Screening for Environmental Hazards at Sites with Contaminated Soil and Groundwater

Volume 2: Background Documentation for the Development of Tier 1 Environmental Action Levels

Appendices 2-9

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DISCLAIMER

This document, *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (Fall 2011), is a technical report prepared by staff of the Hawai'i Department of Health (HDOH), Environmental Management Division. The document updates and replaces the document *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (Interim Final, March 2009 and interim updates).

The document provides guidance for identification and evaluation of environmental hazards associated with contaminated soil and groundwater. The Environmental Action Levels (EALs) presented in this document and the accompanying text are specifically *not* intended to serve as: 1) a stand-alone decision making tool, 2) guidance for the preparation of baseline environmental risk assessments, 3) a rule to determine if a waste is hazardous under the state or federal regulations, or 4) a rule to determine when the release of hazardous substances must be reported to the HDOH.

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VOLUME 2: BACKGROUND DOCUMENTATION FOR THE DEVELOPMENT OF TIER 1 SOIL AND GROUNDWATER ACTION LEVELS

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GLOSSARY OF TERMS

AWQC: Aquatic Water Quality Criteria
CCC: Criterion for Continuous Concentration
CCM: Criterion for Maximum Concentration
EPA: Environmental Protection Agency
ESL: Environmental Screening Level
FVC: Final Chronic Value
HIDOH: Hawai'i Department of Health
HH: Human Health-consumption of aquatic organisms
LOEL: Lowest-Observed-Effects Level
MADEP: Massachusetts Department of Environmental Protection
MCL: Maximum Concentration Level
MOEE: Ontario Ministry of Environment and Energy
MTBE: Methyl tert-Butyl Ethylene
PCE: Tetrachloroethylene
PRG: Preliminary Remediation Goals
RBSL: Risk-Based Screening Level
RSL: Regional Screening Level
RWQCB: Regional Water Quality Control Board
TPH: Total Petroleum Hydrocarbons
USEPA: U.S. Environmental Protection Agency
USDOE: U.S. Department of Energy

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APPENDIX 2

SUMMARY OF HUMAN HEALTH DIRECT EXPOSURE MODELS AND DEFAULT INPUT PARAMETER VALUES

USEPA REGIONAL SCREENING LEVELS USER'S GUIDE (JUNE 2011, TEXT ONLY)

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EQUATIONS FOR DERIVATION OF RISK-BASED SCREENING LEVELS FOR SOIL, INDOOR AIR AND DRINKINGWATER

1.0 Introduction

This appendix summarizes models and exposure assumptions used to generate risk-based action levels for soil, tapwater and indoor air that are incorporated into the HDOH Tier 1 Environmental Action Levels presented in Appendix 1. Risk-based action levels for soil and tapwater follow models and assumptions used to develop the USEPA Regional Screening Levels (RSLs, USEPA 2011). The RSLs represent a consolidation of Preliminary Remedial Goals (PRGs) previously published by individual USEPA regions. Previous editions of the HDOH guidance in particular referenced PRGs developed and published by USEPA Region IX (USEPA 2004a).

A copy of the 2011 USEPA RSL User's Guide is attached. This document presents a detailed discussion of the equations and assumptions used to calculate the RLSs. Risk-based soil action levels were developed for the following exposure scenarios:

- Residential direct exposure;
- Commercial/Industrial;
- Construction/Trench Workers.

The USEPA soil RSLs take into account the following routes of exposure:

- Incidental ingestion;
- Inhalation of vapors or dust;
- Dermal absorption.

Soil exposure assumptions for the Outdoor (vs indoor) Worker RSLs were referred to for incorporation in the Appendix 1 lookup tables (refer to Table I-2 in Appendix 1). The primary difference is an assumed soil ingestion rate of 100 mg/day vs 50 mg/day, respectively.

The USEPA RSL guidance only presents risk-based soil action levels for residential and commercial/industrial land use scenarios. A third set of action levels is incorporated into the HDOH Tier 1 EALs for construction and trench workers. A summary of exposure assumptions for all scenarios is provided in Table 1. References for the development of this exposure scenario are discussed in more detail below and in Appendix 1. The soil action levels can be used in site-specific Environmental Hazard Evaluations to evaluate in contaminants in deep or otherwise isolated soils to help target remedial efforts.

Soil action levels for contaminants that pose noncancer health risks were calculated for a target hazard quotient of both 1.0, following the approach used by USEPA, as well as more conservative hazard quotient of 0.2. Soil action levels based on a hazard quotient of 0.2 are carried forward for inclusion in the Tier 1 EAL lookup tables (refer to table A, B and I series). This was done in order to take into account potential cumulative affects posed by the presence of multiple contaminants with similar health effects. In most instances, this results in HDOH soil action levels for noncancer concerns that are one-fifth of the USEPA RSLs. In cases where the USEPA RSL exceeds the theoretical soil saturation level for a given chemical (Csat), however, the difference will be less. As discussed in Appendix 1, Csat is used as the upper limit for direct exposure soil action levels. The USEPA RSL and adjusted DOH action level will be identical both if the RSL and the DOH action level exceed this value. HDOH action levels for some chemicals may also differ slightly from the original USEPA RSL due to rounding inconsistencies between input values in the respective HDOH and USEPA spreadsheets.

The USEPA RSLs for tapwater take into account a similar set of assumed exposure routes:

- Direct ingestion of water;
- Inhalation of vapors during showering or other activities.

Equations used to develop the RSLs and similarly used to develop action levels for this guidance are presented in the attached USEPA RSL User's Guide.

The soil leaching model used in the USEPA RSL guidance was not referred to for use in the Tier 1 EALs. An alternative model used to develop soil action levels for this potential environmental hazard is discussed in Appendix 1.

2.0 Construction/Trench Workers Exposure Scenario

Direct-exposure screening levels for deep soils are calculated based on a construction/trench worker exposure scenario. Exposure assumptions are summarized in Table 1. The assumed exposed skin area and soil ingestion rate are based on guidance presented in the Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites (USEPA 2002). The inhalation rate, body weight, averaging time and target hazard quotient are set equal to assumptions used in the USEPA RSLs (USEPA 2011) for consistency with screening levels for occupational exposure assumptions. The soil adherence factor is taken from trench-worker exposure scenario assumptions developed by the Massachusetts Department of Environmental Protection for use in calculating screening levels for Deep soils (MADEP 1994).

The Massachusetts Department of Environmental Protection assumes exposure durations of three months for noncarcinogens (plus use of subchronic RfDs) and seven years for carcinogens. A seven year (versus three month) exposure duration for carcinogens is used in part because shorter exposure durations were considered to be beyond the limits of cancer risk models. For the purposes of this document, a one-time, three month exposure duration to exposed soils at a site was considered to be inadequate. This may be particularly true for utility workers who re-visit a site numerous times over several years for routine maintenance of underground utilities. As noted in Table 1, a total exposure duration of seven years is assumed for both carcinogens and noncarcinogens. An exposure frequency of 20 days (4 weeks) per year for 7 years yields a total of 140 days total exposure. Construction workers may receive 140 days (roughly 6 months) of exposure in a single year and never visit the site again. Using chronic RfDs (generally less stringent that subchronic RfDs) and spreading the total exposure time over seven years is somewhat conservative but is consistent with the utility worker scenario. A target risk of 1E-06 was used to calculate soil screening levels for carcinogens. A target hazard quotient of 0.2 was used to calculate soil screening levels for noncarcinogens. This is consistent with assumption used to develop screening levels for residential and industrial/commercial exposure scenarios.

The emission of vapors from contaminated soil is based on part on the calculation of a "Volatilization Factor" on a chemical-specific basis (USEPA 2011, see equation in attached RSL guidance manual). A key parameter in this calculation is the term "Q/C," defined as the inversion of the ration of the mean concentration of a VOC in air to the volatilization flux at the center of site (see VF equation in attachment). A default value of 68.81 is assigned to Q/C for standard residential and commercial/industrial site scenarios. A default Q/C value of 14.31 is assigned for use in trench worker exposure models for calculation of soil action levels for VOCs in order to take into account the potential for poor air flow in trenches (see Table I-3 in Appendix 1).

"Particulate Emission Factors (PEFs)" are intended to relate the concentration of a chemical in soil to the concentration of the chemical in air-born dust. The PEF used for residential and occupational exposure scenarios (1.316E+09 mg-kg/mg/m3) was taken directly from the USEPA Region IX Preliminary Remediation Goals guidance document (USEPA 2011). The PEF reflects a concentration of air-born particulate matter of approximately 0.76 ug/m3. This PEF and associated concentration of air-born dust was not considered to be adequately conservative of conditions that may occur at construction sites. A revised PEF for this exposure scenario was derived through use of a "Dust Emission Factor" for construction sites developed by the USEPA. The Dust Emission Factor of 1.2 tons of dust per month, per acre is based on USEPA field studies at apartment complex and commercial center developments in semi-

arid areas (USEPA 1974, 1985). Derivation of the construction-site PEF is summarized in Table 4. The derived PEF (1.44E+06 mg-kg/mg/m3) corresponds to a concentration of air-born dust of approximately 700 ug/m3.

3.0 INDOOR AIR

Target levels for indoor air were calculated based on equations incorporated into vapor intrusion spreadsheets published by the USEPA (USEPA 2004b). Refer to Appendix 4 for a copy of this guidance and a more detailed discussion of the equations. The equations are reproduced below for reference.

Equation 1: Residential Exposures to Carcinogenic Contaminants in Indoor Air

$$C_{air}(ug/m^3) = \frac{TR \ x \ AT_c}{EF_{res} \ x \ ED_{res} \ x \ URF}$$

Equation 2: Occupational Exposures to Carcinogenic Contaminants in Indoor Air

$$C_{air}(ug/m^3) = \frac{TR \ x \ AT_c}{EF_{occ} \ x \ ED_{occ} \ x \ URF}$$

Equation 3: Residential Exposures to Noncarcinogenic Contaminants in Indoor Air

$$C_{air}(ug/m^3) = \frac{THQ \ x \ AT_{nc} \ x \ RfC}{EF_{res} \ x \ ED_{res}}$$

Equation 4: Occupational Exposures to Noncarcinogenic Contaminants in Indoor Air

$$C_{air}(ug/m^3) = \frac{THQ \ x \ AT_{nc} \ x \ RfC}{EF_{occ} \ x \ ED_{occ}}$$

where URF is the unit risk factor carcinogens $(ug/m3)^{-1}$ for and RfC carcinogens (ug/m3) is the reference concentration for noncarcinogens. A summary of URFs and RfCs for specific chemicals is provided in Table H and E-3 of Appendix 1.

REFERENCES

MADEP, 1994, *Background Documentation for the Development of the MCP Numerical Standards:* Massachusetts Department of Environmental Protection, Bureau of Waste Site Cleanup and Office of Research and Standards, April 1994.

USEPA, 1974, Development of Emission Factors for Fugitive Dust Sources: U.S. Environmental Protection Agency, Publication No. EPA-450/3-74-037, (prepared by Cowherd, C., Axetell, K., Guenther, C., and Jutze, G., Midwest Research Institute).

USEPA, 1985, Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources: U.S. Environmental Protection Agency, Office of Air and Radiation, Publication No. AP-42, Fourth Edition, September 1985.

USEPA, 2002, Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites: U.S. Environmental Protection Agency, Solid Waste and Emergency Response, OSWER 9355.4-24, December 2002.

USEPA, 2004a, Preliminary Remediation Goals: U.S. Environmental Protection Agency, Region IX, October 2002, www.epa.gov/region09/waste/sfund/prg/intro.htm.

USEPA, 2004b, *User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapor Intrusion Into Buildings*: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, www.epa.gov/oerrpage/superfundrisk/airmodel/.

USEPA, 2011a, *Regional Screening Levels*: U.S. Environmental Protection Agency, June 2011, prepared by Oak Ridge National Laboratories, http://epaprgs. ornl.gov/chemicals/index.shtml

USEPA, 2011b, *Exposure Factors Handbook*: U.S. Environmental Protection Agency, Office of Research and Development. September 2011, EPA/600/R-090/052F www.epa.gov

TABLE 1. HUMAN EXPOSURE PARAMETER DEFINITIONS AND DEFAULT VALUES

Symbol	Definition (units)	Default	References (refer to USEPA 2002 for full references)
CSFo	Cancer slope factor oral $(mg/kg\text{-}d)^{-1}$	--	Chemical specific - Appendix 1, Table H
CSFi	Cancer slope factor inhaled $(mg/kg\text{-}d)^{-1}$	--	Chemical specific - Appendix 1, Table H
RfDo	Reference dose oral (mg/kg-d)	--	Chemical specific - Appendix 1, Table H
RfDi	Reference dose inhaled (mg/kg-d)	--	Chemical specific - Appendix 1, Table H
TRr/o	Target cancer risk - residential, occupational/ industrial exposure scenario	10^{-6}	USEPA 2011a. See Appendix 1 Table I series and text for exceptions
*TRctw	Target cancer risk - construction/trench worker exposure scenario	10^{-5}	HIDOH (see Appendix 1)
THQ	Target hazard quotient	0.2	USEPA 2011a. See Appendix 1 Table I series and text for exceptions
BWa	Body weight, adult (kg)	70	USEPA 2011a
BWc	Body weight, child (kg)	15	USEPA 2011a
ATc	Average time – carcinogens (days)	25,550	USEPA 2011a
ATn	Average time – noncarcinogens (days)	ED*365	USEPA 2011a
SAar	Exposed surface area, adult res. (cm^2/day)	5,700	USEPA 2011a
SAaw	Exposed surface area, adult occ. (cm^2/day)	3,300	USEPA 2011a
SAc	Exposed surface area, child (cm^2/day)	2,800	USEPA 2011a
*SAac/tw	Exposed surface area, construction/trench worker (cm^2/day)	5,800	USEPA 2011b
AFar	Adherence factor, adult res. (mg/cm^2)	0.07	USEPA 2011a
AFaw	Adherence factor, occupational (mg/cm^2)	0.20	USEPA 2011a
*AFctw	Adherence factor, construction/trench worker (mg/cm^2)	0.51	Massachusetts DEP (1994)
AFc	Adherence factor, child (mg/cm^2)	0.20	USEPA 2011a
ABS	Skin absorption (unitless): chemical specific	--	USEPA 2011a
IRAa	Inhalation rate – adult (m^3/day)	20	USEPA 2011a
IRAc	Inhalation rate – child (m^3/day)	10	USEPA 2011a
*IRActw	Inhalation rate – construction/trench worker (m^3/day)	20	USEPA 2011b
IRWa	Drinking water ingestion – adult (L/day)	2	USEPA 2011a
IRWc	Drinking water ingestion – child (L/day)	1	PEA Cal-EPA (DTSC, 1994)
IRSa	Soil ingestion – adult (mg/day)	100	USEPA 2011a
IRSc	Soil ingestion – child (mg/day)	200	USEPA 2011a)
IRSo	Soil ingestion – occupational (mg/day)	50	USEPA 2011a
*IRSctw	Soil ingestion–construction/trench worker (mg/day)	330	USEPA 2002
EFr	Exposure frequency – residential (d/y)	350	USEPA 2011a
EFo	Exposure frequency – occupational (d/y)	250	USEPA 2011a
*EFctw	Exposure frequency – construction/trench worker (d/y)	20	Massachusetts DEP (1994)
EDr	Exposure duration – residential (years)	30	USEPA 2011a
EDc	Exposure duration – child (years)	6[a]	USEPA 2011a
EDo	Exposure duration – occupational (years)	25	USEPA 2011a
*EDctw	Exposure duration – construction/trench worker (years)	7	modified from Massachusetts DEP (1994)
IFSadj	Ingestion factor, soils ([mg-yr]/[kg-d])	114	USEPA 2011a
SFSadj	Skin contact factor, soils ([mg-yr]/[kg-d])	361	USEPA 2011a
InhFadj	Inhalation factor ([m^3-yr]/[kg-d])	11	USEPA 2011a
IFWadj	Ingestion factor, water ([1-yr]/[kg-d])	1.1	USEPA 2011a
VFw	Volatilization factor for water ($L/m^{3)}$	0.5	USEPA 2011a
PEFres/oc	Particulate emission factor (m^3/kg) - residential/occupational exposure scenarios	1.32E+09	USEPA 2011a
*PEFctw	Particulate emission factor (m^3/kg) - construction/trench worker exposure scenarios	1.44E+06	Based on Construction Site Dust Emission Factors (USEPA 1974, 1985). See attached table.
VFs	Volatilization factor for soil (m3/kg)	-	Chemical specific (USEPA 2002, 2011a)
sat	Soil saturation concentration (mg/kg)	-	Chemical specific (USEPA 2002, 2011a)

TABLE 2. VOLATILIZATION FACTOR PARAMETER DEFINITIONS AND DEFAULT VALUES

Parameter	Definition (units)	Default
VF_s	Volatilization factor M^3/kg)	--
D_A	Apparent diffusivity (cm^2/s)	--
$Q/C_{default}$	Inverse of the mean conc. at the center of a 0.5-acre square source (g/m^2-s per kg/m^3)	68.81 (USEPA 2011a)
Q/C_{trench}	Inverse of the mean conc. at the center of a 0.5-acre square source (g/m^2-s per kg/m^3)	14.31 (USEPA 2002)
T	Exposure interval (s)	9.5×10^8
rho_b	Dry soil bulk density (g/cm^3)	1.5
$theta_a$	Air filled soil porosity (L_{air}/L_{soil})	0.28 or n-w
n	Total soil porosity (L_{pore}/L_{soil})	0.43 or 1 – (b/s)
$theta_w$	Water-filled soil porosity (L_{water}/L_{soil})	0.15
rho_s	Soil particle density (g/cm^3)	2.65
Di	Diffusivity in air (cm^2/s)	Chemical-specific
H	Henry's Law constant (atm-m^3/mol)	Chemical-specific
H'	Dimensionless Henry's Law constant	Calculated from H by multiplying by 41 (USEPA 1991a)
D_w	Diffusivity in water (cm^2/s)	Chemical-specific
K_d	Soil-water partition coefficient (cm3/g) = Koc x foc	Chemical-specific
K_{oc}	Soil organic carbon-water partition coefficient (cm^3/g)	Chemical-specific
f_{oc}	Fraction organic carbon in soil (g/g)	0.006 (0.6%)

TABLE 3. PARTICULATE EMISSION FACTOR PARAMETER DEFINITIONS AND DEFAULT VALUES - RESIDENTIAL/OCCUPATIONAL SCENARIOS

Parameter	Definition (units)	Default
*PEF	Particulate emission factor (m^3/kg)	1.316×10^9
Q/C	Inverse of the mean concentration at the center of a 0.5-acre-square source (g/m^2-s per kg/m^3)	90.80
V	Fraction of vegetative cover (unitless)	0.5
Um	Mean annual windspeed (m/s)	4.69
Ut	Equivalent threshold value of windspeed at 7 m (m/s) 11.32	11.32
F(x)	Function dependent on Um/Ut derived using Cowherd (1985) (unitless)	0.194

* Concentration dust in air (mg/m^3) = 1/(PEF x (1 kg/1,000,000 mg)) = 0.0007 mg/m^3

TABLE 4. PARTICULATE EMISSION FACTOR FOR CONSTRUCTION/TRENCH WORKER EXPOSURE SCENARIO

Dust Generated (moderate to heavy construction) (M_{dust}):			
Dust Emission Factor (EF):	1.2 2400 1089	tons/mo-acre lbs/mo-acre kgs/mo-acre	USEPA 1974, 1985 conversion conversion
Volume Air Passing Over Site Per Month Per Acre (V_{air}):			
Length Perpendicular To Wind (L):	1 43560 4047 64	acre ft^2 m^2 m	Default EF area conversion conversion L=Area^$^{0.5}$
Air Mixing Zone Height (MZ): Ave Wind Speed (V): Seconds per 30.4 Day Month (S): Volume Air (Volume-air):	2 4.69 2.63E+06 1.57E+09	m m/s sec/month m^3	model assumption USEPA 2004 (default PRG value) conversion Volume-air=LxMZxVxS
Average Concentration Dust in Air ($C_{dust-air}$):			
Concentration Dust ($C_{dust-air}$)	6.95E-07 0.695	kg/m^3 mg/m^3	(Cair = M_{dust}/Volume-air) conversion
Particulate Emission Factor (PEF):			
Concentration soil in dust ($C_{dust-soil}$): PEF:	1,000,000 1.44E+06	mg/kg (mg/kg)/ (mg/m^3)	Model assumption - 100% (1000000 mg/kg) of dust is derived from on-site soil. PEF=$C_{dust-soil}/C_{dust-air}$

Attachment

Text of USEPA Region IX Preliminary Remediation Goals Document (June 2011)

Mid-Atlantic Risk Assessment

User's Guide (May 2011)

Disclaimer

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This guidance sets forth a recommended, but not mandatory, approach based upon currently available information with respect to risk assessment for response actions at CERCLA sites. This document does not establish binding rules. Alternative approaches for risk assessment may be found to be more appropriate at specific sites (e.g., where site circumstances do not match the underlying assumptions, conditions and models of the guidance). The decision whether to use an alternative approach and a description of any such approach should be documented for such sites. Accordingly, when comments are received at individual CERCLA sites questioning the use of the approaches recommended in this guidance, the comments should be considered and an explanation provided for the selected approach.

It should also be noted that the screening levels (SLs) in these tables are based upon human health risk and do not address potential ecological risk. Some sites in sensitive ecological settings may also need to be evaluated for potential ecological risk. EPA's guidance "Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment" http://www.epa.gov/oswer/riskassessment/ecorisk/ecorisk.htm contains an eight step process for using benchmarks for ecological effects in the remedy selection process.

1. Introduction

The purpose of this website is to provide default screening tables and a calculator to assist Remedial Project Managers (RPMs), On Scene Coordinators (OSC's), risk assessors and others involved in decision-making concerning CERCLA hazardous waste sites and to determine whether levels of contamination found at the site may warrant further investigation or site cleanup, or whether no further investigation or action may be required.

Users within and outside the CERCLA program should use the tables or calculator results at their own discretion and they should take care to understand the assumptions incorporated in these results and to apply the SLs appropriately.

The SLs presented in the Generic Tables are chemical-specific concentrations for individual contaminants in air, drinking water and soil that may warrant further investigation or site cleanup. The SLs generated from the calculator may be site-specifc concentrations for individual chemicals in soil, air, water and fish. **It should be emphasized that SLs are not cleanup standards**. SLs should not be used as cleanup levels for a CERCLA site until the

other remedy selections identified in the relevant portions of the National Contingency Plan (NCP), 40 CFR Part 300, have been evaluated and considered. PRGs (Preliminary Remediation Goals) is a term used to describe a project team's early and evolving identification of possible remedial goals. PRGs may be initially identified early in the Remedial Investigation/ Feasibility Study (RI/FS) process (e.g., at RI scoping) to select appropriate detection limits for RI sampling. Typically, it is necessary for PRGs to be more generic early in the process and to become more refined and site-specific as data collection and assessment progress. The SLs identified on this website are likely to serve as PRGs early in the process--e.g., at RI scoping and at screening of chemicals of potential concern (COPCs) for the baseline risk assessment. However, once the baseline risk assessment has been performed, PRGs can be derived from the calculator using site-specific risks, and the SLs in the Generic Tables are less likely to apply. PRGs developed in the FS will usually be based on site-specific risks and Applicable or Relevant and Appropriate Requirements (ARARs) and not on generic SLs.

2. Understanding the Screening Tables

2.1 General Considerations

Risk-based SLs are derived from equations combining exposure assumptions with chemical-specific toxicity values.

2.2 Exposure Assumptions

Generic SLs are based on default exposure parameters and factors that represent Reasonable Maximum Exposure (RME) conditions for long-term/chronic exposures and are based on the methods outlined in EPA's Risk Assessment Guidance for Superfund, Part B Manual (1991) and Soil Screening Guidance documents (1996 and 2002).

Site-specific information may warrant modifying the default parameters in the equations and calculating site-specific SLs, which may differ from the values in these tables. In completing such calculations, the user should answer some fundamental questions about the site. For example, information is needed on the contaminants detected at the site, the land use, impacted media and the likely pathways for human exposure.

Whether these generic SLs or site-specific screening levels are used, it is important to clearly demonstrate the equations and exposure parameters used in deriving SLs at a site. A discussion of the assumptions used in the SL calculations should be included in the documentation for a CERCLA site.

2.3 Toxicity Values

In 2003, EPA's Superfund program revised its hierarchy of human health toxicity values, providing three tiers of toxicity values (http://www.epa.gov/oswer/riskassessment/pdf/hhmemo.pdf). Three tier 3 sources were identified in that guidance, but it was acknowledged that additional tier 3 sources may exist. The 2003 guidance did not attempt to rank or put the identified tier 3 sources into a hierarchy of their own. However, when developing the screening tables and calculator presented on this website, EPA needed to establish a hierarchy among the tier 3 sources. The toxicity values used as "defaults" in these tables and calculator are consistent with the 2003

guidance. Toxicity values from the following sources in the order in which they are presented below are used as the defaults in these tables and calculator.

1. EPA's Integrated Risk Information System (IRIS)

2. The Provisional Peer Reviewed Toxicity Values (PPRTVs) derived by EPA's Superfund Health Risk Technical Support Center (STSC) for the EPA Superfund program.

3. The Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs)

4. The California Environmental Protection Agency (OEHHA) Office of Environmental Health Hazard Assessment's Chronic Reference Exposure Levels (RELS) from December 18, 2008 and the Cancer Potency Values from July 21, 2009.

5. In the Fall 2009, this new source of toxicity values used was added: screening toxicity values in an appendix to certain PPRTV assessments. While we have less confidence in a screening toxicity value than in a PPRTV, we put these ahead of HEAST toxicity values because these appendix screening toxicity values are more recent and use current EPA methodologies in the derivation, and because the PPRTV appendix screening toxicity values also receive external peer review.

6. The EPA Superfund program's Health Effects Assessment Summary. (Note that the HEAST website of toxicity values for chemical contaminants is not open to users outside of EPA, but values can be obtained for use on Superfund sites by contacting Rich Kapuscinski at Kapuscinski.Rich@epa.gov).

Users of these screening tables and calculator wishing to consider using other toxicity values, including toxicity values from additional sources, may find the discussions and seven preferences on selecting toxicity values in the attached Environmental Council of States paper useful for this purpose (ECOS website, ECOS paper).

When using toxicity values, users are encouraged to carefully review the basis for the value and to document the basis of toxicity values used on a CERCLA site.

2.3.1 Reference Doses

The current, or recently completed, EPA toxicity assessments used in these screening tables (IRIS and PPRTVs) define a reference dose, or RfD, as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, or using categorical regression, with uncertainty factors generally applied to reflect limitations of the data used. RfDs are generally the toxicity value used most often in evaluating noncancer health effects at Superfund sites. Various types of RfDs are available depending on the critical effect (developmental or other) and the length of exposure being evaluated (chronic or subchronic). Some of the SLs in these tables also use Agency for Toxic Substances and Disease Registry (ATSDR) chronic oral minimal risk levels (MRLs) as an oral chronic RfD. Screening toxicity values in an appendix to certain PPRTV assessments were added to the hierarchy in the fall of 2009. The HEAST RfDs used in these SLs were based upon then current EPA toxicity methodologies, but did not use the more recent benchmark dose or

categorical regression methodologies. Chronic oral reference doses and ATSDR chronic oral MRLs are expressed in units of (mg/kg-day).

2.3.1.1 Chronic Reference Doses

Chronic oral RfDs are specifically developed to be protective for long-term exposure to a compound. As a guideline for Superfund program risk assessments, chronic oral RfDs generally should be used to evaluate the potential noncarcinogenic effects associated with exposure periods greater than 7 years (approximately 10 percent of a human lifetime). However, this is not a bright line. Note, that ATSDR defines chronic exposure as greater than 1 year for use of their values. The calculator requires the user to select between chronic and subchronic toxicity values.

2.3.1.2 Subchronic Reference Doses

Subchronic oral RfDs are specifically developed to be protective for short-term exposure to a compound. As a guideline for Superfund program risk assessments, subchronic oral RfDs should generally be used to evaluate the potential noncarcinogenic effects of exposure periods between two weeks and seven years. However, this is not a bright line. Note, that ATSDR defines subchronic exposure as less than 1 year for use of their values. The calculator requires the user to select between chronic and subchronic toxicity values.

2.3.2 Reference Concentrations

The current, or recently completed, EPA toxicity assessments used in these screening tables (IRIS and PPRTV assessments) define a reference concentration (RfC) as an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark concentration, or using categorical regression with uncertainty factors generally applied to reflect limitations of the data used. Various types of RfCs are available depending on the critical effect (developmental or other) and the length of exposure being evaluated (chronic or subchronic). These screening tables also use ATSDR chronic inhalation MRLs as a chronic RfC, intermediate inhalation MRLs as a subchronic RfC and California Environmental Protection Agency (chronic) Reference Exposure Levels (RELs) as chronic RfCs. Screening toxicity values in an appendix to certain PPRTV assessments were added to the hierarchy in the fall of 2009. These screening tables may also use some RfCs from EPA’s HEAST tables.

2.3.2.1 Chronic Reference Concentrations

The chronic inhalation reference concentration is generally used for continuous or near continuous inhalation exposures that occur for 7 years or more. However, this is not a bright line, and ATSDR chronic MRLs are based on exposures longer than 1 year. EPA chronic inhalation reference concentrations are expressed in units of (mg/m3). Cal EPA RELs are presented in µg/m3 and have been converted to mg/m3 for use in these screening tables. Some ATSDR inhalation MRLs are derived in parts per million (ppm) and some in mg/m3. For use in this table all were converted into mg/m3. The calculator requires the user to select between chronic and subchronic toxicity values.

2.3.2.2 Subchronic reference Concentrations

The subchronic inhalation reference concentration is generally used for exposures that are between 2 weeks and 7 years. However, this is not a bright line, and ATSDR subchronic MRLs are based on exposures less than 1 year. EPA subchronic inhalation reference concentrations are expressed in units of (mg/m3). Cal EPA RELs are presented in µg/m3 and have been converted to mg/m3 for use in these screening tables. Some ATSDR intermediate inhalation MRLs are derived in parts per million (ppm) and some in mg/m3. For use in this table all were converted into mg/m3. The calculator requires the user to select between chronic and subchronic toxicity values.

2.3.3 Slope Factors

A slope factor and the accompanying weight-of-evidence determination are the toxicity data most commonly used to evaluate potential human carcinogenic risks. Generally, the slope factor is a plausible upper-bound estimate of the probability of a response per unit intake of a chemical over a lifetime. The slope factor is used in risk assessments to estimate an upper-bound lifetime probability of an individual developing cancer as a result of exposure to a particular level of a potential carcinogen. Slope factors should always be accompanied by the weight-of-evidence classification to indicate the strength of the evidence that the agent is a human carcinogen.

Oral slope factors are toxicity values for evaluating the probability of an individual developing cancer from oral exposure to contaminant levels over a lifetime. Oral slope factors are expressed in units of (mg/kg-day)-1. When available, oral slope factors from EPA’s IRIS or PPRTV assessments are used. The ATSDR does not derive cancer toxicity values (e.g. slope factors or inhalation unit risks). Some oral slope factors used in these screening tables were derived by the California Environmental Protection Agency, whose methodologies are quite similar to those used by EPA’s IRIS and PPRTV assessments. Screening toxicity values in an appendix to certain PPRTV assessments were added to the hierarchy in the fall of 2009. When oral slope factors are not available in IRIS then PPRTVs, Cal EPA assessments, PPRTV appendices or values from HEAST are used.

2.3.4 Inhalation Unit Risk

The IUR is defined as the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 µg/m3 in air. Inhalation unit risk toxicity values are expressed in units of (µg/m3)-1.

When available, inhalation unit risk values from EPA’s IRIS or PPRTV assessments are used. The ATSDR does not derive cancer toxicity values (e.g. slope factors or inhalation unit risks). Some inhalation unit risk values used in these screening tables were derived by the California Environmental Protection Agency, whose methodologies are quite similar to those used by EPA’s IRIS and PPRTV assessments. Screening toxicity values in an appendix to certain PPRTV assessments were added to the hierarchy in the fall of 2009. When inhalation unit risk values are not available in IRIS then PPRTVs, Cal EPA assessments, PPRTV appendices or values from HEAST are used.

2.3.5 Toxicity Equivalence Factors

Some chemicals are members of the same family and exhibit similar toxicological properties; however, they differ in the degree of toxicity. Therefore, a toxicity equivalence factor (TEF)

must first be applied to adjust the measured concentrations to a toxicity equivalent concentration.

The following table contains the various dioxin-like toxicity equivalency factors for Dioxins, Furans and PCBs (Van den Berg et al. 2006), which are the World Health Organization 2005 values.

Dioxin Toxicity Equivalence Factors

	Dioxins and Furans		**TEF**
Chlorinated dibenzo-p-dioxins			
	2,3,7,8-TCDD		1
	1,2,3,7,8-PeCDD		1
	1,2,3,4,7,8-HxCDD		0.1
	1,2,3,6,7,8-HxCDD		0.1
	1,2,3,7,8,9-HxCDD		0.1
	1,2,3,4,6,7,8-HpCDD		0.01
	OCDD		0.0003
Chlorinated dibenzofurans			
	2,3,7,8-TCDF		0.1
	1,2,3,7,8-PeCDF		0.03
	2,3,4,7,8-PeCDF		0.3
	1,2,3,4,7,8-HxCDF		0.1
	1,2,3,6,7,8-HxCDF		0.1
	1,2,3,7,8,9-HxCDF		0.1
	2,3,4,6,7,8-HxCDF		0.1
	1,2,3,4,6,7,8-HpCDF		0.01
	1,2,3,4,7,8,9-HpCDF		0.01
	OCDF		0.0003
PCBs			
	IUPAC No.	**Structure**	
>Non-*ortho*	77	3,3',4,4'-TetraCB	0.0001
	81	3,4,4',5-TetraCB	0.0003
	126	3,3',4,4',5-PeCB	0.1
	169	3,3',4,4',5,5'-HxCB	0.03
>Mono-*ortho*	105	2,3,3',4,4'-PeCB	0.00003
	114	2,3,4,4',5-PeCB	0.00003
	118	2,3',4,4',5-PeCB	0.00003
	123	2',3,4,4',5-PeCB	0.00003
	156	2,3,3',4,4',5-HxCB	0.00003
	157	2,3,3',4,4',5'-HxCB	0.00003
	167	2,3',4,4',5,5'-HxCB	0.00003

	189	2,3,3',4,4',5,5'-HpCB	0.00003
>Di-*ortho**	170	2,2',3,3',4,4',5-HpCB	0.0001
	180	2,2',3,4,4',5,5'-HpCB	0.00001

* Di-ortho values come from Ahlborg, U.G., et al. (1994), which are the WHO 1994 values from Toxic equivalency factors for dioxin-like PCBs: Report on WHO-ECEH and IPCS consultation, December 1993 Chemosphere, Volume 28, Issue 6, March 1994, Pages 1049-1067.

Carcinogenic polycyclic aromatic hydrocarbons

Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons (EPA/600/R-93/089, July 1993), recommends that a toxicity equivalency factor (TEF) be used to convert concentrations of carcinogenic polycyclic aromatic hydrocarbons (cPAHs) to an equivalent concentration of benzo(a)pyrene when assessing the cancer risks posed by these substances from oral exposures. These TEFs are based on the potency of each compound relative to that of benzo(a)pyrene. For the toxicity value database, these TEFs have been applied to the toxicity values. Although this is not in complete agreement with the direction in the aforementioned documents, this approach was used so that toxicity values could be generated for each cPAH. Additionally, it should be noted that computationally it makes little difference whether the TEFs are applied to the concentrations of cPAHs found in environmental samples or to the toxicity values as long as the TEFs are not applied to both. However, if the adjusted toxicity values are used, the user will need to sum the risks from all cPAHs as part of the risk assessment to derive a total risk from all cPAHs. A total risk from all cPAHs is what is derived when the TEFs are applied to the environmental concentrations of cPAHs and not to the toxicity values. These TEFs are not needed and should not be used with the Cal EPA Inhalation Unit Risk Values used, nor should they be used when calculating non-cancer risk. See FAQ no. 15.

The following table presents the TEFs for cPAHs recommended in *Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons*.

Toxicity Equivalency Factors for Carcinogenic Polycyclic Aromatic Hydrocarbons

Compound	TEF
Benzo(a)pyrene	1.0
Benz(a)anthracene	0.1
Benzo(b) fluoranthene	0.1
Benzo(k) fluoranthene	0.01
Chrysene	0.001
Dibenz(a,h) anthracene	1.0
Indeno(1,2,3-c,d) pyrene	0.1

2.4 Chemical-specific Parameters

Several chemical specific parameters are needed for development of the SLs.

2.4.1 Sources

Many sources are used to populate the database of chemical-specific parameters. They are briefly described below.

1. The Estimation Programs Interface (EPI) SuiteTM was developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC). These programs estimate various chemical-specific properties. The calculations for these SL tables use the experimental values for a property over the estimated values.

2. EPA Soil Screening Level (SSL) Exhibit C-1.

3. WATER8, which has been replaced with WATER9.

4. Syracuse Research Corporation (SRC). 2005. CHEMFATE Database. SRC. Syracuse, NY. Accessed July 2005.

5. Syracuse Research Corporation (SRC). 2005. PHYSPROP Database. SRC. Syracuse, NY. Accessed July 2005.

6. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds. Knovel, 2003. (http://www.knovel.com).

7. EPA Soil Screening Level (SSL) Table C.4 (http://www.epa.gov/superfund/health/conmedia/soil/index.htm).

8. Baes, C.F. 1984. Oak Ridge National Laboratory. A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture. http://homer.ornl.gov/baes/documents/ornl5786.html. Values are also found in Superfund Chemical Data Matrix (SCDM) (http://www.epa.gov/superfund/sites/npl/hrsres/tools/scdm.htm).

9. NIOSH Pocket Guide to Chemical Hazards (NPG), NIOSH Publication No. 97-140, February 2004. (http://www.cdc.gov/niosh/npg/npg.html).

10. CRC Handbook of Chemistry and Physics . (Various Editions)

11. Perry'sChemical Engineers' Handbook (Various Editions).McGraw-Hill. Online version available at:http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=2203&VerticalID=0. Green, Don W.; Perry, Robert H. (2008).

12. Lange's Handbook of Chemistry (Various Editions). Online version available at:http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1347&VerticalID=0. Speight, James G. (2005). McGraw-Hill.

13. U.S. EPA 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Final.

OSWER 9285.7-02EP.July 2004. Document and website http://www.epa.gov/oswer/riskassessment/ragse/index.htm">http://www.epa.gov/oswe

2.4.2 Hierarchy by Parameter

Generally the hierarchies below will work for organic and inorganic compounds.

1. Organic Carbon Partition Coefficient (K_{oc}) (L/kg). Not applicable for inorganics. EPI estimated values; SSL, Yaw estimated values; EPI experimental values; Yaw Experimental values

2. Dermal Permeability Constant (K_p) (cm/hr). EPI estimated values; RAGS Part E.

3. Molecular Weight (MW) (g/mole). EPI; CRC89; PERRY; LANGE; YAWS

4. Water Solubility (S) (mg/L). EPI experimatal values; SSL; CRC; PERRY; LANGE; YAWS experimental values; Yaws estimated values; EPI estimated values; PHYSPROP

5. Unitless Henry's Law Constant (H'). EPI experimental values; SSL; YAWS experimental values; EPI estimated values; PHYSPROP

6. Henry's Law Constant (atm-m3/mole). EPI experimental values; SSL; YAWS experimental values; EPI estimated values; PHYSPROP

7. Diffusivity in Air (D_{ia}) (cm2/s). WATER9 equations; SSL

8. Diffusivity in Water (D_{ia}) (cm2/s). WATER9 equations; SSL

9. Fish Bioconcentration Factor (BCF) (L/kg). EPI experimental values; EPI estimated values

10. Soil-Water Partition Coefficient (K_d) (cm3/g). SSL; BAES

11. Density (g/cm3). CRC; PERRY; LANGE; IRIS

3. Using the SL Tables

The "Generic Tables" page provides generic concentrations in the absence of site-specific exposure assessments. These concentrations can be used for:

Prioritizing multiple sites or operable units or areas of concern within a facility or exposure units

Setting risk-based detection limits for contaminants of potential concern (COPCs)

Focusing future site investigation and risk assessment efforts (e.g., selecting COPCs for the baseline risk assessment)

Identifying contamination which may warrant cleanup

Identifying sites, or portions of sites, which warrant no further action or investigation

Initial cleanup goals when site-specific data are lacking

Generic SLs are provided for multiple exposure pathways and for chemicals with both carcinogenic and noncarcinogenic effects. A Summary Table is provided that contains SLs corresponding to either a 10-6 risk level for carcinogens or a Hazard Quotient (HQ) of 1 for non-carcinogens. The summary table identifies whether the SL is based on cancer or noncancer effects by including a "c" or "n" after the SL. The Supporting Tables provide SLs corresponding to a 10-6 risk level for carcinogens and an HQ of 1 for noncarcinogens. Site specific SLs corresponding to an HQ of less than 1 may be appropriate for those sites where multiple chemicals are present that have RfDs or RfCs based on the same toxic endpoint. Site specific SLs based upon a cancer risk greater than 10-6 can be calculated and may be appropriate based upon site specific considerations. However, caution is recommended to ensure that cumulative cancer risk for all actual and potential carcinogenic contaminants found at the site does not have a residual (after site cleanup, or when it has been determined that no site cleanup is required) cancer risk exceeding 10-4. Also, changing the target risk or HI may change the balance between the cancer and noncancer endpoints. At some concentrations, the cancer-risk concerns predominate; at other concentrations, noncancer-HI concerns predominate. The user must take care to consider both when adjusting target risks and hazards.

Tables are provided in either MS Excel or in PDF format. The following lists the tables provided and a description of what is contained in each:

Summary Table - provides a list of contaminants, toxicity values, MCLs and the lesser (more protective) of the cancer and noncancer SLs for resident soil, industrial soil, resident air, industrial air and tapwater.

Residential Soil Supporting Table - provides a list of contaminants, toxicity values and the cancer and noncancer SLs for resident soil.

Industrial Soil Supporting Table - provides a list of contaminants, toxicity values and the cancer and noncancer SLs for industrial soil.

Residential Air Supporting Table - provides a list of contaminants, toxicity values and the cancer and noncancer SLs for resident air.

Industrial Air Supporting Table - provides a list of contaminants, toxicity values and the cancer and noncancer SLs for industrial air.

Residential Tapwater Supporting Table - provides a list of contaminants, toxicity values, MCLs and the cancer and noncancer SLs for tapwater.

3.1 Developing a Conceptual Site Model

When using generic SLs at a site, the exposure pathways of concern and site conditions should match those used in developing the SLs presented here. (Note, however, that future uses may not match current uses. Future uses are potential site uses that may occur in the future. At Superfund sites, future uses should be considered as well as current uses. RAGS Part A, Chapter 6, provides guidance on selecting future-use receptors.) Thus, it is necessary to develop a conceptual site model (CSM) to identify likely contaminant source areas, exposure pathways, and potential receptors. This information can be used to determine the applicability of SLs at the site and the need for additional information. The final CSM diagram

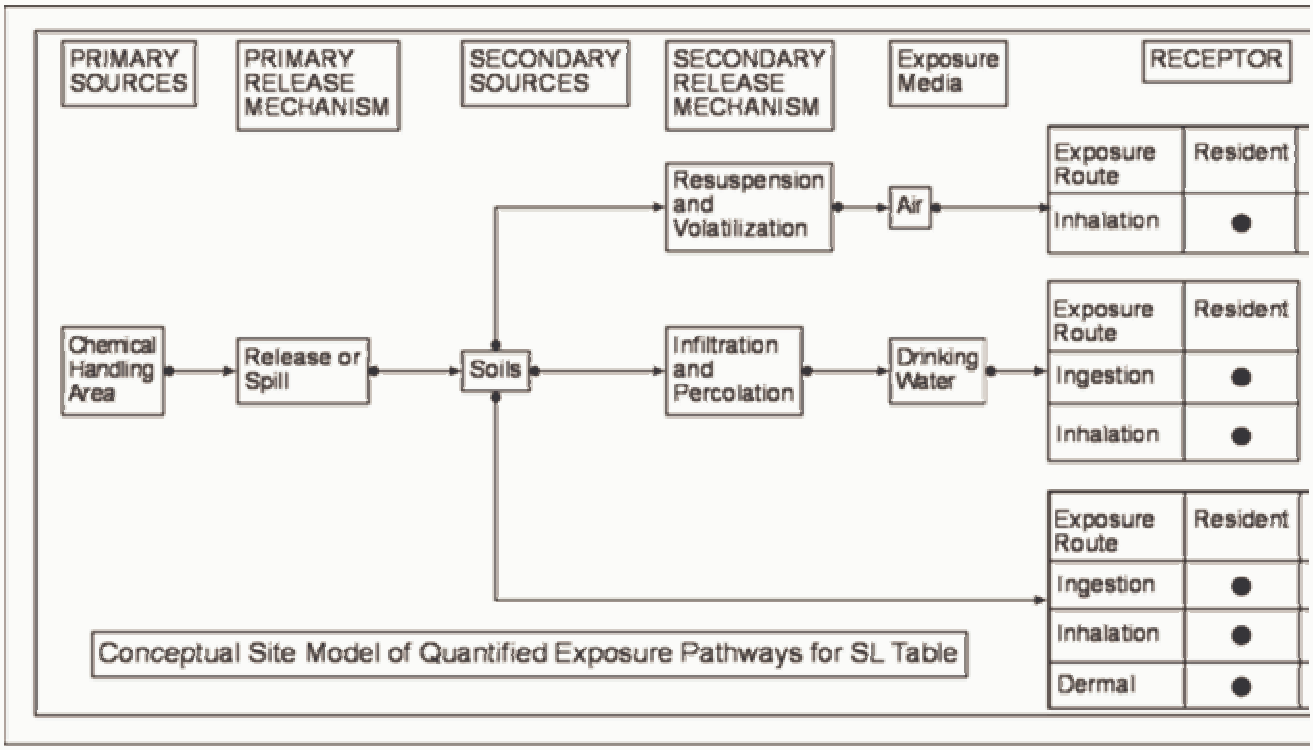
represents linkages among contaminant sources, release mechanisms, exposure pathways, and routes and receptors based on historical information. It summarizes the understanding of the contamination problem. A separate CSM for ecological receptors can be useful. Part 2 and Attachment A of the Soil Screening Guidance for Superfund: Users Guide (EPA 1996) contains the steps for developing a CSM.

As a final check, the CSM should address the following questions:

> Are there potential ecological concerns?
>
> Is there potential for land use other than those used in the SL calculations (i.e., residential and commercial/industrial)?
>
> Are there other likely human exposure pathways that were not considered in development of the SLs?
>
> Are there unusual site conditions (e.g. large areas of contamination, high fugitive dust levels, potential for indoor air contamination)?

The SLs and later PRGs may need to be adjusted to reflect the answers to these questions.

Below is a potential CSM of the quantified pathways addressed in the SL Tables.



3.2 Background

EPA may be concerned with two types of background at sites: naturally occurring and anthropogenic. Natural background is usually limited to metals whereas anthropogenic (i.e. human-made) “background” includes both organic and inorganic contaminants.

Please note that the SL tables, which are purely risk-based, may yield SLs lower than naturally occurring background concentrations of some chemicals in some areas. However, background considerations may be incorporated into the assessment and investigation of sites, as acknowledged in existing EPA guidance. Background levels should be addressed as they are for other contaminants at CERCLA sites. For further information see EPA's guidance Role of Background in the CERCLA Cleanup Program, April 2002, (OSWER 9285.6-07P) and Guidance for Comparing Background and Chemical Concentration in Soil for CERCLA Sites, September 2002, (OSWER 9285.7-41).

Generally EPA does not clean up below natural background. In some cases, the predictive risk-based models generate SL concentrations that lie within or even below typical background concentrations for the same element or compound. Arsenic, aluminum, iron and manganese are common elements in soils that have background levels that may exceed risk-based SLs. This does not mean that these metals cannot be site-related, or that these metals should automatically be attributed to background. Attribution of chemicals to background is a site-specific decision; consult your regional risk assessor.

Where anthropogenic “background” levels exceed SLs and EPA has determined that a response action is necessary and feasible, EPA's goal will be to develop a comprehensive response to the widespread contamination. This will often require coordination with different authorities that have jurisdiction over the sources of contamination in the area.

3.3 Potential Problems

As with any risk based screening table or tool, the potential exists for misapplication. In most cases, this results from not understanding the intended use of the SLs or PRGs. In order to prevent misuse of the SLs, the following should be avoided:

Applying SLs to a site without adequately developing a conceptual site model that identifies relevant exposure pathways and exposure scenarios.

Not considering the effects from the presence of multiple contaminants, where appropriate.

Use of the SLs as cleanup levels without adequate consideration of the other NCP remedy selection criteria on CERCLA sites.

Use of SL as cleanup levels without verifying numbers with a toxicologist or regional risk assessor.

Use of outdated SLs when tables have been superseded by more recent values.

Not considering the effects of additivity when screening multiple chemicals.

Applying inappropriate target risks or changing a cancer target risk without considering its effect on noncancer, or vice versa.

Not performing additional screening for pathways not included in these SLs (e.g,. vapor intrusion, fish consumption).

Adjusting SLs upward by factors of 10 or 100 without consulting a toxicologist or regional risk assessor.

4. Technical Support Documentation

The SLs consider human exposure to individual contaminants in air, drinking water and soil. The equations and technical discussion are aimed at developing risk-based SLs or PRGs. The following text presents the land use equations and their exposure routes. Table 1 presents the definitions of the variables and their default values. Any alternative values or assumptions used in developing SLs on a site should be presented with supporting rationale in the decision document on CERCLA sites.

4.1 Residential Soil

4.1.1 Noncancer

The residential soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{res\text{-}sol\text{-}nc\text{-}ing}\left(mg/kg\right)=\frac{THQ\times AT_r\left(\frac{365\ days}{year}\times ED_c\left(6\ years\right)\right)\times BW_c\left(15\ Kg\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_c\left(6\ year\right)\times\frac{1}{RfD_o\left(\frac{mg}{Kg\text{-}day}\right)}\times IRS_c\left(\frac{200\ mg}{day}\right)\times\frac{10^{-6}k}{1\ mg}}$$

inhalation of particulates emitted from soil,

$$SL_{res\text{-}sol\text{-}nc\text{-}inh}\left(mg/kg\right)=\frac{THQ\times AT_r\left(\frac{365\ days}{year}\times ED_c\left(6\ years\right)\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_c\left(6\ year\right)\times ET_{rs}\left(\frac{24\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times\frac{1}{RfC\left(mg\right.}}$$

dermal contact with soil,

$$SL_{res\text{-}sol\text{-}nc\text{-}der}\left(mg/kg\right)=\frac{THQ\times AT_r\left(\frac{365\ days}{year}\times ED_c\left(6\ years\right)\right)\times BW_c}{EF_r\left(\frac{350\ days}{year}\right)\times ED_c\left(6\ year\right)\times\frac{1}{\left(RfD_o\left(\frac{mg}{Kg\text{-}day}\right)\times GIABS\right)}\times SA_c\left(\frac{2800}{da}\right.}$$

Total.

$$SL_{res\text{-}sol\text{-}nc\text{-}tot}\left(mg/kg\right)=\frac{1}{\frac{1}{SL_{res\text{-}sol\text{-}nc\text{-}ing}}+\frac{1}{SL_{res\text{-}sol\text{-}nc\text{-}der}}+\frac{1}{SL_{res\text{-}sol\text{-}nc\text{-}inh}}}$$

4.1.2 Carcinogenic

The residential soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{res\text{-}sol\text{-}ca\text{-}ing}\,(mg/kg) = \frac{TR \times AT_r\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times EF_r\left(\frac{350\ days}{year}\right) \times IFS_{adj}\left(\frac{114\ mg\text{-}Year}{Kg\text{-}day}\right) \times \left(\frac{10^{-6}Kg}{mg}\right)}$$

where:

$$IFS_{adj}\left(\frac{114\ mg\text{-}Year}{Kg\text{-}day}\right) = \frac{ED_c\,(6\ years) \times IRS_c\left(\frac{200\ mg}{day}\right)}{BW_c\,(15\ Kg)} + \frac{ED_r\text{-}ED_c\,(24\ years) \times IRS_a\left(\frac{100\ mg}{day}\right)}{BW_a\,(70\ Kg)}$$

inhalation of particulates emitted from soil,

$$SL_{res\text{-}sol\text{-}ca\text{-}inh}\,(mg/kg) = \frac{TR \times AT_r\left(\frac{365\ days}{year} \times LT\,(70\ y\right.}{IUR\left(\mu g/m^3\right)^{-1} \times \left(\frac{1000\ \mu g}{mg}\right) \times EF_r\left(\frac{350\ days}{year}\right) \times \left(\frac{1}{VF_s\left(\frac{m^3}{Kg}\right)} + \frac{1}{PEF_w\left(\frac{m^3}{Kg}\right)}\right.}$$

dermal contact with soil,

$$SL_{res\text{-}sol\text{-}ca\text{-}der}\,(mg/kg) = \frac{TR \times AT_r\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right) \times EF_r\left(\frac{350\ days}{year}\right) \times DFS_{adj}\left(\frac{361\ mg\text{-}Year}{Kg\text{-}day}\right) \times ABS_d \times}$$

where:

$$DFS_{adj}\left(\frac{361\ mg\text{-}Year}{Kg\text{-}day}\right) = \frac{ED_c\,(6\ years) \times SA_c\left(\frac{2800\ cm^2}{day}\right) \times AF_c\left(\frac{0.2\ mg}{cm^2}\right)}{BW_c\,(15\ Kg)} + \frac{ED_r\text{-}ED_c\,(24\ years) \times S}{E}$$

Total.

$$SL_{res\text{-}sol\text{-}ca\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{res\text{-}sol\text{-}ca\text{-}ing}} + \frac{1}{SL_{res\text{-}sol\text{-}ca\text{-}der}} + \frac{1}{SL_{res\text{-}sol\text{-}ca\text{-}inh}}}$$

4.1.3 Mutagenic

The residential soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{res\text{-}sol\text{-}mu\text{-}ing}\left(mg/kg\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times EF_r\left(\frac{350\ days}{year}\right)\times IFSM_{adj}\left(\frac{489.5\ mg\text{-}Year}{Kg\text{-}day}\right)\times\left(\frac{10^{\cdots}}{n}\right.}$$

where:

$$IFSM_{adj}\left(\frac{489.5\ mg\text{-}Year}{Kg\text{-}day}\right)=\frac{ED_{0\text{-}2}\left(yr\right)\times IRS_c\left(\frac{200\ mg}{day}\right)\times 10}{BW_c\left(15\ Kg\right)}+\frac{ED_{2\text{-}6}\left(yr\right)\times IRS_c\left(\frac{200\ mg}{day}\right)\times 3}{BW_c\left(15\ Kg\right)}+\frac{ED_{6\text{-}16}\left(yr\right)\times IRS_a\left(\frac{100\ mg}{day}\right)\times 3}{BW_a\left(70\ Kg\right)}+\frac{ED_{16\text{-}30}\left(yr\right)\times IRS_a\left(\frac{100\ mg}{day}\right)\times 1}{BW_a\left(70\ Kg\right)}$$

inhalation of particulates emitted from soil,

$$SL_{res\text{-}sol\text{-}mu\text{-}inh}\left(mg/kg\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ET_{rs}\left(\frac{24\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times\left(\frac{1000\ \mu g}{mg}\right)\times\left(\left(ED_{0\text{-}2}\left(yrs\right)\times IUR\left(\mu g/m^3\right)^{-1}\times 10\right)+\left(ED_{2\text{-}6}\left(yrs\right)\times IUR\left(\mu g/m^3\right)^{-1}\times 3\right)+\left(ED_{6\text{-}16}\left(yrs\right)\times IUR\left(\mu g/m^3\right)^{-1}\times 3\right)+\left(ED_{16\text{-}30}\left(yrs\right)\times IUR\left(\mu g/m^3\right)^{-1}\times 1\right)\right)}$$

dermal contact with soil,

$$SL_{res\text{-}sol\text{-}mu\text{-}der}\left(mg/kg\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right)\times EF_r\left(\frac{350\ days}{year}\right)\times DFSM_{adj}\left(\frac{1445\ mg\text{-}Year}{Kg\text{-}day}\right)\times AB}$$

where:

$$DFSM_{adj}\left(\frac{1445\ mg\text{-}Year}{Kg\text{-}day}\right)=\frac{ED_{0\text{-}2}\left(yr\right)\times AF_c\left(\frac{0.2\ mg}{cm^2}\right)\times SA_c\left(\frac{2800\ cm^2}{day}\right)\times 10}{BW_c\left(15\ Kg\right)}+\frac{ED_{2\text{-}6}\left(yr\right)\times AF_c\left(\frac{0}{}\right.}{E}+\frac{ED_{6\text{-}16}\left(yr\right)\times AF_a\left(\frac{0.07\ mg}{cm^2}\right)\times SA_a\left(\frac{5700\ cm^2}{day}\right)\times 3}{BW_a\left(70\ Kg\right)}+\frac{ED_{16\text{-}30}\left(yr\right)\times AF_a}{}$$

Total.

$$SL_{res\text{-}sol\text{-}mu\text{-}tot}\left(mg/kg\right)=\frac{1}{\frac{1}{SL_{res\text{-}sol\text{-}mu\text{-}ing}}+\frac{1}{SL_{res\text{-}sol\text{-}mu\text{-}der}}+\frac{1}{SL_{res\text{-}sol\text{-}mu\text{-}inh}}}$$

4.1.4 Vinyl Chloride - Carcinogenic

The residential soil land use equations, presented here, contain the following exposure routes:

incidental ingestion of soil,

$$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}ing}\,(mg/kg) = \frac{TR}{\left(\dfrac{CSF_o\left(\dfrac{mg}{Kg\text{-}day}\right)^{-1} \times EF_r\left(\dfrac{350\ days}{year}\right) \times IFS_{adj}\left(\dfrac{114\ mg\text{-}yr}{kg\text{-}d}\right) \times \dfrac{10^{-6}Kg}{1\ mg}}{AT\left(\dfrac{365\ days}{year} \times LT\ (70\ years)\right)}\right) + \left(\dfrac{CSF_o\left(\dfrac{mg}{Kg\text{-}day}\right)^{-1} \times IRS_c\left(\dfrac{200\ mg}{day}\right) \times \dfrac{10^{-6}Kg}{1\ mg}}{BW_c\ (15\ kg)}\right)}$$

inhalation of particulates emitted from soil,

$$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}inh}\,(mg/kg) = \frac{TR}{\left(\dfrac{IUR\left(\mu g/m^3\right)^{-1} \times EF\left(\dfrac{350\ days}{year}\right) \times ED\ (30\ years) \times ET_{rs}\left(\dfrac{24\ hours}{day}\right) \times \left(\right.}{AT\left(\dfrac{365\ days}{year} \times LT\ (70\ years)\right) \times VF\left(\dfrac{m^3}{kg}\right)}\right) + \left(\dfrac{IUR\left(\mu g/m^3\right)^{-1}}{VF\left(\dfrac{m^3}{kg}\right)} \times \left(\dfrac{1000\ \mu g}{mg}\right)\right)}$$

dermal contact with soil,

$$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}der}\,(mg/kg) = \frac{TR}{\left(\dfrac{\dfrac{CSF_o\left(\dfrac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS} \times EF_r\left(\dfrac{350\ days}{year}\right) \times DFS_{adj}\left(\dfrac{361\ mg\text{-}yr}{kg\text{-}day}\right) \times ABS_d \times 1}{AT_r\left(\dfrac{365\ days}{year} \times LT\ (70\ years)\right)}\right) + \left(\dfrac{\dfrac{CSF_o\left(\dfrac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS} \times SA_c\left(\dfrac{2800\ cm^2}{day}\right) \times AF_c\left(\dfrac{0.2\ mg}{cm^2}\right) \times ABS \times \dfrac{10^{-6}Kg}{1\ mg}}{BW_c\ (15\ kg)}\right)}$$

Total.

$$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}tot}\ (mg/kg) = \frac{1}{\frac{1}{SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}ing}} + \frac{1}{SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}der}} + \frac{1}{SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}inh}}}$$

A number of studies have shown that inadvertent ingestion of soil is common among children 6 years old and younger (Calabrese et al. 1989, Davis et al. 1990, Van Wijnen et al. 1990). Therefore, the dose method uses an age-adjusted soil ingestion factor that takes into account the difference in daily soil ingestion rates, body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 30 years old. The equation is presented below. This health-protective approach is chosen to take into account the higher daily rates of soil ingestion in children as well as the longer duration of exposure that is anticipated for a long-term resident. For more on this method, see RAGS Part B.

4.2 Composite Worker Soil

This landuse is for developing industrial default screening levels that are presented in the Generic Tables.

4.2.1 Noncancer

The composite worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{w\text{-}sol\text{-}nc\text{-}ing}\ (mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\ (25\ years)\right) \times BW_{ow}\ (70\ Kg)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times \frac{1}{RfD_o\left(\frac{mg}{kg\text{-}day}\right)} \times IR_{ow}\left(100\ \frac{mg}{day}\right) \times \left(\right.}$$

inhalation of particulates emitted from soil,

$$SL_{w\text{-}sol\text{-}nc\text{-}inh}\ (mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\ (25\ yea\right.}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times ET_{ws}\left(\frac{8\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \frac{}{RfC}}$$

dermal exposure,

$$SL_{w\text{-}sol\text{-}nc\text{-}der}\ (mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\ (25\ years)\right)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times \left(\frac{1}{RfD_o\left(\frac{mg}{kg\text{-}day}\right) \times GIABS}\right) \times SA_{ow}\left(\right.}$$

Total.

$$SL_{w\text{-}sol\text{-}nc\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{w\text{-}sol\text{-}nc\text{-}ing}} + \frac{1}{SL_{w\text{-}sol\text{-}nc\text{-}der}} + \frac{1}{SL_{w\text{-}sol\text{-}nc\text{-}inh}}}$$

4.2.2 Carcinogenic

The composite worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{w\text{-}sol\text{-}ca\text{-}ing}\,(mg/kg) = \frac{TR \times AT_{ow}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times BW_{ow}\ (70\ Kg)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times CSF_{o}\left(\frac{mg}{kg\text{-}day}\right)^{-1} \times IR_{ow}\left(100\ \frac{mg}{day}\right) \times}$$

inhalation of particulates emitted from soil,

$$SL_{w\text{-}sol\text{-}ca\text{-}inh}\,(mg/kg) = \frac{TR \times AT_{ow}\left(\frac{365\ days}{year} \times LT\ (70\right.}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times ET_{ws}\left(\frac{8\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times IUR}$$

dermal exposure,

$$SL_{w\text{-}sol\text{-}ca\text{-}der}\,(mg/kg) = \frac{TR \times AT_{ow}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times BW}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{ow}\ (25\ years) \times \left(\frac{CSF_{o}\left(\frac{mg}{kg\text{-}day}\right)^{-1}}{GIABS}\right) \times SA_{ow}\left(\frac{3300}{da}\right.}$$

Total.

$$SL_{w\text{-}sol\text{-}ca\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{w\text{-}sol\text{-}ca\text{-}ing}} + \frac{1}{SL_{w\text{-}sol\text{-}ca\text{-}der}} + \frac{1}{SL_{w\text{-}sol\text{-}ca\text{-}inh}}}$$

4.3 Indoor Worker Soil

The indoor worker soil land use is not provided in the Generic Tables but SLs can be created by using the Calculator to modify the exposure parameters for the composite worker to match the equations that follow.

4.3.1 Noncancer

The indoor worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{iw\text{-}nc\text{-}ing}\ (mg/kg) = \frac{THQ \times AT_{iw}\left(\frac{365\ days}{year} \times ED_{iw}\ (25\ years)\right) \times BW_{iw}\ (70\ Kg)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{iw}\ (25\ years) \times \frac{1}{RfD_o\left(\frac{mg}{kg\text{-}day}\right)} \times IR_{iw}\left(50\ \frac{mg}{day}\right) \times \left(\frac{10^{-6}}{1\ m}\right.}$$

inhalation of particulates emitted from soil,

$$SL_{iw\text{-}nc\text{-}inh}\ (mg/kg) = \frac{THQ \times AT_{iw}\left(\frac{365\ days}{year} \times ED_{iw}\ (25\ years)\right)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{iw}\ (25\ years) \times ET_{ws}\left(\frac{8\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \frac{1}{RfC\left(\frac{mg}{}\right.}}$$

Total.

$$SL_{iw\text{-}nc\text{-}tot}\ (mg/kg) = \frac{1}{\frac{1}{SL_{iw\text{-}nc\text{-}ing}} + \frac{1}{SL_{iw\text{-}nc\text{-}inh}}}$$

4.3.2 Carcinogenic

The indoor worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{iw\text{-}ca\text{-}ing}\ (mg/kg) = \frac{TR \times AT_{iw}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times BW_{iw}\ (70\ Kg)}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{iw}\ (25\ years) \times CSF_o\left(\frac{mg}{kg\text{-}day}\right)^{-1} \times IR_{iw}\left(50\ \frac{mg}{day}\right) \times \left(\frac{10^{-6}}{1\ n}\right.}$$

inhalation of particulates emitted from soil,

$$SL_{iw\text{-}ca\text{-}inh}\ (mg/kg) = \frac{TR \times AT_{iw}\left(\frac{365\ days}{year} \times LT\ (70\ yea\right.}{EF_{iw}\left(250\ \frac{days}{year}\right) \times ED_{iw}\ (25\ years) \times ET_{ws}\left(\frac{8\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times IUR\left(\mu g/\right.}$$

Total.

$$SL_{iw\text{-}ca\text{-}tot}\ (mg/kg) = \frac{1}{\frac{1}{SL_{iw\text{-}ca\text{-}ing}} + \frac{1}{SL_{iw\text{-}ca\text{-}inh}}}$$

4.4 Outdoor Worker Soil

The outdoor worker soil land use is not provided in the Generic Tables but SLs can be created by using the Calculator to modify the exposure parameters for the composite worker to match the equations that follow.

4.4.1 Noncancer

The outdoor worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{ow\text{-}sol\text{-}nc\text{-}ing}\,(mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\,(25\ years)\right) \times BW_{ow}\,(70\ Kg)}{EF_{ow}\left(225\ \frac{days}{year}\right) \times ED_{ow}\,(25\ years) \times \frac{1}{RfD_o\left(\frac{mg}{kg\text{-}day}\right)} \times IR_{ow}\left(100\ \frac{mg}{day}\right)}$$

inhalation of particulates emitted from soil,

$$SL_{ow\text{-}sol\text{-}nc\text{-}inh}\,(mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\,(25\ ye\right.}{EF_{ow}\left(225\ \frac{days}{year}\right) \times ED_{ow}\,(25\ years) \times ET_{ws}\left(\frac{8\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \frac{}{Rf}}$$

dermal exposure,

$$SL_{ow\text{-}sol\text{-}nc\text{-}der}\,(mg/kg) = \frac{THQ \times AT_{ow}\left(\frac{365\ days}{year} \times ED_{ow}\,(25\ years\right.}{EF_{ow}\left(225\ \frac{days}{year}\right) \times ED_{ow}\,(25\ years) \times \left(\frac{1}{RfD_o\left(\frac{mg}{kg\text{-}day}\right) \times GIABS}\right) \times SA_{ow}}$$

Total.

$$SL_{ow\text{-}sol\text{-}nc\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{ow\text{-}sol\text{-}nc\text{-}ing}} + \frac{1}{SL_{ow\text{-}sol\text{-}nc\text{-}der}} + \frac{1}{SL_{ow\text{-}sol\text{-}nc\text{-}inh}}}$$

4.4.2 Carcinogenic

The outdoor worker soil land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil,

$$SL_{ow\text{-}sol\text{-}ca\text{-}ing}\left(mg/kg\right)=\frac{TR\times AT_{ow}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)\times BW_{ow}\left(70\ Kg\right)}{EF_{ow}\left(225\ \frac{days}{year}\right)\times ED_{ow}\left(25\ years\right)\times CSF_{o}\left(\frac{mg}{kg\text{-}day}\right)^{-1}\times IR_{ow}\left(100\ \frac{mg}{day}\right)}$$

inhalation of particulates emitted from soil,

$$SL_{ow\text{-}sol\text{-}ca\text{-}inh}\left(mg/kg\right)=\frac{TR\times AT_{ow}\left(\frac{365\ days}{year}\times LT\left(7\right.\right.}{EF_{ow}\left(225\ \frac{days}{year}\right)\times ED_{ow}\left(25\ years\right)\times ET_{ws}\left(\frac{8\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times IU}$$

dermal exposure,

$$SL_{ow\text{-}sol\text{-}ca\text{-}der}\left(mg/kg\right)=\frac{TR\times AT_{ow}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)\times B}{EF_{ow}\left(225\ \frac{days}{year}\right)\times ED_{ow}\left(25\ years\right)\times\left(\frac{CSF_{o}\left(\frac{mg}{kg\text{-}day}\right)^{-1}}{GIABS}\right)\times SA_{ow}\left(\frac{330}{}\right.}$$

Total.

$$SL_{ow\text{-}sol\text{-}ca\text{-}tot}\left(mg/kg\right)=\frac{1}{\frac{1}{SL_{ow\text{-}sol\text{-}ca\text{-}ing}}+\frac{1}{SL_{ow\text{-}sol\text{-}ca\text{-}der}}+\frac{1}{SL_{ow\text{-}sol\text{-}ca\text{-}inh}}}$$

4.5 Recreational Soil or Sediment

4.5.1 Noncancer

The recreational soil or sediment land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil or sediment,

$$SL_{rec\text{-}sol\text{-}nc\text{-}ing}\left(mg/kg\right)=\frac{THQ\times AT_{rec}\left(\frac{365\ days}{year}\times ED_{recsc}\left(years\right)\right)\times BW_{recsc}\left(Kg\right)}{EF_{recsc}\left(\frac{days}{year}\right)\times ED_{recsc}\left(\ years\right)\times\frac{1}{RfD_{o}\left(\frac{mg}{Kg\text{-}day}\right)}\times IRS_{recsc}\left(\frac{200\ mg}{day}\right.}$$

inhalation of particulates emitted from soil or sediment,

$$SL_{rec\text{-}sol\text{-}nc\text{-}inh}\,(mg/kg) = \frac{THQ \times AT_{rec}\left(\frac{365\ days}{year} \times ED_{recsc}\,(yea\right.}{EF_{recsc}\left(\frac{days}{year}\right) \times ED_{recsc}\,(year) \times ET_{recsc}\left(\frac{hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \frac{}{RfC}}$$

dermal contact with soil or sediment,

$$SL_{rec\text{-}sol\text{-}nc\text{-}der}\,(mg/kg) = \frac{THQ \times AT_{rec}\left(\frac{365\ days}{year} \times ED_{recsc}\,(years)\right) \times E}{EF_{recsc}\left(\frac{days}{year}\right) \times ED_{recsc}\,(year) \times \frac{1}{\left(RfD_o\left(\frac{mg}{Kg\text{-}day}\right) \times GIABS\right)} \times SA_{recsc}}$$

Total.

$$SL_{rec\text{-}sol\text{-}nc\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{rec\text{-}sol\text{-}nc\text{-}ing}} + \frac{1}{SL_{rec\text{-}sol\text{-}nc\text{-}der}} + \frac{1}{SL_{rec\text{-}sol\text{-}nc\text{-}inh}}}$$

4.5.2 Carcinogenic

The recreational soil or sediment land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil or sediment,

$$SL_{rec\text{-}sol\text{-}ca\text{-}ing}\,(mg/kg) = \frac{TR \times AT_{rec}\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times IFS_{adj}\left(\frac{mg}{Kg}\right) \times \left(\frac{10^{-6}Kg}{mg}\right)}$$

where:

$$IFS_{rec\text{-}adj}\left(\frac{mg}{Kg}\right) = \frac{ED_{recsc}\,(years) \times EF_{recsc}\left(\frac{days}{year}\right) \times IRS_{recsc}\left(\frac{200\ mg}{day}\right)}{BW_{recsc}\,(Kg)} + \frac{ED_{recsa}\,(years) \times EF_r}{E}$$

inhalation of particulates emitted from soil or sediment,

$$SL_{rec\text{-}sol\text{-}ca\text{-}inh}\,(mg/kg) = \frac{TR \times AT_{rec}\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}{IUR\left(\mu g/m^3\right)^{-1} \times \left(\frac{1000\ \mu g}{mg}\right) \times EF_{recs}\left(\frac{days}{year}\right) \times \left(\frac{1}{VF_s\left(\frac{m^3}{Kg}\right)} + \frac{1}{PEF_w\left(\frac{m^3}{Kg}\right)}\right)}$$

$$ED_{recs}\,(years) \times ET_{recs}\left(\frac{hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right)$$

dermal contact with soil or sediment,

$$SL_{rec\text{-}sol\text{-}ca\text{-}der}\left(mg/kg\right)=\frac{TR\times AT_{rec}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{\left(\frac{CSF_{o}\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right)\times DFS_{adj}\left(\frac{mg}{Kg}\right)\times ABS_{d}\times\left(\frac{10^{-6}Kg}{mg}\right)}$$

where:

$$DFS_{rec\text{-}adj}\left(\frac{mg}{Kg}\right)=\frac{ED_{recsc}\left(\ years\right)\times EF_{recsc}\left(\frac{days}{year}\right)\times SA_{recsc}\left(\frac{cm^{2}}{day}\right)\times AF_{recsc}\left(\frac{mg}{cm^{2}}\right)}{BW_{recsc}\left(Kg\right)}+\frac{ED_{rec}}{}$$

Total.

$$SL_{rec\text{-}sol\text{-}ca\text{-}tot}\left(mg/kg\right)=\frac{1}{\frac{1}{SL_{rec\text{-}sol\text{-}ca\text{-}ing}}+\frac{1}{SL_{rec\text{-}sol\text{-}ca\text{-}der}}+\frac{1}{SL_{rec\text{-}sol\text{-}ca\text{-}inh}}}$$

4.5.3 Mutagenic

The recreational soil or sediment land use equation, presented here, contains the following exposure routes:

incidental ingestion of soil or sediment,

$$SL_{rec\text{-}sol\text{-}mu\text{-}ing}\left(mg/kg\right)=\frac{TR\times AT_{rec}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{CSF_{o}\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times IFSM_{adj}\left(\frac{mg}{Kg}\right)\times\left(\frac{10^{-6}Kg}{mg}\right)}$$

where:

$$IFSM_{rec\text{-}adj}\left(\frac{mg}{Kg}\right)=\frac{ED_{0\text{-}2}\left(yr\right)\times EF_{0\text{-}2}\left(\frac{days}{year}\right)\times IRS_{0\text{-}2}\left(\frac{200\ mg}{day}\right)\times 10}{BW_{0\text{-}2}\left(Kg\right)}+\frac{ED_{2\text{-}6}\left(yr\right)\times EF_{2\text{-}6}\left(\right.}{B}$$

$$\frac{ED_{6\text{-}16}\left(yr\right)\times EF_{6\text{-}16}\left(\frac{days}{year}\right)\times IRS_{6\text{-}16}\left(\frac{100\ mg}{day}\right)\times 3}{BW_{6\text{-}16}\left(Kg\right)}+\frac{ED_{16\text{-}30}\left(yr\right)\times EF_{16}}{}$$

inhalation of particulates emitted from soil or sediment,

$$SL_{rec\text{-}sol\text{-}mu\text{-}inh}\,(mg/kg) = \frac{TR \times AT_{rec}\left(\frac{365\ da}{year}\right.}{\left(\frac{1\ day}{24\ hours}\right) \times \left(\frac{1000\ \mu g}{mg}\right) \times \left(\frac{1}{VF_s\left(\frac{m^3}{Kg}\right)} + \frac{1}{PEF_w\left(\frac{m^3}{Kg}\right)}\right) \times \left(\left(ED_{0\text{-}2}\,(yrs) \times EF_{0\text{-}2}\left(\frac{days}{year}\right) \times ET_{0\text{-}2}\left(\frac{hours}{day}\right) \times IUR\left(\mu g/m^3\right)^{-1} \times 10\right) + \left(EI\right.\right.}$$

$$\left(ED_{6\text{-}16}\,(yrs) \times EF_{6\text{-}16}\left(\frac{days}{year}\right) \times ET_{6\text{-}16}\left(\frac{hours}{day}\right) \times IUR\left(\mu g/m^3\right)^{-1} \times 3\right) + \Big|$$

dermal contact with soil or sediment,

$$SL_{rec\text{-}sol\text{-}mu\text{-}der}\,(mg/kg) = \frac{TR \times AT_{rec}\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right) \times DFSM_{adj}\left(\frac{mg}{Kg}\right) \times ABS_d \times \left(\frac{10^{-6} Kg}{mg}\right)}$$

where:

$$DFSM_{rec\text{-}adj}\left(\frac{mg}{Kg}\right) = \frac{ED_{0\text{-}2}\,(yr) \times EF_{0\text{-}2}\left(\frac{days}{year}\right) \times AF_{0\text{-}2}\left(\frac{mg}{cm^2}\right) \times SA_{0\text{-}2}\left(\frac{cm^2}{day}\right) \times 10}{BW_{0\text{-}2}\,(Kg)} + \frac{ED_{2\text{-}6}\,(y}{}$$

$$\frac{ED_{6\text{-}16}\,(yr) \times EF_{6\text{-}16}\left(\frac{days}{year}\right) \times AF_{6\text{-}16}\left(\frac{mg}{cm^2}\right) \times SA_{6\text{-}16}\left(\frac{cm^2}{day}\right) \times 3}{BW_{6\text{-}16}\,(Kg)} + \frac{ED_{16\text{-}}}{}$$

Total.

$$SL_{rec\text{-}sol\text{-}mu\text{-}tot}\,(mg/kg) = \frac{1}{\frac{1}{SL_{rec\text{-}sol\text{-}mu\text{-}ing}} + \frac{1}{SL_{rec\text{-}sol\text{-}mu\text{-}der}} + \frac{1}{SL_{rec\text{-}sol\text{-}mu\text{-}inh}}}$$

4.5.4 Vinyl Chloride - Carcinogenic

The recreational soil or sediment land use equations, presented here, contain the following exposure routes:

incidental ingestion of soil or sediment,

$$SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}ing}\left(mg/kg\right)=\frac{TR}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times EF_{recs}\left(\frac{days}{year}\right)\times IFS_{rec\text{-}adj}\left(\frac{mg\text{-}yr}{kg\text{-}d}\right)\times\frac{10^{-6}Kg}{1\ mg}}{AT_{recs}\left(\frac{365\ days}{year}\times LT\ (70\ years)\right)}\right)+\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times IRS_{recsc}\left(\frac{200\ mg}{day}\right)\times\frac{10^{-6}Kg}{1\ mg}}{BW_{recsc}\left(kg\right)}\right)}$$

inhalation of particulates emitted from soil or sediment,

$$SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}inh}\left(mg/kg\right)=\frac{TR}{\left(\frac{IUR\left(\mu g/m^3\right)^{-1}\times EF_{recs}\left(\frac{days}{year}\right)\times ED_{recs}\left(years\right)\times ET_{recs}\left(\frac{hours}{day}\right)\times\left(\right.}{AT_{rec}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)\times VF\left(\frac{m^3}{kg}\right)}\right.\left(\frac{IUR\left(\mu g/m^3\right)^{-1}}{VF\left(\frac{m^3}{kg}\right)}\times\left(\frac{1000\ \mu g}{mg}\right)\right)}$$

dermal contact with soil or sediment,

$$SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}der}\left(mg/kg\right)=\frac{TR}{\left(\frac{\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\times EF_{recs}\left(\frac{days}{year}\right)\times DFS_{rec\text{-}adj}\left(\frac{361\ mg\text{-}yr}{kg\text{-}day}\right)\times ABS_d}{AT_{recs}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}\right.\left(\frac{\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\times SA_{recsc}\left(\frac{cm^2}{day}\right)\times AF_{recsc}\left(\frac{mg}{cm^2}\right)\times ABS\times\frac{10^{-6}Kg}{1\ mg}}{BW_{recsc}\left(kg\right)}\right.}$$

Total.

$$SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}tot}\left(mg/kg\right)=\frac{1}{\frac{1}{SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}ing}}+\frac{1}{SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}der}}+\frac{1}{SL_{rec\text{-}soil\text{-}ca\text{-}vc\text{-}inh}}}$$

A number of studies have shown that inadvertent ingestion of soil is common among children 6 years old and younger (Calabrese et al. 1989, Davis et al. 1990, Van Wijnen et al. 1990). Therefore, the dose method uses an age-adjusted soil ingestion factor that takes into account the difference in daily soil ingestion rates, body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 30 years old. The equation is presented below. This health-protective approach is chosen to take into account the higher daily rates of soil ingestion in children as well as the longer duration of exposure that is anticipated for a long-term resident. For more on this method, see RAGS Part B.

4.6 Recreational Surface Water

4.6.1 Noncarcinogenic

The surface water land use equation, presented here, contains the following exposure routes:

incidental ingestion of water,

$$SL_{rec\text{-}water\text{-}nc\text{-}ing}\left(\mu g/L\right)=\frac{THQ\times AT_{rec}\left(\frac{365\ days}{year}\times ED_{recwc}\left(years\right)\right)\times BW_{recv}}{EF_{recwc}\left(\frac{days}{year}\right)\times ED_{recwc}\left(years\right)\times\frac{1}{RfD_{o}\left(\frac{mg}{kg\text{-}d}\right)}\times IRW_{recwc}\left(\frac{0.05\ L}{hr}\right.}$$

dermal,

FOR INORGANICS:

$$SL_{rec\text{-}water\text{-}nc\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{ug}{cm^2\text{-}event}\right) \times \left(\frac{1000\ cm^3}{L}\right)}{K_p\left(\frac{cm}{hr}\right) \times ET_{recwc}\left(\frac{hours}{event}\right)}$$

FOR ORGANICS:

$$\text{IF } ET_{recwc}\left(\frac{hours}{event}\right) \le t^*\ (hr)\text{, then } SL_{rec\text{-}water\text{-}nc\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{ug}{cm^2\text{-}ev}\right.}{2 \times FA \times K_p\left(\frac{cm}{hr}\right) \sqrt{\frac{6 \times \tau_{ever}}{}}}$$

or,

$$\text{IF } ET_{recwc}\left(\frac{hours}{event}\right) > t^*\ (hr)\text{, then } SL_{rec\text{-}water\text{-}nc\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{}{c}\right.}{FA \times K_p\left(\frac{cm}{hr}\right) \times \left[\frac{ET_{recwc}\left(\frac{ho}{ev}\right.}{1+B}\right.}$$

where:

$$DA_{event}\left(\frac{ug}{cm^2\text{-}event}\right) = \frac{THQ \times AT_{recw}\left(\frac{365\ days}{year} \times ED_{recwc}\ (years)\right) \times \left(\frac{1000\ \mu}{mg}\right.}{\left(\frac{1}{RfD_o\left(\frac{mg}{Kg\text{-}day}\right) \times GIABS}\right) \times EV_{recwc}\left(\frac{events}{day}\right) \times ED_{recwc}\ (years) \times E}$$

Total.

$$SL_{rec\text{-}water\text{-}nc\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{rec\text{-}water\text{-}nc\text{-}ing}} + \frac{1}{SL_{rec\text{-}water\text{-}nc\text{-}der}}}$$

4.6.2 Carcinogenic

The surface water land use equation, presented here, contains the following exposure routes:

incidental ingestion of water,

$$SL_{rec\text{-}water\text{-}ca\text{-}ing}\left(\mu g/L\right)=\frac{TR\times AT_{recw}\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)\times\left(\frac{1000\ \mu g}{mg}\right)}{CSF_{o}\left(\frac{mg}{kg\text{-}day}\right)^{-1}\times IFW_{adj}\left(\frac{L}{Kg}\right)}$$

where:

$$IFW_{adj}\left(\frac{L}{Kg}\right)=\frac{EV_{recwc}\left(\frac{events}{day}\right)\times ED_{recwc}\left(years\right)\times EF_{recwc}\left(\frac{days}{year}\right)\times ET_{recwc}\left(\right.}{BW_{recwc}\left(Kg\right)}$$

$$\frac{EV_{recwa}\left(\frac{events}{day}\right)\times ED_{recwa}\left(years\right)\times EF_{recwa}\left(\frac{days}{year}\right)\times ET_{recwa}\left(\right.}{BW_{recwa}\left(Kg\right)}$$

dermal,

FOR INORGANICS:

$$SL_{rec\text{-}water\text{-}ca\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{ug}{cm^2\text{-}event}\right) \times \left(\frac{1000\ cm^3}{L}\right)}{K_p\left(\frac{cm}{hr}\right) \times ET_{recw\text{-}adj}\left(\frac{hours}{event}\right)}$$

FOR ORGANICS:

$$\text{IF } ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) \le t^*\ (hr), \text{then } SL_{rec\text{-}water\text{-}ca\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{u}{cm^2\text{-}e}\right.}{2 \times FA \times K_p\left(\frac{cm}{hr}\right)\sqrt{\frac{6 \times \tau_{ever}}{}}}$$

or,

$$\text{IF } ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) > t^*\ (hr), \text{then } SL_{rec\text{-}water\text{-}ca\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\right.}{FA \times K_p\left(\frac{cm}{hr}\right) \times \left[\frac{ET_{recw\text{-}adj}\left(\right.}{1+B}\right.}$$

where:

$$DA_{event}\left(\frac{ug}{cm^2\text{-}event}\right) = \frac{TR \times AT_{recw}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right) \times DFW_{adj}\left(\frac{cm^2\text{-}event}{kg}\right)}$$

where :

$$DFW_{adj}\left(\frac{cm^2\text{-}event}{kg}\right) = \frac{EV_{recwc}\left(\frac{events}{day}\right) \times ED_{recwc}\ (years) \times EF_{recwc}\left(\frac{days}{year}\right) \times SA_{recwc}\ (cm}{BW_{recwc}\ (Kg)}$$

$$\frac{EV_{recwa}\left(\frac{events}{day}\right) \times ED_{recwa}\ (years) \times EF_{recwa}\left(\frac{days}{year}\right) \times SA_{recwa}\ (cm}{BW_{recwa}\ (Kg)}$$

and:

$$ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) = \frac{\left(ET_{recwc}\left(\frac{hours}{event}\right) \times ED_{recwc}\ (years) + ET_{recwa}\left(\frac{hours}{event}\right) \times ED_{recwa}\ (y\right.}{ED_{recwc}\ (years) + ED_{recwa}\ (years)}$$

Total.

$$SL_{rec\text{-}water\text{-}ca\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{rec\text{-}water\text{-}ca\text{-}ing}} + \frac{1}{SL_{rec\text{-}water\text{-}ca\text{-}der}}}$$

4.6.3 Mutagenic

The surface water land use equation, presented here, contains the following exposure routes:

incidental ingestion of water,

$$SL_{rec\text{-}water\text{-}mu\text{-}ing}\,(\mu g/L) = \frac{TR \times AT_{recw}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times IFWM_{rec\text{-}adj}\left(\frac{L}{Kg}\right)}$$

where:

$$IFWM_{rec\text{-}adj}\left(\frac{L}{Kg}\right) = \frac{ED_{0\text{-}2}\,(yr) \times EF_{0\text{-}2}\left(\frac{days}{year}\right) \times IRW_{0\text{-}2}\left(\frac{0.05\ L}{hr}\right) \times EV_{0\text{-}2}\left(\frac{events}{day}\right) \times ET_{0\text{-}2}\left(\right.}{BW_{0\text{-}2}\,(Kg)}$$

$$\frac{ED_{2\text{-}6}\,(yr) \times EF_{2\text{-}6}\left(\frac{days}{year}\right) \times IRW_{2\text{-}6}\left(\frac{0.05\ L}{hr}\right) \times EV_{2\text{-}6}\left(\frac{events}{day}\right) \times ET_{2\text{-}6}\left(\right.}{BW_{2\text{-}6}\,(15)}$$

$$\frac{ED_{6\text{-}16}\,(yr) \times EF_{6\text{-}16}\left(\frac{days}{year}\right) \times IRW_{6\text{-}16}\left(\frac{0.05\ L}{hr}\right) \times EV_{6\text{-}16}\left(\frac{events}{day}\right) \times ET_{6}}{BW_{6\text{-}16}\,(Kg)}$$

$$\frac{ED_{16\text{-}30}\,(yr) \times EF_{16\text{-}30}\left(\frac{days}{year}\right) \times IRW_{16\text{-}30}\left(\frac{0.05\ L}{hr}\right) \times EV_{16\text{-}30}\left(\frac{events}{day}\right)}{BW_{16\text{-}30}\,(Kg)}$$

dermal,

FOR INORGANICS:

$$SL_{rec\text{-}water\text{-}mu\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{ug}{cm^2\text{-}\ event}\right) \times \left(\frac{1000\ cm^3}{L}\right)}{K_p\left(\frac{cm}{hr}\right) \times ET_{recw\text{-}madj}\left(\frac{hours}{event}\right)}$$

FOR ORGANICS:

$$\text{IF } ET_{recw\text{-}madj}\left(\frac{hours}{event}\right) \le t^*\ (hr), \text{then } SL_{rec\text{-}water\text{-}mu\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{}{cm^2\text{-}}\right.}{2 \times FA \times K_p\left(\frac{cm}{hr}\right)\sqrt{\frac{6 \times \tau_{ev}}{}}}$$

or,

$$\text{IF } ET_{recw\text{-}madj}\left(\frac{hours}{event}\right) > t^*\ (hr), \text{then } SL_{rec\text{-}water\text{-}mu\text{-}der}\ (\mu g/L) = \frac{DA_{even}}{FA \times K_p\left(\frac{cm}{hr}\right) \times \left[\frac{ET_{recw\text{-}ma}}{1+}\right.}$$

where:

$$DA_{event}\left(\frac{ug}{cm^2\text{-}\ event}\right) = \frac{TR \times AT_{recw}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right) \times DFWM_{rec\text{-}adj}\left(\frac{events\text{-}\ cm^2}{kg}\right)}$$

$$where:\ DFWM_{rec\text{-}adj}\left(\frac{events\text{-}\ cm^2}{kg}\right) = \left[\begin{array}{l} \left(\frac{EV_{recw\ 0\text{-}2}\left(\frac{events}{day}\right) \times ED_{0\text{-}2}\ (years}{BV}\right. \\ \left(\frac{EV_{recw\ 2\text{-}6}\left(\frac{events}{day}\right) \times ED_{2\text{-}6}\ (years}{BV}\right. \\ \left(\frac{EV_{recw\ 6\text{-}16}\left(\frac{events}{day}\right) \times ED_{6\text{-}16}\ (ye}{B}\right. \\ \left(\frac{EV_{recw\ 16\text{-}30}\left(\frac{events}{day}\right) \times ED_{16\text{-}30}\ (}{}\right. \end{array}\right.$$

and:

$$ET_{recw\text{-}madj}\left(\frac{hours}{event}\right) = \frac{\left(\begin{array}{l} ET_{recw\,0\text{-}2}\left(\frac{hours}{event}\right) \times ED_{0\text{-}2}\,(years) + ET_{recw\,2\text{-}6}\left(\frac{hours}{event}\right) \times ED_{2\text{-}6} \\ ET_{recw\,6\text{-}16}\left(\frac{hours}{event}\right) \times ED_{6\text{-}16}\,(years) + ET_{recw\,16\text{-}30}\left(\frac{hours}{event}\right) \times ED \end{array}\right)}{ED_{0\text{-}2}\,(years) + ED_{2\text{-}6}\,(years) + ED_{6\text{-}16}\,(years) + ED_{16\text{-}3}}$$

Total.

$$SL_{rec\text{-}water\text{-}mu\text{-}tot}\,(\mu g/L) = \frac{1}{\frac{1}{SL_{rec\text{-}water\text{-}mu\text{-}ing}} + \frac{1}{SL_{rec\text{-}water\text{-}mu\text{-}der}}}$$

4.6.4 Vinyl Chloride - Carcinogenic

The surface water land use equation, presented here, contains the following exposure routes:

incidental ingestion of water,

$$SL_{rec\text{-}water\text{-}ca\text{-}vc\text{-}ing}\,(\mu g/L) = \frac{TR}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times IFW_{rec\text{-}adj}\left(\frac{L}{Kg}\right) \times \left(\frac{mg}{1000\ \mu g}\right)}{AT_{rec}\left(\frac{365\ days}{year} \times LT\,(70\ years)\right)}\right) + \left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times ET_{recwc}\left(\frac{hr}{day}\right) \times IRW_{recwc}\,\frac{0.05\ L}{hr} \times \left(\frac{mg}{1000\ \mu g}\right)}{BW_{recwc}\,(kg)}\right)}$$

where:

$$IFW_{rec\text{-}adj}\left(\frac{L}{Kg}\right) = \frac{EV_{recwc}\left(\frac{events}{day}\right) \times ED_{recwc}\,(years) \times EF_{recwc}\left(\frac{days}{year}\right) \times ET_{recwc}}{BW_{recwc}\,(Kg)} \frac{EV_{recwa}\left(\frac{events}{day}\right) \times ED_{recwa}\,(years) \times EF_{recwa}\left(\frac{days}{year}\right) \times ET_{recwa}}{BW_{recwa}\,(Kg)}$$

dermal,

$$\text{IF } ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) \le t^{*}\ (hr), \text{then } SL_{rec\text{-}water\text{-}vc\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{ug}{cm^2\text{-}ev}\right.}{2 \times FA \times K_p\left(\frac{cm}{hr}\right)\sqrt{\frac{6 \times \tau_{event}}{}}}$$

or,

$$\text{IF } ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) > t^{*}\ (hr), \text{then } SL_{rec\text{-}water\text{-}vc\text{-}der}\ (\mu g/L) = \frac{DA_{event}\left(\frac{}{c}\right.}{FA \times K_p\left(\frac{cm}{hr}\right) \times \left[\frac{ET_{recw\text{-}adj}\left(\frac{h}{e}\right.}{1+B}\right.}$$

where:

$$DA_{event}\left(\frac{ug}{cm^2\text{-}event}\right) = \frac{TR}{\left(\frac{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}}{GIABS}\right) \times DFW_{adj}\left(\frac{cm^2\text{-}events}{kg}\right)}{AT_{recw}\left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}\right) + \left(\frac{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)}{GIABS}\right.}{E}\right.}$$

where:

$$DFW_{adj}\left(\frac{cm^2\text{-}event}{kg}\right) = \frac{EV_{recwc}\left(\frac{events}{day}\right) \times ED_{recwc}\ (years) \times EF_{recwc}\left(\frac{days}{year}\right) \times SA_c\left(cm^2\right)}{BW_c\ (Kg)} + \cdots$$

and:

$$ET_{recw\text{-}adj}\left(\frac{hours}{event}\right) = \frac{\left(ET_{recwc}\left(\frac{hours}{event}\right) \times ED_{recwc}\ (years)\right) + \left(ET_{recwa}\left(\frac{hours}{event}\right) \times ED_{recwa}\ (y\right.}{ED_{recwc}\ (years) + ED_{recwa}\ (years)}$$

Total.

$$SL_{rec\text{-}water\text{-}ca\text{-}vc\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{rec\text{-}water\text{-}ca\text{-}vc\text{-}ing}} + \frac{1}{SL_{rec\text{-}water\text{-}ca\text{-}vc\text{-}der}}}$$

4.7 Tapwater

The Tapwater calculations do not include the dermal exposure route. It was determined that too many analytes were outside of the EPA Superfund Dermal Risk Assessment Guidance (RAGS Part E)'s Effective Predictive Domain (EPD) to include a dermal permeability constant

(Kp). Some of these were significant analytes, such as persistent chlorinated organics, including PCBs. Kp can be determined from the molecular weight and the logKow for organic compounds. Compounds with very high log Kows are outside of the EPD. Section 3.1.2 of RAGS Part E provides more detail.

4.7.1 Noncarcinogenic

The tapwater land use equation, presented here, contains the following exposure routes:

ingestion of water,

$$SL_{water\text{-}nc\text{-}ing}\ (\mu g/L) = \frac{THQ \times AT_r \left(\frac{365\ days}{year} \times ED_r\ (30\ years)\right) \times BW_a\ (70\ Kg) \times \left(\frac{1000\ \mu g}{mg}\right)}{EF_r \left(350\ \frac{days}{year}\right) \times ED_r\ (30\ years) \times \frac{1}{RfD_o \left(\frac{mg}{kg\text{-}d}\right)} \times IRW_a \left(\frac{2\ L}{day}\right)}$$

inhalation of volatiles,

$$SL_{water\text{-}nc\text{-}inh}\ (\mu g/L) = \frac{THQ \times AT_r \left(\frac{365\ days}{year} \times ED_r\ (30\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{EF_r \left(350\ \frac{days}{year}\right) \times ED_r\ (30\ years) \times ET_{rw} \left(\frac{24\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \frac{1}{RfC \left(\frac{mg}{\ }\right.}}$$

Total.

$$SL_{water\text{-}nc\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{water\text{-}nc\text{-}ing}} + \frac{1}{SL_{water\text{-}nc\text{-}inh}}}$$

4.7.2 Carcinogenic

The tapwater land use equation, presented here, contains the following exposure routes:

ingestion of water,

$$SL_{water\text{-}ca\text{-}ing}\ (\mu g/L) = \frac{TR \times AT_r \left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{EF_r \left(\frac{350\ days}{year}\right) \times CSF_o \left(\frac{mg}{kg\text{-}day}\right)^{-1} \times \left(IFW_{adj} \left(\frac{1.086\ L\text{-}Year}{Kg\text{-}day}\right)\right)}$$

where:

$$IFW_{adj} \left(\frac{1.086\ L\text{-}Year}{Kg\text{-}day}\right) = \frac{ED_c\ (6\ years) \times IRW_c \left(\frac{1\ L}{day}\right)}{BW_c\ (15\ Kg)} + \frac{ED_r\text{-}ED_c\ (24\ years) \times IRW_a \left(\frac{2\ L}{day}\right)}{BW_a\ (70\ Kg)}$$

inhalation of volatiles,

$$SL_{water\text{-}ca\text{-}inh}\ (\mu g/L) = \frac{TR \times AT_r \left(\frac{365\ days}{year} \times LT\ (70\ years)\right)}{EF_r \left(\frac{350\ days}{year}\right) \times ED_r\ (30\ years) \times ET_{rw} \left(\frac{24\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times IUR \left(\mu g/n\right.}$$

Total.

$$SL_{water\text{-}ca\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{water\text{-}ca\text{-}ing}} + \frac{1}{SL_{water\text{-}ca\text{-}inh}}}$$

4.7.3 Mutagenic

The tapwater land use equation, presented here, contains the following exposure routes:

ingestion of water,

$$SL_{water\text{-}mu\text{-}ing}\ (\mu g/L) = \frac{TR \times AT_r \left(\frac{365\ days}{year} \times LT\ (70\ years)\right) \times \left(\frac{1000\ \mu g}{mg}\right)}{CSF_o \left(\frac{mg}{Kg\text{-}day}\right)^{-1} \times EF_r \left(\frac{350\ days}{year}\right) \times IFWM_{adj} \left(\frac{3.39\ L\text{-}Year}{Kg\text{-}day}\right)}$$

where:

$$IFWM_{adj} \left(\frac{3.39\ L\text{-}Year}{Kg\text{-}day}\right) = \frac{ED_{0\text{-}2}\ (yr) \times IRW_c \left(\frac{1\ L}{day}\right) \times 10}{BW_c\ (15\ Kg)} + \frac{ED_{2\text{-}6}\ (yr) \times IRW_c \left(\frac{1\ L}{day}\right) \times 3}{BW_c\ (15\ Kg)} + \frac{ED_{6\text{-}16}\ (yr) \times IRW_a \left(\frac{2\ L}{day}\right) \times 3}{BW_a\ (70\ Kg)} + \frac{ED_{16\text{-}30}\ (yr) \times IRW_a \left(\frac{2\ L}{day}\right) \times 1}{BW_a\ (70\ Kg)}$$

inhalation of volatiles,

$$SL_{water\text{-}mu\text{-}inh}\ (\mu g/L) = \frac{TR \times AT_r \left(\frac{365\ days}{year} \times LT\ (70\ years)\right)}{EF_r \left(\frac{350\ days}{year}\right) \times K \left(\frac{0.5\ L}{m^3}\right) \times ET_{rw} \left(\frac{24\ hours}{day}\right) \times \left(\frac{1\ day}{24\ hours}\right) \times \left(\left(ED_{0\text{-}2}\ (yrs) \times IUR \left(\mu g/m^3\right)^{-1} \times 10\right) + \left(ED_{2\text{-}6}\ (yrs) \times IUR \left(\mu g/m^3\right)^{-1} \times 3\right) + \left(ED_{6\text{-}16}\ (yrs) \times IUR \left(\mu g/m^3\right)^{-1} \times 3\right) + \left(ED_{16\text{-}30}\ (yrs) \times IUR \left(\mu g/m^3\right)^{-1} \times 1\right)\right)}$$

Total.

$$SL_{water\text{-}mu\text{-}tot}\ (\mu g/L) = \frac{1}{\frac{1}{SL_{water\text{-}mu\text{-}ing}} + \frac{1}{SL_{water\text{-}mu\text{-}inh}}}$$

4.7.4 Vinyl Chloride - Carcinogenic

The tapwater land use equation, presented here, contains the following exposure routes:

ingestion of water,

$$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}ing}\left(\mu g/L\right)=\frac{TR}{\left(\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times EF_r\left(\frac{350\ days}{year}\right)\times IFW_{adj}\left(\frac{1.086\ L\text{-}yr}{kg\text{-}day}\right)\times\left(\frac{mg}{1000\ \mu g}\right.}{AT\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}\right.\left.\frac{CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times IRW_c\left(\frac{1\ L}{day}\right)\times\left(\frac{mg}{1000\ \mu g}\right)}{BW_c\left(15\ kg\right)}\right)+$$

inhalation of volatiles,

$$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}inh}\left(\mu g/L\right)=\frac{TR}{\left(\frac{IUR\left(\mu g/m^3\right)^{-1}\times EF\left(\frac{350\ days}{year}\right)\times ED\left(30\ years\right)\times ET_{rw}\left(\frac{24\ hours}{day}\right)\times}{AT\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}\right.\left.IUR\left(\mu g/m^3\right)^{-1}\times K\left(\frac{0.5\ L}{m^3}\right)\right)}$$

Total.

$$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}tot}\left(\mu g/L\right)=\frac{1}{\frac{1}{SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}ing}}+\frac{1}{SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}inh}}}$$

4.8 Resident Air

4.8.1 Noncarcinogenic

Thet air land use equation, presented here, contains the following exposure routes:

inhalation

$$SL_{res\text{-}air\text{-}nc}\left(\mu g/m^3\right)=\frac{THQ\times AT_r\left(\frac{365\ days}{year}\times ED_r\left(30\ years\right)\right)\times\left(\frac{1000\ \mu g}{mg}\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_r\left(30\ years\right)\times ET_{ra}\left(\frac{24\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times\frac{1}{RfC\left(mg/m\right.}}$$

4.8.2 Carcinogenic

The air land use equation, presented here, contains the following exposure routes:

inhalation

$$SL_{res\text{-}air\text{-}ca}\left(\mu g/m^3\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\ (70\ years)\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_r\ (30\ years)\times ET_{ra}\left(\frac{24\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times IUR\left(\mu g/m^3\right.}$$

4.8.3 Vinyl Chloride - Carcinogenic

The air land use equation, presented here, contains the following exposure routes:

inhalation

$$SL_{res\text{-}air\text{-}ca\text{-}vinyl\ chloride}\left(\mu g/m^3\right)=\frac{TR}{IUR\left(\mu g/m^3\right)^{-1}+\left(\frac{IUR\left(\mu g/m^3\right)^{-1}\times EF_r\left(\frac{350\ days}{year}\right)\times ED_r\ (30\ yea}{AT_r\left(\frac{365\ days}{year}\times LT\ (\right.}\right.}$$

4.8.4 Mutagenic

The air land use equation, presented here, contains the following exposure routes:

inhalation

$$SL_{res\text{-}air\text{-}mu}\left(\mu g/m^3\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\ (70\ years)\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ET_{ra}\left(\frac{24\ hours}{day}\right)\times\left(\frac{1\ day}{24\ hours}\right)\times\left(\left(ED_{0\text{-}2}\ (yrs)\times IUR\left(\mu g/m^3\right)^{-1}\times 10\right)+\left(ED_{2\text{-}6}\ (yrs)\times IUR\left(\mu g/m^3\right)^{-1}\times 3\right)+\left(ED_{6\text{-}16}\ (yrs)\times IUR\left(\mu g/m^3\right)^{-1}\times 3\right)+\left(ED_{16\text{-}30}\ (yrs)\times IUR\left(\mu g/m^3\right)^{-1}\times 1\right)\right)}$$

4.9 Worker Air

4.9.1 Noncarcinogenic

The air land use equation, presented here, contains the following exposure routes:

Inhalation

$$SL_{w\text{-}air\text{-}nc}\left(\mu g/m^3\right)=\frac{THQ\times AT_w\left(\frac{365\ days}{year}\times ED_r\left(25\ years\right)\right)\times\left(\frac{1000\ \mu g}{mg}\right)}{EF_w\left(\frac{250\ days}{year}\right)\times ED_w\left(25\ years\right)\times ET_w\left(\frac{8\ hr}{24\ hr}\right)\times\frac{1}{RfC\left(mg/m^3\right)}}$$

4.9.2 Carcinogenic

The air land use equation, presented here, contains the following exposure routes:

Inhalation

$$SL_{w\text{-}air\text{-}ca}\left(\mu g/m^3\right)=\frac{TR\times AT_w\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)}{EF_w\left(\frac{250\ days}{year}\right)\times ED_w\left(25\ years\right)\times ET_w\left(\frac{8\ hr}{24\ hr}\right)\times IUR\left(\mu g/m^3\right)^{-1}}$$

4.10 Ingestion of Fish

The ingestion of fish exposure route is not provided in the Generic Tables but SLs can be created by using the Calculator and the equations that follow:

4.10.1 Noncarcinogenic

The ingestion of fish equation, presented here, contains the following exposure route:

consumption of fish.

$$SL_{res\text{-}fsh\text{-}nc\text{-}ing}\left(mg/kg\right)=\frac{THQ\times AT_r\left(\frac{365\ days}{year}\times ED_r\left(30\ years\right)\right)\times BW_a\left(70\ Kg\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_r\left(30\ year\right)\times\frac{1}{RfD_o\left(\frac{mg}{Kg\text{-}day}\right)}\times IRF_a\left(\frac{5.4\times10^4\ mg}{day}\right)\times}$$

4.10.2 Carcinogenic

The ingestion of fish equation, presented here, contains the following exposure route:

consumption of fish.

$$SL_{res\text{-}fsh\text{-}ca\text{-}ing}\left(mg/kg\right)=\frac{TR\times AT_r\left(\frac{365\ days}{year}\times LT\left(70\ years\right)\right)\times BW_a\left(70\ Kg\right)}{EF_r\left(\frac{350\ days}{year}\right)\times ED_r\left(30\ year\right)\times CSF_o\left(\frac{mg}{Kg\text{-}day}\right)^{-1}\times IRF_a\left(\frac{5.4\times10^4\ mg}{day}\right)}$$

Note: the consumption rate for fish is not age adjusted for this land use. Also the SL calculated for fish is not for soil, like for the agricultural land uses, but is for fish tissue.

4.11 Soil to Groundwater

These equations are used to calculate screening levels in soil (SSLs) that are protective of groundwater. SSLs are either back-calculated from protective risk-based ground water concentrations or based on MCLs. The SSLs were designed for use during the early stages of a site evaluation when information about subsurface conditions may be limited. Because of this constraint, the equations used are based on conservative, simplifying assumptions about the release and transport of contaminants in the subsurface. Migration of contaminants from soil to groundwater can be envisioned as a two-stage process: (1) release of contaminant in soil leachate and (2) transport of the contaminant through the underlying soil and aquifer to a receptor well. The SSL methodology considers both of these fate and transport mechanisms.

SSLs are provided for metals in the Generic Tables based on Kds from the Soil Screening Guidance Exhibit C-4 . According to Appendix C,

> "Exhibit C-4 provides pH-specific soil-water partition coefficients (Kd) for metals. Site-specific soil pH measurements can be used to select appropriate Kd values for these metals. Where site-specific soil pH values are not available, values corresponding to a pH of 6.8 should be used."

If a metal is not listed in Exhibit C-4, Kds were taken from Baes, C. F. 1984. Kds for organic coumponds are calculated from Koc and the fraction of organic carbon in the soil (foc).Kd for metals are listed below.

Chemical	CAS	Kd	Reference
Aluminum	7429-90-5	1.50E+03	Baes, C.F. 1984
Antimony (metallic)	7440-36-0	4.50E+01	SSG 9355.4-23 July 1996
Arsenic, Inorganic	7440-38-2	2.90E+01	SSG 9355.4-23 July 1996
Barium	7440-39-3	4.10E+01	SSG 9355.4-23 July 1996
Beryllium and compounds	7440-41-7	7.90E+02	SSG 9355.4-23 July 1996
Boron And Borates Only	7440-42-8	3.00E+00	Baes, C.F. 1984
Bromate	15541-45-4	7.50E+00	Baes, C.F. 1984
Cadmium (Diet)	7440-43-9	7.50E+01	SSG 9355.4-23 July 1996
Cadmium (Water)	7440-43-9	7.50E+01	SSG 9355.4-23 July 1996
Chlorine	7782-50-5	2.50E-01	Baes, C.F. 1984
Chromium (III) (Insoluble Salts)	16065-83-1	1.80E+06	SSG 9355.4-23 July 1996
Chromium Salts	0-00-3	8.50E+02	Baes, C.F. 1984
Chromium VI (chromic acid mists)	18540-29-9	1.90E+01	SSG 9355.4-23 July 1996

Chromium VI (particulates)	18540-29-9	1.90E+01	SSG 9355.4-23 July 1996
Chromium, Total (1:6 ratio Cr VI : Cr III)	7440-47-3	1.80E+06	SSG 9355.4-23 July 1996
Cobalt	7440-48-4	4.50E+01	Baes, C.F. 1984
Copper	7440-50-8	3.50E+01	Baes, C.F. 1984
Cyanide (CN-)	57-12-5	9.90E+00	SSG 9355.4-23 July 1996
Fluorine (Soluble Fluoride)	7782-41-4	1.50E+02	Baes, C.F. 1984
Iron	7439-89-6	2.50E+01	Baes, C.F. 1984
Lead and Compounds	7439-92-1	9.00E+02	Baes, C.F. 1984
Lithium	7439-93-2	3.00E+02	Baes, C.F. 1984
Magnesium	7439-95-4	4.50E+00	Baes, C.F. 1984
Manganese (Diet)	7439-96-5	6.50E+01	Baes, C.F. 1984
Manganese (Water)	7439-96-5	6.50E+01	Baes, C.F. 1984
Mercury (elemental)	7439-97-6	5.20E+01	SSG 9355.4-23 July 1996
Mercury, Inorganic Salts	0-01-7	5.20E+01	SSG 9355.4-23 July 1996
Molybdenum	7439-98-7	2.00E+01	Baes, C.F. 1984
Nickel Soluble Salts	7440-02-0	6.50E+01	SSG 9355.4-23 July 1996
Phosphorus, White	7723-14-0	3.50E+00	Baes, C.F. 1984
Selenium	7782-49-2	5.00E+00	SSG 9355.4-23 July 1996
Silver	7440-22-4	8.30E+00	SSG 9355.4-23 July 1996
Sodium	7440-23-5	1.00E+02	Baes, C.F. 1984
Strontium, Stable	7440-24-6	3.50E+01	Baes, C.F. 1984
Thallium (Soluble Salts)	7440-28-0	7.10E+01	SSG 9355.4-23 July 1996
Thorium	0-23-2	1.50E+05	Baes, C.F. 1984
Tin	7440-31-5	2.50E+02	Baes, C.F. 1984
Titanium	7440-32-6	1.00E+03	Baes, C.F. 1984
Uranium (Soluble Salts)	0-23-8	4.50E+02	Baes, C.F. 1984
Vanadium and Compounds	0-06-6	1.00E+03	SSG 9355.4-23 July 1996
Vanadium, Metallic	7440-62-2	1.00E+03	SSG 9355.4-23 July 1996
Zinc (Metallic)	7440-66-6	6.20E+01	SSG 9355.4-23 July 1996
Zirconium	7440-67-7	3.00E+03	Baes, C.F. 1984

Because Kds vary greatly by soil type, it is highly recommended that site-specific Kds be determined and used to develop SSLs.

The more protective of the carcinogenic and noncarcinogenic SLs is selected to calculate the SSL.

4.11.1 Noncarcinogenic Tapwater Equations for SSLs

The tapwater equations, presented in Section 4.4.1, are used to calculate the noncarcinogenic SSLs for volatiles and nonvolatiles. If the contaminant is a volatile, both ingestion and inhalation exposure routes are considered. If the contaminant is not a volatile, only ingestion is considered.

4.11.2 Carcinogenic Tapwater Equations for SSLs

The tapwater equations, presented in Section 4.4.2, are used to calculate the carcinogenic SSLs for volatiles and nonvolatiles. Sections 4.4.3 and 4.4.4 present the mutagenic and vinyl chloride equations, respectively. If the contaminant is a volatile, both ingestion and inhalation exposure routes are considered. If the contaminant is not a volatile, only ingestion is considered.

4.11.3 Method 1 for SSL Determination

Method 1 employs a partitioning equation for migration to groundwater and defaults are provided. This method is used to generate the download default tables.

method 1.

$$SSL(mg/kg) = C_w\left(\frac{mg}{L}\right)\times DAF\times\left[K_d\left(\frac{L}{kg}\right)+\left(\frac{\left(\theta_w\left(\frac{L_{water}}{L_{soil}}\right)+\theta_a\left(\frac{L_{air}}{L_{soil}}\right)\times H'\right)}{\rho_b\left(\frac{1.5\ kg}{L}\right)}\right)\right]$$

where:

$$\theta_a\left(\frac{L_{air}}{L_{soil}}\right) = n\left(\frac{L_{water}}{L_{soil}}\right) - \theta_w\left(\frac{0.3\ L_{water}}{L_{soil}}\right);$$

$$n\left(\frac{L_{pore}}{L_{soil}}\right) = 1 - \left(\frac{\rho_b\left(\frac{1.5\ kg}{L}\right)}{\rho_s\left(\frac{2.65\ kg}{L}\right)}\right) \text{ and}$$

$$K_d\left(\frac{L}{kg}\right) = K_{oc}\left(\frac{L}{kg}\right)\times f_{oc}\ (0.002\ \text{unitless})$$

4.11.4 Method 2 for SSL Determination

Method 2 employs a mass-limit equation for migration to groundwater and site-specific information is required. This method can be used in the calculator portion of this website.

method 2.

$$SSL(mg/kg) = \frac{C_w\left(\frac{mg}{L}\right)\times DAF\times I\left(\frac{0.18\ m}{year}\right)\times ED\ (70\ years)}{\rho_b\left(\frac{1.5\ kg}{L}\right)\times d_s\ (m)}$$

4.11.5 Determination of the Dilution Factor

The SSL values in the download tables are based on a dilution factor of 1. If one wishes to use the calculator to calculate screening levels using the SSL guidance for a 0.5 acre source, then a dilution factor of 20 should be used. If all of the parameters needed to calculate a site -specific dilution factor are known, they may be entered.

dilution factor.

$$\text{Dilution Attenuation Factor (DAF)} = 1 + \frac{K\left(\frac{m}{year}\right)\times i\left(\frac{m}{m}\right)\times d\ (m)}{I\left(\frac{0.18\ m}{year}\right)\times L\ (m)}$$

where:

$$d\ (m) = \left(0.0112\times L^2\ (m)\right)^{0.5} + d_a\times\left[1-\exp\left(\frac{-L\ (m)\times I\left(\frac{m}{year}\right)}{K\left(\frac{m}{year}\right)\times i\left(\frac{m}{m}\right)\times d_a\ (m)}\right)\right]$$

4.12 Supporting Equations and Parameter Discussion

There are two parts of the above land use equations that require further explanation. They are the inhalation variables: the particulate emission factor (PEF) and the volatilization factor (VF).

4.12.1 Particulate Emission Factor (PEF)

Inhalation of contaminants adsorbed to respirable particles (PM10) was assessed using a default PEF equal to 1.36 x 109 m^3/kg. This equation relates the contaminant concentration in soil with the concentration of respirable particles in the air due to fugitive dust emissions from contaminated soils. The generic PEF was derived using default values that correspond to a receptor point concentration of approximately 0.76 μ/m^3. The relationship is derived by Cowherd (1985) for a rapid assessment procedure applicable to a typical hazardous waste site, where the surface contamination provides a relatively continuous and constant potential for emission over an extended period of time (e.g., years). This represents an annual average emission rate based on wind erosion that should be compared with chronic health criteria; it is not appropriate for evaluating the potential for more acute exposures. Definitions of the input variables are in Table 1.

With the exception of specific heavy metals, the PEF does not appear to significantly affect most soil screening levels. The equation forms the basis for deriving a generic PEF for the inhalation pathway. For more details regarding

specific parameters used in the PEF model, refer to Soil Screening Guidance: Technical Background Document. The use of alternate values on a specific site should be justified and presented in an Administrative Record if considered in CERCLA remedy selection.

$$PEF_W = \frac{Q}{C_W} \times \frac{3{,}600}{0.036 \times (1-V) \times (U_m/U_t)^3 \times F(x)}$$

where

$$\frac{Q}{C_W} = A \times \exp\left[\frac{(\ln A_s - B)^2}{C}\right]$$

Note: the generic PEF evaluates wind-borne emissions and does not consider dust emissions from traffic or other forms of mechanical disturbance that could lead to greater emissions than assumed here.

4.12.2 Volatilization Factor (VF)

The soil-to-air VF is used to define the relationship between the concentration of the contaminant in soil and the flux of the volatilized contaminant to air. VF is calculated from the equation below using chemical-specific properties and either site-measured or default values for soil moisture, dry bulk density, and fraction of organic carbon in soil. The Soil Screening Guidance: User's Guide describes how to develop site measured values for these parameters.

VF is only calculated for volatile organic compounds (VOCs). VOCs, for the purpose of this guidance, are chemicals with a Henry's Law constant of 1 x 10^{-5} atm-m^3/mole or greater and with a molecular weight of less than 200 g/mole.

$$VF = \frac{\frac{Q}{C_W} \times \left(3.14 \times D_A \times T\right)^{\frac{1}{2}} \times 10^{-4} \left(m^2/cm^2\right)}{2 \times \rho_b \times D_A}$$

where

$$\frac{Q}{C_W} = A \times \exp\left[\frac{(\ln A_s - B)^2}{C}\right] \text{ and}$$

$$D_A = \frac{\left[\left(\theta_a^{10/3} \times D_{ia} \times H' + \theta_w^{10/3} \times D_{iw}\right) / n^2\right]}{\rho_b \times K_d + \theta_w + \theta_a \times H'}$$

Diffusivity in Water (cm2/s)

Diffusivity in water can be calculated from the chemical's molecular weight and density, using the following correlation equation based on WATER9 (U.S. EPA, 2001):

$$D_{iw}\left(\frac{cm^2}{s}\right)=0.0001518\times\left(\frac{T\,^0C+273.16}{298.16}\right)\times\left(\frac{MW\left(\frac{g}{mol}\right)}{\rho\left(\frac{g}{cm^3}\right)}\right)^{-0.6}$$

where

T typically = 25^0 C

If density is not available,

$$D_{iw}\left(\frac{cm^2}{s}\right)=0.000222\times(MW)^{-\left(\frac{2}{3}\right)}$$

If density is not available, diffusivity in water can be calculated using the correlation equation based on U.S. EPA (1987). The value for diffusivity in water must be greater than zero. No maximum limit is enforced.

Diffusivity in Air (cm2/s).

Diffusivity in air can be calculated from the chemical's molecular weight and density, using the following correlation equation based on WATER9 (U.S. EPA, 2001):

$$D_{ia}\left(\frac{cm^2}{s}\right)=\frac{0.00229\times\left(T^{o}C+273.16\right)^{1.5}\times\sqrt{0.034+\left(\frac{1}{MW\left(\frac{g}{mol}\right)}\right)\times MW_{cor}}}{\left(\left(\frac{MW\left(\frac{g}{mol}\right)}{2.5\times\rho\left(\frac{g}{cm^3}\right)}\right)^{0.333}+1.8\right)^2}$$

where

T typically = $25^{o}C$

$MW_{cor} = \left(1-0.000015\times MW^2\right)$ If MW_{cor} is less than 0.4, then MW_{cor} is set to 0.4.

If density is not available,

$$D_{ia}\left(\frac{cm^2}{s}\right)=1.9\times\left(MW\left(\frac{g}{mol}\right)^{-\left(\frac{2}{3}\right)}\right)$$ except for dioxins use, $$D_{ia}\left(\frac{cm^2}{s}\right)=\left(\frac{154}{MW\left(\frac{g}{mol}\right)}\right)^{0.5}\times 0.068$$

If density is not available, diffusivity in air can be calculated using the correlation equation based on U.S. EPA (1987). For dioxins, diffusivity in air can be calculated from the molecular weight using the correlation equation based on EPA's Dioxin Reassessment (U.S. EPA, 2000).

5. Special Considerations

Most of the SLs are readily derived by referring to the above equations. However, there are some cases for which the standard equations do not apply and/or external adjustments to the SLs are recommended. These special case chemicals are discussed below.

5.1 Cadmium

IRIS presents an oral "water" RfD for cadmium for use in assessment of risks to water of 0.0005 mg/kg-day. IRIS also presents an oral "food" RfD for cadmium for use in assessment of risks to soil and biota of 0.001 mg/kg-day. The SLs for Cadmium are based on the oral RfD for "water", which is slightly more conservative (by a factor of 2) than the RfD for "food". Because the SLs are considered screening values, the more conservative RfD is used for cadmium. However, reasonable arguments could be made for applying an RfD for food (instead of the oral RfD for water) for some media such as soils. RAGS Part E, in Exhibit 4-1, presents a GIABS for soil of 2.5% and for water of 5%.

5.2 Lead

EPA has no consensus RfD or CSF for inorganic lead, so it is not possible to calculate SLs as we have done for other chemicals. EPA considers lead to be a special case because of the difficulty in identifying the classic "threshold" needed to develop an RfD.

EPA therefore evaluates lead exposure by using blood-lead modeling, such as the Integrated Exposure-Uptake Biokinetic Model (IEUBK). The EPA Office of Solid Waste has also released a detailed directive on risk assessment and cleanup of residential soil lead. The directive recommends that soil lead levels less than 400 mg/kg are generally safe for residential use. Above that level, the document suggests collecting data and modeling blood-lead levels with the IEUBK model. For the purposes of screening, therefore, 400 mg/kg is recommended for residential soils. For water, we suggest 15 µg/l (the EPA Action Level in water), and for air, the National Ambient Air Quality Standard.

However, caution should be used when both water and soil are being assessed. The IEUBK model shows that if the average soil concentration is 400 mg/kg, an average tap water concentration above 5 µg/L would yield more than 5% of the population above a 10 µg/dL blood-lead level. If the average tap water concentration is 15 µg/L, an average soil concentration greater than 250 mg/kg would yield more than 5% of the population above a 10 µg/dL blood-lead level.

EPA uses a second Adult Lead Model to estimate SLs for an industrial setting. This SL is intended to protect a fetus that may be carried by a pregnant female worker. It is assumed that a cleanup goal that is protective of a fetus will also afford protection for male or female adult workers. The model equations were developed to calculate cleanup goals such that the fetus of a pregnant female worker would not likely have an unsafe concentration of lead in blood.

For more information on EPA's lead models and other lead-related topics, please go to Addressing Lead at Superfund Sites.

5.3 Manganese

The IRIS RfD (0.14 mg/kg-day) includes manganese from all sources, including diet. The author of the IRIS assessment for manganese recommended that the dietary contribution from the normal U.S. diet (an upper limit of 5 mg/day) be subtracted when evaluating non-food (e.g., drinking water or soil) exposures to manganese, leading to a RfD of 0.071 mg/kg-day for non-food items. The explanatory text in IRIS further recommends using a modifying factor of 3 when calculating risks associated with non-food sources due to a number of uncertainties that are discussed in the IRIS file for manganese, leading to a RfD of 0.024 mg/kg-day. This modified RfD has been used in the derivation of some manganese screening levels for soil and water. For more information regarding the Manganese RfD, users are advised to contact the author of the IRIS assessment on Manganese.

5.4 Vanadium Compounds

The oral RfD toxicity value for Vanadium, used in this website, is derived from the IRIS oral RfD for Vanadium Pentoxide by factoring out the molecular weight (MW) of the oxide ion. Vanadium Pentoxide (V205) has a molecular weight of 181.88. The two atoms of Vanadium

contribute 56% of the MW. Vanadium Pentoxide's oral RfD of 9E-03 multiplied by 56% gives a Vanadium oral RfD of 5.04E-03.

5.5 Uranium

"Uranium Soluble Salts" uses the IRIS oral RfD of 3E-03 mg/kg-day. For the insoluble salts of Uranium, the oral RfD of 6E-04 mg/kg-day may be used from the Federal Register, Thursday December 7, 2000. Part II, Environmental Protection Agency. 40 CFR Parts 9, 141, and 142 - National Primary Drinking Water Regulations; Radionuclides; Final Rule. p 76713.

5.6 Chromium (VI)

It is recommended that valence-specific data for chromium be collected when chromium is likely to be an important contaminant at a site, and when hexavalent chromium Cr(VI) may exist. For Cr(VI), IRIS shows an air unit risk of 1.2E-2 per ($\mu g/m^3$). While the exact ratio of Cr(VI) to Cr(III) in the data used to derive the IRIS air unit risk value is not known, it is likely that both Cr(VI) and Cr(III) were present. The RSLs calculated using the IRIS air unit risk assume that the Cr(VI) to Cr(III) ratio is 1:6. Because of various sources of uncertainty, this assumption may overestimate or underestimate the risk calculated. Users are invited to review the document “Toxicological Review of Hexavalent Chromium” in support of the summary information on Cr(VI) on IRIS to determine whether they believe this ratio applies to their projects and to consider consulting with an EPA regional risk assessor.

In the RSL Table, the Cr(VI) specific value (assuming 100% Cr(VI)) is derived by multiplying the IRIS Cr(VI) value by 7. This is considered to be a health-protective assumption, and is also consistent with the State of California's interpretation of the Mancuso study that forms the basis of Cr(VI)'s estimated cancer potency.

If you are working on a chromium site, you may want to contact the appropriate regulatory officials in your region to determine what their position is on this issue.

The Maximum Contaminant Level (MCL) of 100 µg/L for "Chromium (total)", from the EPA's MCL listing is applied to the "Chromium, Total" analyte on this website.

The New Jersey Department of Environmental Protection (NJDEP) recently determined that Cr (VI) by ingestion is likely to be carcinogenic in humans. NJDEP derived a new oral cancer slope factor, based on cancer bioassays conducted by the National Toxicology Program (http://www.state.nj.us/dep/dsr/chromium/soil-cleanup-derivation.pdf). In addition, EPA’s Office of Pesticide Programs (OPP) has concluded that the weight-of-evidence supports that Cr(VI) may act through a mutagenic mode of action following administration via drinking water and has also recommended that Age-Dependent Adjustment Factors (ADAFs) be applied when assessing cancer risks from early-life exposure (< 16 years of age).

Both of these assessments are considered Tier 3 sources and were used to derive the screening levels for Cr(VI). We applied ADAFs for early life exposure via ingestion and inhalation because OPP’s proposed mutagenic mode of action for Cr(VI) occurs in all cells, regardless of type. Application of ADAFs for all exposure pathways results in more health-protective screening levels.

5.7 Aminodinitrotoluenes

The IRIS oral RfD of 2E-03 mg/kg-day for 2,4-Dinitrotoluene is used as a surrogate for 2-Amino-4,6-Dinitrotoluene and 4-Amino-2,6-Dinitrotoluene.

5.8 PCBs

Aroclor 1016 is considered "lowest risk" and assigned appropriate toxicity values. All other Aroclors are assigned the high risk toxicity values.

5.9 Xylenes

The IRIS oral RfD of 2E-01 for xylene, mixture is used as a surrogate for the 3 xylene congeners. The earlier RfD values for some xylene isomers were withdrawn from our electronic version of HEAST.

5.10 Soil Saturation Limit (Csat)

The soil saturation concentration, Csat, corresponds to the contaminant concentration in soil at which the absorptive limits of the soil particles, the solubility limits of the soil pore water, and saturation of soil pore air have been reached. Above this concentration, the soil contaminant may be present in free phase (i.e., nonaqueous phase liquids (NAPLs) for contaminants that are liquid at ambient soil temperatures and pure solid phases for compounds that are solid at ambient soil temperatures).

Equation 4-10 is used to calculate Csat for each volatile contaminant. As an update to RAGS HHEM, Part B (USEPA 1991a), this equation takes into account the amount of contaminant that is in the vapor phase in soil in addition to the amount dissolved in the soil’s pore water and sorbed to soil particles.

Chemical-specific Csat concentrations must be compared with each VF-based SL because a basic principle of the SL volatilization model is not applicable when free-phase contaminants are present. How these cases are handled depends on whether the contaminant is liquid or solid at ambient temperatures. Liquid contaminant that have a VF-based SL that exceeds the Csat concentration are set equal to Csat whereas for solids (e.g., PAHs), soil screening decisions are based on the appropriate SLs for other pathways of concern at the site (e.g., ingestion).

$$C_{sat}=\frac{S\left(\frac{mg}{L}\right)}{\rho_b\left(\frac{Kg}{L}\right)}\times\left(K_d\left(\frac{L}{Kg}\right)\times\rho_b\left(\frac{Kg}{L}\right)+\theta_w\left(\frac{L_{water}}{L_{soil}}\right)+H'\times\theta_a\left(\frac{L_{air}}{L_{soil}}\right)\right)$$

where

$$Kd=K_{oc}\left(\frac{L}{Kg}\right)\times f_{oc}\left(\frac{g}{g}\right),$$

$$\theta_a\left(\frac{L_{air}}{L_{soil}}\right)=n\left(\frac{L_{pore}}{L_{soil}}\right)-\theta_w\left(\frac{L_{water}}{L_{soil}}\right) \text{ and}$$

$$n=1-\left(\frac{\rho_b\left(\frac{Kg}{L}\right)}{\rho_s\left(\frac{Kg}{L}\right)}\right)$$

5.11 SL Theoretical Ceiling Limit

The ceiling limit of 10+5 mg/kg is equivalent to a chemical representing 10% by weight of the soil sample. At this contaminant concentration (and higher), the assumptions for soil contact may be violated (for example, soil adherence and wind-borne dispersion assumptions) due to the presence of the foreign substance itself.

5.12 Target Risk

With the exceptions described previously in Sections 5.6 and 5.7, SLs are chemical concentrations that correspond to fixed levels of risk (i.e., either a one-in-one million [10^{-6}] cancer risk or a noncarcinogenic hazard quotient of 1) in soil, air, and water. In most cases, where a substance causes both cancer and noncancer (systemic) effects, the 10^{-6} cancer risk will result in a more stringent criteria and consequently this value is presented in the printed copy of the Table. SL concentrations that equate to a 10^{-6} cancer risk are indicated by 'ca'. SL concentrations that equate to a hazard quotient of 1 for noncarcinogenic concerns are indicated by 'nc'.

If the SLs are to be used for site screening, it is recommended that both cancer and noncancer-based SLs be used. Both carcinogenic and noncarcinogenic values may be obtained in the Supporting Tables.

Some users of this SL Table may plan to multiply the cancer SL concentrations by 10 or 100 to set 'action levels' for triggering remediation or to set less stringent cleanup levels for a specific site after considering non-risk-based factors such as ambient levels, detection limits, or technological feasibility. This risk management practice recognizes that there may be a range of values that may be 'acceptable' for carcinogenic risk (EPA's risk management range is one-in-a-million [10^{-6}] to one-in-ten thousand [10^{-4}]). However, this practice could lead one to overlook serious noncancer health threats and it is strongly recommended that the user consult with a toxicologist or regional risk assessor before doing this. Carcinogens are indicated by an asterisk ('*') in the SL Table where the noncancer SLs would be exceeded if the cancer value that is displayed is multiplied by 100. ('**') indicate that the noncancer values would be exceeded if the cancer SL were multiplied by 10. There is no range of

'acceptable' noncarcinogenic 'risk' for CERCLA sites. Therefore, the noncancer SLs should not be multiplied by 10 or 100 when setting final cleanup criteria. In the rare case where noncancer SLs are more stringent than cancer SLs set at one-in-one-million risk, a similar approach has been applied (e.g. 'max').

SL concentrations in the printed Table are risk-based, but for soil there are two important exceptions: (1) for several volatile chemicals, SLs may exceed the soil saturation level ('sat') and (2) SLs may exceed a non-risk based 'ceiling limit' concentration of 10^{+5} mg/kg ('max') for relatively less toxic inorganic and semivolatile contaminant. For more information on the 'sat' value in the SL Table, please see the discussion in Section 5.10. For more information on the 'max' value in the SL Table, please see the discussion in Section 5.11.

With respect to applying a 'ceiling limit' for chemicals other than volatiles, it is recognized that this is not a universally accepted approach. Some within the agency argue that all values should be risk-based to allow for scaling (for example, if the risk-based SL is set at a hazard quotient = 1.0, and the user would like to set the hazard quotient to 0.1 to take into account multiple chemicals, then this is as simple as multiplying the risk-based SL by 1/10th). If scaling is necessary, SL users can do this simply by referring to the Supporting Tables at this website where risk-based soil concentrations are presented for all chemicals.

In spite of the fact that applying a ceiling limit is not a universally accepted approach, this table applies a 'max' soil concentration to the SL Table for the following reasons:

> Risk-based SLs for some chemicals in soil exceed unity (>1,000,000 mg/kg), which is not possible.
>
> The ceiling limit of 10+5 mg/kg is equivalent to a chemical representing 10% by weight of the soil sample. At this contaminant concentration (and higher), the assumptions for soil contact may be violated (for example, soil adherence and wind-borne dispersion assumptions) due to the presence of the foreign substance itself.
>
> SLs currently do not address short-term exposures (e.g., pica children and construction workers). Although extremely high soil SLs are likely to represent relatively non-toxic chemicals, such high values may not be justified if in fact more toxicological data were available for evaluating short-term and/or acute exposures.

5.13 Screening Sites with Multiple Contaminants

The screening levels in the tables are calculated under the assumption that only one contaminant is present. Users needing to screen sites with multiple contaminants should consult with their regional risk assessors. The following sections describe how target risks can be changed to screen against multiple contaminants and how the ratio of concentration to RSL can be used to estimate total risk.

5.13.1 Adjusting Target Risk and Target Hazard Quotient

When multiple contaminants are present at a site the target hazard quotient (THQ) may be modified. The following options are among the commonly used methods to modify the THQ:

1. The calculator on this website can be used to generate SLs based on any THQ or target cancer risk (TR) deemed appropriate by the user. The THQ input to the

calculator can be modified from the default of 1. How much it should be modified is a user decision, but it could be based upon the number of contaminants being screened together. For example, if one is screening two contaminants together, then the THQ could be modified to 0.5. If ten contaminants are being screened together, then the THQ could be modified to 0.1. The above example weights each chemical equally; it is also possible to weight the chemicals unequally, as long as the total risk meets the desired goal. The decision of how to weight the chemicals is likely to be site-specific, and it is recommended that this decision be made in consultation with the regional risk assessor.

Note that when the TR or THQ is altered, the relationship between cancer-based and noncancer-based SLs may change. At certain risk levels, the cancer-based number may be more conservative; at different risk levels, the noncancer-based number may be more conservative. The data user needs to consider both cancer and noncancer endpoints.

2. Similar to the above approach of using the calculator to recalculate SLs based on non-default target levels, the values in the screening tables themselves can be addressed directly. Consistent with the above logic, although the EPA Superfund Program has not developed guidance on this, it is not uncommon that Superfund sites are screened at a THQ of 0.1. (The cancer-based SLs are already at a target risk of 1E-6 and are usually not adjusted further in this scenario.) SLs based on a THQ of 0.1 can be derived by dividing a default SL by 10. Again, note that altering the target HQ can change the relationship between cancer-based and noncancer-based screening levels; the data user needs to consider both endpoints. Additional approaches or alternatives may exist. When screening actual or potential Superfund sites, users are encouraged to consult with risk assessors in that EPA Regional Office when evaluating or screening contamination at a site with multiple contaminants to see if they may know of another approach or if they have a preference.

5.13.2 Using RSLs to Sum Risk from Multiple Contaminants

RSLs can be used to estimate the total risk from multiple contaminants at a site as part of a screening procedure used by some regions. This methodology, which does not substitute for a baseline risk assessment, is often called the “sum of the ratios” approach. A step-wise approach follows:

1. Perform an extensive records search and compile existing data.

2. Identify site contaminants in the SL Table. Record the SL concentrations for various media and note whether SL is based on cancer risk (indicated by ‘c') or noncancer hazard (indicated by 'n'). Segregate cancer SLs from non-cancer SLs and exclude (but don't eliminate) non-risk based SLs 's' or 'm'.

3. For cancer risk estimates, take the site-specific concentration (maximum or 95th percentile of the upper confidence on the mean (UCL)) and divide by the SL concentrations that are designated for cancer evaluation 'c'. Multiply this ratio by 10-6 to estimate chemical-specific risk for a reasonable maximum exposure (RME). For multiple pollutants, simply add the risk for each chemical. See equation below.

$$\text{Risk} = \left[\left(\frac{\text{conc}_x}{\text{SL}_x}\right) + \left(\frac{\text{conc}_y}{\text{SL}_y}\right) + \left(\frac{\text{conc}_z}{\text{SL}_z}\right)\right] \times 10^{-6}$$

4. For non-cancer hazard estimates, divide the concentration term by its respective non-cancer SL designated as 'n' and sum the ratios for multiple contaminants. The cumulative ratio represents a non-carcinogenic hazard index (HI). A hazard index of 1 or less is generally considered 'safe'. A ratio greater than 1 suggests further evaluation. Note that carcinogens may also have an associated non-cancer SL that is not listed in the SL Table. To obtain these values, the user should view the Supporting Tables. See equation below.

$$\text{Hazard Index} = \left[\left(\frac{\text{conc}_x}{\text{SL}_x}\right) + \left(\frac{\text{conc}_y}{\text{SL}_y}\right) + \left(\frac{\text{conc}_z}{\text{SL}_z}\right)\right]$$

5.14 Deriving Soil Gas SLs

The air SLs could apply to indoor air from, e.g., a vapor intrusion scenario. To model indoor air concentrations from other media (e.g., soil gas, groundwater), consult with regional experts in vapor intrusion.

For more information on EPA's current understanding of this emerging exposure pathway, please refer to EPA's recent draft guidance Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance) (USEPA 2002) available on the web at: http://www.epa.gov/osw/hazard/correctiveaction/eis/vapor.htm.

5.15 Mutagens

Some of the cancer causing analytes in this tool operate by a mutagenic mode of action for carcinogenesis. There is reason to surmise that some chemicals with a mutagenic mode of action, which would be expected to cause irreversible changes to DNA, would exhibit a greater effect in early-life versus later-life exposure. Cancer risk to children in the context of the U.S. Environmental Protection Agency’s cancer guidelines (U.S. EPA, 2005) includes both early-life exposures that may result in the occurrence of cancer during childhood and early-life exposures that may contribute to cancers later in life. In keeping with this guidance, separate cancer risk equations are presented for mutagens. The mutagen vinyl chloride has a unique set of equations. Consult Supplemental Guidance for Assessing Susceptibility from Early-Life Exposure to Carcinogens, EPA/630/R-03/003F, March 2005 for further information.

http://www.epa.gov/oswer/riskassessment/sghandbook/chemicals.htm provides more detailed information about which contaminants are considered carcinogenic by a mutagenic mode of action. In addition to the previous document's list of these contaminants, Chromium VI is also now considered carcinogenic by a mutagenic mode of action.

6. Using the Calculator

The Calculator can be used to generate site-specific SLs or PRGs. The calculator requires the user to make some simple selections. To use the calculator Select a landuse. Next, select

whether you want Default or Site-specific SLs. Selecting default screening levels will reproduce the results in the generic Generic Tables. Selecting Site-Specific will allow you to change exposure parameters. Now pick your analytes. To pick several in a row, depress the left mouse button and drag, then release. Or hold the Ctrl key down and select multiple analytes that are not in a row. Select the output option. Hit the retrieve button. If you selected Site-Specific, the next page allows you to change exposure parameters. Hit the retreive button. SLs are being calculated. The first table presents the input parameters that were selected. The next table contains the screening levels. This table can be too big to print. The easiest way to manage this table is to move it to a spreadsheet or a database. To copy this table, hold the left mouse key down and drag across the entire table. when done, press Ctrl c to copy. Switch to a spreadsheet and press Ctrl v to paste.

Table 1. Standard Default Factors

Symbol	Definition (units)	Default	Reference
SLs			
$SL_{res\text{-}air\text{-}ca}$	Resident Air Carcinogenic ($\mu g/m^3$)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}air\text{-}ca\text{-}vinyl\ chloride}$	Resident Air Carcinogenic Vinyl Chloride ($\mu g/m^3$)	Vinyl Chloride-specific	Determined in this calculator
$SL_{res\text{-}air\text{-}mu}$	Resident Air Mutagenic ($\mu g/m^3$)	Mutagen-specific	Determined in this calculator
$SL_{res\text{-}air\text{-}nc}$	Resident Air Noncarcinogenic ($\mu g/m^3$)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}fsh\text{-}ca\text{-}ing}$	Resident Fish Carcinogenic (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}fsh\text{-}nc\text{-}ing}$	Resident Fish Noncarcinogenic (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}ca\text{-}ing}$	Resident Tapwater Groundwater Carcinogenic Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}ca\text{-}inh}$	Resident Tapwater Groundwater Carcinogenic Inhalation (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}ca\text{-}tot}$	Resident Tapwater Groundwater Carcinogenic Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}ing}$	Resident Tapwater Groundwater Carcinogenic Vinyl Chloride Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}inh}$	Resident Tapwater Groundwater Carcinogenic Vinyl Chloride Inhalation (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}water\text{-}ca\text{-}vc\text{-}tot}$	Resident Tapwater Groundwater Carcinogenic Vinyl Chloride Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}mu\text{-}ing}$	Resident Tapwater Groundwater Mutagenic Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}mu\text{-}inh}$	Resident Tapwater Groundwater Mutagenic Inhalation (µg/L)	Mutagen-specific	Determined in this calculator

$SL_{water\text{-}mu\text{-}tot}$	Resident Tapwater Groundwater Mutagenic Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}nc\text{-}ing}$	Resident Tapwater Groundwater Noncarcinogenic Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{water\text{-}nc\text{-}inh}$	Resident Tapwater Groundwater Noncarcinogenic Inhalation (µg/L)	Mutagen-specific	Determined in this calculator
$SL_{water\text{-}nc\text{-}tot}$	Resident Tapwater Groundwater Noncarcinogenic Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}ca\text{-}ing}$	Resident Soil Carcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}ca\text{-}der}$	Resident Soil Carcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}ca\text{-}inh}$	Resident Soil Carcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}ca\text{-}tot}$	Resident Soil Carcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}ing}$	Resident Soil Carcinogenic Vinyl Chloride Ingestion (mg/kg)	Vinyl Chloride - specific	Determined in this calculator
$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}der}$	Resident Soil Carcinogenic Vinyl Chloride Dermal (mg/kg)	Vinyl Chloride-specific	Determined in this calculator
$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}inh}$	Resident Soil Carcinogenic Vinyl Chloride Inhalation (mg/kg)	Vinyl Chloride-specific	Determined in this calculator
$SL_{res\text{-}soil\text{-}ca\text{-}vc\text{-}tot}$	Resident Soil Carcinogenic Vinyl Chloride Total (mg/kg)	Vinyl Chloride-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}mu\text{-}ing}$	Resident Soil Mutagenic Ingestion (mg/kg)	Mutagen-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}mu\text{-}der}$	Resident Soil Mutagenic Dermal (mg/kg)	Mutagen-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}mu\text{-}inh}$	Resident Soil Mutagenic Inhalation (mg/kg)	Mutagen-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}mu\text{-}tot}$	Resident Soil Mutagenic Total (mg/kg)	Mutagen-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}nc\text{-}ing}$	Resident Soil Noncarcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}nc\text{-}der}$	Resident Soil Noncarcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}nc\text{-}inh}$	Resident Soil Noncarcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{res\text{-}sol\text{-}nc\text{-}tot}$	Resident Soil Noncarcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}ca\text{-}ing}$	Composite Worker Soil Carcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}ca\text{-}der}$	Composite Worker Soil Carcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}ca\text{-}inh}$	Composite Worker Soil Carcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}ca\text{-}tot}$	Composite Worker Soil Carcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator

$SL_{w\text{-}sol\text{-}nc\text{-}ing}$	Composite Worker Soil Noncarcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}nc\text{-}der}$	Composite Worker Soil Noncarcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}nc\text{-}inh}$	Composite Worker Soil Noncarcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{w\text{-}sol\text{-}nc\text{-}tot}$	Composite Worker Soil Noncarcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}ca\text{-}ing}$	Indoor Worker Soil Carcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}ca\text{-}der}$	Indoor Worker Soil Carcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}ca\text{-}inh}$	Indoor Worker Soil Carcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}ca\text{-}tot}$	Indoor Worker Soil Carcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}nc\text{-}ing}$	Indoor Worker Soil Noncarcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}nc\text{-}der}$	Indoor Worker Soil Noncarcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}nc\text{-}inh}$	Indoor Worker Soil Noncarcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{iw\text{-}sol\text{-}nc\text{-}tot}$	Indoor Worker Soil Noncarcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}ca\text{-}ing}$	Outdoor Worker Soil Carcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}ca\text{-}der}$	Outdoor Worker Soil Carcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}ca\text{-}inh}$	Outdoor Worker Soil Carcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}ca\text{-}tot}$	Outdoor Worker Soil Carcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}nc\text{-}ing}$	Outdoor Worker Soil Noncarcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}nc\text{-}der}$	Outdoor Worker Soil Noncarcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}nc\text{-}inh}$	Outdoor Worker Soil Noncarcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{ow\text{-}sol\text{-}nc\text{-}tot}$	Outdoor Worker Soil Noncarcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}ca\text{-}ing}$	Recreator Soil Carcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator

$SL_{rec\text{-}sol\text{-}ca\text{-}der}$	Recreator Soil Carcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}ca\text{-}inh}$	Recreator Soil Carcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}ca\text{-}tot}$	Recreator Soil Carcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}nc\text{-}ing}$	Recreator Soil Noncarcinogenic Ingestion (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}nc\text{-}der}$	Recreator Soil Noncarcinogenic Dermal (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}nc\text{-}inh}$	Recreator Soil Noncarcinogenic Inhalation (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}sol\text{-}nc\text{-}tot}$	Recreator Soil Noncarcinogenic Total (mg/kg)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}ca\text{-}der}$	Recreator Surface Water Carcinogenic Dermal (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}ca\text{-}ing}$	Recreator Surface Water Carcinogenic Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}ca\text{-}tot}$	Recreator Surface Water Carcinogenic Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}vc\text{-}der}$	Recreator Surface Water Carcinogenic Vinyl Chloride Dermal (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}vc\text{-}ing}$	Recreator Surface Water Carcinogenic Vinyl Chloride Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}vc\text{-}tot}$	Recreator Surface Water Carcinogenic Vinyl Chloride Total (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}nc\text{-}der}$	Recreator Surface Water Non-Carcinogenic Dermal (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}nc\text{-}ing}$	Recreator Surface Water Non-Carcinogenic Ingestion (µg/L)	Contaminant-specific	Determined in this calculator
$SL_{rec\text{-}water\text{-}nc\text{-}tot}$	Recreator Surface Water Non-Carcinogenic Total (µg/L)	Contaminant-specific	Determined in this calculator
Toxicity Values			
RfD_o	Chronic Oral Reference Dose (mg/kg-day)	Contaminant-specific	EPA Superfund hierarchy
RfC	Chronic Inhalation Reference Concentration (mg/m^3)	Contaminant-specific	EPA Superfund hierarchy
CSF_o	Chronic oral Slope Factor $(mg/kg\text{-}day)^{-1}$	Contaminant-specific	EPA Superfund hierarchy
IUR	Chronic Inhalation Unit Risk $(\mu g/m^3)^{-1}$	Contaminant-specific	EPA Superfund hierarchy
Miscellaneous Variables			
TR	target risk	1×10^{-6}	Determined in this calculator
THQ	target hazard quotient	1	Determined in this calculator
K_p	Andelman Volatilization Factor (L/m^3)	0.5	U.S. EPA 1991b (pg. 20)

AT_r	Averaging time - resident (days/year)	365	U.S. EPA 1989 (pg. 6-23)
AT_w	Averaging time - composite worker (days/year)	365	U.S. EPA 1989 (pg. 6-23)
AT_{iw}	Averaging time - indoor worker (days/year)	365	U.S. EPA 1989 (pg. 6-23)
AT_{ow}	Averaging time - outdoor worker (days/year)	365	U.S. EPA 1989 (pg. 6-23)
AT_{rec}	Averaging time - recreator (days/year)	365	U.S. EPA 1989 (pg. 6-23)
LT	Lifetime (years)	70	U.S. EPA 1989 (pg. 6-22)
Ingestion, and Dermal Contact Rates			
IRW_c	Resident Drinking Water Ingestion Rate - Child (L/day)	1	U.S. EPA 1989 (Exhibit 6-11)
IRW_a	Resident Drinking Water Ingestion Rate - Adult (L/day)	2	U.S. EPA 1989 (Exhibit 6-11)
IFW_{adj}	Resident Drinking Water Ingestion Rate - Age-adjusted (L-year/kg-day)	1.086	Calculated using the age adjusted intake factors equation
$IFWM_{adj}$	Resident Mutagenic Drinking Water Ingestion Rate - Age-adjusted (L-year/kg-day)	3.39	Calculated using the age adjusted intake factors equation
IRS_c	Resident Soil Ingestion Rate - Child (mg/day)	200	U.S. EPA 1991a (pg. 15)
IRS_a	Resident Soil Ingestion Rate - Adult (mg/day)	100	U.S. EPA 1991a (pg. 15)
IFS_{adj}	Resident Soil Ingestion Rate - Age-adjusted (mg-year/kg-day)	114	Calculated using the age adjusted intake factors equation
$IFSM_{adj}$	Resident Mutagenic Soil Ingestion Rate - Age-adjusted (mg-year/kg-day)	489.5	Calculated using the age adjusted intake factors equation
IR_{iw}	Indoor Worker Soil Ingestion Rate (mg/day)	50	Calculated using the age adjusted intake factors equation
IR_{ow}	Outdoor Worker Soil Ingestion Rate (mg/day)	100	Calculated using the age adjusted intake factors equation
IRW_{recwc}	Recreator Surface Water Ingestion Rate - Child (L/day)		Calculated using the age adjusted intake factors equation
IRW_{recwa}	Recreator Surface Water Ingestion Rate - Adult (L/day)		Calculated using the age adjusted intake factors equation
$IFW_{rec\text{-}adj}$	Recreator Surface Water Ingestion Rate - Age-adjusted (L-year/kg-day)		Calculated using the age adjusted intake factors equation
$IRW_{0\text{-}2}$	Recreator Surface Water Ingestion Rate - Age Segment 0-2 (L/day)	0.05	U.S. EPA Region 4
$IRW_{2\text{-}6}$	Recreator Surface Water Ingestion Rate - Age Segment 2-6 (L/day)	0.05	U.S. EPA Region 4

IRW_{6-16}	Recreator Surface Water Ingestion Rate - Age Segment 6-16 (L/day)	0.05	U.S. EPA Region 4
IRW_{16-30}	Recreator Surface Water Ingestion Rate - Age Segment 16-30 (L/day)	0.05	U.S. EPA Region 4
$IFWM_{rec-adj}$	Recreator Mutagenic Surface Water Ingestion Rate - Age-adjusted (L-year/kg-day)		Calculated using the age adjusted intake factors equation
IRS_{recsc}	Recreator Soil Ingestion Rate - Child (mg/day)		Calculated using the age adjusted intake factors equation
IRS_{recsa}	Recreator Soil Ingestion Rate - Adult (mg/day)		Calculated using the age adjusted intake factors equation
$IFS_{rec-adj}$	Recreator Soil Ingestion Rate - Age-adjusted (mg-year/kg-day)		Calculated using the age adjusted intake factors equation
IRS_{0-2}	Recreator Soil Ingestion Rate - Age-segment 0-2 (mg/day)	200	U.S. EPA 1991a (pg. 15)
IRS_{2-6}	Recreator Soil Ingestion Rate - Age-segment 2-6 (mg/day)	200	U.S. EPA 1991a (pg. 15)
IRS_{6-16}	Recreator Soil Ingestion Rate - Age-segment 6-16 (mg/day)	100	U.S. EPA 1991a (pg. 15)
IRS_{16-30}	Recreator Soil Ingestion Rate - Age-segment 16-30 (mg/day)	100	U.S. EPA 1991a (pg. 15)
$IFSM_{rec-adj}$	Recreator Mutagenic Soil Ingestion Rate - Age-adjusted (mg-year/kg-day)		Calculated using the age adjusted intake factors equation
DFS_{adj}	Resident soil dermal contact factor- age-adjusted (mg-year/kg-day)	361	Calculated using the age adjusted intake factors equation
$DFSM_{adj}$	Resident Mutagenic soil dermal contact factor- age-adjusted (mg-year/kg-day)	1445	Calculated using the age adjusted intake factors equation
$DFS_{rec-adj}$	Recreator soil dermal contact factor- age-adjusted (mg-year/kg-day)		Calculated using the age adjusted intake factors equation
$DFSM_{rec-adj}$	Recreator Mutagenic soil dermal contact factor- age-adjusted (mg-year/kg-day)		Calculated using the age adjusted intake factors equation
IRF_a	Fish Ingestion Rate (mg/day)	5.4×10^4	U.S. EPA 1991a (pg. 15)
SA_c	Resident soil surface area - child (cm^2)	2800	U.S. EPA 2002 (Exhibit 1-2)
SA_a	Resident soil surface area - adult (cm^2)	5700	U.S. EPA 2002 (Exhibit 1-2)
SA_{ow}	Worker soil surface area - adult (cm^2)	3300	U.S. EPA 2002 (Exhibit 1-2)
SA_{ow}	Worker soil surface area - adult (cm^2)	3300	U.S. EPA 2002 (Exhibit 1-2)

SA_{recsc}	Recreator soil surface area - child (cm^2)		Calculated using the age adjusted intake factors equation
SA_{recsa}	Recreator soil surface area - adult (cm^2)		Calculated using the age adjusted intake factors equation
SA_{0-2}	Recreator soil surface area - age segment 0-2 (cm^2)		
SA_{2-6}	Recreator soil surface area - age segment 2-6 (cm^2)		
SA_{6-16}	Recreator soil surface area - age segment 6-16 (cm^2)		
SA_{16-30}	Recreator soil surface area - age segment 16-30 (cm^2)		
AF_c	Resident soil adherence factor - child (mg/cm^2)	0.2	U.S. EPA 2002 (Exhibit 1-2)
AF_a	Resident soil adherence factor - adult (mg/cm^2)	0.07	U.S. EPA 2002 (Exhibit 1-2)
AF_{ow}	Worker soil adherence factor - child (mg/cm^2)	0.2	U.S. EPA 2002 (Exhibit 1-2)
AF_{recsc}	Recreator soil adherence factor - child (mg/cm^2)		Calculated using the age adjusted intake factors equation
AF_{recsa}	Recreator soil adherence factor - adult (mg/cm^2)		Calculated using the age adjusted intake factors equation
AF_{0-2}	Recreator soil adherence factor - age segment 0-2 (mg/cm^2)		
AF_{2-6}	Recreator soil adherence factor - age segment 2-6 (mg/cm^2)		
AF_{6-16}	Recreator soil adherence factor - age segment 6-16 (mg/cm^2)		
AF_{16-30}	Recreator soil adherence factor - age segment 16-30 (mg/cm^2)		
BW_c	Recreator Body Weight - child (kg)		Calculated using the age adjusted intake factors equation
BW_{recsa}	Recreator Body Weight - adult (kg)		Calculated using the age adjusted intake factors equation
BW_{0-2}	Recreator Body Weight - age segment 0-2 (kg)		
BW_{2-6}	Recreator Body Weight - age segment 2-6 (kg)		
BW_{6-16}	Recreator Body Weight - age segment 6-16 (kg)		
BW_{16-30}	Recreator Body Weight - age segment 16-30 (kg)		
ABS_d	Fraction of contaminant absorbed dermally from soil (unitless)	Contaminant-specific	U.S. EPA 2004 (Exhibit 3-4)

GIABS	Fraction of contaminant absorbed in gastrointestinal tract (unitless) Note: if the GIABS is >50% then it is set to 100% for the calculation of dermal toxicity values.	Contaminant-specific	U.S. EPA 2004 (Exhibit 4-1)
Exposure Frequency, Exposure Duration, and Exposure Time Variables			
EF_r	Resident Exposure Frequency (days/yr)	350	U.S. EPA 1991a (pg. 15)
EF_{iw}	Indoor Worker Exposure Frequency (days/yr)	250	U.S. EPA 1991a (pg. 15)
EF_{ow}	Outdoor Worker Exposure Frequency (days/yr)	225	U.S. EPA 1991a (pg. 15)
EF_{rec}	Recreator Exposure Frequency (days/yr)		Calculated using the age adjusted intake factors equation
EF_{recwc}	Recreator Exposure Frequency - child (days/yr)		Calculated using the age adjusted intake factors equation
EF_{recwa}	Recreator Exposure Frequency - adult (days/yr)		Calculated using the age adjusted intake factors equation
EF_{0-2}	Recreator Exposure Frequency - age segment 0-2 (days/yr)		
EF_{2-6}	Recreator Exposure Frequency - age segment 2-6 (days/yr)		
EF_{6-16}	Recreator Exposure Frequency - age segment 6-16 (days/yr)		
EF_{16-30}	Recreator Exposure Frequency - age segment 16-30 (days/yr)		
ED_r	Resident Exposure Duration (yr)	30	U.S. EPA 1991a (pg. 15)
ED_c	Resident Exposure Duration - child (yr)	6	U.S. EPA 1991a (pg. 15)
ED_a	Resident Exposure Duration - adult (yr)	24	U.S. EPA 1991a (pg. 15)
ED_{iw}	Indoor Worker Exposure Duration - (yr)	25	U.S. EPA 1991a (pg. 15)
ED_{ow}	Outdoor Worker Exposure Duration (yr)	25	U.S. EPA 1991a (pg. 15)
ED_{rec}	Recreator Exposure Duration (yr)		Calculated using the age adjusted intake factors equation
ED_{recsc}	Recreator Exposure Duration - child (yr)		Calculated using the age adjusted intake factors equation
ED_{recsa}	Recreator Exposure Duration - adult (yr)		Calculated using the age adjusted intake factors equation
ED_{0-2}	Exposure Duration - age segment 0-2 (yr)		
ED_{2-6}	Exposure Duration - age segment 2-6 (yr)		

ED_{6-16}	Exposure Duration - age segment 6-16 (yr)		
ED_{16-30}	Exposure Duration - age segment 16-30 (yr)		
ET_{ra}	Resident Ambient Air Exposure Time (hr/hr)	24	
ET_{rs}	Resident Soil Exposure Time (hr/hr)	24	
ET_{recs}	Recreator Soil Exposure Time (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{recsc}	Recreator Soil Exposure Time - child (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{recsa}	Recreator Soil Exposure Time - adult (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{recw}	Recreator Surface Water Exposure Time (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{recwc}	Recreator Surface Water Exposure Time - child (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{recwa}	Recreator Surface Water Exposure Time - adult (hr/hr)		Calculated using the age adjusted intake factors equation
ET_{0-2}	Recreator Exposure Time - age segment 0-2 (hr/hr)		
ET_{2-6}	Recreator Exposure Time - age segment 2-6 (hr/hr)		
ET_{6-16}	Recreator Exposure Time - age segment 6-16 (hr/hr)		
ET_{16-30}	Recreator Exposure Time - age segment 16-30 (hr/hr)		
$ET_{recw-adj}$	Recreator Exposure Time - age-adjusted (hr/hr)		Calculated using the age adjusted intake factors equation
EV_{recwc}	Recreator Events - child (events per day)		Calculated using the age adjusted intake factors equation
EV_{recwa}	Recreator Events - adult (events per day)		Calculated using the age adjusted intake factors equation
EV_{0-2}	Recreator Events - age segment 0-2 (events per day)		
EV_{2-6}	Recreator Events - age segment 2-6 (events per day)		
EV_{6-16}	Recreator Events - age segment 6-16 (events per day)		
EV_{16-30}	Recreator Events - age segment 16-30 (events per day)		
Soil to Groundwater SSL Factor Variables			

I	Infiltration Rate (m/year)	0.18	U.S. EPA. 1996a (pg. 31)
L	source length parallel to ground water flow (m)	site-specific	U.S. EPA. 1996a (pg. 31)
i	hydraulic gradient (m/m)	site-specific	U.S. EPA. 1996a (pg. 31)
K	aquifer hydraulic conductivity (m/year)	site-specific	U.S. EPA. 1996a (pg. 31)
θ_w	water-filled soil porosity (L_{water}/L_{soil})	0.3	U.S. EPA. 1996a (pg. 31)
θ_a	air-filled soil porosity (L_{air}/L_{soil})	$= n-\theta_w$	U.S. EPA. 1996a (pg. 31)
n	total soil porosity(L_{pore}/L_{soil})	$= 1-(\rho_b/\rho_s)$	U.S. EPA. 1996a (pg. 31)
ρ_s	soil particle density (Kg/L)	2.65	U.S. EPA. 1996a (pg. 31)
ρ_b	dry soil bulk density (kg/L)	1.5	U.S. EPA. 1996a (pg. 31)
H'	Dimensionless Henry Law Constant (unitless)	analyte-specific	EPI Suite
K_d	soil-water partition coefficient (L/kg)	$= K_{oc}*f_{oc}$ for organics	U.S. EPA. 1996a (pg. 31)
K_{oc}	soil organic carbon/water partition coefficient (L/kg)	analyte-specific	EPI Suite
f_{oc}	fraction organic carbon in soil (g/g)	0.002	U.S. EPA. 1996a (pg. 31)
d_a	aquifer thickness (m)	site-specific	U.S. EPA. 1996a (pg. 31)
d_s	depth of source (m)	site-specific	U.S. EPA. 1996a (pg. 31)
d	mixing zone depth (m)	site-specific	U.S. EPA. 1996a (pg. 31)
Particulate Emission Factor Variables			
PEF	Particulate Emission Factor - Minneapolis (m^3/kg)	1.36×10^9(region -specific)	Determined in this calculator
Q/C	Inverse of the Mean Concentration at the Center of a 0.5-Acre-Square Source (g/m^2-s per kg/m^3)	93.77 (region-specific)	Determined in this calculator
V	Fraction of Vegetative Cover (unitless)	0.5	U.S. EPA 1996a (pg. 23)
U_m	Mean Annual Wind Speed (m/s)	4.69	U.S. EPA 1996a (pg. 23)
U_t	Equivalent Threshold Value of Wind Speed at 7m (m/s)	11.32	U.S. EPA 1996a (pg. 23)
F(x)	Function Dependent on U_m/U_t (unitless)	0.194	U.S. EPA 1996a (pg. 23)
A	Dispersion constant unitless	PEF and region-specific	U.S. EPA 2002 (pg. D-6 to D-8)
A_s	Areal extent of the site or contamination (acres)	0.5 (range 0.5 to 500)	U.S. EPA 2002 (pg. D-2)

B	Dispersion constant unitless	PEF and region-specific	U.S. EPA 2002 (pg. D-6 to D-8)
C	Dispersion constant unitless	PEF and region-specific	U.S. EPA 2002 (pg. D-6 to D-8)
Volatilization Factor and Soil Saturation Limit Variables			
VF	Volatilization Factor - Los Angeles (m^3/kg)	Contaminant-specific	U.S. EPA. 1996b (pg. 24)
Q/C_w	Inverse of the Mean Concentration at the Center of a 0.5-Acre-Square Source (g/m^2-s per kg/m^3)	68.81	U.S. EPA. 1996b (pg. 24)
D_A	Apparent Diffusivity (cm^2/s)	Contaminant-specific	U.S. EPA. 1996b (pg. 24)
T	Exposure interval (s)	9.5×10^8	U.S. EPA. 1996b (pg. 24)
ρ_b	Dry soil bulk density (g/cm^3)	1.5	U.S. EPA. 1996b (pg. 24)
θ_a	Air-filled soil porosity (L_{air}/L_{soil}) ($n-\theta_w$)	0.28	U.S. EPA. 1996b (pg. 24)
n	Total soil porosity (L_{pore}/L_{soil}) ($1-(\rho_b/\rho_s)$)	0.43	U.S. EPA. 1996b (pg. 24)
θ_w	Water-filled soil porosity (L_{water}/L_{soil})	0.15	U.S. EPA. 1996b (pg. 24)
ρ_s	Soil particle density (g/cm^3)	2.65	U.S. EPA. 1996b (pg. 24)
S	Water Solubility Limit (mg/L)	Contaminant-specific	EPI Suite
D_{ia}	Diffusivity in air (cm^2/s)	Contaminant-specific	U.S. EPA. 2001
H'	Dimensionless Henry's Law Constant	Contaminant-specific	EPI Suite
D_{iw}	Diffusivity in water (cm^2/s)	Contaminant-specific	U.S. EPA. 2001
K_d	Soil-water partition coefficient (L/Kg) ($K_{oc}\times f_{oc}$)	Contaminant-specific	U.S. EPA. 1996b (pg. 24)
K_{oc}	Soil organic carbon-water partition coefficient (L/Kg)	Contaminant-specific	EPI Suite
f_{oc}	Organic carbon content of soil (g/g)	0.006	U.S. EPA. 1996b (pg. 24)

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U.S. EPA 2009. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment) Final. OSWER 9285.7-82. January 2009. Document, memo and website http://www.epa.gov/oswer/riskassessment/ragsf/index.htm

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APPENDIX 3

RELEVANT PORTIONS OF
USER'S GUIDE FOR THE JOHNSON AND ETTINGER (1991) MODEL FOR SUBSURFACE VAPOR INTRUSION INTO BUILDINGS

SENSITIVITY ANALYSIS OF *JOHNSON AND ETTINGER (1991) MODEL*

Hawai'i DOH
Fall 2011

Hawai'i DOH
Fall 2011

USER'S GUIDE FOR EVALUATING SUBSURFACE VAPOR INTRUSION INTO BUILDINGS

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DISCLAIMER

This document presents technical and policy recommendations based on current understanding of the phenomenon of subsurface vapor intrusion. This guidance does not impose any requirements or obligations on the U.S. Environmental Protection Agency (EPA) or on the owner/operators of sites that may be contaminated with volatile and toxic compounds. The sources of authority and requirements for addressing subsurface vapor intrusion are the applicable and relevants statutes and regulations.. This guidance addresses the assumptions and limitations that need to be considered in the evaluation of the vapor intrusion pathway. This guidance provides instructions on the use of the vapor transport model that originally was developed by P. Johnson and R. Ettinger in 1991 and subsequently modified by EPA in 1998, 2001, and again in November 2002. On November 29, 2002 EPA published Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Federal Register: November 29, 2002 Volume 67, Number 230 Page 71169-71172). This document is intended to be a companion for that guidance. Users of this guidance are reminded that the science and policies concerning vapor intrusion are complex and evolving.

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WHAT'S NEW IN THIS VERSION!

This revised version of the User's Guide corresponds with the release of Version 3.1 of the Johnson and Ettinger (1991) model (J&E) spreadsheets for estimating subsurface vapor intrusion into buildings. Several things have changed within the models since Version 2 was released in December 2000 and since the original version was released in September 1998. The following represent the major changes in Version 3.1 to be consistent with Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Quality from Groundwater and Soils dated November 25, 2002 as referenced below:

1. Table 1 lists the chemicals that are commonly found at contaminated sites. This list has been expanded from the list of chemicals included in Version 2 of the model. We have also applied certain criteria to determine whether it is appropriate to run the model for these contaminants. Only those contaminants for which all of the toxicological or physical chemical properties needed to make an assessment of the indoor inhalation risk are included in the spreadsheets. A chemical is considered to be sufficiently toxic if the vapor concentration of the pure component poses an incremental life time cancer risk greater than 1×10^{-6} or the noncancer hazard index is greater than 1. A chemical is considered to be sufficiently volatile if its Henry's law constant is 1×10^{-5} atm-m^3/mole or greater. The final chemical list for Version 3 includes 108 chemicals.

2. **Chemical Property Data -** The source of chemical data used in the calculation is primarily EPA's Superfund Chemical Data Matrix (SCDM) database. EPA's WATER9 database is used for chemicals not included in the SCDM database. Appendix B contains other data sources. Henry's Law value for cumene is incorrect in the above listed reference. The correct value was determined by using EPA's system performs automated reasoning in chemistry algorithms found in "Prediction of Chemical Reactivity Parameters and Physical Properties of Organic Compounds from Molecular Structure Using SPARE." EPA-2003.

3. **Toxicity Values –** EPA's Integrated Risk Information System (IRIS) is the generally preferred source of carcinogenic unit risks and non-carcinogenic reference concentrations (RfCs) for inhalation exposure.[1] The following two sources were consulted, in order of preference, when IRIS values were not available: provisional toxicity values recommended by EPA's National Center for Environmental Assessment (NCEA) and EPA's Health Effects Assessment Summary Tables (HEAST). If no inhalation toxicity data could be obtained from IRIS, NCEA, or HEAST, extrapolated unit risks and/or RfCs using toxicity data for oral exposure (cancer slope factors and/or reference doses, respectively) from these same sources

[1] U.S. EPA. 2002. Integrated Risk Information System (IRIS). http://www.epa.gov/iriswebp/iris/index.html. November.

using the same preference order were used.[2] Note that for most compounds, extrapolation from oral data introduces considerable uncertainty into the resulting inhalation value. Values obtained from inhalation studies or from pharmacokinetic modeling applied to oral doses will be less uncertain than those calculated using the equations noted in footnote 2.

IRIS currently does not include carcinogenicity data for trichloroethylene (TCE), a volatile contaminant frequently encountered at hazardous waste sites. The original carcinogenicity assessment for TCE, which was based on a health risk assessment conducted in the late 1980's, was withdrawn from IRIS in 1994. The Superfund Technical Support Center has continued to recommend use of the cancer slope factor from the withdrawn assessment, until a reassessment of the carcinogenicity of TCE is completed. In 2001, the Agency published a draft of the TCE toxicity assessment for public comment.[3] Using this guidance, TCE target concentrations for the draft vapor intrusion guidance were calculated using a cancer slope factor identified in that document, which is available on the NCEA web site. This slope factor was selected because it is based on state-of-the-art methodology. However, because this document is still undergoing review, the slope factor and the target concentrations calculated for TCE are subject to change and should be considered "provisional" values.

Toxicity databases such as IRIS are routinely updated as new information becomes available; the data included in the lookup tables are current as of December 2003. Users of these models are strongly encouraged to research the latest toxicity values for contaminants of interest from the sources noted above. In the next year, IRIS reassessments are expected for several contaminants commonly found in subsurface contamination whose inhalation toxicity values are currently based on extrapolation.

4. Assumption and Limitations

The Johnson and Ettinger (J&E) Model was developed for use as a screening level model and, consequently, is based on a number of simplifying assumptions regarding contaminant distribution and occurrence, subsurface characteristics, transport mechanisms, and building construction. The assumptions of the J&E Model as implemented in EPA's spreadsheet version are listed in Section 2.11, Section 5, and

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[2] The oral-to-inhalation extrapolations assume an adult inhalation rate (IR) of 20 m^3/day and an adult body weight (BW) of 70 kg. Unit risks (URs) were extrapolated from cancer slope factors (CSFs) using the following equation:

$$UR\ (\mu g/m^3)^{-1} = CSF\ (mg/kg/d)^{-1} * IR\ (m^3/d) * (1/BW)(kg^{-1}) * (10^{-3}\ mg/\mu g)$$

Reference concentrations (RfCs) were extrapolated from reference doses (RfDs) using the following equation:

$$RfC\ (mg/m^3) = RfD\ (mg/kg/d) * (1/IR)\ (m3/d)^{-1}\ (\ BW\ (kg)$$

[3] US EPA, Trichloroethylene Health Risk Assessment: Synthesis and Characterization – External Review Draft, Office of Research and Development, EPA/600/P-01-002A, August, 2001.

Table 12 along with an assessment of the likelihood that the assumptions can be verified through field evaluation.

5. Soil Parameters

A list of generally reasonable, yet conservative, model input parameters for selected soil and sampling related parameters are provided in Tables 7 and 8. These tables also provide the practical range, typical or mean value (if applicable), and most conservative value for these parameters. For building parameters with low uncertainty and sensitivity, only a single "fixed" value corresponding to the mean or typical value is provided in Table 9. Soil-dependent properties are provided in Table 10 for soils classified according to the US Soil Conservation Soil (SCS) system. If site soils are not classified according to the US SCS, Table 11 can be used to assist in selecting an appropriate SCS soil type corresponding to the available site lithologic information. Note that the selection of the soil texture class should be biased towards the coarsest soil type of significance, as determined by the site characterization program. These input parameters were developed considering soil-physics science, available studies of building characteristics, and expert opinion. Consequently, the input parameters listed in Tables 7 and 8 are considered default parameters for a first-tier assessment, which should in most cases provide a reasonably (but not overly) conservative estimate of the vapor intrusion attenuation factor for a site. The soil water filled porosity (θ_w) is dependent on the soil type and the default value was removed from the model set up. Users must define soil type or input a value for the porosity.

6. Building Parameters

Building Air Exchange Rate (Default Value = 0.25 hr^{-1})

Results from 22 studies for which building air exchange data are available were summarized in Hers et al. (2001). When all the data were analyzed, the 10th, 50th, and 90th percentile values were 0.21, 0.51, and 1.48 air exchanges per hour (AEH). Air exchange rates varied depending on season and climatic region. For example, for the winter season and coldest climatic area (Region 1, Great Lakes area and extreme northeast US), the 10th, 50th, and 90th percentile values were 0.11, 0.27, and 0.71 AEH. In contrast, for the winter season and warmest climatic area [Region 4 (southern California, Texas, Florida, Georgia)], the 10th, 50th, and 90th percentile values were 0.24, 0.48, and 1.13 AEH. For this guidance, a default value of 0.25 for air exchange rate was selected to represent the lower end of these distributions. The previous version of the guidance included a default value of 0.45 exchanges per hour.

Building Area and Subsurface Foundation Area (Default Value = 10 m by 10 m)

A Michigan study indicates that a 111.5 m^2 area approximately corresponds to the 10th percentile floor space area for residential single family dwellings, based on statistics compiled by the U.S. Department of Commerce (DOC) and U.S. Housing and Urban Development (HUD). The previous median value was 9.61 m x 9.61 m.

Building Mixing Height (Default Value = 2.44 m for slab-on-grade scenario; = 3.66 m for basement scenario)

The J&E Model assumes that subsurface volatiles migrating into the building are completely mixed within the building volume, which is determined by the building area and mixing height. The building mixing height will depend on a number of factors including the building height, the heating, ventilation and air conditioning (HVAC) system operation, environmental factors such as indoor-outdoor pressure differentials and wind loading, and seasonal factors. For a single-story house, the variation in mixing height can be approximated by the room height. For a multi-story house or apartment building, the mixing height will be greatest for houses with HVAC systems that result in significant air circulation (e.g., forced-air heating systems). Mixing heights will be less for houses using electrical baseboard heaters. It is likely that mixing height is, to some degree, correlated to the building air exchange rate.

There are little data available that provide for direct inference of mixing height. There are few sites, with a small number of houses where indoor air concentrations were above background, and where both measurements at ground level and the second floor were made (CDOT, Redfields, Eau Claire). Persons familiar with the data sets for these sites indicate that in most cases a fairly significant reduction in concentrations (factor of two or greater) was observed, although at one site (Eau Claire, "S" residence), the indoor TCE concentrations were similar in both the basement and second floor of the house. For the CDOT site apartments, there was an approximate five-fold reduction between the concentrations measured for the first floor and second floor units. Less mixing would be expected for an apartment because there are less cross-floor connections than for a house. The default value chosen for a basement house scenario (3.66 m) would be representative of a two-fold reduction or attenuation in vapor concentrations between floors.

Crack Width (0.1 cm) and Crack Ratio (Default Value = 0.0002 for basement house; = 0.0038 for slab-on-grade house)

The crack width and crack ratio are related. Assuming a square house and that the only crack is a continuous edge crack between the foundation slab and wall ("perimeter crack"), the crack ratio and crack width are related as follows:

$$Crack\,Ratio = \frac{4(CrackWidth / \sqrt{SubsurfaceFoundation\,Area}}{SubsurfaceFoundationArea}$$

There is little information available on crack width or crack ratio. One approach used by radon researchers is to back calculate crack ratios using a model for soil gas flow through cracks and the results of measured soil gas flow rates into a building. For example, the back-calculated values for a slab/wall edge crack based on soil gas-entry rates reported in Nazaroff (1992), Revzan et al. (1991), and Nazaroff et al. (1985) range from approximately 0.0001 to 0.001. Another possible approach is to measure crack openings although this, in practice, is difficult to do. Figley and Snodgrass (1992) present data from ten houses where edge crack measurements were made. At the eight houses where cracks were observed, the cracks' widths ranged from hairline cracks up to 5 mm wide, while the total crack length per house ranged from 2.5 m to 17.3 m. Most crack widths were less than 1 mm. The suggested defaults for crack ratio is regulatory guidance, literature and models also vary. In ASTM E1739-95, a default crack ratio of 0.01 is used. The crack ratios suggested in the VOLASOIL model (developed by the Dutch Ministry of Environment) range from 0.0001 to 0.0000001. The VOLASOIL model values correspond to values for a "good" and "bad" foundation, respectively. The crack ratio used by J&E (1991) for illustrative purposes ranged from 0.001 to 0.01. The selected default values fall within the ranges observed.

Q_{soil} (Default Value = 5 L/min)

The method used to estimate the vapor flowrate into a building (Q_{soil}) is an analytical solution for two-dimensional soil gas flow to a small horizontal drain (Nazaroff 1992) ("Perimeter Crack Model"). Use of this model can be problematic in that Q_{soil} values are sensitive to soil-air permeability and consequently a wide range in flows can be predicted.

An alternate empirical approach was selected to determine the Q_{soil} value. This new approach is based on trace tests (i.e., mass balance approach). When soil gas advection is the primary mechanism for tracer intrusion into a building, the Q_{soil} value is estimated by measuring the concentrations of a chemical tracer in indoor air, outdoor air, and in soil vapor below a building, and measuring the building ventilation rate (Hers et al. 2000a; Fischer et al. 1996; Garbesi et al. 1993; Rezvan et al. 1991; Barbesi and Sectro 1989). The Q_{soil} values measured using this technique were compared to predicted rates using the Perimeter Crack model, for sites with coarse-grained soils. The Perimeter Crack model predictions are both higher and lower than the measured values, but overall are within one order of magnitude of the measured values. Although the Q_{soil} predicted by the models and measured using field tracer tests are uncertain, the results suggest that a "typical" range for houses on coarse-grained soils is on the order of 1 to 10 L/min. A disadvantage with the tracer

test approach is that there are only limited data, and there do not appear to be any tracer studies for field sites with fine-grained soils.

Because the advective flow zone is relatively limited in extent, the soil type adjacent to the building foundation is of importance. In many cases, coarse-grained imported fill is placed below foundations, and either coarse-grained fill, or disturbed, loose fill is placed adjacent to the foundation walls. Therefore, a conservative approach for the purposes of this guidance is to assume that soil gas flow will be controlled by coarse-grained soil, and not to rely on the possible reduction in flow that would be caused by fine-grained soils near the house foundation. For these reasons, a soil gas flow rate of 5 L/min (midpoint between 1 and 10 L/min) was chosen as the input value.

7. Convenience Changes

- Default values for soil bulk densities have been added to the lookup tables for the various soil types.
- Default values for soil water-filled porosity have been updated within the lookup tables for soil properties for the various soil types.
- The chemical data list has been expanded to include 108 chemicals. Chemical physical properties were reviewed and updated where applicable to provide the user with more accurate values.
- All of the lookup functions within the models were modified to include an exact match parameter, rather than a closest match. The models would previously return data for CAS Numbers not in the lookup tables. Although the DATENTER sheet informed the user that this CAS Number was not found, it would return values on the CHEMPROPS sheet that was the closest match. This caused some confusion and therefore was changed.
- CAS number and soil type pick lists were added to the cells within the models where the user is required to provide data in a specific format. The pick lists were added to assist the user from entering data that are not an acceptable parameter.
- All models were modified to require the user to specify the soil type of each stratum. In addition, a button was added that allows the user to automatically retrieve the default values for the soil type selected. These additions were added as a convenience to the user and soil selection can be ignored should site-specific data be available.
- All models were modified to include an input for the average vapor flow rate into the building (Q_{soil}) in liters/minute (L/min). This value can be left blank and the model will calculate the value of Q_{soil} as was done in previous versions.

- All models were also modified to include a button that will reset the default value on the DATENTER sheet. This button will allow the user to clear all values and reset the default values or reset only those values that have a default value. The user is also allowed to specify whether the values should be reset for the basement or slab-on-grade scenario.

SECTION 1

INTRODUCTION TO THE VAPOR INTRUSION MODEL THEORY AND APPLICATION

Volatilization of contaminants located in subsurface soils or in groundwater, and the subsequent mass transport of these vapors into indoor spaces constitutes a potential inhalation exposure pathway, which may need to be evaluated when preparing risk assessments. Likewise, this potential indoor inhalation exposure pathway may need evaluation when estimating a risk-based soil or groundwater concentration below which associated adverse health effects are unlikely.

Johnson and Ettinger (J&E) (1991) introduced a screening-level model that incorporates both convective and diffusive mechanisms for estimating the transport of contaminant vapors emanating from either subsurface soils or groundwater into indoor spaces located directly above the source of contamination. In their article, J&E reported that the results of the model were in qualitative agreement with published experimental case histories and in good qualitative and quantitative agreement with detailed three-dimensional numerical modeling of radon transport into houses.

The J&E Model is a one-dimensional analytical solution to convective and diffusive vapor transport into indoor spaces and provides an estimated attenuation coefficient that relates the vapor concentration in the indoor space to the vapor concentration at the source of contamination. The model is constructed as both a steady-state solution to vapor transport (infinite or non-diminishing source) and as a quasi-steady-state solution (finite or diminishing source). Inputs to the model include chemical properties of the contaminant, saturated and unsaturated zone soil properties, and structural properties of the building.

This manual provides documentation and instructions for using the vapor intrusion model as provided in the accompanying spreadsheets.

Model results (both screening and advanced) are provided as either a risk-based soil or groundwater concentration, or as an estimate of the actual incremental risks associated with a user-defined initial concentration. That is to say that the model will reverse-calculate an “acceptable” soil or groundwater concentration given a user-defined risk level (i.e., target risk level or target hazard quotient), or the model may be used to forward-calculate an incremental cancer risk or hazard quotient based on an initial soil or groundwater concentration.

The infinite source models for soil contamination and groundwater contamination should be used as first-tier screening tools. In these models, all but the most sensitive model parameters have

been set equal to central tendency or upper bound values. Values for the most sensitive parameters may be user-defined.

More rigorous estimates may be obtained using site-specific data and the finite source model for soil contamination. Because the source of groundwater contamination may be located upgradient of the enclosed structure for which the indoor inhalation pathway is to be assessed, the advanced model for contaminated groundwater is based on an infinite source of contamination, however, site-specific values for all other model parameters may be user-defined.

In addition to the finite and infinite source models referred to above, two models that allow the user to input empirical soil gas concentration and sampling depth information directly into the spreadsheets. These models will subsequently estimate the resulting steady-state indoor air concentrations and associated health risks.

Because of the paucity of empirical data available for either bench-scale or field-scale verification of the accuracy of these models, as well as for other vapor intrusion models, the user is advised to consider the variation in input parameters and to explore and quantify the impacts of assumptions on the uncertainty of model results. At a minimum, a range of results should be generated based on variation of the most sensitive model parameters.

SECTION 2

MODEL THEORY

Chemical fate and transport within soils and between the soil column and enclosed spaces are determined by a number of physical and chemical processes. This section presents the theoretical framework on which the J&E Model is based, taking into account the most significant of these processes. In addition, this section also presents the theoretical basis for estimating values for some of the most sensitive model parameters when empirical field data are lacking. The fundamental theoretical development of this model was performed by J&E (1991).

2.1 MODEL SETTING

Consider a contaminant vapor source (C_{source}) located some distance (L_T) below the floor of an enclosed building constructed with a basement or constructed slab-on-grade. The source of contamination is either a soil-incorporated volatile contaminant or a volatile contaminant in solution with groundwater below the top of the water table.

Figure 1 is a simplified conceptual diagram of the scenario where the source of contamination is incorporated in soil and buried some distance below the enclosed space floor. At the top boundary of contamination, molecular diffusion moves the volatilized contaminant toward the soil surface until it reaches the zone of influence of the building. Here convective air movement within the soil column transports the vapors through cracks between the foundation and the basement slab floor. This convective sweep effect is induced by a negative pressure within the structure caused by a combination of wind effects and stack effects due to building heating and mechanical ventilation.

Figure 2 illustrates the scenario where the source of contamination is below the top of the water table. Here the contaminant must diffuse through a capillary zone immediately above the water table and through the subsequent unsaturated or vadose zone before convection transports the vapors into the structure.

The suggested minimum site characterization information for a first-tier evaluation of the vapor intrusion pathway includes: site conceptual model, nature and extent of contamination distribution, soil lithologic descriptions, groundwater concentrations, and/or possibly near source soil vapor concentrations. The number of samples and measurements needed to establish this information varies by site, and it is not possible to provide a hard and fast rule.

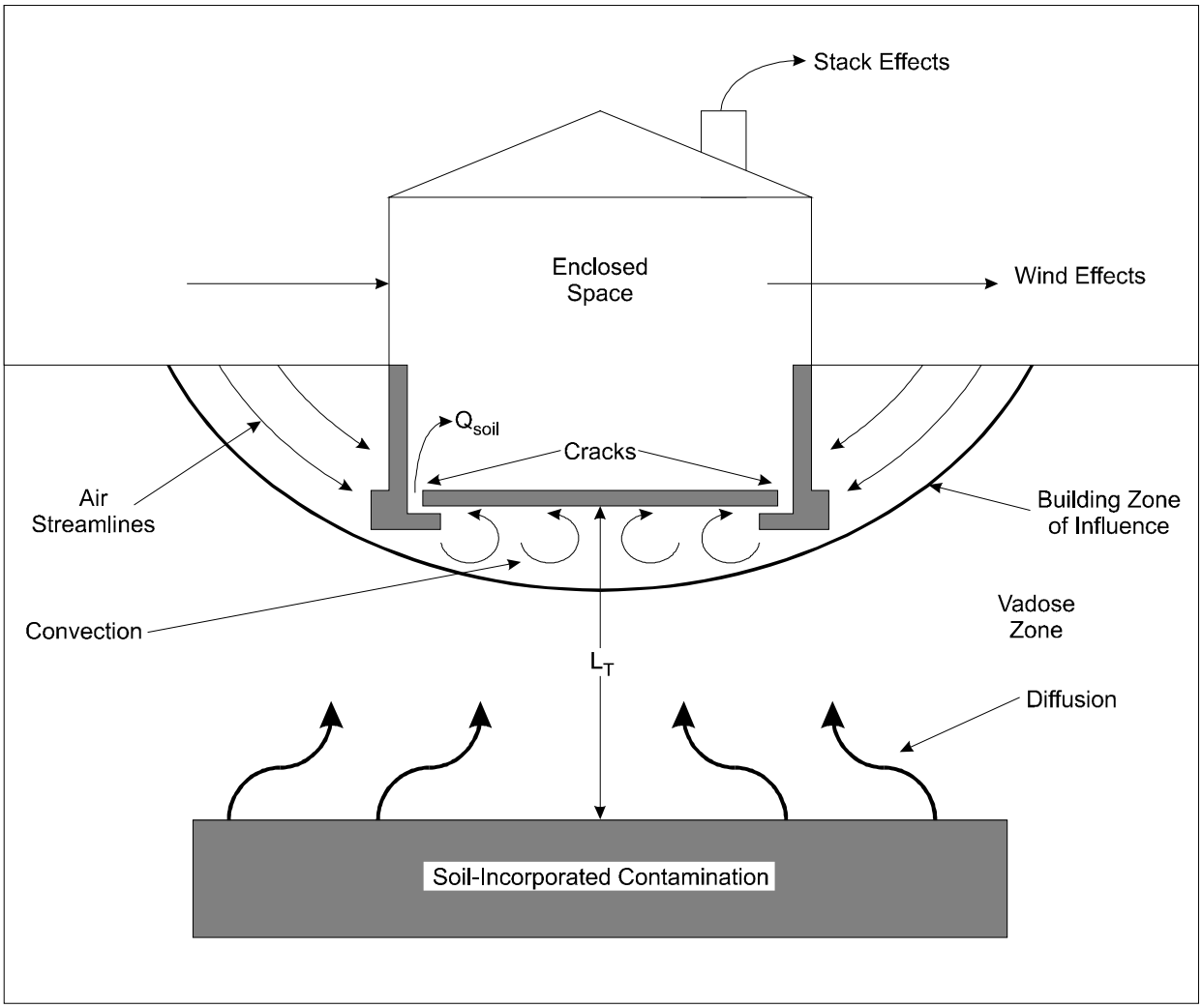


Figure 1. Pathway for Subsurface Vapor Intrusion into Indoor Air

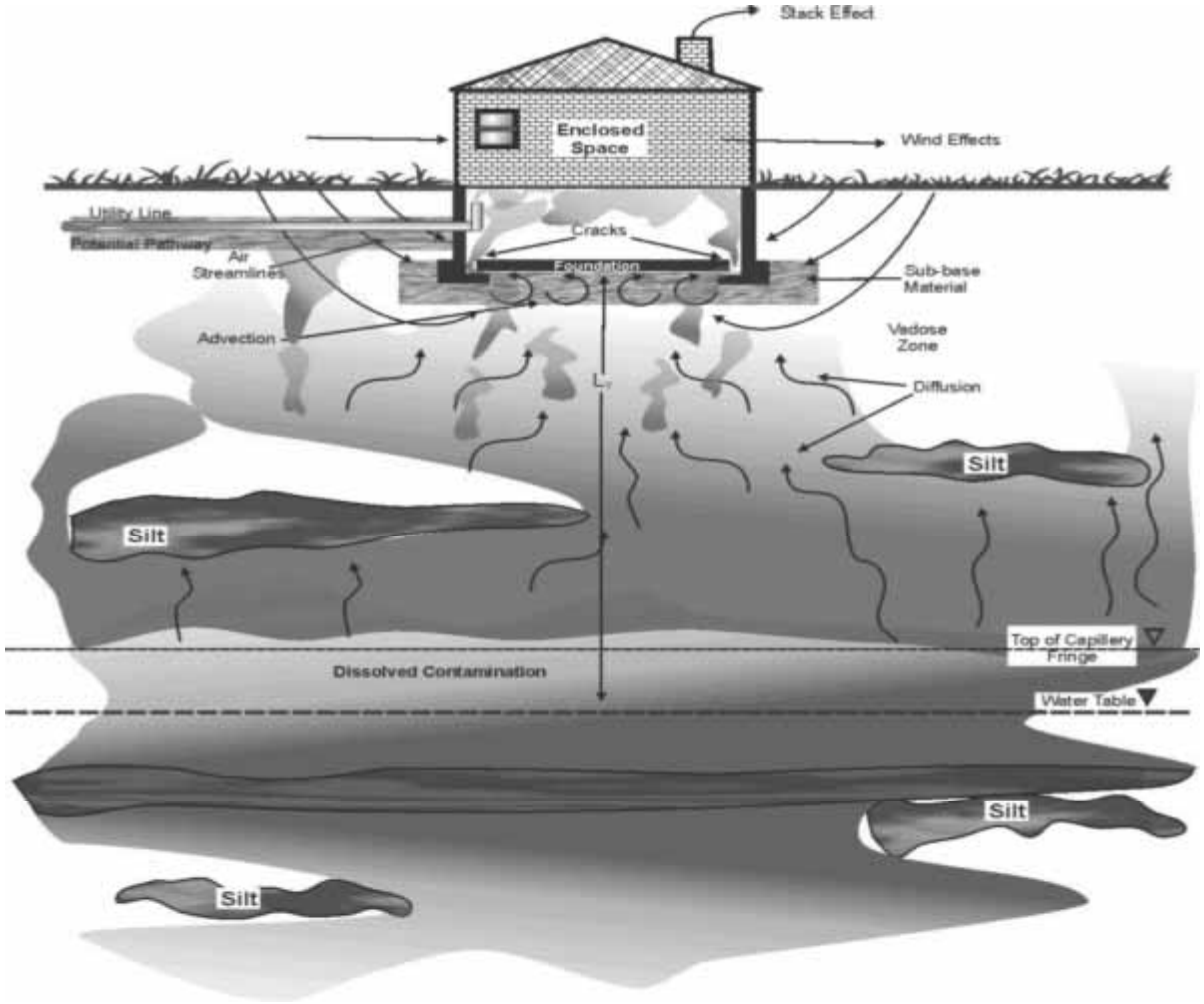


Figure 2. Vapor Pathway into Buildings

Based on the conceptual site model, the user can select the appropriate spreadsheet corresponding to the vapor source at the site and determine whether to use the screening level spreadsheet (which accommodates only one soil type above the capillary fringe) or the more advanced version (which allows up to three layers above the capillary fringe). As most of the inputs to the J&E Model are not collected during a typical site characterization, conservative inputs are typically estimated or inferred from available data and other non-site specific sources of information.

Table 1 lists 114 chemicals that may be found at hazardous waste sites and it indicates whether the chemical is sufficiently toxic and volatile to result in a potentially unacceptable indoor inhalation risk. It also provides a column for checking off the chemicals found or reasonably suspected to be present in the subsurface at a site. Under this approach, a chemical is considered sufficiently toxic if the vapor concentration of the pure component poses an incremental lifetime cancer risk greater than 10^{-6} or results in a non-cancer hazard index greater than one. A chemical is considered sufficiently volatile if its Henry's Law Constant is 1×10^{-5} atm-m^3/mol or greater (EPA, 1991). It is assumed that if a chemical does not meet both of these criteria, it need not be further considered as part of the evaluation. Table 1 also identifies six chemicals that meet the toxicity and volatility criteria but are not included in the vapor intrusion models because one or more of the needed physical or chemical properties has not been found in the literature.

The rate of soil gas entry (Q_{soil}) or average vapor flow rate into the building is a function solely of convection; however, the vapor concentration entering the structure may be limited by either convection or diffusion depending upon the magnitude of the source-building separation (L_T).

2.2 VAPOR CONCENTRATION AT THE SOURCE OF CONTAMAINATION

With a general concept of the problem under consideration, the solution begins with an estimate of the vapor concentration at the source of contamination.

In the case of soil contamination, the initial concentration (C_R) does not contain a residual-phase (e.g., nonaqueous-phase liquid or solid); and in the case of contaminated groundwater, the initial contaminant concentration (C_W) is less than the aqueous solubility limit (i.e., in solution with water).

Given these initial conditions, C_{source} for soil contamination may be estimated from Johnson et al. (1990) as:

$$C_{source} = \frac{H'_{TS}\, C_R\, \rho_b}{\theta_w + K_d \rho_b + H'_{TS}\, \theta_a} \qquad (1)$$

where C_{source} = Vapor concentration at the source of contamination, g/cm^3-v

H'_{TS} = Henry's law constant at the system (soil) temperature, dimensionless

TABLE 1. SCREENING LIST OF CHEMICALS

CAS No.	Chemical	Is Chemical Sufficiently Toxic?[1]	Is Chemical Sufficiently Volatile?[2]	Check Here if Known or Reasonably Suspected to be Present [3]
83329	Acenaphthene	YES	YES	
75070	Acetaldehyde	YES	YES	
67641	Acetone	YES	YES	
75058	Acetronitrile	YES	YES	
98862	Acetophenone	YES	YES	
107028	Acrolein	YES	YES	
107131	Acrylonitrile	YES	YES	
309002	Aldrin	YES	YES	
319846	Alpha-HCH (alpha-BHC)	YES	YES	
62533	Aniline	YES	NO	NA
120127	Anthracene	NO	YES	NA
56553	Benz(a)anthracene	YES	NO	NA
100527	Benzaldehyde	YES	YES	
71432	Benzene	YES	YES	
50328	Benzo(a)pyrene	YES	NO	NA
205992	Benzo(b)fluoranthene	YES	YES	
207089	Benzo(k)fluoranthene	NO	NO	NA
65850	Benzoic Acid	NO	NO	NA
100516	Benzyl alcohol	YES	NO	NA
100447	Benzylchloride	YES	YES	
91587	Beta-Chloronaphthalene [3]	YES	YES	
319857	Beta-HCH(beta-BHC)	YES	NO	NA
92524	Biphenyl	YES	YES	
111444	Bis(2-chloroethyl)ether	YES	YES	
108601	Bis(2-chloroisopropyl)ether [3]	YES	YES	
117817	Bis(2-ethylhexyl)phthalate	NO	NO	NA
542881	Bis(chloromethyl)ether [3]	YES	YES	
75274	Bromodichloromethane	YES	YES	
75252	Bromoform	YES	YES	
106990	1,3-Butadiene	YES	YES	
71363	Butanol	YES	NO	NA
85687	Butyl benzyl phthalate	NO	NO	NA
86748	Carbazole	YES	NO	NA
75150	Carbon disulfide	YES	YES	
56235	Carbon tetrachloride	YES	YES	
57749	Chlordane	YES	YES	

(continued)

CAS No.	Chemical	Is Chemical Sufficiently Toxic?[1]	Is Chemical Sufficiently Volatile?[2]	Check Here if Known or Reasonably Suspected to be Present [3]
126998	2-Chloro-1,3-butadiene(chloroprene)	YES	YES	
108907	Chlorobenzend	YES	YES	
109693	1-Chlorobutane	YES	YES	
124481	Chlorodibromomethane	YES	YES	
75456	Chlorodifluoromethane	YES	YES	
75003	Chloroethane (ethyl chloride)	YES	YES	
67663	Chloroform	YES	YES	
95578	2-Chlorophenol	YES	YES	
75296	2-Chloropropane	YES	YES	
218019	Chrysene	YES	YES	
156592	Cis-1,2-Dichloroethylene	YES	YES	
123739	Crotonaldehyde(2-butenal)	YES	YES	
998828	Cumene	YES	YES	
72548	DDD	YES	NO	NA
72559	DDE	YES	YES	
50293	DDT	YES	NO	NA
53703	Dibenz(a,h)anthracene	YES	NO	NA
132649	Dibenzofuran	YES	YES	
96128	1,2-Dibromo-3-chloropropane [3]	YES	YES	
106934	1,2-Dibromoethane(ethylene dibromide)	YES	YES	
541731	1,3-Dichlorobenzene	YES	YES	
95501	1,2-Dichlorobenzene	YES	YES	
106467	1,4-Dichlorobenzene	YES	YES	
91941	3,3-Dichlorobenzidine	YES	NO	NA
75718	Dichlorodifluoromethane	YES	YES	
75343	1,1-Dichloroethane	YES	YES	
107062	1,2-dichloroethane	YES	YES	
75354	1,1-Dichloroethylene	YES	YES	
120832	2,4-Dichloroephenol	YES	NO	NA
78875	1,2-Dichloropropane	YES	YES	
542756	1,3-Dichloropropene	YES	YES	
60571	Dieldrin	YES	YES	
84662	Diethylphthalate	YES	NO	NA
105679	2,4-Dimethylphenol	YES	NO	NA
131113	Dimethylphthalate	NA	NO	NA
84742	Di-n-butyl phthalate	NO	NO	NA

(continued)

CAS No.	Chemical	Is Chemical Sufficiently Toxic?[1]	Is Chemical Sufficiently Volatile?[2]	Check Here if Known or Reasonably Suspected to be Present [3]
534521	4,6 Dinitro-2methylphenol (4, 6-dinitro-o-cresol)	YES	NO	NA
51285	2,4-Dinitrophenol	YES	NO	NA
121142	2,4-Dinitrotoluene	YES	NO	NA
606202	2,6-Dinitrotoluene	YES	NO	NA
117840	Di-n-octyl phthalate	NO	YES	NA
115297	Endosulfan	YES	YES	
72208	Endrin	YES	NO	NA
106898	Epichlorohydrin [3]	YES	YES	
60297	Ethyl ether	YES	YES	
141786	Ethylacetate	YES	YES	
100414	Ethylbenzene	YES	YES	
75218	Ethylene oxide	YES	YES	
97632	Ethylmethacrylate	YES	YES	
206440	Fluoranthene	NO	YES	NA
86737	Fluorene	YES	YES	
110009	Furane	YES	YES	
58899	Gamma-HCH(Lindane)	YES	YES	
76448	Heptachlor	YES	YES	
1024573	Heptachlor epoxide	YES	NO	NA
87683	Hexachloro-1,3-butadiene	YES	YES	
118741	Hexachlorobenzene	YES	YES	
77474	Hexachlorocyclopentadiene	YES	YES	
67721	Hexachloroethane	YES	YES	
110543	Hexane	YES	YES	
74908	Hydrogene cyanide	YES	YES	
193395	Indeno (1,2,3-cd)pyrene	NO	NO	NA
78831	Isobutanol	YES	YES	
78591	Isophorone	YES	NO	NA
7439976	Mercury (elemental)	YES	YES	
126987	Methacrylonitrile	YES	YES	
72435	Methoxychlor	YES	YES	
79209	Methy acetate	YES	YES	
96333	Methyl acrylate	YES	YES	
74839	Methyl bromide	YES	YES	
74873	Methyl chloride (chloromethane)	YES	YES	
108872	Methylcyclohexane	YES	YES	

(continued)

CAS No.	Chemical	Is Chemical Sufficiently Toxic?[1]	Is Chemical Sufficiently Volatile?[2]	Check Here if Known or Reasonably Suspected to be Present [3]
74953	Methylene bromide	YES	YES	
75092	Methylene chloride	YES	YES	
78933	Methylethylketone (2-butanone)	YES	YES	
108101	Methylisobutylketone (4-methyl-2-pentanone)	YES	YES	
80626	Methylmethacrylate	YES	YES	
91576	2-Methylnaphthalene	YES	YES	
108394	3-Methylphenol(m-cresol)	YES	NO	NA
95487	2-Methylphenol(o-cresol)	YES	NO	NA
106455	4-Methylphenol (p-cresol)	YES	NO	NA
99081	m-Nitrotoluene	YES	NO	NA
1634044	MTBE	YES	YES	
108383	m-Xylene	YES	YES	
91203	Naphthalene	YES	YES	
104518	n-Butylbenzene	YES	YES	
98953	Nitrobenzene	YES	YES	
100027	4-Nitrophenol	YES	NO	NA
79469	2-Nitropropane	YES	YES	
924163	N-nitroso-di-n-butylamine [3]	YES	YES	
621647	N-Nitroso-di-n-propylamine	YES	NO	NA
86306	N-Nitrosodiphenylamine	YES	NO	NA
103651	n-Propylbenzene	YES	YES	
88722	o-Nitrotoluene	YES	YES	
95476	o-Xylene	YES	YES	
106478	p-Chloroaniline	YES	NO	NA
87865	Pentachlorophenol	YES	NO	NA
108952	Phenol	YES	NO	NA
99990	p-Nitrotoluene	YES	NO	NA
106423	p-Xylene	YES	YES	
129000	Pyrene	YES	YES	
110861	Pyridine	YES	NO	NA
135988	Sec-Butylbenzene	YES	YES	
100425	Styrene	YES	YES	
98066	Tert-Butylbenzene	YES	YES	
630206	1,1,1,2-Tetrachloroethane	YES	YES	
79345	1,1,2,2,-Tetrachloroethane	YES	YES	
127184	Tetrachloroethylene	YES	YES	

(continued)

CAS No.	Chemical	Is Chemical Sufficiently Toxic?[1]	Is Chemical Sufficiently Volatile?[2]	Check Here if Known or Reasonably Suspected to be Present [3]
108883	Toluene	YES	YES	
8001352	Toxaphen	YES	NO	NA
156605	Trans-1,2-Dichloroethylene	YES	YES	
76131	1,1,2-Trichloro-1,2,2-trifluoroethane	YES	YES	
120821	1,2,4-Trichlorobenzene	YES	YES	
79005	1,1,2-Trichloroethane	YES	YES	
71556	1,1,1-Trichloroethane	YES	YES	
79016	Trichloroethylene	YES	YES	
75694	Trichlorofluoromethane	YES	YES	
95954	2,4,5-Trichlorophenol	YES	NO	NA
88062	2,4,6-Trichlorophenol	YES	NO	NA
96184	1,2,3-Trichloropropane	YES	YES	
95636	1,2,4-Trimethylbenzene	YES	YES	
108678	1,3,5-Trimethylbenzene	YES	YES	
108054	Vinyl acetate	YES	YES	
75014	Vinyl chloride (chloroethene)	YES	YES	

[1] A chemical is considered sufficiently toxic if the vapor concentration of the pure component poses an incremental lifetime cancer risk greater than 10^{-6} or a non-cancer hazard index greater than 1.

[2] A chemical is considered sufficiently volatile if its Henry's law constant is 1×10^{-5} atm-m^3/mol or greater.

[3] One or more of the physical chemical properties required to run the indoor air vapor intrusion models was not found during a literature search conducted March 2003.

C_R = Initial soil concentration, g/g

ρ_b = Soil dry bulk density, g/cm^3

θ_w = Soil water-filled porosity, cm^3/cm^3

K_d = Soil-water partition coefficient, cm^3/g (= K_{oc} x f_{oc})

θ_a = Soil air-filled porosity, cm^3/cm^3

K_{oc} = Soil organic carbon partition coefficient, cm^3/g

f_{oc} = Soil organic carbon weight fraction.

If the initial soil concentration includes a residual phase, the user is referred to the NAPL-SCREEN or NAPL-ADV models as discussed in Appendix A. These models estimate indoor air concentrations and associated risks for up to 10 user-defined contaminants that comprise a residual phase mixture in soils.

C_{source} for groundwater contamination is estimated assuming that the vapor and aqueous-phases are in local equilibrium according to Henry's law such that:

$$C_{source} = H'_{TS} C_w \qquad (2)$$

where C_{source} = Vapor concentration at the source of contamination, g/cm^3-v

H'_{TS} = Henry's law constant at the system (groundwater) temperature, dimensionless

C_w = Groundwater concentration, g/cm^3-w.

The dimensionless form of the Henry's law constant at the system temperature (i.e., at the average soil/groundwater temperature) may be estimated using the Clapeyron equation by:

$$H'_{TS} = \frac{\exp\left[-\frac{\Delta H_{v,TS}}{R_c}\left(\frac{1}{T_S} - \frac{1}{T_R}\right)\right] H_R}{R T_S} \qquad (3)$$

where H'_{TS} = Henry's law constant at the system temperature, dimensionless

$\Delta H_{v,TS}$ = Enthalpy of vaporization at the system temperature, cal/mol

T_S = System temperature, °K

T_R = Henry's law constant reference temperature, ^oK

H_R = Henry's law constant at the reference temperature, atm-m^3/mol

R_C = Gas constant (= 1.9872 cal/mol - ^oK)

R = Gas constant (= 8.205 E-05 atm-m^3/mol-^oK).

The enthalpy of vaporization at the system temperature can be calculated from Lyman et al. (1990) as:

$$\Delta H_{v,TS} = \Delta H_{v,b}\left[\frac{(1-T_S/T_C)}{(1-T_B/T_C)}\right]^n \qquad (4)$$

where $\Delta H_{v,TS}$ = Enthalpy of vaporization at the system temperature, cal/mol

$\Delta H_{v,b}$ = Enthalpy of vaporization at the normal boiling point, cal/mol

T_S = System temperature, ^oK

T_C = Critical temperature, ^oK

T_B = Normal boiling point, ^oK

n = Constant, unitless.

Table 2 gives the value of n as a function of the ratio T_B/T_C.

TABLE 2. VALUES OF EXPONENT n AS A FUNCTION OF T_B/T_C

T_B/T_C	N
< 0.57	0.30
0.57 - 0.71	0.74 (T_B/T_C) - 0.116
> 0.71	0.41

2.3 DIFFUSION THROUGH THE CAPILLARY ZONE

Directly above the water table, a saturated capillary zone exists whereby groundwater is held within the soil pores at less than atmospheric pressure (Freeze and Cherry, 1979). Between drainage and wetting conditions, the saturated water content varies but is always less than the fully saturated water content which is equal to the soil total porosity. This is the result of air entrapment in the pores during the wetting process (Gillham, 1984). Upon rewetting, the air content of the capillary zone will be higher than after main drainage. Therefore, the air content will vary as a function of groundwater recharge and discharge. At the saturated water content, Freijer (1994) found that the relative vapor-phase diffusion coefficient was almost zero. This implies that all remaining air-filled soil pores are disconnected and thus blocked for gas diffusion. As the air-filled porosity increased, however, the relative diffusion coefficient indicated the presence of connected air-filled pores that corresponded to the air-entry pressure head. The air-entry pressure head corresponds with the top of the saturated capillary zone. Therefore, to allow for the calculation of the effective diffusion coefficient by lumping the gas-phase and aqueous-phase together, the water-filled soil porosity in the capillary zone ($\theta_{w,cz}$) is calculated at the air-entry pressure head (h) according to the procedures of Waitz et al. (1996) and the van Genuchten equation (van Genuchten, 1980) for the water retention curve:

$$\theta_{w,cz} = \theta_r + \frac{\theta_s - \theta_r}{\left[1 + (\alpha_1 h)^N\right]^M} \qquad (5)$$

where $\theta_{w,cz}$ = Water-filled porosity in the capillary zone, cm^3/cm^3

θ_r = Residual soil water content, cm^3/cm^3

θ_s = Saturated soil water content, cm^3/cm^3

α_1 = Point of inflection in the water retention curve where $d\,\theta_w/dh$ is maximal, cm^{-1}

h = Air-entry pressure head, cm (= $1/\alpha_1$ and assumed to be positive)

N = van Genuchten curve shape parameter, dimensionless

M = 1 - (1/N).

With a calculated value of $\theta_{w,cz}$ within the capillary zone at the air-entry pressure head, the air-filled porosity within the capillary zone ($\theta_{a,cz}$) corresponding to the minimum value at which gas diffusion is relevant is calculated as the total porosity (n) minus $\theta_{w,cz}$.

Hers (2002) computed the SCS class average values of the water filled porosity and the height of the capillary zone SCS soil textural classifications. Table 3 provides the class average values for each of the SCS soil types. These data replace the mean values developed by Schaap and

Leij (1998) included in the previous U.S. Environmental Protection Agency (EPA) version of the J&E Models. With the class average values presented in Table 3, a general estimate can be made of the values of $\theta_{w,cz}$ and $\theta_{a,cz}$ for each soil textural classification.

The total concentration effective diffusion coefficient across the capillary zone (D_{cz}^{eff}) may then be calculated using the Millington and Quirk (1961) model as:

$$D_{cz}^{eff} = D_a\left(\theta_{a,cz}^{3.33} / n_{cz}^2\right) + \left(D_w / H'_{TS}\right)\left(\theta_{w,cz}^{3.33} / n_{cz}^2\right) \qquad (6)$$

where D_{cz}^{eff} = Effective diffusion coefficient across the capillary zone, cm^2/s

D_a = Diffusivity in air, cm^2/s

$\theta_{a,cz}$ = Soil air-filled porosity in the capillary zone, cm^3/cm^3

n_{cz} = Soil total porosity in the capillary zone, cm^3/cm^3

D_w = Diffusivity in water, cm^2/s

H'_{TS} = Henry's law constant at the system temperature, dimensionless

$\theta_{w,cz}$ = Soil water-filled porosity in the capillary zone, cm^3/cm^3.

According to Fick's law of diffusion, the rate of mass transfer across the capillary zone can be approximated by the expression:

$$E = A\left(C_{source} - C_{g0}\right)D_{cz}^{eff} / L_{cz} \qquad (7)$$

where E = Rate of mass transfer, g/s

A = Cross-sectional area through which vapors pass, cm^2

C_{source} = Vapor concentration within the capillary zone, g/cm^3-v

C_{g0} = A known vapor concentration at the top of the capillary zone, g/cm^3-v (C_{g0} is assumed to be zero as diffusion proceeds upward)

D_{cz}^{eff} = Effective diffusion coefficient across the capillary zone, cm^2/s

L_{cz} = Thickness of capillary zone, cm.

TABLE 3. CLASS AVERAGE VALUES OF THE VAN GENUCHTEN SOIL WATER RETENTION PARAMETERS FOR THE 12 SCS SOIL TEXTURAL CLASSIFICATIONS

Soil texture (USDA)	Saturated water content, θ_s	Residual water Content, θ_r	van Genuchten parameters		
			α_1 (1/cm)	N	M
Clay	0.459	0.098	0.01496	1.253	0.2019
Clay loam	0.442	0.079	0.01581	1.416	0.2938
Loam	0.399	0.061	0.01112	1.472	0.3207
Loamy sand	0.390	0.049	0.03475	1.746	0.4273
Silt	0.489	0.050	0.00658	1.679	0.4044
Silty loam	0.439	0.065	0.00506	1.663	0.3987
Silty clay	0.481	0.111	0.01622	1.321	0.2430
Silty clay loam	0.482	0.090	0.00839	1.521	0.3425
Sand	0.375	0.053	0.03524	3.177	0.6852
Sandy clay	0.385	0.117	0.03342	1.208	0.1722
Sandy clay loam	0.384	0.063	0.02109	1.330	0.2481
Sandy loam	0.387	0.039	0.02667	1.449	0.3099

The value of C_{source} is calculated using Equation 2; the value of A is assumed to be 1 cm^2; and the value of D_{cz}^{eff} is calculated by Equation 6. What remains is a way to estimate a value for L_{cz}.

Lohman (1972) and Fetter (1994) estimated the rise of the capillary zone above the water table using the phenomenon of capillary such that water molecules are subject to an upward attractive force due to surface tension at the air-water interface and the molecular attraction of the liquid and solid phases. The rise of the capillary zone can thus be estimated using the equation for the height of capillary rise in a bundle of tubes of various diameters equivalent to the diameters between varying soil grain sizes. Fetter (1994) estimated the mean rise of the capillary zone as:

$$L_{cz} = \frac{2 \ \alpha_2 \ COS \ \lambda}{\rho_w \ g \ R} \qquad (8)$$

where L_{cz} = Mean rise of the capillary zone, cm

α_2 = Surface tension of water, g/s (= 73)

λ = Angle of the water meniscus with the capillary tube, degrees (assumed to be zero)

ρ_w = Density of water, g/cm^3 (= 0.999)

g = Acceleration due to gravity, cm/s^2 (= 980)

R = Mean interparticle pore radius, cm

and;

$$R = 0.2D \qquad (9)$$

where R = Mean interparticle pore radius, cm

D = Mean particle diameter, cm.

Assuming that the default values of the parameters given in Equation 8 are for groundwater between 5° and 25^oC, Equation 8 reduces to:

$$L_{cz} = \frac{0.15}{R} \quad . \qquad (10)$$

Nielson and Rogers (1990) estimated the arithmetic mean particle diameter for each of the 12 SCS soil textural classifications at the mathematical centroid calculated from its classification area (Figure 3). Table 4 shows the centroid compositions and mean particle sizes of the 12 SCS soil textural classes.

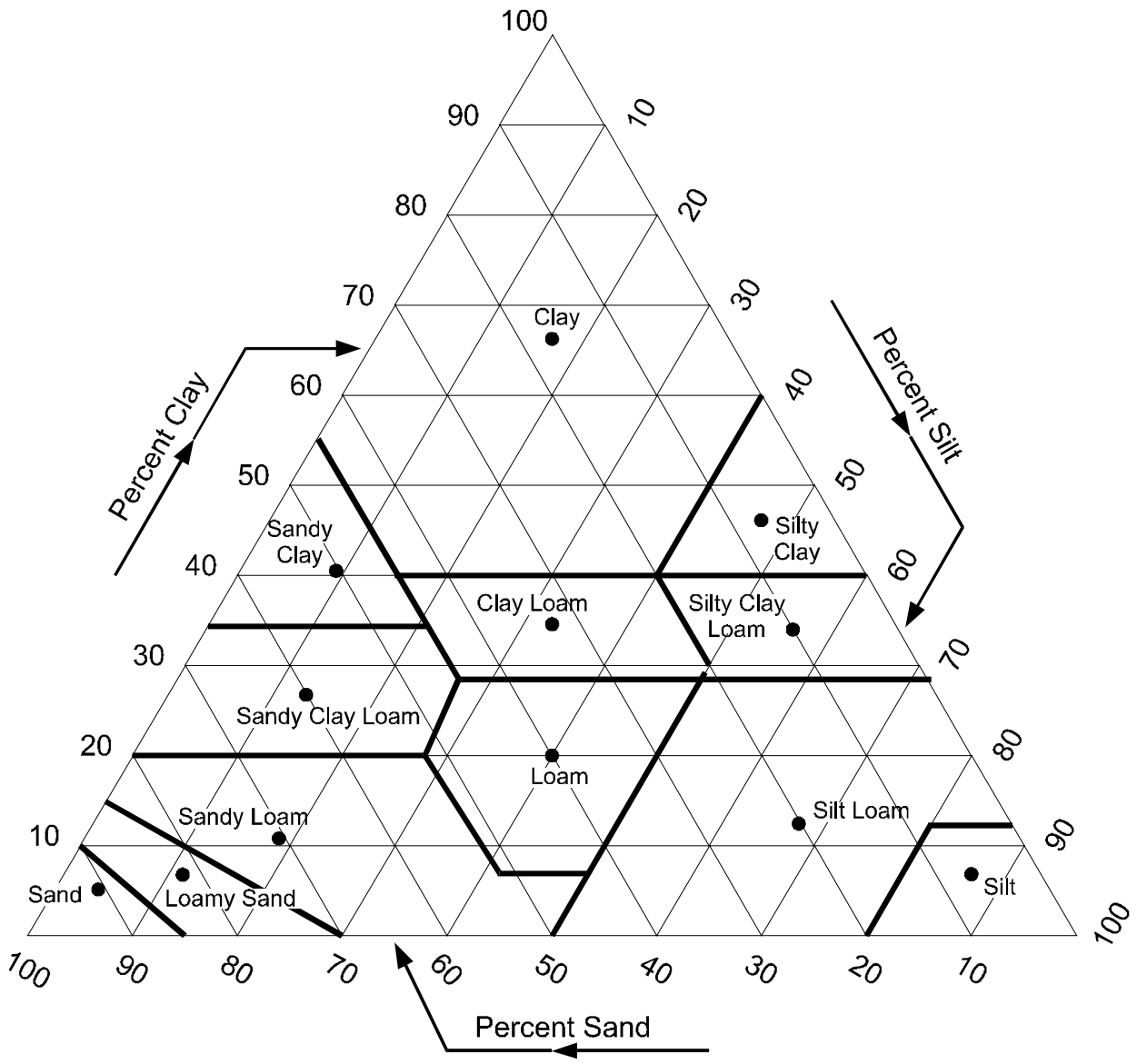


Figure 3. U.S. Soil Conservation Service Classification Chart Showing Centroid Compositions (Solid Circles)

TABLE 4. CENTROID COMPOSITIONS, MEAN PARTICLE DIAMETERS AND DRY BULK DENSITY OF THE 12 SCS SOIL TEXTURAL CLASSIFICATIONS

Textural class	% clay	% silt	% sand	Arithmetic mean particle diameter, cm	Dry Bulk Density g/cm^3
Sand	3.33	5.00	91.67	0.044	1.66
Loamy sand	6.25	11.25	82.50	0.040	1.62
Sandy loam	10.81	27.22	61.97	0.030	1.62
Sandy clay loam	26.73	12.56	60.71	0.029	1.63
Sandy clay	41.67	6.67	51.66	0.025	1.63
Loam	18.83	41.01	40.16	0.020	1.59
Clay loam	33.50	34.00	32.50	0.016	1.48
Silt loam	12.57	65.69	21.74	0.011	1.49
Clay	64.83	16.55	18.62	0.0092	1.43
Silty clay loam	33.50	56.50	10.00	0.0056	1.63
Silt	6.00	87.00	7.00	0.0046	1.35
Silty clay	46.67	46.67	6.66	0.0039	1.38

Given the mean particle diameter data in Table 4, the mean thickness of the capillary zone may then be estimated using Equations 9 and 10.

2.4 DIFFUSION THROUGH THE UNSATURATED ZONE

The effective diffusion coefficient within the unsaturated zone may also be estimated using the same form as Equation 6:

$$D_i^{eff} = D_a\left(\theta_{a,i}^{3.33} / n_i^2\right) + \left(D_w / H'_{TS}\right)\left(\theta_{w,i}^{3.33} / n_i^2\right) \qquad (11)$$

where D_i^{eff} = Effective diffusion coefficient across soil layer i, cm^2/s

D_a = Diffusivity in air, cm^2/s

$\theta_{a,i}$ = Soil air-filled porosity of layer i, cm^3/cm^3

n_i = Soil total porosity of layer i, cm^3/cm^3

D_w = Diffusivity in water, cm^2/s

$\theta_{w,i}$ = Soil water-filled porosity of layer i, cm^3/cm^3

H'_{TS} = Henry's law constant at the system temperature, dimensionless

The overall effective diffusion coefficient for systems composed of n distinct soil layers between the source of contamination and the enclosed space floor is:

$$D_T^{eff} = \frac{L_T}{\sum_{i=0}^{n} L_i / D_i^{eff}} \qquad (12)$$

where D_T^{eff} = Total overall effective diffusion coefficient, cm^2/s

L_i = Thickness of soil layer i, cm

D_i^{eff} = Effective diffusion coefficient across soil layer i, cm^2/s

L_T = Distance between the source of contamination and the bottom of the enclosed space floor, cm.

Note that in the case of cracks in the floor of the enclosed space, the value of L_T does not include the thickness of the floor, nor does the denominator of Equation 12 include the thickness of the floor and the associated effective diffusion coefficient across the crack(s). An unlimited number of soil layers, including the capillary zone, may be included in Equation 12, but all layers must be located between the source of contamination and the enclosed space floor.

2.5 THE INFINITE SOURCE SOLUTION TO CONVECTIVE AND DIFFUSIVE TRANSPORT

Under the assumption that mass transfer is steady-state, J&E (1991) give the solution for the attenuation coefficient (α) as:

$$\alpha = \frac{\left[\left(\frac{D_T^{eff}\ A_B}{Q_{building}\ L_T}\right) x \exp\left(\frac{Q_{soil}\ L_{crack}}{D^{crack}\ A_{crack}}\right)\right]}{\left[\exp\left(\frac{Q_{soil}\ L_{crack}}{D_{crack}\ A_{crack}}\right)+\left(\frac{D_T^{eff}\ A_B}{Q_{building}\ L_T}\right)+\left(\frac{D_T^{eff}\ A_B}{Q_{soil}\ L_T}\right)\left[\exp\left(\frac{Q_{soil}\ L_{crack}}{D^{crack}\ A_{crack}}\right)-1\right]\right]} \quad (13)$$

where α = Steady-state attenuation coefficient, unitless

D_T^{eff} = Total overall effective diffusion coefficient, cm^2/s

A_B = Area of the enclosed space below grade, cm^2

$Q_{building}$ = Building ventilation rate, cm^3/s

L_T = Source-building separation, cm

Q_{soil} = Volumetric flow rate of soil gas into the enclosed space, cm^3/s

L_{crack} = Enclosed space foundation or slab thickness, cm

A_{crack} = Area of total cracks, cm^2

D_{crack} = Effective diffusion coefficient through the cracks, cm^2/s (assumed equivalent to D_i^{eff} of soil layer i in contact with the floor).

The total overall effective diffusion coefficient is calculated by Equation 12. The value of A_B includes the area of the floor in contact with the underlying soil and the total wall area below grade. The building ventilation rate ($Q_{building}$) may be calculated as:

$$Q_{building} = (L_B\ W_B\ H_B\ ER)/3{,}600\ s/h \quad (14)$$

where $Q_{building}$ = Building ventilation rate, cm^3/s

L_B = Length of building, cm

W_B = Width of building, cm

H_B = Height of building, cm

ER = Air exchange rate, (1/h).

The building dimensions in Equation 14 are those dimensions representing the total "living" space of the building; this assumes that the total air volume within the structure is well mixed and that any vapor contaminant entering the structure is instantaneously and homogeneously distributed.

The volumetric flow rate of soil gas entering the building (Q_{soil}) is calculated by the analytical solution of Nazaroff (1988) such that:

$$Q_{soil} = \frac{2\,\pi \Delta P\; k_v\; X_{crack}}{\mu\, \ln\left(2\, Z_{crack} / r_{crack}\right)} \qquad (15)$$

where Q_{soil} = Volumetric flow rate of soil gas entering the building, cm^3/s

π = 3.14159

ΔP = Pressure differential between the soil surface and the enclosed space, $g/cm\text{-}s^2$

k_v = Soil vapor permeability, cm^2

X_{crack} = Floor-wall seam perimeter, cm

μ = Viscosity of air, g/cm-s

Z_{crack} = Crack depth below grade, cm

r_{crack} = Equivalent crack radius, cm.

Equation 15 is an analytical solution to vapor transport solely by pressure-driven air flow to an idealized cylinder buried some distance (Z_{crack}) below grade; the length of the cylinder is taken to be equal to the building floor-wall seam perimeter (X_{crack}). The cylinder, therefore, represents that portion of the building below grade through which vapors pass. The equivalent radius of the floor-wall seam crack (r_{crack}) is given in J&E (1991) as:

$$r_{crack} = \eta\left(A_B / X_{crack}\right) \qquad (16)$$

where r_{crack} = Equivalent crack radius, cm

η = A_{crack}/A_B, $(0 \leq \eta \leq 1)$

A_B = Area of the enclosed space below grade, cm^2

X_{crack} = Floor-wall seam perimeter, cm.

The variable r_{crack} is actually the product of the fixed crack-to-total area ratio (η) and the hydraulic radius of the idealized cylinder, which is equal to the total area (A_B) divided by that portion of the cylinder perimeter in contact with the soil gas (X_{crack}). Therefore, if the dimensions of the enclosed space below grade (A_B) and/or the floor-wall seam perimeter (X_{crack}) vary, and the crack-to-total area ratio (η) remains constant, the value of r_{crack} must also vary. The total area of cracks (A_{crack}) is the product of η and A_B.

Equation 15 requires that the soil column properties within the zone of influence of the building (e.g., porosities, bulk density, etc.) be homogeneous, that the soil be isotropic with respect to vapor permeability, and that the pressure within the building be less than atmospheric.

Equation 13 contains the exponent of the following dimensionless group:

$$\left(\frac{Q_{soil}\, L_{crack}}{D^{crack}\, A_{crack}} \right) \quad . \tag{17}$$

This dimensionless group represents the equivalent Peclet number for transport through the building foundation. As the value of this group approaches infinity, the value of α approaches:

$$\frac{\left(\dfrac{D_T^{eff}\, A_B}{Q_{building}\, L_T} \right)}{\left(\dfrac{D_T^{eff}\, A_B}{Q_{soil}\, L_T} \right) + 1} \quad . \tag{18}$$

In the accompanying spreadsheets, if the exponent of Equation 17 is too great to be calculated, the value of α is set equal to Equation 18.

With a calculated value of α, the steady-state vapor-phase concentration of the contaminant in the building ($C_{building}$) is calculated as:

$$C_{building} = \alpha C_{source} \quad . \tag{19}$$

2.6 THE FINITE SOURCE SOLUTION TO CONVECTIVE AND DIFFUSIVE TRANSPORT

If the thickness of soil contamination is known, the finite source solution of J&E (1991) can be employed such that the time-averaged attenuation coefficient (<α>) may be calculated as:

$$\langle\alpha\rangle = \frac{\rho_b\, C_R\, \Delta H_c\, A_B}{Q_{building}\, C_{source}\, \tau} \left(\frac{L_T^0}{\Delta H_c} \right) \left[\left(\beta^2 + 2\,\Psi\,\tau \right)^{1/2} - \beta \right] \tag{20}$$

where

<α>	= Time-averaged finite source attenuation coefficient, unitless
ρ_b	= Soil dry bulk density at the source of contamination, g/cm^3
C_R	= Initial soil concentration, g/g
ΔH_c	= Initial thickness of contamination, cm
A_B	= Area of enclosed space below grade, cm^2
$Q_{building}$	= Building ventilation rate, cm^3/s
C_{source}	= Vapor concentration at the source of contamination, g/cm^3-v
τ	= Exposure interval, s
L_T^0	= Source-building separation at time = 0, cm

and;

$$\beta = \left(\frac{D_T^{eff}\, A_B}{L_T^O\, Q_{soil}} \right) \left[1 - \exp\left(-\frac{Q_{soil}\, L_{crack}}{D^{crack}\, A_{crack}} \right) \right] + 1 \tag{21}$$

and;

$$\Psi = \frac{D_T^{eff}\, C_{source}}{\left(L_T^O \right)^2\, \rho_b\, C_R} \quad . \tag{22}$$

Implicit in Equation 20 is the assumption that source depletion occurs from the top boundary of the contaminated zone as contaminant volatilizes and moves upward toward the soil surface. This creates a hypothetical "dry zone" (δ) that grows with time; conversely, the "wet zone" of contamination retreats proportionally. When the thickness of the depletion zone (δ) is equal to the initial thickness of contamination (ΔH_c), the source is totally depleted. The unitless expression $(L_T^0/\Delta H_c)[(\beta^2 + 2\,\Psi\tau)^{1/2} - \beta]$ in Equation 20 represents the cumulative fraction of the depletion zone at the end of the exposure interval τ. Multiplying this expression by the remainder of Equation 20 results in the time-averaged finite source attenuation coefficient ($\langle\alpha\rangle$).

With a calculated value for $\langle\alpha\rangle$, the time-averaged vapor concentration in the building ($C_{building}$) is:

$$C_{building} = \langle\alpha\rangle C_{source} \quad . \tag{23}$$

For extended exposure intervals (e.g., 30 years), the time for source depletion may be less than the exposure interval. The time for source depletion (τ_D) may be calculated by:

$$\tau_D = \frac{\left[\Delta H_c / L_T^O + \beta\right]^2 - \beta^2}{2\,\Psi} \quad . \tag{24}$$

If the exposure interval (τ) is greater than the time for source depletion (τ_D), the time-averaged building vapor concentration may be calculated by a mass balance such that:

$$C_{building} = \frac{\rho_b\, C_R\, \Delta H_c\, A_B}{Q_{building}\ \tau} \tag{25}$$

where $C_{building}$ = Time-averaged vapor concentration in the building, g/cm^3-v

ρ_b = Soil dry bulk density at the source of contamination, g/cm^3

C_R = Initial soil concentration, g/g

ΔH_c = Initial thickness of contamination, cm

A_B = Area of enclosed space below grade, cm^2

$Q_{building}$ = Building ventilation rate, cm^3/s

τ = Exposure interval, s.

2.7 THE SOIL GAS MODELS

Use of the J&E Model has typically relied on a theoretical partitioning of the total volume soil concentration into the sorbed, aqueous, and vapor phases. The model has also relied on a theoretical approximation of vapor transport by diffusion and convection from the source of emissions to the building floor in contact with the soil. Use of measured soil gas concentrations directly beneath the building floor instead of theoretical vapor concentrations and vapor transport has obvious advantages that would help to reduce the uncertainty in the indoor air concentration estimates made by the model.

The soil gas models (SG-SCREEN and SG-ADV) are designed to allow the user to input measured soil gas concentration and sampling depth information directly into the spreadsheets. In the new models, the value of the user-defined soil gas concentration is assigned as the value of C_{source} in Equation 19. The steady-state (infinite source) attenuation coefficient (α) in Equation 19 is calculated using Equation 13. The steady-state solution for the attenuation coefficient is used because no evaluation has been made regarding the size and total mass of the source of emissions. The source of emissions, therefore, cannot be depleted over time. The soil gas models estimate the steady-state indoor air concentration over the exposure duration. For a detailed discussion of using the soil gas models as well as soil gas sampling, see Section 4 of this document.

2.8 SOIL VAPOR PERMEABILITY

Soil vapor permeability (k_v) is one of the most sensitive model parameters associated with convective transport of vapors within the zone of influence of the building. Soil vapor permeability is typically measured from field pneumatic tests. If field data are lacking, however, an estimate of the value of k_v can be made with limited data.

Soil intrinsic permeability is a property of the medium alone that varies with the size and shape of connected soil pore openings. Intrinsic permeability (k_i) can be estimated from the soil saturated hydraulic conductivity:

$$k_i = \frac{K_s \mu_w}{\rho_w \, g} \qquad (26)$$

where k_i = Soil intrinsic permeability, cm^2

K_s = Soil saturated hydraulic conductivity, cm/s

μ_w = Dynamic viscosity of water, g/cm-s (= 0.01307 at 10^oC)

ρ_w = Density of water, g/cm^3 (= 0.999)

g = Acceleration due to gravity, cm/s^2 (= 980.665).

Schaap and Leij (1998) computed the SCS class average values of the saturated hydraulic conductivity (K_s) for each of the 12 SCS soil textural classifications (Table 5). With these values, a general estimate of the value of k_i can be made by soil type. As an alternative, in situ measurements of the site-specific saturated hydraulic conductivity can be made and the results input into Equation 26 to compute the value of the soil intrinsic permeability.

Effective permeability is the permeability of the porous medium to a fluid when more than one fluid is present; it is a function of the degree of saturation. The relative air permeability of soil (k_{rg}) is the effective air permeability divided by the intrinsic permeability and therefore takes into account the effects of the degree of water saturation on air permeability.

TABLE 5. CLASS AVERAGE VALUES OF SATURATED HYDRAULIC CONDUCTIVITY FOR THE 12 SCS SOIL TEXTURAL CLASSIFICATIONS

Soil texture , USDA	Class average saturated hydraulic conductivity, cm/h
Sand	26.78
Loamy sand	4.38
Sandy loam	1.60
Sandy clay loam	0.55
Sandy clay	0.47
Loam	0.50
Clay loam	0.34
Silt loam	0.76
Clay	0.61
Silty clay loam	0.46
Silt	1.82
Silty clay	0.40

Parker et al. (1987) extended the relative air permeability model of van Genuchten (1980) to allow estimation of the relative permeabilities of air and water in a two- or three-phase system:

$$k_{rg} = (1 - S_{te})^{1/2} \left(1 - S_{te}^{1/M}\right)^{2M} \qquad (27)$$

where k_{rg} = Relative air permeability, unitless ($0 \le k_{rg} \le 1$)

S_{te} = Effective total fluid saturation, unitless

M = van Genuchten shape parameter, unitless.

Given a two-phase system (i.e., air and water), the effective total fluid saturation (S_{te}) is calculated as:

$$S_{te} = \frac{(\theta_w - \theta_r)}{(n - \theta_r)} \qquad (28)$$

where S_{te} = Effective total fluid saturation, unitless

θ_w = Soil water-filled porosity, cm^3/cm^3

θ_r = Residual soil water content, cm^3/cm^3

n = Soil total porosity, cm^3/cm^3.

Class average values for the parameters θ_r and M by SCS soil type may be obtained from Table 3.

The effective air permeability (k_v) is then the product of the intrinsic permeability (k_i) and the relative air permeability (k_{rg}) at the soil water-filled porosity θ_w.

2.9 CALCULATION OF A RISK-BASED SOIL OR GROUNDWATER CONCENTRATION

Both the infinite source model estimate of the steady-state building concentration and the finite source model estimate of the time-averaged building concentration represent the exposure point concentration used to assess potential risks. Calculation of a risk-based media concentration for a carcinogenic contaminant takes the form:

$$C_C = \frac{TR\, x\, AT_C\, x\, 365\, days/yr}{URF\, x\, EF\, x\, ED\, x\, C_{building}} \qquad (29)$$

where C_C = Risk-based media concentration for carcinogens, µg/kg-soil, or µg/L-water

TR = Target risk level, unitless

AT_C = Averaging time for carcinogens, yr

URF = Unit risk factor, $\mu g/m^3)^{-1}$

EF = Exposure frequency, days/yr

ED = Exposure duration, yr

$C_{building}$ = Vapor concentration in the building, μg/m^3 per μg/kg-soil, or μg/m^3 per μg/L-water.

In the case of a noncarcinogenic contaminant, the risk-based media concentration is calculated by:

$$C_{NC} = \frac{THQ \, x \, AT_{NC} \, x \, 365 \, days/yr}{EF \, x \, ED \, x \, \frac{1}{RfC} \, x \, C_{building}} \qquad (30)$$

where C_{NC} = Risk-based media concentration for noncarcinogens, μg/kg-soil, or μg/L-water

THQ = Target hazard quotient, unitless

AT_{NC} = Averaging time for noncarcinogens, yr

EF = Exposure frequency, days/yr

ED = Exposure duration, yr

RfC = Reference concentration, mg/m^3

$C_{building}$ = Vapor concentration in the building, mg/m^3 per μg/kg-soil, or mg/m^3 per μg/L-water.

The spreadsheets calculate risk-based media concentrations based on a unity initial concentration. That is, soil risk-based concentrations are calculated with an initial hypothetical soil concentration of 1 μg/kg-soil, while for groundwater the initial hypothetical concentration is 1 μg/L-water.

For this reason, the values of C_{source} and $C_{building}$ shown on the INTERCALCS worksheet when reverse-calculating a risk-based media concentration do not represent actual values. For these calculations, the following message will appear on the RESULTS worksheet:

"MESSAGE: The values of C_{source} and $C_{building}$ on the INTERCALCS worksheet are based on unity and do not represent actual values."

When forward-calculating risks from a user-defined initial soil or groundwater concentration, the values of C_{source} and $C_{building}$ on the INTERCALCS worksheet are correct.

2.10 CALCULATION OF INCREMENTAL RISKS

Forward-calculation of incremental risks begins with an actual initial media concentration (i.e., µg/kg-soil or µg/L-water). For carcinogenic contaminants, the risk level is calculated as:

$$Risk = \frac{URF\ x\ EF\ x\ ED\ x\ C_{building}}{AT_C\ x\ 365\ days/yr} \qquad (31)$$

For noncarcinogenic contaminants, the hazard quotient (HQ) is calculated as:

$$HQ = \frac{EF\ x\ ED\ x\ \frac{1}{RfC}\ x\ C_{building}}{AT_{NC}\ x\ 365\ days/yr} \quad . \qquad (32)$$

2.11 MAJOR MODEL ASSUMPTIONS/LIMITATIONS

The following represent the major assumptions/limitations of the J&E Model.

1. Contaminant vapors enter the structure primarily through cracks and openings in the walls and foundation.

2. Convective transport occurs primarily within the building zone of influence and vapor velocities decrease rapidly with increasing distance from the structure.

3. Diffusion dominates vapor transport between the source of contamination and the building zone of influence.

4. All vapors originating from below the building will enter the building unless the floors and walls are perfect vapor barriers.

5. All soil properties in any horizontal plane are homogeneous.

6. The contaminant is homogeneously distributed within the zone of contamination.

7. The areal extent of contamination is greater than that of the building floor in contact with the soil.

8. Vapor transport occurs in the absence of convective water movement within the soil column (i.e., evaporation or infiltration), and in the absence of mechanical dispersion.

9. The model does not account for transformation processes (e.g., biodegradation, hydrolysis, etc.).

10. The soil layer in contact with the structure floor and walls is isotropic with respect to permeability.

11. Both the building ventilation rate and the difference in dynamic pressure between the interior of the structure and the soil surface are constant values.

Use of the J&E Model as a first-tier screening tool to identify sites needing further assessment requires careful evaluation of the assumptions listed in the previous section to determine whether any conditions exist that would render the J&E Model inappropriate for the site. If the model is deemed applicable at the site, care must be taken to ensure reasonably conservative and self-consistent model parameters are used as input to the model. Considering the limited site data typically available in preliminary site assessments, the J&E Model can be expected to predict only whether or not a risk-based exposure level will be exceeded at the site. Precise prediction of concentration levels is not possible with this approach.

The suggested minimum site characterization information for a first tier evaluation of the vapor intrusion pathway includes: site conceptual model, nature and extent of contamination distribution, soil lithologic descriptions, groundwater concentrations, and/or possibly near source soil vapor concentrations. The number of samples and measurements needed to establish this information varies by site and it's not possible to provide a hard and fast rule. Bulk soil concentrations should not be used unless appropriately preserved during sampling.

Based on the conceptual site model (CSM), the user can select the appropriate spreadsheet corresponding to the vapor source at the site and determine whether to use the screening level spreadsheet (which allows only one soil type above the capillary fringe) or the more advanced version (which allows up to three layers above the capillary fringe). Because most of the inputs to the J&E Model are not collected during a typical site characterization, conservative inputs have to be estimated or inferred from available data and other non-site-specific sources of information.

The uncertainty in determining key model parameters and sensitivity of the J&E Model to those key model parameters is qualitatively described in Table 6. As shown in the table, building-related parameters will moderate to high uncertainty and model sensitivity include: Qsoil, building crack ratio, building air-exchange rate, and building mixing height. Building-related parameters with low uncertainty and sensitivity include: foundation area, depth to base of foundation, and foundation slab thickness. Of the soil-dependent properties, the soil moisture parameters clearly are of critical importance for the attenuation value calculations.

TABLE 6. UNCERTAINTY AND SENSITIVITY OF KEY PARAMETERS FOR THE VAPOR INTRUSION MODEL

Input Parameter	Parameter Uncertainty Or Variability	Parameter Sensitivity			
		Shallower Contamination Building Underpressurized	Deeper Contamination Building Underpressurized	Shallower Contamination Building Not Underpressurized	Deeper Contamination Building Not Underpressurized
Soil Total Porosity (η)	Low	Low	Low	Low	Low
Soil Water-filled Porosity (θ_w)	Moderate to High	Low to Moderate	Moderate to High	Moderate to High	Moderate to High
Capillary Zone Water-filled Porosity ($\theta_{n,\,cz}$)	Moderate to High	Moderate to High	Moderate to High	Moderate to High	Moderate to High
Thickness of Capillary Zone (L_{cz})	Moderate to High	Moderate to High	Moderate to High	Moderate to High	Moderate to High
Soft Dry Bulk Density (ρ_b)	Low	Low	Low	Low	Low
Average Vapor Flowrate into a Building (Q_{soil})	High	Moderate to High	Low to Moderate	N/A	N/A
Soil Vapor Permeability(K_v)	High	Moderate to High	Low to Moderate	N/A	N/A
Soil to Building Pressure Differential (ΔP)	Moderate	Moderate	Low to Moderate	N/A	N/A
Henry's Law Constant (for single chemical) (H)	Low to Moderate	Low to Moderate	Low to Moderate	Low to Moderate	Low to Moderate
Diffusivity in Air (D_A)	Low	Low	Low	Low	Low
Indoor Air Exchange Rate (ER)	Moderate	Moderate	Moderate	Moderate	Moderate
Enclosed Space Height (H_B)	Moderate	Moderate	Moderate	Moderate	Moderate
Area of Enclosed Space Below Grade (A_B)	Low to Moderate	Low to Moderate	Low to Moderate	Low to Moderate	Low to Moderate
Depth Below Grade to Bottom of Enclosed Space (L_F)	Low	Low	Low	Low	Low
Crack-to-Total Area Ratio (η)	High	Low	Low	Moderate to High	Low to Moderate
Enclosed Space Floor Thickness (L_{crack})	Low	Low	Low	Low	Low

SECTION 3

SOIL AND GROUNDWATER MODEL APPLICATION

This section provides step-by-step instructions on how to implement the soil and groundwater contamination versions of the J&E Model using the spreadsheets. This section also discusses application of the soil gas versions of the model. The user provides data and selects certain input options, and views model results via a series of worksheets. Error messages are provided within both the data entry worksheet and the results worksheet to warn the user that entered data are missing or outside of permitted limits.

The J&E Model as constructed within the accompanying spreadsheets requires a range of input variables depending on whether a screening-level or advanced model is chosen. Table 7 provides a list of all major input variables, the range of practical values for each variable, the default value for each variable, and the relative model sensitivity and uncertainty of each variable. Table 7 also includes references for each value or range of values.

Table 8 indicates the results of an increase in the value of each input parameter. The results are shown as either an increase or a decrease in the building concentration ($C_{building}$) of the pollutant. An increase in the building concentration will result in an increase in the risk when forward-calculating from an initial soil or groundwater concentration. When reverse-calculating to a risk-based "acceptable" soil or groundwater concentration, an increase in the hypothetical unit building concentration will result in a lower "acceptable" soil or groundwater concentration.

A list of reasonably conservative model input parameters for building-related parameters is provided in Table 9, which also provides the practical range, typical or mean value (if applicable), and most conservative value for these parameters. For building parameters with low uncertainty and sensitivity, only a single "fixed" value corresponding to the mean or typical value is provided in Table 9. Soil-dependent properties are provided in Table 10 for soils classified according to the US SCS system. If site soils are not classified according to the US SCS, Table 11 can be used to assist in selecting an appropriate SCS soil type corresponding to the available site lithologic information. Note that the selection of the soil texture class should be biased towards the coarsest soil type of significance, as determined by the site characterization program.

TABLE 7. RANGE OF VALUES FOR SELECTED INPUT PARAMETERS

Input parameter	Practical range of values	Default value
Soil water-filled porosity (θ_w)	0.04 – 0.33 cm^3/cm^3[a]	Soil dependent see Table 10
Soil vapor permeability (k_v)	10^{-6} – 10^{-12} cm^2[b,c]	10^{-8} cm^2[d]
Soil-building pressure differential (ΔP)	0 – 20 Pa[3]	4 Pa[f]
Media initial concentration (C_R, C_w)	User-defined	NA
Depth to bottom of soil contamination (L_b)	User-defined	NA
Depth to top of concentration (L_T)	User-defined	NA
Floor-wall seam gap (w)	0.05 – 1.0 cm[e]	0.1 cm[e]
Soil organic carbon fraction (f_{oc})	0.001 – 0.006[a]	0.002[a]
Indoor air exchange rate (ER)	0.18 – 1.26 (H^{-1})[g]	0.25 (h^{-1})[g,h]
Soil total porosity (n)	0.34 – 0.53 cm^3/cm^3[a]	0.43 cm^3/cm^3[a]
Soil dry bulk density (ρ_b)	1.25 – 1.75 g/cm^3[a]	1.5 g/cm^3[a]

[a]U.S. EPA (1996a and b).
[b]Johnson and Ettinger (1991).
[c]Nazaroff (1988).
[d]Based on transition point between diffusion and convection dominated transport from Johnson and Ettinger (1991).
[e]Eaton and Scott (1984); Loureiro et al. (1990).
[f]Loureiro et al. (1990); Grimsrud et al. (1983).
[g]Koontz and Rector (1995).
[h]Parker et al. (1990).
[i]U.S. DOE (1995).

TABLE 8. EFFECT ON BUILDING CONCENTRATION FROM AN INCREASE IN INPUT PARAMETER VALUES

Input parameter	Change in parameter value	Effect on building concentration
Soil water-filled porosity (θ_w)	Increase	Decrease
Soil vapor permeability (k_v)	Increase	Increase
Soil-building pressure differential (ΔP)	Increase	Increase
Media initial concentration (C_R, C_w)[a]	Increase	Increase
Depth to bottom of soil contamination (L_b)[b]	Increase	Increase
Depth to top of concentration (L_T)	Increase	Decrease
Floor-wall seam gap (w)	Increase	Increase
Soil organic carbon fraction (f_{oc})	Increase	Decrease
Indoor air exchange rate (ER)	Increase	Decrease
Building volume[c] (L_B x W_B x H_B)	Increase	Decrease
Soil total porosity (n)	Increase	Increase
Soil dry bulk density (ρ_b)	Increase	Decrease

[a] This parameter is applicable only when forward-calculating risk.
[b] Applicable only to advanced model for soil contamination.
[c] Used with building air exchange rate to calculate building ventilation rate.

TABLE 9. BUILDING-RELATED PARAMETERS FOR THE VAPOR INTRUSION MODEL

Input Parameter	Units	Fixed or Variable	Typical or Mean Value	Range	Conservative Value	Default Value
Total Porosity	cm^3/cm^3	Fixed	Specific to soil texture, see Table 10			
Unsaturated Zone Water-filled Porosity	cm^3/cm^3	Variable	Specific to soil texture, see Table 10			
Capillary Transition zone Water-filled Porosity	cm^3/cm^3	Fixed	Specific to soil texture, see Table 10			
Capillary Transition Zone height	cm^3/cm^3	Fixed	Specific to soil texture, see Table 10			
Q_{soil}	L/min	Variable	Specific to soil texture, see Table 10			
Soil air permeability	m^2	Variable	Specific to soil texture, see Table 10			
Building Depressurization	Pa	Variable	4	0-15	15	N/A
Henry's law constant (for single chemical)	-	Fixed	Specific to chemical, see Appendix B			
Free-Air Diffusion Coefficient (single chemical)	-	Fixed	Specific to chemical, see Appendix B			
Building Air exchange Rate	hr^{-1}	Variable	0.5	0.1-1.5	0.1	0.25
Building Mixing height – Basement scenario	m	Variable	3.66	2.44-4.88	2.44	3.66
Building Mixing height – Slab-on-grade scenario	m	Variable	2.44	2.13-3.05	2.13	2.44
Building Footprint Area – Basement Scenario	m^2	Variable	120	80-200+	80	100
Building Footprint Area – Slab-on-Grade Scenario	m^2	Variable	120	80-200+	80	100
Subsurface Foundation area – Basement Scenario	m^2	Variable	208	152-313+	152	180
Subsurface Foundation area – Slab-on-Grade Scenario	m^2	Fixed	127	85-208+	85	106
Depth to Base of Foundation – Basement Scenario	m	Fixed	2	N/A	N/A	2
Depth to Base of Foundation – Slab-on-Grade Scenario	m	Fixed	0.15	N/A	N/A	0.15
Perimeter Crack Width	mm	Variable	1	0.5-5	5	1
Building Crack ratio – Slab-on-Grade Scenario	dimensionless	Variable	0.00038	0.00019-0.0019	0.0019	3.77×10^{-4}
Building Crack ratio – Basement Scenario	dimensionless	Variable	0.0002	0.0001-0.001	0.001	2.2×10^{-4}
Crack Dust Water-Filled Porosity	cm^3/cm^3	Fixed	Dry	N/A	N/A	Dry
Building Foundation Slab Thickness	m	Fixed	0.1	N/A	N/A	0.1

TABLE 10. SOIL-DEPENDENT PROPERTIES FOR THE VAPOR INTRUSION MODEL - FIRST TIER ASSESSMENT

U.S. Soil Conservation Service (SCS) Soil Texture	Saturated Water Content Total Porosity θ_s (cm^3/cm^3)	Residual Water Content θ_r (cm^3/cm^3)	Unsaturated Zone Water-Filled Porosity: Mean or Typical ($FC_{1/3bar}+\theta_r$)/2 $\theta_{w,unsat}$ (cm^3/cm^3)	Range $\theta_{w,unsat}$ (cm^3/cm^3)	Conservative $\theta_{w,unsat}$ (cm^3/cm^3)	Modeled $\theta_{w,unsat}$ (cm^3/cm^3)	Capillary Transition Zone: Saturated Water Content Total Porosity θ_s (cm^3/cm^3)	$\theta_{w,cap}$ Cap @ air-entry	Height Cap Zone Fetter (94) (cm)
Clay	0.459	0.098	0.215	0.098-0.33	0.098	0.215	0.459	0.412	81.5
Clay Loam	0.442	0.079	0.168	0.079-0.26	0.079	0.168	0.442	0.375	46.9
Loam	0.399	0.061	0.148	0.061-0.24	0.061	0.148	0.399	0.332	37.5
Loamy Sand	0.39	0.049	0.076	0.049-0.1	0.049	0.076	0.39	0.303	18.8
Silt	0.489	0.05	0.167	0.05-0.28	0.050	0.167	0.489	0.382	163.0
Silt Loam	0.439	0.065	0.180	0.065-0.3	0.065	0.180	0.439	0.349	68.2
Silty Clay	0.481	0.111	0.216	0.11-0.32	0.111	0.216	0.481	0.424	192.0
Silty Clay Loam	0.482	0.09	0.198	0.09-0.31	0.090	0.198	0.482	0.399	133.9
Sand	0.375	0.053	0.054	0.053-0.055	0.053	0.054	0.375	0.253	17.0
Sandy Clay	0.385	0.117	0.197	0.117-0.28	0.117	0.197	0.385	0.355	30.0
Sandy Clay Loam	0.384	0.063	0.146	0.063-0.23	0.063	0.146	0.384	0.333	25.9
Sandy Loam	0.387	0.039	0.103	0.039-0.17	0.039	0.103	0.387	0.320	25.0
Loamy Sand	0.39	0.049	0.076	0.049-0.1	0.049	0.076	0.39	0.303	18.8

TABLE 11. GUIDANCE FOR SELECTION OF SOIL TYPE

If your boring log indicates that the following materials are the predominant soil types …	**Then you should use the following texture classification when obtaining the attenuation factor**
Sand or Gravel or **Sand and Gravel**, with less than about 12 % fines, where "fines" are smaller than 0.075 mm in size.	Sand
Sand or Silty Sand, with about 12 % to 25 % fines	Loamy Sand
Silty Sand, with about 20 % to 50 % fines	Sandy Loam
Silt and Sand or Silty Sand or Clayey, Silty Sand or Sandy Silt or Clayey, Sandy Silt, with about 45 to 75 % fines	Loam
Sandy Silt or Silt, with about 50 to 85 % fines	Silt Loam

These input parameters were developed from the best available soil-physics science, available studies of building characteristics, and international-expert opinion. Consequently, the input parameters listed in Tables 9 and 10 are considered default parameters for a first-tier assessment, which should in most cases provide a reasonably (but not overly) conservative estimate of the vapor intrusion attenuation factor for a site. Justification for the building-related and soil-dependent parameters values selected as default values for the J&E Model is described below.

3.1 JUSTIFICATION OF DEFAULT SOIL-DEPENDENT PROPERTIES

The default soil-dependent parameters recommended for a first tier assessment (Table 10) represent mean or typical values, rather than the most conservative value, in order to avoid overly conservative estimates of attenuation factors. Note, however, that the range of values for some

soil properties can be very large, particularly in the case of moisture content and hydraulic conductivity. Consequently, selecting a soil type and corresponding typical soil property value may not accurately or conservatively represent a given site. Note also that Table 9 does not provide estimates of soil properties for very coarse soil types, such as gravel, gravelly sand, and sandy gravel, etc., which also may be present in the vadose zone. Consequently, in cases where the vadose zone is characterized by very coarse materials, the J&E Model may not provide a conservative estimate of attenuation factor.

As discussed above, the J&E Model is sensitive to the value of soil moisture content. Unfortunately, there is little information available on measured moisture contents below buildings. Therefore, the typical approach is to use a water retention model (e.g., van Genuchten model) to approximate moisture contents. For the unsaturated zone, the selected default value for soil moisture is a value equal to halfway between the residual saturation value and field capacity, using the van Genuchten model-predicted values for U.S. SCS soil types. For the capillary transition zone, a moisture content corresponding to the air entry pressure head is calculated by using the van Genuchten model. When compared to other available water retention models, the van Genuchten model yields somewhat lower water contents, which results in more conservative estimates of attenuation factor. The soil moisture contents listed in Table 10 are based on agricultural samples, which are likely to have higher water contents than soils below building foundations and, consequently result in less-conservative estimates of the attenuation factor.

3.2 JUSTIFICATION OF DEFAULT BUILDING-RELATED PROPERTIES

Building Air Exchange Rate (Default Value = 0.25 AEH)

The results of 22 studies for which building air exchange rates are reported in Hers et al. (2001). Ventilation rates vary widely from approximately 0.1 AEH for energy efficient “air-tight” houses (built in cold climates) (Fellin and Otson, 1996) to over 2 AEH (AHRAE (1985); upper range). In general, ventilation rates will be higher in summer months when natural ventilation rates are highest. Murray and Burmaster (1995) conducted one of the most comprehensive studies of U.S. residential air exchange rates (sample size of 2844 houses). The data set was analyzed on a seasonal basis and according to climatic region. When all the data were analyzed, the 10th, 50th and 90th percentile values were 0.21, 0.51 and 1.48 AEH. Air exchange rates varied depending on season and climatic region. For example, for the winter season and coldest climatic area (Region 1, e.g., Great Lakes area and extreme northeast U.S.), the 10th, 50th , and 90th percentile values were 0.11, 0.27 and 0.71 AEH, respectively.. In contrast, for the winter season and warmest climatic area [Region 4 (southern California, Texas, Florida, Georgia)], the 10th, 50th, and 90th percentile values were 0.24, 0.48 and 1.13 AEH, respectively. Although building air exchange rates would be higher during the summer months, vapor intrusion during winter months (when house depressurization is expected to be most significant) would be of greatest concern. For this guidance, a default value of 0.25 for air exchange rate was selected to represent the lower end of these distributions.

Crack Width and Crack Ratio (Default Value = 0.0002 for basement house; = 0.0038 for slab-on-grade house)

The crack width and crack ratio are related. Assuming a square house and that the only crack is a continuous edge crack between the foundation slab and wall ("perimeter crack"), the crack ratio and crack width are related as follows:

Crack Ratio = Crack Width x 4 x (Subsurface Foundation Area)^0.5/Subsurface Foundation Area

Little information is available on crack width or crack ratio. One approach used by radon researchers is to back-calculate crack ratios using a model for soil gas flow through cracks and the results of measured soil gas flow rates into a building. For example, the back-calculated values for a slab/wall edge crack based on soil gas-entry rates reported in Nazaroff (1992), Revzan *et al.* (1991), and Nazaroff *et al.* (1985) range from about 0.0001 to 0.001. Another possible approach is to measure crack openings although this, in practice, is difficult to do. Figley and Snodgrass (1992) present data from 10 houses where edge crack measurements were made. At the eight houses where cracks were observed, the crack widths ranged from hairline cracks up to 5 mm wide, while the total crack length per house ranged from 2.5 m to 17.3 m. Most crack widths were less than 1 mm. The suggested defaults for crack ratio in regulatory guidance, literature, and models also vary. In ASTM E1739-95, a default crack ratio of 0.01 is used. The crack ratios suggested in the VOLASOIL model (developed by the Dutch Ministry of Environment) range from 0.0001 to 0.000001. The VOLASOIL model values correspond to values for a "good" and "bad" foundation, respectively. The crack ratio used by J&E (1991) for illustrative purposes ranged from 0.001 to 0.01. The selected default values fall within the ranges observed.

Building Area and Subsurface Foundation Area (Default Value = 10 m by 10 m)

The default building area is based on the following information:

- Default values used in the Superfund User's Guide (9.61 m by 9.61 m or 92.4 m^2)
- Default values used by the State of Michigan, as documented in Part 201, Generic Groundwater and Soil Volatilization to Indoor Air Inhalation Criteria: Technical Support Document (10.5 m by 10.5 m of 111.5 m^2).

The Michigan guidance document indicates that the 111.5 m^2 area approximately corresponds to the 10th percentile floor space area for a residential single-family dwelling, based on statistics compiled by the U.S. Department of Commerce (DOC) and U.S. Housing and Urban Development (HUD). The typical, upper, and lower ranges presented in Table 9 are subjectively chosen values. The subsurface foundation area is a function of the building area, and depth to the base of the foundation, which is fixed.

Building Mixing Height (Default Value = 2.44 m for slab-on-grade scenario; = 3.66 m for basement scenario)

The J&E Model assumes that subsurface volatiles migrating into the building are completely mixed within the building volume, which is determined by the building area and mixing height. The building mixing height will depend on a number of factors including building height; heating, ventilation, and air conditioning (HVAC) system operation, environmental factors such as indoor-outdoor pressure differentials and wind loading, and seasonal factors. For a single-story house, the variation in mixing height can be approximated by using the room height. For a multi-story house or apartment building, the mixing height will be greatest for houses with HVAC systems that result in significant air circulation (e.g., forced-air heating systems). Mixing heights would likely be less for houses with electrical baseboard heaters. It is likely that mixing height is, to some degree, correlated to the building air exchange rate.

Little data are available that provides for direct inference of mixing height. There are few sites, with a small number of houses where indoor air concentrations were above background, and where both measurements at ground level and the second floor were made Colorado Department of Transportation (CDOT), Redfields, Eau Claire). Persons familiar with the data sets for these sites indicate that in most cases a fairly significant reduction in concentrations (factor of two or greater) was observed, although at one site (Eau Claire, "S" residence), the indoor trichloroethylene (TCE) concentrations were similar in both the basement and second floor of the house. For the CDOT site apartments, there was an approximate five-fold reduction between the concentrations measured for the first floor and second floor units (Mr. Jeff Kurtz, EMSI, personal communication, June 2002). Less mixing would be expected for an apartment because there are less cross-floor connections than for a house. The value chosen for a basement house scenario (3.66 m) would be representative of a two-fold reduction or attenuation in vapor concentrations between floors.

Q_{soil} (Default Value = 5 L/min)

The method often used with the J&E Model for estimating the soil gas advection rate (Q_{soil}) through the building envelope is an analytical solution for two-dimensional soil gas flow to a small horizontal drain (Nazaroff 1992) ("Perimeter Crack Model"). Use of this model can be problematic in that Q_{soil} values are sensitive to soil-air permeability and consequently a wide range in flows can be predicted.

An alternate empirical approach is to select a Q_{soil} value on the basis of tracer tests (i.e., mass balance approach). When soil gas advection is the primary mechanism for tracer intrusion into a building, the Q_{soil} can be estimated by measuring the concentrations of a chemical tracer in indoor air, in outdoor air, and in soil vapor below a building, and by measuring the building ventilation rate (Hers et al. 2000a; Fischer et al. 1996; Garbesi et al. 1993; Rezvan et al. 1991; Garbesi and Sextro, 1989). For sites with coarse-grained soils (Table 10). The Q_{soil} values measured using this technique are compared to predicted rates using the Perimeter Crack model. The Perimeter Crack model predictions are both higher and lower than the measured values, but overall are within one order of magnitude of the measured values. Although the Q_{soil} values predicted by the models and measured

using field tracer tests are uncertain, the results suggest that a "typical" range for houses on coarse-grained soils is on the order of 1 to 10 L/min. A disadvantage with the tracer test approach is that only limited data are available and there do not appear to be any tracer studies for field sites with fine-grained soils.

It is also important to recognize that the advective zone of influence for soil gas flow is limited to soil immediately adjacent to the building foundation. Some data on pressure coupling provide insight on the extent of the advective flow zone. For example, Garbesi *et al.* (1993) report a pressure coupling between the soil and experimental basement (*i.e.*, relative to that between the basement and atmosphere) equal to 96 percent directly below the slab, between 29 percent and 44 percent at 1 m below the basement floor slab, and between 0.7 percent and 27 percent at a horizontal distance of 2 m from the basement wall. At the Chatterton site (research site investigated by the author), the pressure coupling immediately below the building floor slab ranged from 90 to 95 percent and at a depth of 0.5 m was on the order of 50 percent. These results indicate that the advective zone of influence will likely be limited to a zone within 1 to 2 m of the building foundation.

Because the advective flow zone is relatively limited in extent, the soil type adjacent to the building foundation is of importance. In many cases, coarse-grained imported fill is placed below foundations, and either coarse-grained fill, or disturbed, loose fill is placed adjacent to the foundation walls. Therefore, a conservative approach for the purposes of this guidance is to assume that soil gas flow will be controlled by coarse-grained soil, and not rely on the possible reduction in flow that would be caused by fine-grained soils near to the house foundation. For these reasons, a soil gas flow rate of 5 L/min (midpoint between 1 and 10 L/min) was chosen as the input value.

3.3 RUNNING THE MODELS

Eight different models are provided in MICROSOFT EXCEL formats.

1. Models for Soil Contamination:
   SL-SCREEN-Feb 04.XLS
   SL-ADV-Feb 04.XLS

2. Models for Groundwater Contamination:
   GW-SCREEN-Feb 04.XLS
   GW-ADV-Feb 04.XLS

3. Model for Soil Gas Contamination
   SG-SCREEN-Feb 04.xls
   SG-ADV-Feb 04.xls

4. Models for Non Aqueous Phase Liquids
   NAPL-SCREEN-Feb 04.xls

NAPL-ADV-Feb 04.xls

Both the screening-level models and the advanced models allow the user to calculate a risk-based media concentration or incremental risks from an actual starting concentration in soil or in groundwater. Data entry within the screening-level models is limited to the most sensitive model parameters and incorporates only one soil stratum above the contamination. The advanced models provide the user with the ability to enter data for all of the model parameters and also incorporate up to three individual soil strata above the contamination for which soil properties may be varied.

To run any of the models, simply open the appropriate model file within MICROSOFT EXCEL. Each model is constructed of the following worksheets:

1. DATENTER (Data Entry Sheet)
2. CHEMPROPS (Chemical Properties Sheet)
3. INTERCALCS (Intermediate Calculations Sheet)
4. RESULTS (Results Sheet)
5. VLOOKUP (Lookup Tables).

The following is an explanation of what is contained in each worksheet, how to enter data, how to interpret model results, and how to add/revise the chemical properties data found in the VLOOKUP Tables. As examples, Appendix C contains all the worksheets for the advanced soil contamination model SL-ADV.

3.4 THE DATA ENTRY SHEET (DATENTER)

Figure 4 is an example of a data entry sheet. In this case, it shows the data entry sheet for the screening-level model for contaminated groundwater (GW-SCREEN). Figure 5 is an example of an advanced model data entry sheet (GW-ADV). Note that the screening-level model sheet requires entry of considerably less data than does the advanced sheet. To enter data, simply position the cursor within the appropriate box and type the value; all other cells are protected.

Error Messages

In the case of the screening-level models, all error messages will appear in red type below the applicable row of data entry boxes. For the advanced models, error messages may appear on the data entry sheet or in the lower portion of the results sheet. Error messages will occur if required entry data are missing or if data are out of range or do not conform to model conventions. The error message will tell the user what kind of error has occurred.

GW-SCREEN
Version 3.1; 02/04

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES [X]

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION
(enter "X" in "YES" box and initial groundwater conc. below)

YES [ ]

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (μg/L)	Chemical
56235		Carbon tetrachloride

MORE ↓

ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to water table, L_{WT} (cm)	ENTER SCS soil type directly above water table	ENTER Average soil/ groundwater temperature, T_S (^{0}C)	ENTER Average vapor flow rate into bldg. (Leave blank to calculate) Q_{soil} (L/m)
200	400	SC	10	5

MORE ↓

ENTER Vadose zone SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined vandose zone soil vapor permeability, k_v (cm^2)	ENTER Vadose zone SCS soil type (Lookup Soil Parameters)	ENTER Vadose zone soil dry bulk density, ρ_b^V (g/cm^3)	ENTER Vadose zone soil total porosity, n^V (unitless)	ENTER Vadose zone soil water-filled porosity, θ_w^V (cm^3/cm^3)
SC			SC	1.63	0.385	0.197

MORE ↓

ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)	ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)
1.0E-06	1	70	30	30	350
Used to calculate risk-based groundwater concentration.					

Figure 4. GW-SCREEN Data Entry Sheet

GW-ADV
Version 3.1; 02/04

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES [X]

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION (enter "X" in "YES" box and initial groundwater conc. below

YES [ ]

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (µg/L)	Chemical
56235		Carbon tetrachloride

MORE ↓

ENTER Average soil/ groundwater temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to water table, L_{WT} (cm)	ENTER Totals must add up to value of L_{WT} (cell G28) Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum directly above water table, (Enter A, B, or C)	ENTER SCS soil type directly above water table	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
10	200	400	300	50	50	C	SC	C		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
C	1.43	0.459	0.215	S	1.66	0.375	0.054	SC	1.63	0.385	0.197

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
10	40	1000	1000	366	0.1	0.25	5

MORE ↓

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	30	30	350	1.0E-06	1
				Used to calculate risk-based groundwater concentration.	

END

Figure 5. GW-ADV Data Entry Sheet

Figure 6 is an example of an error message appearing on the data entry sheet. Figure 7 illustrates error messages appearing within the message and error summary section on the results sheet (advanced models only).

Entering Data

Each data entry sheet requires the user to input values for model variables. Data required for the soil contamination scenario will differ from that required for the groundwater contamination scenario. In addition, data required for the screening-level models will differ from that required for the advanced models.

Model Variables--

The following is a list of all data entry variables required for evaluating either a risk-based media concentration or the incremental risks due to actual contamination. A description for which model(s) the variable is appropriate is given in parenthesis after the name of the variable. In addition, notes on how the variable is used in the calculations and how to determine appropriate values of the variable are given below the variable name. A quick determination of which variables are required for a specific model can be made by reviewing the data entry sheet for the model chosen. Example data entry sheets for each model can be found in Appendix D.

1. *Calculate Risk-Based Concentration* or *Calculate Incremental Risks from Actual Concentration* (All Soil and Groundwater Models)

   The model will calculate either a risk-based soil or groundwater concentration or incremental risks but cannot calculate both simultaneously. Enter an "X" in only one box.

2. *Chemical CAS No.* (All Models)

   Enter the appropriate CAS number for the chemical you wish to evaluate; do not enter dashes. The CAS number entered must exactly match that of the chemical, or the error message "CAS No. not found" will appear in the "Chemical" box. Once the correct CAS number is entered, the name of the chemical will automatically appear in the "Chemical" box. A total of 108 chemicals and their associated properties are included with each model; see Section 3.7 for instructions on adding/revising chemicals.

GW-SCREEN
Version 3.1; 02/04

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES [X]

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION
(enter "X" in "YES" box and initial groundwater conc. below)

YES [X]

Cannot calculate risk-based concentration and incremental risk simultaneously.

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (μg/L)	Chemical
56235		Carbon tetrachloride

Figure 6. Example Error Message on Data Entry Sheet

RISK-BASED SOIL CONCENTRATION CALCULATIONS:

Indoor exposure soil conc., carcinogen (μg/kg)	Indoor exposure soil conc., noncarcinogen (μg/kg)	Risk-based indoor exposure soil conc., (μg/kg)	Soil saturation conc., C_{sat} (μg/kg)	Final indoor exposure soil conc., (μg/kg)
NA	NA	NA	3.09E+05	NA

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
8.0E-08	7.9E-04

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

SCROLL DOWN TO "END"

ERROR: Combined thickness of strata A + B + C must be = depth below grade to top of contamination.

Figure 7. Example Error Message on Results Sheet

3. *Initial Soil or Groundwater Concentration* (All Soil and Groundwater Models) (L_w)

Enter a value only if incremental risks are to be calculated. Be sure to enter the concentration in units of µg/kg (wet weight basis soil) or µg/L (groundwater). Typically, this value represents the average concentration within the zone of contamination. If descriptive statistics are not available to quantify the uncertainty in the average value, the maximum value may be used as an upper bound estimate.

4. *Average Soil/Groundwater Temperature* (All Models) (T_s)

The soil/groundwater temperature is used to correct the Henry's law constant to the specified temperature. Figure 8 from U.S. EPA (1995) shows the average temperature of shallow groundwater in the continental United States. Shallow groundwater temperatures may be used to approximate subsurface soil temperatures greater than 1 to 2 meters below the ground surface. Another source of information may be your State groundwater protection regulatory agency.

5. *Depth Below Grade to Bottom of Enclosed Space Floor* (All Models) (L_F)

Enter the depth to the <u>bottom</u> of the floor in contact with the soil. The default value for slab-on-grade and basement construction is 15 cm and 200 cm, respectively.

6. *Depth Below Grade to Top of Contamination* (Soil Models Only) (L_T)

Enter the depth to the top of soil contamination. If the contamination begins at the soil surface, enter the depth below grade to the <u>bottom</u> of the enclosed space floor. The depth to the top of contamination must be greater than or equal to the depth to the bottom of the floor.

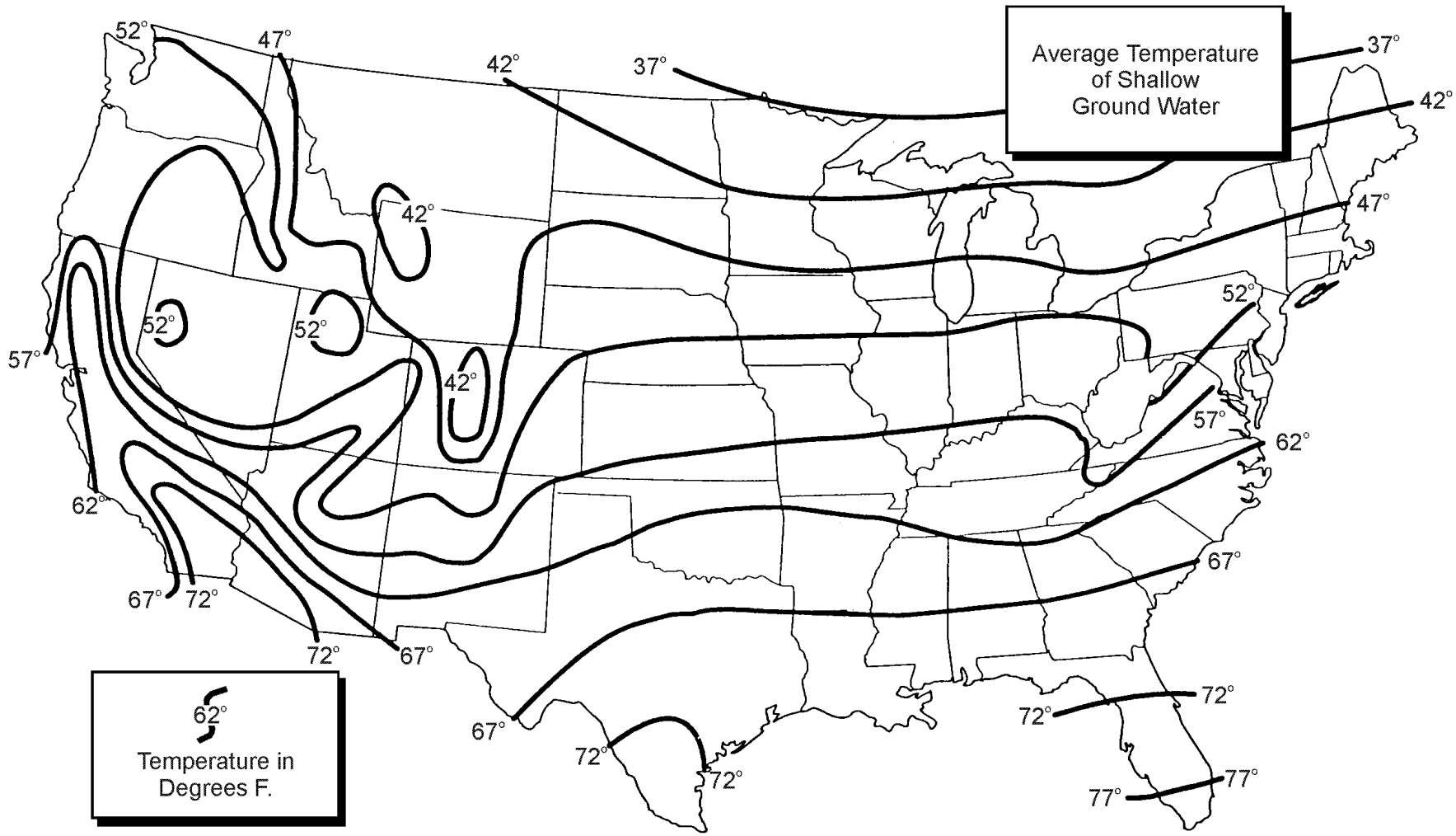


Figure 8. Average Shallow Groundwater Temperature in the United States

7. *Depth Below Grade to Water Table* (Groundwater Models Only) (L_{wt})

Enter the depth to the top of the water table (i.e., where the pressure head is equal to zero and the pressure is atmospheric).

Note: The thickness of the capillary zone is calculated based on the SCS soil textural classification above the top of the water table. The depth below grade to the top of the water table minus the thickness of the capillary zone must be greater than the depth below grade to the bottom of the enclosed space floor. This means that the top of the capillary zone is always below the floor.

8. *Depth Below Grade to Bottom of Contamination* (Advanced Soil Model Only) (L_B)

This value is used to calculate the thickness of soil contamination. A value greater than zero and greater than the depth to the top of contamination will automatically invoke the finite source model. If the thickness of contamination is unknown, two options are available:

1. Entering a value of zero will automatically invoke the infinite source model.

2. Enter the depth to the top of the water table. This will invoke the finite source model under the assumption that contamination extends from the top of contamination previously entered down to the top of the water table.

9. *Thickness of Soil Stratum "X"* (Advanced Models Only) (h_x, x = A, B, or C)

In the advanced models, the user can define up to three soil strata between the soil surface and the top of contamination or to the soil gas sampling depth, as appropriate. These strata are listed as A, B, and C. Stratum A extends down from the soil surface, Stratum B is below Stratum A, and Stratum C is the deepest stratum. The thickness of Stratum A must be at least as thick as the depth below grade to the bottom of the enclosed space floor. The combined thickness of all strata must be equal to the depth to the top of contamination, or to the soil gas sampling depth, as appropriate. If soil strata B and/or C are not to be considered, a value of zero must be entered for each stratum not included in the analysis.

10. *Soil Stratum A SCS Soil Type* (Advanced Models Only) (SES – soil)

Enter one of the following SCS soil type abbreviations:

Abbreviation	SCS Soil Type
C	Clay
CL	Clay loam
L	Loam
LS	Loamy sand
S	Sand
SC	Sandy clay
SCL	Sandy clay loam
SI	Silt
SIC	Silty clay
SICL	Silty clay loam
SIL	Silty loam
SL	Sandy loam

The SCS soil textural classification can be determined by using either the ATSM Standard Test Method for Particle-Size Analysis of Soils (D422-63) or by using the analytical procedures found in the U.S. Natural Resources Conservation Service (NRCS) Soil Survey Laboratory Methods Manual, Soil Survey Laboratory Investigations Report No. 42. After determining the particle size distribution of a soil sample, the SCS soil textural classification can be determined using the SCS classification chart in Figure 7.

The SCS soil type along with the Stratum A soil water-filled porosity is used to estimate the soil vapor permeability of Stratum A which is in contact with the floor and walls of the enclosed space below grade. Alternatively, the user may define a soil vapor permeability (see Variable No. 11).

11. *User-Defined Stratum A Soil Vapor Permeability* (Advanced Models Only)(K_v)

As an alternative to estimating the soil vapor permeability of soil Stratum A, the user may define the soil vapor permeability. As a general guide, the following represent the practical range of vapor permeabilities:

Soil type	Soil vapor permeability, cm^2
Medium sand	1.0×10^{-7} to 1.0×10^{-6}
Fine sand	1.0×10^{-8} to 1.0×10^{-7}
Silty sand	1.0×10^{-9} to 1.0×10^{-8}
Clayey silts	1.0×10^{-10} to 1.0×10^{-9}

12. *Vadose Zone SCS Soil Type* (Screening Models Only) (SCS – soil)

Because the screening-level models accommodate only one soil stratum above the top of contamination or soil gas sampling depth, enter the SCS soil type from the list given in Variable No. 10.

13. *User-Defined Vadose Zone Soil Vapor Permeability* (Screening Models Only) (K_v)

For the same reason cited in No. 12 above, the user may alternatively define a soil vapor permeability. Use the list of values given in Variable No. 11 as a general guide.

14. *Soil Stratum Directly Above the Water Table* (Advanced Groundwater Models Only) (A, B, or C)

Enter either A, B, or C as the soil stratum directly above the water table. This value must be the letter of the deepest stratum for which a thickness value has been specified under Variable No. 9.

15. *SCS Soil Type Directly Above Water Table* (Groundwater Models Only) (SCS – soil)

Enter the correct SCS soil type from the list given in Variable No. 10 for the soil type directly above the water table. The soil type entered is used to estimate the rise (thickness) of the capillary zone.

16. *Stratum "X" Soil Dry Bulk Density* (Advanced Models Only) (P_x, x = A, B, or C)

Identify the soil type for each strata and accept the default value or enter a site-specific value for the average soil dry bulk density. Dry bulk density is used in a number of intermediate calculations and is normally determined by field measurements (ASTM D 2937 Method).

17. *Stratum "X" Soil Total Porosity* (Advanced Models Only) (n^x, x = A, B, or C)

Total soil porosity (n) is determined as:

$$n = 1\ \rho_b/\rho_s$$

where ρ_b is the soil dry bulk density (g/cm^3) and ρ_s is the soil particle density (usually 2.65 g/cm^3).

18. *Stratum "X" Soil Water-Filled Porosity* (Advanced Models Only) (θ_w^x, X = a, b, or c)

Enter the average long-term volumetric soil moisture content; this is typically a depth-averaged value for the appropriate soil stratum. A long-term average value is typically not readily available. Do not use values based on episodic measurements unless they are representative of long-term conditions. Table 10 provides a soil-specific range of typical value for specified soils. The user must define soil type or input site-specific values.

One option is to use a model to estimate the long-term average soil water-filled porosities of each soil stratum between the enclosed space floor and the top of contamination. The HYDRUS model version 5.0 (Vogel et al., 1996) is a public domain code for simulating one-dimensional water flow, solute transport, and heat movement in variably-saturated soils. The water flow simulation module of HYDRUS will generate soil water content as a function of depth and time given actual daily precipitation data. Model input requirements include either the soil hydraulic properties of van Genuchten (1980) or those of Brooks and Corey (1966). The van Genuchten soil hydraulic properties required are the same as those given in Tables 3 and 4 (i.e., θ_s, θ_r, N, α_1, and K_s). The HYDRUS model is available from the U.S. Department of Agriculture (USDA) - Agricultural Research Service in Riverside, California via their internet website at http://www.ussl.ars.usda.gov/MODELS/HYDRUS.HTM. One and two-dimensional commercial versions of HYDRUS (Windows versions) are available at the International Ground Water Modeling Center website at http://www.mines.edu/research/igwmc/software/. Schaap and Leij (1998) have recently developed a Windows program entitled ROSETTA for estimating the van Genuchten soil hydraulic properties based on a limited or more extended set of input

data. The ROSETTA program can be found at the USDA website: http://www.ussl.ars.usda.gov/MODELS/rosetta/rosetta.htm. The van Genuchten hydraulic properties can then be input into HYDRUS to estimate soil moisture content.

19. *Stratum "X" Soil Organic Carbon Fraction* (Advanced Soil Models Only) (f_{oc}^{x}, X = A, B, or c)

Enter the depth-averaged soil organic carbon fraction for the stratum specified. Soil organic carbon is measured by burning off soil carbon in a controlled-temperature oven. This parameter, along with the chemical's organic carbon partition coefficient (K_{oc}), is used to determine the soil-water partition coefficient (K_d).

20. *Vadose Zone Soil Dry Bulk Density* (Screening Models Only) (ρ^A)

Because the screening-level models accommodate only one soil stratum above the top of contamination, identify the soil type and accept the default values or enter the depth-averaged soil dry bulk density. The universal default value is 1.5 g/cm^3, which is consistent with U.S. EPA (1996a and b) for subsurface soils.

21. *Vadose Zone Soil Total Porosity* (Screening Models Only) (m^A)

Because the screening-level models accommodate only one soil stratum above the top of contamination, enter the depth-averaged soil total porosity. The default value is 0.43, which is consistent with U.S. EPA (1996a and b) for subsurface soils.

22. *Vadose Zone Soil Water-Filled Porosity* (Screening Models Only) (θ_w^A)

Because the screening-level models accommodate only one soil stratum above the top of contamination, enter the depth-averaged soil water-filled porosity. The default value is 0.30, which is consistent with U.S. EPA (1996a and b) for subsurface soils.

23. *Vadose Zone Soil Organic Carbon Fraction* (Soil Screening Model Only) (f_{oc}^A)

Because the screening-level models accommodate only one soil stratum above the top of contamination, enter the depth-averaged soil organic carbon fraction. The default value is 0.002, which is consistent with U.S. EPA (1996a and b) for subsurface soils.

24. *Enclosed Space Floor Thickness* (Advanced Models Only) (L_{crack})

Enter the thickness of the floor slab. All models operate under the assumption that the floor in contact with the underlying soil is composed of impermeable concrete

whether constructed as a basement floor or slab-on-grade. The default value is 10 cm, which is consistent with J&E (1991).

25. *Soil-Building Pressure Differential* (Advanced Models Only) (ΔP)

Because of wind effects on the structure, stack effects due to heating of the interior air, and unbalanced mechanical ventilation, a negative pressure with respect to the soil surface is generated within the structure. This pressure differential (ΔP) induces a flow of soil gas through the soil matrix and into the structure through cracks, gaps, and openings in the foundation. The effective range of values of ΔP is 0-20 pascals (Pa) (Loureiro et al., 1990; Eaton and Scott, 1984). Individual average values for wind effects and stack effects are approximately 2 Pa (Nazaroff et al., 1985; Put and Meijer, 1989). Typical values for the combined effects of wind pressures and heating are 4 to 5 Pa (Loureiro et al., 1990; Grimsrud et al., 1983). A conservative default value of ΔP was therefore chosen to be 4 Pa (40 g/cm-s^2).

For more information on estimating site-specific values of ΔP, the user is referred to Nazaroff et al. (1987) and Grimsrud et al. (1983).

26. *Enclosed Space Floor Length* (Advanced Models Only) (L_B)

The default value is 1000 cm (see Variable No. 28).

27. *Enclosed Space Floor Width* (Advanced Models Only) (W_B)

The default value is 1000 cm (see Variable No. 28).

28. *Enclosed Space Height* (Advanced Models Only) (H_B)

For a single story home, the variation in mixing height will be the greatest for houses with HVAC systems that result in significant air circulation (e.g., forced air heat pump). Mixing heights would be less for houses with electrical baseboard heaters. The mixing height is approximated by the room height. The default value is 2.44 meters for a single story house without a basement.

For a single story house with a basement less mixing would be expected because of the cross floor connections. The default values for a house with a basement is 3.66 m. This value represents a two-fold reduction in vapor concentrations between the floors.

29. *Floor-Wall Seam Crack Width* (Advanced Models Only) (W)

The conceptual model used in the spreadsheets follows that of Loureiro et al. (1990) and Nazaroff (1988) and is illustrated in Figure 9. The model is based on a single-

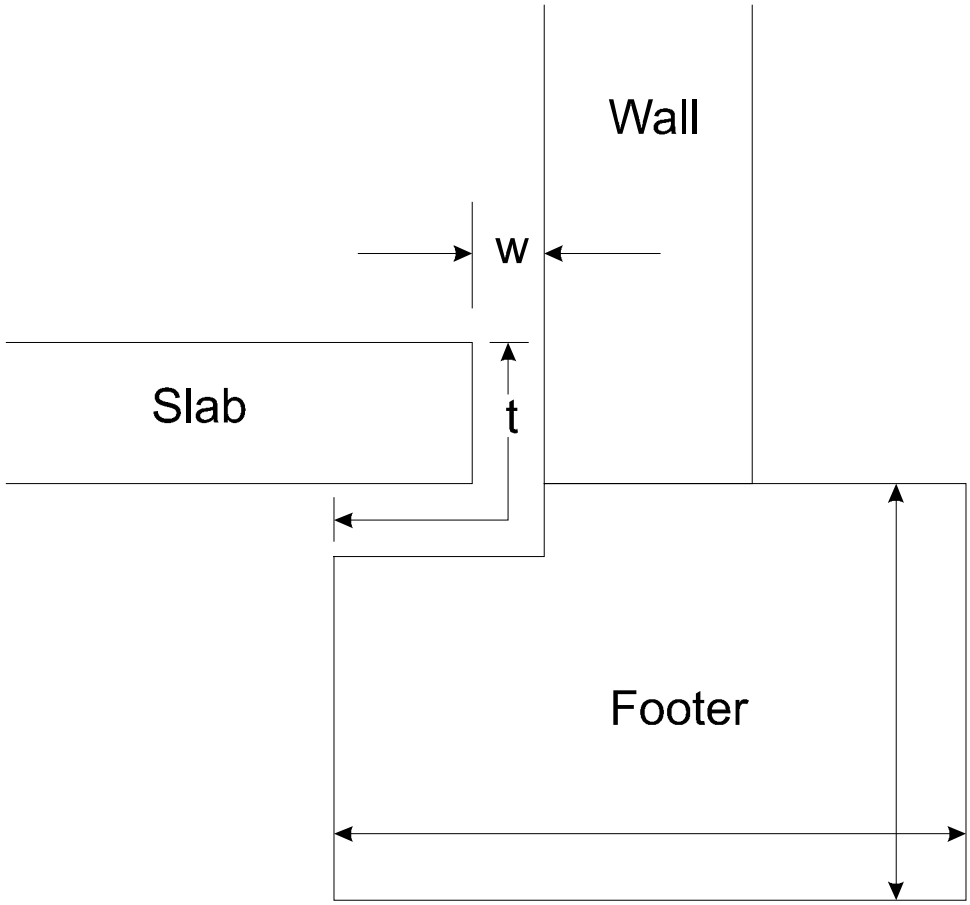


Figure 9. Floor Slab and Foundation

family house with a poured concrete basement floor and wall foundations, or constructed slab-on-grade in similar fashion. A gap is assumed to exist at the junction between the floor and the foundation along the perimeter of the floor. The gap exists as a result of building design or concrete shrinkage. This gap is assumed to be the only opening in the understructure of the house and therefore the only route for soil gas entry.

Eaton and Scott (1984) reported typical open areas of approximately 300 cm^2 for the joints between walls and floor slabs of residential structures in Canada. Therefore, given the default floor length and width of 1000 cm, a gap width (w) of 0.1 cm equates to a total gap area of 900 cm^2, which is reasonable given the findings of Eaton and Scott. This value of the gap width is also consistent with the typical value reported in Loureiro et al. (1990). The default value of the floor-wall seam crack width was therefore set equal to 0.1 cm.

30. *Indoor Air Exchange Rate* (Advanced Models Only) (ER)

The indoor air exchange rate is used along with the building dimensions to calculate the building ventilation rate. The default value of the indoor air exchange rate is 0.25/h. This value is consistent with the 10th percentile of houses in all regions of the U.S., as reported in Koontz and Rector (1995). This value is also consistent with the range of the control group of 331 houses in a study conducted by Parker et al. (1990) to compare data with that of 292 houses with energy-efficient features in the Pacific Northwest.

31. *Averaging Time for Carcinogens* (All Models) (AT_c)

Enter the averaging time in units of years. The default value is 70 years.

32. *Averaging Time for Noncarcinogens* (All Models) (AT_{nc})

Enter the averaging time in units of years. The averaging time for noncarcinogens is set equal to the exposure duration. The default value for residential exposure from U.S. EPA (1996a and b) is 30 years.

33. *Exposure Duration* (All Models) (ED)

Enter the exposure duration in units of years. The default value for residential exposure from U.S. EPA (1996a and b) is 30 years.

34. *Exposure Frequency* (All Models) (EF)

Enter the exposure frequency in units of days/yr. The default value for residential exposure from U.S. EPA (1996a and b) is 350 days/yr.

35. *Target Risk for Carcinogens* (All Soil and Groundwater Models) (TR)

If a risk-based media concentration is to be calculated, enter the target risk-level. The default value is 1×10^{-6}.

36. *Target Hazard quotient for Noncarcinogens* (All Soil and Groundwater Models) (THQ)

If a risk-based media concentration is to be calculated, enter the target hazard quotient. The default value is 1.

The remaining four worksheets include the results sheet (RESULTS) and three ancillary sheets. The ancillary sheets include the chemical properties sheet (CHEMPROPS), the intermediate calculations sheet (INTERCALCS), and the lookup tables (VLOOKUP).

3.5 THE RESULTS SHEET (RESULTS)

Once all data are entered in the data entry sheet, the model results may be viewed on the RESULTS sheet. For the soil and groundwater models, calculations are presented as either a risk-based soil or groundwater concentration, or the incremental risks associated with an initial soil or groundwater concentration. In the case of the advanced models, the user should check the message and error summary below the results section to ensure that no error messages appear. If one or more error messages appear, re-enter the appropriate data.

The RESULTS worksheet shows the indoor exposure soil or groundwater concentration for either a carcinogen or noncarcinogen as appropriate. When a contaminant is both a carcinogen and a noncarcinogen, the risk-based indoor exposure concentration is set equal to the lower of these two values. In addition, the soil saturation concentration (C_{sat}) or the aqueous solubility limit (S) is also displayed for the soil and groundwater models, respectively.

The equilibrium vapor concentration at the source of contamination is limited by the value of C_{sat} for soil contamination and by the value of S for groundwater contamination, as appropriate. For a single contaminant, the vapor concentration directly above the source of soil contamination cannot be greater than that associated with the soil saturation concentration; for groundwater contamination, the vapor concentration cannot be greater than that associated with the solubility limit. As a result, subsurface soil concentrations greater than C_{sat} and groundwater concentrations greater than S will not produce higher vapor concentrations. Therefore, if the indoor vapor concentration predicted from a soil concentration greater than or equal to the value of C_{sat} and it does not exceed the health-based limit in indoor air (target risk or target hazard quotient), the vapor intrusion pathway will not be of concern for that particular chemical. The same is true for an indoor vapor concentration predicted from a groundwater concentration greater than or equal to the value of S. That does not necessarily mean, however, that the subsurface contamination will not be of concern from a groundwater protection standpoint, (ingestion) and the potential for free-phase contamination (e.g., NAPL) must also be addressed.

For subsurface soils, the physical state of a contaminant at the soil temperature plays a significant role. When a contaminant is a liquid (or gas) at the soil temperature, the upper limit of the soil screening level is set at C_{sat}. This tends to reduce the potential for NAPL to exist within the vadose zone. The case is different for a subsurface contaminant that is a solid at the soil temperature. In this case, the screening level is not limited by C_{sat} because of the reduced possibility of leaching to the water table. If the model estimates a risk-based screening level greater than C_{sat} for a solid in soils, the model will display the final soil concentration as "NOC" or Not of Concern for the vapor intrusion pathway.

In the case of groundwater contamination, the physical state of the contaminant is not an issue in that the contamination has already reached the water table. Because the equilibrium vapor concentration at the source of emissions cannot be higher than that associated with the solubility limit, the vapor concentration is calculated at the solubility limit if the user enters a groundwater concentration greater than the value of S when forward-calculating risk. When reverse-calculating a risk-based groundwater concentration, the model will display the final groundwater concentration as "NOC" for the vapor intrusion pathway if the model calculates a risk-based level greater than or equal to the value of S. It should be noted, however, that if the soil properties or other conditions specified in the DATENTER worksheet are changed, the final risk-based soil or groundwater concentration must be remodeled.

It should also be understood that if a contaminant is labeled "Not of Concern" for the vapor intrusion pathway, all other relevant exposure pathways must be considered for both contaminated soils and groundwater.

3.6 THE CHEMICAL PROPERTIES SHEET (CHEMPROPS)

The chemical properties sheet provides a summary of the chemical and toxicological properties of the chemical selected for analysis. These data are retrieved from the VLOOKUP sheet by CAS number. All data in the chemical properties sheet are protected.

3.7 THE INTERMEDIATE CALCULATIONS SHEET (INTERCALS)

The intermediate calculations sheet provides solutions to intermediate variables. Review of the values of the intermediate variables may be helpful in an analysis of the cause-and-effect relationships between input values and model results. All data in the intermediate calculations sheet are protected.

3.8 THE LOOKUP TABLES (VLOOKUP)

The VLOOKUP sheet contains two lookup tables from which individual data are retrieved for a number of model calculations. The first table is the Soil Properties Lookup Table. This table contains the average soil water retention curve data of Hers (2002) and Schaap and Leij (1998) and the mean grain diameter data of Nielson and Rogers (1990) by SCS soil type, and the mean dry bulk density from Leij, Stevens, et al (1994).

3.9 ADDING, DELETING, OR REVISING CHEMICALS

Data for any chemical may be edited, new chemicals added, or existing chemicals deleted from the Chemical Properties Lookup Table within the VLOOKUP worksheet. To begin an editing

session, the user must unprotect (unseal) the worksheet (the password is "ABC" in capital letters); editing of individual elements or addition and deletion of chemicals may then proceed. Space has been allocated for up to 260 chemicals in the lookup table. Row number 284 is the last row that may be used to add new chemicals. After the editing session is complete, the user must sort all the data in the lookup table (except the column headers) in ascending order by CAS number. After sorting is complete, the worksheet should again be protected (sealed).

SECTION 4

SOIL GAS MODEL APPLICATION

Two additional models have been added to allow the user to input measured soil gas concentration and sampling depth data directly into the spreadsheet. These models eliminate the need for theoretical partitioning of a total volume soil concentration or a groundwater concentration into discrete phases. This section provides instructions for using the soil gas models.

4.1 RUNNING THE MODELS

Two models are provided as MICROSOFT EXCEL spreadsheets. The screening-level model is titled SG-SCREEN.xls (EXCEL). The advanced model is titled SG-ADV.xls.

Both the screening-level and advanced models allow the user to calculate steady-state indoor air concentrations and incremental risks from user-defined soil gas concentration data. The models do not allow for reverse-calculation of a risk-based soil or groundwater concentration. As with the soil and groundwater screening-level models, the SG-SCREEN model operates under the assumption that the soil column properties are homogeneous and isotropic from the soil surface to an infinite depth. In addition, the SG-SCREEN model uses the same default values for the building properties as the SL-SCREEN and GW-SCREEN models. The advanced model allows the user to specify up to three different soil strata from the bottom of the building floor in contact with the soil to the soil gas sampling depth. Finally, the advanced model allows the user to specify values for all of the model variables.

To run the models, simply open the appropriate file within either MICROSOFT EXCEL worksheet. Each model is constructed of the following worksheets:

1. DATENTER (Data Entry Sheet)
2. CHEMPROPS (Chemical Properties Sheet)
3. INTERCALCS (Intermediate Calculations Sheet)
4. RESULTS (Results Sheet)
5. VLOOKUP (Lookup Tables)

Each worksheet follows the form of the worksheets in the soil and groundwater models. See Section 4.2 for a description of each worksheet.

The DATENTER worksheet of each of the soil gas models is different than those of the soil and groundwater models. Figure 10 shows the DATA ENTER worksheet of the SG-ADV model. Note that there is no option for running the model to calculate a risk-based media concentration. As with the other models, the user enters the CAS number of the chemical of interest. This automatically retrieves the chemical and toxicological data for that chemical. The CAS number must match one of the chemicals listed in the VLOOKUP worksheet, or the message "CAS No. not found" will appear in the "Chemical" box. The user also has the opportunity to add new chemicals to the data base. Next, the user must enter a value for the soil gas concentration of the chemical of interest. The user may enter this value in units of $\mu g/m^3$ or parts-per-million by volume (ppmv). If the soil gas concentration is entered in units of ppmv, the concentration is converted to units of $\mu g/m^3$ by:

$$C_g' = \frac{C_g \times MW}{R \times T_S} \qquad (33)$$

where C_g' = Soil gas concentration, $\mu g/m^3$

C_g = Soil gas concentration, ppmv

MW = Molecular weight, g/mol

R = Gas constant (= 8.205 E-05 atm-m^3/mol-^oK)

T_S = System (soil) temperature, ^oK.

In the soil gas models, the steady-state indoor air concentration is calculated by Equation 19 (i.e., $C_{building} = \alpha\ C_{source}$). The value of the vapor concentration at the source of emissions (C_{source}) is assigned the value of the user-defined soil gas concentration. The value of the steady-state attenuation coefficient (α) in Equation 19 is calculated by Equation 13. Because no evaluation has been made of the extent of the source of emissions, steady-state conditions (i.e., a non-diminishing source) must be assumed.

The SG-SCREEN model operates under the assumption of homogeneously distributed soil properties and isotropic conditions with respect to soil vapor permeability from the soil surface to an infinite depth. The SG-ADV model, on the other hand, allows the user to specify up to three different soil strata between the building floor in contact with the soil and the soil gas sampling depth. Soil properties within these three strata may be varied to allow for different diffusion resistances to vapor transport.

4.2 SOIL GAS SAMPLING

In order to use the soil gas models, soil gas concentrations must be measured at one or more depths below ground surface (bgs). The user is advised to take samples directly under building slabs

SG-ADV
Version 3.1; 02/04

Reset to Defaults

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Soil gas conc., C_g ($\mu g/m^3$)	OR	ENTER Soil gas conc., C_g (ppmv)	Chemical
	Soil Gas Concentration Data			
71432			2.00E+01	Benzene

MORE ↓

ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Soil gas sampling depth below grade, L_s (cm)	ENTER Average soil temperature, T_S (°C)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of Ls (cell F24)					
200	400	10	200	100	100	L		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
	1.5	0.43	0.15		1.5	0.43	0.25		1.7	0.38	0.3

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
10	40	1000	1000	366	0.1	0.25	5

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)
70	30	30	350

END

Figure 10. SG-ADV Data Entry Worksheet

or basement floors when possible. This can be accomplished by drilling through the floor and sampling through the drilled hole. Alternatively, an angle-boring rig can be used to sample beneath the floor from outside the footprint of the building. When sampling directly beneath the floor is not possible, enough samples adjacent to the structure should be taken to adequately estimate an average concentration based on reasonable spatial and temporal scales.

Soil gas measurements can be made using several techniques; however, active whole-air sampling methods and active or passive sorbent sampling methods are usually employed. Typically, a whole-air sampling method is used whereby a non-reactive sampling probe is inserted into the soil to a prescribed depth. This can be accomplished manually using a "slam bar," or a percussion power drill, or the probe can be inserted into the ground using a device such as a Geoprobe.® The Geoprobe® device is attached to the rear of a specially customized vehicle. In the field, the rear of the vehicle is placed over the sample location and hydraulically raised on its base. The weight of the vehicle is then used to push the sampling probe into the soil. A built-in hammer mechanism allows the probe to be driven to predetermined depths up to 50 feet depending on the type of soil encountered. Soil gas samples can be withdrawn directly from the probe rods, or flexible tubing can be connected to the probe tips at depth for sample withdrawal.

Whole-air sampling is typically accomplished using an evacuated Summa or equivalent canister, or by evacuation to a Tedlar bag. Normal operation includes the use of an in-line flow controller and a sintered stainless steel filter to minimize particles becoming entrained in the sample atmosphere. For a 6-liter Summa canister, a normal sampling flow rate for a 24-hr integrated sample might be on the order of 1.5 ml/min; however, higher sampling rates can be used for grab samples. The sampling rate chosen, however, must not be so high as to allow for ambient air inleakage between the annulus of the probe and the surrounding soils. Depending on the target compounds, excessive air inleakage can dilute the sample (in some cases below the analytical detection limits).

One way to check for inleakage is to test an aliquot of the sample gas for either nitrogen or oxygen content before the sample is routed to the canister or Tedlar bag. To test for nitrogen in real- or near real-time requires a portable gas chromatograph/mass spectrometer (GC/MS). A portable oxygen meter, however, can be used to test for sample oxygen content in real-time with a typical accuracy of one-half of one percent. If air inleakage is detected by the presence of excessive nitrogen or oxygen, the seal around the sample probe at the soil surface as well as all sampling equipment connections and fittings should be checked. Finally, the flow rate may need to be reduced to decrease or eliminate the air inleakage.

The collection and concentration of soil gas contaminants can be greatly affected by the components of the sampling system. It is imperative to use materials that are inert to the contaminants of concern. Areas of sample collection that need particular attention are:

- The seal at the soil surface around the sample probe
- Use of a probe constructed of stainless steel or other inert material
- Minimization of the use of porous or synthetic materials (i.e., PTFE, rubber, or most plastics) that may adsorb soil gas and cause cross-contamination

- Purging of the sample probe and collection system before sampling
- Leak-check of sampling equipment to reduce air infiltration
- Keeping the length of all sample transfer lines as short as possible to minimize condensation of extracted gas in the lines.

The choice of analytical methods for whole-air soil gas sampling depends on the contaminants of concern. Concentrations of volatile organic compounds (VOCs) in the soil gas are typically determined using EPA Method TO-14 or TO-15. In the case of semi-volatile compounds, an active sorbent sampling methodology can be used. In this case, a low-volume sampling pump is normally used to withdraw the soil gas, which is then routed to a polyurethane foam (PUF) plug. Vapor concentrations of semi-volatile contaminants sorbed to the PUF are then determined using EPA Method TO-10. The active soil gas sampling equipment can be assembled to allow for both canister sampling for volatiles and PUF sampling for semi-volatiles.

Passive sorbent sampling involves burial of solid sorbent sampling devices called cartridges or cassettes to a depth of normally 5 feet or less. The cassettes may be configured with one or more sorbents depending on the list of target analytes, and are typically left in-ground for 72 to 120 hours or longer. During this time period, the vapor-phase soil gas contaminants pass through the cassette and are adsorbed as the soil gas moves toward the soil surface by diffusion and/or convection. Analytical methods for sorbent sampling depend on the target analytes and the sorbent used and may include EPA Method TO-10 or a modified EPA Method TO-1. Vapor-phase concentrations for some solid sorbent sampling systems are determined using the total mass of each contaminant recovered, the time in-ground, the cross-sectional area of the cassette, the diffusivity of the compound in air, and a quasi-empirical adsorption rate constant.

Recent EPA technology verification reports produced by the EPA National Exposure Research Laboratory (EPA 1998, 1998a) concluded, at least for two such systems, that the sorbent methodologies accurately accounted for the presence of most of the soil gas contaminants in the studies. Further, the reports concluded that the sorbent systems showed detection of contaminants at low concentrations not reported using an active whole-air sampling system. For one system, however, it was noted that as the vapor concentrations reported for the whole-air sampling system increased by 1 to 4 orders-of-magnitude, the associated concentrations reported for the sorbent system increased only marginally. Perhaps the best use of such passive sorbent sampling methods is to help confirm which contaminants are present in the soil gas and not necessarily contaminant concentrations.

An excellent discussion of soil gas measurement methods and limitations can be found in the ASTM Standard Guide for Soil Gas Monitoring in the Vadose Zone D5314-92e1. ASTM Standard Guides are available from the ASTM website at:

http://www.astm.org.

In addition, soil gas measurement method summaries can be found in the EPA Standard Operating Procedures for Soil Gas Sampling (SOP No. 2042) developed by the EPA Environmental Response

Team (ERT) in Edison, New Jersey. This document can be downloaded from the ERT Compendium of Standard Operating Procedures at the following website:

http://www.ert.org/media_resrcs/media_resrcs.asp.

Data Quality and Data Quality Objectives

The results of soil gas sampling must meet the applicable requirements for data quality and satisfy the data quality objectives of the study for which they are intended. Data quality objectives are qualitative and quantitative statements derived from the data quality objectives process that clarify study objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used to support site decisions. Data quality objectives are formulated in the first phase of a sampling project.

In the second phase of the project, a Quality Assurance Project Plan (QAPP) translates these requirements into measurement performance specifications and quality assurance/quality control procedures to provide the data necessary to satisfy the user's needs. The QAPP is the critical planning document for any environmental data collection operation because it documents how quality assurance and quality control activities will be implemented during the life of the project. Development of the data quality objectives and the QAPP for soil gas sampling should follow the guidance provided by EPA's Quality Assurance Division of the Office of Research and Development. Guidance documents concerning the development and integration of the data quality objectives and the QAPP can be obtained from the EPA website at:

http://epa.gov/ncerqa/qa/qa_docs.html.

In addition to the above guidance, the EPA Regional Office and/or other appropriate regulatory agency should be consulted concerning specific sampling requirements.

4.3 ASSUMPTIONS AND LIMITATIONS OF THE SOIL GAS MODEL

As discussed previously, the soil gas models operate under the assumption of steady-state conditions. This means that enough time has passed for the vapor plume to have reached the building of interest directly above the source of contamination and that the vapor concentrations have reached their maximum values. Depending on the depth at which the soil gas is sampled, diffusion of the soil gas toward the building is a function of the soil properties between the building floor in contact with the soil and the sampling depth. Convection of the soil gas into the structure is a function of the building properties and the effective soil vapor permeability. Assumptions and limitations of the soil gas models are the same as those in Section 2.11 with the exception of the source vapor concentration that is determined empirically through soil gas sampling.

The user should also recognize the inherent limitations of soil gas sampling. First, the geologic variability of the subsurface may be considerable. This may be especially problematic for

shallow soil gas sampling because soil moisture content can vary widely as a function of precipitation events and surface runoff. The soil moisture content has an exponential effect on the rate of vapor diffusion. Transformation processes such as biodegradation can also occur in shallow subsurface soils. In some cases, only a relatively thin stratum of bioactive soil can greatly reduce the emission flux toward the soil surface. Finally, subsurface phase equilibria is a dynamic process resulting in varying vapor-phase concentrations over time at the same sampling location and depth. These factors can result in significant differences in measured soil gas concentrations over relatively small spatial and temporal scales.

For these reasons, the planning phase of the soil gas-sampling program should carefully consider the inherent uncertainties in site-specific sampling and analytical data. In the final analysis, the extent of soil gas sampling is a trade-off between sampling costs and the degree of certainty required in the soil gas concentration data.

SECTION 5

ASSUMPTIONS AND LIMITATIONS OF THE J&E MODEL

The J&E Model is a one-dimensional analytical solution to diffusive and convective transport of vapors into indoor spaces. The model is formulated as an attenuation factor that relates the vapor concentration in the indoor space to the vapor concentration at the source. It was developed for use as a screening level model and consequently is based on a number of simplifying assumptions regarding contaminant distribution and occurrence, subsurface characteristics, transport mechanisms, and building construction.

EPA is suggesting that the J&E Model be used at Resource Conservation and Recovery Act (RCRA) Corrective Action Sites, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)/Superfund Sites, and voluntary cleanup sites. EPA is not recommending that the J&E Model be used for sites contaminated with petroleum products if the products were derived from Underground Storage Tanks. The J&E Model does not account for contaminant attenuation (biodegradation, hydrolysis, sorption, and oxidation/reduction). Attenuation is potentially a significant concern for these type of sites. EPA is recommending that investigators use OSWER Directive 9610.17: Use of Risk Based Decision-Making in UST Corrective Action Programs to evaluate these types of sites.

The J&E Model as implemented by EPA assumes homogeneous soil layers with isotropic properties that characterize the subsurface. The first tier spreadsheet versions allow only one layer; the advanced spreadsheet versions allow up to three layers. Sources of contaminants that can be modeled include dissolved, sorbed, or vapor sources where the concentrations are below the aqueous solubility limit, the soil saturation concentration, and/or the pure component vapor concentration. The contaminants are assumed to be homogeneously distributed at the source. All but one of the spreadsheets assumes an infinite source. The exception is the advanced model for a bulk soil source, which allows for a finite source. For the groundwater and bulk soil models, the vapor concentration at the source is calculated assuming equilibrium partitioning. Vapor from the source is assumed to diffuse directly upward (one-dimensional transport) through uncontaminated soil (including an uncontaminated capillary fringe if groundwater is the vapor source) to the base of a building foundation, where convection carries the vapor through cracks and openings in the foundation into the building. Both diffusive and convective transport processes are assumed to be at steady state. Neither sorption nor biodegradation is accounted for in the transport of vapor from the source to the base of the building.

The assumptions described above and in Table 12 suggest a number of conditions that preclude the use of the Non-NAPL Models as implemented by EPA. These conditions include:

TABLE 12. ASSUMPTIONS AND LIMITATIONS OF THE VAPOR INTRUSION MODEL

Assumption	Implication	Field Evaluation
Contaminant		
No contaminant free-liquid/precipitate phase present	J&E Model not representative of NAPL partitioning from source	NAPL or not at site–easier to evaluation for floating product or soil contamination sites. Most DNAPL sites with DNAPL below the water table defy easy characterization.
Contaminant is homogeneously distributed within the zone of contamination		
No contaminant sources or sinks in the building.	Indoor sources of contaminants and/or sorption of vapors on materials may confound interpretation of results.	Survey building for sources, assessment of sinks unlikely
Equilibrium partitioning at contaminant source.	Groundwater flow rates are low enough so that there are no mass transfer limitations at the source.	Not likely
Chemical or biological transformations are not significant (model will predict more intrusion)	Tendency to over predict vapor intrusion for degradable compounds	From literature
Subsurface Characteristics		
Soil is homogeneous within any horizontal plane	Stratigraphy can be described by horizontal layers (not tilted layers)	Observe pattern of layers and unconformities Note: In simplified J&E Model layering is not considered
All soil properties in any horizontal plane are homogeneous		
The top of the capillary fringe must be below the bottom of the building floor in contact with the soil.		
EPA version of JE Model assumes the capillary fringe is uncontaminated.		
Transport Mechanisms		
One-dimensional transport	Source is directly below building, stratigraphy does not influence flow direction, no effect of two- or three-dimensional flow patterns.	Observe location of source, observe stratigraphy, pipeline conduits, not likely to assess two- and three-dimensional pattern.
Two separate flow zones, one diffusive one convective.	No diffusion (dispersion) in the convective flow zone. Plug flow in convective zone	Not likely
Vapor-phase diffusion is the dominant mechanism for transporting contaminant vapors from contaminant sources located away from the foundation to the soil region near the foundation	Neglects atmospheric pressure variation effects, others?	Not likely

(continued)

Assumption	Implication	Field Evaluation
Straight-line gradient in diffusive flow zone.	Inaccuracy in flux estimate at match point between diffusive and convective sections of the model.	Not likely
Diffusion through soil moisture will be insignificant (except for compounds with very low Henry's Law Constant	Transport through air phase only. Good for volatiles. Only low volatility compounds would fail this and they are probably not the compounds of concern for vapor intrusion	From literature value of Henry's Law Constant.
Convective transport is likely to be most significant in the region very close to a basement, or a foundation, and vapor velocities decrease rapidly with increasing distance from a structure		Not likely
Vapor flow described by Darcy's law	Porous media flow assumption.	Observations of fractured rock, fractured clay, karst, macropores, preferential flow channels.
Steady State convection	Flow not affected by barometric pressure, infiltration, etc.	Not likely
Uniform convective flow near the foundation	Flow rate does not vary by location	Not likely
Uniform convective velocity through crack or porous medium	No variation within cracks and openings and constant pressure field between interior spaces and the soil surface	Not likely
Significant convective transport only occurs in the vapor phase	Movement of soil water not included in vapor impact	Not likely
All contaminant vapors originating from directly below the basement will enter the basement, unless the floor and walls are perfect vapor barriers. (Makes model over est. vapors as none can flow around the building)	Model does not allow vapors to flow around the structure and not enter the building	Not likely
Contaminant vapors enter structures primarily through cracks and openings in the walls and foundation	Flow through the wall and foundation material itself neglected	Observe numbers of cracks and openings. Assessment of contribution from construction materials themselves not likely

- The presence or suspected presence of residual or free-product non-aqueous phase liquids (LNAPL, DNAPL, fuels, solvents, etc.) in the subsurface.
- The presence of heterogeneous geologic materials (other than the three layers allowed in the advanced spreadsheets) between the vapor source and building. The J&E Model does not apply to geologic materials that are fractured, contain macropores or other preferential pathways, or are composed of karst.

- Sites where significant lateral flow of vapors occurs. These can include geologic layers that deflect contaminants from a strictly upward motion and buried pipelines or conduits that form preferential paths. Significantly different permeability contrasts between layers are likely to cause lateral flow of vapors. The model assumes the source of contaminants is directly below the potential receptors.
- Very shallow groundwater where the building foundation is wetted by the groundwater.
- Very small building air exchange rates (e.g., < 0.25/h)
- Buildings with crawlspace structures or other significant openings to the subsurface (e.g., earthen floors, stone buildings, etc.). The EPA spreadsheet only allows for either slab on grade or basement construction.
- Contaminated groundwater sites with large fluctuations in the water table elevation. In these cases, the capillary fringe is likely to be contaminated; whereas in the groundwater source spreadsheets, the capillary fringe is assumed to be uncontaminated.

In theory the above limitations are readily conceptualized, but in practice the presence of these limiting conditions may be difficult to verify even when extensive site characterization data are available. Conditions that are particularly difficult to verify in the field include the presence of residual non-aqueous phase liquids (NAPLs) in the unsaturated zone and the presence and influence of macropores, fractures and other preferential pathways in the subsurface. Additionally, in the initial stages of evaluation, especially at the screening level, information about building construction and water table fluctuations may not be available. Even the conceptually simple assumptions (e.g., one-dimensional flow, lack of preferential pathways) may be difficult to assess when there are little site data available.

The vapor equilibrium models employed to estimate the vapor concentration at the source of soil contamination is applicable only if "low" concentrations of the compound(s) are sorbed to organic carbon in the soil, dissolved in soil moisture, and present as vapor within the air-filled soil pores (i.e., a three-phase system). The vapor equilibrium models do not account for a residual phase NAPLs. If residual phase contaminants are present in the soil column, the user is referred to either the NAPL-SCREEN or NAPL-ADV model (Appendix A), as appropriate.

In the case of contaminated groundwater, the vapor equilibrium model operates under the assumption that the contaminant is present at levels below the water solubility limit. If the user-defined soil concentration is greater than the soil saturation concentration (C_{sat}) or if the groundwater concentration is greater than the solubility limit (S), the equilibrium vapor concentration will be calculated at the value of C_{sat} or S as appropriate.

The user is also reminded that when estimating a risk-based soil concentration, the model will compare the calculated soil concentration with the soil saturation concentration above which a residual phase is likely to occur. The soil saturation concentration (C_{sat}) is calculated as in U.S. EPA (1996a and b). If the risk-based concentration is greater than the saturation concentration and the contaminant is a liquid or gas at the soil temperature, the final soil concentration will be set equal to the soil saturation concentration. This tends to eliminate the possibility of allowing a liquid residual phase to exist within the soil column, which may leach to the water table. If the risk-based soil concentration is greater than C_{sat} and the contaminant is a solid, the contaminant is not of concern for the vapor intrusion pathway.

Likewise, the groundwater models will compare the calculated risk-based groundwater concentration to the aqueous solubility limit of the compound. If the risk-based groundwater concentration is greater than the solubility limit, the contaminant is not of concern for the vapor intrusion pathway.

Finally, it should be recognized that the procedures used to estimate both the soil saturation concentration and the aqueous solubility limit do not consider the effects of multiple contaminants. The estimated values, therefore, may be artificially high such that a residual phase may actually exist at somewhat lower concentrations.

The procedures used to estimate the soil vapor permeability of the soil stratum in contact with the building floor and walls assume isotropic soils and steady-state soil moisture content. In addition, the calculations do not account for preferential vapor pathways due to soil fractures, vegetation root pathways, or the effects of a gravel layer below the floor slab or backfill. These items may act to increase the vapor permeability of in situ soils.

If in situ pneumatic tests are used to measure site vapor permeability, care must be taken to ensure adequate sampling to reduce the possibility of missing important soil structure effects due to anisotropy.

Single-point in situ pneumatic tests are typically conducted by measuring the pressure in a probe as a metered flow of air is passed through the probe and into the soil. Garbesi et al. (1996), however, demonstrated that soil vapor permeability increases with the sampling length scale. Using a dual-probe dynamic pressure sampling apparatus, Garbesi et al. (1996) demonstrated that the average soil vapor permeability typically increases up to a constant value as the distance between the source probe and detector probe increases. On a length scale typical of a house (3 to 10 m), use of the dual-probe sampling technique found that the soil permeability was approximately 10 to 20 times higher than that measured by the single-point method. Although arguably the most accurate means of determining in situ soil vapor permeability, the techniques of Garbesi et al. (1996) are complex and require specialized equipment.

Another method for determining the intrinsic permeability of soil is to conduct empirical measurements of the saturated hydraulic conductivity (K_s). These data are then input into Equation

26. The resulting value of k_i is then multiplied by the relative air permeability (k_{rg}) calculated by Equation 27 to yield the effective air permeability of the soil.

Estimation of the rise of the capillary zone is based on the equation for the rise of a liquid in a capillary tube. The procedure assumes that the interstitial space between the soil particles is equivalent to the capillary tube diameter and that the resulting rise of water occurs under steady-state soil column drainage conditions. In actuality, the height of the capillary zone is uneven or fingered due to the variation in the actual in situ particle size distribution. In addition, the groundwater models do not account for the episodic rise and fall of the water table or the capillary zone due to aquifer recharge and discharge. As constructed, the groundwater models do not allow the top of the capillary zone to be above the bottom of the building floor in contact with the soil. The user should be aware, however, that in reality the top of the capillary zone may rise to levels above the floor in some cases.

Diffusion across the capillary zone is estimated based on lumping vapor and aqueous-phase diffusion together within the calculation of the effective diffusion coefficient. To allow for vapor-phase diffusion within the capillary zone, the air-filled soil pores must be connected. In reality, the capillary zone may be comprised of a tension-saturated zone immediately above the water table and the deep portion of the vadose zone within which the soil water content is strongly dependent on the pressure head. Diffusion across the tension-saturated zone is dominated by liquid-phase diffusion, which is typically four orders of magnitude less than vapor-phase diffusion. Therefore, a large concentration gradient may exist between the top of the water table and the top of the tension-saturated zone (McCarthy and Johnson, 1993).

Lumping vapor and aqueous-phase diffusion together is a less-intensive, although less-rigorous, method for estimating the effective diffusion coefficient. The result is typically a higher effective diffusion coefficient relative to separate solutions for aqueous diffusion across the tension-saturated zone and both vapor and aqueous diffusion across the unsaturated portion of the vadose zone.

To minimize the possible overestimation of the effective diffusion coefficient, the soil air-filled porosity within the capillary zone is estimated based on the air-entry pressure head, which corresponds with the water-filled porosity at which the interstitial air-filled pores first become connected. The user should be aware that this procedure is inherently conservative if a significant concentration gradient exists across the tension-saturated zone. This conservatism may be somewhat offset in that the model does not consider any episodic rise in the level of the water table. During such events, water that had previously been part of the saturated zone (and hence contain higher contaminant concentrations) is redistributed in the vadose zone resulting in temporary elevations in soil gas concentrations.

The model assumes that all vapors from underlying soils will enter the building through gaps and openings in the walls, floor, and foundation. This implies that a constant pressure field is generated between the interior spaces and the soil surface and that the vapors are intercepted within the pressure field and transported into the building. This assumption is inherently conservative in

that it neglects periods of near zero pressure differentials (e.g., during mild weather when windows are left open).

As with the estimation procedure for soil vapor permeability, the model assumes isotropic soils in the horizontal direction; vertical anisotropy is accounted for by a series of isotropic soil strata above the top of contamination. Soil properties within the zone of soil contamination are assumed to be identical to those of the soil stratum directly above the contamination and extend downward to an infinite depth. Solute transports by convection (e.g., water infiltration) and by mechanical dispersion are neglected. Transformation processes (e.g., biodegradation, hydrolysis, etc.) are also neglected.

The J&E Model treats the entire building as a single chamber with instantaneous and homogeneous vapor dispersion. It therefore neglects contaminant sinks and the room-to-room variation in vapor concentration due to unbalanced mechanical and/or natural ventilation.

5.1 SOURCE VAPOR CONCENTRATION

As applied in the accompanying spreadsheets, the vapor equilibrium model employed to estimate the vapor concentration at the source of soil contamination is applicable in the limit of "low" concentrations where compounds are sorbed to organic carbon in the soil, dissolved is soil moisture, and present as vapor within the air-filled soil pores (i.e., a three-phase system). The model does not account for a residual phase (e.g., NAPL). If residual phase contaminants are present in the soil column, the user is referred to either the NAPL-SCREEN or NAPL-ADV model, as appropriate.

In the case of contaminated groundwater, the vapor equilibrium model operates under the assumption that the contaminant is present at levels below the water solubility limit. If the user-defined soil concentration is greater than the soil saturation concentration (C_{sat}) or if the groundwater concentration is greater than the solubility limit (S), the equilibrium vapor concentration will be calculated at the value of C_{sat} or S as appropriate.

The user is also reminded that when estimating a risk-based soil concentration, the model will compare the calculated soil concentration with the soil saturation concentration above which a residual phase is likely to occur. The soil saturation concentration (C_{sat}) is calculated as in U.S. EPA (1996a and b). If the risk-based concentration is greater than the saturation concentration and the contaminant is a liquid or gas at the soil temperature, the final soil concentration will be set equal to the soil saturation concentration. This tends to eliminate the possibility of allowing a liquid residual phase to exist within the soil column, which may leach to the water table. If the risk-based soil concentration is greater than C_{sat} and the contaminant is a solid, the contaminant is not of concern for the vapor intrusion pathway.

Likewise, the groundwater models will compare the calculated risk-based groundwater concentration to the aqueous solubility limit of the compound. If the risk-based groundwater

concentration is greater than the solubility limit, the contaminant is not of concern for the vapor intrusion pathway.

Finally, it should be recognized that the procedures used to estimate both the soil saturation concentration and the aqueous solubility limit do not consider the effects of multiple contaminants. The estimated values, therefore, may be artificially high such that a residual phase may actually exist at somewhat lower concentrations.

5.2 SOIL VAPOR PERMEABILITY

The procedures used to estimate the soil vapor permeability of the soil stratum in contact with the building floor and walls assumes isotropic soils and steady-state soil moisture content. In addition, the calculations do not account for preferential vapor pathways due to soil fractures, vegetation root pathways, or the effects of a gravel layer below the floor slab or backfill which may act to increase the vapor permeability with respect to in situ soils.

If in situ pneumatic tests are used to measure site vapor permeability, care must be taken to ensure adequate sampling to reduce the possibility of missing important soil structure effects due to anisotropy.

Single point in situ pneumatic tests are typically conducted by measuring the pressure in a probe as a metered flow of air is passed through the probe and into the soil. Garbesi et al. (1996), however, demonstrated that soil vapor permeability increases with the sampling length scale. Using a dual-probe dynamic pressure sampling apparatus, Garbesi et al. (1996) demonstrated that the average soil vapor permeability typically increases up to a constant value as the distance between the source probe and detector probe increases. On a length scale typical of a house (3 to 10 m) use of the dual-probe sampling technique found that the soil permeability was approximately 10 to 20 times higher than that measured by the single point method. Although arguably the most accurate means of determining in situ soil vapor permeability, the techniques of Garbesi et al. (1996) are complex and require specialized equipment.

Another method for determining the intrinsic permeability of soil is to conduct empirical measurements of the saturated hydraulic conductivity (K_s). These data are then input into Equation 26. The resulting value of k_i is then multiplied by the relative air permeability (k_{rg}) calculated by Equation 27 to yield the effective air permeability of the soil.

5.3 RISE OF AND DIFFUSION ACROSS THE CAPILLARY ZONE

Estimation of the rise of the capillary zone is based on the equation for the rise of a liquid in a capillary tube. The procedure assumes that the interstitial space between the soil particles is equivalent to the capillary tube diameter and that the resulting rise of water occurs under steady-state soil column drainage conditions. In actuality, the height of the capillary zone is uneven or fingered due to the variation in the actual in situ particle size distribution. In addition, the groundwater

models do not account for the episodic rise and fall of the water table or the capillary zone due to aquifer recharge and discharge. As constructed, the groundwater models do not allow the top of the capillary zone to be above the bottom of the building floor in contact with the soil. The user should be aware, however, that in reality the top of the capillary zone might rise to levels above the floor in some cases.

Diffusion across the capillary zone is estimated based on lumping vapor and aqueous-phase diffusion together within the calculation of the effective diffusion coefficient. To allow for vapor-phase diffusion within the capillary zone, the air-filled soil pores must be connected. In reality, the capillary zone may be comprised of a tension-saturated zone immediately above the water table and the deep portion of the vadose zone within which the soil water content is a strongly dependent on the pressure head. Diffusion across the tension-saturated zone is dominated by liquid-phase diffusion which is typically four orders of magnitude less than vapor-phase diffusion. Therefore, a large concentration gradient may exist between the top of the water table and the top of the tension-saturated zone (McCarthy and Johnson, 1993).

Lumping vapor and aqueous-phase diffusion together is a less intensive, although less rigorous, method for estimating the effective diffusion coefficient. The result is typically a higher effective diffusion coefficient relative to separate solutions for aqueous diffusion across the tension-saturated zone and both vapor and aqueous diffusion across the unsaturated portion of the vadose zone.

To minimize the possible over estimation of the effective diffusion coefficient, the soil air-filled porosity within the capillary zone is estimated based on the air-entry pressure head, which corresponds with the water-filled porosity at which the interstitial air-filled pores first become connected. The user should be aware that this procedure is inherently conservative if a significant concentration gradient exists across the tension-saturated zone. This conservatism may be somewhat offset in that the model does not consider any episodic rise in the level of the water table. During such events, water which had previously been part of the saturated zone (and hence contain higher contaminant concentrations) is redistributed in the vadose zone resulting in temporary elevations in soil gas concentrations.

5.4 DIFFUSIVE AND CONVECTIVE TRANSPORT INTO THE STRUCTURE

The following is a discussion of the major assumptions and limitations of the J&E Model for diffusive and convective vapor transport into buildings.

The model assumes that all vapors from underlying soils will enter the building through gaps and openings in the walls, floor, and foundation. This implies that a constant pressure field is generated between the interior spaces and the soil surface and that the vapors are intercepted within the pressure field and transported into the building. This assumption is inherently conservative in that it neglects periods of near zero pressure differentials (e.g., during mild weather when windows are left open).

As with the estimation procedure for soil vapor permeability, the model assumes isotropic soils in the horizontal direction; vertical anisotropy is accounted for by a series of isotropic soil strata above the top of contamination. Soil properties within the zone of soil contamination are assumed to be identical to those of the soil stratum directly above the contamination and extend downward to an infinite depth. Solute transports by convection (e.g., water infiltration) and by mechanical dispersion are neglected. Transformation processes (e.g., biodegradation, hydrolysis, etc.) are also neglected.

An empirical field study (Fitzpatrick and Fitzgerald, 1997) indicated that the model may be overly conservative for nonchlorinated species (e.g., benzene, toluene, ethylbenzene and xylene) but in some cases, may underpredict indoor concentrations for chlorinated species. The authors contribute the likely cause for this discrepancy to the significant biodegradation of the nonchlorinated compounds.

The J&E Model treats the entire building as a single chamber with instantaneous and homogeneous vapor dispersion. It therefore neglects contaminant sinks and the room-to-room variation in vapor concentration due to unbalanced mechanical and/or natural ventilation.

Finally, convective vapor flow from the soil matrix into the building is represented as an idealized cylinder buried below grade. This cylinder represents the total area of the structure below the soil surface (walls and floor). The total crack or gap area is assumed to be a fixed fraction of this area. Because of the presence of basement walls, the actual vapor entry rate is expected to be 50 to 100 percent of that provided by the idealized geometry (Johnson and Ettinger, 1991).

SECTION 6

INTERPRETATION OF RESULTS

The models described herein are theoretical approximations of complex physical and chemical processes and as such should not be used in a deterministic fashion (i.e., to generate a single outcome). At the least, a range of outcomes should be explored focusing on the most sensitive model input variables. In general, using the default values for input variables will result in higher indoor air concentrations and thus higher incremental risks or lower risk-based media concentrations. With a realistic range of outcomes, the risk manager may assess the uncertainty in the model predictions.

From a conceptual point of view, the vapor intrusion model provides a theoretical description of the processes involved in vapor intrusion from subsurface soils or groundwater into indoor structures. A combination of modeling and sampling methods is also possible to reduce the uncertainty of the calculated indoor air concentrations. Typically this involves field methods for measuring soil gas very near or below an actual structure. It should be understood, however, that soil gas sampling results outside the footprint of the building may or may not be representative of the soil gas concentrations directly below the structure. For solid building floors in contact with the soil (e.g., concrete slabs), the soil gas directly beneath the floor may be considerably higher than that adjacent to the structure. This is typically due to a vapor pooling effect underneath the near impermeable floor. Once a representative average concentration is determined, all vapor directly below the areal extent of the building is presumed to enter the structure. The soil gas concentration, along with the building ventilation rate and the soil gas flow rate into the building, will determine the indoor concentration. When using the soil gas models, it must be remembered that no analysis has been made concerning the source of contamination. Therefore, the calculated indoor concentration is assumed to be steady-state. The procedures described in API (1998) can be used to calibrate the diffusion transport considerations of the J&E Model as well as for calibrating the Model for transformation processes (e.g., biodegradation). The reader is also referred to U.S. EPA (1992) for a more detailed discussion of applying soil gas measurements to indoor vapor intrusion.

Finally, calibration and verification of the model have been limited due to the paucity of suitable data. Research is needed to provide spatially and temporally correlated measurements during different seasons, at different locations, with different buildings, and over a range of different contaminants such that the accuracy of the model may be determined. Appendix E contains bibliography and references.

APPENDIX A

USER'S GUIDE FOR NON-AQUEOUS PHASE LIQUIDS

Purpose

The NAPL-SCREEN and NAPL-ADV models are designed to forward calculate incremental cancer risks or noncarcinogenic hazard quotients due to subsurface soil vapor intrusion into buildings. The models are specifically designed to handle nonaqueous phase liquids or solids in soils. The user may specify up to 10 soil contaminants, the concentrations of which form a residual phase mixture. A residual phase mixture occurs when the sorbed phase, aqueous phase, and vapor phase of each chemical have reached saturation in soil. Concentrations above this saturation limit for all of the specified chemicals of a mixture will result in a fourth or residual phase (i.e., nonaqueous phase liquid or solid).

Other vapor intrusion models (SL-SCREEN, SL-ADV, SG-SCREEN, SG-ADV, GW-SCREEN, and GW-ADV) handled only a single contaminant and only when the soil concentration was at or below the soil saturation limit (i.e., a three-phase system). Use of these models when a residual phase is present, results in an overprediction of the soil vapor concentration and subsequently the building vapor concentration.

Residual Phase Theory

The three-phase system models estimate the equilibrium soil vapor concentration at the emission source (C_{source}) using the procedures from Johnson et al. (1990):

$$C_{source} = \frac{H'_{TS} C_R \rho_b}{\theta_w + K_d \rho_b + H'_{TS} \theta_a} \qquad (1)$$

where:

C_{source}	=	Vapor concentration at the source of contamination, g/cm^3
H'_{TS}	=	Henry's law constant at the soil temperature, dimensionless
C_R	=	Initial soil concentration, g/g
ρ_b	=	Soil dry bulk density, g/cm^3
θ_w	=	Soil water-filled porosity, cm^3/cm^3
K_d	=	Soil-water partition coefficient, cm^3/g (= $K_{oc} \times f_{oc}$)
θ_a	=	Soil air-filled porosity, cm^3/cm^3
K_{oc}	=	Soil organic carbon partition coefficient, cm^3/g
f_{oc}	=	Soil organic carbon weight fraction.

In Equation 1, the equilibrium vapor concentration is proportional to the soil concentration up to the soil saturation limit. When a residual phase is present, however, the vapor concentration is independent of the soil concentration but proportional to the mole fraction of the individual component of the residual phase mixture. In this case, the equilibrium vapor concentration must be calculated numerically for a series of time-steps. For each time-step, the mass of each constituent that is volatilized is calculated using Raoult's law and the appropriate mole fraction. At the end of each time-step, the total mass lost is subtracted from the initial mass and the mole fractions are recomputed for the next time-step.

The NAPL-SCREEN and NAPL-ADV models use the procedures of Johnson et al. (2001) to calculate the equilibrium vapor concentration at the source of emissions for each time-step. Within each model, the user-defined initial soil concentration of each component in the mixture is checked to see if a residual phase is present. This is done by calculating the product of the activity coefficient of component *i* in water (α_i) and the mole fraction of *i* dissolved in soil moisture (y_i) such that:

$$\alpha_i y_i = \frac{M_i}{\left[\left(P_i^v(T_S)\theta_a V / RT_S\right) + \left(M^{H2O} / \alpha_i\right) + \left(K_{d,i} M_{soil} / \alpha_i MW_{H2O}\right)\delta\left(M^{H2O}\right)\right]} \quad (2)$$

where:

M_i	=	Initial moles of component *i* in soil, moles
$P_i^v(T_S)$	=	Vapor pressure of *i* at the average soil temperature, atm
θ_a	=	Soil air-filled porosity, cm^3/cm^3
V	=	Volume of contaminated soil, cm^3
R	=	Ideal gas constant, 82.05 atm-cm^3/mol-^oK
T_S	=	Average soil temperature, ^oK
M^{H_2O}	=	Total moles in soil moisture dissolved phase, moles
α_i	=	Activity coefficient of *i* in water, unitless
$K_{d,i}$	=	Soil-water partition coefficient of *i*, cm^3/g
M_{soil}	=	Total mass of contaminated soil, g
MW_{H2O}	=	Molecular weight of water, 18 g/mol
$\delta(M^{H_2O})$	=	1 if $M^{H_2O} > 0$, and
$\delta(M^{H_2O})$	=	0 if $M^{H_2O} = 0$.

If the sum of all the values of $\alpha_i y_i$ for all of the components of the mixture is less than 1, the mixture does not contain a residual phase and the models are not applicable. In such cases, the SL-SCREEN or SL-ADV model can be used to estimate the building concentration.

Once it has been determined that a residual phase does exists, the mole fraction of each component (x_i) is determined by iteratively solving Equations 3 and 4 subject to the constraint that the sum of all the mole fractions equals unity ($\Sigma x_i = 1$):

$$x_i = \frac{M_i}{\left[\left(P_i^v(T_S)\theta_a V / RT_S\right) + M^{HC} + \left(M^{H2O} / \alpha_i\right) + \left(K_{d,i} M_{soil} / \alpha_i MW_{H2O}\right)\delta\left(M^{H2O}\right)\right]} \quad (3)$$

and,

$$x_i = \frac{M_i^{HC}}{M^{HC}} \quad (4)$$

where M_i^{HC} is the number of moles of component i in residual phase and M^{HC} is the total number of moles of all components in residual phase. The solution is simplified by assuming that M^{H_2O} is approximately equal to the number of moles of water in the soil moisture. With the mole fraction of each component at the initial time-step, the equilibrium vapor concentration at the source of emissions is calculated by Raoult's law:

$$C_{source} = \frac{x_i P_i^v(T_S) MW_i}{RT_S} \qquad (5)$$

where MW_i is the molecular weight of component i (g/mol).

At the beginning of each succeeding time-step, the number of moles of each chemical remaining in the soil from the previous time-step are again checked to see if a residual phase is present using Equation 2. When a residual phase is no longer present, the equilibrium vapor concentration at the source of emissions is calculated by:

$$C_{source} = \frac{\alpha_i y_i P_i^v(T_S) MW_i}{RT_S}. \qquad (6)$$

Ancillary Calculations

The activity coefficient of component i in water (α_i) is estimated from its solubility. Because hydrocarbons are typically sparingly soluble in water, the following generalization has been applied to compounds that are liquid or solid at the average soil temperature:

$$\alpha_i = (1/y_i) = (55.55 \text{ moles/L}) MW_i / S_i \qquad (7)$$

where S_i is the solubility of component i (g/L). For gases at the average soil temperature, the corresponding relationship is:

$$\alpha_i = (1/y_i)\left(1atm / P_i^v(T_S)\right) = (55.55 \text{ moles}/L)\left(MW_i(1\ atm)/S_i P_i^v(T_S)\right). \qquad (8)$$

Assuming that the vapor behaves as an ideal gas with a relatively constant enthalpy of vaporization between 70°F and the average soil temperature, the Claussius-Clapeyron equation can be used to estimate the vapor pressure at the desired temperature:

$$P^v(T_S) = P^v(T_R) \times \exp\left[\left(\frac{T_B \times T_R}{(T_B - T_R)}\right)\left(\frac{1}{T_S} - \frac{1}{T_R}\right)\ln\left(\frac{P^v(T_R)}{P_B}\right)\right] \qquad (9)$$

where: $P^v(T_S)$ = Vapor pressure at the desired temperature T_S, atm
$P^v(T_R)$ = Vapor pressure at the reference temperature T_R, atm

T_B	=	Normal boiling point, ^oK
T_R	=	Vapor pressure reference temperature, ^oK
T_S	=	The desired temperature, ^oK
P_B	=	Normal boiling point pressure = 1 atm.

Building Concentration

The vapor concentration within the building or enclosed space ($C_{building}$) is calculated using the steady-state solution of Johnson and Ettinger (1991) such that:

$$C_{building} = \alpha C_{source} . \qquad (10)$$

The steady-state attenuation coefficient (α) is calculated by:

$$\alpha = \frac{\left[\left(\frac{D_T^{eff} A_B}{Q_{building} L_T}\right) \times \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)\right]}{\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) + \left(\frac{D_T^{eff} A_B}{Q_{building} L_T}\right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) - 1\right]\right]} \qquad (11)$$

where:

α	=	Steady-state attenuation coefficient, unitless
D_T^{eff}	=	Total overall effective diffusion coefficient, cm^2/s
A_B	=	Area of the enclosed space below grade, cm^2
$Q_{building}$	=	Building ventilation rate, cm^3/s
L_T	=	Source-building separation, cm
Q_{soil}	=	Volumetric flow rate of soil gas into the enclosed space, cm^3/s
L_{crack}	=	Enclosed space foundation or slab thickness, cm
A_{crack}	=	Area of total cracks, cm^2
D^{crack}	=	Effective diffusion coefficient through the cracks, cm^2/s.

The reader is referred to Section 2.5 of this Guidance for a more detailed discussion of the derivation of Equation 11 and procedures for determining values for model input parameters. Except for the calculation of the equilibrium vapor concentration at the source of emissions, NAPL-SCREEN is identical to the three-phase model SL-SCREEN and NAPL-ADV is identical to the three-phase model SL-ADV.

The NAPL-SCREEN and NAPL-ADV models explicitly solve for the time-averaged building concentration over the exposure duration using a forward finite-difference numerical approach. For each time-step δt:

$$M_i(t+\delta t) = M_i(t) - \delta t\left(C_{building} \times Q_{building} / MW_i\right) \qquad (12)$$

where $M_i\ (t)$ is the number of moles of component i in soil at the previous time and $M_i(t+\delta t)$ is the number of moles at the new time. The time-step interval is variable as a function of the percent of mass lost over the time-step. The user may specify a minimum and maximum percent loss allowed; these values are applied to the single component of the residual phase mixture with the highest mass loss rate during each time-step interval. If the user-specified maximum percent loss is exceeded, the next time-step interval is reduced by half; likewise, if the user-specified minimum percent loss is not achieved, the next time-step interval is increased by a factor of two. The instantaneous building concentration at time = t is calculated using Equation 10 for each time-step. The time-averaged building concentration is estimated using a trapezoidal approximation of the integral.

Model Assumptions and Limitations

The NAPL-SCREEN and NAPL-ADV models operate under the assumption that sufficient time has elapsed since the time of initial soil contamination for steady-state conditions to have been achieved. This means that the subsurface vapor plume has reached the bottom of the enclosed space floor and that the vapor concentration has reached its maximum value. An estimate of the time required to reach near steady-state conditions (τ_{ss}) can be made using the following equations from API (1998):

$$\tau_{ss} \cong \frac{R_v \theta_a L_T^{\ 2}}{D^{eff}} \qquad (13)$$

and,

$$R_v = 1 + \frac{\theta_w}{\theta_a H'_{TS}} + \frac{\rho_b K_d}{\theta_a H'_{TS}} \qquad (14)$$

and,

$$D^{eff} = D_a \frac{\theta_a^{\ 10/3}}{n^2} + \left(\frac{D_w}{H'_{TS}} \right) \frac{\theta_w^{\ 10/3}}{n^2} \qquad (15)$$

where R_v is the unitless vapor phase retardation factor, L_T is the source-building separation (cm), D^{eff} is the effective diffusion coefficient (cm^2/s), D_a is the diffusivity in air (cm^2/s), D_w is the diffusivity in water (cm^2/s), and n is the soil total porosity (cm^3/cm^3). The NAPL-SCREEN and NAPL-ADV models are applicable only when the elapsed time since initial soil contamination meets or exceeds the value of τ_{ss} (see **Using the Models**).

Emission source depletion is calculated by estimating the rate of vapor loss as a function of time such that the mass lost at each time-step is subtracted from a finite mass of contamination at the source. This requires the model user to estimate the dimensions of the emission source, e.g., the length, width, and thickness of the contaminated zone. The model should only be used, therefore,

when the extent of soil contamination has been sufficiently determined. It should be noted that because the NAPL-SCREEN and NAPL-ADV models are one-dimensional, the areal extent of soil contamination (i.e., length × width) can be less than but not greater than the areal extent of the building floor in contact with the soil.

Each model treats the contaminated zone directly below the building as a box containing a finite mass of each specified compound. The initial contamination contained within the box is assumed to be homogeneously distributed. After each time-step, the remaining contamination is assumed to be instantaneously redistributed within the box to homogeneous conditions. The diffusion path length from the top of contamination to the bottom of the enclosed space floor therefore remains constant with time. Use of this simplifying assumption means that the degree of NAPL soil saturation is not required in the calculation of the total overall effective diffusion coefficient (D_T^{eff}).

As time proceeds, the concentration of the mixture of compounds within the soil column may reach the soil saturation limit. Below this point, a residual phase will cease to exist and the vapor concentration of each chemical will decrease proportional to its total volume soil concentration. Theoretically, the vapor concentration will decrease asymptotically, approaching but never reaching zero. Because of the nature of the numerical solution to equilibrium vapor concentration, however, compounds with high effective diffusion coefficients (e.g., vinyl chloride) may reach zero soil concentrations while other less volatile contaminants will not. If the initial soil concentrations are significantly higher than their respective values of the soil saturation concentration, a residual phase may persist up to the user-defined exposure duration.

Model assumptions and limitations concerning vapor transport and vapor intrusion into buildings are those specified for the three-phase models.

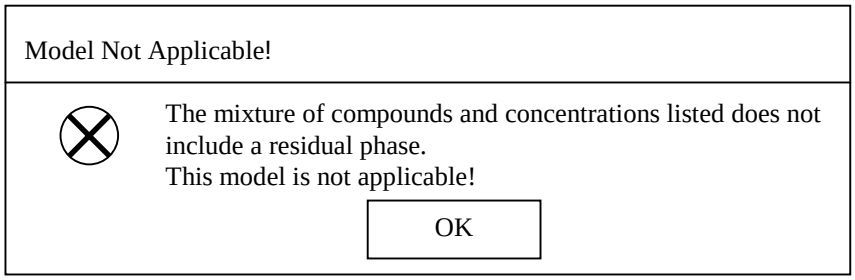
Using the Models

Each model is constructed as a Microsoft® Excel workbook containing five worksheets. The DATENTER worksheet is the data entry worksheet and also provides model results. The VLOOKUP worksheet contains the "Chemical Properties Lookup Table" with listed chemicals and associated chemical and toxicological properties. It should be noted that the toxicological properties for many of these chemicals were derived by route-to-route extrapolation. In addition, the VLOOKUP worksheet includes the "Soil Properties Lookup Table" containing values for model intermediate variables used in estimating the soil vapor permeability. The CHEMPROPS worksheet provides a summary of the chemical and toxicological properties of the soil contaminants selected by the user. In addition, the CHEMPROPS worksheet provides calculated values for the soil saturation concentration (C_{sat}) and the time to reach steady-state conditions (τ_{ss}) once all required data are entered into the DATENTER worksheet. The INTERCALCS worksheet contains calculated values of intermediate model variables. Finally, the COMPUTE worksheet contains the numerical solutions for equilibrium vapor concentration and building vapor concentration as a function of time.

Both models use the Microsoft® SOLVER add-in algorithms to simultaneously solve Equations 3 and 4 for each of up to 10 chemicals specified by the user. In order to run NAPL-SCREEN or NAPL-ADV, the SOLVER add-in must be loaded into EXCEL. The user is referred to the EXCEL instructions for loading the SOLVER add-in.

On the DATENTER worksheet, the user may specify up to 10 soil contaminants by CAS number along with associated soil concentrations in units of mg/kg. The CAS number entered must match exactly one of the 93 chemicals listed in the VLOOKUP worksheet or the error message "CAS No. not found" will appear in the "Chemical" box. If the list of chemicals and concentrations entered does not constitute a residual phase, the error message in Figure 1 will appear after starting the model.

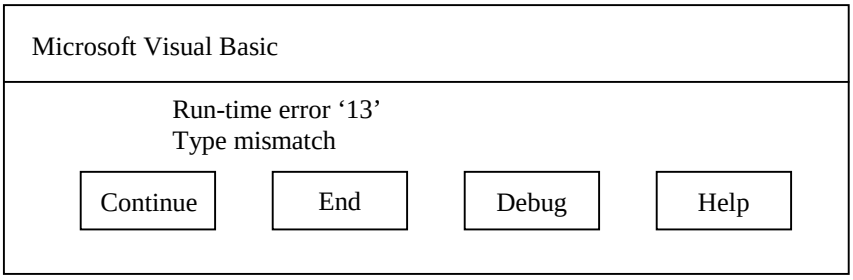
Figure 1. Residual Phase Error Message



If this error message box appears, use either the SL-SCREEN or SL-ADV model to estimate subsurface vapor intrusion into the building.

After starting the model calculations, other error message boxes may appear if data entry values are missing on the DATENTER worksheet or if entered values do not conform to model assumptions. If such an error message box appears, fill-in missing data or re-enter data as appropriate. If entered data values are outside the expected range or if text values are entered where numeric values are expected, the model calculation macro will be suspended and the run-time error message in Figure 2 will appear.

Figure 2. Run-Time Error Message



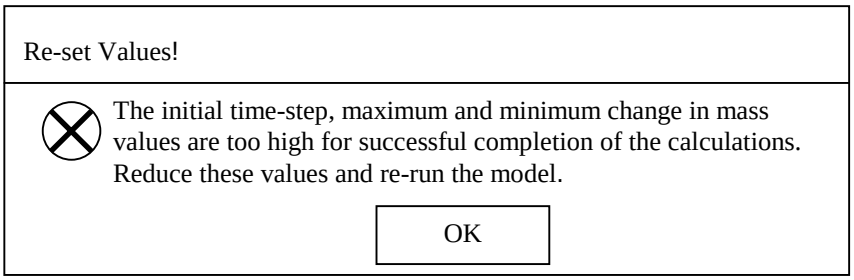
Should this error message appear, click on the "End" button to terminate the macro and return to the DATENTER worksheet. At this point, the user should review all of the entered values and make the appropriate corrections.

In addition to contaminant data, soil properties data, zone of contamination data, and exposure assumptions must also be specified in the DATENTER worksheet. Similar to the SL-SCREEN three-phase model, the NAPL-SCREEN model allows for only one soil stratum between the top of contamination and the bottom of the building floor in contact with the soil. In addition, the NAPL-SCREEN model uses built-in default values for all building variables (e.g., building dimensions, air exchange rate, total crack area, etc.). These default values are for single-family detached residences; therefore, the NAPL-SCREEN model should only be used for the residential exposure scenario.

The NAPL-ADV model, like the SL-ADV model, allows for up to three different soil strata between the top of contamination and the bottom of the building floor. In addition, the NAPL-ADV model allows the user to enter values for all model variables. This allows for the estimation of soil vapor intrusion into buildings other than single-family residences.

For each model, the user must also enter the duration of the first (initial) time-step interval. The maximum and minimum change in mass for each time-step must also be specified. The values of the initial time-step interval, and the maximum and minimum change in mass are <u>important</u>. If these values are too low, the model will calculate very small increments in the mass lost over time which will greatly extend the run-time of the model. In general, if the concentrations of the least volatile chemicals in the mixture are well above their respective values of the soil saturation concentration, a relatively large initial time-step interval, and maximum and minimum change in mass should be specified (e.g., 4 days, 10%, and 5%, respectively). For comparison, the value of the soil saturation concentration (C_{sat}) for each chemical specified by the user may be found in the CHEMPROPS worksheet after all data have been entered on the DATENTER worksheet. If, however, the soil concentrations of the most volatile constituents are very close to their respective saturation limits, large values of the initial time-step interval, and the maximum and minimum change in mass will result in the error message in Figure 3 after starting the model.

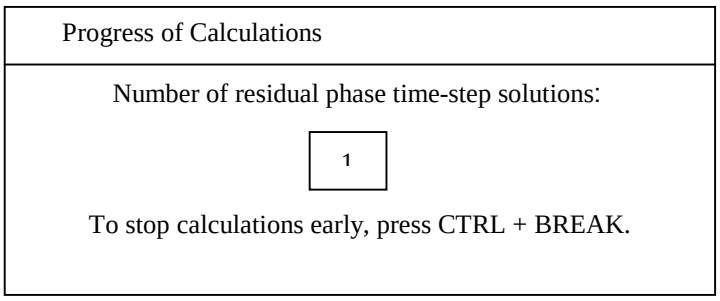
Figure 3. Time-Step and Change in Mass Error Message



Should this error message occur, reduce the value of the initial time-step interval and the values of the maximum and minimum change in mass to smaller values and re-run the model. The error message will be repeated until the values of these variables are sufficiently small.

After all required data are entered into the DATENTER worksheet, the model is run by clicking on the "Execute Model" button which will change from reading "Execute" to "Stand by...". In addition, the message box in Figure 4 will appear keeping a running count of the number of residual phase time-step solutions achieved by the model.

Figure 4. Progress of Calculations Message Box

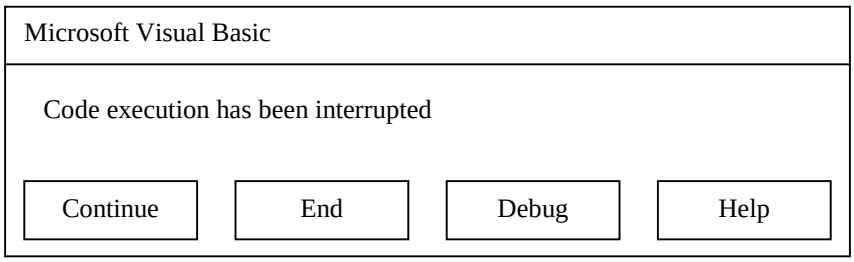


Each SOLVER trial solution can also be seen running in the status bar at the bottom of the screen. When the model is finished calculating, the "Execute Model" button will read "Done" and the Progress of Calculations message box in Figure 4 will disappear. The time-averaged building concentrations, incremental cancer risks, and/or hazard quotients will then be displayed under the "RESULTS" section of the DATENTER worksheet. In addition, an "X" will appear beside the calculated risk or hazard quotient of each contaminant for which a route-to-route extrapolation was employed. It should be noted that a route-to-route extrapolation was used for any chemical without a unit risk factor (URF) or a reference concentration (RfC). Therefore, the user should evaluate the resulting cancer risks and/or hazard quotients of such chemicals. Once a solution has been achieved and the user wishes to save the results, the file should be saved under a new file name. If the user wishes to delete <u>all</u> of the data previously entered on the DATENTER worksheet, this may be accomplished by clicking on the "Clear Data Entry Sheet" button.

Stopping Calculations Early

As mentioned previously, the user-defined values of the initial time-step interval, and the maximum and minimum change in mass should be chosen carefully. If the model run-time is excessive or if the user simply wishes to terminate the calculations, the model may be stopped by pressing CTRL + BREAK. If termination occurs in-between SOLVER solutions, the message box in Figure 5 will appear.

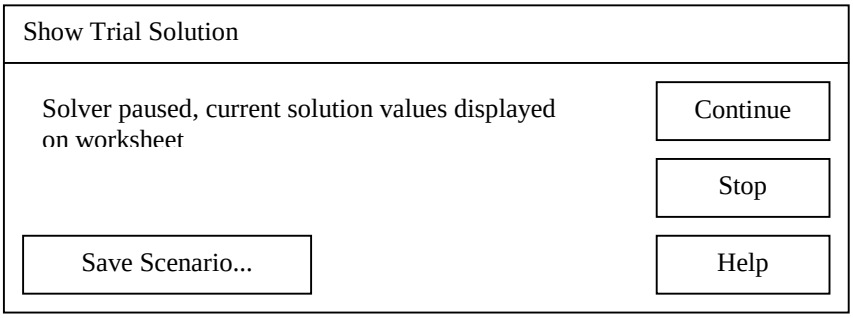
Figure 5. Code Interruption Message Box



If this message box appears, click on the "End" button to terminate the macro.

If the termination occurs during a SOLVER solution, the message box in Figure 6 will appear. If this message box appears, click on the "Stop" button. This will stop the SOLVER solution but not the program macro. Depending on where in the macro code the interruption occurs, the model may continue to operate after clicking on the "Stop" button in Figure 6. If this happens, press CTRL + BREAK again. At this point, the message box in Figure 5 will appear; click on the "End" button to terminate the macro.

Figure 6. Solver Interruption Message Box



At this point, the user may examine the model results up to the point of termination on the COMPUTE worksheet. The values of the "Change in mass", the "Time-step interval", and the "Cumulative time" should be examined to determine if changes are necessary in the values of the initial time-step interval, and the maximum and minimum change in mass. After these or any other values are changed on the DATENTER worksheet, the model may be re-run by clicking on the "Execute Model" button.

Step-By-Step Procedures for Running the Models

The following gives the step-by-step procedures for running either the NAPL-SCREEN or the NAPL-ADV model.

1. On the DATENTER worksheet, enter the CAS number of each soil contaminant in the residual phase mixture (do not include dashes in the CAS numbers). After the CAS numbers have been entered, the respective chemical names will appear in the "Chemical" box.

2. On the DATENTER worksheet, enter the soil concentration of each contaminant in units of mg/kg as well as values for all remaining variables except the "Initial time-step", the "Maximum change in mass", and the "Minimum change in mass".

3. On the CHEMPROPS worksheet, note the calculated values of the "Time to steady state" (τ_{ss}) for each contaminant. Calculated values of the time-averaged building concentration and associated risks for contaminants with values of τ_{ss} greater than the actual elapsed time since initial soil contamination will be artificially high.

4. On the CHEMPROPS worksheet, note the calculated values of the "Soil saturation concentration" (C_{sat}) for each contaminant. Use these data to help determine appropriate user-defined values for the initial time-step, and the maximum and minimum change in mass. Typical values for these variables might be 2 days, 7%, and 4%, respectively, but may be considerably higher or lower depending on the number of chemicals in the analysis and the starting soil concentrations (see the discussion on page 8).

5. Click on the "Execute Model" button to begin the model calculations. If data are missing on the DATENTER worksheet, or entered values do not conform to model assumptions, an error message box will appear after the model is started informing the user of the type of error encountered. Enter the appropriate values on the DATENTER worksheet and re-run the model. Once the model has successfully started, note the number of residual phase time-step solutions achieved by the model in the Progress of Calculations message box (Figure 4). Use this information to help establish new values for the initial time-step interval and the maximum and minimum change in mass if the number of time-steps needs to be increased or decreased.

6. When the NAPL-SCREEN model has finished calculating, check column "O" on the COMPUTE worksheet to determine how many time-steps were calculated while a residual phase was present; one time-step is equal to one row (when using the NAPL-ADV model check column "P"). A residual phase is present when the value in column "O" or "P", as appropriate, is equal to 1.000. In general, a greater number of time-steps means a more accurate estimate of the time-averaged building concentration. If the starting soil concentrations of the most volatile contaminants are very close to their respective values of C_{sat}, a minimum of 5 to 10 time-steps should be calculated by the model. For all other cases, a reasonable number of time-steps is between 40 and 70. To increase the number of time-steps calculated by the model, decrease the values of the initial time-step interval and the maximum and minimum change in mass. The opposite is true when the number of time-steps is to be decreased.

7. If the message box in Figure 1 appears after starting the model, the mixture of compounds and concentrations specified does not include a residual phase. Use the SL-SCREEN or SL-ADV model to calculate indoor air concentrations and risks for each contaminant separately.

8. If the message box in Figure 3 appears after starting the model, reduce the input values of the initial time-step, and maximum and minimum change in mass and re-run the model.

9. If the run-time of the model is excessive, terminate the model macro by pressing CTRL + BREAK (see the discussion under **Stopping Calculations Early** on pages 9 and 10). Examine the calculated values of the "Change in mass", the "Time-step interval", and the "Cumulative time" on the COMPUTE worksheet. Re-enter new lower values for the initial time-step interval, and the maximum and minimum change in mass and re-run the model.

10. After successful completion of a model run, note the calculated values of the "Time-averaged building concentration", "Incremental cancer risk", and/or "Hazard quotient" in the "RESULTS" section of the DATENTER worksheet. Also note for which contaminants a route-to-route extrapolation was employed. <u>If the model results are to be retained, save the file under a new file name</u>.

Adding, Deleting or Revising Chemical Data

Additional chemicals can be listed in the "Chemical Properties Lookup Table" within the VLOOKUP worksheet. To add, delete or revise chemicals, the VLOOKUP worksheet must be unprotected using the password "ABC" in capital letters. Row number 171 is the last row that may be used to add new chemicals. If new chemicals are added or chemicals deleted, the user must sort all the data in the "Chemical Properties Lookup Table" (except the column headers) in ascending order by CAS number. After sorting is complete, the worksheet should again be protected.

APPENDIX E

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Ground Water Monitoring&Remediation

Evaluation of the Johnson and Ettinger Model for Prediction of Indoor Air Quality

by Ian Hers, Reidar Zapf-Gilje, Paul C. Johnson, and Loretta Li

Abstract

Screening level models are now commonly used to estimate vapor intrusion for subsurface volatile organic compounds (VOCs). Significant uncertainty is associated with processes and models and, to date, there has been only limited field-based evaluation of models for this pathway. To address these limitations, a comprehensive evaluation of the Johnson and Ettinger (J&E) model is provided through sensitivity analysis, comparisons of model-predicted to measured vapor intrusion for 11 petroleum hydrocarbon and chlorinated solvent sites, and review of radon and flux chamber studies. Significant intrusion was measured at five of 12 sites with measured vapor attenuation ratios (α_m's) (indoor air/source vapor) ranging from $\sim 1 \times 10^{-6}$ to 1×10^{-4}. Higher attenuation ratios were measured for studies using radon, inert tracers, and flux chambers; however, these ratios are conservative owing to boundary conditions and tracer properties that are different than those at most VOC-contaminated sites. Reasonable predictions were obtained using the J&E model with comparisons indicating that model-predicted vapor attenuation ratios (α_p's) were on the same order, or less than the α_m's. For several sites, the α_m were approximately two orders of magnitude less than the α_p's indicating that the J&E model is conservative in these cases. The model comparisons highlight the importance in using appropriate input parameters for the J&E model. The regulatory implications associated with use of the J&E model to derive screening criteria are also discussed.

Introduction

The use of models to predict indoor air quality associated with volatile organic compound (VOC) contamination in soil and ground water is now commonplace (ASTM 1995; Johnson et al. 1998, Hers et al. 2002). Screening models typically used for this pathway are the Johnson and Ettinger (1991) model (henceforth referred to as the J&E model), or variants thereof. Processes controlling the intrusion of VOC vapors into buildings are not well understood, the accuracy of the J&E model is uncertain, and there have been only limited comparisons of model predictions to field data. There are also substantial differences in the way in which the J&E model is used for regulatory purposes.

To address these limitations, this paper presents a comprehensive evaluation of the J&E model based on theoretical considerations and field data from petroleum hydrocarbon and chlorinated solvent sites, and radon and flux chamber studies. Data sources are published studies, consultant or agency reports, and a field-based research program conducted by the authors. Included in the data sets analyzed are several recent groundbreaking investigations at chlorinated solvent sites.

The paper begins with an analysis of methods for estimating input parameters for the J&E model and their effect on model sensitivity and uncertainty. This analysis provides the needed context for the methods employed to interpret the field data used for this study. It is also important because it is essential that model attributes and potential limitations be understood before using field data to evaluate the predictive capabilities of a model. Field-based methods for the evaluation of vapor attenuation ratio (α), defined as the indoor air concentration divided by the source vapor concentration, are evaluated next. The primary focus is measured vapor attenuation ratios (α_m) from 11 sites with petroleum hydrocarbon and chlorinated solvent contamination. Information from tracer studies using radon or an injected tracer such as sulpher hexafluoride (SF_6), and flux chamber studies are also reviewed. The measured α_m from field studies are compared to model-predicted vapor attenuation ratios (α_p) using the J&E model. Trends in the data are qualitatively evaluated and possible factors affecting vapor intrusion are considered. The paper also comments on the use of the J&E model to derive regulatory screening criteria.

J&E Model Input Parameters, Sensitivity, and Uncertainty

The basic form of the J&E model couples one-dimensional steady-state diffusion through soil, and diffusion and advection through a building envelope (i.e., foundation). A simple "box" model, which assumes uniform and instantaneous mixing of chemicals within the building enclosure, is used to estimate the indoor air concentration. Model sensitivity and uncertainty analysis and input needed for comparisons of

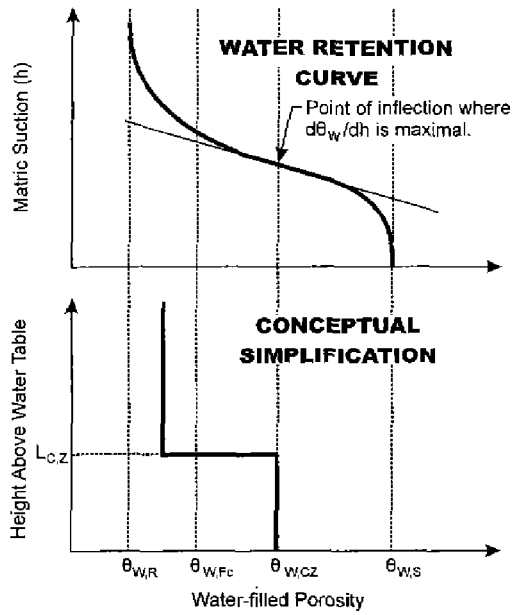

Figure 1. Conceptual simplification of water retention curve for purposes of estimating moisture contents and capillary rise ($\theta_{W,R}$, $\theta_{W,FC}$, $\theta_{W,CZ}$, $\theta_{W,S}$ are the residual, field capacity, capillary zone, and saturated water contents).

model predictions to field data all require estimation of effective diffusion coefficient and soil gas advection rate. Because the available data varied, different methods were used to estimate these input parameters and interpret field data. The estimation methods subsequently used in this paper are discussed in the following sections.

Estimation of Effective Diffusion Coefficient (Air-Filled and Total Porosity)

The J&E model uses the Millington and Quirck (1961) relationship to estimate the effective diffusion coefficient (D_T^{eff}), as follows:

$$D^T_{eff} = (\theta_a^{(10/3)} / \theta^2) * D_{air} + 1/H' * (\theta_w^{(10/3)} / \theta^2) * D_{water}$$

where θ_a, θ_w, and θ are the air-filled, water-filled, and total porosity; D_{air} and D_{water} are free-air and free-water diffusion coefficients (L^2T^{-1}); and H' is the dimensionless Henry's law constant.

A common method for estimating air-filled and total porosity directly uses the measured soil moisture content and bulk density. A potential disadvantage is that soil disturbance during sampling can lead to inaccurate moisture, density, and hence, porosity estimates. Samples obtained adjacent to buildings may not be representative of conditions below buildings owing to the drying of soil that can occur.

A second method involves the use of the van Genuchten (VG) model (van Genuchten 1980) to predict the water retention parameters for U.S. Soil Conservation Service (SCS) soil types, based on VG model curve-fit parameters computed by Schaap and Leij (1998) (Simplified VG method). This method, developed by Environmental Quality Management Inc. (EQM 2000), is incorporated in U.S. EPA guidance for this pathway. The VG model parameters are, in turn, used to develop a simplified step function for water-filled porosity (Figure 1). The capillary zone ($\theta_{w,cz}$) water-filled porosity is equal to the moisture content at the inflection point in the water retention curve where $d\theta_w/dh$ is maximal, as suggested by Waitz et al. (1996) (where θ_w and h equal the water-filled porosity and matric suction, respectively). Vapor-phase diffusion becomes negligible once the water-filled porosity exceeds the $\theta_{w,cz}$. The height of the capillary zone is estimated using an equation for capillary rise in a tube (Fetter 1994), and mean particle size for the SCS soil textural classifications (Nielson and Rogers 1990). The water-filled porosity above the capillary zone is user defined; we suggest a practical range below a building is between the residual water content and field capacity.

The simplified VG model likely predicts lower than actual water-filled porosity in soil, for the capillary transition zone (Figure 1). Because diffusion rates are much higher in air than water, this simplification likely results in conservative (high) diffusion estimates through the capillary transition zone. However, this conservatism may be counterbalanced by nonrepresentative assumptions for the ground water contamination source. The common paradigm for prediction of cross-media VOC transport is that dissolved chemicals are present below a static water table, and that transport through the capillary transition zone is limited to vapor- and aqueous-phase diffusion. In reality, there will be some lateral ground water flow and dispersive mixing of chemicals in the tension-saturated zone, and vertical movement of chemicals as a result of water-table fluctuations. There is limited information on VOC migration in the capillary transition zone. One study, involving a large chamber, showed that the pore-water concentrations in the tension-saturated zone were similar to those below the water table, and showed a sharp decline in concentrations near the top of the tension-saturated zone (McCarthy and Johnson 1993). The implication is that a more representative top boundary for dissolved ground water contaminants may be some distance above the water table.

Estimation of Soil Gas Advection Rate (Q_{soil})

The method often used with the J&E model for estimating the soil gas advection rate (Q_{soil}) through the building envelope is an analytical solution for two-dimensional soil gas flow to a small horizontal drain (Nazaroff 1992). This model is used to simulate gas flow to an edge crack located at the perimeter of a building (perimeter crack model). The Q_{soil} (L^3T^{-1}) is estimated as follows:

$$Q_{soil} = \frac{2\,\pi\,k_a\,\Delta P\,X_{crack}}{\mu\,\ln\left(\frac{2\,z_{crack}}{r_{crack}}\right)} \qquad (2)$$

where k_a is the soil-air permeability (L^2), ΔP is the pressure difference between the building and ambient air, X_{crack} is the perimeter crack length (L), μ is the gas viscosity ($M\,L^{-1}\,T^{-1}$), z_{crack} is the depth to edge crack (L), and r_{crack} is the crack radius (L). The ratio of cracks to total subsurface foundation area (i.e., base and walls) (η) can be expressed as

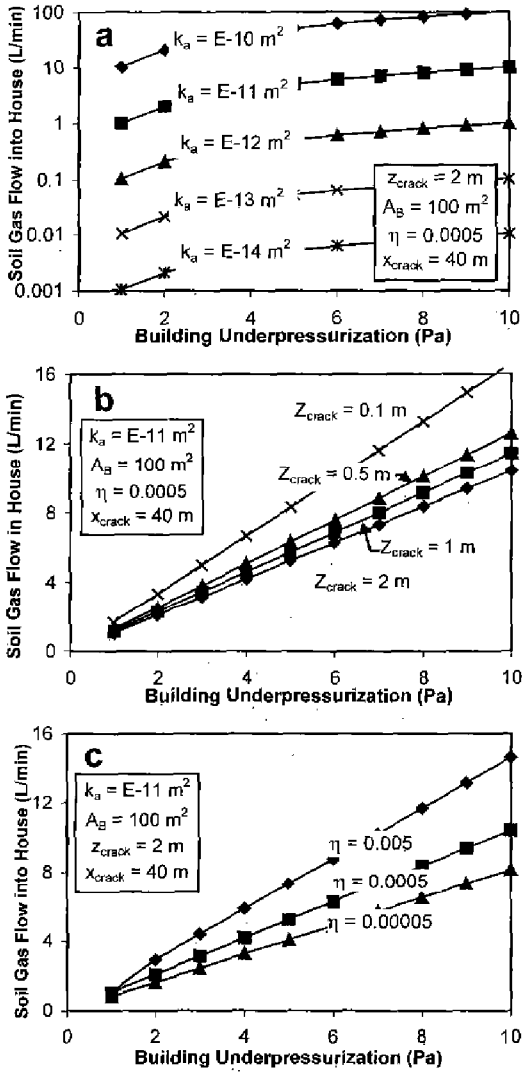

Figure 2. Sensitivity of soil gas flow to perimeter crack model (used in J&E model) to (a) soil-air permeability (k_a), (b) depth to perimeter crack (z_{crack}), and (c) crack ratio (η). X_{crack} = perimeter crack length, A_b = subsurface foundation area.

$$\eta = \frac{z_{crack} X_{crack}}{A_B} \tag{3}$$

where A_B is the subsurface foundation area (L^2). The perimeter crack model accounts for both soil gas flow through soil and the foundation, but is most sensitive to the soil-air permeability based on the analysis presented in Figure 2. For the range of values chosen for k_a, η, ΔP, and z_{crack}, by far the greatest variation is obtained for k_a with the predicted Q_{soil} ranging between ~0.001 and 100 L/min.

One method of estimating soil-air permeability is to use published values for saturated hydraulic conductivity and water retention parameters for a particular soil type (EQM 2000). This method involves the following steps: (1) obtain saturated hydraulic conductivity for soil texture type (Schaap and Leij 1998); (2) estimate intrinsic permeability from saturated hydraulic conductivity; (3) estimate effective total fluid saturation at field capacity; (4) estimate relative air permeability using the relationship proposed by Parker et al. (1987); and (5) calculate effective soil-air permeability (relative air permeability multiplied by intrinsic permeability). The soil-air permeability can also be measured in the field (Garbesi and Sextro 1995; Hers and Zapf-Gilje 1998); however, this type of testing is rarely performed.

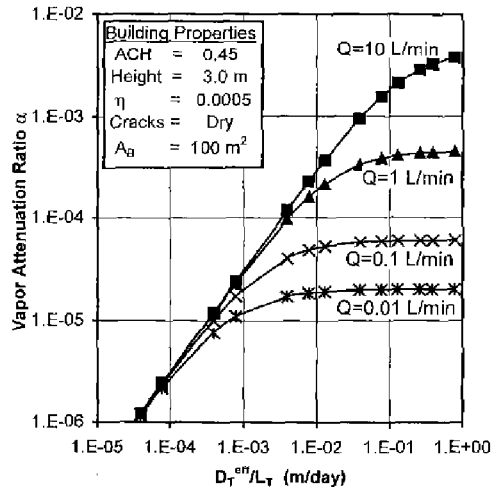

Figure 3. Sensitivity of vapor attenuation ratio (benzene) to soil-gas flow rate (Q) into building using perimeter crack model with dry dust-filled concrete cracks with total porosity = 0.3 Height = building height, Q = Q_{soil} ACH = air exchanges per hour (other symbols previously defined).

The Q_{soil} can also be estimated from a tracer test mass balance. When soil-gas advection is the primary mechanism for tracer intrusion into a building, the Q_{soil} can be estimated by measuring the concentrations of a chemical tracer in indoor air, outdoor air, and in soil vapor below a building, and measuring the building ventilation rate (Hers et al. 2002; Fischer et al. 1996; Garbesi et al. 1993; Rezvan et al. 1991; Garbesi and Sextro, 1989). The Q_{soil} values measured using this technique are compared to predicted rates using the perimeter crack model, for sites with coarse-grained soils (Table 1). The perimeter crack model predictions are both higher and lower than the measured values, but overall are within one order of magnitude of the measured values. Although the Q_{soil} predicted by models and measured using field tracer tests are uncertain, the results suggest that a "typical" range for houses on coarse-grained soils is on the order of 1 to 10 L/min.

J&E Model Sensitivity for Key Input Parameters

The sensitivity of the benzene α_p predicted by the J&E model is evaluated as a function of soil gas flow (Q_{soil}), the effective diffusion coefficient (D_T^{eff}), and contamination depth (L_T) (Figure 3). The D_T^{eff}/L_T ratio captures the influence of soil properties and depth to contamination source on α_p. For BTEX and most chlorinated solvent compounds, chemical-specific variation in the D_T^{eff}/L_T ratio is not significant because the free-air diffusion coefficients vary by only a factor of two, and the Henry's law constants vary by a factor of 10 (D_T^{eff}/L_T is less sensitive to H′ than D_{air}). Because the effective diffusion coefficient is calculated using the Millington and Quirck (1961) relationship, the soil properties of relevance are the air-filled and total porosity. A high D_T^{eff}/L_T ratio is asso-

Table 1
Comparison of Measured and Model-Predicted Soil Gas Flow Rates Into Buildings

Site	Foundation Type	ΔP (Pa)	Subsurface Foundation Area (m^2)	Crack Ratio η	Depth to Perimeter Crack (m)	$k_{soil-air}$ (Darcy)	Soil Gas Flow Rates Measured Tracer (L/min)	Soil Gas Flow Rates Predicted PCM (L/min)
Chatterton Site (Hers et al. 2000)	Slab-on-grade	30	57	0.00033	0.3	10	2.7	29
	Slab-on-grade	10	57	0.00033	0.3	10	4.2	9.6
	Slab-on-grade	10	57	0.0001	0.3	10	2.9	8.2
Alameda Site Fischer et al. (1996)	Slab-on-grade	3	50	**0.0001**	0.2	10	1.4	2.4
Central California Site Garbese & Sextro (1989)	Filled hollow block basement w/coating	30	128	**0.0001**	2.5	3	67	8.3
Ben Lomond Garbesi et al. (1993)	Experimental basement	10	26	0.00075	1.8	6	9.7	2.3
Spokane Valley Houses Revzan et al. (1991)	Poured concrete basements	5	220	0.0001	2	200	102	110

Notes: Bold print values assumed, all other values measured, ΔP = building underpressurization, PCM = Perimeter Crack model.

Table 2
Qualitative Summary of Sensitive Parameters for the J&E Model

	Building Depressurized (Advection and Diffusion)	Building Not Depressurized (Diffusion Only)
High D_T^{eff}/L_T (shallow and/or dry soil)	Q_{soil} (advection controlled)	Building foundation cracks
Moderate D_T^{eff}/L_T	Q_{soil} and moisture content (MC)	Building foundation cracks and MC
Low D_T^{eff}/L_T (deep and/or wet soil)	Moisture content (diffusion controlled)	Moisture content (MC)

Note: Indoor air concentrations are directly proportional to source concentrations, building mixing height and ventilation rate.

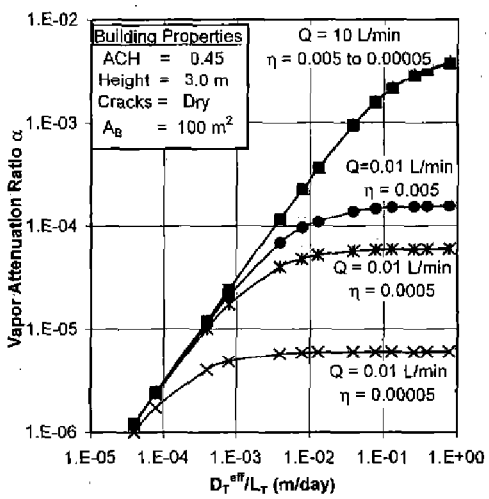

Figure 4. Sensitivity of vapor attenuation ratio (benzene) to soil-gas flow rate (Q) using perimeter crack model and foundation crack ratio (η) (other symbols previously defined).

ciated with dry soils and/or shallow contamination, whereas a low D_T^{eff}/L_T ratio is associated with wet soils and/or deep contamination. Based on the analysis in the sections that follow, sensitive parameters for the J&E model are also qualitatively summarized in Table 2.

Sensitivity of α_p to Q_{soil}

For sensitivity analysis purposes, a Q_{soil} range of 0.01 to 10 L/min was chosen because it is considered representative of most houses or small buildings. The results indicate that Q_{soil} begins to have a significant influence on α_p when D_T^{eff}/L_T values are moderate to relatively large (>~0.001 m/day) (Figure 3). The J&E model is described to be advection controlled for this scenario. When D_T^{eff}/L_T is relatively small (<~0.001 m/day), α_p is not sensitive to Q_{soil}. The J&E model is described to be diffusion controlled for this scenario. The D_T^{eff}/L_T for case studies subsequently evaluated in this paper ranged from ~0.002 to 0.1 m/day. For these D_T^{eff}/L_T values, the maximum error in prediction caused by a four order of magnitude variation in Q_{soil} ranges from 3X to 100X.

Sensitivity of α_p to Crack Ratio

The influence of crack ratio (η) on α_p was evaluated for two different Q_{soil} values (Figure 4). For Q_{soil} = 10 L/min, α_p is not sensitive to η. When Q_{soil} = 0.01 L/min, a two order of magnitude change in η causes up to 25X change in α_p. The sensitivity of α_p to η increases as Q_{soil} decreases, with sensitivity highest for the diffusion-only case (i.e., Q_{soil} = 0). The crack ratio is of little importance for smaller D_T^{eff}/L_T or Q_{soil} >~1 L/min, which means that for the majority of sites crack ratio will not be important.

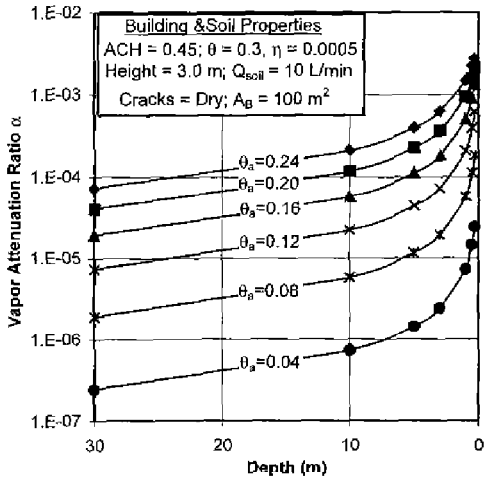

Figure 5. Sensitivity of vapor attenuation ratio (benzene) to water-filled porosity (θa). Other symbols previously defined.

Sensitivity of α_p to Air-Filled Porosity (Moisture Content)

The effect of air-filled porosity and depth to contamination was evaluated for a soil with moisture contents ranging from 3.6% to 15.6% (dry weight) and a constant total porosity of 0.3 (Figure 5). This variation in moisture content is potentially representative of the difference between a dry soil below a building compared to a wet soil within the capillary transition zone. The corresponding air-filled porosities are between 0.04 and 0.26. A Q_{soil} value of 10 L/min was assumed. For a constant depth to contamination, a 4X change in moisture content causes approximately or more than two orders of magnitude change in α_p. For a constant moisture content, α_p becomes sensitive to depth to contamination, at shallow depths. It is clear that soil layers with high moisture content will have a significant effect on the diffusive flux and vapor intrusion.

J&E Model Uncertainty for Range of Values

Vapor attenuation ratios predicted by the J&E model are provided for a range of soil gas advection rates and building properties, as a function of D_T^{eff}/L_T (Figure 6). For illustrative purposes, upper and lower soil-gas advection rates were estimated for four U.S. SCS soil textures (sand, loamy sand, sandy loam, and silt) using published values for saturated hydraulic conductivity and the perimeter crack model. The soil type only applies to soil immediately adjacent to the building, because the radius-of-influence for soil-gas advection is relatively limited. The estimated Q_{soil} values are highly uncertain; however, we note that the predicted values for sand (1 to 10 L/min) are consistent with the results of tracer tests for coarse-grained soils. The uncertainty in Q_{soil} increases for finer-grained soils because the influence of permeable soil layers and preferential pathways (e.g., utility backfill) becomes more important. It is suggested that the Q_{soil} for sand be used when near the foundation soil is not well characterized.

The building properties input to the model are the crack ratio, dust-filled crack moisture content, building height, building air exchanges, and building foundation size. The upper and lower building properties given are subjectively considered to represent the range of values that would be encountered at most sites, based on available information and the author's experience (Hers and Zapf-Gilje 1998; Hers et al. 2001). The subsurface foundation area is for a house with a shallow basement or slab-on-grade foundation. Slightly lower α_p's would be predicted for a deep basement with larger foundation area.

The graphs in Figure 6 illustrate the effect of variation in Q_{soil} and building properties on vapor attenuation ratio, but do not address uncertainty in D_T^{eff}/L_T, which is primarily caused by soil moisture content. To gain insight into uncertainty in model predictions owing to moisture content, a possible range in D_T^{eff}/L_T was evaluated for two hypothetical scenarios. The first scenario (Site 1) assumes a shallow soil vapor source (1.5 m depth) situated well above the water table. The second scenario (Site 2) assumes a relatively deep water table (6 m depth) and contamination that is limited to a dissolved ground water plume. Both sites were assumed to have uniform SCS loamy sand soil. The approach taken was to first obtain a plausible best estimate, and upper and lower range for D_T^{eff}/L_T. For Site 1, a constant air-filled porosity halfway between the residual water content and field capacity was assumed. For Site 2, the simplified VG method was used to estimate the air-filled and total porosity for the capillary zone. As shown in Table 3, the resulting porosities are expressed as relative water saturation values where $S = \theta_w/\theta$ and $\theta_a = \theta(1-S)$. The reason for using relative saturation values in the uncertainty analysis is that the air-filled and total porosity are expected to be strongly correlated. Therefore, uncertainty would be overestimated if these parameters are allowed to vary independently. This is prevented through the use of the relative saturation values. The uncertainty ranges given for total porosity and relative saturation are considered reasonable values for a well-characterized site.

Using the best estimate values and uncertainty ranges, the best estimate, lower and upper ranges are provided for the normalized effective diffusion coefficient (D_T^{eff}/L_T) (Table 3 and Figure 6). For Site 1, the upper and lower D_T^{eff}/L_T values vary by a factor of 2.4. For Site 2, the uncertainty is greater (factor of 23) because the sensitivity of D_T^{eff}/L_T to air-filled porosity within the capillary zone is high because moisture content is also high.

The overall uncertainty in the vapor attenuation ratio will be dependent on the available data. If there is information only on the contamination depth, the range in α_p can vary three to four orders of magnitude. When information on soil properties is also available, the uncertainty in D_T^{eff}/L_T and Q_{soil} is reduced resulting in α_p that vary over two orders of magnitude (Figure 6). When good quality site-specific data is available for both soil properties (e.g., moisture content) and building properties (e.g., ventilation rate, mixing height), it may be possible to reduce the uncertainty in α_p to approximately one order of magnitude.

Field-Based Methods for Evaluation of Vapor Intrusion

Three field-based approaches or methods are used to evaluate vapor intrusion: the indoor VOC method, the tracer method, and the flux chamber method. The *indoor VOC method* involves measurement of VOC concentrations in indoor air and at the contamination source. The α_m will vary depending on the contamination scenario. For sites with dissolved ground water plumes, the α_m is calculated using a

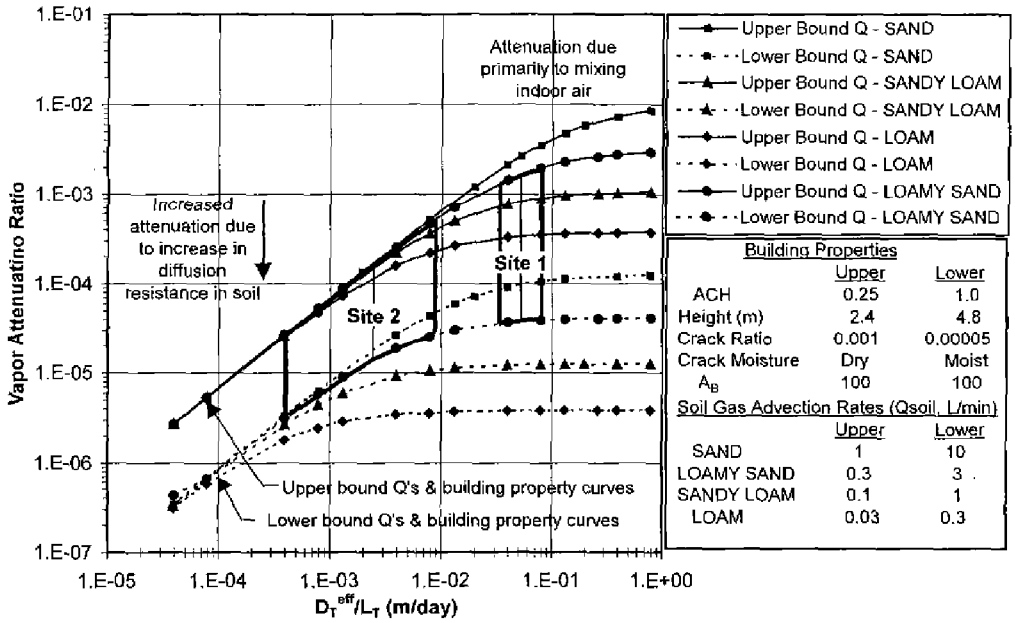

Figure 6. Predicted vapor attenuation ratio (benzene) for vapor concentrations at source and indoor air using Johnson and Ettinger (1991) model. Figure adapted from Johnson et al. (1998). Dry dust-filled cracks: Total porosity = 0.3; moist dust-filled cracks: water-filled porosity = 0.1, and total porosity = 0.3.

Table 3
Uncertainty Analysis for Normalized Effective Diffusion Coefficient

Parameters	Best Estimate Values Site 1	Site 2	Uncertainty
Input Parameters			
Contamination	Above WT	Dissolved in Gdw	N/A
Contamination depth (m)	1.5	6.0	constant
U.S. SCS soil classification	Sandy Loam	Sandy Loam	N/A
Total porosity (θ)	0.390	0.390	+/- 10%
S_R (θ_w/θ) above CZ (S)	0.265	0.265	+/- 25%
Height of CZ (L_{cz}) (m)	N/A	0.250	+/- 25%
S_R (θ_w/θ) in CZ (S_{cz})	N/A	0.821	+12/-10%
Calculated Values			
D_T^{eff}/L_T lower est. (m/day)	0.0325	0.00038	
D_T^{eff}/L_T best est. (m/day)	0.0512	0.00248	
D_T^{eff}/L_T lowest est. (m/day)	0.0775	0.00861	
D_T^{eff}/L_T upper/lower range	2.4	23	

Notes: CZ = capillary zone, S_R = relative saturation, Gdw = Ground water, WT = water table.

predicted source vapor concentration (i.e., directly above the water table) estimated using the Henry's law constant assuming equilibrium partitioning between the dissolved and vapor phases. When measured source vapor concentrations are available, the α can be directly calculated. Because some deviation from equilibrium conditions would be expected, the α_{in} estimated using ground water and soil vapor data are not directly comparable. A key challenge for this approach is that there are numerous other "background" sources of VOCs in indoor and outdoor air for most chemicals of concern at contaminated sites (Hers et al. 2001). The intrusion of soil vapor into buildings is also highly dependent on site-specific conditions and may vary over time. These factors complicate the interpretation of indoor air measurements when the goal is to deduce the subsurface-derived component.

The *tracer method* involves measurement of the indoor air concentration of a tracer injected below ground (SF_6), or a natural tracer such as radon (Fisher et al. 1996; Garbesi et al. 1993). The measured vapor intrusion for the tracer is, in turn, used to infer intrusion for the VOC of interest. Key factors affecting this approach are that boundary conditions for a tracer injected below a building may be different than those for the VOC of interest (e.g., if contamination is relatively deep) and that typically, an essentially inert tracer is used. When compared to the tracer, the mass loss or attenuation through sorption and/or biodegradation will be greater for most VOCs of interest. For these reasons, the tracer method will typically provide a conservative estimate of intrusion.

The *flux chamber* method involves measurement of soil-gas flow and/or VOC flux through cracks or openings in a building foundation. There are only a few published reports documenting the use of flux chambers to measure VOC flux into buildings (Figley and Snodgrass 1992; Hers and Zapf-Gilje 1998). Challenges for this approach are that these tests are difficult and costly to perform, and the uncertainty associated with "scaling up" the results for a small crack to an entire building.

Results and Discussion of Field Studies and Model Predictions

Indoor VOC Method

Vapor attenuation ratios are evaluated for 11 sites. The sites represent studies available to the authors with reasonable quality field data, and are for residential houses, ground-floor

Table 4
Measured and Model-Predicted Vapour Attenuation Ratios

Site & Reference	Contaminant or Tracer	Building and Foundation Type	Soil Conditions	Depth (m)[1]	Chemical	Source Concentration (ug/L)	N Indoor Air[2]	α_m Statistic	Measured α_m	J&E model α_p[3]	Comments
Indoor VOC Method											
"Virginia (Motiva) Site", Fan and Quinn (2000)	petroleum HC, NAPL above water	SFR, basements, attached garages, cement block foundations	claystone saprolite k ~ 0.01 darcy	0.5	benzene	V: 410	13	50th	<8.3E-6	3.70E-06	
"Chatterton Site" Delta, B.C. Canada Hers et al. (1998) Hers et al.(2000a)	BTX petro-chemical plant, NAPL above water table	research greenhouse slab-on-grade poured concrete 2 mm edge crack	surface silt to f. sand, under-lain by m.sand with k ~ 10 darcies	1.4	benzene	V: 15,000	3-4	Avg	< 5.3E-7	1.3E-05	C1: ΔP= 0 Pa, η = 3.3E-4
					toluene	V: 20,000	3-4	Avg	< 1.9E-6	1.3E-05	C1: ΔP= 0 Pa, η = 3.3E-4
					benzene	V: 15,000	3-4	Avg	4.0E-07	5.9E-05	C2: ΔP= 2.5 Pa, η = 1E-4
					toluene	V: 20,000	3-4	Avg	5.9E-07	5.9E-05	C2: ΔP= 2.5 Pa, η = 1E-4
					benzene	V: 15,000	3-4	Avg	9.9E-05	7.8E-05	C3: ΔP= 10 Pa, η = 1E-4
					toluene	V: 20,000	3-4	Avg	1.3E-04	7.8E-05	C3: ΔP= 10 Pa, η = 1E-4
					benzene	V: 15,000	3-4	Avg	7.2E-06	8.0E-05	C4: ΔP= 10 Pa, η = 3.3E-4
					toluene	V: 20,000	3-4	Avg	3.4E-05	8.0E-05	C4: ΔP= 10 Pa, η = 3.3E-4
					benzene	V: 15,000	3-4	Avg	5.8E-06	2.9E-05	C5: ΔP= 30 Pa, η = 3.3E-4
					toluene	V: 20,000	3-4	Avg	2.2E-05	2.9E-05	C5: ΔP= 30 Pa, η = 3.3E-4
"Paulsboro Site", NJ USA, Laubacher et al. (1997)	gasoline NAPL above water table	SFR basement	sand, some silt	2.74	benzene	V: 576	15	Avg	<1.6E-6	4.3E-04	
"Alameda (Air Station) Site", CA, USA Fischer et al.(1996)	gasoline NAPL above water table	small commercial building, slab-on-grade poured concrete	sand k ~ 1 to 3 darcy	0.7	benzene	V: 200	1	N/A	<9E-6	2.45E-04	
				0.7	iso-pentene	V: 28,000	1	N/A	< 9E-7	2.46E-04	
"Mass. DEP Sites" USA, Fitzpatrick & Fitzgerald (1996)	petroleum hydrocarbon	N/A (3 sites)	N/A	N/A	benzene	N/A	-	N/A	1E-5 to 4E-5	INS INS	
"Midwest School Site" USA, Moseley and Meyer (1992)	petroleum HC NAPL above water table	Built 50's, at-grade construction, crawl-space, large paved area	sand & gravel, discontinuous clay lenses	~ 3	benzene total HC	N/A	N/A	N/A	HC-like odours -- 1E-4	INS	crawlspace conc.: benzene ~ 8.3 mg/m^3, Total HC ~ 500 mg/m^3
"CDOT HDQ Site" Colorado, USA Johnson et al. (2000)	chlorinated solvents, dissolved plume	mostly apartments, few SFRs, mostly slab-on-grade, few crawl-spaces & basements, AC mostly window units, heating natural gas, baseboard, and/or fireplaces	weathered & fractured claystone above water table	4.6	1,1 DCE	G: 10-10,000	115-150	Geom 90th	4.8E-06		a_m values for houses above plume with DCE groundwater concentration > 10 ug/L
					1,1 DCE	G: 10-10,000			2.0E-05		
					TCE	G: 3-3,000	115-150	Geom 90th	1.4E-05		
					TCE	G: 3-3,000			7.0E-05		
					1,1,1 TCA	G: 10-1,000	115-150	Geom 90th	1.7E-05		
					1,1,1 TCA	G: 10-1,000			6.6E-05		
					above 3 CS		115-150	Geom 90th	1.2E-05	8.6E-05	average for 3 chlorinated solvents (CS)
					above 3 CS				5.2E-05	2.4E-04[4]	
"Redfields Site" Colorado, USA Envirogroup (1999)	chlorinated solvents, dissolved plume	SFRs, built 50's and 60's, mostly basements or crawlspaces, no combustion air intakes	clay & silt, some sand layers, mostly sand or silt near WT	6.1 to 7.3	1,1 DCE	G: 10-1,000	65	50th	1.50E-05	INS	a_m values for houses above plume with DCE groundwater concentration > 10 ug/L
					1,1 DCE	G: 10-1,000	65	Avg	7.60E-05		
					1,1 DCE	G: 10-1,000	65	90th	1.20E-04		
Hamilton Site Colorado, USA (2001), unpublished	chlorinated solvents, dis-solved plume	SFRs built 50's most basements	primarily sand & & gravel, some clay & silt layers	9.7 to 11	1,1 DCE	G: 15-30	32	50th	6.80E-05	INS	Gravel at water table
						G: 15-30	32	90th	1.40E-04		
"Lowry (Air Force Base) Site" Colorado, USA Versar (2000)	chlorinated solvents, dissolved	SFR: mostly basements some crawlspaces	silty sand to silt, generally silty sand near water table	6.1 to 7	1,1 DCE	G: 1.4-1.9	>50	50th	2.20E-05	INS	max G a_{sl} = 6.2E-04
					TCE	G: 120-170	>50	50th	2.20E-05		max G a_{sl} = 1.2E-03
					1,1 DCE	V: > 29	>50	50th	6.50E-04		max V_{SS} a_m = 8.3E-03
					TCE	V: > 1,000	>50	50th	7.70E-04		max V_{SS} a_m = 1.4E-02
"Mountain View Site" California, USA Wu (2000)	chlorinated solvents, leach-field & dissolved[5]	SFRs, built 1998, at-grade construction with moisture vapor barrier	mostly silty/ clayey sand & gravel, some sand or silt lenses	1.5	TCE	V: 84	14	Max	2.80E-04	INS	a_m shallow vapour
						V: 84	14	2nd[6]	<1.3E-5		
				10.7	TCE	G: 735	14	Max	7.80E-05		a_m groundwater, depth to groundwater = 10.7 m
						G: 735	14	2nd	<3.6E-5		
"Mass. DEP Sites" USA, Fitzpatrick & Fitzgerald (1996)	chlorinated solvents	N/A (19 sites)	N/A	N/A	CS	N/A	N/A	N/A	2E-6 to to 1E-1	INS	high a_m associated with highly permeable building envelopes (earthern floor, block walls & sumps)
Tracer and Flux Chamber Tests											
"Central California Site", Garbesi & Sextro (1989)	SF_6	SFR, basement poured slab, block walls coated with asphalt	sandy loam to loamy sand, k = 0.1 to 10 darcies	sub-slab	SF_6	N/A	N/A	N/A	~ 1E-3	N/A	ΔP = 30 Pa
"Alameda Site" Fischer et al. (1996)	SF_6	small commercial, slab on-grade, concrete	sand, k = 1 to 3 darcy	sub-slab	SF_6	N/A	N/A	N/A	2E-4 to 4E-4	N/A	ΔP ~ 3 (estimate based on wind loading)
U.S. Sites Little et al.(1992)	radon	SFRs	N/A	sub-slab	radon	N/A	N/A	N/A	1.6E-3[7]	N/A	
"Spokane River Valley Sites", WA, USA, Rezvan et al. (1992)	radon	SFRs (14), 8 houses slab-on-grade, 6 basement	highly permeable sand & gravel, k ~ 200 darcies	sub-slab	radon	N/A	N/A	N/A	~ 7.9E-3 to to 4.5E-2	N/A	winter conditions, mean house volume = 500 m^3, ACH = 0.5/hr

Notes: [1]Depth to contamination from underside of foundation slab; [2]N = Number of indoor air samples tested; [3]Best estimate unless otherwise noted; [4]Upper range; [5]Contamination likely in unsaturated zone; [6]2nd highest α_m value; [7]Alpha (α) estimated using mean radon content of soil combined with appropriate constant divided by radon concentration in U.S. homes (55 Bq m-3); [6]N/A = not available or applicable, SFR = single family residence, SF_6 = sulpher hexafluoride; V = vapor, V_{ss} = sub-slab, G = ground water, bgs = below ground surface, HC = hydrocarbon, AC = air-conditioning, INS = insufficient data, ACH = air exchanges per hour, WT = water table, CS = chlorinated solvents.

Table 5
Input Parameter Values Used for Johnson and Ettinger (1991) Model[1]

Parameter	Virginia Site	Chatterton Site	Paulsboro Site	Alameda Site	Midwest Site	CDOT HDQ Site	Redfields Site	Hamilton Site	Lowry Site	Mountain West Site
US SCS soil type used for D_T^{eff}/L_T	N/A	N/A	N/A	N/A	N/A	N/A	Loamy Sand	Sand	Loamy Sand	N/A
Depth to contamination (L_T) (m)	0.5	1.4	2.74	0.7	3.0	4.8	6.1	10.3	0.25[1] 6.1[3]	1.5[2] 10.7[3]
Total porosity unsaturated zone (θ)	0.43	0.36	0.39	0.36	0.4	0.4	0.39	0.375	0.39	0.41
Air-filled θ unsaturated zone (θ_a)	0.28	0.21	0.23	0.22	0.25	0.26	0.287	0.319	0.287	0.2
Height of capillary zone (L_c) (m)	N/A	N/A	N/A	N/A	N/A	0.2	0.25		0.17	0.25
Total θ capillary zone (θ_c)	N/A	N/A	N/A	N/A	N/A	0.4	0.39	0.375	0.39	0.41
Air-filled θ capillary zone ($\theta_{a,c}$)	N/A	N/A	N/A	N/A	N/A	0.08	0.07	0.12	0.07	0.1
D_T^{eff}/L_T (m/day)	0.12[4]	0.023[4]	0.014[4]	0.054[4] 0.050[5]	0.016[6]	3.4E-3[6]	2.4E-3[7]	8.4E-3[7]	0.49[8] 2.4E-3[9]	0.013[10] 1.5E-3[11]
Soil-air permeability k_a (10^{-12} m^2)	0.01	10	10	3	—	N/A[12]	—	—	—	—
Building underpressurization (Pa)	1	0, 2.5, 10, 30	5	3	—	N/A[12]	—	—	—	—
Foundation crack ratio (η)	1.5E-03	3.3E-4 to 1E-4	1.E-04	1.E-04	—	1.E-04	—	—	—	—
x_{crack} (m)	55.9	26.8	27.6	26.8	—	N/A[12]	—	—	—	—
z_{crack} (m)	2.0	0.3	2.13	0.2	—	N/A[12]	—	—	—	—
Q_{soil} (L/min)	0.0016	8.2 to 29	2.8	2.2	—	10	—	—	—	—
Total θ dust-filled cracks (θ_{crack})	0.43	0.25	0.25	0.25	—	0.4	—	—	—	—
Air-filled θ dust-filled cracks ($\theta_{a,crack}$)	0.28	0.25	0.25	0.25	—	0.26	—	—	—	—
Air exchange per hour (ACH)	0.76	0.42 to 14.3	0.42	2.1	—	0.45	—	—	—	—
Building mixing height (m)	2.0	2.19	2.74	2.4	—	3.0	—	—	—	—
Subsurface building area (A_B) (m^2)	186	57	39	50	—	89	—	—	—	—

Notes: [1]Depth to sub-slab soil gas probes; [2]Depth to shallow gas probes; [3]Depth to ground water; [4]Benzene; [5]Iso-pentene; [6]Average 1, 1 DCE, TCE and 1,1,1 TCA; [7]1,1,DCE; [8]DCE for sub-slab vapor source (TCE value is 0.43); [9]DCE for ground water source (value for TCE is 2.2E-03); [10]TCE for shallow vapor source; [11]TCE for ground water source; [12]Q_{soil} is etimated directly; therefore x_{crack}, z_{crack}, ΔP and k_a not needed; [13]Building foundation thickness not included since has negligible effect.

apartments, or small commercial buildings. Site characteristics and estimated input parameters are summarized, and measured and J&E model-predicted vapor attenuation ratios (α_m and α_p) are compared (Tables 4 and 5, Figure 7). In most cases, the vapor attenuation ratios are estimated by the authors using site data; in a few cases, the ratios given in references cited in Table 4 are reported. This has led to differences in the statistical estimators used to characterize the variability in α_m and α_p. For completeness, the vapor attenuation ratios reported for several Massachusetts sites are also included in Table 4; these sites are not included in the 11 case study sites discussed later.

The quality and quantity of site characterization data, and ability to distinguish measured indoor air concentrations from background VOC sources varies from site to site. For three sites, the VOC concentrations in a relatively large number of houses above the contaminant plume were significantly greater than house concentrations in background areas, resulting in fairly reliable α_m estimates. For the remaining sites, either the vapor-derived VOC concentrations in indoor air were significant in only a small subset of houses above the contaminant plume, or there was no significant difference between above plume and background indoor air concentrations. The vapor attenuation ratio is not measurable when there is no significant vapor-derived component; however, the indoor air concentrations can be used to calculate upper bound α_m values, represented as "less than" values in Table 4, and dashed lines in Figure 7.

For each site (except Chatterton), a predictive "envelope" for α_p was generated. A best estimate D_T^{eff}/L_T was directly calculated when reasonably good quality moisture content data was available. When good quality data was not available, the U.S. SCS soil texture class was inferred based on soil descriptions and the simplified VG method was used to calculate D_T^{eff}/L_T. We recognize that inference of soil texture is approximate and subjective. The upper and lower bound D_T^{eff}/L_T values were approximated using the same variability calculated for the two hypothetical sites discussed earlier (Table 3). The upper and lower bounds for Q_{soil} and building properties are the curves presented in Figure 6. A Q_{soil} range of 1 to 10 L/min (i.e., representative of sand) was assumed for all sites (except Virginia) because either coarse soils were present below building foundations, or there was no information on soil type (in these cases, sand was assumed to be present below foundations). Based on the fine-grained near-foundation soils at the Virginia site, a Q_{soil} range of 0.03 to 0.3 L/min (i.e., representative of loam) was assumed. When there was sufficient information on building properties and soil gas advection potential, the J&E model-predicted α_p was also estimated (represented as symbols in Figure 7). For the Chatterton site, only the best estimate α_p were plotted because testing at this site involved an experimental building and test cases not representative of generalized predictive envelopes in Figure 6.

Measured Vapor Attenuation Ratios at Petroleum Hydrocarbon Sites

Case study sites with petroleum hydrocarbon contamination have coarse-grained soils (except for the Virgina site) and

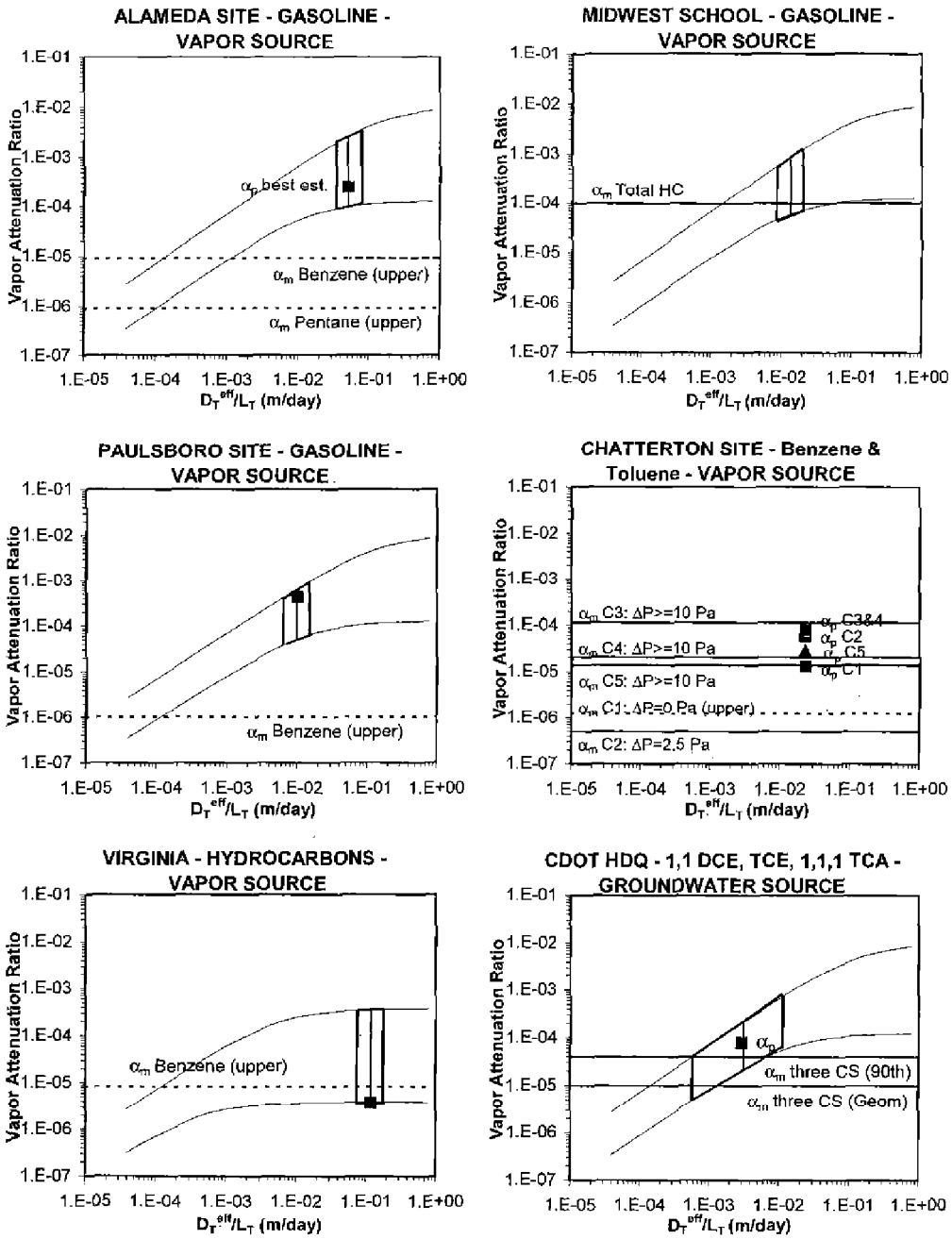

Figure 7a. Comparison between measured and J&E model-predicted vapor attenuation ratio (benzene). Upper and lower bound curves from Figure 6 are included. Dashed lines indicate that α_m is upper bound value. Symbols are best estimate α_p values.

shallow to moderate depths to contamination (0.5 to 3 m). Extensive residual nonaqueous phase liquid (NAPL) is present above the water table at the Chatterton site. There is evidence for some residual NAPL above the water table at the Alameda, Paulsboro, Virginia, and Midwest School sites. Indoor air testing was limited to a single or small number of buildings at each case study site. For petroleum sites, near-source vapor concentrations are available and therefore the α_m is directly calculated (vapor α_m).

At the Virginia, Chatterton (depressurization (ΔP) = 0 Pa case), Paulsboro, and Alameda sites, there was no difference between indoor air concentrations measured in building(s) above the plume and in background areas, indicating that the α_m are unknown. For these sites, the α_m calculated using the measured indoor air concentrations are upper-bound values and range from $< 4.0 \times 10^{-7}$ to $< 9.0 \times 10^{-6}$. For the Chatterton ΔP = 2.5 Pa case, there was a statistically significant difference in indoor and background indoor air concentrations; however, the α_m remained low (4.0×10^{-7} to 5.9×10^{-7}). For the Chatterton ΔP = 10 and 30 Pa cases, there was a significant increase in indoor air concentrations and α_m.

At the Midwest School site, hydrocarbon-like odors were noted indoors during a period of relatively heavy rains and high water table in September 1992. Subsequent analysis of indoor

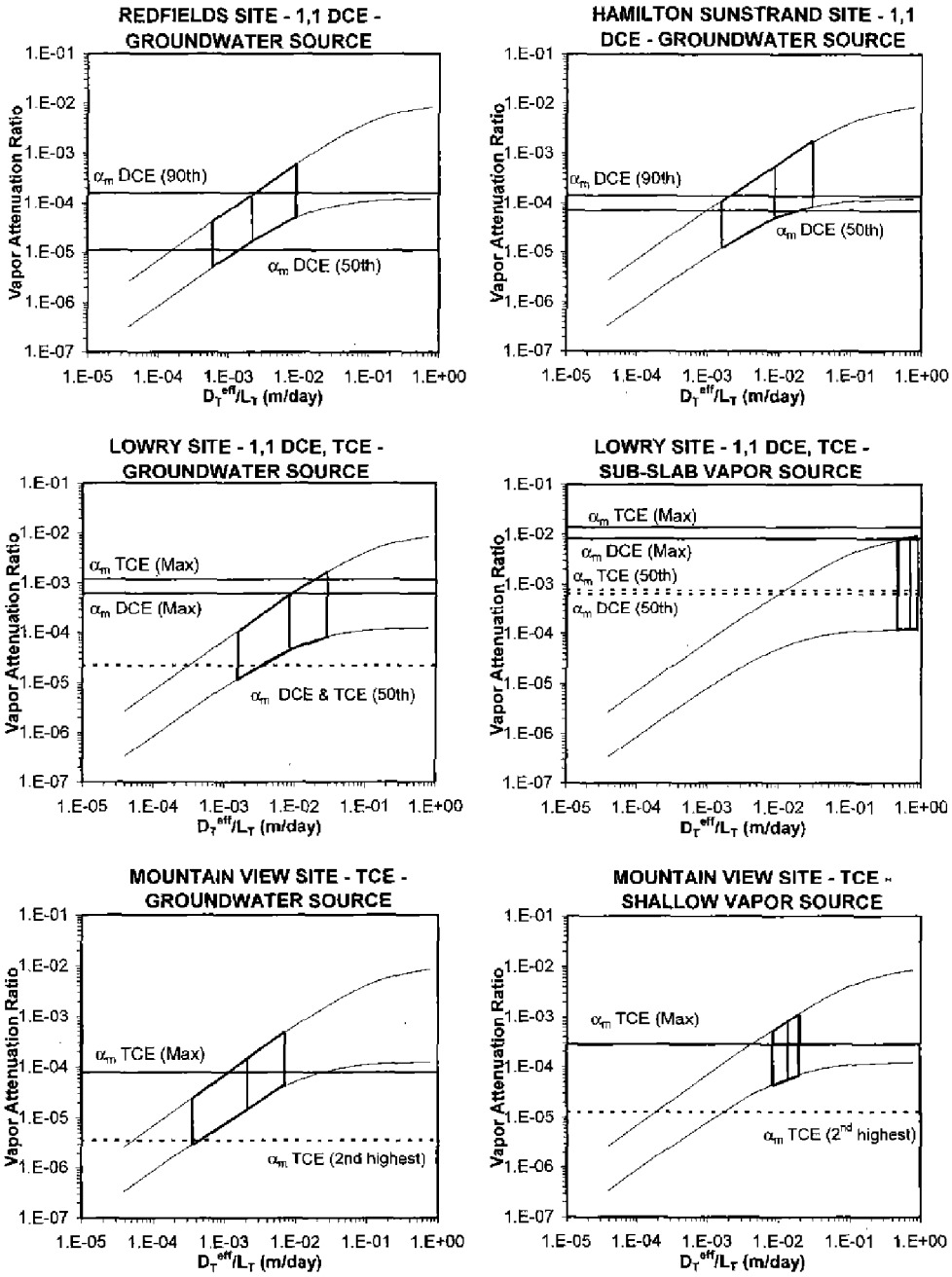

Figure 7b. Comparison between measured and J&E model-predicted vapor attenuation ratio (benzene). Upper and lower bound curves from Figure 6 are included. Dashed lines indicate that α_m is upper bound.

air during October 1992 indicated that hydrocarbon concentrations in indoor air were elevated but could not be conclusively distinguished from background sources at this time. However, the benzene (8 mg/m^3) and total hydrocarbon concentrations (500 mg/m^3) in an unventilated crawlspace below the ground floor were well above background levels. Based on a rough estimate of the source vapor concentrations and odor thresholds for hydrocarbons, the α_m may have been on the order of 1×10^{-4}.

Field data, including soil vapor profiles, indicate there was significant bioattenuation of hydrocarbon vapors for the Alameda and Chatterton ($\Delta P = 0$ and 2.5 Pa cases) sites. This is consistent with other studies indicating that biodegradation can result in significant vadose zone attenuation of hydrocarbon vapors, provided sufficient O_2 is present (Ostendorf and Kampbell 1991; Ririe and Sweeney 1995). For higher underpressurizations (10 and 30 Pa), at the Chatterton site hydrocarbon vapor concentrations were elevated because of increased vapor flux from deeper soil, and reduced travel times (Hers et al. 2002). The relatively high α_m at the Chatterton site are from the combined effect of shallow contamination, relatively permeable soils, and high building underpressurizations.

The Paulsboro and Midwest School sites had elevated

hydrocarbon vapor levels directly below the building slab. For the Midwest School site, we speculate that elevated indoor hydrocarbon concentrations may have been a result of limited biodegradation owing to a large building and paved area, which reduced oxygen recharge, combined with factors that contributed to vapor intrusion into the building. These factors include building construction (i.e., crawlspace) and/or a sanitary sewer that was located near the water table within the hydrocarbon plume, which may have acted as a preferential pathway. At the Virginia site, contamination was shallow but no significant vapor intrusion was measured possibly because of the presence of fine-grained soils and/or building construction (i.e., tight foundations).

Comparison to Model Predictions for Petroleum Hydrocarbon Sites

Comparisons for the Chatterton ($\Delta P = 0$ and 2.5 Pa cases), Paulsboro, and Alameda sites indicate that the best estimate α_p are one to two orders of magnitude higher than the measured or upper bound α_m indicating the J&E model results in conservative predictions for these sites. Comparisons for the Chatterton ($\Delta P = 10$ and 30 Pa cases) and Virginia sites indicate the best estimate α_p are similar to the α_m. The high soil-gas advection rates for the Chatterton site resulted in significant vapor intrusion rates and hence similar α_p and α_m. For the Virginia site, the α_p is lower than at other sites owing to the influence of the fine-grained soils. For the Midwest site, the predictive envelope for α_p also intersects the α_m; however, the α_m is highly uncertain.

Measured Vapor Attenuation Ratios at Chlorinated Solvent Sites

At four case study sites with chlorinated solvent contamination (CDOT, Redfields, Hamilton, and Lowry), dissolved plumes have migrated below houses (Table 4). The depth to the water table at these sites ranged from ~4.8 to 10.7 m below ground surface. The ground water plumes at these sites are relatively long and narrow, resulting in significant spatial variability in dissolved ground water concentrations. At the fifth site (Mountain View), houses were constructed on top of a former leach field where chlorinated solvents had been disposed of. Therefore, in addition to ground water, shallow soil is likely contaminated at this site. Soil grain size at the sites is variable (Table 4). For all sites, the α_m are estimated using vapor concentrations predicted from ground water data (ground water α_m). For the Lowry and Mountain View sites, soil vapor data were also available; therefore, the α_m is also directly calculated using vapor data (unless otherwise noted, the α_m given below are for the ground water source scenario).

For the CDOT site, the differences in three chlorinated solvent concentrations (1,1 DCE, TCE, and 1,1,1 TCA) in houses above the plume and at background locations are statistically significant. However, the ground water and indoor air data were found to be unreliable at the periphery of the plume and therefore low ground water and indoor air concentrations were removed from the database prior to calculating the α_m. The resulting database comprises several hundred tests from apartments and houses. The methodology used to estimate α_m is further described in Johnson et al. (2000). The geometric mean and 90th percentile α_m for the CDOT site are 1.0×10^{-5} and 5.2×10^{-5}. Analysis of the intrusion database for the site indicated no strong correlation between seasons and α_m, or difference between basement and slab-on-grade construction (personal communication, Dr. Jeff Kurtz, EMSI Inc.).

For the Redfields site, the difference in 1,1 DCE concentrations in houses above the plume and at background locations are statistically significant. A data screening procedure similar to that used for the CDOT site resulted in α_m only being estimated in areas where the 1,1 DCE concentrations in ground water exceeded 10 µg/L. A visual interpolation method was used to estimate ground water concentrations below houses. The resulting database comprises 65 houses nearest to the Redfields site. The 50th and 90th percentile α_m for the Redfields site are 1.1×10^{-5} and 1.2×10^{-4}. Synoptic data for the Redfields site indicated a slight correlation between indoor 1,1 DCE concentrations and season, for some houses, with winter-time values that were two to three times higher than summer-time values (personal communication, Dr. David Folkes 2000).

For the Hamilton site, the difference in 1,1 DCE concentrations in houses above the plume and at background locations are statistically significant. Because ground water data was limited, the attenuation ratio analysis is for a strip of 32 houses parallel and closest to the long axis of the plume (and wells) in the area with 1,1 DCE concentrations above ~10 µg/L. The 50th and 90th percentile α_m for the Hamilton site are 6.8×10^{-5} and 1.4×10^{-4}.

At the Lowry site, the database evaluated consists of more than a year of quarterly testing at 13 houses above and near the periphery of the plume. Concurrent testing of indoor air, and subslab vapor concentrations for houses with slab-on-grade or basement construction, and crawlspace air for houses with crawlspaces was conducted. At one house, the maximum TCE and 1,1 DCE concentrations in indoor air were 51 µg/m^3 and 0.91 µg/m^3, suggesting significant vapor intrusion. At three other houses, the TCE concentrations in indoor air were mostly between 5 and 15 µg/m^3. Compared to published background data for TCE (Hers et al. 2001) and data for houses along the periphery of the plume, it is possible that concentrations at these three houses included a soil vapor-derived component. The indoor air concentrations were at background levels in remaining houses.

Measured vapor attenuation ratios are estimated for a subset of four Lowry houses with nearby ground water data. For this data subset, the maximum indoor air TCE concentration was 51 µg/m^3, but exceeded 5 µg/m^3 in only one house. Therefore, most α_m are upper bound values. When all data are used, the 50th percentile and maximum ground water α_m are 2.2×10^{-5} and 1.2×10^{-3} for TCE, and 2.2×10^{-5} and 6.2×10^{-4} for 1,1 DCE. The maximum, as opposed to 90th percentile α_m, was calculated owing to the relatively limited number of tests for this site. The Lowry subslab vapor concentrations were highly variable and elevated below certain houses (e.g., TCE up to 10,000 µg/m^3), but near background levels below other houses above the plume. An analysis of the house data subset where indoor air TCE concentrations exceeded 5 µg/m^3 and/or subslab TCE concentrations exceeded 1000 µg/m^3 indicated that the 50th percentile and maximum subslab vapor α_m are 7.7×10^{-4} and 1.4×10^{-2}. Available synoptic data for the Lowry site indicated no significant seasonal variation in subslab or indoor air concentrations.

At the Mountain View site, indoor air in seven houses

above the contaminated area and two "background" houses in a noncontaminated area was tested on two occasions. The indoor TCE concentration in one house was 12 and 25 $\mu g/m^3$, whereas the TCE concentrations in remaining houses were at background levels (0.26 to 1.1 $\mu g/m^3$) (Wu 2000). The maximum ground water α_m is 7.8×10^{-5} while the shallow vapor maximum α_m is 2.8×10^{-4}.

When all five sites are evaluated, the results can be summarized as follows. The 50th percentile (or geometric mean) and 90th percentile (or maximum) α_m values for the ground water to indoor air pathway were remarkably similar for all sites (approximately 1×10^{-5} and 1×10^{-4}, respectively). For individual sites, there is significant house-to-house variability in α_m (e.g., two order of magnitude difference for Redfields site); however, based on the available data there appear to be only slight, if any, seasonally induced variations in vapor intrusion, and similar intrusion rates for houses with basement and slab-on-grade construction. Potential sources of variability in α_m include inaccurate estimation of water table ground water concentrations below houses, geological heterogeneity, differences in house construction and depressurization, and differences in ventilation rates and house activities during indoor air testing. At the Lowry and Mountain View sites, no significant vapor intrusion could be measured for most houses. One likely reason for the generally nonsignificant intrusion is that ground water concentrations are lower at these sites, compared to the CDOT, Redfields, and Hamilton sites. Another possible factor for the Mountain View site is the building construction, which consists of at-grade foundation slab with (moisture) vapor barrier. Overall, the results suggest that geologic conditions and diffusion rates have the greatest influence on vapor intrusion rates at the chlorinated solvent sites, and that building factors are less important.

Comparison to Model Predictions for Chlorinated Solvent Sites

Comparisons for sites with the most reliable data (CDOT, Redfields, and Hamilton) indicates that the predictive envelope for the α_p intersects the α_m. The centroid of the predictive envelope is in all cases higher than the 50th percentile α_m suggesting, on average, the J&E model would result in conservative predictions. For the CDOT site, the best estimate α_p is approximately eight times higher than the 50th percentile α_m. For the Lowry site, the predictive envelope is below the α_m for one house with significant vapor intrusion, indicating a nonconservative prediction in this case. For the Mountain View site, the predictive envelope for α_p intersects the maximum α_m. Overall, the J&E model in most cases results in conservative predictions (i.e., α_p is higher than α_m). However, the comparisons highlight the potential for nonconservative predictions if a combination of low Q_{soil} and low D_T^{eff}/L_T are used.

Tracer Method

There are several sites where tracer tests can be used to estimate α, which range from ~2×10^{-4} at the Alameda site to 4.5×10^{-2} at the Spokane River (Valley) sites (Table 4). The Spokane River sites were calculated using an assumed average house volume (500 m^3) and building ventilation rate (air changes per hour (ACH) = 0.5 $hour^{-1}$)) and therefore are approximate. Soils at the Spokane River site are very permeable, and α is based on winter conditions (i.e., highest expected seasonal building depressurization); therefore, the α for this site is considered an upper range value. It should be remembered that tracer studies represent α values for near-field boundary conditions and, therefore, are not representative of intrusion at many sites contaminated with VOCs. The tracer test α values are, however, consistent with the upper range of the J&E model predictions (Figure 6).

Flux Chamber Method

A method that has been used for radon assessments is the equivalent leakage area (ELA) method (Grimsrud et al. 1982; CSGB 1986). The ELA is obtained by developing an empirical relationship between the soil-gas flow into a building and building depressurization. Soil-gas flows are measured using flux chambers and mass flow meters. In one study involving multiple measurements of soil-gas flow through various building foundation cracks at 10 houses in Saskatchewan, Canada, the total house foundation ELA for the foundation edge cracks and utility penetrations ranged from 0.15 to 16.4 cm^2 (Figley and Snodgrass 1992). The contribution to total ELA from untrapped floor drains, present at a few houses, was excluded from this analysis since untrapped drains are uncommon in newer construction. For example, the National Building Code of Canada (1995) requires sealing of floor drainage systems that have the potential to allow soil-gas entry (Section 9.13.8.3).

The measured total ELA can be used to estimate soil-gas intrusion rates using the method in Figley (1997). A building depressurization representative of severe winter conditions (10 Pa), as proposed by Figley (1997), and possible values for the house volume (500 m^3) and building ventilation rate (0.3 ACH) produces α values between 3.6×10^{-4} and 3.8×10^{-2}. The α obtained in this manner is conservative because it assumes an unlimited and uniform soil-vapor source directly below the foundation slab (i.e., contaminants in vapor are replenished as fast as they are swept into the building).

Flux chamber tests have also been used to measure VOC flux rates through concrete cracks (Schmidt and Zdeb 1997; Hers and Zapf-Gilje 1998). Both studies indicated detectable VOCs were measured in soil gas transmitted through cracks, and the study by Hers and Zapf-Gilje (1998) indicated that the scaled-up flux for the entire building was of the same order as flux measured by the indoor VOC method.

Regulatory Implications

The J&E model is widely used for regulatory and guidance purposes in North America. Several agencies have developed generic screening criteria for the vapor intrusion pathway (Massachusetts 1993; Michigan 1998; Connecticut 1998). Semigeneric soil standards have been developed in Canada, based on two soil types (fine- and coarse-grained) and two building types (CCME 2000). Guidance recently developed by the U.S. EPA consists of a multitiered framework to evaluate the soil vapor intrusion pathway (U.S. EPA 2002). A primary (initial) screening step is used to identify sites with significant potential for vapor intrusion (e.g., odors, product in sumps or directly below foundation), and where indoor air monitoring and/or engineering controls is warranted. A secondary screening step involves the use of semigeneric curves for α, based

on soil type and depth, and target breathing concentrations in indoor air to back-calculate acceptable source ground water and soil vapor concentrations. Depending on the results of the secondary screening, there is the option to conduct a site-specific pathway assessment.

Derivation of regulatory criteria requires the prediction of cross-media transfer of contaminants, and vapor transport and intrusion into buildings. For the regulatory agencies cited previously (excluding Massachusetts), cross-media transfer between VOCs in ground water and soil vapor is predicted using the Henry's law constant assuming equilibrium partitioning. Under the Massachusetts guidance, the Henry's law constant is divided by 10 to account for source vapor concentrations that are typically lower than those predicted assuming equilibrium partitioning. The vapor attenuation ratios incorporated into regulatory criteria depend on whether the assumed contamination scenario is a dissolved ground water plume or an unsaturated zone contamination source. For a ground water source, the α incorporates vapor transport through both the capillary transition zone and unsaturated zone. For an unsaturated zone source, the α incorporates transport through just the unsaturated zone. For the agencies cited previously, the ground water source α ranges from 4.6×10^{-6} to 1.5×10^{-3} whereas the vapor source α ranges from 3.9×10^{-7} to 6.2×10^{-3}. An analysis of the previous regulatory criteria indicates that the key factor affecting the α is the Q_{soil} value chosen or estimated for predictive purposes. Of lessor importance is the assumed generic or semigeneric soil type.

When vapor attenuation ratios incorporated in regulatory criteria are compared to measured ratios for field studies presented in this paper, it is apparent that the low end of the regulatory range may not be conservative for some sites. Of greatest concern would be sites with nonbiodegradable chemicals, shallow to moderate depth contamination, and high advection potential (i.e., coarse soil, high building underpressurization).

Conclusions and Recommendations

A comprehensive evaluation of the J&E model characteristics and sensitivity, and comparisons of measured to model-predicted vapor attenuation ratios (α_m and α_p), have been provided for residential houses, ground-floor apartments, and small commercial buildings. Based on this analysis, the following conclusions can be drawn:

1. The J&E model is moderately too highly sensitive to soil-gas advection rate into the building (Q_{soil}), at D_T^{eff}/L_T values above $\sim 1 \times 10^{-3}$. Except when Q_{soil} is low, the J&E model is relatively insensitive to building foundation properties. At best, the range or uncertainty in J&E model predictions is about one order of magnitude when relatively good quality site-specific data is available.
2. Estimation of effective diffusion coefficient is subject to considerable uncertainty. Some of this uncertainty can be reduced through better site characterization, including careful lithological descriptions, testing of moisture content, grain size distribution and water retention, and appropriate consideration of the effect of surface barriers on soil moisture content.
3. Several radon and VOC tracer studies indicate that measured Q_{soil} values at coarse-grained soil sites, for single family residences, ranged from ~ 1 to 10 L/min. Depending on the input values chosen, much lower Q_{soil} values can be predicted using the soil-gas advection model typically used in conjunction with the J&E model.
4. There are only a limited number of high quality and comprehensive field studies that can be used to help validate models for the vapor intrusion pathway.
5. For petroleum hydrocarbon sites, the vapor α_m for the Chatterton site (high ΔP cases) and Midwest site were on the order of 1×10^{-5} to 1×10^{-4} (the Midwest value is uncertain). For the remaining cases and sites, the possible upper bound vapor α_m ranged from $\sim 5 \times 10^{-7}$ to 1×10^{-5}.
6. For chlorinated solvent sites, the ground water α_m were on the order of 1×10^{-6} to 1×10^{-4} for the three sites with the most reliable data sets (CDOT, Redfields, and Hamilton). For one site with a smaller and somewhat less reliable data set (Lowry), the maximum ground water α_m was $\sim 1 \times 10^{-3}$ while the maximum subslab vapor α_m was $\sim 1 \times 10^{-2}$.
7. For the tracer and flux chamber studies, the α_m was on the order of 1×10^{-4} to 1×10^{-2}. In the context of VOC intrusion, these α_m represent conservative upper bounds owing to boundary conditions and tracer properties that are generally different than those at VOC-contaminated sites.
8. For almost all case studies, the best estimate J&E model-predicted α_p were one to two orders of magnitude less than the 50th percentile or median α_m, indicating that when best estimate and average conditions are evaluated, the J&E model predictions are conservative. There were a few cases studies where the best estimate α_p was less than the 90th percentile or maximum α_m, indicating the J&E model predictions are nonconservative for a small subset of houses or apartments. The comparisons also highlight the potential for non-conservative model predictions if a combination of low Q_{soil} and low D_T^{eff}/L_T are used.

The observed variability in α_m between different field sites, and individual houses at some sites, highlights the complexity of processes affecting vapor intrusion. Numerous factors potentially affect the vapor intrusion pathway including biodegradation, chemical transformation, sorption, contaminant source depletion, geologic heterogeneity, soil properties (moisture content, permeability, organic carbon content), building properties, meteorological conditions, and building ventilation rates. In light of this complexity, it is important to recognize the vapor intrusion modeling paradigm typically followed is a compartmental model for steady-state one-dimensional diffusion through soil, and diffusion and advection through a building foundation having an idealized edge or perimeter crack (J&E model). Often, a homogeneous soil is assumed, although it is relatively easy to model diffusion for multiple soil layers assuming site information is available (Johnson et al. 1998). Simulation of vapor transport through the building foundation and mixing of VOCs within the building airspace is highly simplified. Although not used for this study, it is noted that the J&E model has been modified to include first-order biodegradation for a dominant soil layer (Johnson et al. 1998) and oxygen-limited first-order biodegradation (Johnson et al. 2001).

Notwithstanding the above, the question remains: Can the

J&E model (or other similar screening models) be reliably used for the vapor intrusion pathway? Our answer is a qualified yes, provided that appropriate input values are used and the model sensitivity, uncertainty, and limitations are recognized. The answer may also depend on what the model is used for. For example, the use of the J&E model to set generic criteria is problematic owing to model sensitivity and uncertainty, and the wide range in possible site conditions. In our opinion, a semigeneric approach that incorporates site-specific information on critical factors affecting vapor intrusion (e.g., Q_{soil} and soil properties) improves on a single criteria approach. The technically preferred approach is to use the J&E model on a fully site-specific basis, and to calibrate model predictions using soil vapor profiles, and when possible, indoor air data. In all cases, an appropriate framework for model use and understanding of model characteristics is essential when using models for regulatory purposes.

Several data gaps and sources of uncertainty remain. Additional field-based studies should be conducted to evaluate the vapor intrusion pathway for different site conditions, and to more fully assess specific factors affecting vapor intrusion. Data that would contribute to a more in-depth pathway analysis include soil properties such as moisture content and porosity, soil vapor concentration profiles below buildings, building properties such as depressurization, and meteorological data. Further evaluation of biodegradation kinetics for hydrocarbon vapors, effect of surface barriers (e.g., buildings) on biodegradation, and chlorinated solvent transformation processes are also needed.

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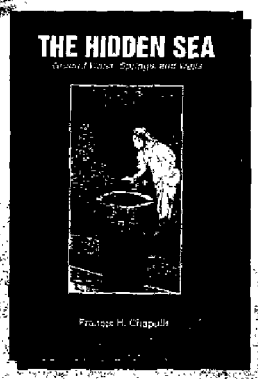

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APPENDIX 4

EXAMPLE PRINTOUTS OF VAPOR INTRUSION MODELS

1. Groundwater to indoor air, residential exposure scenario.
2. Groundwater to indoor air, commercial/industrial exposure scenario.
3. Soil to indoor air, residential exposure scenario.
4. Soil to indoor air, commercial/industrial exposure scenario.
5. Soil Gas to indoor air, residential exposure scenario.
6. Soil Gas to indoor air, commercial/industrial exposure scenario.

Hawai'i DOH
Fall 2011

GW-ADV
Version 3.0; 02/03

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES: X

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION (enter "X" in "YES" box and initial groundwater conc. below)

YES:

Groundwater Vapor Emissions To Indoor Air
Residential Exposure Scenario
High Permeability Soil Scenario

FOR EXAMPLE ONLY

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (µg/L)	Chemical
127184		Tetrachloroethylene

MORE ↓

ENTER Average soil/ groundwater temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to water table, L_{WT} (cm)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum directly above water table, (Enter A, B, or C)	ENTER SCS soil type directly above water table	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of L_{WT} (cell G28)							
15	15	300	100	200		B	CL	S		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
S	1.50	0.430	0.15	CL	1.5	0.43	0.3				

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
15	40	961	961	244	0.1	1	5

MORE ↓

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	30	30	350	1.0E-06	0.2
				Used to calculate risk-based groundwater concentration.	

END

DATA ENTRY SHEET

Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Henry's law constant at reference temperature, H ($atm\text{-}m^3/mol$)	Henry's law constant reference temperature, T_R (^oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Pure component water solubility, S (mg/L)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
5.00E-02	9.50E-06	1.76E-02	25	8,288	394.40	620.20	9.49E+01	2.06E+02	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

Exposure duration, τ (sec)	Source-building separation, L_T (cm)	Stratum A soil air-filled porosity, θ_a^A (cm^3/cm^3)	Stratum B soil air-filled porosity, θ_a^B (cm^3/cm^3)	Stratum C soil air-filled porosity, θ_a^C (cm^3/cm^3)	Stratum A effective total fluid saturation, S_{te} (cm^3/cm^3)	Stratum A soil intrinsic permeability, k_i (cm^2)	Stratum A soil relative air permeability, k_{rg} (cm^2)	Stratum A soil effective vapor permeability, k_v (cm^2)	Thickness of capillary zone, L_{cz} (cm)	Total porosity in capillary zone, n_{cz} (cm^3/cm^3)	Air-filled porosity in capillary zone, $\theta_{a,cz}$ (cm^3/cm^3)	Water-filled porosity in capillary zone, $\theta_{w,cz}$ (cm^3/cm^3)	Floor-wall seam perimeter, X_{crack} (cm)
9.46E+08	285	0.280	0.130	ERROR	0.257	1.00E-07	0.703	7.04E-08	46.88	0.43	0.055	0.375	3,844

Bldg. ventilation rate, $Q_{building}$ (cm^3/s)	Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. groundwater temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. groundwater temperature, H_{TS} (atm-m^3/mol)	Henry's law constant at ave. groundwater temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Stratum A effective diffusion coefficient, D^{eff}_A (cm^2/s)	Stratum B effective diffusion coefficient, D^{eff}_B (cm^2/s)	Stratum C effective diffusion coefficient, D^{eff}_C (cm^2/s)	Capillary zone effective diffusion coefficient, D^{eff}_{cz} (cm^2/s)	Total overall effective diffusion coefficient, D^{eff}_T (cm^2/s)	Diffusion path length, L_d (cm)
6.26E+04	9.24E+05	4.16E-04	15	9,502	1.01E-02	4.26E-01	1.77E-04	3.90E-03	3.05E-04	0.00E+00	2.18E-05	1.06E-04	285

Convection path length, L_p (cm)	Source vapor conc., C_{source} ($\mu g/m^3$)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ ($\mu g/m^3$)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
15	4.26E+02	0.10	8.33E+01	3.90E-03	3.84E+02	#NUM!	5.49E-06	2.34E-03	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

RISK-BASED GROUNDWATER CONCENTRATION CALCULATIONS:

Indoor exposure groundwater conc., carcinogen (µg/L)	Indoor exposure groundwater conc., noncarcinogen (µg/L)	Risk-based indoor exposure groundwater conc., (µg/L)	Pure component water solubility, S (µg/L)	Final indoor exposure groundwater conc., (µg/L)
1.77E+02	2.41E+04	1.77E+02	2.06E+05	1.77E+02

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
NA	NA

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

MESSAGE: The values of Csource and Cbuilding on the INTERCALCS worksheet are based on unity and do not represent actual values.

SCROLL DOWN TO "END"

END

DATA ENTRY SHEET

Soil Properties Lookup Table

SCS Soil Type	K_s (cm/h)	α_1 (1/cm)	N (unitless)	M (unitless)	n (cm^3/cm^3)	θ_r (cm^3/cm^3)	Mean Grain Diameter (cm)	Bulk Density (g/cm^3)	θ_w (cm^3/cm^3)	SCS Soil Name
C	0.61	0.01496	1.253	0.2019	0.459	0.098	0.0092	1.43	0.215	Clay
CL	0.34	0.01581	1.416	0.2938	0.442	0.079	0.016	1.48	0.168	Clay Loam
L	0.50	0.01112	1.472	0.3207	0.399	0.061	0.020	1.59	0.148	Loam
LS	4.38	0.03475	1.746	0.4273	0.390	0.049	0.040	1.62	0.076	Loamy Sand
S	26.78	0.03524	3.177	0.6852	0.375	0.053	0.044	1.66	0.054	Sand
SC	0.47	0.03342	1.208	0.1722	0.385	0.117	0.025	1.63	0.197	Sandy Clay
SCL	0.55	0.02109	1.330	0.2481	0.384	0.063	0.029	1.63	0.146	Sandy Clay Loam
SI	1.82	0.00658	1.679	0.4044	0.489	0.050	0.0046	1.35	0.167	Silt
SIC	0.40	0.01622	1.321	0.2430	0.481	0.111	0.0039	1.38	0.216	Silty Clay
SICL	0.46	0.00839	1.521	0.3425	0.482	0.090	0.0056	1.37	0.198	Silty Clay Loam
SIL	0.76	0.00506	1.663	0.3987	0.439	0.065	0.011	1.49	0.180	Silt Loam
SL	1.60	0.02667	1.449	0.3099	0.387	0.039	0.030	1.62	0.103	Sandy Loam

For example only. Constants reflect values presented in Appendix 1, Table H of the HEER Office EHE guidance and may have been modified in later editions of the guidance

Chemical Properties Lookup Table

CAS No.	Chemical	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Pure component water solubility, S (mg/L)	Henry's law constant H' (unitless)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	URF extrapolated (X)	RfC extrapolated (X)
127184	Tetrachloroethylene	9.49E+01	5.00E-02	9.50E-06	2.06E+02	7.20E-01	1.76E-02	25	394.40	620.20	8,288	5.9E-06	2.7E-01	L	

Hawai'i DOH
Fall 2011

GW-ADV
Version 3.0; 02/03

Reset to Defaults

CALCULATE RISK-BASED GROUNDWATER CONCENTRATION (enter "X" in "YES" box)

YES: X

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL GROUNDWATER CONCENTRATION (enter "X" in "YES" box and initial groundwater conc. below)

YES:

Groundwater Vapor Emissions To Indoor Air
Commercial/Industrial Exposure Scenario
High Permeability Soil Scenario

FOR EXAMPLE ONLY

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial groundwater conc., C_W (µg/L)	Chemical
127184		Tetrachloroethylene

MORE ↓

ENTER Average soil/ groundwater temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to water table, L_{WT} (cm)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum directly above water table, (Enter A, B, or C)	ENTER SCS soil type directly above water table	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of L_{WT} (cell G28)							
15	15	300	100	200		B	CL	S		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
S	1.50	0.430	0.15	CL	1.5	0.43	0.3				

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
15	40	961	961	244	0.1	2	5

MORE ↓

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	25	25	250	1.0E-06	0.2
				Used to calculate risk-based groundwater concentration.	

END

DATA ENTRY SHEET

Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Henry's law constant at reference temperature, H ($atm\text{-}m^3/mol$)	Henry's law constant reference temperature, T_R (^oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Pure component water solubility, S (mg/L)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
5.00E-02	9.50E-06	1.76E-02	25	8,288	394.40	620.20	9.49E+01	2.06E+02	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

Exposure duration, τ (sec)	Source-building separation, L_T (cm)	Stratum A soil air-filled porosity, θ_a^A (cm^3/cm^3)	Stratum B soil air-filled porosity, θ_a^B (cm^3/cm^3)	Stratum C soil air-filled porosity, θ_a^C (cm^3/cm^3)	Stratum A effective total fluid saturation, S_{te} (cm^3/cm^3)	Stratum A soil intrinsic permeability, k_i (cm^2)	Stratum A soil relative air permeability, k_{rg} (cm^2)	Stratum A soil effective vapor permeability, k_v (cm^2)	Thickness of capillary zone, L_{cz} (cm)	Total porosity in capillary zone, n_{cz} (cm^3/cm^3)	Air-filled porosity in capillary zone, $\theta_{a,cz}$ (cm^3/cm^3)	Water-filled porosity in capillary zone, $\theta_{w,cz}$ (cm^3/cm^3)	Floor-wall seam perimeter, X_{crack} (cm)
7.88E+08	285	0.280	0.130	ERROR	0.257	1.00E-07	0.703	7.04E-08	46.88	0.43	0.055	0.375	3,844

Bldg. ventilation rate, $Q_{building}$ (cm^3/s)	Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. groundwater temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. groundwater temperature, H_{TS} (atm-m^3/mol)	Henry's law constant at ave. groundwater temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Stratum A effective diffusion coefficient, D^{eff}_A (cm^2/s)	Stratum B effective diffusion coefficient, D^{eff}_B (cm^2/s)	Stratum C effective diffusion coefficient, D^{eff}_C (cm^2/s)	Capillary zone effective diffusion coefficient, D^{eff}_{cz} (cm^2/s)	Total overall effective diffusion coefficient, D^{eff}_T (cm^2/s)	Diffusion path length, L_d (cm)
1.25E+05	9.24E+05	4.16E-04	15	9,502	1.01E-02	4.26E-01	1.77E-04	3.90E-03	3.05E-04	0.00E+00	2.18E-05	1.06E-04	285

Convection path length, L_p (cm)	Source vapor conc., C_{source} ($\mu g/m^3$)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ ($\mu g/m^3$)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
15	4.26E+02	0.10	8.33E+01	3.90E-03	3.84E+02	#NUM!	2.74E-06	1.17E-03	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

RISK-BASED GROUNDWATER CONCENTRATION CALCULATIONS:

Indoor exposure groundwater conc., carcinogen (µg/L)	Indoor exposure groundwater conc., noncarcinogen (µg/L)	Risk-based indoor exposure groundwater conc., (µg/L)	Pure component water solubility, S (µg/L)	Final indoor exposure groundwater conc., (µg/L)
5.93E+02	6.75E+04	5.93E+02	2.06E+05	5.93E+02

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
NA	NA

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

MESSAGE: The values of Csource and Cbuilding on the INTERCALCS worksheet are based on unity and do not represent actual values.

SCROLL DOWN TO "END"

END

DATA ENTRY SHEET

Soil Properties Lookup Table

SCS Soil Type	K_s (cm/h)	α_1 (1/cm)	N (unitless)	M (unitless)	n (cm^3/cm^3)	θ_r (cm^3/cm^3)	Mean Grain Diameter (cm)	Bulk Density (g/cm^3)	θ_w (cm^3/cm^3)	SCS Soil Name
C	0.61	0.01496	1.253	0.2019	0.459	0.098	0.0092	1.43	0.215	Clay
CL	0.34	0.01581	1.416	0.2938	0.442	0.079	0.016	1.48	0.168	Clay Loam
L	0.50	0.01112	1.472	0.3207	0.399	0.061	0.020	1.59	0.148	Loam
LS	4.38	0.03475	1.746	0.4273	0.390	0.049	0.040	1.62	0.076	Loamy Sand
S	26.78	0.03524	3.177	0.6852	0.375	0.053	0.044	1.66	0.054	Sand
SC	0.47	0.03342	1.208	0.1722	0.385	0.117	0.025	1.63	0.197	Sandy Clay
SCL	0.55	0.02109	1.330	0.2481	0.384	0.063	0.029	1.63	0.146	Sandy Clay Loam
SI	1.82	0.00658	1.679	0.4044	0.489	0.050	0.0046	1.35	0.167	Silt
SIC	0.40	0.01622	1.321	0.2430	0.481	0.111	0.0039	1.38	0.216	Silty Clay
SICL	0.46	0.00839	1.521	0.3425	0.482	0.090	0.0056	1.37	0.198	Silty Clay Loam
SIL	0.76	0.00506	1.663	0.3987	0.439	0.065	0.011	1.49	0.180	Silt Loam
SL	1.60	0.02667	1.449	0.3099	0.387	0.039	0.030	1.62	0.103	Sandy Loam

For example only. Constants reflect values presented in Appendix 1, Table H of the HEER Office EHE guidance and may have been modified in later editions of the guidance

Chemical Properties Lookup Table

CAS No.	Chemical	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Pure component water solubility, S (mg/L)	Henry's law constant H' (unitless)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Unit risk factor, URF ($\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	URF extrapolated (X)	RfC extrapolated (X)
127184	Tetrachloroethylene	9.49E+01	5.00E-02	9.50E-06	2.06E+02	7.20E-01	1.76E-02	25	394.40	620.20	8,288	5.9E-06	2.7E-01	L	

Hawai'i DOH
Fall 2011

SL-ADV
Version 3.0; 02/03

Reset to Defaults

CALCULATE RISK-BASED SOIL CONCENTRATION (enter "X" in "YES" box)

YES: X

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL SOIL CONCENTRATION (enter "X" in "YES" box and initial soil conc. below)

YES:

Soil Vapor Emissions To Indoor Air
Residential Exposure Scenario

FOR EXAMPLE ONLY

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial soil conc., C_R (µg/kg)	Chemical
127184		Tetrachloroethylene

MORE ↓

ENTER Average soil temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to top of contamination, L_t (cm)	ENTER Depth below grade to bottom of contamination, (enter value of 0 if value is unknown) L_b (cm)	ENTER Totals must add up to value of L_t (cell G28) Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
20	15	15	215	15			S		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum A soil organic carbon fraction, f_{oc}^A (unitless)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum B soil organic carbon fraction, f_{oc}^B (unitless)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)	ENTER Stratum C soil organic carbon fraction, f_{oc}^C (unitless)
S	1.5	0.43	0.15	0.006										

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP (g/cm-s^2)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
15	40	961	961	244	0.1	1	5

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	30	30	350	1.0E-06	0.2
				Used to calculate risk-based soil concentration.	

END

DATA ENTRY SHEET

Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Pure component water solubility, S (mg/L)	Unit risk factor, URF ($\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	Physical state at soil temperature, (S,L,G)
5.00E-02	9.50E-06	1.76E-02	25	8,288	394.40	620.20	9.49E+01	2.06E+02	5.9E-06	2.7E-01	L

END

DATA ENTRY SHEET

Exposure duration, τ (sec)	Source-building separation, L_T (cm)	Stratum A soil air-filled porosity, θ_a^A (cm^3/cm^3)	Stratum B soil air-filled porosity, θ_a^B (cm^3/cm^3)	Stratum C soil air-filled porosity, θ_a^C (cm^3/cm^3)	Stratum A effective total fluid saturation, S_{te} (cm^3/cm^3)	Stratum A soil intrinsic permeability, k_i (cm^2)	Stratum A soil relative air permeability, k_{rg} (cm^2)	Stratum A soil effective vapor permeability, k_v (cm^2)	Floor-wall seam perimeter, X_{crack} (cm)	Initial soil concentration used, C_R (µg/kg)	Bldg. ventilation rate, $Q_{building}$ (cm^3/s)
9.46E+08	1	0.280	ERROR	ERROR	0.257	1.01E-07	0.703	7.10E-08	3,844	1.00E+00	6.26E+04

Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. soil temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. soil temperature, H_{TS} (atm-m^3/mol)	Henry's law constant at ave. soil temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Stratum A effective diffusion coefficient, D^{eff}_A (cm^2/s)	Stratum B effective diffusion coefficient, D^{eff}_B (cm^2/s)	Stratum C effective diffusion coefficient, D^{eff}_C (cm^2/s)	Total overall effective diffusion coefficient, D^{eff}_T (cm^2/s)	Diffusion path length, L_d (cm)	Convection path length, L_p (cm)
9.24E+05	4.16E-04	15	9,451	1.34E-02	5.56E-01	1.78E-04	3.90E-03	0.00E+00	0.00E+00	3.90E-03	1	15

Soil-water partition coefficient, K_d (cm^3/g)	Source vapor conc., C_{source} (µg/m^3)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $\exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ (µg/m^3)	Finite source β term (unitless)	Finite source ψ term $(sec)^{-1}$	Time for source depletion, τ_D (sec)	Exposure duration > time for source depletion (YES/NO)
5.69E-01	7.19E+02	0.10	8.33E+01	3.90E-03	3.84E+02	#NUM!	NA	NA	4.42E+01	1.87E-03	1.54E+07	YES

Finite source indoor attenuation coefficient, <α> (unitless)	Mass limit bldg. conc., $C_{building}$ (µg/m^3)	Finite source bldg. conc., $C_{building}$ (µg/m^3)	Final finite source bldg. conc., $C_{building}$ (µg/m^3)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
NA	4.68E-03	NA	4.68E-03	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

RISK-BASED SOIL CONCENTRATION CALCULATIONS:

Indoor exposure soil conc., carcinogen (µg/kg)	Indoor exposure soil conc., noncarcinogen (µg/kg)	Risk-based indoor exposure soil conc., (µg/kg)	Soil saturation conc., C_{sat} (µg/kg)	Final indoor exposure soil conc., (µg/kg)
8.82E+01	1.20E+04	8.82E+01	1.59E+05	8.82E+01

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
NA	NA

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

MESSAGE: The values of Csource and Cbuilding on the INTERCALCS worksheet are based on unity and do not represent actual values.

SCROLL DOWN TO "END"

END

DATA ENTRY SHEET

Soil Properties Lookup Table

SCS Soil Type	K_s (cm/h)	α_1 (1/cm)	N (unitless)	M (unitless)	n (cm^3/cm^3)	θ_r (cm^3/cm^3)	Mean Grain Diameter (cm)	Bulk Density (g/cm^3)	θ_w (cm^3/cm^3)	SCS Soil Name
C	0.61	0.01496	1.253	0.2019	0.459	0.098	0.0092	1.43	0.215	Clay
CL	0.34	0.01581	1.416	0.2938	0.442	0.079	0.016	1.48	0.168	Clay Loam
L	0.50	0.01112	1.472	0.3207	0.399	0.061	0.020	1.59	0.148	Loam
LS	4.38	0.03475	1.746	0.4273	0.390	0.049	0.040	1.62	0.076	Loamy Sand
S	26.78	0.03524	3.177	0.6852	0.375	0.053	0.044	1.66	0.054	Sand
SC	0.47	0.03342	1.208	0.1722	0.385	0.117	0.025	1.63	0.197	Sandy Clay
SCL	0.55	0.02109	1.330	0.2481	0.384	0.063	0.029	1.63	0.146	Sandy Clay Loam
SI	1.82	0.00658	1.679	0.4044	0.489	0.050	0.0046	1.35	0.167	Silt
SIC	0.40	0.01622	1.321	0.2430	0.481	0.111	0.0039	1.38	0.216	Silty Clay
SICL	0.46	0.00839	1.521	0.3425	0.482	0.090	0.0056	1.37	0.198	Silty Clay Loam
SIL	0.76	0.00506	1.663	0.3987	0.439	0.065	0.011	1.49	0.180	Silt Loam
SL	1.60	0.02667	1.449	0.3099	0.387	0.039	0.030	1.62	0.103	Sandy Loam

For example only. Constants reflect values presented in Appendix 1, Table H of the HEER Office EHE guidance and may have been modified in later editions of the guidance

Chemical Properties Lookup Table

CAS No.	Chemical	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Pure component water solubility, S (mg/L)	Henry's law constant H' (unitless)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	Physical state at soil temperature, (S,L,G)	URF extrapolated (X)	RfC extrapolated (X)
127184	Tetrachloroethylene	9.49E+01	5.00E-02	9.50E-06	2.06E+02	7.20E-01	1.76E-02	25	394.40	620.20	8,288	5.9E-06	2.7E-01	L		

Hawai'i DOH
Fall 2011

SL-ADV
Version 3.0; 02/03

Reset to Defaults

CALCULATE RISK-BASED SOIL CONCENTRATION (enter "X" in "YES" box)

YES: X

OR

CALCULATE INCREMENTAL RISKS FROM ACTUAL SOIL CONCENTRATION (enter "X" in "YES" box and initial soil conc. below)

YES:

Soil Vapor Emissions To Indoor Air
Commercial/Industrial Exposure Scenario

FOR EXAMPLE ONLY

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Initial soil conc., C_R (µg/kg)	Chemical
127184		Tetrachloroethylene

MORE ↓

ENTER Average soil temperature, T_S (°C)	ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Depth below grade to top of contamination, L_t (cm)	ENTER Depth below grade to bottom of contamination, (enter value of 0 if value is unknown) L_b (cm)	ENTER Totals must add up to value of L_t (cell G28) Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
20	15	15	215	15			S		

MORE ↓

ENTER Stratum A SCS soil type (Lookup Soil Parameters)	ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum A soil organic carbon fraction, f_{oc}^A (unitless)	ENTER Stratum B SCS soil type (Lookup Soil Parameters)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum B soil organic carbon fraction, f_{oc}^B (unitless)	ENTER Stratum C SCS soil type (Lookup Soil Parameters)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)	ENTER Stratum C soil organic carbon fraction, f_{oc}^C (unitless)
S	1.5	0.43	0.15	0.006										

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP (g/cm-s^2)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)	ENTER Average vapor flow rate into bldg. OR Leave blank to calculate Q_{soil} (L/m)
15	40	961	961	244	0.1	2	5

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)	ENTER Target risk for carcinogens, TR (unitless)	ENTER Target hazard quotient for noncarcinogens, THQ (unitless)
70	25	25	250	1.0E-06	0.2
				Used to calculate risk-based soil concentration.	

END

DATA ENTRY SHEET

Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Pure component water solubility, S (mg/L)	Unit risk factor, URF ($\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	Physical state at soil temperature, (S,L,G)
5.00E-02	9.50E-06	1.76E-02	25	8,288	394.40	620.20	9.49E+01	2.06E+02	5.9E-06	2.7E-01	L

END

DATA ENTRY SHEET

Exposure duration, τ (sec)	Source-building separation, L_T (cm)	Stratum A soil air-filled porosity, θ_a^A (cm^3/cm^3)	Stratum B soil air-filled porosity, θ_a^B (cm^3/cm^3)	Stratum C soil air-filled porosity, θ_a^C (cm^3/cm^3)	Stratum A effective total fluid saturation, S_{te} (cm^3/cm^3)	Stratum A soil intrinsic permeability, k_i (cm^2)	Stratum A soil relative air permeability, k_{rg} (cm^2)	Stratum A soil effective vapor permeability, k_v (cm^2)	Floor-wall seam perimeter, X_{crack} (cm)	Initial soil concentration used, C_R (µg/kg)	Bldg. ventilation rate, $Q_{building}$ (cm^3/s)
7.88E+08	1	0.280	ERROR	ERROR	0.257	1.01E-07	0.703	7.10E-08	3,844	1.00E+00	1.25E+05

Area of enclosed space below grade, A_B (cm^2)	Crack-to-total area ratio, η (unitless)	Crack depth below grade, Z_{crack} (cm)	Enthalpy of vaporization at ave. soil temperature, $\Delta H_{v,TS}$ (cal/mol)	Henry's law constant at ave. soil temperature, H_{TS} (atm-m^3/mol)	Henry's law constant at ave. soil temperature, H'_{TS} (unitless)	Vapor viscosity at ave. soil temperature, μ_{TS} (g/cm-s)	Stratum A effective diffusion coefficient, D^{eff}_A (cm^2/s)	Stratum B effective diffusion coefficient, D^{eff}_B (cm^2/s)	Stratum C effective diffusion coefficient, D^{eff}_C (cm^2/s)	Total overall effective diffusion coefficient, D^{eff}_T (cm^2/s)	Diffusion path length, L_d (cm)	Convection path length, L_p (cm)
9.24E+05	4.16E-04	15	9,451	1.34E-02	5.56E-01	1.78E-04	3.90E-03	0.00E+00	0.00E+00	3.90E-03	1	15

Soil-water partition coefficient, K_d (cm^3/g)	Source vapor conc., C_{source} (µg/m^3)	Crack radius, r_{crack} (cm)	Average vapor flow rate into bldg., Q_{soil} (cm^3/s)	Crack effective diffusion coefficient, D^{crack} (cm^2/s)	Area of crack, A_{crack} (cm^2)	Exponent of equivalent foundation Peclet number, $\exp(Pe^f)$ (unitless)	Infinite source indoor attenuation coefficient, α (unitless)	Infinite source bldg. conc., $C_{building}$ (µg/m^3)	Finite source β term (unitless)	Finite source ψ term $(sec)^{-1}$	Time for source depletion, τ_D (sec)	Exposure duration > time for source depletion (YES/NO)
5.69E-01	7.19E+02	0.10	8.33E+01	3.90E-03	3.84E+02	#NUM!	NA	NA	4.42E+01	1.87E-03	1.54E+07	YES

Finite source indoor attenuation coefficient, <α> (unitless)	Mass limit bldg. conc., $C_{building}$ (µg/m^3)	Finite source bldg. conc., $C_{building}$ (µg/m^3)	Final finite source bldg. conc., $C_{building}$ (µg/m^3)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)
NA	2.81E-03	NA	2.81E-03	5.9E-06	2.7E-01

END

DATA ENTRY SHEET

RISK-BASED SOIL CONCENTRATION CALCULATIONS:

Indoor exposure soil conc., carcinogen (µg/kg)	Indoor exposure soil conc., noncarcinogen (µg/kg)	Risk-based indoor exposure soil conc., (µg/kg)	Soil saturation conc., C_{sat} (µg/kg)	Final indoor exposure soil conc., (µg/kg)
2.47E+02	2.81E+04	2.47E+02	1.59E+05	2.47E+02

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
NA	NA

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

MESSAGE: The values of Csource and Cbuilding on the INTERCALCS worksheet are based on unity and do not represent actual values.

SCROLL DOWN TO "END"

END

DATA ENTRY SHEET

Soil Properties Lookup Table

SCS Soil Type	K_s (cm/h)	α_1 (1/cm)	N (unitless)	M (unitless)	n (cm^3/cm^3)	θ_r (cm^3/cm^3)	Mean Grain Diameter (cm)	Bulk Density (g/cm^3)	θ_w (cm^3/cm^3)	SCS Soil Name
C	0.61	0.01496	1.253	0.2019	0.459	0.098	0.0092	1.43	0.215	Clay
CL	0.34	0.01581	1.416	0.2938	0.442	0.079	0.016	1.48	0.168	Clay Loam
L	0.50	0.01112	1.472	0.3207	0.399	0.061	0.020	1.59	0.148	Loam
LS	4.38	0.03475	1.746	0.4273	0.390	0.049	0.040	1.62	0.076	Loamy Sand
S	26.78	0.03524	3.177	0.6852	0.375	0.053	0.044	1.66	0.054	Sand
SC	0.47	0.03342	1.208	0.1722	0.385	0.117	0.025	1.63	0.197	Sandy Clay
SCL	0.55	0.02109	1.330	0.2481	0.384	0.063	0.029	1.63	0.146	Sandy Clay Loam
SI	1.82	0.00658	1.679	0.4044	0.489	0.050	0.0046	1.35	0.167	Silt
SIC	0.40	0.01622	1.321	0.2430	0.481	0.111	0.0039	1.38	0.216	Silty Clay
SICL	0.46	0.00839	1.521	0.3425	0.482	0.090	0.0056	1.37	0.198	Silty Clay Loam
SIL	0.76	0.00506	1.663	0.3987	0.439	0.065	0.011	1.49	0.180	Silt Loam
SL	1.60	0.02667	1.449	0.3099	0.387	0.039	0.030	1.62	0.103	Sandy Loam

For example only. Constants reflect values presented in Appendix 1, Table H of the HEER Office EHE guidance and may have been modified in later editions of the guidance

Chemical Properties Lookup Table

CAS No.	Chemical	Organic carbon partition coefficient, K_{oc} (cm^3/g)	Diffusivity in air, D_a (cm^2/s)	Diffusivity in water, D_w (cm^2/s)	Pure component water solubility, S (mg/L)	Henry's law constant H' (unitless)	Henry's law constant at reference temperature, H (atm-m^3/mol)	Henry's law constant reference temperature, T_R (^oC)	Normal boiling point, T_B (^oK)	Critical temperature, T_C (^oK)	Enthalpy of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal/mol)	Unit risk factor, URF $(\mu g/m^3)^{-1}$	Reference conc., RfC (mg/m^3)	Physical state at soil temperature, (S,L,G)	URF extrapolated (X)	RfC extrapolated (X)
127184	Tetrachloroethylene	9.49E+01	5.00E-02	9.50E-06	2.06E+02	7.20E-01	1.76E-02	25	394.40	620.20	8,288	5.9E-06	2.7E-01	L		

Hawai'i DOH
Fall 2011

SG-ADV
Version 1.0; 03/01

SOIL VOC EMISSIONS TO INDOOR AIR
RESIDENTIAL EXPOSURE SCENARIO
HIGH-PERMEABILITY (SANDY) SOILS
SOIL GAS:INDOOR AIR ATTENUATION FACTOR = 0.001

Soil Gas Concentration Data

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Soil gas conc., C_g ($\mu g/m^3$)	OR	ENTER Soil gas conc., C_g (ppmv)	Chemical
127184	3.88E+02			Tetrachloroethylene

Enter soil gas concentration in only one set of units.

MORE ↓

ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Soil gas sampling depth below grade, L_s (cm)	ENTER Average soil temperature, T_S (°C)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of Ls (cell C24)					
15	15	10	15			S		

MORE ↓

ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER Stratum C soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
1.5	0.43	0.15						

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)
15	40	961	961	244	0.1	1

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)
70	30	30	350

END

Diffusivity in air, Da (cm2/s)	Diffusivity in water, Dw (cm2/s)	Henry's law constant at reference temperature, H (atm-m3/mol)	Henry's law constant reference temperature, TR (oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H\varpi,\beta$ (cal/mol)	Normal boiling point, TB (oK)	Critical temperature, TC (oK)	Molecular weight, MW (g/mol)	Unit risk factor, URF (mg/m3)-1	Reference conc., RfC (mg/m3)
7.20E-02	8.20E-06	1.84E-02	25	8,288	394.40	620.20	165.83	5.9E-06	6.0E-01

END

Exposure duration, t (sec)	Source-**building** separation, LT (cm)	Stratum A **air-filled** porosity, qaA (cm3/cm3)	Stratum B soil air-filled porosity, qaB (cm3/cm3)	Stratum C air-filled porosity, qaC (cm3/cm3)	Stratum A effective total fluid saturation, Ste (cm3/cm3)	Stratum A soil intrinsic permeability, ki (cm2)	Stratum A soil relative air permeability, krg (cm2)	Stratum A soil effective vapor permeability, kv (cm2)	Floor-wall seam perimeter, Xcrack (cm)	Soil gas conc. (mg/m3)	Bldg. ventilation rate, Qbuilding (cm3/s)
9.46E+08	1	0.28	ERROR	ERROR	0.25729443	9.92425E-08	0.703228129	6.97901E-08	3844	388.1	62594.20111

Area of enclosed space **below** grade, AB (cm2)	Crack-**to-total** area ratio, h (unitless)	Crack **depth** below grade, Zcrack (cm)	Enthalpy of **vaporization at** ave. soil temperature, DHv,TS (cal/mol)	Henry's law **constant at** ave. soil temperature, HTS (atm-m3/mol)	Henry's law **constant at** ave. soil temperature, H'TS (unitless)	Vapor **viscosity at** ave. soil temperature, mTS (g/cm-s)	Stratum A **effective** diffusion coefficient, DeffA (cm2/s)	Stratum B effective diffusion coefficient, DeffB (cm2/s)	Stratum C **effective** diffusion coefficient, DeffC (cm2/s)	Total overall effective diffusion coefficient, DeffT (cm2/s)	Diffusion path length, Ld (cm)
923521	0.000416233	15	9552.934617	7.83E-03	0.337067044	0.000175414	5.62E-03	0	0	0.005616299	1

Convection path length, **Lp** (cm)	Source vapor **conc.,** Csource (mg/m3)	Crack **radius,** rcrack (cm)	Average vapor flow rate **into bldg.,** Qsoil (cm3/s)	Crack effective diffusion **coefficient,** Dcrack (cm2/s)	Area of **crack,** Acrack (cm2)	Exponent of equivalent foundation Peclet **number,** exp(Pef) (unitless)	Infinite source indoor attenuation **coefficient,** a (unitless)	Infinite source bldg. **conc.,** Cbuilding (ug/m3)	Unit risk **factor,** URF (mg/m3)-1	Reference **conc.,** RfC (mg/m3)
15	388.1	0.1	67.38925148	0.005616299	384.4	2.211E+203	0.001062797	0.412471487	0.0000059	0.6

END

Qsoil (L/min)
4.0

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
1.0E-06	6.6E-04

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

SCROLL DOWN TO "END"

END

SG-ADV
Version 1.0; 03/01

SOIL VOC EMISSIONS TO INDOOR AIR
COMMERCIAL/INDUSTRIAL EXPOSURE SCENARIO
HIGH-PERMEABILITY (SANDY) SOILS
SOIL GAS:INDOOR AIR ATTENUATION FACTOR = 0.0005

Soil Gas Concentration Data

ENTER Chemical CAS No. (numbers only, no dashes)	ENTER Soil gas conc., C_g ($\mu g/m^3$)	OR	ENTER Soil gas conc., C_g (ppmv)	Chemical
127184	1.30E+03			Tetrachloroethylene

Enter soil gas concentration in only one set of units.

MORE ↓

ENTER Depth below grade to bottom of enclosed space floor, L_F (cm)	ENTER Soil gas sampling depth below grade, L_s (cm)	ENTER Average soil temperature, T_S (°C)	ENTER Thickness of soil stratum A, h_A (cm)	ENTER Thickness of soil stratum B, (Enter value or 0) h_B (cm)	ENTER Thickness of soil stratum C, (Enter value or 0) h_C (cm)	ENTER Soil stratum A SCS soil type (used to estimate soil vapor permeability)	OR	ENTER User-defined stratum A soil vapor permeability, k_v (cm^2)
			Totals must add up to value of Ls (cell C24)					
15	15	10	15			S		

MORE ↓

ENTER Stratum A soil dry bulk density, ρ_b^A (g/cm^3)	ENTER Stratum A soil total porosity, n^A (unitless)	ENTER Stratum A soil water-filled porosity, θ_w^A (cm^3/cm^3)	ENTER Stratum B soil dry bulk density, ρ_b^B (g/cm^3)	ENTER Stratum B soil total porosity, n^B (unitless)	ENTER Stratum B soil water-filled porosity, θ_w^B (cm^3/cm^3)	ENTER Stratum C soil dry bulk density, ρ_b^C (g/cm^3)	ENTER soil total porosity, n^C (unitless)	ENTER Stratum C soil water-filled porosity, θ_w^C (cm^3/cm^3)
1.5	0.43	0.15						

MORE ↓

ENTER Enclosed space floor thickness, L_{crack} (cm)	ENTER Soil-bldg. pressure differential, ΔP ($g/cm\text{-}s^2$)	ENTER Enclosed space floor length, L_B (cm)	ENTER Enclosed space floor width, W_B (cm)	ENTER Enclosed space height, H_B (cm)	ENTER Floor-wall seam crack width, w (cm)	ENTER Indoor air exchange rate, ER (1/h)
15	40	961	961	244	0.1	2

ENTER Averaging time for carcinogens, AT_C (yrs)	ENTER Averaging time for noncarcinogens, AT_{NC} (yrs)	ENTER Exposure duration, ED (yrs)	ENTER Exposure frequency, EF (days/yr)
70	25	25	250

END

Diffusivity in air, Da (cm2/s)	Diffusivity in water, Dw (cm2/s)	Henry's law constant at reference temperature, H (atm-m3/mol)	Henry's law constant reference temperature, TR (oC)	Enthalpy of vaporization at the normal boiling point, $\Delta H\varpi,\beta$ (cal/mol)	Normal boiling point, TB (oK)	Critical temperature, TC (oK)	Molecular weight, MW (g/mol)	Unit risk factor, URF (mg/m3)-1	Reference conc., RfC (mg/m3)
7.20E-02	8.20E-06	1.84E-02	25	8,288	394.40	620.20	165.83	5.9E-06	6.0E-01

END

Exposure duration, t (sec)	Source-**building** separation, LT (cm)	Stratum A **air-filled** porosity, qaA (cm3/cm3)	Stratum B soil air-filled porosity, qaB (cm3/cm3)	Stratum C air-filled porosity, qaC (cm3/cm3)	Stratum A effective total fluid saturation, Ste (cm3/cm3)	Stratum A soil intrinsic permeability, ki (cm2)	Stratum A soil relative air permeability, krg (cm2)	Stratum A soil effective vapor permeability, kv (cm2)	Floor-wall seam perimeter, Xcrack (cm)	Soil gas conc. (mg/m3)	Bldg. ventilation rate, Qbuilding (cm3/s)
7.88E+08	1	0.28	ERROR	ERROR	0.25729443	9.92425E-08	0.703228129	6.97901E-08	3844	1304	125188.4022

Area of enclosed space **below** grade, AB (cm2)	Crack-**to-total** area ratio, h (unitless)	Crack **depth** below grade, Zcrack (cm)	Enthalpy of **vaporization at** ave. soil temperature, DHv,TS (cal/mol)	Henry's law **constant at** ave. soil temperature, HTS (atm-m3/mol)	Henry's law **constant at** ave. soil temperature, H'TS (unitless)	Vapor **viscosity at** ave. soil temperature, mTS (g/cm-s)	Stratum A **effective** diffusion coefficient, DeffA (cm2/s)	Stratum B effective diffusion coefficient, DeffB (cm2/s)	Stratum C **effective** diffusion coefficient, DeffC (cm2/s)	Total overall effective diffusion coefficient, DeffT (cm2/s)	Diffusion path length, Ld (cm)
923521	0.000416233	15	9552.934617	7.83E-03	0.337067044	0.000175414	5.62E-03	0	0	0.005616299	1

Convection path length, **Lp** (cm)	Source vapor **conc.,** Csource (mg/m3)	Crack **radius,** rcrack (cm)	Average vapor flow rate **into bldg.,** Qsoil (cm3/s)	Crack effective diffusion **coefficient,** Dcrack (cm2/s)	Area of **crack,** Acrack (cm2)	Exponent of equivalent foundation Peclet **number,** exp(Pef) (unitless)	Infinite source indoor attenuation **coefficient,** a (unitless)	Infinite source bldg. **conc.,** Cbuilding	Unit risk **factor,** URF (mg/m3)-1	Reference **conc.,** RfC (mg/m3)
15	1304	0.1	67.38925148	0.005616299	384.4	2.211E+203	0.000531398	0.692943596	0.0000059	0.6

END

Qsoil (L/min)
4.0

INCREMENTAL RISK CALCULATIONS:

Incremental risk from vapor intrusion to indoor air, carcinogen (unitless)	Hazard quotient from vapor intrusion to indoor air, noncarcinogen (unitless)
1.0E-06	7.9E-04

MESSAGE AND ERROR SUMMARY BELOW: (DO NOT USE RESULTS IF ERRORS ARE PRESENT)

SCROLL DOWN TO "END"

END

APPENDIX 5

DEVELOPMENT OF SOIL LEACHING SCREENING LEVELS

- Massachusetts Department of Environment Protection (MADEP 1994)
- USEPA Soil Screening Level Guidance (USEPA 2002)
- Hawai'i Department of Health (HDOH 1995)

Hawai'i DOH
Fall 2011

BACKGROUND DOCUMENTATION

FOR THE DEVELOPMENT OF THE

MASSACHUSETTS MCP NUMERICAL STANDARDS

Massachusetts Department of Environmental Protection
Bureau of Waste Site Cleanup
and
Office of Research and Standards

April 1994

Note: This appendix provides relevant sections and appendices from the 1994 MADEP publication entitled "Background Documentation for the Development of the Massachusetts Contingency Plan Numerical Standards". The MADEP method was also adopted for use by the Ontario Ministry of Environment and Energy (MOEE 1996) to develop soil screening levels for leaching concerns.

MCP APPENDIX F

DEVELOPMENT OF

DILUTION/ATTENUATION FACTORS
(DAFs)

FOR THE LEACHING-BASED

SOIL STANDARDS

DEVELOPMENT OF DILUTION/ATTENUATION FACTORS (DAFs) FOR THE LEACHING-BASED SOIL STANDARDS

INTRODUCTION

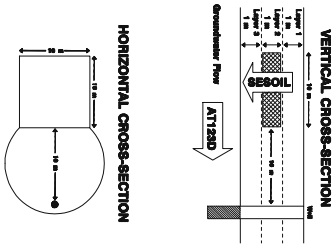
The Massachusetts Department of Environmental Protection has developed dilution attenuation factors (DAFs) in order to establish soil cleanup criteria for the protection of groundwater from leaching of residual contaminants in soil. DEP has adopted the modeling approach utilized by the State of Oregon in a similar process. This report describes the model and its application toward the development of DAFs for Massachusetts for a limited number of compounds of concern, and the subsequent development of one regression algorithm that relates DAFs developed by Oregon to those applicable in Massachusetts, and another algorithm that relates DAFs to chemical specific parameters. The pathway to groundwater is only one consideration in the final determination of an acceptable soil cleanup level.

THE OREGON MODEL

The Oregon model (Anderson, 1992) assumes a generic setting for a release of contaminant in the unsaturated zone and then applies the combination of SESOIL and AT123D models to estimate impact of the initial soil loading on a receptor assumed directly downgradient of the site via the groundwater pathway. The SESOIL and AT123D models, while previously individually developed (see References, Bonazountas, 1984 and Yeh, 1981), are a part of the risk assessment Graphical Exposure Modeling System (GEMS) developed by USEPA. A pc-based version of this (PCGEMS) was developed for USEPA by General Sciences Corporation (1989). The two models can now be linked so that SESOIL can pass leachate loadings to the saturated zone AT123D model.

The Oregon model's site setting (see Figure 1) assumes a 3-meter thick unsaturated zone, divided into three 1-meter layers. Contamination is initially released in the middle layer, as might occur for a leaking tank or for a residual contaminant remaining after some remedial excavation with clean cover backfill, and is uniformly distributed in this layer over a 10 meter by 10 meter area. The unsaturated zone and aquifer are assumed to be the same sandy soil with uniform properties. The upper and lower unsaturated zone layers are initially clean, as is the aquifer.

FIGURE 1
CONCEPTUAL SETTING



Source: Anderson (1991)

SESOIL inputs include the soil type parameters, chemical properties, application rates, and the climatic conditions of the area. The model is run as a transient monthly estimator of leachate volumes and concentrations. Initially, no other transport mechanisms other than leaching, partitioning, and volatilization were considered. Oregon used default values in SESOIL for Portland Oregon climatic conditions, but distributed total precipitation uniformly over the year.

SESOIL was initially found to overestimate losses via volatilization. A parameter, the volatilization fraction (VOLF), was introduced to allow adjustment of losses through this pathway and allow a site-specific calibration. This factor may be varied in time and space. The Oregon study used a uniform VOLF factor of 0.2, based on consultation with a panel of experts. One other soil-related parameter is the disconnectedness index. This parameter varies for and within soil types. Two values are given as SESOIL defaults, and the larger, 7.5, has been used in the simulations. An increase in this parameter appears to result in a higher soil moisture, lower leachate rates, and somewhat lower DAFs (i.e., is more conservative) for the compounds run.

AT123D inputs include general aquifer properties, source configuration, loadings to groundwater, soil partition coefficients, and dispersivity values. The aquifer is assumed to be infinitely wide and thick. The pc-based version of AT123D accepts monthly transient loading rates calculated by SESOIL, and also provides a preprocessor for input file preparation and editing. In utilizing the model, the center of the 10 by 10 meter source area is assumed to be at coordinates 0,0,0. The positive x-axis is in the direction of flow. Calculated concentrations are maximum along the x-axis (y=0) and at the water table surface (z=0). Since the receptor is assumed to be 10 meters from the downgradient edge of the source area, the concentration at x=15, y=0, and z=0 represents the receptor location. Oregon used longitudinal, transverse, and vertical dispersivities of 20m, 2m, and 2m, respectively. These values seem high for a sandy aquifer, but the values have been retained to be consistent with the Oregon base values and to be protective of the Commonwealth's sensitive aquifers on Cape Cod. DAFs are proportional to the dispersivities, particularly sensitive to the vertical dispersivity.

Oregon ran the model for 10 indicator compounds and then developed a multiple linear regression model relating the DAF to the organic partition coefficient (K_{oc}) and the Henry's Law constant (H) to provide preliminary DAFs for sixty other organic compounds. Soil cleanup levels were generated based on the regression algorithm and a safe drinking water level for each compound. In some cases, risk based levels determined by other pathways were lower than the levels required to protect groundwater. In these instances, the lower value was selected as the soil target level. A similar approach was taken to develop the MCP Method 1 Standards, as described in Section 5.3.

SIMULATIONS FOR MASSACHUSETTS

The approach taken to develop DAFs for Massachusetts was to determine the effect that varying the location (changing the climatic conditions from Portland, Oregon to Boston, Massachusetts in SESOIL) would have on the Oregon calculated DAFs. If the model system was essentially linear with respect to loading, then DAFs already calculated for Oregon would be directly related to DAFs appropriate for Massachusetts, and the general algorithm developed by Oregon (with coefficients adjusted) could also be used to estimated DAFs for other compounds. To this end, model runs were made using the Oregon input values for SESOIL and AT123D with the exception of climate parameter values. Eight indicator compounds were selected: benzene, toluene, ethylbenzene, o-xylene, trichloroethene, tetrachloroethene, 1,1,1-trichloroethane, and naphthalene.

The input values for SESOIL are shown in Tables F-1 through F-4, and those for AT123D are shown on Table F-5. Depending on the mobility of the compound through the transport pathway, model runs varied from 2 years to 6 years as necessary to determine the maximum concentration attained at the receptor location for a specific compound. A point to consider in the adoption of the Oregon values, or adjustments to them, is the need to agree with the physio-chemical parameters that were used to generate the DAFs. Even in the eight indicator compounds selected, various accepted databases provide some widely varying values for S, H and K_{oc}. For example, for PCE, H is reported with an order of magnitude difference, and values of K_{oc} and solubility differing by a factor of 2 are reported for ethylbenzene in the literature.

Output concentrations at the selected receptor location demonstrated a cyclical nature due to seasonal variations in precipitation and net recharge. Maximum concentrations were not always attained in the first cycle due to seasonal variability. However, the model output appeared to be linear with respect to the initial loading, allowing soil cleanup levels to be estimated based on the linear DAF approach. Table F-6 shows the model-based DAFs for Oregon and Massachusetts, and also, based on listed safe drinking water levels and the estimated DAFs for Massachusetts, what soil target levels would be for the eight indicator compounds run.

TABLE F-1
CLIMATE PARAMETER VALUES
FOR THE SESOIL MODEL

Default climate values for Boston as contained in the SESOIL model. Latitude = 42 degrees.

TABLE F-2
SOIL PARAMETER VALUES
FOR THE SESOIL MODEL

Intrinsic permeability =$1x10^{-7}$ cm^2
Source area=1,000,000 cm^2
Porosity =0.3
Disconnectedness index = 7.5
Soil bulk density = 1.5 gm/cm^3
Soil organic carbon = 0.1%

Layer 1 thickness = 100 cm
Layer 2 thickness = 100 cm
Layer 3 thickness = 100 cm
No further sublayering specified

Clay content = 0%

All other parameters set to zero except those to indicate uniform parameters in all layers.

TABLE F-3
APPLICATIONS DATA
FOR SESOIL MODEL

Application month = October only
layer = 2
rate = 1500 microgm/cm^2
year = 1 only

Based on the area, thickness and bulk density, this produces an initial concentration of 10 ppm. No other sources are added.

Volatile fraction (VOLF) = 0.2

Uniform in time and space.

All other parameter values set to zero.

TABLE F-4
CHEMICAL DATA FOR SESOIL MODEL

Compound	MW	K_{oc} ml/g	S mg/L	H atm-m^3/mol	DA cm^2/sec
benzene	78	83	1780	0.0055	0.109
ethylbenzene	106	575	161	0.00343	0.093
toluene	92	270	535	0.00668	0.100
o-xylene	106	302	171	0.00527	0.093
TCE	131	124	1100	0.00912	0.083
PCE	166	468	200	0.00204	0.075
1,1,1-TCA	133	157	730	0.0231	0.080
naphthalene	128	1288	31	0.00118	0.085

MW = molecular weight
K_{oc} = organic carbon partition coefficient
S = solubility in water
H = Henry's Law constant
DA = diffusion coefficient in air

TABLE F-5
AT123D MODEL INPUT PARAMETER VALUES

Soil bulk density	=	1.5 g/cc
Porosity	=	0.3
Hydraulic conductivity	=	0.5 m/hr
Hydraulic gradient	=	0.005
Longitudinal dispersivity	=	20.0 m
Transverse dispersivity	=	2.0 m
Vertical dispersivity	=	2.0 m

Loading (kg/hr) passed by SESOIL link program
Distribution coefficient = K_{oc} * fraction organic carbon
Source area = 10 m by 10 m, centered at 0,0
initial z penetration = 0

Degradation rates initially zero

TABLE F-6
MODEL OUTPUT DRAFT DAFS
COMPARISON AND SOIL LEVELS

Oregon Compound	Mass DAF	DAF	DRINKING WATER LEVEL mg/L	SOIL TARGET LEVEL ppm
benzene	44.4	56.5	0.005	0.28
ethylbenzene	103.5	121.1	0.700	84.8
toluene	64.5	80.6	1.000	80.6
o-xylene	65.4	83.3	10.000	833.3
TCE	65.4	76.3	0.005	0.38
PCE	73.0	86.2	0.005	0.43
1,1,1-TCA	133.2	169.2	0.200	33.8
naphthalene	207.0	222.2	0.280	62.2

STATISTICAL RELATIONSHIPS

A linear regression was run on the eight DAF data pairs with DAFs for Oregon as the independent variable. The model was :

$$DAF_{Mass} = A + B*DAF_{Oregon}$$

That is, the regression was not forced through the origin. For the eight data pairs, the equation was

$$DAF_{Mass} = 12.39 + 1.053*DAF_{Oregon}$$

with an r of 0.9913. Thus, over the range of data spanned by these eight compounds, the correlation appears good. Table F-7 shows a comparison of the DAFs calculated by the model and those by the linear regression equation above for the eight indicator compounds. Differences between the two methods are less than 10 percent.

A multiple linear regression algorithm for DAF(Mass) as a function of K_{oc} and H was also developed along the same lines as that developed by Oregon. This allows the calculation of DAFs for compounds for which Oregon did not consider, and which also may be used exclusively from the linear regression cited above. Two models were considered:

(a) $DAF = A + B*H + C*K_{oc}$, and
(b) $DAF = B*H + C*K_{oc}$.

where A, B, and C are regression coefficients. As with the Oregon analysis, it proved that the constant term was not statistically different from zero, and the simpler second model was adopted. Regression analysis yielded:

$$DAF = 6207 * H + 0.166 * K_{oc}$$

The fit here is somewhat better than the r-squared value of .956 for the Oregon model in that one compound with a large residual (carbon tetrachloride with a residual of 30) was not used here, and the average difference is much smaller with the eight compounds than for Oregon's ten. Table F-8 shows the relationship between the model DAFs and the regression expression predicted values. Only one compound varies more than 10 percent while six of the eight have percent differences less than five.

TABLE F-7
COMPARISON BETWEEN MODEL DAFS
AND LINEAR REGRESSION DAFS
BASED ON OREGON DAFS

Compound	Model DAF	Regr. DAF	%Diff.
benzene	56.5	59.1	4.60
ethylbenzene	121.1	121.4	0.25
toluene	80.6	80.3	-0.37
o-xylene	83.3	81.3	-2.40
TCE	76.3	81.3	6.55
PCE	86.2	89.3	3.60
1,1,1-TCA	169.2	152.6	-9.81
naphthalene	222.2	230.4	3.69

TABLE F-8
RESULTS OF THE MULTIPLE LINEAR REGRESSION
EQUATION FOR H AND KOC

Compound	Model DAF	Predicted	% Diff.
benzene	56.5	47.9	-15.2
ethylbenzene	121.1	116.7	- 3.6
toluene	80.6	86.3	7.1
o-xylene	83.3	82.8	- 0.5
TCE	76.3	77.2	1.2
PCE	86.2	90.4	4.9
1,1,1-TCA	169.2	169.4	0.1
naphthalene	222.2	221.1	- 0.5

BIODEGRADATION

It is intuitive that biodegradation may play an important role in attenuating the potential impact of residual contaminants in soils on groundwater. However, there are a great many site-specific conditions that will determine actual biodegradation rates. Further, literature values cover a wide range and the exact conditions under which they were estimated are rarely known. Literature values should be applied only with great caution

to any estimation of contaminant fate and transport. In order to evaluate the potential effect of biodegradation, rate constants cited by Howard et al (1991) were input to the model for the five compounds of the eight indicator compounds known to degrade aerobically. This eliminated the chlorinated compounds TCE, PCE, and 1,1,1-TCA. In addition, one additional rate for benzene (0.002/day from the California LUFT guidance) was also run. Four runs were made for benzene as the most critical compound, at the California rate, at the high and low rates cited by Howard and at the geometric mean of the Howard high and low rates. Only one rate, the low Howard value, was used for each of the other four compounds. The reason for this will be seen shortly.

The degradation rates in Howard appear to be high, with half lives for the BTEX compounds on the order of days. This implies that within a year, residual concentrations in soil would be reduced by biodegradation several (three to six) orders of magnitude. Table F-9 presents the results of the model runs.

For all situations except for the two lowest rates for benzene, the DAFs become huge. In essence, this indicates that only trace amounts of the contaminants ever reach the groundwater table. Soil target level estimation using large DAFs and the linear approach should be done only with extreme caution. A contaminant in the subsurface will attempt to reach equilibrium concentrations in the air, moisture and sorbed to soil. At some total concentration, equilibrium solubility in moisture would be exceeded, indicating the probable presence of free product. In this case, the linearity and basic assumptions in the model may be violated. Of further consideration are the potential toxic effects on the biological population as concentrations of the compounds increase. For these circumstances, estimation of soil target levels considering biodegradation is very difficult.

TABLE F-9
RESULTS OF THE BIODEGRADATION RUNS

Compound	Rate in Soil 1/day	Rate in Water 1/day	DAF
benzene	0.002	0.001 *	84.7
benzene	0.0433	0.000963	2178.
benzene	0.0775	0.00817	1.5×10^{4}
benzene	0.1386	0.0693	5.7×10^{7}
toluene	0.0315	0.02475	8.7×10^{6}
ethylbenzene	0.0693	0.00304	1.8×10^{13}
o-xylene	0.02475	0.001899	2.8×10^{5}
naphthalene	0.01444	0.00269	8.6×10^{10}

* Note: Odencrantz's article on the California LUFT parameter values did not cite a rate for water. This was assumed here to be half that in soil. Note that not much more degradation occurs in the aquifer due to the rapid travel time to the receptor of about 11 to 12 days (large longitudinal dispersivity and low retardation).

SENSITIVITY

A detailed sensitivity analysis was not done at this point in time. However, Oregon did perform some sensitivity analyses, and sensitivity of these models as applied in California's LUFT program is discussed in another article (Odencrantz, et al, 1992)

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Superfund

SUPPLEMENTAL GUIDANCE FOR DEVELOPING SOIL SCREENING LEVELS FOR SUPERFUND SITES

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SUPPLEMENTAL GUIDANCE FOR DEVELOPING SOIL SCREENING LEVELS FOR SUPERFUND SITES

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Disclaimer

This document provides guidance to EPA Regions concerning how the Agency intends to exercise its discretion in implementing one aspect of the CERCLA remedy selection process. The guidance is designed to implement national policy on these issues.

The statutory provisions and EPA regulations described in this document contain legally binding requirements. However, this document does not substitute for those provisions or regulations, nor is it a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. Any decisions regarding a particular remedy selection decision will be made based on the statute and regulations, and EPA decisionmakers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. EPA may change this guidance in the future.

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LIST OF ACRONYMS

ABS	Absorption fraction
AF	Skin-soil Adherence Factor
ARAR	Applicable or Relevant and Appropriate Requirement
ASTM	American Society for Testing and Materials
AT	Averaging Time
ATSDR	Agency for Toxic Substances and Disease Registry
BW	Body Weight
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
C/I	Commercial/Industrial
C_{sat}	Soil Saturation Limit
CSF	Cancer Slope Factor
CSGWPP	Comprehensive State Ground Water Protection Plan
CSM	Conceptual Site Model
DAF	Dilution Attenuation Factor
DDT	p,p'-Dichlorodiphenyltrichloroethane
DOD	Department of Defense
DOE	Department of Energy
DQO	Data Quality Objectives
Eco-SSLs	Ecological Soil Screening Levels
ED	Exposure Duration
EF	Exposure Frequency
EPA	Environmental Protection Agency
EV	Event Frequency
HBL	Health Based Level
HEAST	Health Effects Assessment Summary Tables
HELP	Hydrologic Evaluation of Landfill Performance
HI	Hazard Index
HQ	Hazard Quotient
IC	Institutional Control
IF	Age-adjusted Soil Ingestion Factor
IR	Soil Ingestion Rate
IRIS	Integrated Risk Information System
ISC3	Industrial Source Complex Dispersion Model
MCL	Maximum Contaminant Level (in water)
MCLG	Maximum Contaminant Level Goal (in water)
MRL	Minimal Risk Level
NAPL	Nonaqueous Phase Liquid
NPDWR	National Primary Drinking Water Regulations
NPL	National Priorities List
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response

LIST OF ACRONYMS
(Continued)

PAH	Polycyclic Aromatic Hydrocarbon
PA/SI	Preliminary Assessment/Site Inspection
PCB	Polychlorinated biphenyl
PEF	Particulate Emission Factor
PRG	Preliminary Remediation Goal
QA/QC	Quality Assurance/Quality Control
Q/C	Site-Specific Dispersion Factor
RAGS	Risk Assessment Guidance for Superfund
RAS	Regulatory Analytical Services
RBCA	Risk-based Corrective Action
RCRA	Resource Conservation and Recovery Act
RfC	Reference Concentration
RfD	Reference Dose
RI/FS	Remedial Investigation/Feasibility Study
RME	Reasonable Maximum Exposure
SA	Surface Area
SAP	Sampling and Analysis Plan
SCDM	Superfund Chemical Data Matrix
SCS	Soil Classification System
SPLP	Synthetic Precipitation Leachate Procedure
SSG	Soil Screening Guidance
SSL	Soil Screening Level
TBD	Technical Background Document
TC	Soil-to-dust Transfer Coefficient
THQ	Target Hazard Quotient
TR	Target Cancer Risk
TRW	Technical Review Workgroup for Lead
UCL	Upper Confidence Limit
URF	Unit Risk Factor
VF	Volatilization Factor
VOC	Volatile Organic Compound

Migration to Ground Water.

This guidance calculates commercial/industrial SSLs for the ingestion of leachate-contaminated ground water using the same set of equations and default input values presented in the 1996 *SSG*. Thus, the generic SSLs for this pathway are the same under commercial/industrial and residential land use scenarios.

EPA has adopted this approach for two reasons. First, it protects off-site receptors, including residents, who may ingest contaminated ground water that migrates from the site. Second, it protects potentially potable ground water aquifers that may exist beneath commercial/ industrial properties. (See text box for EPA's policy on ground water classification). Thus, this approach is appropriate for protecting ground water resources and human health; however, it may necessitate that sites meet stringent SSLs if the migration to ground water pathway applies, regardless of future land use.

Ground Water Classification

In order to demonstrate that the ingestion of ground water exposure pathway is not applicable for a site, site managers may either perform a detailed fate and transport analysis (as discussed in the *TBD* to the 1996 *SSG*), or may show that the underlying ground water has been classified as non-potable. EPA's current policy regarding ground water classification for Superfund sites is outlined in an OSWER directive (U.S. EPA, 1997e). EPA evaluates ground water at a site according to the federal ground water classification system, which includes four classes:

1 - sole source aquifers;
2A - currently used for drinking water;
2B - potentially usable for drinking water; and
3 - not usable for drinking water.

Generally, this pathway applies to all potentially potable water (i.e., classes 1, 2A, and 2B), unless the state has made a different determination through a process analogous to the Comprehensive State Ground Water Protection Plan (CSGWPP). Through this process, ground water classification is based on an aquifer or watershed analysis of relevant hydrogeological information, with public participation, in consultation with water suppliers, and using a methodology that is consistently applied throughout the state. If a state has no CSGWPP or similar plan, EPA will defer to the state's ground water classification only if it is more protective than EPA's. As of February 2001, 11 states (AL, CT, DE, GA, IL, MA, NH, NV, OK, VT, and WI) have approved CSGWPP plans.

The simple site-specific ground water approach consists of two steps. First, it employs a simple linear equilibrium soil/water partition equation to estimate the contaminant concentration in soil leachate. Alternatively, the synthetic precipitation leachate procedure (SPLP) can be used to estimate this concentration. Next, a simple water balance equation is used to calculate a dilution factor to account for reduction of soil leachate concentration from mixing in an aquifer. This calculation is based on conservative, simplified assumptions about the release and transport of contaminants in the subsurface (see Exhibit 4-3). These assumptions should be reviewed for consistency with the CSM to determine the applicability of SSLs to the migration to ground water pathway.

Equation 4-10 is the soil/water partition equation; it is appropriate for calculating SSLs corresponding to target leachate contaminant concentrations in the zone of contamination. Equations 4-11 and 4-12 are appropriate for determining the dilution attenuation factor (DAF) by which concentrations are reduced when leachate mixes with a clean aquifer. Because of the wide variability in subsurface conditions that affect contaminant migration in ground water, default values are not provided for input parameters for these dilution equations. Instead, EPA has

developed two possible default DAFs (DAF=20 and DAF=1) that are appropriate for deriving generic SSLs for this pathway. The selection of a default DAF is discussed in Appendix A, and the derivation of these defaults is described in the *TBD* to the 1996 *SSG*. The default DAFs also can be used for calculating simple site-specific SSLs, or the site manager can develop a site-specific DAF using equations 4-11 and 4-12.

To calculate SSLs for the migration to ground water pathway, the acceptable ground water concentration is multiplied by the DAF to obtain a target soil leachate concentration (C_w).[12] For example, if the DAF is 20 and the acceptable ground water concentration is 0.05 mg/L, the target soil leachate concentration would be 1.0 mg/L. Next, the partition equation is used to calculate the total soil concentration (i.e., SSL) corresponding to this soil leachate concentration. Alternatively, if a leach test is used, the target soil leachate concentration is compared directly to extract concentrations from the leach tests.

Exhibit 4-3

Simplifying Assumptions for the SSL Migration to Ground Water Pathway

- Infinite source (i.e., steady-state concentrations are maintained over the exposure period)
- Uniformly distributed contamination from the surface to the top of the aquifer
- No contaminant attenuation (i.e., adsorption, biodegradation, chemical degradation) in soil
- Instantaneous and linear equilibrium soil/water partitioning
- Unconfined, unconsolidated aquifer with homogeneous and isotropic hydrologic properties
- Receptor well at the downgradient edge of the source and screened within the plume
- No contaminant attenuation in the aquifer
- No NAPLs present (if NAPLs are present, the SSLs do not apply)

For more information on the development of SSLs for this pathway, please consult the 1996 *SSG*.

Mass-Limit SSLs. Equations 4-13 and 4-14 present models for calculating mass-limit SSLs for the outdoor inhalation of volatiles and migration to ground water pathways, respectively. These models can be used only if the depth and area of contamination are known or can be estimated with confidence. These equations are identical to those in the 1996 *SSG*. Please consult that guidance for information on using mass-limit SSL models.

[12] The acceptable ground water concentration is, in order of preference: a non-zero Maximum Contaminant Level Goal (MCLG), a Maximum Contaminant Level (MCL), or a health-based level (HBL) calculated based on an ingestion rate of 2L/day and a target cancer risk of $1x10^{-6}$ or an HQ of 1. These values are presented in Appendix C.

Equation 4-10
Soil Screening Level Partitioning Equation for Migration to Ground Water

$$\text{Screening Level in Soil (mg/kg)} = C_w \left[K_D + \frac{(\theta_w + \theta_a H')}{\rho_b} \right]$$

Parameter/Definition (units)	Default
C_w/target soil leachate concentration (mg/L)	(nonzero MCLG, MCL, or HBL)[a] × dilution factor
K_d/soil-water partition coefficient (L/kg)	for organics: $K_d = K_{oc} \times f_{oc}$ for inorganics: see Appendix C[b]
K_{oc}/soil organic carbon/water partition coefficient (L/kg)	chemical-specific[c]
f_{oc}/fraction organic carbon in soil (g/g)	**0.002 (0.2%)**
θ_w/water-filled soil porosity (L_{water}/L_{soil})	**0.3**
θ_a/air-filled soil porosity (L_{air}/L_{soil})	$n - \theta_w$
ρ_b/dry soil bulk density (kg/L)	**1.5**
n/soil porosity (L_{pore}/L_{soil})	$1 - (\rho_b/\rho_s)$
ρ_s/soil particle density (kg/L)	2.65
H′/dimensionless Henry's law constant	chemical-specific[c] (assume to be zero for inorganic contaminants except mercury)

[a] Chemical-specific (see Appendix C).
[b] Assume a pH of 6.8 when selecting default K_d values for metals.
[c] See Appendix C.

Equation 4-11
Derivation of Dilution Attenuation Factor

$$\text{Dilution Attenuation Factor (DAF)} = 1 + \frac{K \times i \times d}{I \times L}$$

Parameter/Definition (units)	Default
DAF/dilution attenuation factor (unitless)	**20 or 1 (0.5-acre source)**
K/aquifer hydraulic conductivity (m/yr)	**Site-specific**
i/hydraulic gradient (m/m)	**Site-specific**
I/infiltration rate (m/yr)	**Site-specific**
d/mixing zone depth (m)	**Site-specific**
L/source length parallel to ground water flow (m)	**Site-specific**

Equation 4-12
Estimation of Mixing Zone Depth

$$d = (0.0112 L^2)^{0.5} + d_a(1 - \exp[(-L \times I)/(K \times i \times d_a)])$$

Parameter/Definition (units)	Default
d/mixing zone depth (m)	**Site-specific**
L/source length parallel to ground water flow (m)	**Site-specific**
I/infiltration rate (m/yr)	**Site-specific**
K/aquifer hydraulic conductivity (m/yr)	**Site-specific**
i/hydraulic gradient (m/m)	**Site-specific**
d_a/aquifer thickness (m)	**Site-specific**

Equation 4-13
Mass-Limit Volatilization Factor
- Commercial/Industrial Scenario

$$VF = Q/C_{vol} \times \frac{[T \times (3.15 \times 10^7 s/yr)]}{(\rho_b \times d_s \times 10^6 g/Mg)}$$

Parameter/Definition (units)	Default
d_s/average source depth (m)	**site-specific**
T/exposure interval (yr)	**30**
Q/C_{vol} /inverse of the ratio of the geometric mean air concentration to the volatilization flux at the center of a square source (g/m^2-s per kg/m^3)	**68.18[a]**
ρ_b/dry soil bulk density (kg/L or Mg/m^3)	**1.5**

[a] Assumes a 0.5 acre emission source

Equation 4-14
Mass-Limit Soil Screening Level for Migration to Ground Water

$$\text{Screening Level in Soil (mg/kg)} = \frac{(C_w \times I \times ED)}{\rho_b \times d_s}$$

Parameter/Definition (units)	Default
C_w/target soil leachate concentration (mg/L)	(nonzero MCLG, MCL, or HBL)[a] × dilution factor
d_s/depth of source (m)	**site-specific**
I/infiltration rate (m/yr)	**0.18**
ED/exposure duration (yr)	70
ρ_b/dry soil bulk density (kg/L)	**1.5**

[a] Chemical-specific, see Appendix C.

Hawai'i Department of Health RBCA Guidance (Tier 2 methodology for evaluation of leaching of chemicals from soil)

Reference: HIDOH, 1995, *Risk-Based Corrective Action and Decision Making at Sites With Contaminated Soil and Groundwater*: State of Hawai'i, Department of Health, December, 1995 (revised June, 1996).

RISK-BASED CORRECTIVE ACTION AND DECISION MAKING AT SITES WITH CONTAMINATED SOIL AND GROUNDWATER

VOLUME I

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Errata:

Table of Contents; Addenda noted.
Chapter 1, table 1-1 and 1-2, Chapter 2, Table 2-2, Appendix F, Table 1; drinking water standard for vinyl chloride corrected.
Chapter 1, pages 3-4; groundwater action level discussion revised for clarity.
Chapter 1, page 7; text in paragraph three revised to describe Table 1-1.
Chapter 1, page 13; NS term defined in Table 1-1 notes.
Chapter 2, page 17; introduction revised for clarity.
Chapter 2, pages 20-21; groundwater action level discussion revised for clarity.
Chapter 2, page 28, Appendix E, page E-1; definition of volatile contaminant corrected.
Chapter 2, Table 2-6, Appendix C, Table 3, Appendix E, Table 2; molecular weight for toluene corrected.
Chapter 2, Table 2-9, Appendix E, Table 4; soil and particle density units corrected to kg/m^3.
Appendix F, Table 1; revised for clarity with respect maximum groundwater protection soil action level, SESOIL model results for benzene and toluene in Table 1d corrected.
QUIKSOIL spreadsheet; SAL calculation corrected to match equation in RBCA manual.

Addenda:

Addendum # 1 (February 1996): Provides additional guidance on determining the extent of soil contamination at sites and choosing soil contaminant concentrations for use in RBCA models.

Addendum #2 (June 1996, second update): February, 1996, version of addendum added nine contaminants to Tier 1 lookup tables. June, 1996, updates include: text revised for clarity; dioxin (2,3,7,8 TCDD), chlordane, and carbon tetrachloride added to Tier 1 lookup tables; soil action levels for Di-n-octyl phthalate corrected; groundwater action levels for 4,4 DDE corrected; molecular weight for 4,4 DDE corrected; physio-chemical constants for PCBs noted (for potential use in modeling).

Addendum # 3 (June 1996): RBCA manual Appendix K: Supporting Data for Tier 1 Soil Action Levels Generated Using SESOIL.

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EXECUTIVE SUMMARY

This report presents and describes a refined, risk-based corrective action (RBCA) process that has been implemented by the Hawai‘i Department of Health (DOH) for assessment and remediation of sites with contaminated soil and groundwater. Chapter 1 presents a revision of Tier 1, DOH-recommended ("default") action levels for soil and groundwater in accordance with advances made in quantitative direct-exposure and contaminant fate-and-transport models. To reflect their purpose to serve as a guide to site remedial actions but not necessarily to serve as strict "cleanup numbers", DOH has chosen to refer to the revised criteria as soil and groundwater "action" levels.

Tier 1 soil and groundwater action levels appropriate for a given site are chosen from a lookup table based on the location of the site with respect to potential impact on drinking-water resources and annual rainfall at the site. Soil and groundwater action levels for contaminants not listed in the report can be obtained from the DOH.

Groundwater action levels adhere to state and federal surface water and drinking water standards. As a minimum, groundwater action levels are set to be protective against potential adverse impact to surface water ecosystems. For sites where drinking water resources may also be impacted, groundwater action levels are refined as needed to additionally meet drinking water standards.

Soil action levels are set to be protective of direct, residential exposure to impacted soils and adverse groundwater impact due to remobilization (e.g., leaching) of contaminants from the soil. Soil action levels are generated with the aid of computer-assisted, risk-based, direct-exposure models and vadose-zone leaching models. Action levels are contaminant-specific and based on both the potential mobility and toxicity of the contaminant.

The Tier 1 soil action levels presented in the lookup table may be overly conservative for small areas of impacted soil (e.g., less than one-half acre). Chapter 2 provides guidelines for use of the models on a Tier 2, site-specific basis. In Tier 2 site assessments, DOH allows a controlled use of the Tier 1 models to generate more site-specific soil action levels without the need for a full-scale, time-consuming, and generally costly "risk assessment (Tier 3)." Site-specific factors that can be taken into account in Tier 2 assessments include the actual volume of impacted soil at the site and the geology and hydrogeology of the site. User-friendly computer spreadsheets are available from DOH for use in Tier 2 site evaluations. For further guidance on Tier 2 procedures refer Chapter 2 of this document. DOH should be consulted prior to a facility undertaking a full-scale (Tier 3) risk assessment.

Impacted sites with contaminant concentrations in excess Tier 1 soil or groundwater action levels required to initiate followup "action," whether this be remediation to default action levels (Tier 1), limited refinement of soil action levels to reflect more site-specific data (Tier 2), or full refinement of soil action levels based on a detailed, site-specific risk assessment (Tier 3).

TIER 2 SOIL ACTION LEVEL - OBJECTIVES

Groundwater Protection Objectives

The importance of Hawaii's groundwater and surface water resources cannot be overemphasized. Essentially 100% Hawaii's drinking water comes from groundwater resources. The quality of the state's inland and coastal surface waters is intricately tied to the quality of the islands groundwater and likewise plays a crucial role in the ecological and, in turn, economic health of the state.

Tier 2 soil action levels for groundwater-protection concerns must be set to meet the following objectives:

1) Leachate that infiltrates through the vadose zone and recharges any groundwater system must not cause the groundwater to be impacted at greater than DOH standards for surface water (either marine or fresh water, whichever is the more stringent).

2) Leachate that infiltrates through the vadose zone and recharges a groundwater system that is a current or potential source of drinking water must not lead to a groundwater impact that exceeds either surface water <u>or</u> drinking water standards.

3) Due to the heightened threat of groundwater impact, residual contamination present in the vadose-zone should not exceed Tier 1, theoretical saturation levels for individual contaminants of concern.

The delineation and utility of groundwater systems on the islands should be made in accordance with the DOH policy statement "Determination of Groundwater Utility at Leaking Underground Storage Tank Sites (HIDOH, 1995b)." For the purposes of both Tier 1 and Tier 2 site evaluations, DOH assumes that all leachate that infiltrates through the vadose zone will impact a groundwater system. It is further assumed that all groundwater systems are potentially interconnected to bodies of surface water (streams, rivers, lakes, marshes, coastal waters, etc.) and that all of these surface water bodies are ecologically important.

DOH groundwater action levels for common contaminants of concern are repeated in Table 2-2. As discussed in Chapter 1, groundwater action levels for any site are initially set to meet surface water quality criteria. This is intended to be protective of aquatic ecosystems should contaminated groundwater migrate or otherwise be

discharged into a body of surface water. The criteria presented are based on state and federal acute or, when available, chronic surface water standards. For sites where the groundwater of concern is a current or potential source of drinking water ("Drinking Water Source Threatened" in Table 1-1), action levels are adjusted where needed to ensure that state drinking water standards or alternative drinking water criteria are additionally met. Note that drinking water standards are substituted for surface water standards where the latter have not been established (e.g., benzo(a)pyrene).

Direct-Exposure Objectives

In addition to addressing groundwater protection concerns, Tier 2 SALs ultimately applied to a site must be also be protective of residential exposure to impacted soils through inhalation, ingestion, and dermal absorption. With the exception of only a few compounds, most notably benzo(a)pyrene and PCBs, direct-exposure soil action levels generated are set to meet a one-in-a-million (10^{-6}) cancer risk for carcinogenic contaminants and a hazard quotient of "1" for non-carcinogenic contaminants. The use of alternative direct-exposure objectives and assumptions at a site must be justified and documented in a Tier 3 risk assessment that is submitted to DOH for review and approval.

GENERATION OF TIER 2 SALs FOR GROUNDWATER-PROTECTION CONCERNS - SESOIL APPLICATION

SESOIL Computer Application

RiskPro's SESOIL vadose-zone contaminant fate and transport computer application (GSC, 1993, Version 1.07) developed by General Sciences Corporation (GSC) or updates to the application must be used for Tier 2 evaluations of potential groundwater impact unless otherwise approved or directed by DOH. An overview of the RiskPro SESOIL application is presented in "The New SESOIL User's Guide (August, 1994)" published by the Wisconsin Department of Natural Resources (Hetrick et al., 1994). Excerpts from the publication are provided in Appendix B. A sensitivity analysis of SESOIL conducted by the Wisconsin Department of Natural Resources (WDNR, 1993) is included in the appendix.

Other versions of the SESOIL application may be inappropriate for use in either Tier 2 or Tier 3 site evaluations. An example of unacceptable versions of SESOIL include the SESOIL module in the 1995 "Decision Support Software" computer application put forth by the American Petroleum Institute (API, 1994). Output from this version of SESOIL provides only a yearly resolution of groundwater impact, rather than monthly as in the original version of the application.

A table of SESOIL-generated SALs based on the default Tier 1 site scenario are presented in Appendix F for variable depths to groundwater. As an alternative to re-running SESOIL models at sites where depth to groundwater may be an important

factor in setting groundwater protection SALs, facilities can refer to SALs presented in Appendix F for use in Tier 2 assessments. The default SALs should be multiplied by the appropriate site dilution attenuation factor, as described below, in order to generate a final groundwater protection SAL for the site.

Unless otherwise approved or directed by DOH, use of SESOIL to generate soil action levels for Tier 2 (or Tier 3) purposes must follow assumptions and procedures described in this chapter. Note that for Tier 3 site evaluations, any vadose-zone application can be used provided that the application generates at least a monthly resolution for groundwater impact. If the model results are not as conservative as would have been produced using the GSC version of SESOIL, however, then the discrepancy should be discussed and justified in the Tier 3 report and use of the application approved by DOH.

SESOIL Model Procedures

Procedures regarding use of SESOIL to generate initial Tier 2 SALs are described below. Each step corresponds to an input module of the application. Fill out and submit the SESOIL worksheet provided in Appendix D (attachment D2) for each mode run. A summary of the input data parameters and default values used in the Tier 1 models is provided in Table 2-3. A complete description and discussion of the Tier 1 default parameter values is provided in Appendix C.

Step 1: Input Model Simulation Information

Note the site name, DOH ID number, and contaminant modeled in the module heading. "Raingage station" refers to the source of climate data used in the simulation. The number of years of climate data input will normally be "1" (climate data is repeated in subsequent model simulation years). The model simulation time will vary based on the physio-chemical nature of the contaminant and the hydrogeology of the site. (Due to memory limitations, the IBM 466DX used for Tier 1 could not run SESOIL simulations greater than 25 years in length.)

Step 2: Input Climate Data

Input data from the most correlative climate station (an optional climate data set is available with the RiskPro SESOIL application). Evapotranspiration can be directly calculated from input cloud cover, humidity, and albedo data. For most climate stations, however, these data are not available. If this is the case, input a value of "0" for monthly cloud cover, humidity, and albedo data and input evapotranspiration as a fraction of total rainfall based on the island location of the site as follows (data from Atlas of Hawai'i, 1983): Ni'ihau: 72% total rainfall, Kaua'i: 24% total rainfall, O'ahu: 36% total rainfall, Moloka'i: 54% total rainfall, Maui: 27% total rainfall, Lāna'i: 66% total rainfall, Kaho'olawe: 70% total rainfall, and Hawai'i: 44% total rainfall. Note that evapotranspiration data must be input as cm/day.

Where appropriate climate data are not available, determine the annual rainfall for the site based on maps provided in Appendix G. Refer to the default climate data provided in Table 2-4 and modify the default monthly precipitation (total 200cm/year) to reflect actual annual rainfall determined for the site (e.g., for sites with 100cm of annual rainfall the default precipitation data would be multiplied by a factor of 0.5). Input evapotranspiration as the appropriate, daily fraction of total rainfall based on the island that the site is located on (see above).

Step 3: Input Soil Property Data

Input site-specific soil property data where supported by information gained during the site investigation or related published reports. Otherwise, use the default, Tier 1 parameter values noted in Table 2-3. For sites where mixtures of contaminants are present (e.g., petroleum releases), assume that an organic carbon content of no more than 0.1% is available for sorption of any given contaminant.

The data input into the soil property module are applied to the uppermost layer of the geologic model and then used as default values for subsequent layers. Input a value of "0" for the default soil permeability. Layer-specific permeability will be set in the "Soil Column Properties" module (step 6).

The default soil property data presented in Table 2-3 are based on information published by the U.S. Department of Agriculture (Foote et al., 1972; USDOA, 1976; USDOA, 1992) and the University of Hawai'i - Mānoa Water Resources Research Center (Miller et al., 1988; Mink and Lau, 1990), and also on discussions with local experts of Hawaii's soils and hydrogeology (Table 2-5). Refer to the discussion in Appendix C and the DOH Tier 1 document for additional discussion regarding soil and bedrock properties in Hawai'i.

Step 4: Input Physio-Chemical Constants for Contaminant

Default physio-chemical constants and biodegradation rates for common contaminants are provided in tables 2-6 and 2-7. These constants should be used for both the SESOIL and direct-exposure models unless otherwise approved or directed by DOH. Contact the DOH Solid and Hazardous Waste Branch for information regarding contaminants not listed in the table. A value of "0" will normally be input for the hydrolysis and complexation constants noted in the module. Refer to Appendix C for a discussion on the source and justification of the default physio-chemical constants and biodegradation rates provided. Input physio-chemical constants can be supplemented with site-specific soil data where available (e.g., soil batch tests, etc.).

Step 5: Input Application Data

Input a value of "25" for the number of years of model simulation data. This should be sufficient for most model simulations. The number of soil layers input is governed by the geologic profile determined for the site. **Include a 1cm- thick layer at the base**

of the column and input the same soil/bedrock properties as the layer overlying it. In the model simulation, this 1cm-thick layer directly overlies groundwater. Inclusion of a thin, basal layer is used to improve the precision of the SESOIL output data regarding the mass of contaminant moving from the vadose-zone into the groundwater (used in step 7).

The input application area reflects the areal extent of impacted soil and is used in conjunction with layer thickness to calculate contaminant mass. SESOIL automatically generates the site latitude based on the input climate station. The spill mode should be set to "Instantaneous" to reflect the one-time presence of residual contamination in the model impacted layer (i.e., no continuous source). "Pollutant Load" should be set to "Concentration" to reflect soil contaminant concentration as input in the next module. Washload simulations are not applicable for Tier 2 models.

Step 6: Input Soil Column Properties

Input thickness and permeability data for each geologic layer. Refer to the default permeability data provided in Table 2-5 where site-specific data are not available. The number of soil sublayers will normally be set to one.

For the layers underlying the uppermost unit, input a value of "1" for all soil-property, factoring parameters except organic carbon (OC). For organic carbon, input factors that reflect site-specific data where available. For sites where site-specific OC data are not available, assume an organic carbon content of 0.0001% for all lithified (rock) units and for all sediment and soil layers situated at greater than 3 meters depth (following assumptions used in Tier 1) and adjust the input OC factor values accordingly. For sites where mixtures of contaminants are present (e.g., petroleum), assume a maximum of 0.1% OC for soils within three meters of the surface and 0.0001% OC for all lithified units and for all layers situated at greater than 3 meters depth.

Step 7: Input Pollutant Loading Data

Input a value of "0" for the first data-input year of the "mass transformed", "sink", and "ligand" columns unless otherwise approved or directed by DOH. The input factor will be repeated for all subsequent years of data. **Input a value of "0.2" for "volatilization factor" to limit contaminant loss due to volatilization to 20% of the maximum possible (required).** Note that unlike the factors noted above the volatilization factor must be repeated for <u>every</u> simulation year. (Click on the column heading and use the column math function to expedite data input.) The application erroneously assumes a volatilization factor of 1 for all months where no data is input.

Input a value of "0" for the monthly pollutant load of each year of input data (i.e., the number of data-input years noted in Step 5) except the first month of the first year. Following the procedures outlined in Appendix D, adjust the input soil concentration for the 1st year, 1st month until the model is calibrated to target groundwater-

protection objective. **(Do not include assumed dilution of leachate at this point!)**

Step 8: Extract Groundwater-Impact SAL from Output Data.

Extract the SESOIL-generated SAL from the calibrated output file by following the procedures outlined in Appendix D. Change the SAL units to mg/kg. The final, site SAL for groundwater-protection concerns will be calculated by multiplying the SESOIL-generated SAL by the dilution attenuation factor determined for the site, as discussed below.

Unedited (except for format) output files for SESOIL model simulations must be included with the report documenting the derivation of each Tier 2 soil action level. The version of SESOIL used to generate the Tier 2 soil action levels must be clearly indicated in the report. Warning messages in the output file regarding input rainfall and permeability data are based on the input of extremely variable data and are intended to prompt the user to recheck the input data modules. If the input data is correct then the warnings can generally be ignored.

GENERATION OF TIER 2 SALs FOR GROUNDWATER-PROTECTION CONCERNS - QUIKSOIL SPREADSHEET

The QUIKSOIL spreadsheet model is based on a simple contaminant partitioning equation that approximates the dissolved-phase ("leachate") concentration of the contaminant in impacted soil based on the physio-chemical nature of the contaminant and the soil. The model is based on an equation presented in ASTM's "Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (Table X2.1, ASTM, 1994)" for calculation of soil leaching factors:

$$SAL = C_w \times (Kd + (\theta_w + (\theta_a \times H'))/\rho_b),$$

where C_w is the target groundwater action level for the site (mg/L), Kd is the soil-water partition coefficient (L/Kg), θ_w and θ_a are the water- and air-filled porosities, H' is the Henry's law constant (unitless) and ρ_b is the soil bulk density.

Procedures regarding use of the QUIKSOIL spreadsheet to generate Tier 2 SALs are as follows:

Step 1. Check with the DOH Solid and Hazardous Waste Branch to ensure that the spreadsheet you have is the most up-to-date version.

Step 2. Input physio-chemical constants for the contaminant being evaluated. Constants for common contaminants are provided at the end of the spreadsheet (use "cut & paste" function of spreadsheet; refer also to Table 2-6). Contact the DOH Solid and Hazardous Waste Branch to obtain constants for contaminants not listed.

Step 3. Input site data where available. (Model will use default, conservative parameter values where site data is not available.)

Step 4. Input the target groundwater standard for the site (refer to Table 2-2). Do not include assumptions regarding dilution of leachate. Contact the DOH Solid and Hazardous Waste Branch to obtain groundwater criteria for contaminants not listed in Table 2-2.

Step 5. Spreadsheet generates the contaminants Tier 2 SAL for groundwater-protection concerns at the site. Complete the information at the end of the first page of the spreadsheet. Include a copy of the spreadsheet for each contaminant modeled with the Tier 2 report submitted to DOH for review and approval.

An example printout of the QUIKSOIL spreadsheet is provided in Appendix H.

Users of the QUIKSOIL spreadsheet should be aware that the model does not incorporate DOH-acceptable assumptions regarding the fate and transport of the "leachate" in the vadose zone. With respect to the more comprehensive SESOIL application, the QUIKSOIL spreadsheet generates overly conservative SALs for contaminants that are highly biodegradable (e.g., half-life < 50 days) or highly volatile (e.g., Henry's Law constant > 0.01atm-m^3/mol) or sites where the base of the impacted soil is situated greater than ten meters from groundwater. For contaminants or sites with these attributes, DOH strongly encourages use of the SESOIL application to generate groundwater-protection SALs.

CALCULATION OF FINAL SALs FOR GROUNDWATER-PROTECTION CONCERNS

SALs generated with SESOIL (either Tier 1 SESOIL SALs provided in Appendix F or Tier 2, site-specific SESOIL SALs) or QUIKSOIL should be further refined on a site-specific basis to account for dilution of leachate as it mixes with groundwater. Because the relationship between leachate concentration and soil concentration is assumed to be linear (i.e., Freundich number in SESOIL application set to "1"), refinement of a SESOIL- or QUIKSOIL-generated SAL is a simple matter of multiplying the SAL by a leachate dilution attenuation factor (DAF) calculated for the site.

Site-specific dilution attenuation factors are generated using the DOH spreadsheet entitled "DAF" (refer to example in Appendix I). The DAF equation relates the volume of recharge water infiltrating into groundwater beneath a site during a year to the volume of impacted groundwater passing beneath the site during that year as follows:

$$DAF = 1 + ((V_s \times d_m) \times n_{eff})/(I \times L),$$

where "V_s" (meters/year) is groundwater seepage velocity, "D_m" (meters) is the mixing depth of the leachate in groundwater, "n_{eff}" (m^3/m^3) is the fraction effective porosity, "I" (meters/year) is infiltration rate, and "L" (meters) is source length parallel to

groundwater flow.

Annual groundwater recharge is reported in the yearly summaries of SESOIL output files. If Tier 1, SESOIL-generated SALs or SALs based on the QUIKSOIL spreadsheet are used for the site then groundwater recharge can be estimated as an island-specific fraction of total annual rainfall. Assume the following recharge with respect to the location of the site (data from Atlas of Hawai'i, 1983): Ni'ihau: 5% total rainfall, Kaua'i: 16% total rainfall, O'ahu: 36% total rainfall, Moloka'i: 16% total rainfall, Maui: 30% total rainfall, Lāna'i: 12% total rainfall, Kaho'olawe: 10% total rainfall, and Hawai'i: 31% total rainfall.

The spreadsheet calculates groundwater velocity (seepage) as:

$$V_s = (K \times h)/n_{eff}$$

where "K" is the hydraulic conductivity of the groundwater bearing media in meters per year, "h" is the hydraulic gradient.

Mixing zone depth is calculated by relating source length parallel to groundwater flow, aquifer thickness (d_a, meters), and the hydraulic conductivity of the groundwater-bearing media as follows:

$$d_m = (0.0112 \times L^2)^{0.5} + d_a(1 - \exp[(-L \times I)/(K \times h \times d_a)]).$$

The dilution factor equation presented above is used in ASTM's "Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites" (Table X2.1, ASTM, 1994). The mixing-zone depth equation is based on an equation published in EPA's *Technical Background Document for Soil Screening Guidance* (USEPA, 1994d).

Mixing-zone depths calculated using the equation will typically range between one and ten meters. The ASTM document referenced recommends a default mixing-zone depth of two meters. DAFs generated by the equations presented typically range from 1 to 10, dependent largely on annual rainfall, the hydraulic conductivity of the groundwater-bearing media, and the hydraulic gradient of the groundwater.

GENERATION OF TIER 2 SALs FOR DIRECT-EXPOSURE CONCERNS

Direct-Exposure Model Equations

The risk-based, deterministic models incorporated into the DETIER2 spreadsheet are based on slight modifications of direct-exposure models presented in the Second Half, 1994, and First Half, 1995, editions of EPA Region IX's "Preliminary Remediation Goals (PRGs)" (Appendix E, USEPA, 1994a, 1995). The equations used in the PRG models reflect guidance provided in the California EPA document entitled "Preliminary Endangerment Guidance Manual, January, 1994" (CAEPA, 1994). A copy of this

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APPENDIX 6

DEVELOPMENT OF CARBON RANGE AND TOTAL PETROLEUM HYDROCARBON RISK-BASED ACTION LEVELS

- Summary of 2011 HEER Office TPH Soil Gas Study (Pending)
- 2002 Massachusetts VPH-EPH Guidance
- Overview of gasoline composition (NEIWPCC, 2003)
- Measurement of TPH in soil gas: TO-15 vs TO-17 (Hayes 2007)

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Characterizing Risks Posed by Petroleum Contaminated Sites:

Implementation of the MADEP VPH/EPH Approach

FINAL POLICY

October 31, 2002

Policy #WSC-02-411

This Policy provides guidance for parties conducting response actions under the Massachusetts Contingency Plan (MCP) on the use and application of the Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) methods to characterize risks posed by releases of petroleum products to the environment. This Policy updates and replaces draft documents that were issued on October 31, 1997 and June 2001. Parties who are currently using criteria and guidance contained in the June 2001 draft document may do so until May 1, 2003. A summary of significant changes between these earlier drafts and this Final Policy is provided in Appendix 6.

The information contained in this document is intended solely as guidance. This Policy does not create any substantive or procedural rights, and is not enforceable by any party in any administrative proceeding with the Commonwealth. This Policy provides recommendations and guidance on approaches the Department considers acceptable for meeting the performance standards set forth in the MCP and discussed in this document. These performance standards include, but are not limited to, the Response Action Performance Standards of section 310 CMR 40.0191 of the MCP. Parties using this guidance should be aware that there may be other acceptable alternatives for achieving and documenting compliance with the general regulatory requirements and performance standards of the MCP, including those of 310 CMR 40.0191. The regulatory citations in this document should not be relied upon as a complete list of the applicable regulatory requirements.

This Policy and further information on the development and application of the aliphatic/aromatic hydrocarbon evaluative technique employed by the Department, referred to as the "VPH/EPH" approach, may be obtained at http://www.state.ma.us/dep/bwsc/vph_eph.htm

10/31/02
Date

Signature on Original

Deirdre C. Menoyo
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Bureau of Waste Site Cleanup

This information is available in alternate format. Call Aprel McCabe, ADA Coordinator at 1

DEP on the World Wide Web: http://www.mass.gov/dep

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LIST OF ACRONYMS

AAS	Atomic Absorption Spectroscopy
APH	Air-Phase Petroleum Hydrocarbons
AQWC	Ambient Water Quality Criteria
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CEP	Critical Exposure Pathway
EDB	Ethylene Dibromide
EPA	Environmental Protection Agency
EPC	Exposure Point Concentration
EPH	Extractable Petroleum Hydrocarbons
eV	Electron Volt
FID	Flame Ionization Detector
GC	Gas Chromatography or Gas Chromatograph
GC/FID	Gas Chromatograph/Flame Ionization Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GRO	Gasoline Range Organics
GW	Groundwater
HVAC	Heating, Ventilation, Air-conditioning
ICP-AES	Inductively coupled plasma atomic emissions spectroscopy
IR	Infra-red
LNAPL	Light Non-Aqueous Phase Liquids
LSP	Licensed Site Professional
MADEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MtBE	Methyl tertiary butylether
NAPL	Non-Aqueous Phase Liquids
NRS	Numerical Ranking System
OTP	Ortho-terphenyl
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
ppbV	Parts-per-billion by volume
ppmV	Parts-per-million by volume
QA/QC	Quality Assurance/Quality Control
RAF	Relative Absorption Factor
RAO	Response Action Outcome
RfC	Reference Concentration
RfD	Reference Dose
RL	Reporting Limit
SIM	Selective Ion Monitoring
SW	Surface Water
TIC	Tentatively Identified Compound
TOV	Total Organic Vapor
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UCL	Upper Concentration Limit
UCM	Unresolved Complex Mixture
UST	Underground Storage Tank
UV	Ultra-violet
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons
WSC	Waste Site Cleanup

1.0 INTRODUCTION

1.1 Background

Spills and releases of petroleum fuels are the leading source of environmental contamination in Massachusetts. Because petroleum products are a complex and highly variable mixture of hundreds of individual hydrocarbon compounds, however, characterizing the risks posed by petroleum-contaminated soil and water has proven to be difficult and inexact.

Traditional approaches have focused on the identification and evaluation of specific indicator compounds, like benzene, and/or the quantitation of a "Total Petroleum Hydrocarbon" (TPH) value. The limitations of an "indicator only" approach have long been recognized, especially at gasoline-contaminated sites, and it is clear that focusing on a select few compounds cannot adequately characterize the risks posed by all hydrocarbons present. While the quantitation of a TPH value is a step in the right direction, in that an attempt is being made to account for all compounds present, traditional TPH methods and approaches provide little or no information on the composition or toxicity of generated data.

In response to these shortcomings, the Massachusetts Department of Environmental Protection (MADEP) published a document in August 1994 entitled *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*. This document presented a new toxicological approach to characterize and evaluate risks posed by petroleum-contaminated sites, by breaking down TPH into collective aliphatic and aromatic fractions.

To support and implement this new toxicological approach, MADEP developed two analytical methods that differentiate and quantitate collective concentrations of aliphatic and aromatic hydrocarbons in soil and water. These methods, for *Volatile Petroleum Hydrocarbons* (VPH) and *Extractable Petroleum Hydrocarbons* (EPH), were issued in draft form in August 1995, and as final procedures in January 1998. At present, MADEP is in the process of finalizing a method for *Air-Phase Petroleum Hydrocarbons* (APH), which will allow for the collective quantitation of aliphatic and aromatic hydrocarbons in air. A draft APH method was issued by the agency in February 2000.

MADEP has integrated this new approach into the Massachusetts Contingency Plan (MCP), by developing and promulgating soil and groundwater cleanup standards for the aliphatic and aromatic ranges of interest. These standards became effective on October 31, 1997. Parties undertaking cleanup actions at petroleum-contaminated sites in Massachusetts now have the means to quickly and easily address risks posed by these complex mixtures, by the optional use of the generic *Method 1* cleanup standards. Conversely, such parties may elect to develop site-specific cleanup standards via use of a *Method 2* or *Method 3* risk assessment process.

1.2 Purpose and Scope

The purpose of this document is to (1) provide a succinct summary of key provisions of the "VPH/EPH" approach, (2) provide greater detail and specificity on important elements of this new approach, and (3) provide technical and regulatory insight, guidance, and ***Rules of Thumb*** to assist Licensed Site Professionals and others in understanding and applying this approach in a practical and cost-effective manner.

Rules of Thumb are suggestions and recommendations on how to approach, evaluate, and resolve investigatory, assessment, and remedial issues. In most cases, they are based upon reasonably conservative or "worst case" assumptions and considerations, and are intended to assist competent professionals in "ruling out" items of concern, or affirming a need to proceed to a more comprehensive level of evaluation. These rules are based upon current information, and are designed to be protective at most, but not all sites. Derivation details are provided in "Background/Support Documentation for the Development of Publication Guidelines and Rules of Thumb", available at: http://www.state.ma.us/dep/bwsc/vph_eph.htm.

Rules of Thumb **may only be applied to the specific situations described in this document, as such guidelines are predicated upon a designated scenario and are reflective of the totality of conservative assumptions incorporated into that scenario. Changing any developmental element of these guidelines and/or applying them to situations not detailed in this document may not be sufficiently protective. Moreover, the use of these rules may not be appropriate at sites with complex or highly heterogeneous contaminant conditions or migration pathways, or at sites or portions of sites with highly sensitive receptors (e.g., drinking water wells).**

While striving to be as useful and complete as possible, nothing in this document should be viewed as limiting or obviating the need for the exercise of good professional judgment.

1.3 Applicability

The provisions of this document are applicable at sites contaminated by releases of one or more petroleum fuels and/or lubricating oils. The guidance contained in this policy is designed to help Licensed Site Professionals (LSPs) and others comply with the risk-based/performance-based requirements of the MCP to adequately investigate and assess releases of oil and waste oil to the environment.

The MCP – since 1988 – has required that parties conducting response actions at disposal sites document or achieve a level of no significant risk of harm to human health, safety, public welfare, and the environment. Because the MCP is performance-based, it does not dictate the specific means by which one demonstrates compliance with these standards. From a practical point of view, however, most parties did not have ready access to the tools and procedures needed to adequately characterize the total risks posed by petroleum contamination – until promulgation of the VPH/EPH approach, analytical methodologies, and Method 1 cleanup standards in 1997. For this reason, MADEP has adopted a prospective and retrospective position on the application of the VPH/EPH approach:

1.3.1 Site Closure on or after October 31, 1997

Since October 31, 1997, MADEP has provided parties conducting response actions a means to easily and adequately assess risks posed by petroleum contaminants. Therefore, all sites closed on or after this date (e.g., by filing of a Response Action Outcome Statement) must demonstrate compliance with this standard, by use of the VPH/EPH approach, or by use of another scientifically valid and health-protective approach. In these cases, the use of an "indicator only" approach is NOT acceptable.

There are no "grand fathering" provisions for sites that were not closed out prior to October 31, 1997. However, this document provides guidance on how one might utilize and/or "convert" old data obtained prior to this date, to more fully assess risks pursuant to the VPH/EPH approach, and support a post-1997 closure submittal.

Notwithstanding the implementation of this new approach, it should be noted that the MCP retains a cleanup standard for Total Petroleum Hydrocarbons (TPH), which is set conservatively at the lowest EPH fractional cleanup standard (typically C_{11}-C_{22} Aromatic Hydrocarbons). Parties may continue to use a TPH approach to characterize heavier petroleum products (i.e., $>C_9$), using the EPH method (in the TPH screening mode) or other scientifically valid and defensible method (See Section 3.7.1).

1.3.2 Site Closure Prior to October 31, 1997

In general, MADEP will not require reevaluation of petroleum-contaminated sites properly closed prior to October 31, 1997. Nonetheless, the agency reserves the right to do so, in cases where direct and compelling exposure concerns are believed to be present, and where human health is being directly threatened. Such concerns may exist at sites where (1) a release of gasoline has impacted a drinking water well, or (2) a release of gasoline has resulted in persistent, long-term odors or vapors within an occupied structure.

In cases where parties voluntarily conduct VPH/EPH testing at sites closed prior to October 31, 1997 (e.g., pursuant to a property transfer evaluation), the applicable "re-opener" language is contained at 310 CMR 40.0317(17). Under the provisions of this section of the MCP, a notification obligation would exist for this newly obtained VPH/EPH data if such information would change or negate the findings of the closure document (e.g., RAO, LSP Evaluation Opinion).

2.0 SUMMARY OF VPH/EPH APPROACH

2.1 The Concept

Petroleum is a mixture of hundreds of hydrocarbon compounds. Industry specifications for refined products, such as gasoline and diesel fuel, are based upon physical and performance-based criteria, not upon a specific chemical formulation. As such, the composition of petroleum products released to the environment are complex and variable, and are a function of (1) the origin and chemistry of the parent crude oil, (2) refining and blending processes, and (3) the use of performance-enhancing additives. Once released to the environment, the chemistry of a petroleum product is further altered by contaminant fate and transport processes, such as leaching, volatilization, and biodegradation.

It would be extremely difficult and expensive to identify and quantitate every single hydrocarbon compound present in petroleum-contaminated media. Even if this activity was accomplished, there is little toxicological data available for the vast majority of petroleum constituents. While there are limited data available on the toxicity of some petroleum fuels, the chemistry of weathered products typically encountered at contaminated sites may be quite different from the chemistry of the fresh product that was the subject of toxicological evaluation.

Based upon an evaluation of information and data available on the chemistry and toxicity of petroleum products, however, it is possible to make some broad observations and conclusions:

- ◊ petroleum products are comprised mainly of aliphatic/alicyclic and aromatic hydrocarbon compounds;
- ◊ aromatic hydrocarbons appear to be more toxic than aliphatic compounds; and
- ◊ the toxicity of aliphatic compounds appears to be related to their carbon number/molecular weights.

These three precepts are the foundation of the VPH/EPH approach. Specifically, under this approach, the **non-cancer** toxicity of petroleum-contaminated media is established by (1) determining the collective concentrations of specified ranges of aliphatic and aromatic hydrocarbons, and (2) assigning a toxicity value (e.g., Reference Dose) to each range. Toxicity values are determined on the basis of a review and/or extrapolation of available toxicological data on hydrocarbon mixtures and specific hydrocarbon compounds. The complete breakdown for all ranges of interest is summarized in Table 2-1.

Table 2-1: Toxicological Approach for Non-Cancer Health Effects

Hydrocarbon Fraction	Reference Dose (mg/kg/day)
C5-C8 Aliphatic Hydrocarbons	0.04[a]
C9-C18 Aliphatic Hydrocarbons	0.1[a]
C19-C36 Aliphatic Hydrocarbons	2.0[a]
C9-C22 Aromatic Hydrocarbons	0.03

[a] updated values (2002)

Cancer effects are evaluated separately, by the identification and quantitation of those specific hydrocarbon compounds, like benzene and certain polycyclic aromatic hydrocarbons (PAHs), which are designated carcinogens. Additional information and details on this approach are provided in the MADEP publication *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, August, 1994, and as amended, available at http://www.state.ma.us/dep/bwsc/vph_eph.htm.

2.2 Hydrocarbon Fractions of Interest

Although the non-cancer toxicity of petroleum-contaminated media can be adequately described by division into the four hydrocarbon fractions listed above, MADEP has chosen to designate six hydrocarbon fractions of interest, because of the following analytical and program considerations:

- ◊ EPA analytical methods have traditionally used one approach for the analysis of volatile organics (i.e., purge and trap), and another for the analysis of semi-volatile/extractable organics (i.e., solvent extraction). To facilitate use by commercial laboratories accustomed to such division, the VPH and EPH methods developed by MADEP maintain this distinction. Moreover, because of the large carbon range covered by the new approach (i.e., C5 to C36), it would be difficult to detect all fractions using just one method: the volatile/purgeable methods can adequately cover the lighter hydrocarbons, but not the heavier fractions (>C12), while, due to losses of low molecular weight hydrocarbons that occur during the sample preparation process, extractable methods are generally unable to reliably detect lighter fractions (<C9).

- ◊ Given the need for two analytical methods, and a desire to minimize use of both methods on all samples, a decision was made to break up the C9-C18 Aliphatic range, to enable detection of all gasoline-range hydrocarbons in the VPH method. In this manner, it would only be necessary to use the VPH procedure to characterize gasoline releases.

For these reasons, it was necessary and desirable to divide the aliphatic and aromatic hydrocarbon ranges of interest into six separate entities; three detected by the VPH method, and three detected by the EPH Method, as listed in Table 2-2.

Table 2-2: Hydrocarbon Fractions of Interest

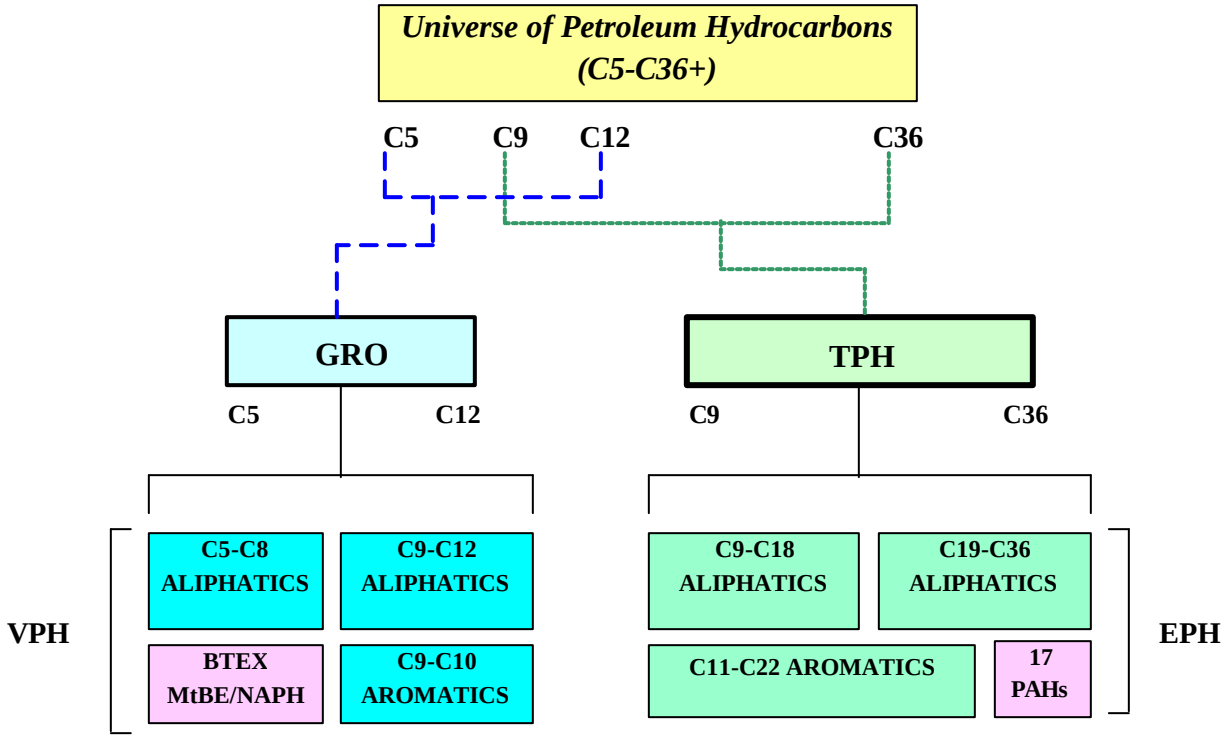
Toxicologically Defined Hydrocarbon Fraction	Analytical/Program Defined Hydrocarbon Fraction	Analytical Method	Reference Dose (mg/kg/day)
C5-C8 Aliphatics	C5-C8 Aliphatics	VPH	0.04[a]
C9-C18 Aliphatics	C9-C12 Aliphatics	VPH	0.1[a]
	C9-C18 Aliphatics	EPH	0.1[a]
C19-C36 Aliphatics	C19-C36 Aliphatics	EPH	2.0[a]
C9-C22 Aromatics	C9-C10 Aromatics	VPH	0.03
	C11-C22 Aromatics	EPH	0.03

[a] updated value (2002)

2.3 Relationship of VPH/EPH to TPH and Gasoline Range Organics (GRO)

The relationship between TPH, GRO, VPH and EPH is graphically displayed in Figure 2-1.

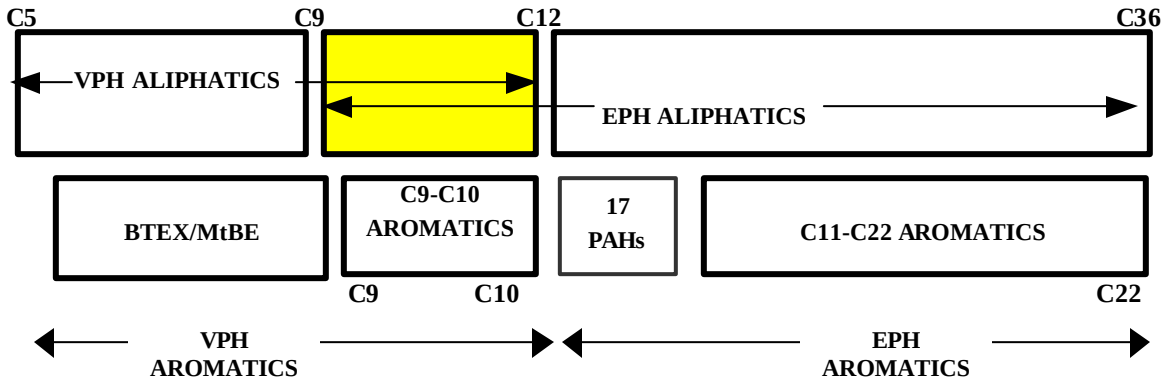
Figure 2-1: Relationship of GRO, TPH, VPH, and EPH



As can be seen in Figure 2-1, if the concentrations of the three EPH fractions and target PAH analytes were added together, it would be equal to a traditional "TPH" value. Similarly, if the three VPH fractions and BTEX/MtBE/naphthalene concentrations were added together, it would equal a GRO value.

It may also be noted that an overlap exists between the VPH and EPH methods, in that C9-C12 aliphatic hydrocarbons are quantitated by both methods. This overlap, further discussed in Section 4.2.3, is graphically illustrated in Figure 2-2.

Figure 2-2: Overlap of VPH and EPH Test Methods



Note that there is no overlap in the aromatic fractions: the C9-C10 Aromatic fraction from the VPH method ends just before naphthalene, and the C11-C22 Aromatic fraction from the EPH method starts just after naphthalene.

2.4 Additional Research and Data Needs

MADEP continues to gather and review information and data on petroleum hydrocarbon chemistry and toxicity. Recent efforts have focused on the review and evaluation of previously unavailable oral and inhalation toxicological data, which has lead to some revisions to the recommended RfD and RfC values for hydrocarbon fractions of interest (see Table 4-13). Additional study is also needed to better evaluate ecological risks posed by aliphatic and aromatic hydrocarbons.

On a national level, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has published a number of documents relating to this subject. TPHCWG is comprised of representatives from the oil industry, Department of Defense, EPA, state agencies, environmental consulting firms, and academia. This group has recommended an aliphatic/aromatic fractional approach similar to the MADEP approach. Additional information and recommendations have also been provided on petroleum chemistry, hydrocarbon fate and transport, and analytical methodologies.

A number of TPHCWG publications are available on the World Wide Web at http://www.aehs.com/

3.0 ANALYTICAL METHODS

In order to use the VPH/EPH toxicological approach, it is necessary to be able to measure the collective concentrations of aliphatic and aromatic hydrocarbons in impacted media. Because conventional TPH and EPA test methods cannot produce this type of data, MADEP has developed and published two detailed analytical methods for Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH). Both methods are gas chromatography (GC) techniques, and are modifications of traditional EPA procedures contained in SW-846. As such, most laboratories that have conducted volatile and extractable organic analyses in the past should be able to perform these techniques.

3.1 Gas Chromatography

Chromatography is the separation of compounds or groups of compounds in a complex mixture. In gas chromatography, hydrocarbons in a sample are transferred to the vapor phase by purging (VPH) or heating (EPH). The gaseous sample then flows through a (100 meter long +/-) *capillary column* to a detector. A chemical coating on the walls of the column first sorbs, and then desorbs each compound in the sample, with the heavier molecular weight compounds being "detained" longer than the lighter compounds. In this manner, analytes exit or *elute* from the column in a predictable and reproducible manner, based upon the structure, molecular weight, and boiling point of the compound.

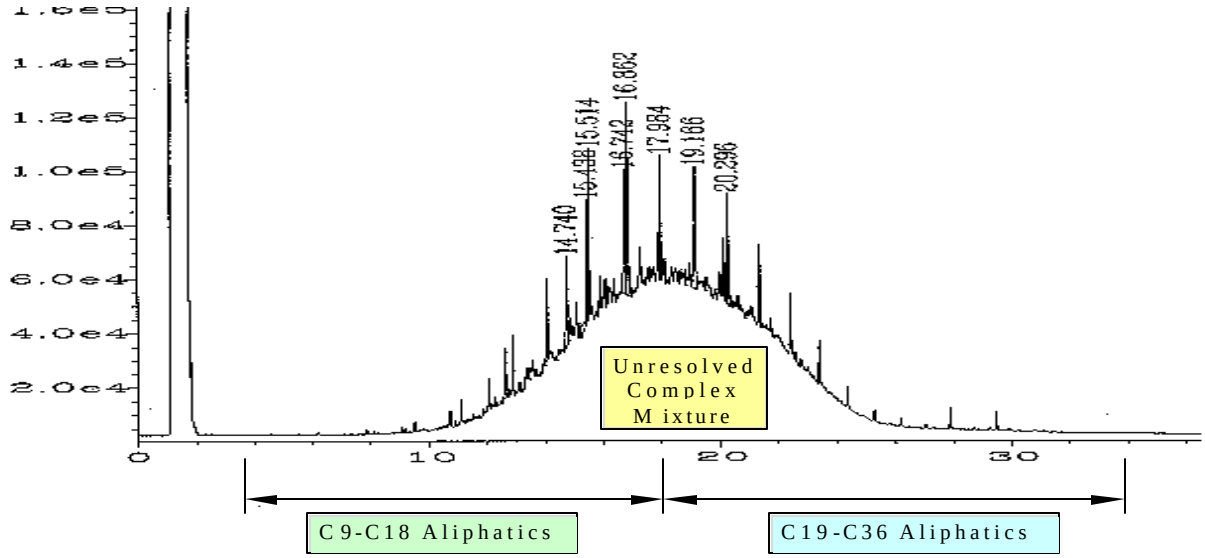
Once they elute from the column, analytes pass through a detector, where the presence of each compound produces a small electrical current, proportional to its mass. This current is then amplified and used to produce a chromatogram, which is simply a plot of electrical (detector) response over time. Each peak on a chromatogram represents one or more individual compounds. Compounds are identified based upon their *retention times*, which is the time (in minutes) it takes the compound to travel through the column. Compounds or ranges of interest are quantitated by an *integration* process that calculates the area beneath the chromatographic peak(s), for comparison to mass/area ratios derived from the injection of *calibration standards* of known mass or concentration.

To transfer the hydrocarbons within a sample medium into a gas chromatograph, and into a gaseous phase, various sample preparation techniques may be used. Volatiles within water samples are generally *purged* with an inert gas, which strips the dissolved volatile compounds from the aqueous phase into the gaseous phase, where they are initially retained on a *trap* containing an appropriate sorbent. This trap is then rapidly heated to desorb the analytes, and load them onto a chromatographic column. Volatiles within soils are first extracted with a solvent (e.g., methanol), then mixed with water and purged. Heavier non-volatile hydrocarbons in both water and soil samples are generally extracted with a solvent (e.g., methylene chloride); the extract is then injected into a gas chromatograph, where it is heated and vaporized into a gaseous state.

A key and novel requirement of the VPH/EPH approach is the need to separate or *fractionate* hydrocarbon mixtures into collective groupings of aliphatic and aromatic hydrocarbons. This fractionation is something that is not done in conventional TPH or Gasoline Range Organic analyses, or the EPA volatile/extractable methodologies detailed in SW-846. There are several different ways to accomplish this task, each with advantages and disadvantages. The recommended MADEP analytical methods use detector selectivity and a chemical exchange process to fractionate samples, but other techniques may also be acceptable and cost-effective.

An example of an EPH (GC/FID) chromatogram of the aliphatic portion of a weathered #2 Fuel Oil soil sample is provided in Figure 3-1.

Figure 3-1: Sample Chromatogram - #2 Fuel Oil



Note that the "x" axis is the retention time, in minutes, and the "y" axis is the detector signal strength. The retention time of some of the individual peaks are printed above those peaks. Note also the presence of a large chromatographic "hump" between 10 and 26 minutes, indicating the presence of an *Unresolved Complex Mixture (UCM);* this feature is an important issue discussed in more detail below.

3.2 MADEP Analytical Methodologies

MADEP has developed and published two analytical methodologies for the detection of Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) in soil and water. Both methods separate complex hydrocarbon

mixtures into collective fractions of aliphatic and aromatic hydrocarbons, and produce data that can be directly compared to MCP *Method 1* cleanup standards. MADEP has also issued a draft methodology for the detection of Air-Phase Petroleum Hydrocarbons (APH), to identify and quantitate collective ranges of aliphatic and aromatic hydrocarbons in air and soil gas.

The VPH, EPH, and APH methods were developed to allow a meaningful evaluation of the risks posed by hydrocarbon mixtures. Other procedures may also be available to fulfill this objective, or, perhaps more importantly, other data quality objectives. For example, it may be more cost-effective to use (or initially use) EPA Method TO-14 to evaluate indoor air quality, and establish whether a subsurface hydrocarbon transport pathway is present at a disposal site; if there is no pathway, there is no need to evaluate risks via the APH procedure.

3.2.1 Volatile Petroleum Hydrocarbons (VPH)

The MADEP VPH Method (1998) is a *Purge and Trap, GC/PID/FID* procedure. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can be quantitated in soil or water matrices. In addition to these fractional ranges, the VPH method may also be used to concurrently identify and quantitate individual concentrations of the *Target VPH Analytes* benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE); and naphthalene.

Samples are analyzed using a *purge-and-trap* sample preparation/concentration procedure. The gas chromatograph is temperature-programmed to facilitate separation of hydrocarbon compounds. Detection is achieved by a photoionization detector (PID) and flame ionization detector (FID) in series. The PID chromatogram is used to determine the individual concentrations of Target Analytes and the collective fractional concentration of aromatic hydrocarbons in the C9 through C10 range. The FID chromatogram is used to determine the collective fractional concentrations of aliphatic hydrocarbons within the C5 through C8 and C9 through C12 ranges. Individual "marker" compounds are used to establish the beginning and end of the hydrocarbon ranges of interest.

The MADEP VPH method relies upon the selectivity of the PID detector to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. Specifically, the PID will preferentially respond to hydrocarbon compounds with *pi* or double carbon (C=C) bonds, but will not respond well to hydrocarbon compounds with single carbon (C-C) *sigma* bonds. Because aromatic compounds have at least one benzene ring with three double bonds, they respond well to a PID; straight, branched, and cyclic aliphatic compounds with single carbon bonds respond poorly. Conversely, the FID is more of a universal detector, and will respond equally well to both aliphatic and aromatic hydrocarbons.

Because the PID can detect sample analytes without destroying them, compounds eluting from the chromatographic column are first passed through the PID, and then through the FID, where they are combusted in a hydrogen flame. In theory, the FID will detect the total concentrations of all petroleum hydrocarbons in the sample, and the PID will detect only (or mostly) aromatic compounds. By subtracting the PID from the FID response, it would be possible to quantitate just the aliphatic compounds. However, reality deviates from this theoretical ideal in the following ways:

- *Pi* bonds are present in hydrocarbon compounds other than aromatics - most notably alkenes, which are present in gasoline. Therefore, alkenes will be quantitated as aromatics. However, this bias is not deemed to be a major methodological limitation, due to the fact that (a) alkenes are typically not found in high concentrations in most petroleum products, and (b) alkenes may be more toxicologically similar to aromatics than to aliphatics.

- A more problematic issue is the fact that aliphatic compounds will produce some measurable response on a PID, especially heavier-molecular-weight branched and cyclic alkanes. Collectively, this response can become significant if there are a lot of these types of aliphatic compounds present, and will result in a falsely inflated quantitation of aromatics. Since a good portion of the hydrocarbons in the C9-C12 range of gasoline are in fact substituted aromatic compounds, this analytical overquantitation is not a major problem. However, other products, like kerosene and Jet A fuel, contain predominately aliphatic compounds within this range, and therefore use of the PID/FID approach can lead to significant overquantitation of the aromatic fraction.

Steps can be taken to minimize overquantitation of the aromatic fraction. Using a low energy PID lamp (e.g., 9.5 eV) will further diminish aliphatic response. Where essential, other techniques, such as chemical fractionation and/or use of a GC/MS approach, may be used to ensure more accurate data in this regard.

3.2.2 Extractable Petroleum Hydrocarbons (EPH)

The MADEP EPH Method (1998) is a *solvent extraction/fractionation GC/FID* procedure. Using this method, the collective concentrations of C9-C18 Aliphatic, C19-C36 Aliphatic, and C11-C22 Aromatic Hydrocarbons can be quantitated in soil or water matrices. In addition to these fractional ranges, the EPH method may also be used to concurrently identify and quantitate individual concentrations of the 17 Polycyclic Aromatic Hydrocarbon (PAH) *Target EPH Analytes*.

Soil and water samples are extracted with methylene chloride, solvent exchanged into hexane, and loaded onto a silica gel cartridge or column. The silica gel cartridge/column is rinsed with hexane to strip aliphatic compounds, and the resultant extract is collected and labeled. The silica gel cartridge/column is then rinsed with methylene chloride, to strip aromatic compounds, and the resultant extract is collected and labeled. The two extracts are then analyzed separately by direct injection into a temperature-programmed GC/FID. Individual target PAH compounds are identified by GC/FID analysis of the aromatic extract.

There are two important methodological elements that should be considered when reviewing EPH data:

- The MADEP EPH method relies upon a solvent-exchange/silica-gel-fractionation process to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. This fractionation process is a sensitive yet critical element of the analytical approach; small errors at this stage can result in significant over or underquantitation of aromatic and aliphatic ranges. For this reason, the method specifies use of *Fractionation Surrogates* to verify proper separation of the aliphatic and aromatic fractions.

- Like any GC/FID procedure, an *unresolved complex mixture (UCM) or "hump"* will typically be observed on the chromatogram of a heavier molecular weight petroleum product, particularly weathered products. (See Figure 3-1). A UCM is produced when many individual hydrocarbon compounds are eluting from the capillary column at the same time, overwhelming and preventing the detector signal from returning to baseline. Nevertheless, it is important that these compounds are included in the sample quantitation calculation, and for that reason the EPH method specifies the use of a *forced or projected baseline* when integrating chromatographic areas of fractional ranges. **If a laboratory does not takes steps to ensure this integration technique, resultant fractional range data may significantly under-report true hydrocarbon concentrations.**

The EPH method also contains an option to forego the solvent-exchange/silica-gel-fractionation process, to obtain a Total Petroleum Hydrocarbon (TPH) concentration. While this data will provide little information on the chemistry or toxicity of the petroleum mixture, it can provide a cost-effective analytical screening value, for comparison with TPH reporting and cleanup standards.

3.2.3 Air-Phase Petroleum Hydrocarbons (APH)

The draft MADEP APH method (2000) *is a GC/MS procedure*. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can be quantitated in air or soil gas matrices. In addition to these fractional ranges, the APH method may also be used to concurrently identify and quantitate individual vapor-phase concentrations of the *Target APH Analytes* 1,3-butadiene, benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE), naphthalene, and 2-methylnaphthalene.

Samples are collected in SUMMA ® passivated stainless steel canisters (other collection techniques are permissible and may be more appropriate for certain data quality objectives). A specified volume of sample is withdrawn from the canister through a mass flow controller using a vacuum pump. The sample is cryogenically concentrated to a volume of less than one mL in a nickel trap filled with nonsilanized glass beads. Following preconcentration, the sample is refocused at the head of a capillary column on a gas chromatograph using a cryofocusing accessory. This step further reduces the sample volume to less than one microliter for injection.

The sample is then injected into a gas chromatograph, which is used to separate the compounds and hydrocarbon fractions of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantitated using characteristic ions. Collective concentrations of C_9-C_{10} Aromatic Hydrocarbons are quantitated using extracted ions. Collective concentrations of aliphatic hydrocarbon fractions are quantitated using a total ion chromatogram, subtracting out Target APH Analytes and C_9-C_{10} Aromatic Hydrocarbons. It is important to note that the final APH method may contain modifications of the above procedures.

Air testing, whether by the APH procedure or other methodologies, is a specialty service that is not as widely available as soil and water analytical services. However, unlike the VPH and EPH methods, MADEP does not expect use of the APH method will be required at most petroleum contaminated sites, for the reasons listed below:

- Most releases of petroleum products do not result in an indoor air impact;
- For those sites where an indoor air impact is a potential concern, it is usually possible to evaluate and/or rule-out indoor air contamination problems using low-cost soil gas analytical screening techniques, as further detailed in Section 4.3.1; and
- Where indoor air sampling is required to evaluate a potential subsurface vapor transport pathway, traditional EPA procedures (e.g., EPA Method TO-14) may be used to determine if an impact is likely (based upon concentration of target analytes and qualitative presence of hydrocarbon peaks). The use of the APH (or similar) procedure would only be necessary if contamination is confirmed, and a quantitative risk assessment is required.

3.3 VPH/EPH Target Analytes

Although both the VPH and the EPH methods are capable of providing quantitation of Target Analytes (concurrent with the quantitation of aliphatic and aromatic ranges), because they are GC methods which identify analytes solely on the basis of retention times, they can produce "false positive" or over-inflated concentration data for these individual compounds. For example, the large peak eluting at 14.740 minutes in Figure 3-1 may be identified by the EPH method as hexadecane, because a hexadecane standard run as part of the calibration procedures eluted at this retention time. However, it is possible that hexadecane is not present in this sample at all, and some other (unknown) hydrocarbon compound is present which elutes at precisely this same time; or it is possible that hexadecane is indeed present, but that 2 or 3 other hydrocarbon compounds are *co-eluting* with hexadecane at precisely this time, which will lead to an overquantitation of the hexadecane concentration.

Although the sample-extract cleanup and fractionation procedures specified in the EPH method will tend to minimize interferences of this nature (by removing aliphatic compounds that may co-elute with the PAH Target Analytes), the only way to get positive identification and quantitation of these Target Analytes is to use a GC/MS analytical technique, like EPA Method 8270 for the PAHs, and EPA Method 8260 for BTEX/MtBE. For this reason, a laboratory may advise a client to use the VPH and EPH methods to quantitate the aliphatic/aromatic fractional ranges, but a GC/MS method to quantitate individual (Target) analytes. This approach is acceptable, although it may increase analytical costs.

To save money, it may be a worthwhile gamble to quantitate Target Analytes using the VPH/EPH Methods for samples that are believed to be relatively free from contamination - for example, when trying to confirm a "clean closure" at a tank removal site. If significant concentrations of Target Analytes are in fact found to be present, a re-analysis can be done using GC/MS, to provide a definitive determination in this regard (if the laboratory was instructed to retain the sample extract from the VPH/EPH samples, the cost for this re-analysis would be reduced).

3.4 Sampling Procedures and Requirements for the VPH/EPH Methods

Sample collection and preservation are critical elements in the VPH and EPH methodologies. A summary of requirements in this regard is provided in Table 3-1; detailed step-by-step sampling recommendations are provided in Appendix 1.

Sample preservation is essential. **VPH and EPH aqueous samples must be preserved in a manner that prevents biodegradation of hydrocarbons**. ***Simply cooling these samples is not sufficient.*** Biodegradation can be prevented by addition of acids (e.g., HCl to pH <2) or by the addition of bases (e.g., Trisodium Phosphate Dodecahydrate to pH > 11). *Note that acid preservation can significantly degrade levels of MtBE in aqueous samples (see Appendix 1).*

VPH soil samples must be preserved in a manner that (1) prevents sample losses due to volatilization, and (2) prevents sample losses due to biodegradation. There is now considerable evidence and data demonstrating substantial losses of volatile petroleum hydrocarbons from unpreserved sampling containers. The recommended preservation technique is to immerse VPH soil samples in methanol *at the time of collection*. Alternative techniques will be considered only if sufficient data are available to demonstrate the efficacy of sample preservation. Currently, only one alternative has been shown to provide acceptable preservation: the use of specially designed sealed-tube devices that obtain an air-tight soil sample.

Table 3-1: Sample Collection, Preservation, and Holding Times

Method	Matrix	Container	Preservation	Holding Time
VPH	Aqueous	40 mL VOC vial w/Teflon-lined septa screw caps; fill completely to zero headspace	pH <2 (add 3-4 drops of 1:1 HCl); cool to 4°C. Where MtBE is of concern, use 0.40– 0.44 grams TSP to raise pH > 11 (see Appendix 1)	14 days
	Soil	VOC vial or container; add 15g to 40mL vial; 25g to 60 mL vial	1 mL methanol per 1g soil (+/- 25%); cool to 4°C	28 days
EPH	Aqueous	1-Liter amber glass bottle with Teflon-lined screw cap	pH<2 (add 5 mL of 1:1 HCl); cool to 4°C	Extract within 14 days; analyze extract within 40 days
	Soil	4-oz (120 mL) +/- widemouth amber glass jar with Teflon-lined screw cap	cool to 4°C	Extract within 7 days; analyze extract within 40 days

Such devices have been shown to maintain sample integrity for 48 hours, by which time the sample must be extruded and preserved in methanol. Additional detail on the preservation of VPH aqueous and soil samples is provided in Appendix 1. Information and guidance on shipping methanol-preserved samples is contained in Appendix 2.

3.5 Modifications of the VPH/EPH/APH Methods

The MADEP VPH, EPH, and APH analytical techniques are "performance-based" methods, which means that modifications to specified procedures are allowable, as long as acceptable performance is demonstrated and documented.

The most common modification of the VPH and EPH methods involves the use of a GC/MS technique to identify and quantitate collective ranges of aliphatic and/or aromatic hydrocarbons. Under this approach, a mass spectrometer is used to break up the hydrocarbon molecules in a sample into fragments with certain masses and charges. A computer program is then used to search for specified fragments that are indicative of an aliphatic and/or aromatic hydrocarbon structure. Quantitation of a collective hydrocarbon range is accomplished by comparing the total mass of these selected fragments with the mass of fragments produced by calibration standards.

While MADEP believes that a GC/MS approach has promise, it has not yet issued guidelines or recommendations in this regard. Until such time as this occurs, all laboratories conducting such modifications must be able to provide complete documentation on their procedures, and must be able to demonstrate that their methodology is capable of generating data of a known level of accuracy and precision. Specific questions that a data user might want to address to laboratories include:

- *What "ions" (fragments) were used to quantitate specific aliphatic and/or aromatic hydrocarbon ranges? How were these ions chosen? Because hydrocarbon molecules fragment in different manners and proportions, how do the fragmentation patterns of the calibration standards correlate to the fragmentation patterns of the hydrocarbons likely contained in the sample?*

- *What studies did the laboratory do to validate the method? Were "neat" petroleum products analyzed? Fresh and/or "weathered"?*

- *Based upon the choice of quantitating ions and the results of the validation studies, under what (sample chemistry) conditions would a positive or negative identification and/or quantitating bias be expected?*

While MADEP encourages laboratories to develop "better mouse traps", ultimately, it is the responsibility of the data user to determine the validity and application of data obtained from modified methods. Parties unfamiliar with analytical chemistry and/or laboratory operations are advised to seek expert advice in such matters, and understand the nature, extent, and implication of all method modifications.

3.6 Data Quality and Report Content

Because the VPH and EPH methods are performance-based, and because MADEP does not (at this time) have a laboratory certification program for non-drinking/non-wastewater matrices, it is incumbent upon the laboratory and data users to take steps to ensure and document the quality of analytical data, consistent with the provisions and requirements of 310 CMR 40.0017.

The VPH and EPH methods have detailed and specific Quality Assurance and Quality Control (QA/QC) requirements, and a required data reporting content, which is provided in Appendix 3. The reporting content is designed to ensure that data users can easily ascertain (1) what is being reported, (2) basic sample and QA/QC information, (3) whether significant modifications were made to the recommended methods, (4) whether all recommended QA/QC steps were taken, and (5) whether all specified QA/QC and performance standards were met. *While it is not necessary to obtain and provide data in exactly the same form and order detailed on the reporting sheets provided in Appendix 3, data users should insist that all indicated information and statements be provided.*

Although a comprehensive review of all QA/QC information and data is beyond the ability and/or resources of most data users, there are several quick and easy steps that can and should be taken to help ensure the accuracy and reliability of VPH/EPH/APH data, by simply reviewing the information and data required in the data report:

- ◊ ***All sample information specified in Appendix 3 should be provided, describing the sample matrix, condition of containers, and sample preservation***. VPH samples that were not preserved in the field with methanol (or sampled/preserved in an acceptable alternative manner) are highly suspect.

- ◊ ***The dates of sample collection, receipt by laboratory, extraction (EPH) and analyses should be provided.*** Samples held beyond the recommended holding times are suspect, especially EPH soil samples that are preserved only by refrigeration.

- ◊ ***A percent moisture value should be reported for all soil samples***, to ensure that such data have been adjusted to a "dry weight" reporting basis.

- ◊ ***The analytical units must be clearly indicated,*** and should be appropriate for the matrix under evaluation (i.e., µg/g, mg/kg, or µg/kg for soil; µg/L or mg/L for water; µg/m^3 or ppbv for air).

- ◊ ***Reporting Limits (RLs) should be specified for each aliphatic and aromatic range and each Target Analyte***. The VPH, EPH, and APH methods contain specific procedures and requirements on how to establish Reporting Limits, which are the minimum concentration values that a laboratory can discern and report with sufficient confidence. These values must be experimentally determined by each laboratory. Note that expected RLs for the aliphatic and aromatic ranges in water are between 50 and 100 µg/L; expected RLs for the aliphatic and aromatic ranges in soil are between 2 and 10 mg/kg; expected RLs for the aliphatic and aromatic fractions in air are between 25 and 100 µg/m^3.

- ◊ ***The percent recovery of sample surrogates should be provided, along with the acceptable range***. A surrogate is a (non-petroleum) chemical compound added ("spiked") into each VPH and EPH water and soil sample prior to extraction and analyses. The purpose of surrogate spiking is to determine the efficiency and accuracy of sample extraction (EPH), sample purging (VPH), and instrument analyses. Surrogate recovery is expressed in terms of percent recovery; for example, if 1000 µg of the surrogate compound ortho-terphenyl (OTP) is spiked onto a 10 gram soil sample that is to be analyzed by the EPH method (yielding a theoretical concentration of 100 µg/g), and the resultant analysis quantified OTP at 70 µg/g, the percent recovery would be 70%. Although sample data with surrogate recoveries outside of the stated acceptance range should be carefully evaluated, they need not be summarily dismissed or considered categorically unusable. For example, data associated with a surrogate recovery greater than specified limits may be appropriate to use as an "upper limit" value; data associated with a surrogate recovery lower than specified limits may be appropriate to use as a "lower limit", and would constitute knowledge of a release if exceeding Reportable Concentrations. Note that low recoveries are not uncommon (or unexpected) in clay/organic soil matrices. Also, low recoveries of sample surrogates may be observed in VPH soil samples with high moisture content.

- ◊ ***For the EPH Method, the percent recovery of Fractionation Surrogates should be provided, along with the acceptable range***. In the EPH method, a sample extract is loaded onto silica gel, followed by a hexane rinse, to

remove and collect aliphatics, and a methylene chloride rinse, to remove and collect aromatics. However, because of the weakly polar nature of naphthalene and substituted naphthalenes, they are easily "stripped" into the aliphatic fraction - an especially problematic occurrence in water samples, as the naphthalenes constitute a large percentage of the water-soluble fraction of fuel oils. To monitor whether this action is occurring, Fractionation Surrogates are added directly to the sample extract just prior to the silica gel fractionation step (as opposed to the sample surrogates, which are added to the soil and water samples prior to extraction, to evaluate extraction efficiency). The currently recommended Fractionation Surrogates are 2-Fluorobiphenyl and 2-Bromonaphthalene - two compounds that are not normally present in petroleum, and that have polarities similar to naphthalene. Both compounds should be detected in the aromatic fraction within the specified acceptable percent recovery ranges.

Note: Changes and refinements to the EPH Method may affect the use and selection of Fractionation Surrogates.

◊ ***The laboratory should clearly indicate whether the reported VPH/EPH/APH fractional range concentrations include or do not include the concentration of Target Analytes, and the range(s) in which the Target Analytes elute.*** By definition, these ranges exclude Target Analytes, which are evaluated separately. (Absent this exclusion, Target Analytes like BTEX and PAHs would be "double counted" - once in the collective range concentrations, and once in a separate Target Analyte evaluation). If the laboratory did not subtract out the concentrations of these Target Analytes (perhaps they only provided range data), the data user may make this adjustment. It is also permissible for a data user to adjust a range concentration value by excluding the concentration(s) of non-petroleum analytes eluting within that hydrocarbon range (e.g., TCE eluting within a C5-C8 Aliphatic Hydrocarbon range). Note that unadjusted data are also acceptable to MADEP - they are just overly conservative.

◊ ***The laboratory must clearly indicate whether significant modifications were made to MADEP VPH/EPH/APH methods, and if so, should detail the nature and extent of these modifications***. Examples of "significant modifications" are specifically listed in Section 11 of each method. Note that MADEP encourages innovation, where appropriate.

◊ ***The laboratory should clearly indicate whether it has followed and met the QA/QC program and performance standards specified by the MADEP VPH/EPH/APH Methods.*** Such an affirmation is contained in the required laboratory report content. Note that on some samples, it will not be possible to meet all QA/QC specifications, and that such data need not be summarily dismissed as unacceptable, as long as an appropriate explanation is provided, and as long as limitations inherent in the data are acceptable for the given application and use of the data.

◊ ***A report narrative should be provided, if necessary, to document and explain any deviations from the method, analytical problems, and/or QA/QC issues.*** Laboratories using modifications of the method should have on file a written Standard Operating Procedure, which should be referenced or provided as appropriate. While a failure to perform or meet the data reporting and performance standards specified above does not necessarily mean that the provided data are not of sufficient quality, it does place the burden on the data user to make this determination.

◊ ***The laboratory should certify under the pains and penalties of perjury that the information contained in the data report form is accurate and complete.*** This attestation should be done via the signature of a responsible laboratory representative.

While minimum standards are specified in the methods, to ensure a minimum level of quality for all data, there is an expectation that laboratories should be able to achieve better results on most samples. In selecting a laboratory, a data user should make sufficient inquiry into the experience of the laboratory performing these (and any other) analytical methods, and on the QA/QC program in operation to monitor, document, and improve analytical quality. In addition, the scope of laboratory services should be negotiated and clearly articulated "up front", to ensure that the data user is procuring (and the laboratory is receiving compensation for) all desired information and data (e.g., QA/QC data, narrative reports, data usability discussions, etc.).

Additional guidance and recommendations on data quality issues for the VPH/EPH methods (as wells as most other common EPA methods) can be downloaded from MADEP at: http://www.state.ma.us/dep/bwsc/files/data/QAQCDocs.htm

Analytical data and testing should not be viewed as a commodity, but as a highly technical and sophisticated professional service, requiring the same level of scrutiny and oversight as any other professional service that will be relied upon by a Licensed Site Professional in rendering a waste site cleanup opinion.

3.7 Other Hydrocarbon Testing Methods

The VPH and EPH methods were developed to provide data on the chemistry and toxicity of complex hydrocarbon mixtures, to facilitate risk evaluations and to complement MADEP Method 1 cleanup standards. However, in cases where the total concentrations of hydrocarbons are relatively low, use of these fractionation procedures may be "overkill", and a "total petroleum hydrocarbon" (and Target Analyte) evaluation may suffice. Moreover, risk characterization is not the only site assessment objective or concern at disposal sites; other characterization needs may include: petroleum product identification, petroleum source identification, and/or Remediation Waste characterization. In these cases, other analytical procedures may be more appropriate and cost-effective.

A summary of other possible analytical approaches and methodologies in this regard is provided in Table 3-2.

Table 3-2: Other Analytical Approaches

Objective	Analytical Approach	Conditions/Caveats/Comments
Characterization of Remediation Wastes	TPH, VOCs, and/or jar headspace screening. Metals, PCBs and/or TCLP often required	Need to check with disposal or recycling facility for requirements
Risk Assessment & Compliance with Cleanup Standards	TPH via an appropriate methodology. Characterize Target Analytes as needed with EPA SW-846 methodologies	Applicable for low levels of C9 and heavier hydrocarbons (i.e., when TPH concentrations will likely < TPH cleanup standards)
Determining Type of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting	Also recommended to differentiate petrogenic vs. pryrogenic PAHs
Determining Source of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting; quantitation of biomarkers	Not always definitive; requires interpretative expertise

3.7.1 Total Petroleum Hydrocarbons (TPH)

Though a widely used and conceptually-simple testing parameter, there is no universal definition of TPH, and the term is essentially defined by the analytical method chosen by the laboratory. To further complicate this matter, many laboratories use undefined and inconsistent "modifications" of published methodologies to detect and quantitate TPH concentration values (e.g., Modified EPA Method 8100). This situation has lead to a significant degree of confusion over the application, comparability, and quality of TPH data.

The MCP provides a definition of TPH at 310 CMR 40.0006:

> *<u>Total Petroleum Hydrocarbons</u> and <u>TPH</u> each mean the total or cumulative concentration of hydrocarbons with boiling points equal to or greater than 150°C [C_9] and associated with a petroleum product, as measured by standard analytical techniques and/or by procedures approved by the Department, excluding the individual compounds listed at 310 CMR 40.0974(2).*

This definition reflects the fact that the vast majority of "TPH" analyses traditionally conducted in Massachusetts involved the use of an extraction solvent (e.g., Method 418.1), which leads to the loss of lighter hydrocarbons (<C9) present in the sample. Based upon this definition, the following rules and recommendations would apply to parties electing to use a TPH analytical method to support a risk assessment or document compliance with an MCP Method 1 TPH cleanup standard:

- The TPH method and resultant data may only be used to characterize releases of petroleum products that consist of hydrocarbons primarily in the C9 to C36 range. In other words, it may only be used in lieu of an EPH procedure, not a VPH procedure. Guidance on when an EPH procedure is appropriate is contained in Table 4-6.

- In addition to the TPH analysis, all appropriate Target Analytes must also be addressed. Guidance in this regard is contained in Tables 4-3 and 4-5.

- For analytical procedures that utilize a GC/FID technique, the TPH quantitation value must be based upon the integration to baseline of all peak areas from n-Nonane (C9) to n-Hexatriacontane (C36).

- As the MCP specifically excludes "individual compounds listed at 310 CMR 40.0974(2)" from its definition of TPH, it is acceptable to adjust gross TPH values by subtracting out the collective concentrations of these individual compounds. Note that, for all intents and purposes, the "individual compounds listed at 310 CMR 40.0974(2)" are synonymous with the EPH Target Analytes listed in Tables 4-3 and 4-5.

While the MCP defines TPH to be C9 and heavier hydrocarbons, there are some TPH and/or "Gasoline Range Organics" methodologies that may collectively quantitate lighter hydrocarbons in the range of C5-C12. Typically, these methods involve the use of a purge-and-trap or headspace development technique, followed by a GC/FID analytical procedure. While these procedures may NOT be used to obtain TPH data for comparison to the MCP Method 1 cleanup standards (because of the definition of TPH at 40.0006), they can be used as a screening tool for VPH range contaminants. Specifically, if the TOTAL concentration of hydrocarbons within the C5-C12 range (excluding VPH Target Analytes) is less than the lowest VPH Method 1 standard (usually C9-C10 Aromatic Hydrocarbons), it would be safe to assume that hydrocarbon levels are within all fractional standards.

While use of TPH methods may offer certain advantages, it is the responsibility of the party using and submitting such data to ensure that the specific technique and procedure(s) used is appropriate for the disposal site in question, and that appropriate Quality Assurance and Quality Control (QA/QC) measures are taken to monitor and document the quality and usability of the generated data. In general, MADEP expects all such methods to achieve a level of QA/QC consistent with the VPH and EPH methods.

A tabulation of commonly and/or historically available TPH analytical techniques is provided in Table 3-3.

Table 3-3: Common/Available TPH Testing Methods

Method	Technique	Comments
MADEP EPH	Extraction with methylene chloride & GC/FID analysis	Use in the "TPH" screening mode by eliminating the fractionation step per Section 1.5 of EPH Method
EPA Method 1664	Extraction with n-hexane & gravimetric analyses	New method (1999) to replace Method 418.1 (Freon extraction with IR analyses)
Modified EPA Method 8100	Extraction with appropriate solvent & GC/FID analysis	Must ensure quantitation in C9-C36 range with forced baseline integration if data is used to support MCP TPH cleanup standard
Modified EPA Method 8015	Purge-and-trap or headspace sample preparation & GC/FID analysis	Must ensure quantitation in the C5-C12 range with forced baseline integration if data is to be used to screen samples for compliance with MCP VPH cleanup standards

3.7.2 Environmental Forensic Techniques

In conducting a characterization of a petroleum-contaminated site, it may be necessary and/or desirable to identify the types of petroleum product present and/or the source of their release to the environment. In recent years, new analytical testing techniques have evolved to facilitate evaluations of this nature, and support an evolving specialization known as "environmental forensics".

In order to identify the types and/or source of petroleum products that were detected at a site, (up to) a three-step analytical regiment is recommended:

- Initially, samples should be analyzed by a high-resolution gas chromatography/flame ionization detection (GC/FID) methodology. Such techniques have been utilized for many years, and are a useful "first cut" to help identify the boiling-point range of the hydrocarbon mixtures present in the sample, which can then be used to make judgments on the type(s) of petroleum product(s) released at the site (e.g., #2 fuel oil vs. #6 fuel oil). In some cases, the data obtained in this manner is sufficiently conclusive to satisfy site characterization objectives.

In other cases, however, the contamination is highly weathered, and/or intermingled with hydrocarbons of pyrogenic origin (e.g., coal ash, soot, engine emissions).

- In situations where a GC/FID evaluation is inconclusive, additional analytical characterization by a gas chromatography/mass spectrometry (GC/MS) "advanced chemical fingerprinting" technique may be advisable. These methodologies focus on the identification and quantitation of polycyclic aromatic hydrocarbons (PAHs). Although most people are familiar with the 17 priority pollutant PAH compounds quantitated by the MADEP EPH method and EPA Method 8270, there are in fact many more PAH compounds present in petroleum products. Using a GC/MS technique and sophisticated quantitation algorithm, it is possible to identify and quantitate collective groupings of these PAH compounds based upon their structure, e.g., naphthalene with a side chain containing 1 carbon atom; naphthalene with a side chain containing 2 carbon atoms, etc. The presence and distribution of these side chains can then be used to help establish the type of petroleum product(s) present at the site. Moreover, this same information – often plotted as histograms – may also be used to differentiate petroleum-derived (petrogenic) hydrocarbons from combustion-derived (pyrogenic) hydrocarbons (given that the latter are predominated by the parent PAH compound, while the former are predominated by the alkylated side chain PAH compounds).

- Data on the distribution of alkylated PAHs can often provide definitive information on the type(s) of petroleum products present at a site, and even some evidence on the specific source(s) of release. However, in order to obtain more definitive proof of the source of a petroleum release, one additional analytical tool should be considered: the identification and quantitation of biomarkers. Biomarkers are chemical compounds present in petroleum products that are the remnants of the biological life (e.g., algae, plants, bacteria) that help create the parent crude oil. While certain biomarkers are identifiable using a GC/FID methodology (e.g., pristane and phytane), the most useful compounds in this regard (e.g., terpanes and steranes) are identified using a GC/MS technique in a selected ion monitoring (SIM) mode. Because each crude oil source has a distinct "fingerprint" of biomarkers, it is often possible to identify the specific source of a release of petroleum at a site using this approach (e.g., using a statistical/multivariate component analyses), though weathering processes may sometimes decrease confidence in such conclusions.

At the present time, advanced chemical fingerprinting is an innovative technology used by only a small number of laboratories. Given this status, and given the sophistication, complexity, and professional judgment inherent in these approaches, it is essential that data users seek out facilities and personnel with the appropriate expertise and experience.

3.8 Analytical Screening Techniques

The use of analytical screening techniques is encouraged, to provide timely and cost-effective data. As the sophistication and reliability of so-called "field" methods continue to increase, the distinction between conventional laboratory and analytical screening techniques becomes less defined, and less important. However, with this increased capability and performance comes an increased need to demonstrate and document a commensurate level of quality assurance/quality control (QA/QC), consistent with the provisions and requirements of 310 CMR 40.0017.

Various levels/approaches are possible:

◊ Screening techniques may be used solely to direct remedial actions and/or sampling programs for conventional VPH/EPH testing. Because such screening data will not be used in a "stand alone" capacity, QA/QC requirements are not as critical.

◊ Screening techniques may also be employed to obtain data that will be used, in whole or in part, to assess risks and/or determine compliance with cleanup standards, and/or to support the representativeness of ("lab") data used in the risk assessment process. While it is understood that such screening methodologies may lack the qualitative or quantitative accuracy of conventional VPH/EPH testing, *the same level of QA/QC will be expected, within the limits and bounds of the stated application of the data*.

The use of screening techniques depends upon, or may be enhanced by, the use of assumptions and conditions. This approach is acceptable, as long as conservative assumptions are made, and the use of such methods and assumptions are appropriate, given contaminant chemistry, site conditions, and area receptors. A tabulation of commonly used screening techniques, and recommended applications and *Rules of Thumb*, are provided in Table 3-4.

Table 3-4
VPH/EPH Analytical Screening Techniques

Technique	Description	Range	Applications	Limitations	Recommendations
PID/FID Headspace	Soil or water sample is placed in sealed container & headspace is allowed to develop. PID and/or FID meter is then used to test the headspace for total volatile organic compounds (VOCs). Reference: Recommended DEP jar headspace procedure	VPH	Excellent screening tool for gasoline; good tool for kerosene, jet fuel and fresh fuel oil. Best used to direct remedial operations, and provide first-cut site characterization data. PID preferentially responds to the more toxic aromatic compounds.	Not appropriate for heavy mineral/ lube/fuel oils or weathered diesel/#2 fuel oil. PID can be non-linear and/or erratic for gasoline headspace vapors > 150 ppmv. PID response lessened by high humidity/ moisture (instrument dependent). Additional confirmatory analyses usually required.	For gasoline, excluding clays & organic soils, headspace readings less than 100 ppmv usually means that all VPH fractions are below 100 µg/g. Confirmatory analyses needed.
PID/FID Soil Gas	Soil gas is extracted from a probe and analyzed with a PID and/or FID meter. Reference: see Section 4.3.1.1	VPH & EPH	Use to investigate soil gas/indoor air pathways, and evaluate sites with g.w. concentrations > GW-2 Method 1 standards. PID preferentially responds to the more toxic aromatic compounds.	Instrument response is flow-dependent; must ensure adequate flow rates. PID response affected by high moisture & high petroleum vapor concentrations (>150 ppmv). FID will respond to pipeline/naturally-occurring methane.	See recommendations in Section 4.3.1.1 and Table 4-9.
UV Fluorescence & Absorbance	The absorbance or fluorescence of a UV light source is used to directly quantitate the aromatic content of soil sample. Extraction solvent, such as methanol or Isopropyl alcohol, must be used. Reference: ASTM 5831-95	VPH & EPH	Good screening tool for petroleum products with significant aromatic content (e.g., diesel/#2 fuel oil and gasoline). UV Fluorescence has lower detection limits than absorbance, but is not as linear. UV methods target the more toxic aromatic fractions.	Does not respond to aliphatics; not appropriate for petroleum products that are primarily aliphatics (mineral oils or dielectric fluids). May pick up naturally occurring humic acids - calcium oxide can be used to decrease interference.	Calibrate with aromatic standard, like C11-C22 EPH standard, for direct measurement of aromatic hydrocarbons. For diesel/#2 fuel oil, assume aliphatic content is twice aromatic. This approach may significantly over-predict aliphatic content of highly weathered diesel/#2 fuel oil. Confirmatory analysis recommended for representative/worst-case samples.
Emulsion-Based TPH Methods	Hydrocarbons are extracted from a soil sample with a solvent (e.g. methanol), and a surfactant is added to create an emulsion. Optical sensor is used to measure extract turbidity	EPH	Gives "TPH" screening values, quantitating both aromatic and aliphatic hydrocarbons. Best correlation shown with diesel/#2 fuel oil.	Does not discriminate between aliphatics and aromatics. Interference possible in organic-rich and clay soils. Not recommend for gasoline.	For diesel/#2 fuel oil, assume 60% C11-C22 Aromatics and 40% C9-C18 Aliphatics.
Immunoassay Test Kits	Soil or water samples analyzed by antibody-antigen reaction. Enzyme conjugates used to allow colorimetric analysis of antigen (contaminant) conc. Soil extraction with methanol. Reference: EPA 4030/4035	VPH & EPH	Can be used to detect specific compounds or groups of compounds (e.g., BTEX and PAHs). "TPH" methods usually target naphthalene, and assume correlation to TPH.	Because antibodies bind with specific antigens (contaminants), cannot directly quantitate collective aliphatic/aromatic fractions or total hydrocarbons. Not effective for lube/hydraulic oils.	No general assumptions can be made. Each kit and application has to be individually evaluated.
Fiber-Optic Chemical Sensors	Probe with hydrophobic/organo-phyllic optical fiber is lowered into a well. Change in refraction index used to est. hydrocarbon conc. in groundwater	VPH & EPH	Allows in-situ measurements of volatile and semi-volatile dissolved hydrocarbons. Results calibrated to a p-xylene response. In-situ vapor measurement also possible.	Response decreases with increasing solubility; response to benzene 10 times less than p-xylene. Significant calibration/cleaning requirements between uses.	Insufficient information available to offer general recommendations.

3.8.1 Principles of Operation, Biases, and Calibration

All screening techniques and instruments are predicated upon certain principles of operation, detection, and calibration. Many have limitations and biases that need to be understood and accommodated. For example, an immunoassay "TPH" test method may be designed to detect the presence of naphthalene, and then extrapolate a TPH concentration based upon an assumption on the percentage of naphthalene in fresh fuel oil. Thus, two important assumptions and biases are present: (a) the concentration of a single compound (naphthalene) can be used to determine the concentration of a product which is made up of numerous (perhaps hundreds of) hydrocarbon compounds, and (b) the chemistry of a fresh fuel oil standard can be used to estimate the chemistry of a field sample. As such, a highly weathered fuel oil sample, or a fuel product low in naphthalene (e.g., mineral oils) may not yield reliable results.

To effectively use analytical/screening techniques, especially for risk and cleanup decisions, it is incumbent upon the data user to:

1. understand the application and limitations of the screening method(s) of interest;

2. consider site-specific contaminant/mixture chemistry and fate/transport processes; and

3. determine the precision and accuracy boundaries of the generated data, to see if they meet the desired data quality objectives and site characterization needs (e.g., if data can be considered accurate at 100 µg/g +/- 300%, and the cleanup standard is 500 µg/g, it may be acceptable).

In general, the following recommendations are offered:

◊ Techniques that detect a structural class and/or range of compounds are preferred, as opposed to methods that rely upon one specific indicator compound. Techniques that detect a range of compounds include PID/FID headspace techniques, UV absorbance/fluorescence, and emulsion-based TPH techniques. Procedures that target a single indicator compound require sufficient site-specific correlative and confirmatory data.

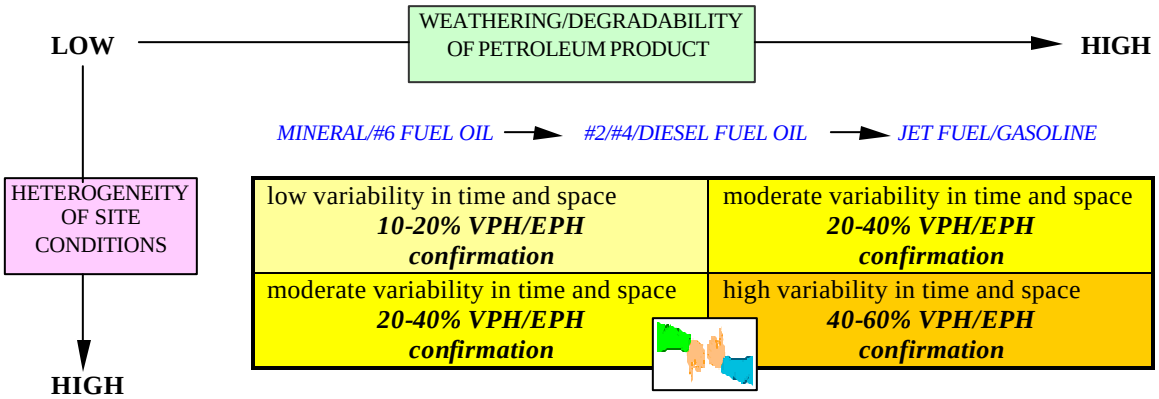
◊ Techniques that target aromatic hydrocarbons are preferred, as opposed to methods that target aliphatic compounds, due to the fact that aromatic hydrocarbons are, as a class, more toxic and mobile than aliphatic hydrocarbons. *On the whole, it is better to be able to accurately quantitate collective aromatic hydrocarbons, and estimate aliphatics, than to accurately quantitate collective aliphatic hydrocarbons, and estimate aromatics*. Techniques that target aromatics include PID headspace and UV absorbance/fluorescence.

◊ Techniques that involve a quick "shake out" extraction technique for soil analyses may not be sufficient for clay or organic-rich soils, due to partitioning efficiencies.

3.8.2 Recommended Approach

For small sites, such as residential underground storage tank (UST) excavations, screening techniques are perhaps best used to direct soil removal operations, identify areas for assessment and/or confirmatory VPH/EPH laboratory analysis, and/or provide a database to support the representativeness of decision-quality data. For larger sites, the use of screening data as a substitute and complement for VPH/EPH laboratory data may provide a better and less expensive approach to site characterization. For example, for the price of a single EPH test (approximately $200), it may be possible to perform 4 to 10 field screening analyses. So, for a sampling and analytical budget of $2000, it may make sense to take 8 EPH samples, and 8 to 20 field-screening samples, rather than (just) 10 EPH samples. The minimum number of VPH/EPH laboratory samples needed to understand contaminant chemistry, and provide confidence in screening data, is necessarily site-specific. The key variables are the heterogeneity of site conditions (stratigraphic/microbiological), source vs. migration areas, and the degradability of the petroleum product(s). Generalized *Rules of Thumb* in this regard are provided in Table 3-5. Note that additional confirmatory sampling would be indicated if sufficient correlation could not be established between the VPH/EPH values and screening/TPH values.

Table 3-5: Recommended Minimum VPH/EPH Laboratory Confirmation Data Needed to Support Analytical Screening



3.9 Drinking Water Testing Methods

When testing a potable drinking water supply, the use of the VPH/EPH analytical methods should be limited to quantitation of hydrocarbon ranges of interest; specific analytes of interest should be quantitated using the appropriate EPA "500" series drinking water methods.

4.0 CLEANUP STANDARDS

The Massachusetts Contingency Plan (MCP) provides three methods to assess risks and determine *how clean is clean enough*:

- ◊ Method 1 - generic cleanup standards in soil and groundwater
- ◊ Method 2 - site-specific modification of generic cleanup standards
- ◊ Method 3 - completely site-specific risk assessment

The easiest approach is Method 1, in that cleanup standards have already been established by MADEP. In support of the VPH/EPH approach, 6 generic standards have been developed and promulgated for the aliphatic and aromatic fractions of interest. A conservative TPH standard has also been retained, to allow continued use of such methods. *Note that it is not necessary to meet a TPH cleanup standard (or Reportable Concentration) if all 3 EPH fractional standards are achieved [see 310 CMR 40.0973(7) and 40.0360(2)].*

Because the Method 1 standards are generic, and were calculated assuming conservative site conditions, they can overestimate risk at some sites. In such cases, use of a Method 2 or 3 alternative approach may be advisable and cost effective. Guidance and recommendations in this regard are provided in Table 4-1.

For complete information and guidance on the use of the MCP risk assessment methods, consult the Massachusetts Contingency Plan at 310 CMR 40.0900, and MADEP's *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan*, available at http://www.state.ma.us/dep/ors/orspubs.htm .

Table 4-1: Choosing an MCP Risk Assessment/Cleanup Method

Method	Consider Using If.....	Significant Limitations
1	♦ simple/small site ♦ contamination in soil and gw only ♦ cleanup to Method 1 standards is feasible	◊ cannot be (solely) used if sign. sediment contam ◊ cannot be (solely) used if sign. indoor air impacts [see 40.0942]
2	♦ groundwater concentrations > GW-2 standards ♦ groundwater concentrations > GW-3 standards ♦ sites in GW-1 areas and C9-C10 or C11-C22 Aromatic fraction(s) in soil > Method 1 stds	◊ can't use if sign. sediment contamination ◊ can't use if sign. indoor air impacts [see 40.0942]
3	♦ complex/large sites ♦ sites with indoor air impacts ♦ sites with sediment contamination ♦ sites with soil/gw > Method 1 standards	◊ can't achieve permanent solution if: (1) more than 0.5 inches NAPL, or (2) above drinking water std in GW-1 area; or (3) soil conc above Upper Conc Limits (UCLs) unless deeper than 15' or below engineered barrier; or (4) gw conc > UCL

4.1 Exposure Point Concentrations

Regardless of the risk assessment method selected, it is necessary to calculate Exposure Point Concentrations in media and pathways of interest.

4.1.1 Groundwater EPCs

In accordance with the provisions of 310 CMR 40.0924(2)(a)(1.), when using a Method 1 or 2 Risk Characterization approach, EACH well and/or groundwater monitoring point is a separate Exposure Point, and data from each well is considered a separate Exposure Point Concentration. Accordingly, the (temporal) average concentration of dissolved analytes in EACH monitoring well cannot exceed appropriate GW-1, GW-2, and/or GW-3 standards (i.e., spatial averaging of data among wells is not permitted). More flexibility is allowed in a Method 3 risk assessment, with the exception of GW-1 areas [40.0924(2)(b)(2.)].

Because groundwater is a dynamic medium, a single "snapshot in time" is generally not sufficient to characterize contaminant levels, and calculate Exposure Point Calculations. ***Except for petroleum products with a low water soluble fraction, it is generally not possible to adequately characterize groundwater quality on the basis of a single round of sampling.*** Seasonal and antecedent precipitation events can significantly influence groundwater quality in any given well on any given day. Over the course of a year, temporal fluctuations in the concentration of dissolved analytes in monitoring wells can be substantial; variation by factors of 2-3 are common at most sites, and factors of up to 5-10 are possible, especially for water table wells, and when monitoring low levels of analytes (i.e., < 50 µg/L).

The amount of spatial and temporal monitoring data needed to make reasonable and meaningful conclusions on groundwater quality is necessarily a site-specific decision, based upon (1) the type/water-solubility of the petroleum product(s) released, (2) the homogeneity of the formation, (3) the sensitivity of potential pollutant receptors, (4) the magnitude of contaminant concentrations (with respect to the standard(s) of interest), and (5) the degree of confidence and understanding of the Conceptual Site Model.

Table 4-2 provides the minimum recommended number of rounds of groundwater sampling at petroleum-contaminated sites where NAPL is not present. A preferred approach is to obtain at least 4 measurements over a 1-year period, coinciding with seasonal variations. **In cases where less than 1 year of quarterly monitoring has been performed, it is necessary to consider and address expected variations in analyte concentrations over time (especially in cases where limited sample data is *just below* the applicable standard).**

Table 4-2 Minimum Recommended Quarterly Rounds of Groundwater Monitoring at Sites Where NAPL is Not Present

Location/GW Category	Gasoline/ JP-4	Diesel/#2-4 Fuel/Kerosene	Mineral/Lube/#6 Fuel Oil
< 800 feet from water supply	4+	3-4	2-3
GW-2	2-3	2	1
GW-3	1-2	1-2	1

It is important to stress that the recommendations provided above are for *quarterly* sampling efforts, with each quarter comprising a 3-month time period coinciding with spring, summer, fall, and/or winter conditions. Multiple sampling rounds in any given season, while providing potentially useful site data, cannot be considered equivalent to multiple samples over multiple seasonal conditions.

Beyond the general concerns and recommendations provided above for all sites, additional monitoring efforts are necessary at sites where groundwater remediation has been undertaken, to determine if contaminant "rebound" has occurred (i.e., a significant increase in dissolved groundwater contaminant concentrations that occurs as contaminants partition and diffuse from and near soil solids). In such cases, groundwater monitoring should be systematically conducted for at least 6 - 9 months after the termination of all remedial activities.

4.1.2 Soil EPCs

A general discussion of issues and recommendations for the development and calculation of soil Exposure Point Concentrations (EPCs) is contained in *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan.* Of particular interest at petroleum-contaminated sites is the evaluation of subsurface soil contamination associated with releases from Underground Storage Tanks (USTs). In this regard, when obtaining soil samples at an UST grave for the purposes of determining an EPC, it is necessary to specifically investigate whether a "hot spot" exists within the groundwater table fluctuation zone (i.e., the "smear zone"). For gasoline and fresh diesel/fuel oil releases, this action may be easily accomplished by headspace analysis of samples from sidewall excavations using a PID meter. In cases where headspace concentrations within this smear zone are equal to or greater than 10 times other locations on the sidewall, soil samples from this zone should be discretely collected/composited (either as the sidewall sample or with other sidewall samples) for appropriate analyses.

4.1.3 Indoor Air EPCs

Extensive guidance on this subject is provided in the *MADEP Indoor Air Sampling and Evaluation Guide*, available at http://www.state.ma.us/dep/ors/files/indair.pdf. When evaluating indoor air impacts at disposal sites, however, it is important to understand and differentiate sampling and evaluation objectives and requirements.

Specifically, when the objective is to calculate indoor air EPCs for the purpose of conducting a quantitative risk assessment, temporal and/or spatial averaging of data may be appropriate. Conversely, when the objective is to determine whether a Critical Exposure Pathway (CEP) is present at a home or school, averaging of this nature is NOT appropriate; rather, data from "worse case" site conditions are of interest. Additional discussions in this regard are provided in Section 4.3.

4.2 Method 1 Cleanup Standards

Generic soil and groundwater cleanup standards have been developed by MADEP for the 3 hydrocarbon fractions detected using the VPH analytical procedure (i.e., C5-C8 Aliphatics, C9-C12 Aliphatics, and C9-C10 Aromatics) and the 3 hydrocarbon fractions detected using the EPH analytical procedure (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics). These standards are designed to be protective at most sites, and were developed using a series of conservative site scenarios to evaluate risks to human health, public welfare, and the environment via a number of exposure pathways and concerns, including direct contact, ingestion, leaching (soil), and volatilization (groundwater).

Method 1 cleanup standards have been developed for 3 categories of groundwater (see 310 CMR 40.0932):

- ◊ **GW-1 Standards** - applicable in (GW-1) areas where groundwater is or may be used for drinking water purposes. The GW-1 standards are based upon ingestion/use of groundwater as a potable water supply.

- ◊ **GW-2 Standards** - applicable in areas within 30 feet of an occupied structure if the depth to groundwater is less than 15 feet from the ground surface. GW-2 standards are based upon inhalation exposures that could occur to occupants of a building impacted by volatile compounds which partition from shallow groundwater.

- ◊ **GW-3 Standards** - applicable at all sites. GW-3 standards consider impacts to aquatic receptors in surface water bodies that receive recharge from a contaminated groundwater plume.

Based upon the above, it can be seen that any given disposal site may fall in one, two, or all three categories. At sites where more than one category applies, groundwater contaminants must be at or below all applicable GW standards in all applicable categories in order to demonstrate a condition of "No Significant Risk" per Method 1.

Method 1 cleanup standards have also been developed for 3 categories of soil (see 310 CMR 40.0933):

- ◊ **S-1 Standards** - applicable to soils that are accessible or potentially accessible, and where the frequency and/or intensity of exposure is high.

- ◊ **S-2 Standards** - applicable to less accessible soils, with lower exposure potential.

- ◊ **S-3 Standards** - applicable to isolated soils, and/or soils where the frequency and/or intensity of exposure is low.

Because all soil standards consider leaching impacts to underlying groundwater, and because there are 3 groundwater categories, there is a matrix of nine possible Method 1 soil standards for each contaminant (e.g., S-1/GW-1, S-1/GW-2, etc.). As with the GW standards, any given disposal site may fall in one or more of these nine soil standards. At sites where more than one category applies, soil contaminants must be at or below all applicable "S-x/GW-y" standards in all applicable categories in order to demonstrate a condition of "No Significant Risk" per Method 1.

In addition to the human health and environmental exposures described above, all Method 1 standards are bounded by certain *basement* and *ceiling* conditions established by MADEP. As a lower limit, no Method 1 standard is set below a background or analytical reporting limit, even if the risked-based concentration was less than this value. On the other extreme, no Method 1 standard is set above a series of "ceiling" concentrations established for classes of soil and groundwater contaminants. Ceiling levels were established to account for exposure pathways and factors that were not considered in developing these generic standards, including "public welfare" concerns related to odors. The ceiling level in groundwater is set at 50,000 µg/L; the ceiling levels in soil are 100, 500, 1000, 2500, and 5000 µg/g, depending upon the soil category (i.e., S-1, S-2, or S-3) and the vapor pressure and/or Odor Index of the compound or hydrocarbon range of interest. Additional information on ceiling levels and Method 1 standards are provided in the MADEP publication *Background Documentation for the Development of the MCP Numerical Standards*, April 1994, and as amended, which is available and may be downloaded from http://www.state.ma.us/dep/ors/orspubs.htm.

4.2.1 Using Method 1 VPH/EPH Fractional Standards

Using Method 1 to characterize a petroleum release is a two step process:

- Step 1 - identify and evaluate individual Target Analytes of interest, to address specific hydrocarbon constituents of concern, including carcinogenic compounds; and

- Step 2 - identify and evaluate aliphatic/aromatic fractions of interest, to address the rest of the hydrocarbon mixture.

Note: When using Method 1 fractional standards, it is necessary to have some actual (VPH/EPH) fractional range data. Although it is possible to make assumptions on the aliphatic/aromatic breakdown of TPH and GRO data, and demonstrate compliance with cleanup standards without any VPH/EPH data, such actions must be undertaken as part of a Method 3 Risk Characterization process. Alternatively, TPH data may continue to be compared directly to Method 1 TPH standards, at sites contaminated by heavier petroleum products.

4.2.2 Target Analytes

Target Analytes are those constituents of petroleum which have traditionally been used to characterize environmental pollution, and for which MADEP has specific Method 1 cleanup standards: benzene, toluene, ethylbenzene, xylenes, MtBE, lead, Ethylene Dibromide, and the 17 "priority pollutant" PAHs. *By definition, Target Analytes are not counted within the VPH and EPH Aliphatic and Aromatic hydrocarbon fractions.*

It is not necessary to test all media and all petroleum releases for all Target Analytes; this decision is site-specific, based upon (1) the type (chemistry) of the petroleum product(s) released, (2) fate and transport considerations, and (3) the sensitivity of area receptors. Guidance and *Rules of Thumb* on the most commonly released petroleum products, based upon Total Organic Vapor (TOV) headspace screening and/or TPH data, are provided in Table 4-3.

Table 4-3: Recommended Target Analyte List for Petroleum Products

Petroleum Product	Media	Headspace TOV	TPH	Recommended Target Analytes
Gasoline	soil	------	-----	benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
	gw	-----	-----	benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
#2 Fuel/Diesel	soil	≥100 ppmv	-----	benzene, toluene, ethylbenzene, xylenes, naphthalene
		-----	>500 µg/g	acenaphthene, naphthalene, 2-methylnaphthalene, phenanthrene
	gw	------	-----	acenaphthene, naphthalene, 2-methylnaphthalene, phenanthrene; in GW-1, test also for BTEX, MtBE[1]
#3-#6 Fuel Jet Fuels Kerosene Lube Oils Hydraulic Oils	soil	≥100 ppmv	-------	benzene, toluene, ethylbenzene, xylenes, naphthalene
		--------	------	17 priority pollutant PAHs, unless justification not to
	gw	------	-----	If in GW-1 area, test for BTEX and 17 priority pollutant PAHs
Waste Oils	soil	≥ 10 ppmv	-----	BTEX/VOCs, PAHs, PCBs, heavy metals
		-----	-----	PAHs, PCBs, heavy metals
	gw	-----	-----	BTEX/VOCs, PAHs, PCBs, heavy metals

[1]While MtBE is not an additive in fuel oils, it may become present during the transport and distribution process due to mixing of residue product

4.2.2.1 Petroleum Product Additives

The topic of petroleum product additives warrants special consideration with respect to the selection of Target Analytes.

Since 1923, organic, inorganic, and/or organo-metallic compounds have been added to petroleum products to enhance performance characteristics or address operational or air pollution concerns. While additives of this nature have been numerous – and often proprietary – the list of common additives with significant environmental concerns is relatively small. Details in this regard are presented in Table 4-4.

Table 4-4: Common Gasoline Additives (Massachusetts)

Additive	Purpose	Amount Added	Peak Years	Analytical Methods (soil/groundwater)
alkyl leads (tetraethyl lead; tetramethyl lead)	anti-knock/octane enhancer	1-2.5 grams/gal	1923-1981 (automotive gasoline)	Total Pb via ICP-AES (EPA 6010B) or AAS (EPA 7000); alkyl Pb by California LUFT/ DHS or other proced.
		2-4 grams/gal	1920s-present (aviation gasoline)	
Ethylene Dibromide (EDB)	"scavenger" in leaded gasoline	variable	1923-1981 (cont use in aviation gasoline	EPA Method 8260B or EPA Method 8021B
MtBE	octane enhancer	1-8% by volume	1979-1991	MADEP VPH; EPA Method 8260B[a]
	oxygenate	10-15 % by volume	1991-present	MADEP VPH; EPA Method 826OB[a]

[a] acidification of aqueous samples can lead to significant breakdown of MtBE

4.2.2.2 Petroleum Product Additives as Target Analytes

Rules of Thumb on the selection and analysis of specific petroleum product additives as Target Analytes are provided below:

- Given its history of use as an octane enhancer and oxygenate in New England, *MtBE* should always be considered a soil and groundwater Target Analyte of concern (all soil and groundwater categories) at disposal sites where a release of unleaded gasoline occurred or likely occurred after 1979.

- In addition to unleaded gasoline, *MtBE* should also be considered a groundwater Target Analyte of concern within the GW-1 areas of disposal sites where a release of #2 fuel/diesel oil occurred or likely occurred after 1979. Although not (purposely) added to these products, it is believed that trace levels of MtBE are introduced into stocks of #2 fuel/diesel oil during the storage and transportation process. Recent studies have identified the presence of low to moderate concentrations of MtBE within the groundwater at sites contaminated (solely) by a release of #2 fuel/diesel oil.

- *Lead* and *Ethylene Dibromide* should be considered groundwater Target Analytes of concern within the GW-1 areas of disposal sites where a release of gasoline occurred or likely occurred prior to 1988. In addition, *Lead* should be considered a soil Target Analyte of concern within the S-1 areas of disposal sites where a release of leaded gasoline occurred or likely occurred prior to 1988. Because alkyl lead complexes are expected to break down into inorganic salts within a 15-year timeframe, use of a "total lead" methodology (e.g., AA/ ICP) is generally appropriate and sufficient in such cases.

- *Lead* and *Ethylene Dibromide* should be considered soil and groundwater Target Analytes of concern (all soil/groundwater categories) at disposal sites where a release of leaded gasoline occurred or likely occurred after 1987. Due to their toxicities, it may be necessary to use analytical methods capable of detecting and quantitating the specific alkyl lead compounds of concern (e.g., tetraethyl lead). Although there are few published methods for alkyl lead analysis, one procedure is provided in the California LUFT Manual (http://www.swrcb.ca.gov/general/publications/docs/luft-manual-1989.pdf)

A summary of the above recommendations is provided in Table 4-5.

4.2.2.3 Ethanol

Because of its persistence and mobility in the environment, which has lead to wide-scale groundwater contamination, the use of MtBE as a gasoline additive will likely be reduced or eliminated in the coming years. The most likely replacement for MtBE is ethanol, which is already a widely used oxygenate in

Table 4-5: Recommended Target Analyte List for Petroleum Additives

Petroleum Product Released at Site	Date of Release	Recommended Target Analyte(s)	Soil Category			Groundwater Category		
			S-1	S-2	S-3	GW-1	GW-2	GW-3
Unleaded Gasoline	≥1979	MtBE	✓	✓	✓	✓	✓	✓
#2 Fuel/Diesel Oil	≥1979	MtBE[1]				✓		
Leaded Gasoline	≤1987	Total Lead	✓			✓		
		EDB				✓		
Leaded Gasoline	>1987	Lead/alkyl leads	✓	✓	✓	✓		✓
		EDB	✓	✓	✓	✓	✓	✓

[1]While MtBE is not an additive in fuel oils, it may become present during the transport and distribution process due to mixing of residue product

certain parts of the United States, and, in fact, has already been identified at some gasoline release sites in Massachusetts. To date, MADEP has not established a Method 1 standard for ethanol, though it is considered a "hazardous material" under the MCP (see 310 CMR 40.1600). Until such time as the use of ethanol becomes more widespread in Massachusetts, it is not necessary to routinely test for this additive at disposal sites, except as noted below:

- In cases where ethanol is *known* to have been present in gasoline released at a disposal site (e.g., based upon information provided by a service station owner), sampling and analysis for ethanol should be *considered*, based upon the nature of site conditions and sensitivity of surrounding receptors;

- In cases where a release of gasoline has contaminated a drinking water supply, and where ethanol is *known* or *suspected* to be present in the gasoline released at the site (e.g., lack of MtBE contamination), a sample of the drinking water should be analyzed for ethanol.

Note that while ethanol is believed to be less toxic than MtBE, and, unlike MtBE, readily biodegradable under both aerobic and anaerobic conditions, elevated concentrations in the environment may result in certain adverse impacts:

- Due to cosolvency effects, the presence of high concentrations of ethanol may lead to increased levels of gasoline constituents in groundwater, including the Target Analytes benzene, toluene, ethylbenzene, and xylenes (BTEX).

- Because of its highly biodegradable nature, ethanol exerts a high biochemical oxygen demand that can quickly deplete oxygen (and nutrient) levels in the area of contamination, which may lead to longer plumes of BTEX and other dissolved gasoline hydrocarbons. This phenomenon has implications to natural attenuation considerations, and bearing on the design of enhanced and engineered bioremediation systems at such sites.

4.2.2.4 Additional Petroleum Additives

In general, beyond the recommendations contained above, it is not necessary to routinely test for additional petroleum product additives at disposal sites. At disposal sites where releases of gasoline or diesel fuel have impacted drinking water supplies, however, samples of the impacted drinking water should be analyzed (a) by EPA Method 8260B for all method analytes and for Tentatively Identified Compounds (TICs), and (b) for the metals listed in Method EPA 6010B, excluding the common "background" elements calcium, iron, manganese, and sodium. Such an action is appropriate given (i) the wide variety of chemical additives in

petroleum products, (ii) the relative mobility of volatile organic compounds and certain metal salts and complexes, and (iii) the sensitivity of the exposure pathway.

4.2.3 Hydrocarbon Fractions of Interest

It is not necessary to test all media and all petroleum releases for all 6 VPH/EPH hydrocarbon fractions; this decision is also site-specific, based upon (1) the type (chemistry) of the petroleum product(s) released, (2) fate and transport considerations, and (3) the sensitivity of area receptors. Guidance and *Rules of Thumb* on ranges of interest, as determined by either the VPH or EPH test method, are provided in Table 4-6 for the most commonly released petroleum products.

When using a Method 1 approach, each VPH/EPH fraction is treated as if it were a single entity or unique chemical. The general rules that apply to Method 1 Risk Characterization, such as averaging data and hot spot determinations, also apply to these aliphatic and aromatic fractions.

Table 4-6: Hydrocarbon Fractions of Interest

Petro Product	Media	VPH	EPH	Comments/Caveats
Gasoline	soil	✓		
	gw	✓		
Fresh Diesel/#2 Fuel	soil	✓	✓	"Fresh" is defined as soil/gw with TOV headspace ≥ 100 ppmv
	gw	✓	✓	
Weathered Diesel/#2 Fuel	soil		✓	"Weathered" defined as soil/gw with TOV headspace < 100 ppmv
	gw		✓	VPH testing recommended if potentially/impacting a water supply
#3-#6 Fuel Oil Hydraulic Oil	soil		✓	
	gw		✓	VPH testing recommended if potentially/impacting a water supply
Mineral/Di-electric Fluids	soil		✓	
	gw		✓	VPH testing recommended if potentially/impacting a water supply
Jet Fuel JP-4 JP-8	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace < 100 ppmv
	gw	✓	✓	
Jet Fuel Jet A / Kerosene	soil		✓	
	gw		✓	VPH testing recommended if potentially/impacting a water supply
Waste Crankcase Oil	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace < 10 ppmv
	gw	✓	✓	
Unknown Oils	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace < 10 ppmv
	gw	✓	✓	

For samples analyzed by both the VPH and EPH test procedure, there are two methodological issues that warrant discussion and clarification:

◊ When a (split) sample is analyzed by both the VPH and EPH methods, it is not necessary to quantitate or address a (VPH) value for C9-C12 Aliphatic Hydrocarbons, as these hydrocarbons are included within the C9-C18 Aliphatic Hydrocarbon range detected by the EPH test method. Note that there may be cases where the C9-C12 Aliphatic concentration via the VPH test method exceeds the C9-C18 Aliphatic concentration quantitated by the EPH method – this dichotomy occurs because the VPH method tends to over-quantitate aliphatics in this range (because the FID is also quantitating aromatic compounds). In general, the EPH method should provide more accurate data for this range.

◊ In cases where Target Analytes are quantitated by both the VPH and EPH methods, naphthalene will be reported by both procedures. Because it is within the dividing region between purgeable and extractable organics, naphthalene is a problem analyte in both methods: it's the heaviest VPH compound, and difficult to purge, while at the same time being the lightest EPH compound, and therefore subject to volatilization losses during the EPH extraction process. *Accordingly, in such cases, the highest reported value should be used.*

4.2.4 Limitations on the Use of Method 1 Cleanup Standards

Because of the generic assumptions used in the development of the Method 1 standards, they are not appropriate, and cannot be (solely) used at all sites. The most significant limitations in this regard for VPH/EPH standards are:

- there must be a Method 1 standard for all Contaminants of Concern (including any non-petroleum contaminants); and

- the contamination must be limited to just soil and groundwater, and cannot be present in sediments, air, or surface water.

4.2.4.1 Hydrocarbons

With respect to Contaminants of Concern, if only petroleum products are present at a site, there should be no limitations on the use of the Method 1 standards, as the collective VPH and EPH fractional ranges should address all detected constituents. Note that these collective range standards eliminate problems that arose in the past when laboratories using a GC/MS technique would report petroleum constituents, such as trimethylbenzenes, which did not have a Method 1 Standard - and which therefore called into question the applicability of Method 1. It also follows that this practice of identifying additional petroleum (non-target) analytes is no longer necessary, as long as the compound in question is a petroleum constituent that is collectively quantitated in a hydrocarbon range of interest (e.g., the trimethylbenzenes are picked up in the C9-C10 Aromatic Hydrocarbon range detected by the VPH test method).

4.2.4.2 Additives

At present, Method 1 standards exist only for lead and MtBE. If other additives are identified at a disposal site, it will be necessary to evaluate risks using a Method 2 or Method 3 risk assessment process.

4.2.4.3 Air-Phase Contamination

With respect to contamination present in a medium other than soil or groundwater, the most common and problematic limitation occurs when hydrocarbon contaminants are present in the ambient or indoor air at a site. Since this exposure was NOT considered in the development of the Method 1 cleanup standards, a Method 3 assessment must be conducted in such cases.

Volatile non-aqueous phase liquids (NAPL), including separate-phase gasoline, kerosene, jet fuels, and fresh diesel/#2 fuel oils, can result in the generation of significant concentrations of volatile petroleum hydrocarbon vapors in the vadose zone, which can potentially impact the indoor air of nearby structures. Purging a monitoring well containing such NAPL prior to obtaining a groundwater sample may underestimate risks of this nature, as the groundwater sample may contain relatively low concentrations of dissolved hydrocarbons. *For this reason, soil gas investigations should be considered at any site at which volatile NAPL has been identified in monitoring wells or test pits, to characterize the risks posed to indoor air quality, and determine whether use of a Method 1 approach is appropriate.*

4.2.5 Odors

Odors are an indication that hydrocarbon compounds are present in another medium (air) beyond soil or groundwater (although a lack of odors does not mean that hydrocarbon compounds are <u>not</u> present). Such odors could constitute a significant risk to human health, and/or a nuisance condition that may be considered a significant risk to public welfare.

For this reason, Method 1 cleanup standards should not be used at sites with the following odor conditions:

- ◊ persistent, long term (>3 months) odors in the ambient air at a disposal site; or
- ◊ persistent, long term (>3 months) odors in the indoor air of a building impacted by a disposal site.

Short term, ephemeral odors, and/or odors noted at depth during subsurface excavation or exploration, would not, by themselves, invalidate the use of a Method 1 approach.

A tabulation of Method 1 Cleanup Standards for the VPH/EPH hydrocarbon fractions, and TPH, is provided in Appendix 4. Note that these values are current as of the date of this publication, but are subject to change. For a current list of cleanup standards (and Reportable Concentrations), consult the most current version of the Massachusetts Contingency Plan.

4.3 Method 2 Risk Characterization

Using Method 2, site-specific fate and transport factors and considerations may be used to modify certain Method 1 standards. The Method 1 standards that are most likely to be exceeded at petroleum contaminated sites, and for which a Method 2 approach may be advisable, are listed in Table 4-7.

Table 4-7: Method 1 Standards Most Likely to be Exceeded

Contaminant	Groundwater		Soil (standards based upon leaching)		
	GW-2 (µg/L)	GW-3 (µg/L)	S-1/GW-1 (µg/g)	S-2/GW-1 (µg/g)	S-3/GW-1 (µg/g)
C5-C8 Aliphatics (VPH)	✓	✓			
C9-C12 Aliphatics (VPH)	✓				
C9-C10 Aromatics (VPH)	✓	✓	✓	✓	✓
C9-C18 Aliphatics (EPH)	✓				
C11-C22 Aromatics (EPH)		✓	✓	✓	✓
benzene			✓	✓	✓
2-Methylnaphthalene			✓	✓	✓
naphthalene			✓	✓	✓

A summary of recommended Method 2 assessment approaches and limitations is provided in Table 4-8.

Table 4-8: Use of Method 2 at Petroleum-Contaminated Sites

Site Condition	Method 2 Assessment Actions	Limitations
groundwater concentration > GW-2 Std	Evaluate potential for dissolved hydrocarbons in groundwater to impact indoor air of adjacent structures	Assessment limited to demonstration of "no impacts" to structure, based upon actual field data
groundwater concentration > GW-3 Std	Evaluate potential for dissolved hydrocarbons in groundwater to impact receiving surface water body	Cannot modify to exceed an Upper Concentration Limit or have ≥ 0.5 inches NAPL
soil concentration > Soil Standard	Evaluate potential for hydrocarbons to leach from soil and impact underlying groundwater	Cannot modify to exceed an appropriate "direct contact" soil-exposure concentration [40.0985(6)]

Two important limitations to a Method 2 approach at petroleum-contaminated sites warrant additional emphasis:

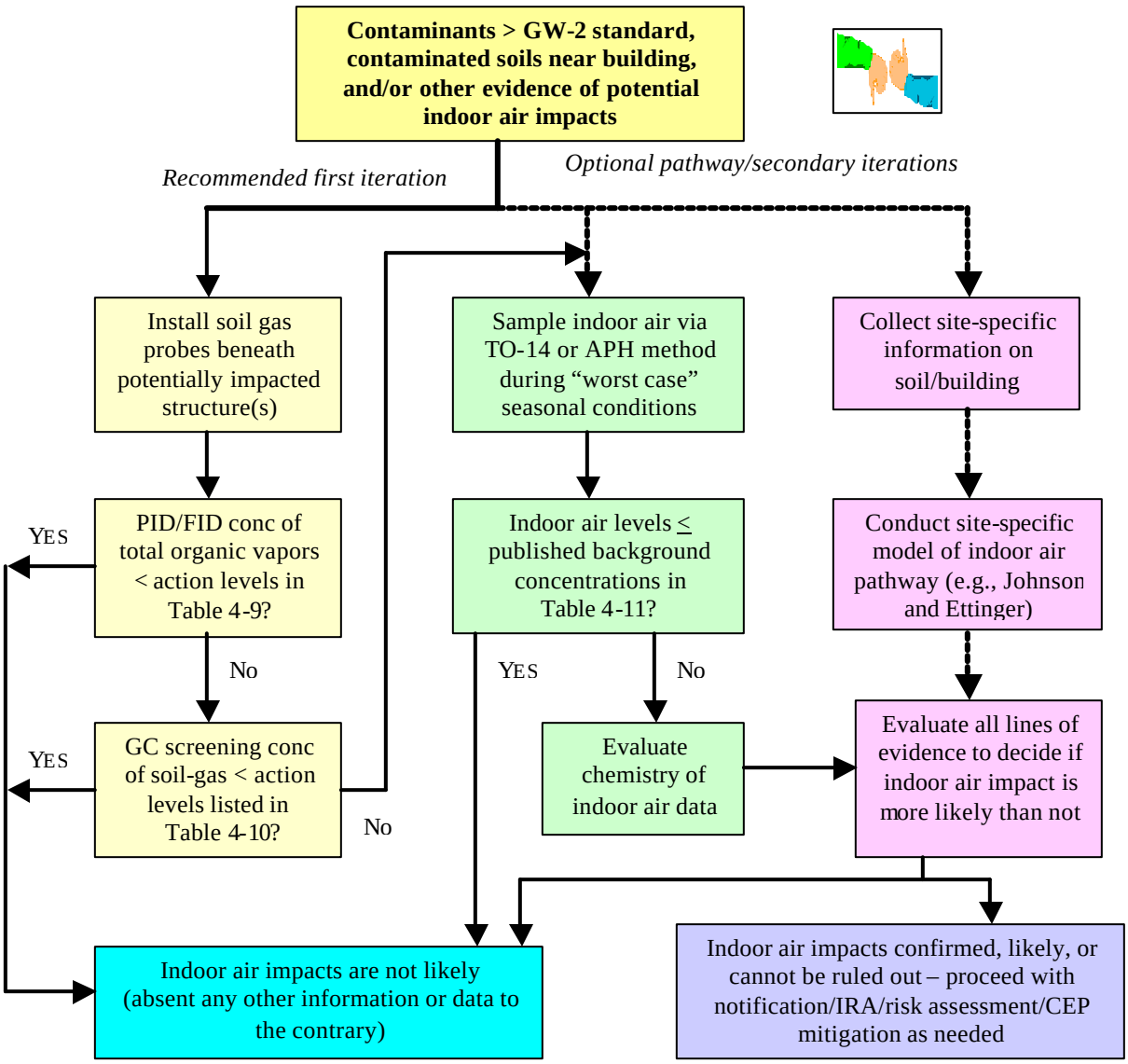
- * Method 2 may **NOT** be used to modify an applicable Method 1 GW-1 standard, including the VPH/EPH fractional standards; and

* Fate and transport models may **NOT** be (solely) used to evaluate or "rule out" an impact to indoor air from dissolved concentrations of the VPH/EPH fractions in groundwater. This prohibition is due to the fact that the GW-2 standards for the VPH/EPH fractions were not directly calculated from a modeling exercise, because of a lack of relevant fate/transport and toxicological information. Thus, because there are no generic modeling assumptions for these fractions, there are no direct site-specific modeling modifications possible via a Method 2 approach.

4.3.1 Using a Method 2 Approach to Demonstrate "No Impact" to Indoor Air

At sites where a Method 1 GW-2 standard is exceeded for a VPH/EPH fraction and/or Target Analyte, a multi-level, progressively structured investigatory program is recommended, to obtain sufficient information and data to determine whether an impact to indoor air has occurred or is likely to occur. This same approach may be used to investigate concerns over the presence of contaminated soils in close proximity to a building. At some sites, conclusions in this regard are relatively clear; at others, a "tool-box" approach may be needed to establish lines of evidence to make such a determination. In most cases, an optimal and cost-effective tool-box approach is to proceed along a continuum of low-cost/conservative-efforts toward higher-cost/more-accurate-techniques, using the cumulative totality of information to rule out impacts as "unlikely", or, when such a decision cannot be supported, arrive at a conclusion that such impacts are in fact likely. This process is illustrated in Figure 4-1.

Figure 4-1: Evaluating Indoor Air Pathway via Method 2



Initially, a relatively inexpensive soil gas screening effort is recommended, utilizing a series of conservative assumptions, in an attempt to rule out exposure/pathway concerns. Sites not screened out at this stage should consider increasingly more sophisticated and invasive actions, up to and including sampling and analysis of indoor air. Step-by-step recommendations are provided below. Additional guidance may be obtained from the *MADEP Indoor Air Sampling and Evaluation Guide*.

4.3.1.1 Level 1 - Soil Gas Screening

a) Install at least one or two soil gas sampling probes beneath the structure of concern (e.g., through the concrete slab of a basement floor). For larger structures, additional probes may be needed. If probes cannot be installed within the footprint of the structure, install soil gas sampling probes along the perimeter of the building, as close as possible to the structure. Locations beneath pavement or other impervious surfaces are preferred to obtain representative conditions.

Soil gas probes located in unpaved areas and/or other areas where rain/snowmelt/surface water infiltration is occurring may not yield representative data. Data from such locations may be biased low, due to displacement and/or solubilization of soil gas vapors during an infiltrative event.

b) Install and sample probes placed within the footprint of the structure in a manner that enables the collection of a soil gas sample from just beneath the lowest (floor/slab) elevation. Probes outside of the footprint of the building should be installed and sampled in a manner that enables the collection of a soil gas sample from a point just below the lowest (floor/slab) elevation.

c) Withdraw a sample of soil gas from each probe, for analysis by a Photoionization Detector (PID) and/or Flame Ionization Detector (FID) meter. The PID should be calibrated to an isobutylene response, the FID to a methane response. Continuous, real-time measurements may be made, or a sample can be pumped to a Tedlar (or equivalent) bag for subsequent PID/FID analyses. Unless a demonstration is made that the sampling technique and equipment is capable of delivering a soil gas sample to the PID/FID meter at an adequate pressure and flow rate, use of the bag technique is recommended. Additional guidance is provided in MADEP's *Policy for the Investigation, Assessment, and Remediation of Petroleum Releases*, April, 1991 (DEP Publication #WSC-401-91), available at http://www.state.ma.us/dep/bwsc/finalpol.htm

D) Compare the readings obtained on the PID and/or FID meters with the screening values in Table 4-9.

Table 4-9: Soil Gas PID/FID Screening Levels for Evaluating Indoor Air Impacts

Hydrocarbon Fraction(s) and Target Analytes which exceed applicable Method 1 GW-2 Standards and/or are present in proximate soils	Indoor air impacts unlikely if below listed value for each hydrocarbon fraction & Target Analyte of interest			
	PID ppmV (Isobutylene response)			FID ppmV (methane response)
	< 10.1 eV	10.1 – 11.4 eV	>11.4 eV	
C5-C8 Aliphatic Hydrocarbons	N/A	7	29	25
C9-C12 Aliphatic Hydrocarbons	3	7	33	19
C9-C10 Aromatic Hydrocarbons	28	29	37	21
C9-C18 Aliphatic Hydrocarbons	3	7	33	19
Toluene	11	12	12	10
Ethylbenzene	4	4	4	3
Total Xylenes	25	26	24	22

- On the left side of the table, identify EACH hydrocarbon fraction(s) and/or Target Analyte(s) which exceed an applicable GW-2 groundwater standard and/or are otherwise of concern.

- If a Photoionization Detector (PID) unit was used to analyze the soil gas, identify the energy level of the (UV) lamp in electron-volts (eV). Identify the ppmV reading listed in the appropriate column, and compare this value to the site value for EACH hydrocarbon range and/or analyte of interest. If EACH site value is less than the listed value for the hydrocarbon range(s) and Target Analyte(s) of interest, impacts to indoor air are not likely.

- If a Flame Ionization Detector (FID) unit was used to sample the soil gas, compare the site value to the value listed in the table. If the site value is less than the listed value for each hydrocarbon range and/or Target Analyte of interest, impacts to indoor air are not likely.

Example: BTEX and aliphatic/aromatic fractions present at site, but GW-2 standards exceeded for only Toluene and C9-C10 Aromatic Hydrocarbons. Soil gas below structure is found to have 25 ppmV (isobutylene calibration) total VOCs via a 10.6 eV PID unit. While this PID reading indicates impacts from C9-C10 Aromatic Hydrocarbons are unlikely (since < 29 ppmV), this data cannot rule out impacts by Toluene (since 25 ppmV > 12 ppmV).

- In situations where soil gas data are available from both a PID and FID, the FID data should be the basis of this evaluation.

- In situations where soil gas data are available from PID units with different lamp (eV) intensities, the data from the highest intensity lamp should be the basis of this evaluation.

The values provided in Table 4-9 are based upon conservative assumptions on (a) likely partitioning and dilution and attenuation factors for the identified hydrocarbon compounds and ranges, (b) response characteristics of commonly available PID and FID units; and (c) empirical observations, experience, and professional judgment. Because of its toxicity and low rate of anaerobic biodegradation, screening values have not been provided for benzene. This table should not be used to rule out impacts for non-listed contaminants, or to rule out impacts at structures with earthen floors, standing water, or open floor sumps.

4.3.1.2 Level 2 - Soil Gas Analysis

If indoor air impacts cannot be ruled out by PID/FID screening, more sophisticated testing is recommended for a soil gas sample obtained in accordance with the recommendations provided in Section 4.3.1.1. Recommendations in this regard follow:

GC SCREENING

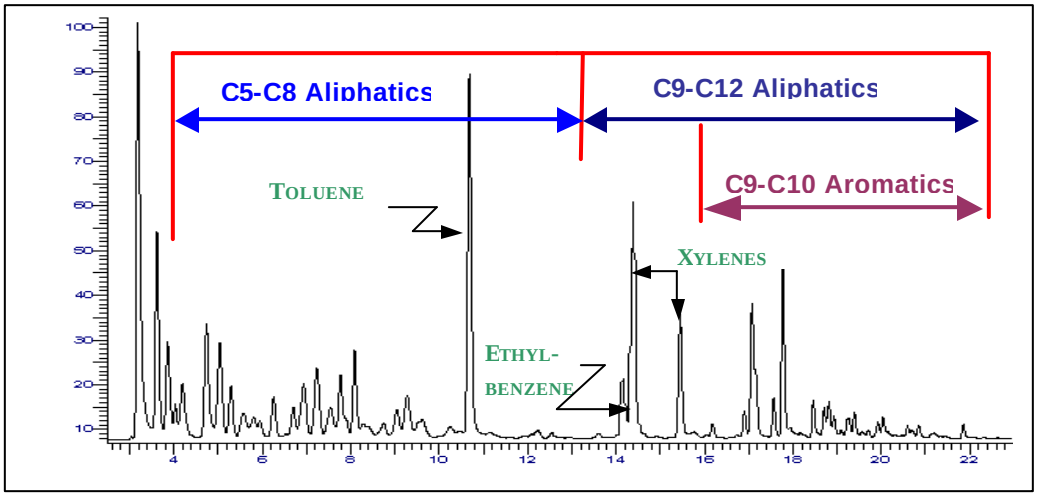
Soil gas samples obtained in a bag, canister, or directly into a gas-tight syringe are analyzed using a GC equipped with a flame ionization detector (FID). In cases where only aromatic contaminants are of interest (i.e., C_9-C_{10} Aromatic Hydrocarbons, toluene, ethylbenzene, and/or xylenes), a GC/PID may be used in lieu of a GC/FID. Even where only aliphatic hydrocarbons are of interest, the use of a PID in series with an FID will lead to more accurate and less conservative data.

A GC/FID sample chromatogram of a fresh gasoline sample is presented in Figure 4-2.

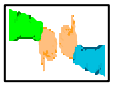
Under this approach, a series of assumptions are used to estimate the concentration of the hydrocarbon range(s) of interest; the more sophistication employed in this effort (i.e., use of GC/PID/FID), the less conservative the assumptions:

C5-C8 Aliphatic Hydrocarbons: On a GC/FID, quantitate all peak elutions between n-pentane and just before n-nonane using a response factor from one or several of the normal alkanes which elute in this range (e.g., n-heptane, n-octane).

Figure 4-2: GC/FID Soil Gas Chromatogram



Conservatively assume that this entire concentration value is C5-C8 Aliphatic Hydrocarbons (even though MtBE and some or all of the BTEX compounds also elute in this range). Compare this value (in $\mu g/m^3$) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate MtBE, benzene, toluene, ethylbenzene, xylenes (BTEX), and naphthalene, and "adjust" the C5-C8 Aliphatic Hydrocarbon value previously obtained by subtracting out the GC/PID $\mu g/m^3$ concentrations of compounds eluting within this range. If this adjusted C5-C8 Aliphatic Hydrocarbon value is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.



C9-C12 Aliphatic Hydrocarbons: On a GC/FID, quantitate all peak elutions between n-nonane and just before naphthalene using response factors from one or several of the normal alkanes which elute in this range (e.g., n-nonane, n-decane). Conservatively assume that this entire concentration value is C9-C12 Aliphatic Hydrocarbons (even though some aromatic compounds are also likely eluting in this range). Compare this value (in $\mu g/m^3$) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate BTEX, naphthalene, and C9-C10 Aromatic Hydrocarbon, and "adjust" the C9-C12 Aliphatic Hydrocarbon value previously obtained by appropriate subtraction from the Aliphatic range. If this adjusted C9-C12 Aliphatic Hydrocarbon value is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.

C9-C10 Aromatic Hydrocarbons: On a GC/FID, quantitate all peak elutions just after the last xylene peak and just before naphthalene using the response factor for 1,2,4-Trimethylbenzene. Conservatively assume that this entire concentration value is C9-C10 Aromatic Hydrocarbons (even though some aliphatic compounds are also likely eluting in this range). Compare this value (in $\mu g/m^3$) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate this range in the same manner. If this GC/PID range concentration is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.

Toluene, Ethylbenzene, Total Xylenes: On a GC/PID or GC/FID, identify and quantitate Target Analyte peak via retention times and response factors/curves established for each analyte. Compare these values ($\mu g/m^3$) with the values listed in Table 4-10. If all data are less than the listed values, measurable indoor air impacts are not likely. If one or more of the analytes are above their respective values, a Level 3 evaluation may be necessary.

NOTE: When using a "field" GC screening technique, all appropriate and necessary quality assurance/quality control procedures must be employed. At a minimum, the following steps would generally be expected:

- Calibration of the GC system at a minimum of 3 concentration levels, using gaseous-phase calibration standards; and
- Daily analysis of a blank sample and mid-range calibration or QC check standard, to ensure and document system performance.

LABORATORY PROCEDURES

Soil gas samples obtained in a bag, canister, or directly into a gas-tight syringe are analyzed using a VPH procedure (modified by changing sample introduction from purge and trap to direct injection/desorption) or by the APH methodology.

Using either the "screening" or laboratory procedure, the concentration of each fraction (in $\mu g/m^3$) should be compared to the soil gas action level indicated in Table 4-10. NOTE: THESE VALUES MAY NOT BE PROTECTIVE AT BUILDINGS WITH EARTHEN FLOORS OR STANDING GROUNDWATER WITHIN A BASEMENT OR CRAWL SPACE AREA.

Table 4-10: Soil Gas GC Screening Levels for Evaluating Indoor Air Impacts

Fraction/Analyte	Measurable Indoor Air Impacts Not Likely if Below (mg/m^3)
C5-C8 Aliphatic Hydrocarbons	111,000
C9-C12 Aliphatic Hydrocarbons	117,000
C9-C10 Aromatic Hydrocarbons	104,000
C9-C18 Aliphatic Hydrocarbons	130,000
Toluene	36,000
Ethylbenzene	13,000
Total Xylenes	94,000

As an alternative to the active soil-gas sampling procedures detailed above, the use of passive/diffusion samplers may also be an appropriate technique to characterize and quantitate hydrocarbon vapors beneath and proximate to structures of concern.

4.3.1.3 Level 3 - Indoor Air Analysis

If soil gas analysis cannot rule out an indoor air impact, direct measurement of indoor air is usually necessary. At least one (2-4 hour) time-weighted sample should be obtained from the lowest occupied level of the structure and analyzed using EPA Method TO-14A/15 or the MADEP Air-Phase Petroleum Hydrocarbon (APH) methodology. (While TO-14A/15 may be used to determine if a pathway is present, the APH method is recommended to evaluate risks from such a pathway). Additional (2-4 hour) time-weighted samples on other levels of the structure could be helpful in evaluating the likelihood of a subsurface vapor infiltration pathway in the event that elevated concentrations of contaminants are identified in the lowest level (e.g., higher concentrations in upper levels could be a potential line of evidence contrary to a subsurface infiltration pathway).

Sampling during Winter or early Spring is usually considered a "worst case" evaluation, due to (a) depressurization of the structure that occurs due to the operation of combustion furnaces and chimney stack effects, (b) lack of building ventilation, (c) presence of frost layer impeding diffusion to the atmosphere, and/or (d) presence of a high groundwater table (Spring). At structures with a central air-conditioning system that obtains make-up air from a basement, worst-case conditions may be during summer months. **Sampling during times of the year that are not considered worst case may not conclusively rule out indoor air impacts.**

Concentrations of hydrocarbon fractions and Target Analytes obtained by this analysis should be evaluated to determine if they are in excess of a "background" condition for that structure. In lieu of determining a site-specific background concentration, the generic values presented in Table 4-11 may be used.

Table 4-11: Estimated Background Indoor Air Concentrations

Fraction/Analyte	Estimated Generic Background	
	mg/m^3	ppbV
C5-C8 Aliphatic Hydrocarbons	85	N/A
C9-C12 Aliphatic Hydrocarbons	90	N/A
C9-C10 Aromatic Hydrocarbons	80	N/A
C9-C18 Aliphatic Hydrocarbons	100	N/A
Benzene	21	6.5
Toluene	29	7.5
Ethylbenzene	10	2.2
Total Xylenes	72	17
Naphthalene	5	1
MtBE	3-18*	1-5*

** concentration of MtBE in ambient air; may be higher in immediate vicinity of gasoline filling stations or if gasoline storage in building (e.g., lawnmower)*

4.3.1.4 Use of Vapor Transport Models

On occasion, it may be necessary or desirable to use predictive/computer models to help evaluate vapor transport issues at disposal sites. This option is most necessary when it is not possible or feasible to obtain soil gas and/or indoor air measurements, or when such data are ambiguous. While use of these techniques can aid in the understanding of the Conceptual Site Model, and facilitate characterization of current and future exposure pathways**, it is MADEP's longstanding position that current exposure pathways should be evaluated/validated with actual site data, to the extent feasible.**

Accordingly, unless precluded by unavoidable logistical constraints and/or "background" interference (e.g., toluene migration into a commercial/industrial site where toluene is used as a raw product*), there is an expectation that (some) actual soil gas and/or indoor air data will be generated during the evaluation of sites with an exceedance of GW-2 standards.* Sufficient explanation and justification must be provided in the appropriate report submittals for sites where such data are not obtained.

Most mathematical evaluations of this vapor transport pathway involve use of the Johnson & Ettinger model. Spreadsheet applications of the model are available for downloading free of charge from MADEP at http://www.state.ma.us/dep/bwsc/files/standard/GW2/GW2.htm and from the US Environmental Protection Agency at http://www.epa.gov/superfund/programs/risk/airmodel/johnson_ettinger.htm.

When using models of this nature, all input parameters and values have to be individually justified as appropriate and/or conservative for the specific site in question; it is not permissible to "pick and chose" generic modeling default values absent such justification. A particularly sensitive modeling parameter in this regard is the vadose zone moisture content **below the structure of concern**, which should be empirically determined on a site-specific basis.

4.3.1.5 Vertical Profiling of Groundwater Contaminants to Evaluate Vapor Transport

In cases where soil gas and/or indoor air data are ambiguous, vertical profiling of groundwater contaminants may provide useful lines of evidence in the evaluation of vapor transport pathways.

Typically, groundwater plumes "dip" as they flow from a source area, due to the infiltration of rainfall and snowmelt. This recharge can result in the formation of a "fresh water lens" above a plume of dissolved contaminants. In such situations, contaminants must diffuse through the (uncontaminated) lens in order to reach the groundwater table/capillary fringe, and partition from the aqueous phase into the gaseous phase. Because of the slow rate of liquid-phase diffusion, the formation of such a fresh water lens can effectively eliminate the vapor transport pathway, by preventing dissolved contaminants from partitioning into the overlying vadose zone.

Predicting the exact point in the path of a plume where vapor generation is "cut off" in this manner is difficult, if not impossible, due to the transient and dynamic nature of the governing parameters. Moreover, plumes that dip will eventually reverse direction and rise toward a groundwater discharge point, where contaminants may again be flowing in close proximity to the groundwater table and aqueous/vapor interface.

Despite these difficulties and unknowns, it may be useful at some sites to profile groundwater contaminant concentrations in the first 5-10 foot interval of the saturated zone, to determine whether a freshwater lens is present at the site in question. Typically, this action is accomplished by advancement of small diameter driven well points, obtaining groundwater samples at 1 to 2 foot depth intervals, for analysis by GC screening or laboratory techniques. Such data, in conjunction with soil gas data and/or other site factors, may provide the necessary weight of evidence to adequately evaluate and/or eliminate this pathway.

4.3.1.6 Response Actions at Sites with Indoor Air Impacts

Evidence of the migration of petroleum vapors from the subsurface into a school building or occupied residential dwelling (above a background condition) represents a Critical Exposure Pathway and Condition of Substantial Release Migration under the Massachusetts Contingency Plan. In such cases, pursuant to the provisions of 310 CMR 40.0414, an Immediate Response Action must be undertaken to evaluate the risks associated with this infiltration, and determine if there is a feasible remedial measure to prevent or mitigate this continued infiltration. *If feasible mitigative options exist, remedial actions must be taken*.

When considering and implementing mitigative options, a hierarchy of remedial efforts is recommended, from least-invasive/least-costly to most-invasive/most-costly. Details are provided in Figure 4.3.

4.3.2 Using a Method 2 Approach to Evaluate Exceedances of Method 1 GW-3 Standards

The Method 1 GW-3 standard most likely to be exceeded at a petroleum-contaminated site is for C9-C10 Aromatic Hydrocarbons. This standard and all Method 1 GW-3 standards were derived based upon an assumption that (a) impacts may occur to ecological receptors in a surface water body at concentrations equal to or greater than the ambient water quality guideline, (b) groundwater from the site is discharging to such a surface water body, and (c) dilution between the groundwater and surface water body is minimal. A summary and description of currently recommended fractional ambient water quality guidelines is provided in Table 4-12.

Using a Method 2 approach, site-specific data, fate and transport factors, and/or predictive models may be used to modify Method 1 GW-3 standards. Recommended fractional fate and transport parameters are provided in Section 4.6. ***Note that per 310 CMR 40.0982(4), a Method 1 GW-3 standard cannot be modified to a concentration in excess of the Upper Concentration Limit for the fraction of interest.***

Figure 4-3: Recommended Hierarchy of Vapor Mitigation Efforts

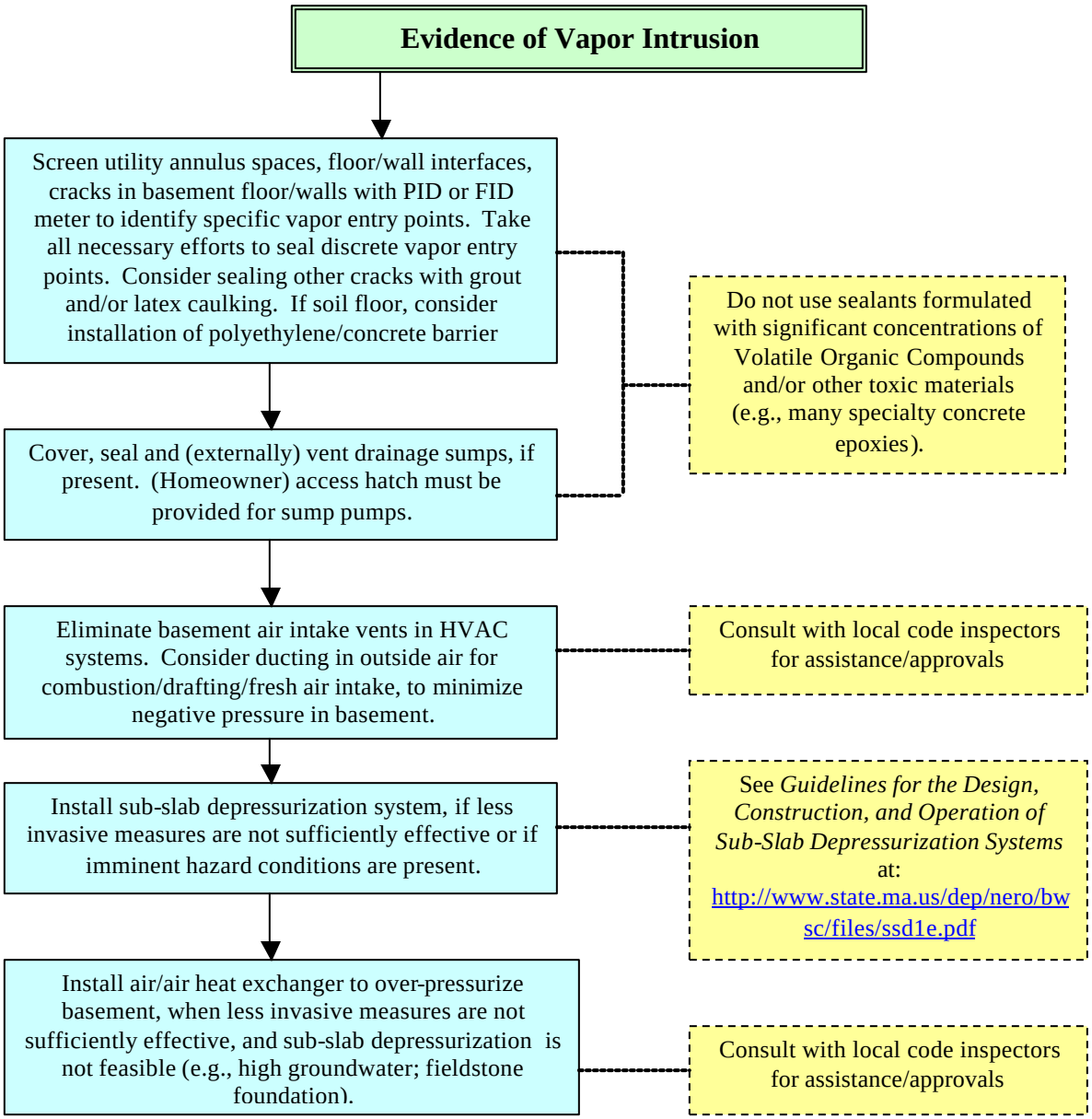


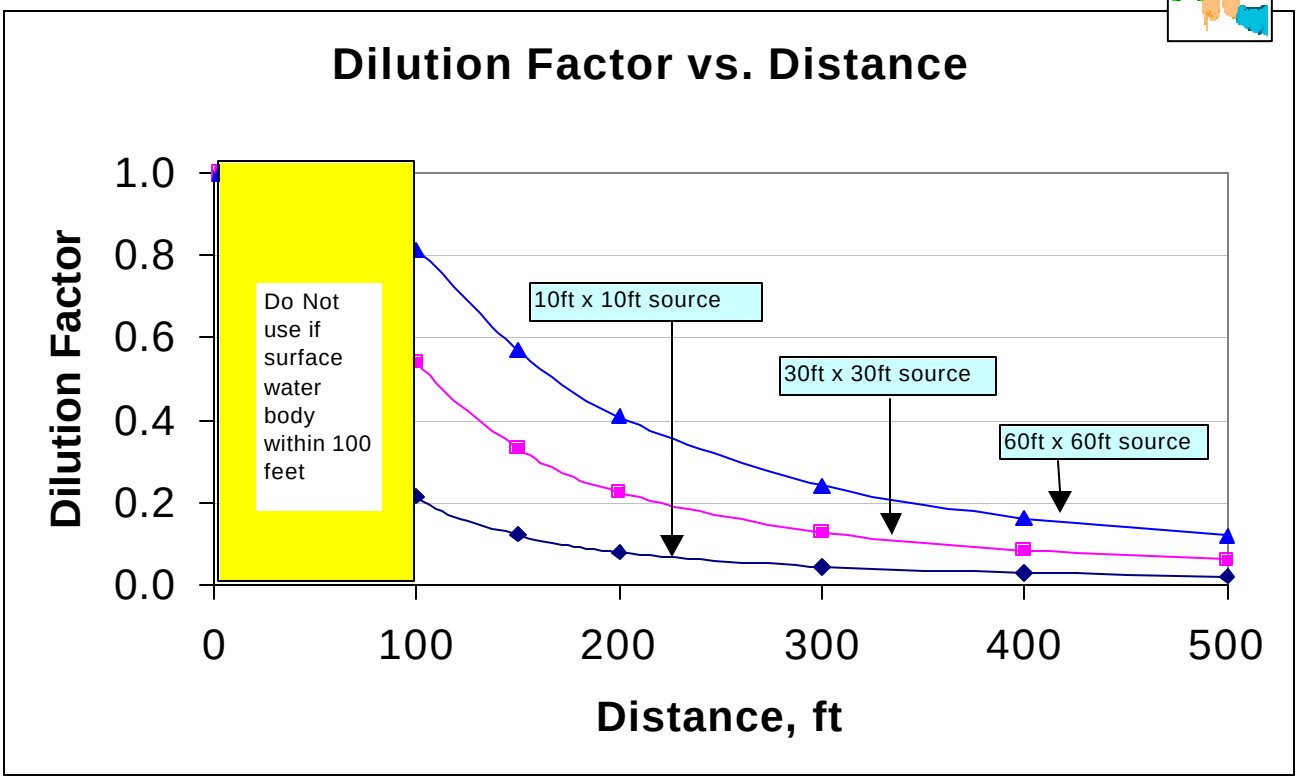
Table 4-12: Recommended Surface Water Quality Guidelines

Fraction	Surface Water Guideline (mg/L)	Basis of Guideline
C5-C8 Aliphatics	250[a]	Acute LC50/10 for Hexane (as surrogate for this range)
C9-C12 Aliphatics	1800	Acute LC50/10 for Decane (as surrogate for this range)
C9-C10 Aromatics	540[a]	Acute LC50/10 for Trimethyllbenzene (as surrogate for this range)
C9-C18 Aliphatics	1800	Acute LC50/10 for Decane (as surrogate for this range)
C19-C36 Aliphatics	2100	Acute EC50/10 for Cyclododecane (as surrogate for this range)
C11-C22 Aromatics	N.A.[a]	Effects may be seen at less than the EPH Reporting Limit; other testing methods (e.g., GC/MS) may be needed on site-specific basis

[a]updated value (2002)

In lieu of site-specific modeling, the conservative dilution factors graphically illustrated in Figure 4-4 may be used as part of a Method 2 evaluation of groundwater-to-surface-water impacts dissolved hydrocarbon contaminants.

Figure 4-4: Groundwater Dilution Factors for Dissolved Hydrocarbons



Equations:

10ft x 10ft source area, DF = 177 (distance in feet)$^{-1.455}$, r^2 = 0.99
30ft x 30ft source area, DF = 303 (distance in feet)$^{-1.365}$, r^2 =0.99
60ft x 60ft source area: DF = 237 (distance in feet)$^{-1.214}$, r^2 = 0.99

The graphs presented in Figure 4-4 are generalized, source-area dependent conservative dilution and dispersion curves for any dissolved groundwater contaminant, including hydrocarbon range fractions and Target Analytes. They were developed using the Domenico and Robbins analytical transport model (1985) assuming an infinite source condition. The only attenuation mechanism considered is hydrodynamic dispersion, and as such may be used for any dissolved organic compound.

The use of these graphs, however, is limited to sites where **ALL** of the following conditions are met:

- ◊ groundwater/contaminant flow is occurring only in an overburden aquifer;
- ◊ there is no "short circuiting" of groundwater/contaminants along preferred flow paths;
- ◊ no fractional range is present at a concentration greater than 100,000 µg/L (i.e., exceeding UCLs); and
- ◊ the nearest downgradient surface water body is at least 100 feet from the impacted well/groundwater area on the site.

Because of modeling uncertainties, and limitations that typically exist on the availability of temporal and spatial groundwater monitoring data, the graphs and equations contained in Figure 4-4 may not be used at sites where the distance to surface water is less than 100 feet.

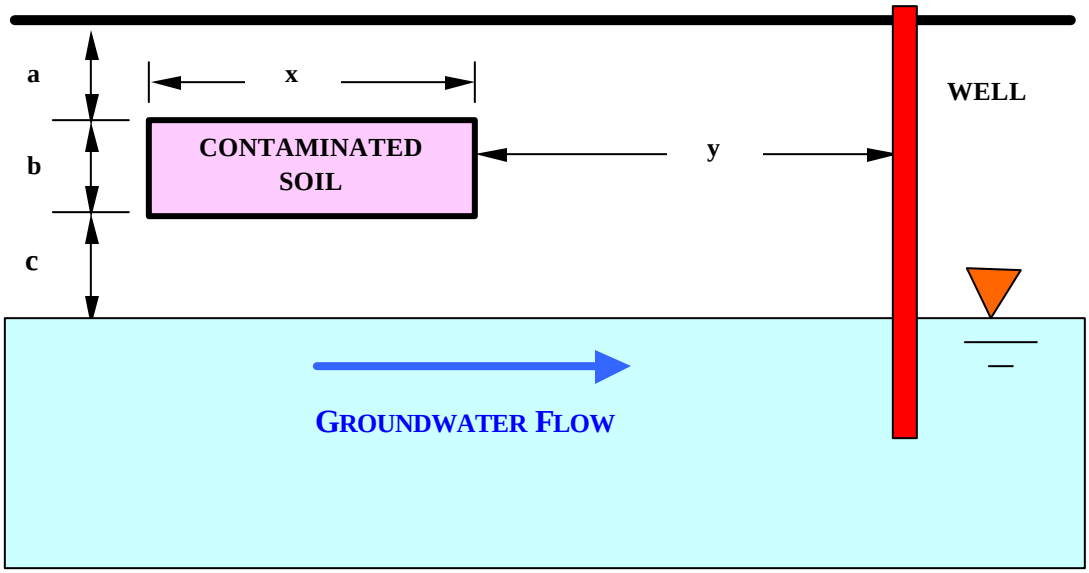
Using Figure 4-4, it is possible to conservatively calculate the concentration of a hydrocarbon range or Target Analyte of interest at some distance from a site (typically, a monitoring well located at a site). For example, at a site in which the source area of contamination is approximately 30ft x 30ft, if the concentration of C_9-C_{10} Aromatic Hydrocarbons in a well located 400 feet from a receiving water is 600 µg/L, a (dimensionless) Dilution Factor of 0.09 is obtained from Figure 4-4. Multiplying this Dilution Factor by 600 µg/L yields 54 µg/L, which would be a conservative estimate of the maximum concentration of C_9-C_{10} Aromatic Hydrocarbons in groundwater that would migrate to this point. An additional dilution factor may then be applied to account for the mixing of groundwater with the surface water, based upon site-specific information and data.

Parties wishing to provide alternative ambient water quality guidelines for the VPH/EPH fractions, and/or provide a site-specific evaluation of environmental impacts, must do so via a MCP Method 3 approach.

4.3.3 Using a Method 2 Approach to Evaluate Leaching

All Method 1 soil standards consider leaching impacts to underlying groundwater. The leaching-based component of the Method 1 standards were derived using the SESOIL and AT123D computer models to evaluate unsaturated and saturated zone transport, as depicted in Figure 4-5.

Figure 4-5: Leaching Scenario Used to Develop Leaching-Based Method 1 Soil Standards



The standards developed by MADEP in 1993 were based upon a deterministic modeling effort, using "point" value input parameters (i.e., in Figure 4-5 a, b, and c = 1 meter, x and y = 10 meters). More recent efforts by MADEP have involved use of a probabilistic modeling approach, using ranges or distributions for input parameters. In all cases, "Dilution and Attenuation Factors" were developed to relate concentrations of soil contaminants in the source area to concentrations of those contaminants in a hypothetical "point of compliance" downgradient monitoring well.

Based upon the assumptions and models used by MADEP, the only VPH/EPH Method 1 soil standard controlled by leaching concerns is C11-C22 Aromatics in GW-1 (drinking water) areas. However, the Method 1 soil cleanup standards for two important Target Analytes - naphthalene and 2-methylnaphthalene - are also controlled by leaching considerations.

Using a Method 2 approach, site-specific data, fate and transport factors, and/or predictive models may be used to modify a Method 1 soil standard that is based upon leaching concerns. In such an exercise, the site-specific soil concentration(s) of a hydrocarbon fraction or Target Analyte of interest is used to predict maximum groundwater concentrations that may be expected in areas beneath and downgradient of the contaminated soil. These

groundwater concentrations are then compared to the appropriate Method 1 or 2 groundwater standards. A modified soil standard derived in this manner is acceptable if:

◊ the maximum predicted groundwater concentration of the contaminant of interest downgradient of the zone of soil contamination is at or below the appropriate Method 1 or 2 GW standard; and

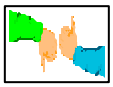
◊ the modified soil standard does not exceed the appropriate S-1, S-2, or S-3 levels which are protective of direct-contact exposure concerns [as listed at 310 CMR 40.0985(6)].

Example: under a Method 2 approach, the S-1/GW-1 Method 1 standard for C11-C22 Aromatic Hydrocarbons can be modified, based upon site-specific leaching considerations, to a maximum concentration of 800 µg/g, which is the level at which the human health risks associated with direct contact controls the setting of this standard.

Note that while the generic Method 1 standards were predicated on a specified or probabilistic downgradient receptor of concern, (e.g., 10 meters downgradient of the source area), actual site-specific conditions and receptors should be used when undertaking a Method 2 evaluation effort (e.g., buildings, surface water bodies, GW-1 areas).

Recommended fractional fate and transport parameters are provided in Section 4.6. For additional information on the calculation of leaching-based Method 1 soil standards, consult *Background Documentation for the Development of the MCP Numerical Standards* (MADEP, 1994 and as amended).

In lieu of or in conjunction with predictive models, the use of groundwater monitoring data is often an acceptable and cost-effective means to evaluate site-specific leaching concerns. In order to have sufficient confidence in such an approach, however, the following site conditions are desirable:



◊ the release occurred at least 24 months ago;
◊ the depth between the zone of soil contamination and groundwater table is less than 6 feet;
◊ the surface(s) overlying the contaminated soil is pervious (i.e., no pavement or buildings);
◊ the number and location of monitoring wells are sufficient to characterize groundwater quality below and downgradient of the zone of soil contamination; and
◊ sufficient temporal monitoring data exist to evaluate seasonal trends.

4.4 Method 3 Risk Characterization

Under Method 3, a completely site-specific evaluation is conducted to determine risks to human health, safety, public welfare, and the environment. Recommended toxicological and fate and transport values for the VPH/EPH fractions in this regard are provided in Tables 4-13 and 4-14, respectively. Although it is not necessary to use any of these values in a Method 3 risk characterization effort, the burden is on the party conducting the assessment to document and defend the selection of alternative assumptions, parameters, and values. Complete details on the Method 3 risk assessment process are provided in *Guidance for Disposal Site Risk Characterization* (MADEP, 1995 and as amended).

4.4.1 Requirements and Limitations of a Method 3 Characterization

While a Method 3 characterization allows a significant degree of flexibility, there are important obligations and limitations:

◊ **Site-specific risks to public welfare must be evaluated.** Under the Massachusetts "superfund" legislation (MGL c. 21E), risks to public welfare are given the same weight as risks to human health, safety, and the environment. In deriving the Method 1 standards, MADEP imposed ceiling levels on acceptable concentrations of contaminants, in an attempt to ensure that each standard would be set at a low enough level to rule out significant impacts to public welfare. "Public welfare" is a difficult standard to articulate, and it is much easier to define a *de minimis* condition, than to define a precise point where a risk to public welfare becomes significant. Nevertheless, parties conducting a Method 3 assessment must make an independent evaluation of all relevant public welfare concerns, and conclude that all such concerns are below a level of *No Significant Risk*.

◊ **Site-specific risks to ecological receptors must be evaluated.** Under the MCP, environmental risk assessment is done via a two-stage process. Stage I is a screening process used to (1) eliminate from further consideration those sites where exposures are clearly unlikely to result in environmental harm, or, on the other extreme, (2)

eliminate from further consideration those sites where harm is readily apparent (i.e., it is clear that remediation is needed, and additional study is not necessary). Those sites that are not eliminated must proceed to a Stage II evaluation, which involves a quantitative, site-specific characterization of the risk to ecological receptors.

◊ **A Method 3 approach cannot be used to modify or eliminate Upper Concentration Limits.** Upper Concentration Limits (UCLs) are "gross" levels of contamination in soil and groundwater that, by their very presence in the environment, constitute a significant risk to public welfare and the environment. Under the provisions of 40.0996(2), the UCL standards are to be applied to the arithmetic average of the concentration of oil or hazardous materials at a site or within a "hot spot". If the average concentrations of site contaminants exceed an applicable UCL value, remediation must be undertaken to treat or encapsulate areas of concern, if feasible. In cases were it is not feasible to remediate such conditions, it may be still possible to obtain an interim site closure by filing a Class C Response Action Outcome, representing a Temporary Solution.

◊ **A Permanent Solution cannot be achieved if drinking water standards are exceeded in a GW-1 area.** In conducting a Method 3 assessment, all applicable or suitably analogous health standards must be identified and achieved. Under the provisions of 310 CMR 40.0993(3)(a), the Massachusetts Drinking Water Quality Standards promulgated in 310 CMR 22.00 are considered applicable in all GW-1 areas. While drinking water standards have been promulgated for a number of Target Analytes (e.g., benzene at 5 µg/L), at the present time, the VPH/EPH fractional ranges are not included on this list. While it is necessary to characterize the risk these factional ranges pose to the water supply of concern, it is not necessary to consider these values "analogous health standards".

4.4.2 Impacts to Indoor Air

Relevant guidance contained in Section 4.3.1 should be considered by parties undertaking an evaluation of impacts to indoor air as part of a Method 3 risk assessment process. The use of the inhalation RfC values provided in Table 4-13 would be a conservative means to quantitate risks via the inhalation pathway, and use of the estimated background concentration values listed in this table would be a conservative means to evaluate Critical Exposure Pathways.

4.4.3 Odors as a Significant Risk to Public Welfare

Under the provisions of 310 CMR 40.0994, the existence of a nuisance condition shall be considered in a characterization of risks to public welfare. Given the low odor recognition thresholds of many petroleum constituents (and breakdown products), the presence of odors at petroleum-contaminated sites can constitute a nuisance condition, and preclude achievement of a condition of No Significant Risk to Public Welfare, *even if a condition of No Significant Risk to Human Health has been achieved.*

Definitive and quantitative guidelines and standards on when a petroleum odor constitutes a nuisance condition and significant risk to public welfare are difficult to articulate. In the context of petroleum-contaminated sites, however, the following ***Rules of Thumb*** are suggested for when an odor condition would generally NOT be considered a nuisance condition:

◊ Odors observed in the subsurface during excavation or boring advancement would generally not be considered a nuisance condition, as long as such odors are not detectable in ambient or indoor air, and as long as there are no plans to excavate or disturb such areas.

◊ Odors observed in the breathing zone of the ambient air, or indoor air of an impacted structure, would generally not be considered a nuisance condition, if such odors do not persist for more than 3 months.

◊ Odors observed in the breathing zone of the ambient air would generally not be considered a nuisance condition if they are discernable less than 10 days a year.

◊ Odors observed in the ambient air or indoor air of an impacted structure would generally not be considered a nuisance condition if the occupants of such a structure do not believe such odors significantly affect or degrade their quality of life.

4.4.4 MADEP Petroleum-Contaminated Site Risk Assessment Short Forms

To streamline the Method 3 risk assessment process, MADEP has developed a series of Risk Assessment "Short Forms" which incorporate the aliphatic and aromatic fractional ranges, for optional use at sites contaminated by various petroleum products. Like other MADEP Short Forms, these spreadsheet-based tools incorporate standardized exposure assumptions and toxicological profiles, and allow the user to input site-specific concentration data. The output is a series of summary tables that describe chemical-specific, medium-specific, and cumulative (total site) risks, which may be used and/or applied as part of a Method 3 risk assessment at petroleum-contaminated sites.

The Short Forms, and supporting documentation, are available for downloading from the MADEP Web site, at http://www.state.ma.us/dep/ors/orspubs.htm

4.5 Recommended Toxicological Parameters

The currently recommended toxicological values for assessing risks associated with the VPH/EPH aliphatic and aromatic hydrocarbon fractions are listed in Table 4-13. Note that these values are subject to change as additional information and data become available to MADEP.

Table 4-13: Recommended VPH/EPH Toxicological & Risk Assessment Parameters

	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics	C11-C22 Aromatics
Chronic Oral RfD (mg/kg/day)	0.04[a]	0.1[a]	0.03	0.1[a]	2.0[a]	0.03
Subchronic Oral RfD (mg/kg/day)	0.4[a]	1.0[a]	0.3	1.0[a]	6[a]	0.3
Chronic Inhalation RfC (mg/m3)	200	200	50[a]	200	N/A	50[a]
Est. Background Indoor Air (mg/m3)	≤85	≤90	≤80	≤100	N/A	≤50
Chronic RAF - Soil Ingestion	1[a]	1[a]	1[a]	1[a]	1[a]	0.36[a]
Chronic RAF - Soil Dermal	1[a]	0.5[a]	0.5[a]	0.5[a]	0.1	0.1[a]
Chronic RAF – Water Ingestion	1	1	0.91	1	1	0.91
Subchronic RAF - Soil Ingestion	1[a]	1[a]	1[a]	1[a]	1[a]	0.36[a]
Subchronic RAF - Soil Dermal	1[a]	0.5[a]	0.5[a]	0.5[a]	0.1	0.18
Subchronic RAF - Water Ingestion	1	1	0.91	1	1	0.91
Ambient Water Quality Guide (mg/L)	250[a]	1800	540[a]	1800	2100	N.A..[a,b]

[a] updated value (2002) [b]see table 4-12

4.6 Recommended Fate and Transport Parameters

For recommended approaches, procedures, and values to conduct fate and transport evaluation/modeling of Target Analytes and hydrocarbon ranges, consult *Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations*, a (1997) publication prepared by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), available at http://www.aehs.com/whatsnew.htm.

Relative to the VPH and EPH hydrocarbon ranges – FOR MODELING PURPOSES ONLY - recommended fractional properties are provided in Table 4-14.

Table 4-14 : Recommended VPH/EPH Fractional Properties for Modeling Purposes

	Equivalent Carbon Number (EC)	Molecular Weight	Vapor Pressure (atms)	Solubility in Water (mg/L)	Henry's Constant, H (dimensionless)	Partition Coeff, Koc (mL/g)	Diffusion Coeff (cm^2/s)	
							air	water
C5-C8 Aliphatics	6.5	93	0.10	11,000	54	2265	0.08	1×10^{-5}
C9-C12 Aliphatics	10.5	149	8.7×10^{-4}	70	65	1.5×10^{5}	0.07	1×10^{-5}
C9-C10 Aromatics	9.5	120	2.9×10^{-3}	51,000	0.33	1778	0.07	1×10^{-5}
C9-C18 Aliphatics	12	170	1.4×10^{-4}	10	69	6.8×10^{5}	0.07	5×10^{-6}
C19-C36 Aliphatics	considered immobile							
C11-C22 Aromatics	14	150	3.2×10^{-5}	5800	0.03	5000	0.06	1×10^{-5}

4.7 Non-Aqueous Phase Liquids (NAPL)

The presence of non-aqueous phase liquids (NAPL) adds significant complexity to the assessment and remediation of petroleum-contaminated sites. Of primary concern are (1) the bulk fluid migration of petroleum NAPL, and potential discharge into underground structures, utilities, and/or surface water bodies, and (2) NAPL acting as a continuing source of soil, groundwater, and/or soil gas contamination. Due to these concerns, under the provisions of 310 CMR 40.0996(4), the presence of a non-aqueous phase liquid having a thickness equal to or greater than 0.5 inches in ***any environmental medium*** is considered an exceedence of an Upper Concentration Limit (UCL).

4.7.1 Upper Concentration Limits

A *single* measurement of $\geq$ 0.5 inches NAPL in a *single* groundwater monitoring well does not necessarily constitute exceedence of a UCL standard:

◊ The standard applies to the formation, not a groundwater monitoring well. Typically, the thickness of NAPL measured in a monitoring well does not correspond to the thickness of NAPL in the surrounding formation. Moreover, seasonal and short-term water table fluctuations and tidal influences will affect apparent levels of petroleum product thickness in monitoring wells, with thickness levels often increasing with a declining water table, and decreasing or "disappearing" with a rising water table. Although the relationship between the thickness of NAPL in a monitoring well and the surrounding formation is not easily established, there may be methods and sites for which reasonable assumptions and conclusions can be reached, based upon:

* an evaluation of formation properties, especially the thickness of the capillary fringe;
* an evaluation of test pit, split-spoon, and/or analytical screening observations within the presumed NAPL "smear zone"; and
* an evaluation of sufficient spatial and temporal monitoring well data, relative to the observed thickness of the NAPL and the elevation of the potentiometric surface.

◊ As with all UCL standards, averaging of data is permissible. In the case of NAPL, however, temporal averaging of data from monitoring wells is generally not appropriate, due to distortions introduced by a falling and rising water table.

◊ It is permissible to spatially average wells within the contiguous area of the NAPL plume, excluding "hot spots", which are defined by the MCP to be discrete areas where the thickness of NAPL is more than 10 times the thickness of surrounding areas.

4.7.2 Apparent NAPL Thickness vs. Actual NAPL Thickness

The occurrence, detection and migration of non-aqueous phase liquids in the subsurface are a complex phenomenon. Many investigators have attempted to develop theoretical and/or empirical methods to correlate the apparent

thickness of NAPL, as measured in a monitoring well, to the actual thickness of that NAPL in the surrounding formation. Most of these methods involve relationships based upon the density of the liquid hydrocarbon (de Pastrovich *et al*., 1979), properties of the geologic medium (Hall *et al*., 1984), height of the capillary fringe (Blake and Hall, 1984; Ballestero *et al*., 1994; and Schiegg, 1985), and/or idealized capillary pressures in homogeneous porous media (Farr *et al*., 1990; and Lenhard and Parker, 1990). Unfortunately, none of the methods or approaches presented to date appears to be sufficiently reliable or reproducible at field sites, especially when significant fluctuations occur in the elevation of the groundwater table.

Despite these limitations, at most sites, it is likely that the *maximum* apparent (measured) thickness of light non-aqueous phase liquid (LNAPL) in a monitoring well is significantly greater than the actual thickness of that LNAPL in the surrounding formation. This phenomenon occurs when a monitoring well is installed into a formation in which mobile LNAPL is pooled on top of the capillary fringe above the water table. In such cases, LNAPL will flow into the monitoring well, depressing the true elevation of the potentiometric surface, until such time as equilibrium is achieved with the level of the LNAPL above the capillary fringe, and the weight/density of the hydrocarbon liquid in the well.

While LNAPL occurrence and measurement is a complicated matter, it is possible to make one simple conclusion: it is usually not possible to adequately characterize this concern without sufficient temporal gauging data. At a minimum, monitoring activities should include at least 4 rounds of gauging during the 4 seasons of the year.

Until such time as additional guidance is available on this topic, site investigators must undertake a "weight of evidence" approach to determine compliance with the 0.5 inch NAPL standard. A conservative approach would be to assume that the maximum (temporal) LNAPL thickness *observed* in a monitoring well is equivalent to the *actual* thickness of LNAPL in the formation. If the spatial average of these values within an area of concern (excluding hot spots) is less than 0.5 inches, compliance has been achieved. If the average of these values – or of a hot spot area – is greater than 0.5 inches, additional evaluations/calculations are needed to relate the observed/apparent thickness to actual formation thickness.

4.7.3 NAPL and Vapor/Indoor Air Impacts

Volatile non-aqueous phase liquids (NAPL), including separate-phase gasoline, kerosene, jet fuels, and fresh diesel/#2 fuel oils, can result in the generation of significant concentrations of volatile petroleum hydrocarbon vapors in the vadose zone, which can potentially impact the indoor air of nearby structures. Purging a monitoring well containing such NAPL prior to obtaining a groundwater sample may underestimate risks of this nature, as the groundwater sample may contain relatively low concentrations of dissolved hydrocarbons. *For this reason, soil gas investigations should be considered at any site at which volatile NAPL has been identified in monitoring wells or test pits, to characterize the risks posed to indoor air quality, and determine whether use of a Method 1 approach is appropriate*

4.8 Elimination of Continuing Sources

Under the provisions of 310 CMR 40.1003(5), a permanent solution cannot be achieved at a site if a continuing source(s) of environmental contamination is present. At petroleum-contaminated sites, the following conditions could constitute a continuing source:

- ◊ *Abandoned Storage Tanks* - any abandoned storage tank containing any amount of mobile and/or soluble petroleum product would be considered a continuing source of environmental contamination, regardless of its current condition, unless such a tank has been closed pursuant to all applicable federal, state, and local regulations.

- ◊ *Septic Tanks/Dry Wells* - any wastewater storage, conveyance, or disposal system containing significant quantities of Non-Aqueous Phase Liquids (NAPL) would be considered a continuing source of environmental contamination, unless such systems are operating in compliance with all applicable federal, state, and local regulations.

- ◊ *Gasoline NAPL* - measurable amounts of gasoline NAPL could constitute a continuing source of environmental contamination, unless modeling, groundwater and/or soil gas monitoring data can demonstrate decreasing concentrations of dissolved and/or vapor-phase contaminants over time.

- ◊ *Gasoline/VPH-contaminated soils* - concentrations of VPH fractions in soil above applicable Method 1 standards could constitute a continuing source of environmental contamination, unless modeling, groundwater and/or soil gas monitoring data can demonstrate decreasing concentrations of dissolved and/or vapor-phase contaminants over time.

4.9 Feasibility of Achieving Background Concentrations

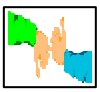
Under the provisions of MGL c. 21E and the MCP, a permanent solution shall, *at a minimum*, achieve a condition of No Significant Risk. However, the statute and regulations go one step further: a permanent solution shall also include measures to reduce contaminant levels in the environment to concentrations that achieve or approach a "background" condition, *to the extent such measures are feasible*. Thus, remedial decisions under the MCP are predicated on two distinct evaluation processes: risk and feasibility. Generic and site-specific procedures and criteria to evaluate and eliminate significant risk are extensively detailed in the MCP and associated guidance documents. Procedures and criteria to evaluate the feasibility of achieving or approaching background are less defined, and are typically considered on a site-by-site basis.

A feasibility evaluation of this nature identifies and weighs the benefits and costs of eliminating or minimizing the mass or volume of contaminants in the environment, beyond a "risk-based" endpoint. The costs of such actions can be generally calculated. The benefits are less quantifiable, but include property-value/economic and non-pecuniary benefits, as well as potential health benefits. With respect to the latter, it is important to understand that all risk-based standards have inherent uncertainties, due to limitations in our understanding of how toxins affect human and ecological receptors; these limitations are especially true and problematic when considering potential synergistic effects of multiple contaminants, and exposures to sensitive populations (e.g., children). While most standards are thought to be conservative, better studies and future data may lead to a different conclusion. A good example in this regard is the risk-based GW-1 standard for MtBE, which in recent years has been lowered by MADEP from 700 µg/L to 70 µg/L (and which may be lowered even further in the future).

While it is necessary to consider the feasibility of achieving or approaching background at petroleum-contaminated sites, certain attributes of petroleum hydrocarbons are germane to the benefit/cost evaluation, and allow for generalized conclusions and recommendations on feasibility issues. Specifically, most of the petroleum hydrocarbons contained in gasoline and lighter fuel oils are biodegradable, under both aerobic and anaerobic conditions. At most sites, residual levels of such contaminants will naturally degrade to levels that achieve or approach a background condition, in a foreseeable time period. In such cases, the "benefit" side of the feasibility equation becomes more an issue of timing than of concentration endpoints: is the benefit of *accelerating* this mass reduction worth the cost?

Based upon the above, certain generic guidelines are offered to streamline background restoration considerations at sites contaminated ONLY with petroleum hydrocarbons:

- ◊ Given the typical "asymptotic" response for contaminant reduction in aquifer systems, at sites contaminated solely by releases of gasoline of diesel?#2 fuel oil, achieving or approaching background concentrations of petroleum hydrocarbons in *groundwater* may generally be considered infeasible, provided that indigenous or enhanced microbial populations present at the site of concern would be expected to naturally degrade petroleum hydrocarbon concentrations.



- ◊ Achieving or approaching background concentrations of petroleum hydrocarbons may generally be considered infeasible in soils that are located beneath a permanent structure.

- ◊ Achieving or approaching background concentrations of petroleum hydrocarbons may generally be considered infeasible at sites where such remedial activities would interrupt vital public services and/or threaten public safety (e.g., energy interruption; traffic disruption).

It is important to stress that the above guidelines pertain <u>only</u> to the feasibility of remediation <u>beyond</u> a risk-based endpoint. Under the MCP, all sites must achieve a condition of No Significant Risk.

Additional policy documents on this subject are currently under development by MADEP; refer to the BWSC publication page at http://www.state.ma.us/dep/bwsc/pubs.htm to track progress/provide input in this regard.

5.0 IMPLEMENTATION ISSUES

5.1 Site Characterization

5.1.1 Analytical Parameters

Recommended Target Analytes and VPH/EPH hydrocarbon ranges of interest for the most commonly released petroleum products are detailed in Tables 4-3, 4-5, and 4-6.

5.1.2 Site and Media Characterization

Site characterization may involve evaluation and/or testing of NAPL, soil, groundwater, surface water, soil gas, ambient air, indoor air, or freshwater or marine sediments. Decisions of this nature are necessarily site-specific, based upon the type and quantity of petroleum product(s) released, depth to groundwater, and sensitivity of potential pollutant receptors.

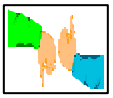
Rules of Thumb for the most commonly released petroleum products and problematic situations are provided below:

NAPL

◊ When gauging a well for the purpose of monitoring the presence and thickness of NAPL, it is essential that all free-phase petroleum product be evacuated from the well after each gauging round, to help ensure that the well remains in good hydraulic communication with the surrounding formation, and accurately reflects dynamic aquifer conditions.

◊ Generally, it is not possible (or meaningful) to attempt to measure the concentration of dissolved petroleum product in a monitoring well which contains a measurable thickness of NAPL.

Soil



◊ When obtaining samples at an UST grave for the purposes of determining an Exposure Point Concentration (EPC), it is necessary to specifically investigate whether a "hot spot" exists within the groundwater table fluctuation zone (i.e., the "smear zone"). For gasoline and fresh diesel/fuel oil releases, this action may be easily accomplished by headspace analysis of samples from sidewall excavations using a PID meter. In cases where headspace concentrations within this smear zone are equal to or greater than 10 times other locations on the sidewall, soil samples from this zone should be discretely collected/composited (either as the sidewall sample or with other sidewall samples) for appropriate analysis.

Groundwater

◊ Regardless of the type of petroleum product released, groundwater characterization should be undertaken at any site where the distance to a groundwater withdrawal well is less than 500 feet.

◊ In most cases, it is necessary to obtain groundwater samples to adequately characterize releases of gasoline, aviation gasoline, and military jet fuels. Exceptions may include: very small releases of product (less than a few gallons), or sites with a deep vadose zone (>30 feet to the groundwater table), **IF** there are no sensitive receptors (e.g., no groundwater withdrawal wells or potentially impacted structures). At sites where the groundwater table is located in bedrock, the use of passive and/or active soil gas sampling is recommended to help determine if NAPL or significant concentrations of dissolved constituents are present in the groundwater.

◊ At sites where there has been a release of diesel/#2 fuel oil, and where excavation is being accomplished to remove a tank or contaminated soil, an attempt should be made to reach the groundwater table using on-site equipment. If reached, visible observations of the presence or absence of NAPL should be documented, and a groundwater and/or soil sample (from within the groundwater fluctuation zone) should be obtained

for analysis by a TPH or EPH methodology. If not reached, the installation of a groundwater monitoring well would generally not be necessary if (a) site data, before or after remediation, document concentrations of EPH fractional ranges below appropriate Method 1 standards, and (b) there are no groundwater withdrawal wells within 500 feet. Further guidance on tank removal is available in *Commonwealth of Massachusetts Underground Storage Tank Closure Assessment Manual*, DEP Policy # WSC-402-96, April, 1996.

◊ At gasoline-contaminated sites, particular attention and emphasis should be placed on the characterization of MtBE in groundwater. This compound, an additive in unleaded gasoline, is extremely soluble and mobile, and can migrate significant distances in groundwater. While most petroleum hydrocarbon plumes tend to biodegrade before significantly "dipping" below the groundwater table, MtBE plumes can "sink" below the typical 10-foot water table well screens in monitoring wells with increasing distance from a source area, necessitating consideration of deeper wells in downgradient plume areas (i.e., beyond about 100 meters from the source area). Moreover, unlike BTEX and other petroleum hydrocarbons, MtBE may not be a good candidate for natural attenuation, as it does not tend to volatilize, sorb to soils, or readily biodegrade. *Recent information and data developed by the USEPA (2002) have disclosed that conventional sampling and analysis techniques can significantly underestimate MtBE concentration in groundwater; additional details and recommendations are provided in Appendix 1.*

◊ When investigating vapor partitioning/transport concerns due to the presence of an open groundwater collection sump in a basement structure, it is recommended that 3-5 sump volumes of water be evacuated (as permitted by site/recharge conditions) immediately prior to sampling, to ensure collection of a representative sub-slab groundwater sample.

Soil Gas/Indoor Air

◊ Testing of soil gas and/or indoor air should be considered at any site where (a) a groundwater sump is present within a potentially impacted structure, (b) an earthen floor is present within a potentially impacted structure, (c) volatile LNAPL is present beneath or near a potentially impacted structure, or (d) contaminated soils are located within 5 feet of a potentially impacted structure (including beneath a basement slab). Note that the current MCP Method 1 soil standards do NOT consider the direct partitioning of volatile contaminants from impacted soils to an overlying or nearby structure, or impacts from groundwater that infiltrates a structure.

◊ When the objective for indoor air sampling is to determine whether a Critical Exposure Pathway (CEP) is present at a home or school, testing must be conducted under "worst case" site conditions; spatial and temporal averaging of indoor air data, while potentially appropriate for determining Exposure Point Concentrations for risk assessment purposes, is NOT appropriate when evaluating CEP conditions. Additional discussions in this regard are provided in Section 4.3.

5.1.3 Filtering of Groundwater Samples

The objective of a groundwater characterization program is to determine the concentrations of contaminants within, and moving through, an aquifer or formation. Groundwater monitoring wells are installed to help meet this objective. However, monitoring wells are not perfect instruments for this purpose, as they can introduce a (false-positive) bias in the form of (a) suspended sediments containing significant concentrations of sorbed (non-dissolved) hydrocarbons, and/or (b) colloidal suspensions of non-aqueous phase liquids (NAPL). In either case, the analyses of water samples from such wells can provide an overquantitation of contaminant levels of concern. For this reason, groundwater samples are sometimes filtered prior to analyses, generally through a 0.45 micron filter. However, filtering in such a manner can produce a (false-negative) bias, by (1) removing particles smaller than 0.45 microns, and/or (2) removing colloids that are in fact contaminants that are moving through a formation.

Recommendations on this issue are outlined below:

◊ The use and sampling of properly installed, constructed, and developed groundwater monitoring wells, using low-flow sampling techniques, is a preferred alternative to filtering. Recommended guidance and a standard operating procedure for low-flow/low-stress groundwater sampling is available from the EPA Region I website at: http://www.epa.gov/region01/measure/well/wellmon.html

- ◊ Samples obtained from potable water supply wells should NOT be filtered prior to analysis.

- ◊ Filtering should generally NOT be conducted in monitoring wells outside the "source area" of a petroleum release. Such wells are designed to determine the dissolved plume migration of petroleum contaminants, and should not contain suspended sediments with significant concentrations of sorbed hydrocarbons, or any NAPL.

- ◊ When filtering samples, the use of an "in line" device is recommended, to minimize handling and disturbance of the sample.

- ◊ When filtering samples, the collection and analysis of a separate (split) non-filtered sample may be appropriate, to help discern biases present in the characterization process, and determine compliance with characterization objectives.

Because of the potential to produce a false-negative/bias, all site investigations that rely upon data obtained from filtered groundwater samples must include an adequate discussion and justification for using such techniques.

5.2 Use of Old and New TPH Data

While the use of the VPH/EPH approach is a preferred means to characterize risks from petroleum products released to the environment, there are significant amounts of historical Total Petroleum Hydrocarbon (TPH) data that have been obtained in the past for contaminated sites. Moreover, the future use of new TPH data may also be appropriate, to screen out problems in a cost-effective manner. For this reason, in addition to the VPH/EPH aliphatic and aromatic range standards, TPH reporting and cleanup standards have been retained in the Massachusetts Contingency Plan. Note, however, that many of the (post 1997 MCP) standards have been changed, in that the TPH standards are now set at the lowest EPH fractional standard (usually C11-C22 Aromatics), as a "worst case" assumption on hydrocarbon chemistry.

There are two ways to use TPH data:

- ◊ TPH data may be used *directly*, by comparison to TPH Reportable Concentrations and Cleanup Standards; or

- ◊ TPH data may be used *indirectly*, by using (conservative) assumptions on hydrocarbon chemistry to break down and "convert" the TPH data into aliphatic and aromatic ranges.

5.2.1 Comparing TPH Data to Reportable Concentrations, Method 1 Cleanup Standards, and UCLs

Soil and groundwater data obtained from a TPH test method may be directly used to ascertain reporting obligations, compliance with MCP Method 1 cleanup standards, and compliance with Upper Concentration Limits (UCLs). Because the TPH standards assume that the entire hydrocarbon mixture is comprised of the most toxic/problematic hydrocarbon fraction, in theory, use of TPH data would be viewed as a conservative screening effort. However, parties electing to proceed in such a fashion should be aware of the following practical conditions and concerns:

- ◊ Effective October 31, 1997, the MCP defines TPH as "the total or cumulative concentration of hydrocarbons with boiling points equal to or greater than 150°C (C9) and associated with a petroleum product...." All data termed TPH must meet this performance standard. Given the lack of standardized testing, calibration, and reporting techniques for TPH test methods, and methodological biases for techniques such as EPA Method 418.1 (Infra-red detection), demonstrating compliance with this definition is a burden that must be met by data users.

- ◊ In lieu of using an ill-defined TPH methodology, parties seeking to use this screening tool should consider using the EPH test method in the "TPH mode". Specifically, the EPH method provides an option to forego the aliphatic/aromatic fractionation step, and generate a GC/FID TPH quantitation value. If this value is low, and below the TPH cleanup standard, compliance has been achieved. If this value is above the TPH cleanup standard, the laboratory can be instructed to then

proceed to the fractionation step, to produce more toxicologically relevant and less conservative fractional data.

◊ Because common TPH test techniques employ a solvent extraction and concentration step, which can lead to significant losses of hydrocarbons lighter than C9, the use of such methods are not appropriate in the characterization of light petroleum products, such as gasoline, aviation gasoline, and certain military jet fuels.

◊ Because the EPH fractional ranges provide a better characterization of hydrocarbon chemistry and risks, such data will take precedence over TPH data. For example, parties that exceed a TPH Method 1 cleanup standard have the option of obtaining EPH fractional range data, to see if the individual fractions comprising the TPH value are within listed standards. Similarly, under the provisions of 310 CMR 40.0360(2), parties that exceed a TPH Reportable Concentration have 120 days to obtain EPH fractional data, and demonstrate that NONE of the fractions exceeds an applicable Reportable Concentration, to avoid reporting.

5.2.2 Converting TPH Data into EPH Fractional Ranges

Since TPH is essentially a summation of the 3 EPH fractions (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics), it is possible to "convert" TPH data into the EPH fractional ranges, by making informed and reasonably conservative judgments on the chemistry of the TPH data. Compositional assumptions for soil data that are believed to be protective at most sites are provided in Table 5-1.

Table 5-1: Recommended TPH Compositional Assumptions in Soil

Petroleum Product	C11-C22 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics
Diesel/#2/Crankcase Oil	60%	40%	0%
#3-#6 Fuel Oil	70%	30%	0%
Kerosene and Jet Fuel	30%	70%	0%
Mineral Oil Dielectric Fluid	20%	40%	40%
Unknown Oil	100%	0%	0%

For water data, only conservative assumptions can be made:

◊ For TPH water data, all of the TPH should be assumed to be the most conservative EPH fractional standard for the groundwater category(ies) of interest, although it is permissible to subtract out the concentrations of Target PAH analytes (e.g., naphthalene), if known;

◊ For Gasoline Range Organic (GRO) water data, the entire GRO concentration should be assumed to be the most conservative VPH fractional standard for the groundwater category(ies) of interest, although it is permissible to subtract out the concentration of Target BTEX/MtBE analytes, if known.

For old GRO soil data, a conservative assumption would be to consider all of the non-BTEX/MtBE hydrocarbons greater than C8 to be C9-C10 Aromatics. (All non-BTEX/MtBE compounds lighter than C9 are aliphatic hydrocarbons). ***Note, however, that if the GRO soil sample was not preserved in methanol, the integrity and validity of this data would be suspect.***

In using and applying assumptions on the composition of petroleum hydrocarbons, it is essential that all relevant factors be carefully considered, including (1) level of certainty of identification of petroleum product(s) released at the site, (2) reliability, validity, and bias of TPH/screening techniques, and (3) sensitivity of pollutant receptors. Given the wide variability in "TPH" analytical methods, and inherent biases of these methods, the determination of a true TPH concentration is not a trivial exercise.

When evaluating risks for Critical Exposure Pathways, such as drinking water wells, the use of assumptions is generally not appropriate, unless it can be demonstrated that such assumptions represent "worst case" conditions.

5.3 VPH/EPH Compositional Variability/Recommended Approach

Because of fate and transport processes that act upon hydrocarbon compounds and mixtures when they are released to the environment, the chemical composition of petroleum contamination will vary across a site of concern. Accordingly, it is not possible to analyze one soil or groundwater sample by the VPH or EPH methods to establish a compositional template, and apply that template to break down TPH data from other parts of the site into aliphatic/aromatic fractional ranges. For example, soil in the saturated zone in the plume migration area will be contaminated with higher concentrations/proportions of more soluble compounds (e.g., aromatics); soils in older spill sites will have higher concentrations/proportions of less soluble/degradable compounds, such as heavy aliphatics and 3-5 ring PAH hydrocarbons.

For small sites, it may be more cost-effective to simply analyze all impacted media samples by VPH and/or EPH test methods, though use of field screening techniques would be desirable to optimize the selection and support the representativeness of such samples. For larger sites, however, cost savings may be realized by using a combination of VPH/EPH test methods and screening techniques to determine the nature and extent of contamination, and calculate Exposure Point Concentrations (EPCs). In such cases, the following would be recommended:

1. obtain VPH/EPH data from *key areas* and *exposure pathways*;
2. supplement VPH/EPH data with screening/TPH data;
3. consider the chemistry of the petroleum products released to the environment, fate and transport factors, the VPH/EPH data, and the conservative compositional parameters recommended in Table 5-1; and
4. determine conservative fractional composition/EPCs for risk assessment purposes and/or comparison with Method 1 standards.

5.4 Other Program Issues

5.4.1 Numerical Ranking System (NRS)

Under the provisions of 310 CMR 40.1500, sites are classified as either Tier I or Tier II on the basis of a numerical score, and scoring criteria are contained within a number of tables throughout this section. Recent additions to the MCP (1999) have provided (human) toxicity scoring criteria for the VPH/EPH fractions at 310 CMR 40.1511. Future revisions to the MCP will include additional VPH/EPH scoring criteria for mobility and persistence; until that occurs, scoring may be accomplished using the values listed in Table 5-2.

Table 5-2: Mobility and Persistence Scoring Criteria for VPH/EPH Fractions

Fraction	Mobility and Persistence Values and Scores										
	Solubility (mg/L)		Vapor Press (mm Hg)		K ow		Degrad Potential		Specific Gravity		Total Score
	Value	Score	Value	Score	Value	Score	Value	Score	Value	Score	
C5-C8 Aliphatics	11	5	80	10	< E+04	5	NP	0	<1	0	20
C9-C12 Aliphatics	0.07	0	0.7	5	> E+04	0	NP	0	<1	0	5
C9-C10 Aromatics	51	5	2	10	<E+04	5	NP	0	<1	0	20
C9-C18 Aliphatics	0.01	0	0.2	5	>E+04	0	NP	0	<1	0	5
C19-C36 Aliphatics	N/A	0	N/A	0	N/A	0	P	10	<1	0	10
C11-C22 Aromatics	5.8	5	0.02	5	>E+04	0	NP	0	<1	0	10

5.4.2 Characterization of Remediation Wastes

For the purpose of characterizing Remediation Wastes, as well as other purposes, the sum of the 3 EPH fractions (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics) is equivalent to a TPH concentration, as defined by the MCP.

5.4.3 Characterization of Remedial Air Emissions

Requirements for the evaluation and/or treatment of remedial air emissions are specified in the MCP at 310 CMR 40.0049. Further guidance in this regard is provided in *Off-Gas Treatment of Point-Source Remedial Air Emissions*, Policy #WSC-94-150, available at http://www.state.ma.us/dep/bwsc/finalpol.htm

For the purposes of characterizing remedial air emissions at petroleum-contaminated sites, the following guidelines may be applied:

- The specification in 310 CMR 40.0049(5) to achieve 95% removal of emitted oil and hazardous materials applies to the collective concentrations of all influent/effluent hydrocarbons, not to individual target analytes and/or hydrocarbon ranges. Therefore, if monitored by the APH method, the collective concentration of all influent Target Analytes and hydrocarbon ranges is compared to the collective concentration of all effluent Target Analytes and hydrocarbon ranges.

- Consistent with the recommendations contained in Section 5.0 of *Off-Gas Treatment of Point-Source Remedial Air Emissions*, it is permissible to monitor influent and effluent vapor concentrations using a portable PID or FID unit. In such cases, the PID unit should be calibrated to an isobutylene response standard, and the FID unit should be calibrated to a methane response standard. At sites where gasoline vapors are being emitted, the PID must be equipped with a minimum 10.0 eV lamp. When using a PID or FID unit to monitor vapor emissions, a reading of 1 ppmV or less can generally be considered a "background" concentration.

- It is permissible to evaluate off-gas remedial emissions using the Emission-Distance Graphs contained in Section 7.3 of *Off-Gas Treatment of Point-Source Remedial Air Emissions*. When using these graphs, the C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C18 Aliphatic Hydrocarbon ranges are considered "Group 4" contaminants, and the C9-C10 Aromatic and C11-C22 Aromatic Hydrocarbon Fractions are considered "Group 3" contaminants.

5.4.4 Characterization of Coal Tar Contaminated Sites

MADEP is evaluating the applicability of the VPH/EPH approach in the characterization of sites contaminated by coal tars. As an interim recommendation, the use of VPH and EPH would appear to be an appropriate approach to characterize the risks posed by the aliphatic and aromatic hydrocarbons that comprise coal tars; because of the chemistry of this material, aliphatic and aromatic ranges quantitated by both the VPH and EPH methods would appear to be necessary, along with all method Target Analytes except MtBE (i.e., BTEX and the 17 Target PAHs). In addition to the aliphatic and aromatic ranges and Target Analytes, additional contaminants of concern for coal tars would include phenolics, cyanide, and trace metals.

SOIL SAMPLES

OPTION 1: In-Field Methanol Preservation Technique

PERFORMANCE STANDARD: **Obtain undisturbed soil sample and immediately preserve with methanol at a ratio of 1 mL methanol per 1 gram soil (+/- 25%).**

Step 1: Choose appropriate sampling container:

60 mL wide mouth packer bottle; or
60 mL straight sided wide mouth bottle; or
60 mL VOA vial; or
40 mL VOA vial

All sampling containers should have an open-top screw cap with Teflon-coated silicone rubber septa or equivalent.

Step 2: Pre-label each container with a unique alpha/numerical designation. Obtain and record tare (empty) weight of each container to nearest 0.1 gram. *This information must be available to the laboratory performing the analyses.*

Step 3: Add 25 mLs of purge and trap grade methanol to 60 mL containers, or 15 mL to 40 mL containers. *It is essential that the methanol be purge and trap grade or equivalent quality*. Immediately cap the container. Make a mark on the 60 mL containers approximately 15 mL above the level of methanol, or a mark on the 40 mL container approximately 10 mL above the level of methanol. The objective is to obtain 25 grams of soil in the 60 mL container, or 15 grams of soil in the 40 mL container, which is approximately 15 and 10 mL of soil volume, respectively, depending upon soil type and moisture content. Other masses of soil are permissible, as long as the ratio of [grams soil]/[mL methanol] is 1:1, +/- 25%. Store at 4°C. *The use of a methanol trip blank prepared in this manner is recommended.*

Step 4: In the field, carefully add soil to the sample container, until the level of methanol in the vial reaches the designated volumetric mark. For wet soil, add slightly beyond the mark. IN NO CASE, HOWEVER, MAY THE LEVEL OF SOIL IN THE CONTAINER RISE ABOVE THE LEVEL OF METHANOL. The use of a 10-30 mL disposable syringe with the end cut off is recommended to obtain an undisturbed soil sample from freshly exposed soils. In such cases, obtain and extrude the soil into sample container, avoiding splashing methanol out of the container.

Optional: use a field electronic balance to ensure addition of desired mass of soil (25 grams to 60 mL containers, 15 grams to 40 mL containers).

Step 5: Use a clean brush or paper towel to remove soil particles from the threads of the sample container and screw cap. Tightly apply and secure screw cap. Gently swirl sample to break up soil aggregate, if necessary, until soil is covered with methanol. DO NOT SHAKE. Duplicate samples obtained in this manner are recommended. A split-sample must also be obtained for a determination of soil moisture content. This sample must NOT be preserved in methanol. HINT: fill this container 1/2 full, to allow screening of the sample headspace by the field investigator or the laboratory.

Step 6: Immediately place containers in cooler for storage in an upright position. Sample vials may be placed in separate sealable bags to protect containers in case of leakage during transport. Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

SOIL SAMPLES (Continued)

OPTION 2: Use of a Sealed-Tube Sampling/Storage Device

PERFORMANCE STANDARD: **Obtain undisturbed soil sample and immediately seal in air-tight container, for shipment to laboratory and immersion in methanol within 48 hours.**

Step 1: Obtain pre-cleaned and/or disposable samplers/containers that allow the collection and air-tight storage of 5- 25 grams of soil.

Step 2: In the field, obtain an undisturbed sample from freshly exposed soil. Immediately seal container, and place in a cooler. Obtain a duplicate sample to enable the determination of soil moisture content (this may be stored/sealed in a conventional container). Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

Step 3: Samples must be extruded and immersed in purge and trap (or equivalent) grade methanol at the laboratory within 48 hours of sampling, at a ratio of 1 mL methanol to 1 gram soil. In no case, however, shall the level of soil in the laboratory container exceed the level of methanol (i.e., the soil must be completely immersed in methanol).

NOTE: Documentation MUST be provided/available on the ability of the sampler/container to provide an air-tight seal in a manner that results in no statistically significant loss of volatile hydrocarbons for at least 48 hours.

OPTION 3: Use of Alternative Collection/Storage/Preservation Techniques

PERFORMANCE STANDARD: **Obtain and store an undisturbed soil sample in a manner that ensures the chemical integrity of the sample by (1) preventing the volatilization of petroleum hydrocarbons heavier than C5, and (2) preventing the biological degradation of petroleum hydrocarbons.**

NOTE: The onus is on the user of such techniques to demonstrate the validity of the procedures used, via reference to published literature and/or other pertinent data.

SAFETY

Methanol is a toxic and flammable liquid, and must be handled with appropriate care. Use in a well-vented area, and avoid inhaling methanol vapors. The use of protective gloves is recommended when handling or transferring methanol. Vials of methanol should always be stored in a cooler with ice at all times, away from sources of ignition such as extreme heat or open flames.

AQUEOUS SAMPLES

MOST VPH/VOC AQUEOUS SAMPLES

All aqueous samples that will not be analyzed within 4 hours of collection must be preserved by pH adjustment, in order to minimize analyte losses due to biodegradation. For most samples, this can be accomplished by acidification of the sample to pH <2, by adding 3-4 drops of 1:1 HCl to a 40 mL vial. The sample should then be stored at 4°C until it is analyzed. In lieu of acidification, samples may also be preserved with an appropriate base to pH > 11.0 (see below).

SAMPLES TO BE ANALYZED FOR MTBE

ISSUE

Traditionally, VPH and VOC aqueous samples have been preserved by addition of an acid (e.g., HCl) to lower the pH of the sample to less than 2.0. While this is still an acceptable approach for petroleum\hydrocarbons and most VOC analytes, recent information and data have indicated that such a technique can lead to significant losses (up to 89%) of MtBE and other ethers (White, H., Lesnik, B., Wilson, J., *Analytical Methods for Fuel Oxygenates*, LUSTLINE Bulletin #42, New England Interstate Water Pollution Control Commission, 2002 (http://www.epa.gov/swerust1/mtbe/LL42Analytical.pdf) Specifically, the combination of a low pH and high temperature sample preparation technique (e.g., heated purge and trap) hydrolyze the ether bonds present in the sample, converting the ethers into alcohols (e.g., TBA).

PRESERVING MTBE SAMPLES

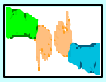
To prevent ether hydrolysis, samples should either (a) not be acidified or (b) not be heated. Because heating the sample may be necessary to achieve proper analyte purging/partitioning, an alternative to acidification is likely to be the most efficient means to prevent hydrolysis. Because ethers are not subject to base-catalyzed hydrolysis, raising the pH of the sample is an acceptable alternative to acidification. Studies by the USEPA have shown that preservation of aqueous samples to a pH greater than 11.0 using trisodium phosphate dodecahydrate will effectively prevent biological degradation of dissolved analytes, and will not result in deleterious effects on other dissolved oxygenates or on BTEX analytes.

PROTOCOL

A recommended protocol to achieve a pH level > 11.0 is to add between 0.40 and 0.44 grams of trisodium phosphate dodecahydrate to a 40 mL vial. For convenience, this can be done in the laboratory prior to sample collection in the field. Because it is more convenient to measure the required amount of trisodium phosphate dodecahydrate on a volume basis rather than by weight, the use of a precalibrated spoon is recommended. In the field, each vial is filled with the aqueous sample and sealed without headspace – as is traditionally done for acidified samples. The sample is then stored at 4°C until it is analyzed.

WHEN IS THIS NEEDED?

Given the Method 1 standard for MtBE in GW-2 and GW-3 areas (i.e., 50,000 µg/L), MADEP will generally not expect or require the use of alternative preservation or analytical protocols for disposal sites located ONLY in such areas, with respect to demonstrating attainment of a condition of No Significant Risk. Nevertheless, such efforts should be considered, and may be necessary, on a case-specific basis, to investigate other site assessment objectives, such as extent of contamination, source identification, etc.



For gasoline releases in GW-1 areas, it is generally expected that some level of assessment will be conducted to confirm the concentration of MtBE using alternative preservation and/or analytical procedures to prevent hydrolysis of ethers. In particular, confirmatory samples would be recommended in the "source area" and in the outer plume (or N.D.) monitoring wells. When sampling a private or public drinking water supply well that is proximate to a release of gasoline and/or #2 fuel oil, it is generally expected that all such samples will be evaluated for the presence of MtBE by use of an alternative preservation and/or analytical procedure.

APPENDIX 2
SHIPPING METHANOL PRESERVED SAMPLES

Shipping of Hazardous Materials

Methanol is considered a hazardous material by the US Department of Transportation (DOT) and the International Air Transport Association (IATA). Shipments of methanol between the field and the laboratory must conform to the rules established in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and the most current edition of the IATA Dangerous Goods Regulations. Consult these documents or your shipping company for complete details, as these regulations may change without notice.

Small Quantity Exemption

The volumes of methanol recommended in the VPH method fall under the small quantity exemption of 49 CFR section 173.4. To qualify for this exemption, all of the following must be met:

- ◊ the maximum volume of methanol in each sample container must not exceed 30 mL
- ◊ the sample container must not be full of methanol
- ◊ the sample container must be securely packed and cushioned in an upright position, and be surrounded by a sorbent material capable of absorbing spills from leaks or breakage of sample containers
- ◊ the package weight must not exceed 64 pounds
- ◊ the volume of methanol per shipping container must not exceed 500 mL
- ◊ the packaging and shipping container must be strong enough to hold up to the intended use
- ◊ the package must not be opened or altered while in transit
- ◊ the shipper must mark the shipping container in accordance with shipping dangerous goods in acceptable quantities, and provide the statement:

"This package conforms to conditions and limitations specified in 49 CFR 173.4"

Shipping Papers

All shipments must be accompanied by shipping papers that include the following:

Proper Shipping Name:	Methyl Alcohol
Hazardous Class:	Flammable Liquid
Identification Number:	UN1230
Total Quantity:	*(mL methanol/container x the number of containers)*
Emergency Response Info:	Methanol MSDS attached
Emergency Response Phone:	*provide appropriate number*
Shipping Exemption:	DOT-E 173.118, Limited Quantity

Labeling & Placarding

Labeling and placarding are not required for valid small quantity exemptions (per 173.118)

APPENDIX 3 - Required VPH Data Report Content

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:		
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:		
Sample Preservatives	Aqueous	☐ N/A ☐ pH≤2 ☐ pH>2 Comment:	
	Soil or Sediment	☐ N/A ☐ Samples NOT preserved in Methanol or air-tight container	mL Methanol/g soil
		☐ Samples rec'd in Methanol: ☐ covering soil ☐ not covering soil	☐ 1:1 +/- 25%
		☐ Samples received in air-tight container:	☐ Other:
Temperature	☐ Received on Ice ☐ Received at 4°C ☐ Other:		

VPH ANALYTICAL RESULTS

Method for Ranges: MADEP VPH 98-1		**Client ID**						
Method for Target Analytes:		**Lab ID**						
VPH Surrogate Standards		**Date Collected**						
PID:		**Date Received**						
FID:		**Date Analyzed**						
		Dilution Factor						
		% Moisture (soil)						
Range/Target Analyte	**Elution Range**	**RL**	**Units**					
Unadjusted C5-C8 Aliphatics[1]	N/A							
Unadjusted C9-C12 Aliphatics[1]	N/A							
Benzene								
Ethylbenzene								
Methyl-tert-butylether								
Naphthalene	N/A							
Toluene								
m- & p- Xylenes								
o-Xylene								
C5-C8 Aliphatic Hydrocarbons[1,2]	N/A							
C9-C12 Aliphatic Hydrocarbons[1,3]	N/A							
C9-C10 Aromatic Hydrocarbons[1]	N/A							
PID Surrogate % Recovery								
FID Surrogate % Recovery								
Surrogate Acceptance Range				70-130%	70-130%	70-130%	70-130%	70-130%

[1] Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range
[2] C_5-C_8 Aliphatic Hydrocarbons exclude the concentration of Target Analytes eluting in that range
[3] C_9-C_{12} Aliphatic Hydrocarbons exclude conc of Target Analytes eluting in that range AND concentration of C_9-C_{10} Aromatic Hydrocarbons

CERTIFICATION

Were all QA/QC procedures REQUIRED by the VPH Method followed? ☐ Yes ☐ No - Details Attached
Were all performance/acceptance standards for required QA/QC procedures achieved? ☐ Yes ☐ No - Details Attached
Were any significant modifications made to the VPH method, as specified in Sect 11.3? ☐ No ☐ Yes - Details Attached

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ **POSITION:** _____

PRINTED NAME: _____ **DATE:** _____

APPENDIX 3 - Supplemental VPH QA/QC data (Optional)

QA/QC DATA

Range/Target Analyte	Range of Elution	Reporting Limit	Lab Method Blank	Duplicate Sample			Lab Fortified Blank	
				Sample	Duplicate	%RPD	Spiking Conc	% Recov
Unadjusted C5-C8 Aliphatics	N/A						N/A	N/A
Unadjusted C9-C12 Aliphatics	N/A						N/A	N/A
Pentane								
2-Methylpentane								
Methyl-t-butylether								
2,2,4-Trimethylpentane								
Benzene								
Toluene								
n-Nonane								
Ethylbenzene								
m- & p- Xylenes								
Naphthalene								
C5-C8 Aliphatics Hydrocarbons	N/A						N/A	N/A
C9-C12 Aliphatics Hydrocarbons	N/A						N/A	N/A
C9-C10 Aromatics Hydrocarbons	N/A						N/A	N/A
Sample Matrix								
Units								
Sample ID number		N/A						
Date Analyzed		N/A						

VPH SOIL PRESERVATION DATA

	Client ID									
	Lab ID									
A	Tare Wt. Jar (g)									
B	Vol Methanol Initially Added (mL)									
C	Wt. Jar & Methanol (g)									
D	Wt Jar, Methanol & Soil (g)									
D-C	Wt. Soil (g)									
E	Est Vol loss Methanol after sampling (mL)									
F	Vol Methanol added after sampling (mL)									
B-E+F	Final Vol Methanol Preservative (mL)									
G	Vol Surrogates/Internal Stds Added (mL)									
H	Volume of Matrix Spikes Added (mL)									

APPENDIX 3 – Required EPH Data Report Content

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:
Aqueous Preservatives	☐ N/A ☐ pH≤2 ☐ pH>2 Comment:
Temperature	☐ Received on Ice ☐ Received at 4 ° C ☐ Other:
Extraction Method	Water: Soil:

EPH ANALYTICAL RESULTS

Method for Ranges: MADEP EPH 98-1		**Client ID**					
Method for Target Analytes:		**Lab ID**					
EPH Surrogate Standards		**Date Collected**					
Aliphatic:		**Date Received**					
Aromatic:		**Date Extracted**					
EPH Fractionation Surrogates		**Date Analyzed**					
		Dilution Factor					
		% Moisture (soil)					
RANGE/TARGET ANALYTE		**RL**	**Units**				
Unadjusted C11-C22 Aromatics[1]							
Diesel PAH Analytes	**Naphthalene**						
	2-Methylnaphthalene						
	Phenanthrene						
	Acenaphthene						
Other Target PAH Analytes							
C9-C18 Aliphatic Hydrocarbons[1]							
C19-C36 Aliphatic Hydrocarbons[1]							
C11-C22 Aromatic Hydrocarbons[1,2]							
Aliphatic Surrogate % Recovery							
Aromatic Surrogate % Recovery							
Sample Surrogate Acceptance Range				40-140%	40-140%	40-140%	40-140%	40-140%
Fractionation Surrogate % Recovery							
Fractionation Surrogate % Recovery							
Fractionation Surrogate Acceptance Range				40-140%	40-140%	40-140%	40-140%	40-140%

[1]Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

[2] C11-C22 Aromatic Hydrocarbons exclude the concentration of Target PAH Analytes

CERTIFICATION

Were all QA/QC procedures REQUIRED by the EPH Method followed? ☐ Yes ☐ No-Details Attached

Were all performance/acceptance standards for the required QA/QC procedures achieved? ☐ Yes ☐ No-Details Attached

Were any significant modifications made to the EPH method, as specified in Section 11.3? ☐ No ☐ Yes-Details Attached

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ **POSITION:** _____

PRINTED NAME: _____ **DATE:** _____

APPENDIX 3 - Recommended TPH Data Report Content

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:
Aqueous Preservatives	☐ N/A ☐ pH≤2 ☐ pH>2 Comment:
Temperature	☐ Received on Ice ☐ Received at 4 ° C ☐ Other:
Extraction Method	Water: Soil:

TPH ANALYTICAL RESULTS

Method: MADEP EPH 98-1		**Client ID**					
Method for Target Analytes:		**Lab ID**					
TPH Surrogate Standards		**Date Collected**					
		Date Received					
		Date Extracted					
		Date Analyzed					
		Dilution Factor					
		% Moisture (soil)					
Range/Target Analyte		**RL**	**Units**				
Unadjusted Total Petroleum Hydrocarbons[1]							
Diesel PAH Analytes	**Naphthalene**						
	2-Methylnaphthalene						
	Phenanthrene						
	Acenaphthene						
Other PAH Target Analytes							
Total Petroleum Hydrocarbons[2]							
Sample Surrogate % Recovery							
Sample Surrogate Acceptance Range				40-140%	40-140%	40-140%	40-140%	40-140%

[1] Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

[2] Total Petroleum Hydrocarbons exclude the concentration of PAH Target Analytes

CERTIFICATION

Were all QA/QC procedures REQUIRED by the EPH Method (for TPH) followed? ☐ Yes ☐ No-Details Attached

Were all performance/acceptance standards for the required QA/QC procedures achieved? ☐ Yes ☐ No-Details Attached

Were any significant modifications made to the EPH method, as specified in Section 11.3? ☐ No ☐ Yes-Details Attached

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ **POSITION:** _____

PRINTED NAME: _____ **DATE:** _____

APPENDIX 3 - Supplemental EPH/TPH QA/QC data (Optional)

Range/Target Analyte	Range of Elution	Reporting Limit	Lab Method Blank	Duplicate Sample			Lab Fortified Blank	
				Sample	Duplicate	%RPD	Spiking Conc	% Recov
Unadjusted C11-C22 Aromatics	N/A						N/A	N/A
Unadjusted TPH	N/A							
C9-C18 Aliphatics	N/A						N/A	N/A
C19-C36 Aliphatics	N/A						N/A	N/A
TPH	N/A						N/A	N/A
Sample Matrix								
Units								
Sample ID number		N/A						
Date Analyzed		N/A						

APPENDIX 4 - VPH/EPH Cleanup Standards and Reportable Concentrations
October 31, 1997

Reportable Concentrations

Fraction/Parameter	RCS-1 (mg/g)	RCS-2 (mg/g)	RCGW-1 (mg/L)	RCGW-2 (mg/L)
C5-C8 Aliphatic Hydrocarbons	100	500	400	1000
C9-C12 Aliphatic Hydrocarbons	1000	2500	1000	1000
C9-C10 Aromatic Hydrocarbons	100	500	200	4000
C9-C18 Aliphatic Hydrocarbons	1000	2500	1000	1000
C19-C36 Aliphatic Hydrocarbons	2500	5000	5000	20,000
C11-C22 Aromatic Hydrocarbons	200	2000	2000	30,000
Total Petroleum Hydrocarbons (TPH)	200	2000	2000	1000

Method 1 Cleanup Standards for Groundwater

Fraction/Parameter	GW-1 (mg/L)	GW-2 (mg/L)	GW-3 (mg/L)
C5-C8 Aliphatic Hydrocarbons	400	1000	4000
C9-C12 Aliphatic Hydrocarbons	4000	1000	20,000
C9-C10 Aromatic Hydrocarbons	200	5000	4000
C9-C18 Aliphatic Hydrocarbons	4000	1000	20,000
C19-C36 Aliphatic Hydrocarbons	5000	N/A	20,000
C11-C22 Aromatic Hydrocarbons	200	50,000	30,000
Total Petroleum Hydrocarbons (TPH)	200	1000	20,000

Method 1 Cleanup Standards for Soil

Fraction/Parameter	GW-1 Areas			GW-2 Areas			GW-3 Areas		
	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)
C5-C8 Aliphatic Hydrocarbons	100	500	500	100	500	500	100	500	500
C9-C12 Aliphatic Hydrocarbons	1000	2500	5000	1000	2500	5000	1000	2500	5000
C9-C10 Aromatic Hydrocarbons	100	100	100	100	500	500	100	500	500
C9-C18 Aliphatic Hydrocarbons	1000	2500	5000	1000	2500	5000	1000	2500	5000
C19-C36 Aliphatic Hydrocarbons	2500	5000	5000	2500	5000	5000	2500	5000	5000
C11-C22 Aromatic Hydrocarbons	200	200	200	800	2000	5000	800	2000	5000
Total Petroleum Hydrocarbons (TPH)	200	200	200	800	2000	5000	800	2000	5000

Upper Concentration Limits (UCLs)

Fraction/Parameter	Groundwater (mg/L)	Soil (mg/g)
C5-C8 Aliphatic Hydrocarbons	100,000	5000
C9-C12 Aliphatic Hydrocarbons	100,000	20,000
C9-C10 Aromatic Hydrocarbons	100,000	5000
C9-C18 Aliphatic Hydrocarbons	100,000	20,000
C19-C36 Aliphatic Hydrocarbons	100,000	20,000
C11-C22 Aromatic Hydrocarbons	100,000	10,000
Total Petroleum Hydrocarbons (TPH)	100,000	10,000

Cleanup Standards are subject to change; consult latest version of the MCP for most up to date values!

APPENDIX 5 - ADDITIONAL REFERENCE/SUPPORT MATERIALS

For a Closer Look.....

The following documents and publications provided additional background, information, and insight into the VPH/EPH approach, guidance, and standards

MADEP Publications

VPH/EPH Approach

◊ *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter, August, 1994* - Original report presenting the toxicological basis of the proposed new VPH/EPH approach.

◊ *Issues Paper: Implementation of VPH/EPH Approach, Public Comment Draft, May, 1996* - Detailed discussion and recommendations on how to develop MCP Method 1 cleanup standards, and otherwise incorporate new VPH/EPH approach into the MCP regulatory process.

◊ *Beyond TPH: Understanding and Using the New VPH/EPH Approach, June, 1997* - Slides and handouts from a day-long training session presented by MADEP in the Spring of 1997.

◊ *#2 Fuel/Diesel Short Form, July, 2002* - An Excel spreadsheet that allows for the site-specific characterization of human health risks for Target Analytes and appropriate aliphatic/aromatic hydrocarbon fractions.

◊ *Reports on the Results of the VPH/EPH Round Robin Testing Programs, June 1997 and January 1998* - Detailed reports outlining the methods and results of two interlaboratory "Round Robin" testing programs undertaken by MADEP to help refine and validate the VPH and EPH analytical test methods.

◊ *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), January, 1998* - Detailed analytical procedure for this GC/PID/FID methodology developed by MADEP.

◊ *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), January, 1998* - Detailed analytical procedure for this silica-gel/fractionation GC/FID method developed by MADEP.

◊ *Draft Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH), February, 2000* – Proposed analytical procedure for this GC/MS methodology developed by MADEP.

◊ *Background Documentation for the Development of VPH/EPH Cleanup Standards and Guidance, October, 2002*, available at http://www.state.ma.us/dep/bwsc/vph_eph.htm.

Related MADEP Regulations and Guidance Documents

◊ *Massachusetts Contingency Plan (MCP), 310 CMR 40.0000* - State regulations that govern the cleanup of sites contaminated by oil or hazardous materials; now includes provisions for VPH/EPH approach and standards.

◊ *Background Documentation for the Development of the MCP Numerical Standards, April, 1994* - Contains information, data, assumptions, approaches, and spreadsheets for development of the MCP Method 1 cleanup standards, excluding VPH/EPH fractional range standards.

◊ *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan, July, 1995* - Comprehensive guidance on how to characterize risks to human and ecological receptors.

APPENDIX 5 - ADDITIONAL REFERENCE/SUPPORT MATERIALS (continued)

Related MADEP Regulations and Guidance Documents (continued)

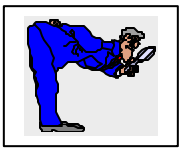
- ◊ *Commonwealth of Massachusetts Underground Storage Tank Closure Assessment Manual, April, 1996* - Outlines requirements and procedures for conducting a closure assessment of underground storage tanks.

- ◊ *Interim Remediation Waste Management Policy for Petroleum Contaminated Soils, April, 1994* - Procedures, requirements, and recommendations for characterizing, classifying, managing, and recycling/disposing of petroleum contaminated soils.

All MADEP publications available on the World Wide Web at http://www.state.ma.us/dep/bwsc/pubs.htm

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Publications

TPHCWG is a national consortium of state regulatory agencies, academia, DOD, DOE, USEPA, ASTDR, petroleum, power and transportation industries, and consulting firms. The goal of this group is to evaluate and propose methods to characterize risks posed by petroleum-contaminated media. TPHCWG has endorsed a toxicological approach similar to the MADEP VPH/EPH approach. Recommendations by this group on evaluating the fate and transport of aliphatic and aromatic hydrocarbon fractions were used by MADEP in developing the cleanup standards and the guidelines and recommendations contained in this policy. TPHCWG plans on publishing a six-volume series of reports on issues of interest; volumes of interest to parties using the VPH/EPH approach are listed below:



- ◊ *Volume I – Analysis of Petroleum Hydrocarbons in Environmental Media (1998)* - Contains an overview of petroleum hydrocarbon characterization and risk assessment, a discussion of available analytical methods, and a proposed GC-Based analytical method, developed by the Working group, that reports hydrocarbon results in equivalent carbon number groups or fractions.

- ◊ *Volume II - Composition of Petroleum Mixtures* – Contains a description of the chemical characteristics and composition of petroleum fuels, with a comprehensive series of tables and references.

- ◊ *Volume III - Selection of TPH Fractions Based upon Fate and Transport Consideration (1997)*- Contains information and data on the physical and chemical properties of hydrocarbons and hydrocarbon mixtures, and recommended algorithms for determining the properties of aliphatic and aromatic fractions.

- ◊ *Volume IV - Development of Fraction-Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH (1997)* - Contains extensive information and data on the toxicological properties of petroleum products and hydrocarbon mixtures, and a proposed approach to characterize risks based upon the collective fractions of aliphatic and aromatic fractions. NOTE: Certain provisions of these recommendations are in conflict with current MADEP positions and requirement, although the agency is currently evaluating recent data presented in this volume.

TPHCWG Publications are being cited as potentially relevant background/reference materials. MADEP is not necessarily endorsing the conclusions and/or recommendations provided in these various documents.

TPHCWG Publications available on the World Wide Web at
http://www.aehs.com/publications/catalog/contents/tph.htm

APPENDIX 6
SUMMARY OF SIGNIFICANT CHANGES MADE TO FINAL IMPLEMENTATION POLICY

BY SECTION		
Section	**Subject**	**Change/Addition**
1.3	Applicability	New explanation of VPH/EPH reporting obligations at closed sites
3.2.3	APH	New explanation of Air-Phase Petroleum Hydrocarbon (APH) method
3.5	Method Modification	New guidance on evaluating modifications to VPH/EPH/APH procedures
3.7	Other Testing Methods	New guidance on use of TPH and other hydrocarbon testing procedures
4.1	Exposure Point Conc.	New Section 4.1 added with additional guidance on determining EPCs
4.2.2	Target Analytes	**Modifications of Table 4-3, additional information and guidance on lead, EDB, MtBE, and other petroleum additives**
4.3	Vapor Pathway	Expanded "tool box" approach to investigate (Figure 4-1) and mitigate (Figure 4-3) subsurface vapor infiltration pathways
4.3.1	Soil Gas Screening	Additional guidance on location of soil gas probes; **new criteria for PID/FID Level 1 Screening (Table 4-9);** additional guidance on Level 2 Screening
4.3.1.1	Soil Gas Guidelines	Certain Target Analytes added to Tables 4-9, 4-10, and 4-11; criteria now relevant to soil contamination, as well as GW-2 exceedances
4.3.1.4	Vapor Transport Models	New reference to DEP policy on use/utility of transport models
4.3.1.5	Groundwater Profiling	New guidance on evaluating indoor air pathways by profiling contaminant concentrations at and below the groundwater table
4.3.2	GW-3 Evaluation	**New Dilution Graphs (Figure4-4) and guidance to evaluate plume dispersion**
4.5	Toxicological parameters	**New RfD and RfC values for certain fractions**
4.6	Fate/Transport Parameters	New aqueous diffusivity coefficients for hydrocarbon fractions
4.7	NAPL	Additional guidance on NAPL monitoring and evaluation
5.4.1	NRS	New recommended mobility and persistence scoring criteria (Table 5-2) for hydrocarbon fractions when using Numerical Ranking System
5.4.3	Remedial Air Emissions	**New recommendations on monitoring and evaluating off-gas treatment for remedial air emissions**
App 1	MtBE analysis	**New information/guidelines on preservation of aqueous samples for MtBE analysis (Due to degradation caused by acidification)**
App 3	VPH/EPH Report Format	Required Reporting Format for VPH/EPH methods
App 5	References	Additional references/support materials for VPH/EPH approach

Shading indicates changes that were made AFTER issuance of FINAL DRAFT document (June 2001)

APPENDIX 6
SUMMARY OF SIGNIFICANT CHANGES MADE TO FINAL IMPLEMENTATION POLICY (Continued)

BY SUBJECT		
Subject	**Section**	**Change/Addition**
APH	3.2.3	New explanation of Air-Phase Petroleum Hydrocarbon (APH) method
Applicability	1.3	New explanation of VPH/EPH reporting obligations at closed sites
Exposure Point Conc.	4.1	New Section 4.1 added with additional guidance on determining EPCs
Fate/Transport Parameters	4.6	New aqueous diffusivity coefficients for hydrocarbon fractions
Groundwater Profiling	4.3.1.5	New guidance on evaluating indoor air pathways by profiling contaminant concentrations at and below the groundwater table
GW-3 Evaluations	4.3.2	**New Dilution Graphs (Figure4-4) and guidance to evaluate plume dispersion**
Method Modifications	3.5	New guidance on evaluating modifications to VPH/EPH/APH procedures
MtBE analysis	App 1	**New information/guidelines on preservation of aqueous samples for MtBE analysis (Due to degradation caused by acidification)**
NAPL	4.7	Additional guidance on NAPL monitoring and evaluation
NRS	5.4.1	New recommended mobility and persistence scoring criteria (Table 5-2) for hydrocarbon fractions when using Numerical Ranking System
Other Testing Methods	3.7	New guidance on use of TPH and other hydrocarbon testing procedures
References	App5	Additional references/support materials for VPH/EPH approach
Remedial Air Emissions	5.4.3	**New recommendations on monitoring and evaluating off-gas treatment for remedial air emissions**
Soil Gas Screening	4.3.1	Additional guidance on location of soil gas probes; **new criteria for PID/FID Level 1 Screening (Table 4-9);** additional guidance on Level 2 Screening
Soil Gas Guidelines	4.3.1.1	Certain Target Analytes added to Table 4-9, 4-10, and 4-11; criteria now relevant to soil contamination, as well as GW-2 exceedances
Target Analytes	4.2.2	**Modifications of Table 4-3, additional information and guidance on lead, EDB, MtBE, and other petroleum additives**
Toxicological Parameters	4.5	**New RfD and RfC values for certain fractions**
Vapor Pathway	4.3	Expanded "tool box" approach to investigate (Figure 4-1) and mitigate (Figure 4-3) subsurface vapor infiltration pathways
Vapor Transport Models	4.3.1.4	New reference to DEP policy on use/utility of transport models
VPH/EPH Report Format	App3	Required Reporting Format for VPH/EPH methods

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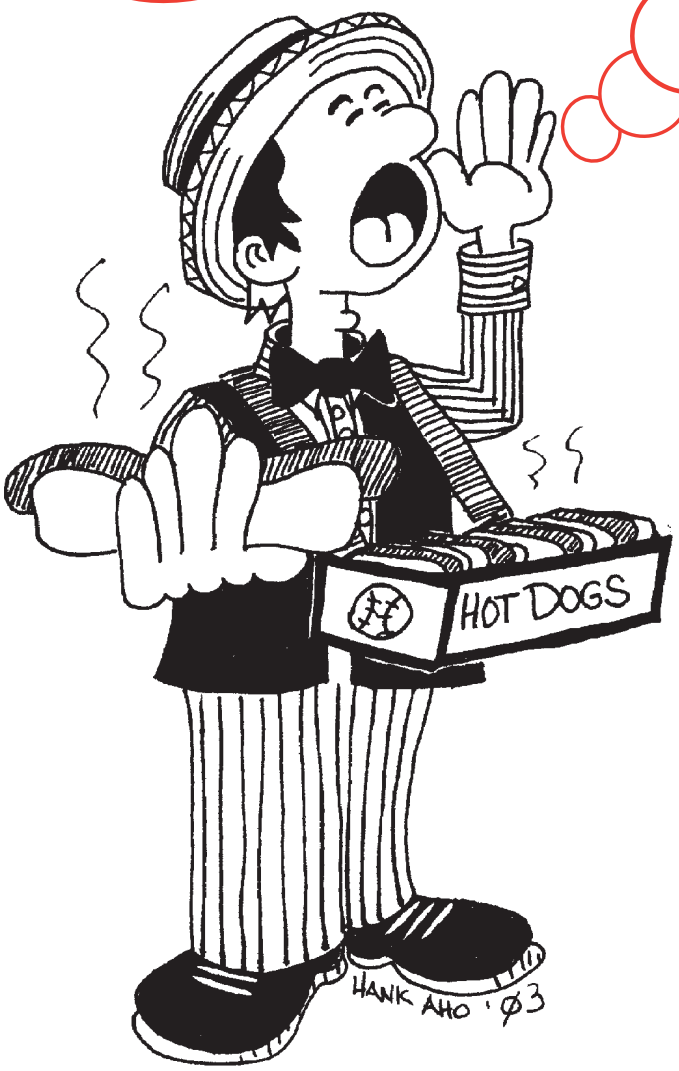
L.U.S.T. LINE

A Report On Federal & State Programs To Control Leaking Underground Storage Tanks

A Hot Dog by Any Other Name Could Be Your Drinking Water



by Patricia Ellis

"Hot dogs, getcher hot dogs!"

The cry of the hot dog vendor at the ballpark. The steaming hot frank with your choice of mustard, ketchup, relish...the captivating aroma and the even more satisfying taste! But let's not stop to think about what's actually in a hot dog. Sure, some of us take comfort in consuming only hot dogs that are "all beef" or "chicken" or Kosher. But what's really in a hot dog? Do we really want to know? And just what has the composition of hot dogs got to do with an article that is ostensibly about leaking underground storage tanks, anyway? Well, it has to do with this propensity to not want to know about those ingredients…even the ingredients in our own drinking water.

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■ **Hot Dogs** *from page 1*

Is Ignorance Bliss?

The drinking water supply systems in the United States are unquestionably the best in the world. Most people can simply turn on the faucet and draw a glass of fresh, clear water that they can put unflinchingly to their lips and drink. Yet, a growing segment of the population uses a filter of some sort, and increasing numbers of people buy bottled water. In fact, in the last 40 years, it is estimated that the U.S. drinking water industry has lost nearly 60 percent of its customers to competitors (currently unregulated) who are "bottled water and point-of-use/point-of-entry providers." (Means et al., 2002) Why?

The reasons are many—taste, odor, color, fad/style, fear (justified or imagined). For those of us on public water supplies, our water suppliers provide us with annual Consumer Confidence Reports (CCRs) that show us that our water has been tested for a variety of contaminants and is safe to drink. But most water suppliers analyze for a couple dozen contaminants at most. The CCRs tell us whether or not these contaminants were detected and at what concentrations.

When these contaminants are detected, even when their concentration may from time to time exhibit a spike above a regulatory threshold, this water is still distributed to us. Generally an accounting gimmick, such as 30-day average concentration, is employed so that it can be claimed that although detected above the limit, the concentration did not exceed "permissible" levels and the water is safe to drink.

For example, if the analytical report for a sample indicates that each of the BTEX compounds is present but at concentrations below their MCLs (5 ppb, 1,000 ppb, 700 ppb, and 10,000 ppb, respectively), is water with up to 11,705 ppb of BTEX really safe to drink? Do we want to drink it knowing that although the levels are reportedly safe, these contaminants are present at all? Do we want our children drinking it? And, health concerns aside, how does it taste? What about other contaminants that are not on this list of only a couple dozen? Are some of them present and, if so, what do we know about them?

Petroleum Cocktail Hour

Petroleum (and the various fuels distilled from petroleum) is composed of hundreds to thousands of individual organic compounds. (Although this article focuses on gasoline, much of the discussion is applicable to other fuels as well.) "Gasoline" is a complex blend of several hundred hydrocarbons (i.e., compounds that contain only hydrogen and carbon atoms) and other organic compounds that typically contain nitrogen, oxygen, or sulfur. The specific composition of any particular blend of gasoline is a function of the petroleum source, refining and blending processes, and additives (Kreamer and Stetzenbach, 1990). The composition also varies with geographic location and from season to season to maintain performance specifications and comply with regulatory requirements.

The primary groups of hydrocarbons in gasoline are the paraffins, olefins, naphthenes, and aromatics (Youngless et al., 1985). Table 1 lists some representative examples for each of the various classes of these organic compounds. Additive packages (which are generally proprietary) vary considerably and typically include compounds that function as antioxidants, antiicers, metal deactivators, detergents, and corrosion inhibitors, among others (Youngless et al., 1985). Some of these compounds are extremely large, complex molecules.

Some components of gasoline may also contain metal species. The most familiar of these, but not the only ones, are the organic lead compounds, which are no longer used in modern unleaded gasolines. In the past, especially with leaded fuels, a wide variety of dyes were incorporated into gasoline blends as well. Table 2 lists a few of the many gasoline additives.

In addition, a significant number of the compounds in gasoline are *unknown* (or unidentified), except for the number of carbon atoms they contain (Kreamer and Stetzenbach, 1990). What do we know about the toxicity of each of the compounds in gasoline? How do they behave in the environment? Which ones are in our drinking water and at what levels?

For an organic contaminant to show up in a water sample, it must be water soluble. It is well known that aromatic hydrocarbons (of which BTEX is probably the best recognized) are the most soluble constituents of gasoline. Table 3 lists 43 common gasoline constituents with solubility greater than 1 mg/L. Two of the nonaromatic compounds in this table have a higher solubility than ethylbenzene (the "E" in BTEX). This list isn't comprehensive, and there are undoubtedly other compounds with similar properties and, hence, significant water solubility.

While these constituents represent pure compound solubility, and individual solubilities from a mixture would be somewhat lower, the point is that there are lots of soluble constituents in gasoline that can appear in groundwater. If a sample is only analyzed for the aromatic fraction, how do we know that some of these other constituents are not also present?

LUSTLine

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Toxicity of Petroleum Constituents

It should come as no surprise to anyone that exposure (e.g., through inhalation, ingestion, or dermal contact) to any of the constituents of gasoline (or any other fuel) at any concentration should be avoided. Exposure to the vapors from most gasoline constituents can cause dizziness, drowsiness, unconsciousness, and other adverse effects on the central nervous system. Prolonged exposure to low concentrations, or brief exposure to higher concentrations, may damage internal organs, cause cancer or birth defects, or may even be fatal. Ingestion of the liquid phase of neat gasoline (and most, if not all, of its individual constituents) is acutely toxic.

So where do we find information on the toxicity of specific constituents? We would expect that one of the best sources is a material safety data sheet (MSDS), and there are many places to find them on the Internet. But they are readily available only for a small percentage of the constituents of gasoline, and, as they only pertain to exposure to a single compound, the effects of exposure to dilute aqueous mixtures are entirely unknown. (This issue is likely to be one of the important public health challenges of this century, and further discussion is way beyond the scope of this article.)

One of the current ways to deal with a large number of organic compounds is to distribute them into smaller groups, each of which has a designated "surrogate." This is the approach adopted by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). In this method, it is presumed that all members of the group have properties that are similar to the surrogate.

But the approach has several drawbacks. First, compound toxicity isn't necessarily the same for each of the group members, and often the toxic characteristics of a significant proportion of the group are unknown. Second, the presence of the surrogate in a sample may not necessarily mean that there are any other compounds in the sample; if they are, they are probably not at the same concentration. Third, the absence of the surrogate in a sample may not necessarily mean that all of the other compounds in the class are also absent from the sample. Fourth, many states are statutorily authorized to regulate only those contaminants that appear on EPA's list (i.e., 40 CFR 302.4, discussed in the "Regulation…" section below).

Sadly, the focus on compound toxicity has been so narrowly concentrated on human carcinogenicity that adverse effects other than cancer are usually conveniently ignored. In almost any discussion of risk management, there is no consideration of the teratogenic (birth defect) or mutagenic (mutation) effects of these toxic compounds—not to mention taste or odor!

We have no idea what contaminants are really in the water we drink (or the hot dogs we eat). Simply because a contaminant isn't listed on an analytical report does not mean that the contaminant is not present in the sample. The truth is that we just don't know, but what we don't know can potentially hurt us.

The issue of exposure to multiple toxicants is likewise given short shrift—exposure to multiple toxic compounds is limited to presumed simple additive effects, if it's considered at all. Yet, it is well recognized that the toxicity of a chemical may be increased (or in some cases even decreased) by simultaneous or consecutive exposure to another chemical (Lu, 1991). There is no consideration of synergistic (multiplicative) effects, or whether mixtures may contain procarcinogens, cocarcinogens, or cancer promoters.

And then there's the issue of whether or not a specific compound is a human carcinogen or just an animal carcinogen. Too often an animal carcinogen is touted as being a human noncarcinogen simply because there isn't any confirmation that the compound causes cancer in humans. However, saying that a compound is a noncarcinogen, when the truth is that there isn't enough information about it to determine whether or not it is a human carcinogen (although the compound is a known animal carcinogen), is being less than honest.

Admittedly, it is difficult (maybe even impossible) to demonstrate with 100 percent certainty that any chemical is a noncarcinogen. But for compounds that are known animal (especially mammalian) carcinogens, ordinary common sense would tell a reasonable person that these are substances with which unnecessary contact should be avoided, even at low concentrations and especially in mixtures that contain substances that may promote cancer.

In theory, a single molecule of a carcinogen can induce cancer. This means that there is no threshold dose and therefore no safe level of exposure to carcinogens. While not all cancer researchers hold this view, the opposing view (i.e., that threshold doses for carcinogens do exist) has yet to be demonstrated, even though large-scale experiments have been conducted for this purpose (Lu, 1991). Further complicating the issue is that unless a fatal quantity of pure product is ingested, most of the toxic effects are slow to develop (10 to 20 years or more in humans) and may be masked by other ailments as we age.

Regulation of Hazardous Substances

Underground storage tanks containing hazardous substances are regulated by the UST program under 40 CFR 280. Additional regulations regarding hazardous substances are found in 40 CFR 302.4 and 40 CFR 261.24. The first of these, CFR 302.4 (U.S. EPA, 2001a), is U.S. EPA's list of approximately 800 Hazardous Substances. Of these substances, only a handful are petroleum hydrocarbons found in fuels, and even fewer are fuel additives. (See Table 4.)

The second regulation, 40 CFR 261.24, is the Toxicity Characteristics (TC) rule for identifying RCRA hazardous wastes. The TC rule specifically exempts "petroleum contaminated" media and debris that fail the test for the toxicity characteristic of 40 CFR 261.24 (U.S. EPA, 2001b). Section 261.24(b) refers to 25 contami-

■ *continued on page 4*

■ **Hot Dogs** *from page 3*

nants (but actually lists 26) that are specifically exempt from consideration as "hazardous wastes," provided they are subject to the corrective action regulations under 40 CFR 280 (the UST regulations). This list of 26 contaminants includes benzene and only two additional chemicals (cresol and pyridine) that *may* be present in gasoline or other petroleum fuels.

We all know that none of the components of gasoline (or other petroleum fuels) are healthy for us, so why is it that so few fuel constituents are officially designated as "toxic" or "hazardous"? Part of the answer is that there are simply too many potentially toxic substances to list; some are unidentified, and adequate toxicity testing hasn't been conducted on others. Although not limited to organic compounds, the Chemical Abstract Service (CAS) assigns unique registration numbers (known as CAS or CASRN) to new chemicals at a rate of about 4,000 per day!!! (See *http://www.cas.org/EO/regsys.html*.)

Another part of the answer is that petroleum fuels as a whole are a critical part of the world economy. They've been used for close to 100 years, so we're familiar with them, we need them, and we consider them to be relatively "safe." Perhaps the primary reason why gasoline is considered "safe" is because UST regulations are relatively effective—at least to the extent that there aren't daily media reports of explosions, fires, and underground rivers of gasoline flowing beneath our feet.

However, as we all know, releases from UST systems do happen, sometimes with immediate and catastrophic effect. Every day there are releases of gasoline (and other fuels) into the environment, and a significant amount of the released fuel eventually winds up in groundwater or surface water or both, some of which is used for drinking water. So how do we know what toxic compounds (if any) are actually in our drinking water?

Identification of Toxic Compounds

Let's assume that we have a water sample that may or may not be contaminated with one or more of the hundreds of petroleum constituents in gasoline. What tests can we conduct to determine what contaminants are in the sample? Several analytical methods are potentially available to us to determine if any contaminants are present in the sample and at what concentrations. Though not the sole source for analytical methods, EPA's compendium of analytical methods, SW-846, (U.S. EPA, 1997) offers us several choices of determinative analytical methods for organic compounds, including: Methods 8015, 8021, 8260, and 8270. Let's look into each of these in ascending numerical order. (See Table 5.)

- **Method 8015** (Nonhalogenated Organics Using GC/FID) explicitly lists 30 compounds, of which only four may be present in gasoline. Only one—methanol—is on the list of hazardous substances. This method may also be used for Gasoline Range Organics (GRO) and Diesel Range Organics (DRO), but other methods (which aren't specified in the scope) may be more applicable. No additional guidance is provided regarding GRO or DRO.

- **Method 8021** (Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors) explicitly lists 57 compounds, of which 10 may be present in gasoline and are also on the list of hazardous substances.

- **Method 8260** (Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry) explicitly lists 107 compounds, of which about a dozen may be found in gasoline and are also on the list of hazardous substances.

- **Method 8270** (Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry) explicitly lists about 250 compounds, of which only a couple are likely to be found in gasoline (although many more could be present in diesel fuel and heavier fuel oils) and are on the list of hazardous substances.

U.S. EPA drinking water methods 502 and 524.2 contain a slightly different list of chemicals.

Of the more than 400 target compounds identified by the four 8000-series methods, approximately 5 percent may be present at any given petroleum release site. "Well and good," you're thinking, "but what's the point of this?"

Absence of Proof Is Not Proof of Absence

Well, the first point of this is that we have no idea what contaminants are really in the water we drink (or the hot dogs we eat). Simply because a contaminant isn't listed on an analytical report does not mean that the contaminant is not present in the sample. (Note that the converse is also true—that is, there is no proof that the contaminant is present.) The truth is that we just don't know, but what we don't know *can* potentially hurt us.

There are a lot of reasons why the presence of a contaminant in a sample might go unrecognized:

- There was no analysis for the contaminant.
- There was an analysis for the contaminant, but an inappropriate method was used.
- The analytical method was applied incorrectly.
- The detection limit is very high.
- Matrix interferences.

In each of these cases, a contaminant could be in a sample, but its presence (and concentration) is undetected (and undetermined). We have to do a better job than we currently do to both anticipate which potential contaminants may be present at a given site and analyze for all of them to determine whether they are in fact present or absent.

In addition to the desirability of knowing all chemicals present for the purpose of conducting a risk assessment, it is important to know all the contaminants present when developing a remediation plan.

In one of my recent projects, carbon filters used as point-of-entry treatment for domestic wells were breaking through in far shorter times than what was expected. After run-

ning Method 8260 plus requesting that all "tics" be identified by a library search, we identified a total of 45 additional chemicals, all potentially having a gasoline source, as being present in the water samples. These additional chemicals all contributed to the loading on the carbon filters and contributed to the early breakthrough. The library search gave estimated concentrations, but none of these compounds had been calibrated against a standard.

I might also have been happier if I hadn't added dissolved lead to the list of analytes because of earlier detections of EDC. Dissolved lead exceeded recommended levels in every sample (pre- and post-carbon filters), and in every well, even where no gasoline components were detected. Further analysis, this time for tetraethyl and tetramethyl lead, the organic lead that would come from leaded gasoline, was negative. Elevated lead levels appeared to be present throughout the aquifer, which would also have to be factored into a risk assessment. While the carbon filters were dealing with the gasoline contamination in the wells, albeit in an expensive manner, the filters had no effect on the dissolved lead.

Further, it isn't enough to have samples analyzed even for all potential contaminants if the samples aren't representative. Samples must be collected from locations where contaminants are most likely to be present, and they must be correctly handled during collection, transport, preparation, and analysis.

Fuel-Specific Analytical Methods

My second point is that the current analytical practices we rely on to determine whether gasoline compounds are present or absent in water (and soil) samples are incomplete and therefore inadequate. Standard operating procedures for Methods 8015, 8021, 8260, and 8270 require calibration for only a few of the many compounds that are present in gasoline, but many compounds are either not present or are unknown.

Target analyte lists must be refined so that they are more representative of the contaminants that are likely to be encountered at fuel-release sites. For example, nearly 90 percent of the analytes listed for Method 8021 are halogenated compounds that would *not* be present at fuel-release sites—why should a sample be analyzed for them and *not* for some of the few hundred other contaminants that may actually be present? If we're going to pay for an analysis for, say, 100 compounds, wouldn't it be more cost-effective if those 100 could be reasonably anticipated to be in the sample?

■ *continued on page 6*

Table 1 Representative Organic Compounds Found in "Gasoline"

Straight Chain Alkanes
- propane
- n-hexane
- n-dodecane

Branched Alkanes
- isobutane
- 2,2-dimethylbutane
- neopentane
- 3-ethylhexane

Cycloalkanes
- cyclohexane
- n-propylcyclopentane
- ethylcyclohexane

Straight Chain Alkenes
- cis-2-butene
- 1-pentene
- trans-2-heptane

Branched Alkenes
- 2-methyl-1-butene
- 4,4-dimethyl-cis-2-pentene

Cycloalkenes
- cyclopentene
- 3-methylcyclopentene

Alkyl Benzenes
- benzene
- toluene
- ethylbenzene
- o-xylene
- m-xylene
- p-xylene
- 1,2-dimethyl-3-ethylbenzene
- 1,2,3-trimethylbenzene
- 1,2,4,5-tetramethylbenzene
- n-propylbenzene

Other Aromatics
- indan
- 1-methylindan
- phenol

Polycyclic Aromatic Hydrocarbons (PAHs)
- naphthalene

Source: Adapted from Cole (1994).

Table 2 Representative Organic Compounds Used as Additives in "Gasoline"

Oxygenates
- methyl *tertiary*-butyl ether (MTBE)
- ethanol
- ethyl *tertiary*-butyl ether (ETBE)
- *tertiary*-butyl alcohol (TBA)
- *tertiary*-amyl ethyl ether (TAEE)
- diisopropyl ether (DIPE)
- *tertiary*-amyl methyl ether (TAME)
- *tertiary*-amyl alcohol (TAA)
- methanol

Anti-knock compounds
- tetra-ethyl lead (TEL)
- tetra-methyl lead (TML)
- methylcyclopentadienyl manganese tricarbonyl (MMT)

Anti-oxidant compounds
- hindered phenols
- phenylene diamines
- aminophenols

Anti-icing compounds
- isopropyl alcohol
- amides/amines
- glycols
- organophosphate ammonimum salts

Corrosion inhibitors
- carboxylic acids
- sulfonates
- amine/alkyl phosphates

Metal deactivators
- disalicylidene amines
- phenolic amines
- thiourea

Ignition controller additives
- tri-*o*-cresol phosphates

Detergents
- aminohydroxyamide
- alkylphenols
- imidazolines

Lead scavengers
- 1,2-dichloroethane (EDC)
- 1,2-dibromoethane (EDB)

Dyes
- azobenzene-4-azo-2-napthol
- benzene-azo-2-napthol
- para-diethyl aminoazobenzene
- 1,4-diisopropylaminoanthraquinone

Source: Adapted from Cummings (1977) and Irwin, et. al. (1997).

■ Hot Dogs *from page 5*

And, in order to credibly evaluate the actual risk posed by contaminants in our water, we absolutely *must* know which contaminants are in the water. In a recent series of articles by Uhler and others (2002, 2003), similar suggestions were made. They suggest a suite of 109 target analytes for the analysis of automotive gasoline using a Modified 8260 method. The list contains the PIANO compounds (Paraffins, Isoparaffins, Aromatics, Naphthenes, and Olefins), useful for recognizing peculiarities that might be inherited from refinery processes (including various major and minor iso-alkanes), and gasoline additives, including the oxygenate additives (alcohols and ethers), lead scavengers (EDC and EDB), and methylcyclopentadienyl manganese tricarbonyl (MMT). Some of this list of compounds can be useful in fingerprinting gasoline for environmental forensic investigations, as well as a basis for conducting a risk assessment.

Just how credible, how "scientifically defensible" is a risk assessment based on omission, neglect, or wishful thinking? To only evaluate the risk posed by some, but not all, contaminants present at a site is like crossing a busy highway but only looking in one direction as you make the attempt. Sure, you may not get hit by a car coming from the direction in which you're looking, but one from the blind side is likely to spoil your day.

Appropriate analytical method(s) already exist in today's marketplace. All that is lacking are appropriate calibration standards and standard operating procedures that have been optimized for analysis of these target analytes. Once it becomes routine to use these standards, risk assessments could be conducted for the contaminants to which receptors are actually exposed, rather than presumed surrogates. This will go a long way toward bolstering the credibility of risk assessment and restoring confidence in the safety of our drinking water.

Take Me Out to the Ballgame

Alternatively, we could opt to accept the status quo…we can slump down in our bleachers, hot dog in one hand, and glass of water (OK, beer) in the other, and blissfully pass away the time. ■

Pat Ellis is a hydrologist with the Delaware Department of Natural Resources and Environmental Control, Tank Management Branch and served as a member of EPA's Blue Ribbon Panel on MTBE. She is a technical advisor and regular contributor to LUSTLine *and can be reached at* Patricia.Ellis@state.de.us.

Table 3
Common Gasoline Constituents Ranked by Solubility (mg/L)

Benzene	1,780
Toluene	515
o-Xylene	220
cis-2-Pentene	203
Cyclopentane	156
Ethylbenzene	152
1-Pentene	148
3-Methyl-1-butene	130
Indan	100
1-Methyl-4-ethylbenzene	95
1,2,3-Trimethylbenzene	77
1-Methyl-2-ethylbenzene	75
Propane	62
1,2,4-Trimethylbenzene	57
Cyclohexane	55
n-Propylbenzene	52
Isopropylbenzene	50
1,3,5-Trimethylbenzene	50
Isobutane	48.9
Methylcyclopentane	42
Pentane	38.5
Naphthalene	31
1-Methyl-naphthalene	28
2-Methyl-naphthalene	25
2,2-Dimethylbutane	18.4
sec-Butylbenzene	17
Methylcyclohexane	14
Isopentane	13.8
2-Methylpentane	13.8
n-Butylbenzene	13.8
3-Methylpentane	12.8
Isobutylbenzene	10.1
Hexane	9.5
2,3-Dimethylpentane	5.25
1,2,4,5-Tetramethylbenzene	3.48
3-Methylhexane	3.3
n-Heptane	2.93
2-Methylhexane	2.54
2,2,4-Trimethylpentane	2.44
2,3,4-Trimethylpentane	2
1-Nonene	1.12

Source: Adapted from Gustafson et al. (1997).

Table 4
Hazardous Substances Listed in 40 CFR 302.4 That May be Present in "Gasoline"

SUBSTANCE	CASRN
1,2-dibromoethane	106934
1,2-dichloroethane	107062
1,3-pentadiene	504609
benzene	71432
cresols	1319773
ortho-cresol	95487
meta-cresol	108394
para-cresol	106445
cyclohexane	110827
ethylbenzene	100414
methanol	67561
naphthalene	91203
phenol	108952
toluene	108883
xylenes	1330207
ortho-xylene	95476
meta-xylene	108383
para-xylene	106423

Source: Adapted from Gustafson et al. (1997).

Table 5 Compounds Present in "Gasoline" That Appear on Target Analyte Lists for Methods in SW-846

COMPOUND	8015*	8021	8260	8270
diethyl ether	x		x	
ethanol	x		x	
methanol	x		x	
pyridine	x		x	
benzene		x	x	
ethylbenzene		x	x	
naphthalene		x	x	x
toluene		x	x	
xylenes		x		
o-xylene		x	x	
m-xylene		x	x	
p-xylene		x	x	
1,2-dibromoethane		x	x	
1,2-dichloroethane		x	x	
tertiary-butyl alcohol			x	
phenol				x

**Method 8015 is also indicated to be applicable for GRO and DRO.*

EPA HQ UPDATE

Analytical Methods Fact Sheet Available

Analytical methods for petroleum hydrocarbons are well established; however, methods that were developed for analysis of petroleum hydrocarbons in water samples may or may not be appropriate for fuel oxygenates. A fact sheet, titled *Analytical Methodologies for Fuel Oxygenates* (EPA 510-F-03-001), outlines the potential problems of analytical methods for common fuel oxygenates and ways to address these problems. It has been distributed to states and regions and is available on the OUST Web site at *www.epa.gov/oust/mtbe/omethods.pdf.*

For more information, contact Hal White at (703) 603-7177.

Senate Passes UST Legislation

On Thursday, May 1, the U.S. Senate passed the Underground Storage Tank Compliance Act (S. 195) by unanimous vote. The legislation provides additional flexibility and authorization of appropriations for preventing and cleaning up releases from USTs. It also includes a dedicated authorization of appropriation for the cleanup of MTBE, mandatory inspection frequencies, additional enforcement tools, and operator training guidelines. Although the House has been working on its version of UST legislation, companion legislation has not been introduced. EPA OUST has been providing technical comments on the proposed legislation.

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APPENDIX 7

DETERMINATION OF GROUNDWATER UTILITY

Hawai'i DOH
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in reply, please refer to:
EMD / SHW

September 19, 1995

POLICY UPDATE
Technical Guidance Manual
for Underground Storage Tank Closure and Release Response

Determination of Groundwater Utility
at Leaking Underground Storage Tank Sites

TO ALL INTERESTED PARTIES:

The Hawai'i Department of Health's Solid and Hazardous Waste Branch, Underground Storage Tank Section, is issuing a policy update to its *Technical Guidance Manual for Underground Storage Tank Closure and Release Response* (August 1992). **This policy update is effective September 13, 1995.**

Recommended cleanup criteria at leaking underground storage tank (LUST) sites depend on, among other things, whether the ground water underlying the site is used or intended for use as a drinking water source. This policy directs owners and operators of USTs to use the aquifer system classification reports developed by the University of Hawai'i at Mānoa's Water Resources Research Center in determining the use of the ground water underlying the site.

This new policy allows for more efficient allocation of limited cleanup resources by ensuring that cleanup requirements applied to a site are appropriate for the use of the site and the surrounding area, while at the same time maintaining effective protection of human health and the environment.

Please bring this policy update to the attention of anyone you know who may have an interest in this matter. Should you have any questions regarding this policy update, please contact the Underground Storage Tank Section at (808) 586-4226.

Sincerely,

STEVEN Y.K. CHANG, P.E., MANAGER
Solid and Hazardous Waste Branch

Attachment

DETERMINATION OF GROUNDWATER UTILITY AT LEAKING UNDERGROUND STORAGE TANK SITES

Background

Soil and groundwater cleanup criteria for remedial activities pursuant to 40 CFR Part 280 Subpart F (RCRA I) and Hawai'i Revised Statutes, Chapters 342L and 128D, are based in part on the utility of the groundwater impacted or potentially impacted by the release. Cleanup criteria for release that threaten sources of drinking water are based primarily on human health concerns. Cleanup criteria for releases that threaten non-drinking water sources are based primarily on ecological/aquatic-life concerns. In general, cleanup criteria for releases that threaten drinking water are much more stringent than for those that do not.

As a useful first approximation, and in order to help maintain consistency in groundwater protection policies within the Department of Health (DOH), the SHWB informally adopted the Underground Injection Control (UIC) line as an initial demarcation between aquifer systems that serve or could potentially serve as sources of drinking water (generally beneath the inland areas of the islands) and those that could not (generally beneath the coastal areas of the islands). The UIC line was established by the DOH Safe Drinking Water Branch (working in cooperation with the Honolulu City & County Board of Water Supply, the U.S. Geological Survey, and the Water Resources Research Center of the University of Hawai'i - Mānoa, among others) for purposes of regulating the location of underground injection wells. Reference to the use of the UIC line for SHWB purposes is made in the document "Technical Guidance Manual for Underground Storage Tank (UST) Closure and Release Response (TGM, August, 1992)," prepared by the UST Section of the SHWB.

In accordance with UIC guidelines, aquifer systems mauka (inland) of the UIC line are by default considered to be current or potential sources of drinking water. Aquifer systems makai (oceanward) of the UIC line are considered by default to not be current or potential sources of drinking water. Correspondingly, cleanup criteria for release sites located mauka of the UIC line are initially set to be protective to drinking water standards. Cleanup criteria for release sites located makai of the UIC line are initially set to be protective to generally less stringent non-drinking water (surface water) standards.

Statement of Problem

The UST section of the SHWB deals with hundreds of facilities with leaking underground storage tank (LUST) sites that are required by federal and state law to report UST-related releases to DOH. Most, if not all, LUST sites are too small to technically or economically warrant a full-scale investigation of the utility of the groundwater that has been or could potentially be impacted by the release. This necessitates the use of approximated, regional groundwater-utility "zones", defined by use of such tools as the UIC line.

Numerous LUST facilities located mauka of the UIC line, however, have requested variance from use of the UIC line to approximate groundwater utility beneath their sites. The requests have been based on the known geology of the site and a position that the release does not threaten an aquifer system that currently or could potentially serve as a source of drinking water. Indeed, many of the subject sites overlie clay-rich, "caprock" coastal plain sediments that are not suitable as sources of drinking water. An extensive, subsurface investigation of the local groundwater system would likely support this at many of the sites if such an investigation was technically and economically feasible. Fortunately, recent research on aquifer systems throughout the islands addresses the bulk of these problem areas.

Aquifer Identification and Classification Technical Report Series

Since establishment of the UIC line, DOH has sponsored additional research regarding the identification, classification, and protection of groundwater resources in Hawai'i. The most important outcome of this research to date has been the "Aquifer Identification and Classification" technical report series published for each island by the Water Resources Research Center (WRRC) at the University of Hawai' i- Mānoa (see references). The reports have been incorporated into the draft Water Resources Protection Plan (March, 1992), prepared by the Department of Land and Natural Resources as part of the Hawai'i Water Plan under provisions set in Chapter 174C of the Hawai'i Revised Statutes. The DOH Office of Hazard Evaluation and Emergency Response currently uses the WRRC aquifer identification and classification reports to screen sites for prioritization.

The WRRC reports systematically review aquifer systems throughout each island and, as one element, indicate whether the aquifer system as a whole can or cannot be utilized as a source of drinking water (aquifer system "utility," second digit in aquifer system status code). Because division of the aquifer systems is based largely on geology, the WRRC aquifer classification system reports address many of the problem areas brought about by reliance on only the UIC line to approximate groundwater utility.

One of the shortcomings of the aquifer system classification reports, recognized by the authors (Mink, personal communication - Attachment A), is a lack of sufficient data to subdivide geologically-defined aquifer "types" into more narrowly-defined "units" based on the variability of groundwater quality within the aquifer system. This can be especially important in coastal areas where groundwater quality within an otherwise "drinking water" aquifer system degrades to below drinking water standards as the freshwater lens pinches out and mixes with saline water within the same geological formation. Examples include much of the basaltic coastal areas of the islands of Kaua'i, Maui, Moloka'i, and Hawai'i.

In these areas, the groundwater specialists consulted generally agreed that the UIC line can serve as a useful and valid tool for approximating the inland boundary of coastal-zone, aquifer system "units" that are not current or potential sources of drinking water (see Attachment A). Over time, continued investigation of Hawai'i's groundwater resources will naturally lead to a refinement of the boundaries between regional aquifer systems and a better breakdown of distinctive units within individual systems.

Policy Statement

Facilities with releases from USTs regulated by the UST Section of the DOH Solid and Hazardous Waste Branch must determine the utility of groundwater (generally drinking water or non-drinking water) that has been or may potentially be impacted by the release. In support of the determination of groundwater utility, the following information should be submitted to the DOH:

1. a review of the known surface and subsurface geology and hydrogeology of the site, including information gained during investigation of the release and information provided in published or unpublished reports that include the subject area (refer to TGM, August 1992 edition for information required in site investigations)

2. a description of all aquifer systems (classification, status, etc.) that have been impacted and/or could potentially be impacted by the release in accordance with the referenced aquifer system classification reports published by the WRRC, and

3. a map showing the location of the release site with respect to the boundaries of impacted or potentially impacted aquifer systems.

In addition, if the UIC line is used to approximate the inland boundaries of coastal-zone, non-drinking water aquifer system units, then the location of the UIC line with respect to the corresponding aquifer system(s) should be included on the map and discussed in the text of the report.

DOH may request additional site-specific geologic, hydrogeologic, and other pertinent information as necessary on a site-by-site basis to make final groundwater utility determinations. In particular, facilities situated near aquifer system boundaries should evaluate the geological accuracy and applicability of the aquifer system maps to their site.

DOH reserves the right to make final decisions of groundwater utility on a site-specific basis, regardless of the location of the site with respect to regional characterizations of aquifer systems. This may become especially important in areas of extensive soil and groundwater contamination, at sites located near important aquifer system boundaries where detailed subsurface data is not available, or in ecologically sensitive areas (e.g., near bodies of surface water).

The review of an aquifer systems status as a source or potential source of drinking water will be for UST section purposes only and the results of the review should not be construed as an official confirmation or refinement of the UIC line in the area of the release site. Injection well applications, if any, will be processed according to UIC regulations, Chapter 23, by the UIC program of the Safe Drinking Water Branch (SDWB) and such applications will not be excluded from UIC restrictions due to designations of what is or is not a source of drinking water that have not been approved by the SDWB.

APPROVED/~~DISAPPROVE~~D

Bruce Anderson

Bruce Anderson, Ph.D., Deputy Director, Environmental Health, Department of Health

9/13/95

Date

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State Water Code, Hawai'i Revised Statutes, Chapter 174C.

Technical Guidance Manual for Underground Storage Tank Closure and Release Response (August, 1992): Hawai'i Department of Health, Solid and Hazardous Waste Branch.

Underground Injection Control, Hawai'i Administrative Rules, Title 11, Chapter 23.

Underground Storage Tanks, Hawai'i Revised Statutes, Chapter 342L.

APPENDIX 8

OTHER SUPPLEMENTAL REFERENCE DOCUMENTS

- Tier 2 Soil Action Levels for Arsenic (HDOH 2010a)
- Tier 2 Soil Action Levels for TEQ Dioxins (HDOH 2010b)
- Use of Laboratory Batch Tests to Evaluate Potential Leaching of Contaminants From Soil (HDOH April 2007)
- Long-Term Management of Petroleum-Contaminated Soil and Groundwater (HDOH June 2007)
- Natural Occurrence of Hexavalent Chromium in Hawai‘I (HDOH January 2011)

Hawai'i DOH
Fall 2011

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In reply, please refer to:
File: EHA/HEER Office
2010-579-RB

October 2010

To: Interested Parties

From: Roger Brewer, Ph.D., Environmental Risk Assessor, HEER

Through: Barbara Brooks, Ph.D., Toxicologist, HEER

Subject: Update to Soil Action Levels for Inorganic Arsenic and Recommended Soil Management Practices

1.0 Introduction

This technical memorandum presents an update to the 2008 Hawai'i Department of Health (HDOH) action levels and corresponding guidance for inorganic arsenic in soil (HDOH 2008a, attached). Categories for management and evaluation of arsenic-contaminated soil have been revised and simplified. Soil action levels for arsenic presented in the 2008 technical memorandum have not been adjusted. This guidance serves as an addendum to the Hazard Evaluation and Emergency Response (HEER) office document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (EHE guidance; HDOH 2008b).

Refer to the June 2010 dioxin technical memorandum for additional guidance on issues common to both dioxin- and arsenic-contaminated soil, including (HDOH 2010a):

- Site characterization;
- Disposal of contaminated soil;
- Engineering controls;
- Institutional controls;
- Management of Category C Soils at Commercial/Industrial Sites;
- Environmental Hazard Management Plans and management of Category C soils at commercial/industrial sites;
- Inclusion of soil above surrounding background in remediation of Category D soils; and
- Hazardous Waste Considerations.

The soil action levels presented herein are not promulgated regulatory standards or required cleanup levels. Alternative proposals may be presented in a site-specific risk assessment.

2.0 Arsenic Soil Management Categories

Updated categories for the evaluation and management of arsenic-contaminated soil are summarized below and in Table 1. These categories replace the scheme presented in the 2008 HDOH technical memorandum (HDOH 2008a):

Category A Soils (natural background): Soils exhibit concentrations of total arsenic <20 mg/kg, and do not appear to have been impacted by local, agricultural or industrial releases of arsenic; not impacted. The natural, background concentration of arsenic in soils in Hawai‘i is typically less than 20 mg/kg. A summary of background concentrations of heavy metals in soil in Hawai’i is in preparation. In the interim, refer to documents published by the Air Force (USAF 2005) and Navy (USN 2006) environmental programs in Hawai‘i. A summary of background concentrations of metals in various soil types on the mainland US has been published by the University of California (UCR 1996) and U.S. Geological Survey (USGS 2001).

Category B Soils (minimally impacted): Total arsenic >20 mg/kg but bioaccessible arsenic <23 mg/kg, indicating probable anthropogenic impacts but at levels within acceptable health risks for long-term exposure; Unrestricted Land Use. HEER expects Category B soils to be generally associated with agricultural fields where arsenic-based herbicides were used for weed control between the years 1915 to 1950. Arsenic levels between individual fields can vary with respect to the location of the field (e.g., high- versus low-rainfall area) as well as the weed control preferences of the sugar companies that managed the fields. Reported concentrations of bioaccessible arsenic are typically below 23 mg/kg in field areas, although exceptions have been identified in some areas. This action level can be easily exceeded in former pesticide storage and mixing areas. In general, bioaccessibility is higher in iron-poor, coralline sands in comparison to iron-rich volcanic soils.

Although not necessary from a health risk standpoint, owners of existing homes where pesticide-related, Category B soils are identified may want to consider measures to minimize exposure to arsenic in the soil as summarized in Table 1 and discussed in the HDOH fact sheet *Arsenic in Hawaiian Soils: Questions and Answers on Health Concerns* (HDOH 2010b; see also 2008c).

HDOH discourages the use of Category B soils with greater than 100 mg/kg *total* arsenic in the fines sol fraction (< 250µm) as fill material in offsite areas without further consultation, even if bioaccessible arsenic meets action levels for unrestricted use. This is intended to limit the movement of contaminated soil to otherwise un-impacted areas, as well as address a potential increase in bioaccessibility with the addition of phosphate fertilizers in lawns or gardens in new developments. Investigations carried out by HDOH in several heavily-impacted community garden soils on the Big Island (>400 mg/kg total

arsenic in the fines soil fraction; HDOH 2007) suggested an increase in bioaccessible arsenic (15-20%) in comparison to equally-contaminated soils in the surrounding areas (1-10%). A limit of total arsenic to 100 mg/kg in fines is intended to approximate the target Category B limit of 23 mg/kg under a worst-case, 25% bioaccessibility for arsenic in iron-rich, volcanic soils.

Category C Soils (moderately impacted): Bioaccessible arsenic between 23 mg/kg and 95 mg/kg; Commercial/Industrial Land Use Only. Category C soils are exemplified by contamination at former pesticide storage and mixing areas and wood treatment facilities. Category C soils have also been identified in community gardens associated with former sugarcane plantations (with elevated arsenic also identified in the adjacent field areas), at the site of a former Canec manufacturing site (see HDOH 2010c), and in some industrial areas believed to have been historically treated with arsenic herbicides for weed control.

Category D Soils (heavily impacted): Bioaccessible arsenic greater than 95 mg/kg; Remedial Actions Required. Category D soils have been identified at a small number of former pesticide mixing areas (e.g., sugarcane operations), former plantation housing areas and wood treatment facilities. Concentrations of total arsenic in soil typically exceed several thousand milligrams per kilogram. These soils are often co-located with heavy dioxin contamination (associated with use of pentachlorophenol) and in some cases triazine pesticides. Pentachlorophenol and triazine pesticides successively replaced the use of arsenic-base herbicides in the 1930s and 1970s, respectively (see HDOH 2010a; refer also to Section 9 in the HEER office Technical Guidance Manual, HDOH 2009).

A site-specific, Environmental Hazard Management Plan (EHMP) must pre prepared for all sites where Category C and D soils are to be left in place for long-term management (HDOH 2008b, 2009). Information to be provided in the EHMP includes:

- To-scale maps that specify the location, thickness and depth of Category C and D soils;
- Summary of the specific environmental hazards potentially posed by the contaminated soil;
- Required institutional and engineering controls (e.g., restricted use, capping requirements, etc.);
- Fugitive dust and storm water runoff control measure;
- Measures for protection of workers involved in future construction or trenching projects that might disturb Category D soils.

Inappropriate reuse of Category C or D soils in offsite areas is of particular concern when excess soil is generated during construction or trenching projects. Clean fill should be used in utility corridors to minimize worker exposure and inadvertent reuse of removed soil in offsite areas. Refer to the HEER office *Environmental Hazard Evaluation* guidance (HDOH 2008b) and *Technical Guidance Manual* (HDOH 2009) for additional information. A copy of the EHMP should be retained by the property owner and lessees, as well submitted to HDOH for inclusion in the public record for the subject site.

3.0 Comparison of Soil Exposure to Dietary Exposure

The unrestricted (e.g., residential) soil action level of 23 mg/kg for bioaccessible, inorganic arsenic equates to a hypothetical, daily exposure dose for a 15kg child of approximately 4.0 micrograms (based on assumed soil ingestion rate, exposure duration and frequency, etc.; see HDOH 2008a). The commercial/industrial action level of 95 mg/kg equates to a daily exposure dose for a 70kg worker of 7.0 micrograms. Actual exposures to arsenic in soil for both children and adults are likely to be much lower due to the conservative nature of the exposure factors used in the calculations.

Exceeding the soil action level and the hypothetical exposure dose does not imply that an adverse health risk will occur, only that additional evaluation is warranted. This is because the Reference Dose (RfD) used to calculate the soil action level (i.e., 0.3 ug/kg-day; USEPA 2010a) incorporates an inherent uncertainty and margin of safety, due to the nature of toxicological risk assessment. As stated in IRIS summary for arsenic, "Risk managers should recognize the considerable flexibility afforded them in formulating regulatory decisions when uncertainty and lack of clear consensus (on toxicity factors) are taken into account."

Arsenic is a naturally occurring element in the earth's soil and water. As such it is naturally present in trace amounts in food. A comparison of exposure to inorganic arsenic in the diet to exposure from soil helps put the stated action levels into perspective, as shown in the table below (see Attachment 2 for detailed explanation):

	Exposure (ug/kg-day)	
Receptor	*Soil	Dietary
Child (15 kg)	4.0	18
Adult (70 kg)	7.0	44

*Exposure to Category B (Child) and C (Adult Worker) soil.

Based on a typical Pacific-Asian diet that is rich heavy in rice and fish, dietary inorganic arsenic exposures are estimate to be as high as 18 ug/day for children (1.2 ug/kg-day for a 15 kg child) and 44 ug/day for adults (0.6 ug/kg-day for a 70 kg adult). Rice accounts for the majority of dietary, inorganic arsenic (see Attachment 2).

Dietary exposure to inorganic arsenic is therefore anticipated to far exceed exposure to arsenic in soil at the stated action levels. The majority of exposure to inorganic arsenic in the diet comes from rice (see Attachment 2), which naturally accumulates arsenic and other elements in the soil when grown under wet conditions. Regular consumption of rice has not been shown to pose a significant health risk due to the presence of arsenic or other metals. Fish contains a significant amount of relatively non-toxic, *organic* arsenic ("fish arsenic") but can also contribute to a small portion of total inorganic arsenic exposure.

4.0 Comparison to 2010 Draft USEPA Arsenic Toxicity Review

The USEPA published draft, proposed changes to the cancer slope factor for inorganic arsenic in February 2010 (USEPA 2010b). The draft USEPA document recommends an *increase* in current cancer slope factors for inorganic arsenic by more than an order of magnitude under some circumstances. In theory this could result in a *reduction* of cancer-based soil action levels by a similar magnitude. As stated in the draft USEPA document: "(This document) has not been formally disseminated by EPA. It does not represent and should not be construed to represent any Agency determination or policy."

The draft USEPA (2010b) cancer slope factors for arsenic are based on doses that are orders of magnitude higher than are typically associated with exposures to soils (e.g., 100s to 1,000s ug/day vs <5 ug/day for exposures to Category B soils. There is considerable debate among both regulators and private entities regarding the applicability of both current and proposed cancer slope factors to very low doses of inorganic arsenic typically associated with exposure to soil as well as rice and other foods (e.g., USSBA 2010, EPRI 2010). As described in the 2008 technical memorandum, HDOH places a higher level of confidence in the noncancer toxicity factors and feels that the use of these factors in the development of soil action levels is more technically supportable for regulatory decisions (HDOH 2008a).

The use of conservative exposure assumptions in conjunction with a comparison to anticipated dietary exposure to inorganic arsenic provide additional lines of evidence to support the adequacy of the soil action levels to help separate low-risk sites from high risk sites and prioritize HDOH resources. HDOH considers the current approach to develop soil action levels as outlined in the 2008 technical memorandum to be appropriate for use in Hawai‘i and does not anticipate the need to adjust them in the foreseeable future.

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Table 1. Summary of Inorganic Arsenic Soil Action Levels and associated soil management categories.

Soil Management Category	Action
Total Arsenic (< 2 mm size fraction)	
Category A Total Arsenic ≤20 mg/kg	**Background.** Within range of expected background conditions in non-agricultural and non-industrial areas. No further action required and no restrictions on land use.
Bioaccessible Arsenic (<250 µm size fraction)	
Category B Total Arsenic >20 mg/kg and Bioaccessible Arsenic ≤23 mg/kg	**Minimally Impacted-Unrestricted Land Use.** Exceeds expected background conditions but at levels anticipated for many agricultural fields where arsenic-based chemicals were used historically. Potential health risks considered to be within the range of acceptable health risks for long-term exposure. Include Category B soil in remedial actions for more heavily contaminated spill areas as practicable in order to reduce exposure (e.g., outer margins of pesticide mixing areas). Offsite reuse of soil for fill material not recommended for soil with >100 mg/kg total arsenic (see text). Use of soil for intermediate (e.g., temporarily inactive portions) or interim (e.g., daily or weekly) cover at a regulated landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions. Although not strictly necessary from a health-risk standpoint, owners of existing homes where pesticide-related, Category B soils are identified may want to consider measures to reduce daily exposure to soil (e.g., maintain lawn cover, ensure good hygiene, thoroughly wash homegrown produce, etc) as described in the HDOH fact sheet *Arsenic in Hawaiian Soils: Questions and Answers on Health Concerns* (HDOH 2010c). For new developments on large, former field areas, notify future homeowners of elevated levels of arsenic on the property and recommend similar, precautionary measures (e.g., include in information provided to home buyers during property transactions, see also HDOH 2008b).
Category C (Bioaccessible Arsenic >23 but ≤95 mg/kg)	**Moderately Impacted-Commercial/Industrial Land Use Only.** Identified at several, former pesticide mixing areas and wood treatment facilities. May be co-located with pentachlorophenol, dioxin and triazine pesticide contamination at agricultural sites. Restriction to commercial/industrial land use is typically required in the absence of remediation or significant institutional and engineered controls and HDOH approval. Use of soil as soil as intermediate (e.g., temporarily inactive portions) or interim (e.g., daily or weekly) cover at a regulated landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions. Preparation of a site-specific, *Environmental Hazard Management Plan* (EHMP) required if soil is left on site for long-term management (HDOH 2008b, 2009). Treatment to reduce bioavailability and/or removal of isolated spill areas is recommended when practicable in order to minimize future management and liability concerns. This includes controls to ensure no off-site dispersion (e.g., dust or surface runoff) or inadvertent excavation and reuse at

	properties with sensitive land uses.
Category D (Bioaccessible Arsenic >95 mg/kg)	**Heavily Impacted-Remedial Actions Required.** Identified at a small number of former pesticide storage and mixing areas (e.g., sugarcane operations), former plantation housing areas and wood treatment facilities. May be co-located with dioxin and triazine pesticide contamination. Remedial actions required under any land use scenario in order to reduce potential exposure. Potentially adverse health risks under both sensitive and commercial/industrial land use scenarios in the absence of significant institutional and/or engineered controls. Disposal of soil at a regulated landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions. Preparation of site-specific EHMP required if left on site.

ATTACHMENT 1

2008 HDOH ARSENIC ACTION LEVEL GUIDANCE

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In reply, please refer to:
File: EHA/HEER Office

TO: Interested Parties

FROM: Roger Brewer
Environmental Risk Assessment
HEER Office

THROUGH: Barbara Brooks
Toxicologist
HEER Office

DATE: June 13, 2008

SUBJECT: Tier 2 Action Levels for Arsenic (update to August 2006 memorandum)

This technical memorandum presents Tier 2 action levels and corresponding guidance for arsenic-contaminated soils. The guidance serves as an addendum to the Hazard Evaluation and Emergency Response (HEER) office document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (HDOH 2008a). The guidance updates and takes precedence over guidance published in August 2006 (HDOH 2006). The update primarily addresses recommendations for the management of Category 2 soils in former agricultural fields. Similar guidance has been prepared for dioxin-contaminated soils (HDOH 2008b)

The guidance is especially intended for use during the redevelopment of former agricultural areas, although it is applicable to any site where releases of arsenic may have occurred. The action levels should be used to help determine the extent and magnitude of arsenic-contaminated soils and help guide the scope of remedial actions needed. The action levels are intended to serve as guidelines only, however, and do not represent strict, regulatory cleanup requirements. Alternative action levels may be proposed for any site in a site-specific, environmental risk assessment.

Overview

The action levels presented are based on concentrations of *bioaccessible* arsenic in soil. *Total* arsenic data are considered appropriate for comparison to anticipated background levels of arsenic in soil but not for use in human health risk assessment or for setting risk-based action levels. An action level of 4.2 mg/kg bioaccessible arsenic is recommended for residential sites. For commercial/industrial sites, an action level of 19 mg/kg bioaccessible arsenic is recommended. Remediation of sites to permit future, unrestricted, residential land use is encouraged when technically and economically feasible. "Residential" use includes both single-family homes and high-density developments, where open spaces essentially serve as residential "backyards." Schools, parks, playgrounds, and other open public spaces that adult and child residents may visit on a regular basis should also be initially assessed under a residential use exposure scenario. Short- and long-term remedial actions in the latter areas may differ from

actions recommended for high-density and single-family residential properties, however, due to greater control over digging and other activities that may expose contaminated soil.

Additional guidance and action levels are provided for sites where the preferred action levels noted above cannot be reasonably met and continued use or redevelopment of the site is still desired. Three categories of arsenic-contaminated soil are defined for both residential and commercial/industrial sites. Residential, Category 1 soils (R-1) are not considered to pose a significant risk to human health under any potential site conditions and can be reused onsite or offsite as desired. Commercial/Industrial, Category 1 soils (C-1) can be used as needed on commercial/industrial sites but should not be used as fill material offsite without prior consultation with HDOH.

Category 2 Residential (R-2) and Commercial/Industrial (C-2) soils are not considered to pose a significant risk to human health under the specified land use. As a best management practice, however, HDOH recommends the removal or capping of Category 2 soils associated with easily identifiable, localized spill areas when feasible (e.g., past pesticide mixing or storage). HDOH does not consider capping or removal of Category 2 soils in large, former field areas to be necessary or practicable.

Category 3 Residential (R-3) and Commercial/Industrial (C-3) soils are considered to pose an unacceptable risk to human health and should be removed from the site or isolated onsite under permanent structures or properly designed caps, as described below.

Remediation of residential and commercial/industrial properties to action levels for Category 2 soils is recommended to the extent technically and economically feasible, however, and should be discussed with the HEER office on a site-by-site basis. Reuse of Category 2 Commercial/Industrial soil for daily cover at a regulated landfill may be acceptable but should be discussed with the landfill operator as well as the HDOH Solid and Hazardous Waste Branch.

Background

Significantly elevated levels of arsenic have been identified in soils from former sugar cane fields and pesticide mixing areas in Hawai‘i, as well as in and around former plantation camps. High levels of arsenic have also been identified in soil samples from at least one former golf course. The presence of the arsenic is believed to be related the use of sodium arsenite and other arsenic-based pesticides in and around the cane fields in the 1920s through 1940s. During this period, up to 200,000 acres of land in Hawai‘i was being cultivated for sugar cane. The arsenic is generally restricted to the upper two feet of the soil column (approximate depth of plowing). Alternative action levels and approaches may be acceptable for contaminated soils situated greater than three feet below ground surface and should be discussed with HDOH on a site-by-site basis.

Current studies have focused on the Kea‘au area of the Big Island. Soils in the area have been described as stony, organic, iron-rich Andisols (Cutler et al., 2006). Concentrations of total arsenic in soils from undeveloped former sugar cane lands in this area have been reported to range from 100-400 mg/kg in the ≤2mm size fraction of the soil and >500 mg/kg in the <250µm size fraction (report pending). Concentrations greater than 1,000 mg/kg have been reported in one former plantation camp area. Background concentrations of arsenic in native soils range from 1.0 mg/kg up to 20 mg/kg. The presence of the arsenic initially posed concerns regarding potential groundwater impacts, uptake in homegrown produce and direct exposure of residents and workers to contaminated soil. Maximum-reported concentrations of bioaccessible arsenic in

soil are far below levels that would cause immediate, acute health affects. Continued exposure to arsenic in heavily contaminated soils over many years or decades could pose long-term, chronic health concerns, however.

Arsenic has not been detected in municipal groundwater wells in the area. Testing of produce from gardens in the Kea‘au area by the Department of Health in 2005 also did not identify levels of arsenic above U.S. norms, even though total arsenic in the garden soils approached or exceeded 300 mg/kg in the $\leq$2mm size fraction. Uptake of the arsenic in edible produce or other plants therefore does not appear to be a significant environmental health concern. These observations suggest that the arsenic is tightly bound to the soil and not significantly mobile. This is further supported by petrologic and leaching studies as well as “bioaccessibility” tests conducted on the soils (Cutler et al., 2006). Despite being relatively immobile, however, elevated levels of arsenic in some areas could still pose a potential chronic health risk to residents and workers who come into regular contact with the soil. The action levels and soil categories discussed below are intended to address this concern.

The evaluation of soil for arsenic has traditionally focused on the *total* amount of arsenic present and comparison to action levels based on a target excess cancer risk of one-in-a-million or 10^{-6}. This has always presented a dilemma in human health risk assessments. Natural, background concentrations of arsenic in soils are typically much higher than risk-based action levels for total arsenic. For example, the residential soil action level for arsenic presented in the HDOH document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater* is 0.42 mg/kg (HDOH 2008a, Appendix 1, Table I-1), while background concentrations of arsenic in soil in Hawai‘i may range up to 20 mg/kg or higher. In addition, much of the arsenic in pesticide-contaminated soil appears to be tightly bound to soil particles and not *available* for uptake in the human body. This portion of the arsenic is essentially nontoxic. These two factors led to a need for further guidance, particularly with respect to the use of *bioaccessible* arsenic data in human health risk assessments and in the development of risk-based, soil action levels.

Bioavailable and Bioaccessible Arsenic

Risk to human health posed by exposure to a contaminant in soil is evaluated in terms of the average daily dose or *intake* of the contaminant for an exposed person (e.g., in milligrams or micrograms per day; USEPA 1989, 2004). Intake can occur through incidental ingestion of soils, inhalation of dust of vapors, and to a lesser extent (for most contaminants) absorption through the skin. Assumptions are made about the fraction of the contaminant that is available for *uptake* in a persons blood stream via the stomach and small intestine. This is referred to as the *bioavailability* of the contaminant (NEPI 2000). The most widely accepted method to determine the bioavailability of a contaminant in soil is through *in vivo* studies where the soil is incorporated into a lab test animal’s diet. In the case of arsenic, the amount that is excreted in the animal’s urine is assumed to represent the fraction that entered the animal’s blood stream and was available for uptake.

In vivo bioavailability tests are time consuming and expensive, however, and not practical for routine site evaluations. As an alternative, faster and more cost-effective laboratory tests have been developed to estimate arsenic bioavailability in soil. These methods, referred to as *in vitro* bioaccessibility tests, utilize an acidic solution intended to mimic a child’s digestive tract (typically a glycine-buffered hydrochloric acid solution at pH 1.5; Ruby 1999; Gron and Andersen, 2003). Soil with a known concentration and mass of arsenic is placed in the solution and allowed to equilibrate for one hour. An extract of the solution is then collected and analyzed

for arsenic. The concentration of arsenic in the solution is used to calculate the total mass of arsenic that was stripped from the soil particles. The ratio of the arsenic mass that went into solution to the original mass of arsenic in the soil is referred to as the *bioaccessible* fraction of arsenic.

The results of *in vitro* bioaccessibility tests for arsenic compare favorably with *in vivo* bioavailability studies (Ruby 1999; Gron and Andersen, 2003). This is supported by studies of arsenic-contaminated soils from the Kea‘au area of the Big Island of Hawai‘i. Samples of the soil were tested for bioavailable arsenic in an *in vivo* monkey study carried out by the University of Florida in 2005 and simultaneously tested for bioaccessible arsenic by *in vitro* methods (report pending publication). The concentration of total arsenic in the samples was approximately 700 mg/kg. The study concluded that the bioavailability of arsenic in the soil ranged from 3.2% to 8.9%. This correlated well with an *in vitro* test carried out on the same soil that yielded an arsenic bioaccessibility of 6.5%. The bioaccessibility of arsenic in soils from the same site was estimated to range from 16% to 20% in a separate study, suggesting that the *in vitro* test method may err on the conservative side in comparison to the more standard *in vivo* method (Cutler et al., 2006). This has been observed in other studies of bioavailability versus bioaccessibility. Bioaccessibility tests on soils from other areas around Kea‘au yielded similar results and again indicated that 80% to >90% of the arsenic in the soil is so tightly bound to soil particles that it is essentially “nontoxic.”

Bioaccessible arsenic was observed to increase with increasing total arsenic concentration (Cutler et al., 2006). This is probably because much of the arsenic in heavily contaminated soils is fixed to low-energy binding sites on soil particles and comparatively easy to remove. Continued stripping of remaining arsenic from progressively higher-energy binding sites requires greater effort (i.e., the arsenic becomes progressively less bioaccessible). Data from the study also indicate that arsenic bioaccessibility (and therefore toxicity) may increase with increasing phosphorous concentration in soil related to the use of fertilizers in gardens. This is because phosphorus is able to out compete arsenic for high-energy binding sites on soil particles. The relationship has not been fully demonstrated, however, and is still under investigation.

Based on a review of published literature and studies conducted to date in Hawai‘i, HDOH considers arsenic bioaccessibility tests to be sufficiently conservative and an important tool in the assessment of arsenic-contaminated properties. Bioaccessible arsenic analyses should always be conducted on the ≤250µm size fraction of the soil since this is the fraction that is most likely to be incidentally ingested. Most soils only contain a small percentage of particles 250µm in size or less. This typically requires the collection of very large samples (several kilograms) to obtain the mass needed for bioaccessibility tests. Appropriate sample handling, processing, and sub-sampling by the lab conducting bioaccessibility testing is essential. Guidance on suggested procedures and quality control for bioaccessibility lab tests will be forthcoming from HDOH. For more information on this subject contact John Peard of the HDOH HEER office (john.peard@doh.hawaii.gov).

Basis of Soil Action Levels

Arsenic action levels and correlative soil categories for residential and commercial/industrial properties are presented in Tables 1 and 2 and summarized in Figure 1. An action level of 20 mg/kg total arsenic in the ≤2mm size soil fraction is recommended to screen out sites where naturally occurring (“background”) concentrations of arsenic are not significantly exceeded (HDOH 2008a). Background total arsenic may approach 50 mg/kg in some areas but this is

considered rare. Analysis of soil samples for bioaccessible arsenic is recommended at sites where total arsenic exceeds anticipated background concentrations.

Action levels for bioaccessible arsenic are presented in Table 1 (residential land use) and Table 2 (commercial/industrial land use). The action levels are based on direct-exposure models used by USEPA to develop soil *Regional Screening Levels* (RSLs) (replace 2004 Preliminary Remediation Goals; USEPA 2008). The USEPA RSLs for arsenic for residential and commercial/industrial land use are 0.39 mg/kg and 1.6 mg/kg, respectively, based on a target excess cancer risk of $1x10^{-6}$ (one-in-a-million). Risk-based action levels for arsenic of 0.42 mg/kg and 1.9 mg/kg are presented in the HDOH document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater*, based on a similar target risk but assuming a slightly lower, dermal absorption factor (HDOH 2008a). Both the USEPA RSLs and the HDOH Tier 1 action levels assume that 100% of the soil arsenic is bioavailable.

The USEPA RSLs and HDOH Tier 1 action levels for total arsenic are far below typical background concentrations of arsenic in soils from Hawai‘i, as well as most of the mainland US. To address this issue, action levels for Category 1 soils in Tables 1 and 2 are based on a target excess cancer risk of $1x10^{-5}$ (one-in-one-hundred-thousand) rather than $1x10^{-6}$. This generates residential and commercial/industrial action levels for bioaccessible arsenic of 4.2 mg/kg and 19 mg/kg, respectively. These action levels serve as useful starting points to help identify arsenic-contaminated sites that warrant further evaluation.

A second set of action levels is used to define soils that are most likely impacted above natural background levels but still may be acceptable for use in residential or commercial/industrial areas if adequate lawns and landscaping are maintained (Category 2 soils). An action level of 23 mg/kg bioaccessible arsenic was selected as an upper limit for soils in residential areas (Table 1). This reflects a noncancer Hazard Quotient of 1.0 and correlates to an excess cancer risk of approximately $5x10^{-5}$. Commercial/industrial action levels based on a similar excess cancer risk of $5x10^{-5}$ and a noncancer Hazard Quotient of 1.0 are 95 mg/kg and 310 mg/kg, respectively. Since the correlative action level for excess cancer risk is less than the action level for noncancer risk, the former (95 mg/kg) was chosen as an upper limit for soils in commercial/industrial areas (Table 2). These action levels are used to define the lower boundary of Category 3 soils.

At concentrations greater than 180 mg/kg, bioaccessible arsenic in soil begins to pose a potentially significant health risk to construction workers and utility workers (HDOH 2008a, refer to Table I-3 in Appendix 1, based on an excess cancer risk of $1x10^{-5}$). As discussed below, this is used as a “ceiling level” for soil that can be isolated under clean soil caps, buildings or paved areas.

The action levels for bioaccessible arsenic were used to group soils into three categories (see Tables 1 and 2). A discussion of potential remedial actions at each site that fall into these soil categories is provided in the following sections. The ultimate action taken at an individual site will be dependent on numerous site-specific factors, including current and planned land use, available options for onsite isolation or offsite disposal, and technical and economic constraints.

Soil Categories and Action Levels for use at Residential Sites

Category 1 Soils (R-1): Bioaccessible Arsenic $\leq$4.2 mg/kg, No Further Action

Long-term exposure to Category 1 (R-1) residential soils is not considered to pose a significant risk to residents. No further action is necessary at sites where the reported concentration of bioaccessible arsenic in soil is equal to or below 4.2 mg/kg.

Utility corridors should be backfilled with clean fill material (e.g., R-1 soils) or at a minimum R-2 soils in order to prevent excavation of contaminated soil and inappropriate reuse in other areas in the future. R-3 soils should not be placed in utility corridors.

Category 2 Soils (R-2): Bioaccessible Arsenic >4.2 mg/kg and ≤23 mg/kg, Consider Removal or Isolation of Localized Spill Areas

Long-term exposure to Category 2 (R-2) residential soils is not considered to pose a significant risk to residents. As a best management practice, however, HDOH recommends the removal or capping of Category 2 soils associated with easily identifiable, localized spill areas when feasible (e.g., past pesticide mixing or storage). HDOH does not consider capping or removal of Category 2 soils in large, former field areas to be necessary or practicable. These issues are discussed in more detail below.

At sites where R-2 soils are discovered in the vicinity of existing homes, residents should be encouraged to minimize exposure to the soil by taking the following precautions:

- Reduce areas of bare soil by planting and maintaining grass or other vegetative cover, or cover barren areas with gravel or pavement.
- Keep children from playing in bare dirt.
- Keep toys, pacifiers, and other items that go into childrens' mouths clean.
- Wash hands and face thoroughly after working or playing in the soil, especially before meals and snacks.
- Wash fruits and vegetables from home gardens before bringing them in the house. Wash again with a brush before eating or cooking to remove any remaining soil particles. Pare root and tuber vegetables before eating or cooking.
- Bring in clean sand for sandboxes and bring in clean soil for garden areas or raised beds.
- Avoid tracking soil into the house and keep the floors of the house clean. Remove work and play shoes before entering the house.

Testing of produce from gardens in the Kea'au area by the Department of Health in 2005 did not identify levels of arsenic above U.S. norms. Uptake of the arsenic in edible produce or other plants does not appear to be a significant environmental health concern in former sugar cane operation areas. Produce should be thoroughly cleaned before cooking or eating, however, in order to avoid accidental ingestion of small amounts of soil.

Category 3 Soils (R-3): Bioaccessible Arsenic >23 mg/kg, Removal or Isolation Recommended

Long-term exposure of residents to Category 3 (R-3) residential soils is considered to pose potentially significant health risks. As discussed above, maximum-reported concentrations of bioaccessible arsenic in soil from former agricultural areas are far below levels that would cause immediate, acute health affects. Continued exposure to arsenic in R-3 soils over many years or decades could pose long-term, chronic health concerns, however.

Offsite disposal of R-3 soils in a permitted landfill facility is recommended when technically and economically feasible. Reuse of some or all of the soil as daily cover at a landfill may also be possible. This should be discussed with the landfill in question as well as with the HDOH Solid and Hazardous Waste Branch. Offsite disposal of soil with bioaccessible arsenic in excess of 180 mg/kg is especially recommended (action level for construction/trench work exposure).

Soils that fall into this category but cannot be disposed offsite due to technical and/or cost constraints should be placed in *soil isolation areas*. Optimally, a soil isolation area would be created under public buildings, private roadways, parking lots and other facilities/structures that constitute a permanent physical barrier that residents are unlikely to disturb in the future. Isolation of R-3 soils under public roadways should be done in coordination with the local transportation authority. Isolation of R-3 soils under permanent structures is preferable to isolation in open areas, due to the increased potential for open areas to be inadvertently disturbed during future gardening, landscaping or subsurface utility work. Soil that cannot be placed under a permanent structure or disposed of offsite should be isolated in well-controlled common areas, rather than on individual residential lots. Contaminated soil should be consolidated in as few isolation areas as possible. Areas where R-3 soils are placed and capped for permanent onsite management must be clearly identified on surveyed, post-redevelopment map(s) of the property. These maps should be included a risk management plan that is provided to HDOH for inclusion in the public file for the site (see "Identification of Soil Isolation Areas" below). Utility corridors should be backfilled with clean fill material (e.g., R-1 soils) when initially installed or following maintenance work in order to prevent excavation and inappropriate reuse of contaminated soil in the future.

Depending on site-specific conditions, permanent covers or caps for soil isolation areas may be constructed of paving materials such as asphalt and concrete ("hard cap") or earthen fill material ("soil cap") that meets R-1 (preferred) or R-2 action levels. A soil cap thickness of 24 inches is recommended for areas where landscaping activities may involve digging deeper than one foot or where gardens may be planted in the future (based on USEPA guidance for lead-contaminated soils, USEPA 2003). A cap of twelve inches may be acceptable in high-density residential redevelopments where gardens will not be allowed and use of the area will be strictly controlled. A clearly identifiable, marker barrier that cannot be easily penetrated with shovels or other handheld digging tools (e.g., orange construction fencing or geotextile webbing) should be placed between the contaminated soil and the overlying clean fill material. A similar marker barrier should be placed below or above gravel, concrete or other hard material placed on top of contaminated soil in order to avoid confusion with former building foundations or road beds.

Permeable marker barriers may be necessary in areas of high rainfall in order to prevent ponding of water during wet seasons. Leaching tests should be carried out on R-3 soils in order to evaluate potential impacts to groundwater (see discussion below).

When R-3 soils are identified at existing homes, removal or permanent capping of the soils should be strongly considered. In the interim, residents should follow the measures outlined for residential R-2 soils to minimize their daily exposure. Children should avoid areas of bare soil and regular work in garden areas.

Soil Categories and Action Levels for use at Commercial/Industrial Sites

Category 1 Soils (C-1): Bioaccessible Arsenic >4.2 mg/kg and ≤19 mg/kg, No Further Action

Long-term exposure to Category 1 (C-1) soils is not considered to pose a significant health risk to workers at commercial or industrial sites. Remediation of soil that exceeds action levels for residential, R-1 (preferred) or R-2 action levels, however, will minimize restrictions on future land use and should be considered when feasible. Note that this may require a more detailed sampling strategy than is typically needed for commercial/industrial properties (e.g., decision units 5,000 ft^2 in size or less). Long-term institutional controls to restrict use of property to commercial/industrial purposes may be required if the site will not be investigated to the level of detail required for future, unrestricted land use to ensure that action levels for Category 2 Residential soils are not exceeded

Category 2 Soils (C-2): Bioaccessible Arsenic >19 mg/kg and ≤95 mg/kg, Consider Removal or Isolation

Long-term exposure to Category 2 (C-2) soils is not considered to pose a significant risk to workers provided that lawns and landscaping are maintained to minimize exposure and control fugitive dust or if the soils. Remediation of commercial/industrial properties to action levels approaching those for C-1 soils or lower is recommended when technically and economically feasible, however, and should be discussed with the HEER office on a site-by-site basis. When selecting remedial options, long-term effectiveness should be given increasing weight as concentrations of bioaccessible arsenic approach the upper boundary for C-2 soils.

For new developments, isolation of C-2 soils under buildings, private roadways and other areas with a permanent cap that workers are unlikely to disturb in the future is recommended when feasible. Isolation of C-2 soils under public roadways should be done in coordination with the local transportation authority. Offsite reuse of C-2 soil as fill material should be avoided. Reuse of some or all of the soil as daily cover in a regulated landfill may be feasible, however. This should be discussed with the landfill in question as well as with the HDOH Solid and Hazardous Waste Branch. Areas of the property where capped or uncapped C-2 soil is located must be clearly identified on surveyed, post-redevelopment map(s) of the property and included in a risk management plan that is documented in the HDOH public file for the site (see "Identification of Soil Isolation Areas" below). Care must be taken to ensure that soil from these areas is not excavated and inadvertently reused in offsite areas where residents could be exposed on a regular basis. Utility corridors should be backfilled with clean fill material (e.g., R-1 soils) when initially installed or following maintenance work in order to prevent excavation and inappropriate reuse of contaminated soil in the future.

At existing facilities, areas of bare C-2 soils should be minimized by maintaining grass or other vegetative cover or by covering bare areas with gravel or pavement. Workers should be encouraged to maintain clean work areas and thoroughly wash hands before breaks and meals.

Category 3 Soils (C-3): Bioaccessible Arsenic >95 mg/kg, Removal or Isolation Recommended

Long-term exposure to Category 3 (C-3) soils is considered to pose potentially significant health risks to workers at commercial or industrial sites. Offsite disposal of C-3 soils is recommended when technically and economically feasible. Offsite disposal of soil with bioaccessible arsenic in excess of 180 mg/kg is especially recommended (action level for construction/trench work exposure). Soil that cannot be removed from the site should be placed in designated isolation areas under public buildings, private roadways, parking lots and other facilities/structures that constitute a permanent physical barrier that residents are unlikely to disturb in the future. Contaminated soil should be consolidated in as few isolation areas as possible. Areas of the property where C-3 soil is located must be clearly identified on surveyed, post-redevelopment map(s) of the property and included in a risk management plan that is documented in the HDOH public file for the site (see "Identification of Soil Isolation Areas" below). Care must be taken to ensure that soil from these areas is not excavated and inadvertently reused in offsite areas where residents could be exposed on a regular basis. Utility corridors should be backfilled with clean fill material (e.g., R-1 soils) in order to prevent inadvertent excavation and reuse of contaminated soil in other areas in the future.

As discussed for residential sites, isolation of contaminated soil under buildings or other permanent structures is preferred over isolation in open areas. If placement of the soil in an open area is necessary, use of areas that are unlikely to be disturbed in the future is preferred. A

minimum cap thickness of twelve inches is generally acceptable for commercial/industrial sites where use of the area will be strictly controlled (USEPA 2003). A clearly identifiable marker barrier should be placed between the contaminated soil and the overlying clean fill material (e.g., orange construction fencing or geotextile webbing). Fencing, geotextile fabric or similar, easily identifiable markers should likewise be placed above any gravel, concrete or other hard material placed on top of contaminated soil in order to avoid confusion with former building foundations or road beds.

Use of Total Arsenic Data

Based on data collected to date, it is possible that a significant portion of former sugar cane land situated in areas of high rainfall (e.g., >100 inches per year) will fall into the R-2 or C-2 soil categories as described above and summarized in Tables 1 and 2. Some of these areas have already been redeveloped for residential houses. Determination of bioaccessible arsenic levels on individual lots with existing homes may not be economically feasible for some residents (current analytical costs $500 to $1000). If site-specific, bioaccessible arsenic data is not affordable for a private homeowner, HDOH recommends that the soil be tested for total arsenic (generally less than $100). The resulting data should then be adjusted using a default *bioavailability* value to estimate bioavailable arsenic concentrations. Based on data collected to date in the Kea‘au area, a 10% bioavailability factor (BF) is recommended for total arsenic values at or below 250 mg/kg. Measured concentrations of total arsenic should be multiplied by 0.1 and the adjusted concentration compared to the action levels in Table 1 or Table 2. For total arsenic above 250 mg/kg, a more conservative bioavailability factor of 20% (0.2) is recommended.

For residential sites, this approach corresponds to an upper limit of 42 mg/kg total arsenic for R-1 soils and 230 mg/kg total arsenic for R-2 soils (10% BF used). For commercial/industrial sites, this corresponds to an upper limit of 190 mg/kg total arsenic for C-1 soils (10% BF used) and 475 mg/kg total arsenic for C-2 soils (20% BF used). Soils that potentially fall into Category 3 for residential or commercial/industrial sites should be tested for bioaccessible arsenic if at all possible. In the absence of bioaccessibility data, it is recommended that children avoid playing or working in gardens or other areas where total arsenic action levels indicate the potential presence of R-3 soils. The default bioaccessibility factors presented were developed based on data from the Kea‘au region and are subject to revision as more data becomes available.

The total arsenic action levels proposed above should not be used for general screening purposes at sites where a formal environmental investigation is being carried out. As previously discussed and as noted in the summary tables, bioaccessible arsenic data should be collected at all sites where total arsenic concentrations exceed an assumed background concentration of 20 mg/kg unless otherwise approved by HDOH.

Soil Sampling Methods

The use of multi-increment field soil sampling and lab sub-sampling techniques is recommended over the use of discrete or traditional composite sampling techniques. This sampling approach allows for the determination of a statistically representative concentration of arsenic within a specific area of investigation or “decision unit.”, such as an individual yard, a park, a garden or a well-defined spill area. Additional guidance on the use of multi-increment and decision unit investigation strategies will be provided in the 2008 update to the HEER office *Technical Guidance Manual.*

Other Potential Environmental Concerns

A discussion of environmental hazards associated with contaminated soil is provided in the HDOH document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (HDOH 2008a). The arsenic action levels presented in this technical memorandum address human-health, direct-exposure hazards only. The action levels do not address potential leaching of arsenic from soil and subsequent impacts to underlying groundwater or potential toxicity to terrestrial flora and fauna. These issues should be evaluated on a site-specific basis as directed by HDOH. Arsenic is not considered to pose significant vapor intrusion or gross contamination hazards.

Based on data collected to date, leaching of arsenic from former sugar cane fields is not anticipated to pose a significant concern in Hawai‘i due to the apparent, relative immobility of the arsenic. Additional field data are needed to support this assumption, however, particularly for soils that exceed the upper action level for R-2 residential soils (i.e., >23 mg/kg bioaccessible arsenic). HDOH recommends that potential leaching of arsenic from soils that exceed 23 mg/kg bioaccessible arsenic be evaluated using the USEPA Synthetic Precipitation Leaching Procedure (SPLP) test or a comparable method. Refer to the HDOH technical memorandum *Use of Laboratory Batch Tests to Evaluate Potential Leaching of Contaminants from Soil* for additional guidance (HDOH 2007).

Assessment of additional pesticides and pesticide-related contaminants in agricultural areas should be carried out as needed based on the past use of the property. Refer to the 2008 update of the HEER office *Technical Guidance Manual* for additional information on target pesticides.

Environmental Hazard Evaluation Plans

Isolation areas where arsenic-contaminated soil is to be capped for permanent onsite management must be clearly identified on surveyed, post-redevelopment map(s) of the property. Areas of soil at commercial/industrial sites that exceed action levels for residential R-1, R-2 and R-3 soils should also be clearly surveyed and mapped. The maps identifying arsenic-impacted soils should be incorporated into an *Environmental Hazard Evaluation Plan* (EHMP, HDOH 2008a) that describes proper management, reuse and disposal of contaminated soil if disturbed during later redevelopment activities. A copy of the plan should be submitted to both HDOH and to the agency(s) that grants permits for construction, trenching, grading or any other activities that could involve future disturbance or excavation of the soil. The need to incorporate the risk management plan and specific land use restrictions in a formal covenant to the property deed should be discussed with HDOH on a site-by-site basis. Additional guidance on EHMPs will be provided in the 2008 update to the HEER office *Technical Guidance Manual*.

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Table 1. Soil categories and recommended actions for Residential Sites.

Total Arsenic (≤ 2 mm size fraction)	**Action**
≤20 mg/kg	Within range of natural background. No further action required and no restrictions on land use.
>20 mg/kg	Exceeds typical background. Re-evaluate local background data as available. Test soil for bioaccessible arsenic if background is potentially exceeded.
Bioaccessible Arsenic (≤250µm size fraction)	**Action**
R-1 Soils (≤4.2 mg/kg)	No further action required and no restrictions on land use.
R-2 Soils (>4.2 but ≤23 mg/kg)	Within USEPA range of acceptable health risk. Consider removal and offsite disposal of small, easily identifiable "hot spots" when possible in order to reduce potential exposure (not required for large, former field areas). Use of soil as daily cover at a regulated landfill may also be possible. For existing homes, consider measures to reduce daily exposure to soil (e.g., maintain lawn cover, ensure good hygiene, thoroughly wash homegrown produce, etc.). For new developments on large, former field areas, notify future homeowners of elevated levels of arsenic on the property (e.g., include in information provided to potential buyers during property transactions).
R-3 Soils (>23 mg/kg)	For existing homes, removal or onsite isolation of exposed soil is strongly recommended. Consider a minimum one-foot cover of clean fill material (two feet in potential garden areas) if soil cannot be removed. An easily identifiable marker barrier should be placed between the contaminated soil and the overlying fill (e.g., orange construction fencing or geotextile/geonet material). In the interim, take measures to reduce daily exposure to soil (e.g., maintain lawn cover, ensure good hygiene, thoroughly wash homegrown produce, etc.). Children should avoid areas of bare soil and regular work in gardens areas. For new residential developments, removal and offsite disposal of soil should be strongly considered. At a minimum, consider removal and offsite disposal of soil with concentrations of bioaccessible arsenic that approach or exceed 180 mg/kg (direct exposure action level for construction and trench workers). Use of soil as daily cover at a regulated landfill may be possible if concentrations of bioaccessible arsenic meet C-2 commercial/industrial soil criteria. If offsite disposal is not feasible but redevelopment of the property is still desired, consider use of soil as structural fill under public buildings, parking lots, private roads, or other paved and well-controlled structures. If capping in open areas is unavoidable, consider a one-foot minimum cap thickness with an easily definable marker barrier placed between the soil and the overlying clean fill (e.g., orange construction fencing or geotextile fabric). Capping of R-3 soils on newly developed, private lots is not recommended due to difficulties in ensuring long-term management of the soil. Backfill utility corridors with clean fill material (e.g., R-1 soils) to avoid excavation and inappropriate reuse of the soil in the future.

Table 1. Soil categories and recommended actions for Residential Sites (cont.).

R-3 Soils (cont.) (>23 mg/kg)	Require formal, long-term institutional controls to ensure appropriate management of soil in the future (e.g., Covenants, Conditions and Restrictions (CC&Rs), deed covenants, risk management plans, etc.). All areas of capped soil should be delineated on a surveyed map of the property to be subsequently included in the risk management plan.

The soil categories and arsenic action levels noted above are intended to be used as guidelines only and do not represent strict, regulatory cleanup requirements.

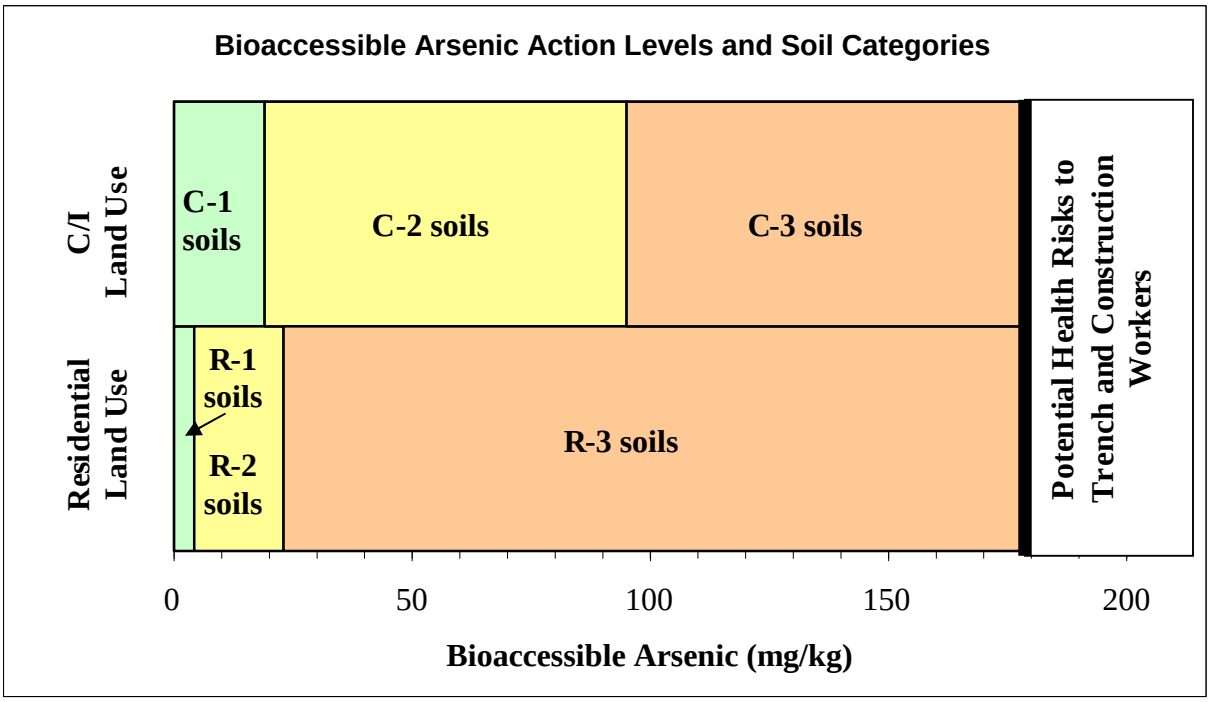
Table 2. Soil categories and recommended actions for Commercial/Industrial Sites.

Total Arsenic (≤ 2 mm size fraction)	**Action**
≤20 mg/kg	Within range of natural background. No further action required and no restrictions on land use.
>20 mg/kg	Exceeds typical background. Re-evaluate local background data as available. Test soil for bioaccessible arsenic if background is potentially exceeded.
Bioaccessible Arsenic (≤250µm size fraction)	**Action**
C-1 Soils (>4.2 mg/kg but ≤19 mg/kg)	No remedial action required. However, consider remediation of commercial/industrial properties to meet Residential R-1 (preferred) or R-2 action levels when feasible in order to minimize restrictions on future land use. Note that this may require a more detailed sampling strategy than typically needed for commercial/industrial properties (e.g., smaller decision units). Require formal, long-term institutional controls to restrict use of property to commercial/industrial purposes if the site will not be investigated to the level of detail required for future, unrestricted land use (i.e., inform potential buyers, deed covenants, risk management plans, etc.).
C-2 Soils (>19 but ≤95 mg/kg)	Remedial actions vary depending on site-specific factors, including current and planned use, available options for onsite isolation or offsite disposal, and technical and economical constraints (see text). Potential actions include: Consider removal and offsite disposal of small, easily identifiable "hot spots" when possible in order to reduce the average concentration of bioaccessible arsenic on the property. Use of C-2 soils as daily cover at a regulated landfill may also be possible. For sites that have already been developed, consider a minimum one-foot cover of clean fill material if the soil cannot be removed. If capping of soil is not feasible, consider measures to reduce daily exposure to soil (e.g., maintain lawn cover, ensure good hygiene, etc.). For new developments, consider isolation of soil under buildings, private roads or other permanent structures if technically and economically feasible. If isolation under permanent structures is not feasible, consider a minimum one-foot cover of clean fill material. Maintain landscaping and lawns in open areas where soil will not be capped. Backfill utility corridors with clean fill material (e.g., R-1 soils) to avoid excavation and inappropriate reuse of contaminated soil in the future. Require formal, long-term institutional controls to restrict use of site to commercial/industrial purposes only and ensure appropriate management of soil if exposed in the future (e.g., inform potential buyers, deed covenants, risk management plans, etc.). All areas of capped soil should be delineated on a surveyed map of the property to be subsequently included in the risk management plan.

Table 2. Soil categories and recommended actions for Commercial/Industrial Sites (cont.).

C-3 Soils (>95 mg/kg)	Removal of soil at existing commercial/industrial sites strongly recommended. At a minimum, consider removal and offsite disposal of soil with concentrations of bioaccessible arsenic that approach or exceed 180 mg/kg (direct exposure action level for construction and trench workers). If C-3 soils cannot be removed for technical or economic reasons, consider a minimum one-foot cover of clean fill material (two feet in potential deep landscaping areas) and placement of an easily identifiable marker barrier between the clean fill and the underlying soil (e.g., orange construction fencing or geotextile/geonet material). For new developments, removal and offsite disposal of soil should be strongly considered. At a minimum, consider removal and offsite disposal of soil with concentrations of bioaccessible arsenic that approach or exceed 180 mg/kg (direct exposure action level for construction and trench workers). If offsite disposal is not feasible but redevelopment of the property is still desired, consider use of soil as structural fill under public buildings, private roads, or other paved and well-controlled structures. If capping in open areas is unavoidable, consider a one-foot minimum cap thickness with an easily definable marker barrier placed between the soil and the overlying clean fill (e.g., orange construction fencing or geotextile/geonet material). Backfill utility corridors with clean fill material (e.g., R-1 soils) to avoid excavation and inappropriate reuse of contaminated soil in the future. Require formal, long-term institutional controls to ensure appropriate management of soil in the future (e.g., inform potential buyers, deed covenants, risk management plans, etc.). All areas of capped soil should be delineated on a surveyed map of the property to be subsequently included in the risk management plan.

The soil categories and arsenic action levels noted above are intended to be used as guidelines only and do not represent strict, regulatory cleanup requirements.



Residential Land Use Soil Categories		Commercial/Industrial Land Use Soil Categories	
R-1	≤4.2 mg/kg	C-1	≤19 mg/kg
R-2	>4.2 mg/kg to ≤23 mg/kg	C-2	>19 mg/kg to ≤95 mg/kg
R-3	>23 mg/kg	C-3	>95 mg/kg
>180 mg/kg: Potential risk to trench & construction workers			

Figure 1. Summary of bioaccessible arsenic action levels and correlative soil categories for residential and commercial/industrial (C/I) land-use scenarios.

ATTACHMENT 2

ESTIMATED DIETARY INTAKE
OF TOTAL AND INORGANIC ARSENIC FOR PACIFIC-ASIAN DIETS

Dietary Exposure to Arsenic

A review of dietary exposure to total and inorganic arsenic was carried out by estimating daily consumption of the following food groups and typical concentrations of arsenic associated with each group:

- cereals & cereal products;
- starch roots and tubers;
- sugars and syrups;
- fats and oils;
- fish, meat and poultry;
- eggs;
- milk and products;
- dried beans, nuts and seeds;
- vegetables;
- fruits; and
- miscellaneous (beverages, condiments, etc.).

Consumption rates of each food group in a typical Filipino diet were compiled based on information published by the Philippine government and used as a surrogate for a typical Pacific-Asian diet (FNRI 2003, see Tables 1 and 2). Data are provided for children (ages 1-5) and the population as a whole (essentially adults). The data are provided for "As Purchased" food (e.g., raw vegetables, uncooked rice, etc.). A summary of the data is provided in Table 1.

Typical concentrations of inorganic and total arsenic in each food group were taken from a study of dietary exposure to arsenic in US children (Schoof et al. 1999, as presented in Yost et al. 2004; refer to Table 2). The data are based on prepared food (i.e., cooked meats and vegetables, including rice). While this is unlikely to introduce significant bias for meats and raw vegetables, the arsenic data for cooked rice cannot be directly compared to consumption data for uncooked rice. As an alternative, the estimated concentration of arsenic in rice is based on the average of 11 types of uncooked rice tested in a separate study (Williams et al 2005, as presented in Juhasz et al. 2006; refer to Table 1). Estimated concentrations of inorganic and total arsenic in seaweed was taken from a study carried out by the United Kingdom Food Standards Agency (UKFSA 2004).

The estimated daily, dietary intake of total arsenic is summarized in Figure 1. The estimated daily intake of inorganic arsenic is summarized in Figure 2. For children age one to five, the average exposure to dietary inorganic arsenic is estimated to be 18 ug/day, with 95% of the arsenic coming from rice. For the mean population (assumed representative of adults in general), the average exposure to dietary inorganic arsenic is estimated to be 44 ug/day, with a similar proportion of the arsenic coming from rice.

Dietary total arsenic is significantly higher, due primarily to the anticipated high consumption of fish and seaweed and the relatively high levels of organic arsenic in these foods. As noted in Table 1 and Figure 1, the average dietary total arsenic for children ages 1-5 is estimated to be 176 ug/day and for the mean population 339 ug/day. The

consumption of fish provides approximately 75% of the total dietary arsenic, with the remainder of the total arsenic contributed by rice and seaweed (Nori seaweed assumed). Although organic arsenic is not considered to be significantly toxic, metabolism to DMA could complicate interpretation of the urine data collected for the target Filipino population.

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Table 1. Estimation of dietary exposure to total arsenic for a typical Filipino diet (surrogate for Pacific-Asian diet).

				Child (6mo-5yr)		Mean Population			
Food Group	**[1]Child Consumption (g/d)**	**[1]Mean Consumption (g/d)**	**Total Arsenic (ug/kg)**	**Daily Dose (ug/d)**	**Percent Total Arsenic Contribution**	**Daily Dose (ug/d)**	**Percent Total Arsenic Contribution**	**[2]Reference**	**Comments**
Cereals	**166**	**364**		**27.09**	**15.40%**	**65.4**	**19.28%**		
Rice & Products	122	303	208	25.4	14.42%	63	18.58%	Williams et al 2005	*in* Juhasz et al 2006
Corn and Products	17	31	38.6	0.66	0.37%	1.20	0.35%	Yost et al., 2004	
Other Cereals and Products	27	30	39.2	1.06	0.60%	1.18	0.35%	Yost et al., 2004	flour
Starch Roots and Tubers	**8**	**19**	**2.8**	**0.02**	**0.01%**	**0.05**	**0.02%**	Yost et al., 2004	potatoes
Sugars and Syrups	**15**	**24**	**23.8**	**0.36**	**0.20%**	**0.57**	**0.17%**	Yost et al., 2004	cane sugar
Fats and Oils	**6**	**18**	**1.8**	**0.01**	**0.01%**	**0.03**	**0.01%**	Yost et al., 2004	butter
Fish, Meat & Poultry	**95**	**185**		**135.61**	**77.08%**	**247.58**	**73.00%**	Yost et al., 2004	
Fish and Products	57	104	2356	134.29	76.34%	245.02	72.25%	Yost et al., 2004	Saltwater fish (Freshwater = 160 ug/kg)
Meat and Products	27	61	13.5	0.36	0.21%	0.82	0.24%	Yost et al., 2004	pork
Poultry and Products	11	20	86.40	0.95	0.54%	1.73	0.51%	Yost et al., 2004	chicken
Eggs	**8**	**13**	**0.98**	**0.01**	**0.00%**	**0.01**	**0.00%**	Yost et al., 2004	
Milk and Products	**179**	**49**		**0.39**	**0.22%**	**0.11**	**0.03%**	Yost et al., 2004	
Whole Milk	158	35	2.2	0.35	0.20%	0.08	0.02%	Yost et al., 2004	
Milk Products	21	14	2.2	0.05	0.03%	0.03	0.01%	Yost et al., 2004	
Dried Beans, Nuts & Seeds	**4**	**10**	**43.7**	**0.17**	**0.10%**	**0.44**	**0.13%**	Yost et al., 2004	
Vegetables	**23**	**111**		**12.08**	**6.87%**	**24.65**	**7.27%**	Yost et al., 2004	
Green Leafy & Yellow	10	31	6.1	0.06	0.03%	0.19	0.06%	Yost et al., 2004	spinach
Other Vegetables	3	80	5.8	0.02	0.01%	0.46	0.14%	Yost et al., 2004	average all other vegetables
Seaweed	0.5	1	24,000	12.00	6.82%	24.00	7.08%	UKSFA 2004	nori seaweed (1/2 MRL of 0.3 mg/kg)
Fruits	**31**	**54**		**0.16**	**0.09%**	**0.26**	**0.08%**	Yost et al., 2004	
Vitamin C-rich Fruits	4	12	2.5	0.01	0.01%	0.03	0.01%	Yost et al., 2004	oranges
Other Fruits	27	42	5.5	0.15	0.08%	0.23	0.07%	Yost et al., 2004	average all other fruits
Miscellaneous	**27**	**39**		**0.02**	**0.01%**	**0.03**	**0.01%**	Yost et al., 2004	
Beverages	26	26	0.8	0.02	0.01%	0.02	0.01%	Yost et al., 2004	tapwater used in cooking
Condiments & Others	1	13	0.8	0.001	0.0005%	0.01	0.003%	Yost et al., 2004	salt
Total Food Consumption:	562	886	**Total:**	**176**	**100.0%**	**339**	**100.0%**		

1. FNRI, 2003. Child = Average 6mo to 5 yrs. "As Purchased," cereals presumable dry weight.

2. See text for full reference.

Table 2. Estimation of dietary exposure to inorganic arsenic for a typical Filipino diet (surrogate for Pacific-Asian diet).

				Child (6mo-5yr)		Mean Population			
Food Group	**[1]Child Consumption (g/d)**	**[1]Mean Consumption (g/d)**	**Inorganic Arsenic (ug/kg)**	**Daily Dose (ug/d)**	**Percent Inorganic Arsenic Contribution**	**Daily Dose (ug/d)**	**Percent Inorganic Arsenic Contribution**	**Reference**	**Comments**
Cereals	**166**	**364**		**17.33**	**96.6%**	**42.6**	**97.5%**		
Rice & Products	122	303	139.0	17.0	94.6%	42	96.4%	Williams et al 2005	*in* Juhasz et al 2006
Corn and Products	17	31	4.4	0.07	0%	0.14	0%	Yost et al., 2004	
Other Cereals and Products	27	30	10.9	0.29	2%	0.33	1%	Yost et al., 2004	flour
Starch Roots and Tubers	**8**	**19**	**0.8**	**0.01**	**0.0%**	**0.02**	**0.0%**	Yost et al., 2004	potatoes
Sugars and Syrups	**15**	**24**	**4.4**	**0.07**	**0%**	**0.11**	**0.2%**	Yost et al., 2004	cane sugar
Fats and Oils	**6**	**18**	**1.2**	**0.01**	**0.0%**	**0.02**	**0.0%**	Yost et al., 2004	butter
Fish, Meat & Poultry	**95**	**185**		**0.08**	**0.5%**	**0.16**	**0.4%**	Yost et al., 2004	
Fish and Products	57	104	1.0	0.06	0.3%	0.10	0.2%	Yost et al., 2004	Saltwater fish (Freshwater = 160 ug/kg)
Meat and Products	27	61	0.67	0.02	0.1%	0.04	0.1%	Yost et al., 2004	pork
Poultry and Products	11	20	0.89	0.01	0.1%	0.02	0.0%	Yost et al., 2004	chicken
Eggs	**8**	**13**	**0.98**	**0.01**	**0.0%**	**0.01**	**0.0%**	Yost et al., 2004	
Milk and Products	**179**	**49**		**0.18**	**1.0%**	**0.05**	0.1%	Yost et al., 2004	
Whole Milk	158	35	1.0	0.16	0.9%	0.04	0.1%	Yost et al., 2004	
Milk Products	21	14	1.0	0.02	0.1%	0.01	0.0%	Yost et al., 2004	
Dried Beans, Nuts & Seeds	**4**	**10**	**4.7**	**0.02**	**0.1%**	**0.05**	**0.1%**	Yost et al., 2004	
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Fruits	**31**	**54**		**0.07**	**0.4%**	**0.12**	**0.3%**	Yost et al., 2004	
Vitamin C-rich Fruits	4	12	2.5	0.01	0.1%	0.03	0.1%	Yost et al., 2004	oranges
Other Fruits	27	42	2.1	0.06	0.3%	0.09	0.2%	Yost et al., 2004	average all other fruits
Miscellaneous	**27**	**39**		**0.02**	**0.1%**	**0.03**	**0.1%**	Yost et al., 2004	
Beverages	26	26	0.8	0.02	0.1%	0.02	0.0%	Yost et al., 2004	tapwater used in cooking
Condiments & Others	1	13	0.8	0.001	0.00%	0.01	0.02%	Yost et al., 2004	salt
Total Food Consumption:	562	886	**Total DD:**	**18**		**44**			

1. FNRI, 2003. Child = Average 6mo to 5 yrs. "As Purchased," cereals presumable dry weight.
2. See text for full reference.

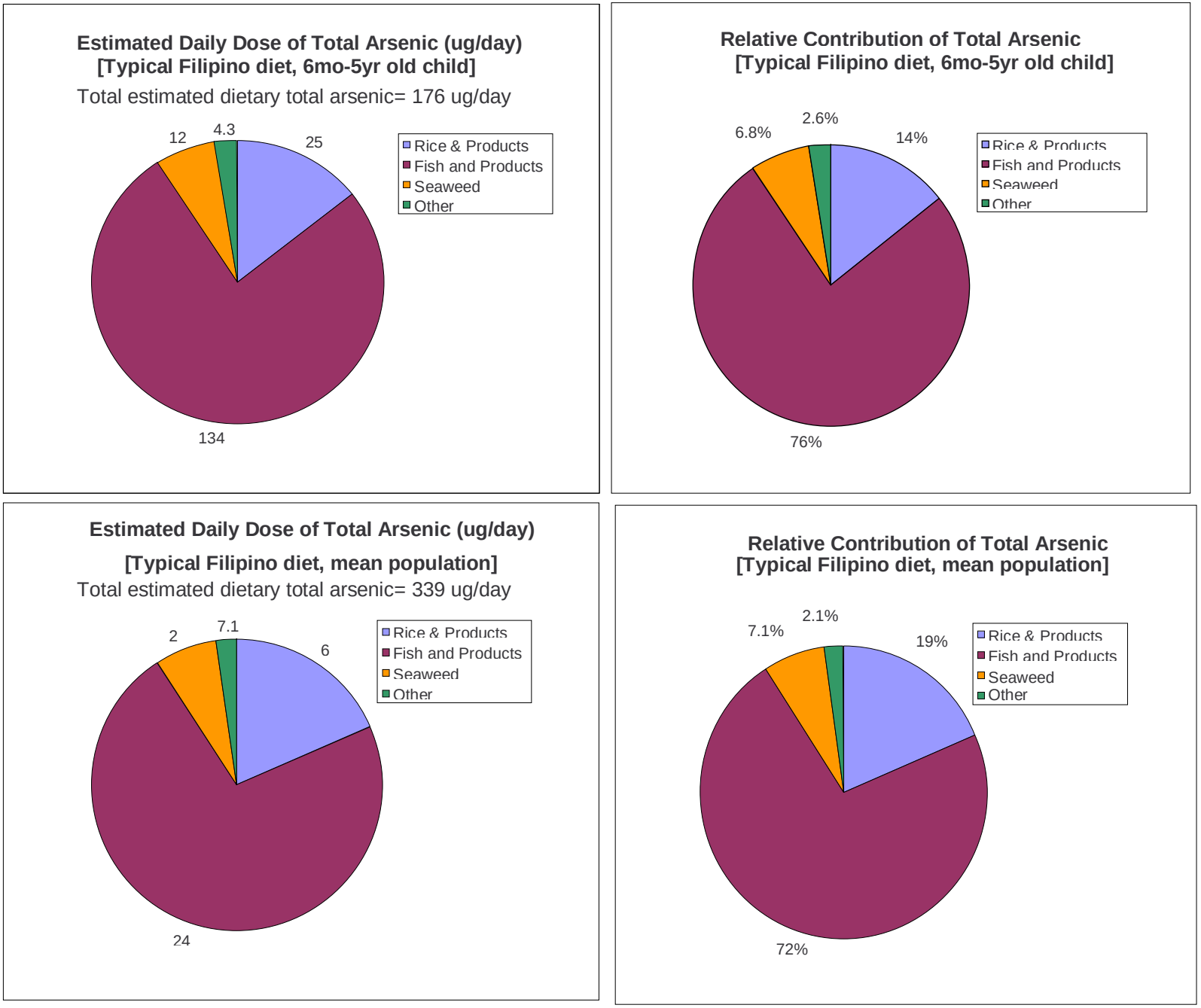

Figure 1. Estimated total arsenic intake based on a typical Filipino diet (surrogate for Pacific-Asian diet, refer to Table 1).

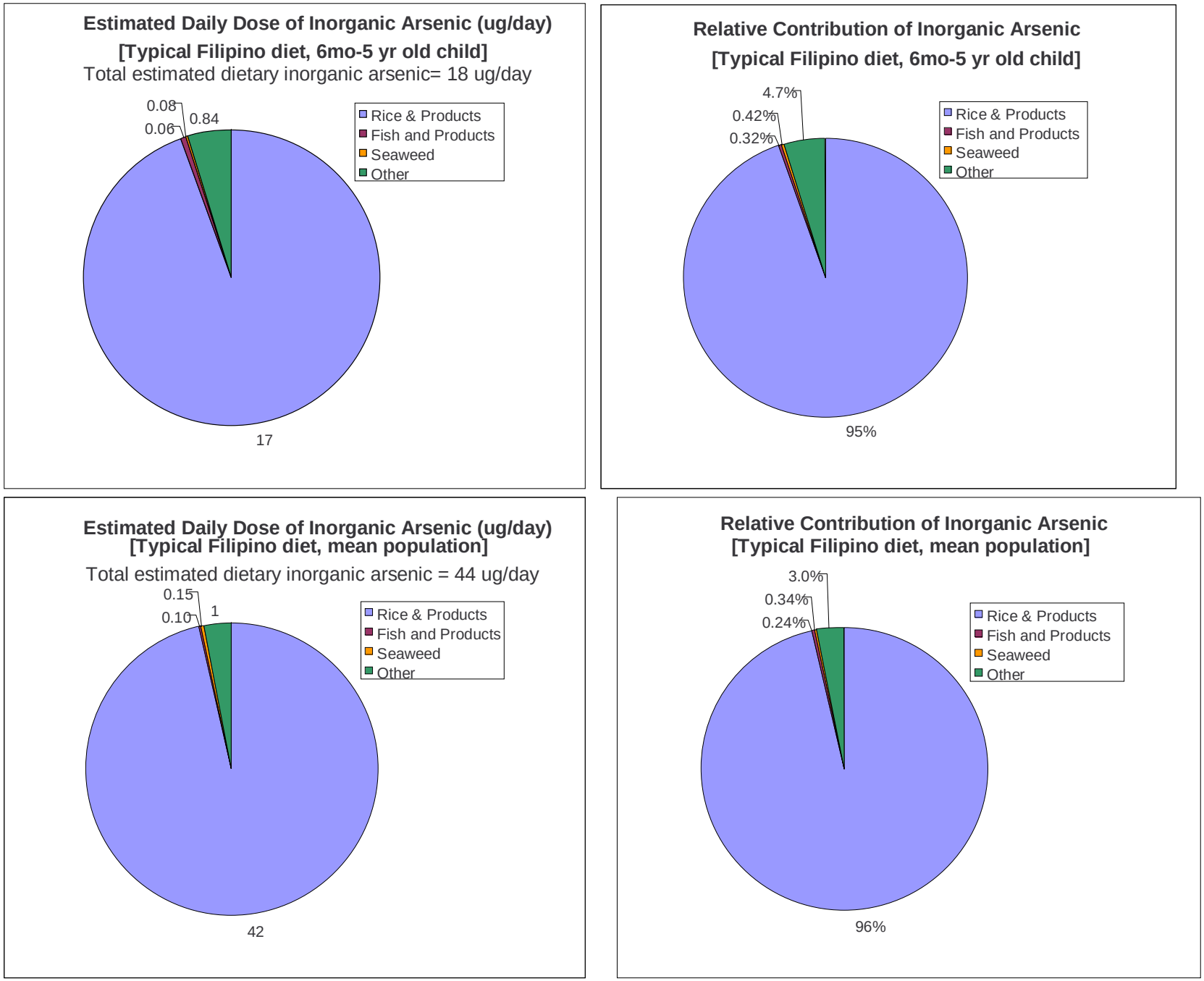

Figure 2. Estimated inorganic arsenic intake based on a typical Filipino diet (surrogate for Pacific-Asian diet, refer to Table 2).

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HONOLULU, HAWAI'I 96801-3378

In reply, please refer to:
File: EHA/HEER Office
2010-389-RB

June 2010

To: Interested Parties

From: Roger Brewer, Ph.D., Environmental Risk Assessor, HEER RB

Through: Barbara Brooks, Ph.D., Toxicologist, HEER BB

Subject: Update to Soil Action Levels for TEQ Dioxins and Recommended Soil Management Practices

1.0 Introduction

This technical memorandum presents an update to Hawai'i Department of Health (HDOH) action levels and corresponding guidance for dioxins and furans ("dioxins") in soil. This guidance serves as an addendum to the Hazard Evaluation and Emergency Response (HEER) office document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (EHE guidance; HDOH 2008a). A summary of the updated action levels and soil management categories is provided in Table 1. A detailed discussion of the development and support of the action levels is provided in Attachment 1 (Supplemental Information), Attachment 2 (Exposure Models) and Attachment 3 (Dietary Exposure to Dioxins).

This guidance supersedes and takes precedence over a technical memorandum on dioxins published by the HEER office in June 2008 and incorporated into the EHE guidance (HDOH 2008b). This memo also presents a modification of the HEER office soil categorization system, based on updates to dioxin action levels and a simplified approach for classification and management of dioxin-contaminated soils. The soil action levels presented herein are not promulgated regulatory standards or required cleanup levels. Alternative proposals may be presented in a site-specific risk assessment. However, the nature of the toxicity factors and exposure assumptions used to in this update are unlikely to allow significant flexibility for less stringent, site-specific action levels in the absence of institutional and/or engineering controls.

The soil action levels presented in this document are intended for comparison to soil data obtained through collection of multi-increment ("incremental") soil samples, as described in the HEER office *Technical Guidance Manual* (HDOH 2009). When combined with *Decision Unit* investigation approaches, multi-increment soil samples offer a more cost-effective and efficient

approach for characterization of a targeted area or volume of soil than traditional, discrete sample approaches. Studies have shown that a small number (e.g., less than <30) of discrete samples is unlikely to adequately capture contaminant heterogeneity and small "hot spots" of elevated contaminant concentrations within a targeted area (e.g., Ramsey et. al. 2005; Jenkins et al. 2005). This can lead to an underestimate of exposure point concentrations for risk assessment purposes, as well as an underestimate of contaminant mass for *in situ* or *ex situ* treatment. Alternative soil sampling schemes should be discussed with the HEER office on a site-by-site basis.

2.0 Updated HDOH TEQ Dioxin Soil Action Levels

The updated Toxicity Equivalent (TEQ) dioxin soil action levels are as follows:

2010 HDOH TEQ Dioxin Soil Action Levels	
≤240 ng/kg	No significant risk to human health under unrestricted (e.g., residential) land use.
≤1,500 ng/kg	No significant risk to human health under commercial/industrial land use (also used as the construction/trench worker action level).

As discussed in Attachments 1-3, the development and justification of the updated soil action levels are based on the following multiple lines of evidence:

- Predominance of less-toxic forms of dioxins in soil (tetrachlorodibenzo-*p*-dioxin or TCDD, generally <<1%);
- Reduced relative bioavailability of dioxins in soil in comparison to published toxicity studies (assumed 60%);
- Uncertainty in published and proposed cancer slope factors and noncancer reference doses for TCDD;
- HDOH preference for the World Health Organization (WHO) body burden approach to evaluate potential health risks posed by chronic exposure to dioxins;
- Comparability of WHO Permissible Tolerable Intake factors for TEQ dioxins to published and draft toxicity factors for health risks published by the U.S. Environmental Protection Agency (USEPA) and other parties;
- Use of WHO Toxicity Equivalent Factors to estimate health risks from non-TCDD dioxins and furans;
- Consideration of typical dietary intake of dioxins with respect to theoretical risk posed by exposure to soil;
- Lack of a significant, added health benefit from the use of lower action levels to further reduce exposure to dioxins in soil;
- HDOH's acknowledgment that remediation of large tracts of agricultural lands where trace levels of dioxins associated with the past use of pentachlorophenol and other agricultural practices have been identified is impractical and unnecessary from a health risk perspective; and

- Recommendation to remediate localized spill areas of heavy dioxin contamination to surrounding background when feasible rather than reliance on purely risk-based action levels.

The updated action levels are used in Section 3 of this technical memorandum to redefine the soil management categories originally presented in the 2008 HEER guidance. Reduction of the soil action level for unrestricted land use from 450 ng/kg, as presented in the 2008 HEER guidance, to 240 ng/kg is not considered to be a significant change from the standpoint of potential risk to human health. HEER does not foresee the need to reopen cases closed under the 2008 action levels or require additional sampling at sites where investigations carried out under the previous guidance have already been completed. For isolated spill areas at sites where remedial action plans have not been finalized or completed, however, parties are encouraged to include *all* soil contaminated above surrounding background in remedial actions to the extent practicable (refer to Section 4).

3.0 Dioxin Soil Management Categories

Updated categories for the evaluation and management of dioxin-contaminated soil are summarized below and summarized in Table 1. These categories replace the scheme presented in the 2008 HEER guidance:

Category A Soils (natural background): Soils exhibit concentrations of TEQ dioxins <20 ng/kg, and do not appear to have been impacted by local, agricultural or industrial releases of dioxin. These soils represent "background" dioxin levels in the absence of agricultural or industrial impacts. Data on dioxins in native, un-impacted soils in Hawai‘i are limited, especially when compared to data on metals (e.g., arsenic). However, based on recent investigations overseen by HEER, the background level of TEQ dioxins in soils in Hawai‘i that have not been impacted by modern agricultural or industrial activities appears to be <20 ng/kg.

Category B Soils (minimally impacted): Soils exhibit concentrations of TEQ dioxins between 20 ng/kg and 240 ng/kg, indicating anthropogenic impacts at levels that are detectable but not considered harmful. HEER expects Category B soils to be generally associated with agricultural fields where dioxin-bearing pesticides were routinely applied in the past. Dioxin levels measured in soils in former agricultural fields range from <20 ng/kg to 100 ng/kg, and up to 200 ng/kg in some areas. HEER believes these dioxins typically represent residues of past applications of pentachlorophenol as an herbicide in sugarcane fields although burning of the fields may have also contributed. At most sites, the pentachlorophenol has degraded to below detectable levels, leaving behind a low-level residue of dioxins. For further discussion, see Section 9 in the HEER *TGM* (HDOH 2009).

Category C Soils (moderately impacted): Soils exhibit concentrations of TEQ dioxins between 240 ng/kg and 1,500 ng/kg. Category C soils are exemplified by contamination at former pesticide storage and mixing areas that included the use of pentachlorophenol and similar pesticides. Soils associated with burn pits or impacted by incinerator ash are also likely to fall into this category.

Category D Soils (heavily impacted): Soils have dioxin concentrations exceeding 1,500 ng/kg. Category D soils are exemplified by heavy contamination at former pesticide mixing areas associated with the use of pentachlorophenol. Concentrations of TEQ dioxins in soil between 10,000 ng/kg and 100,000 ng/kg are not uncommon, with concentrations up to 1,000,000 ng/kg reported at some facilities (>500 mg/kg total dioxins/furans). Pentachlorophenol is typically present at significantly lower concentrations or even below laboratory reporting limits.

4.0 Management of Dioxin-Contaminated Soils

HEER offers the following observations and recommendations for the short-term and long-term management of dioxin-contaminated soil, based on experience with past dioxin response sites.

4.1 Site Characterization

Long-term management of soil with greater than 240 ng/kg TEQ dioxins (or other, approved action levels) will be required at all sites where treatment or removal of this soil is not carried out. Investigation of the site should characterize the lateral and vertical extent of soil contaminated above this action level to the extent practicable, regardless of the current land use of the site, unless otherwise approved by HEER. This includes the need to identify and include Category B soils at commercial/industrial sites in an *Environmental Hazard Management Plan* prepared for that property, even though these soils do no pose a significant health risk to site workers. This will help ensure that the soil is not inadvertently excavated and reused at a more sensitive, offsite location during future subsurface or redevelopment work (e.g., reuse as fill material for a school yard). Potential disposal and management requirements under State and USEPA hazardous waste regulations must also be evaluated and documented.

4.2 Remedial Options

Remedial options typically considered at dioxin response sites are, in order of descending preference, **treatment**, **off-site disposal**, **engineered controls** and **institutional controls**.[1] As discussed in Section 4.3, the added cost of long-term management and potential liability for inappropriate exposure or reuse of the soil in the future should be taken into consideration in the selection of a final remedy.

4.2.1 Treatment

In situ or *ex situ* thermal treatment is considered to be the state-of-the-art method for the destruction of dioxins in contaminated soils, although numerous other remedial options have also

[1] State regulations list remedial options for contaminated soils in the following order of descending preference, to the extent practicable: (a) reuse or recycling; (b) destruction or detoxification; (c) separation, concentration, or volume reduction, followed by reuse, recycling, destruction or detoxification of the residue; (d) immobilization; (e) on-site or off-site disposal, isolation, or containment at an engineered facility in accordance with applicable requirements; and (f) institutional controls or long term monitoring [Hawai‘i Administrative Rules 11-451-8(c)(2)].

been proposed (e.g., Haglund 2007, Kulkarni 2008). The number of companies and facilities that offer thermal treatment is very limited, however, and the cost of thermal treatment can far exceed the short-term costs for other remedial options. For example, the cost to excavate and ship 5,000+ tons of dioxin-contaminated soil from a former pesticide mixing area (PMA) site on O‘ahu to treatment facilities in North America was recently estimated to exceed $3,000/ton. *In situ* thermal treatment of the soil was estimated to approach $1,000/ton. The initial cost to construct an engineered cap over the soil is approximately one-tenth of the total cost for *in situ* treatment.

Treatment of Category D, dioxin-contaminated soil will, in many cases, only be feasible as part of large-scale redevelopment projects that can generate adequate capital funds for this option, e.g., by amortization of cleanup cost, concessions on the land purchase price and/or marginal increases in sales prices of new homes. Capping of the soil at currently unused sites will be necessary in many cases (see *Engineered Controls*). If so, the soil should be capped in an area that will remain accessible for possible removal or *in situ* treatment should cheaper, on-island alternatives come become available in the future (e.g., under parking lots or other open areas, versus under a permanent building). This will allow the property owner and/or responsible party to access and treat the soil in order if they so desire, in order to remove liabilities and depreciation in property value posed by continued long-term management of the soil.

4.2.2 Disposal

Disposal of dioxin-contaminated soil in a permitted landfill is a potentially cost-effective option for remediation of isolated spill areas. As discussed in Section 4.4, however, dioxin-contaminated soil must be evaluated for potential Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous waste restrictions prior to disposal. If the soil is determined to be a hazardous waste, then it cannot be disposed of in a local landfill. If the soil is determined to not be a hazardous waste, then it may be disposed in a municipal landfill or construction & demolition debris landfill, contingent upon acceptance by the landfill operator. Municipal landfills may also be reluctant to accept heavily contaminated soil for disposal due to worker exposure and future liability concerns.

4.2.3 Engineered Controls

The risk posed by dioxin-contaminated soils can be addressed via on-site construction of a physical barrier (a “cap”) to protect the public and the environment from exposure. Containment-based remedies require long-term maintenance and monitoring to ensure the continued integrity of the cap and effectiveness of the remedy. Protocols for long-term management should be included in an *Environmental Hazard Management Plan* prepared for the site, as described in the HEER *Technical Guidance Manual* (HDOH 2009). Specific cap designs will vary depending on site-specific conditions and redevelopment plans.

A clearly identifiable marker barrier (e.g., orange plastic construction fencing) is generally placed between the contaminated soil and the overlying clean fill material. HEER also recommends that a grid of durable, detectable (metallic) and labeled underground warning tape

be placed on top of dioxin-contaminated soils as part of a long-term cap. Similar to the procedures used when burying natural gas pipelines, warning messages and contact information should be printed on the warning tape, for example: "**CAUTION – STOP DIGGING! DIOXIN-CONTAMINATED SOIL BELOW! CONTACT _____ at _____ FOR FURTHER INFORMATION**." The cost for this type of customized warning tape is approximately $200 per 1,000-foot roll; and is available from Safety Systems of Hawai‘i among other vendors.

As discussed above, it is preferable that heavily contaminated soil be capped in an area that will allow access for removal or *in situ* treatment in the future should cheaper, on-island alternatives become available. For additional information, consult the HEER *Technical Guidance Manual* (HEER 2009) and contact HEER staff. HEER plans to update its capping guidance in the near future based on experience gained from current studies.

4.2.4 Institutional controls

Dioxin-contaminated sites may be addressed by the use of institutional controls (ICs) to protect the public and the environment from exposure. For example, use of the property for residences, schools, day care, medical facilities or other sensitive purposes can be restricted in a formal covenant to the deed. Excavation in contaminated areas or reuse of soil from the site without the express consent of HDOH can also be prohibited. Additional information on institutional controls is provided in the HEER *Technical Guidance Manual* (HEER 2009).

4.3 Management of Category C Soils at Commercial/Industrial Sites

Category C soils are not considered to pose health risks under commercial/industrial land use but could pose potential risks under residential or other sensitive land uses. Long-term management of these soils is therefore required if left in place at a commercial/industrial site. Specific issues associated with the long-term management of Category C soils are discussed below.

4.3.1 Include Institutional Controls in EHMPs

Category C soils can be managed in place at commercial/industrial sites with minimal engineering controls provided that care is taken to prevent offsite movement of the soils via windblown dust, storm water runoff and other processes. As discussed in above, however, a potential exists for the inadvertent excavation of these soils, transport to unrestricted/residential land use areas (e.g., schools or residential areas) and reuse of these soils as fill material in areas where the soil could then pose a health risk. Institutional controls should, therefore, be included as one part of the *Environmental Hazard Management Plan* prepared for a commercial/industrial site where Category C soils are left in place.

4.3.2 Include Soil Above Surrounding Background in Remediation of Category D Soils

From a purely risk assessment standpoint, redevelopment of a heavily contaminated site for commercial/industrial purposes only requires remediation of Category D soils, although Category C soils must be managed properly. The boundary between localized "hot spots" of

heavily contaminated soil and the surrounding soils is typically very sharp, however, with a rapid drop off in contaminant concentrations to background (i.e., <20 ng/kg for non-agricultural soils and 20-100 ng/kg for former field areas). The additional area and volume of marginally impacted soil that lies at the margins of the heavily contaminated area will, in many instances, be relatively minor. The inclusion of *all* soil contaminated by the release above the surrounding background in remediation actions is therefore recommended, to the extent practicable, even though the marginally contaminated soil may not pose a significant risk to future users of the site under commercial/industrial land use.

At sites where Category D soils are to be addressed via treatment, disposal, or containment, HEER recommends that the same remedy be used for the full area and volume of soil that is clearly above background for the surrounding area to the extent practicable, for the following reasons:

1. **The added cost of addressing less contaminated soils along with heavily contaminated soils is anticipated to be relatively small.** As described above, sites characterized by isolated spill areas of highly-contaminated soils are typically sharply defined. An expansion of the boundary of the remediation area to include Category C and even Category B soils that are clearly above the surrounding background may significantly increase the long-term reliability of the remedy without an excessive increase in short-term remediation cost and decrease the cost and liability associated with long-term management of the site.

2. **Engineered and institutional controls can be more expensive than initially estimated.** Low up-front capital costs for on-site, long-term management of moderately contaminated soil can mask costs associated with long-term maintenance and oversight of controls as well as future liability associated with inappropriate onsite or offsite reuse of inadvertently exposed soil. This underestimation of the total life-cycle cost can lead to the selection of a remedy that either (1) fails due to inadequately-funded implementation, or (2) ends up exceeding the costs of other remedial options that had been deemed too expensive during the initial evaluation. Full treatment of contaminated soil will also increase the future resale and development value of the property.

Short and long-term remedial actions for sites where Category D soils are identified should be discussed with the HEER office on a site-by-site basis.

4.4 Hazardous Waste Considerations

Hazardous waste issues associated with the long-term management of dioxin-contaminated soil should be discussed with HEER staff on a site-by-site basis and incorporated into an *Environmental Hazard Management Plan* prepared for the site. The burden and feasibility of long-term management of dioxin-contaminated soil at a site can vary greatly depending on the regulatory designation of the soil as a hazardous or nonhazardous waste under RCRA Subtitle C. Dioxin-contaminated soil that is designated as a hazardous waste (see below) cannot be disposed of in any of the permitted, municipal waste landfill or construction and demolition debris landfill

in Hawai‘i. The soil must instead be disposed of at an out-of-state hazardous waste facility, typically at a significantly greater cost and administrative burden. This issue should be considered in selection of a final remedy for a site.

A preliminary Land Disposal Restriction (LDR) determination under RCRA Subtitle C should be made for dioxin-contaminated soils identified in the course of a site investigation (e.g., USEPA 2005). Dioxins associated with the release of a listed waste under RCRA Subtitle C are considered to be hazardous waste at the point that the soil is excavated or “generated.” An example is dioxin-contaminated soil at a wood treatment facility that is associated with the release of pentachlorophenol. If the soil is not excavated then it is not considered to be "generated" and is therefore not subject to an LDR determination. If excavated, the soil is considered to be contaminated with a prohibited waste and must be managed in accordance with LDR restrictions.

Pesticide-contaminated soil associated with past agricultural practices is *exempt* from designation as a hazardous waste, provided that the pesticide was used as intended and containers were cleaned and disposed of in accordance with label information available at that time (40 CFR §262.70 Subpart G: Farmers; USEPA 1986, 2006). This exemption applies to both field areas and pesticide mixing areas. Dioxin-containing soil associated with these types of agricultural sites does not fall under RCRA Subtitle C regulation unless it otherwise fails a hazardous waste characteristics test for other contaminants in the soil (e.g., ignitability, corrosivity, reactivity or exceedence of Toxic Characteristics Leaching Procedure (TCLP) regulatory levels; 40 CFR §261). Note that this exemption will not generally apply to illegal dump sites where disposal of bulk pesticides (vs cleaned containers) occurred. Applicability of this exclusion should be clearly discussed in a site-specific *Environmental Hazard Management Plan* for dioxin-contaminated soil that is capped in place for long-term management, with reference made to the above documents (e.g., 40 CFR §262.70 Subpart G: Farmers; USEPA 1986, 2006) as well as other pertinent information (e.g., past use of subject site for agricultural purposes). Simple reference of this technical memorandum will not be adequate.

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Table 1. Summary of TEQ Dioxin Soil Action Levels and associated soil management categories.

Soil Management Category	Action
Category A (≤20 ng/kg)	**Background.** Within range of expected background conditions in non-agricultural and non-industrial areas. No further action required and no restrictions on land use.
Category B (>20 but ≤240 ng/kg)	**Minimally Impacted.** Exceeds expected background conditions but within range anticipated for agricultural fields. Potential health risks considered to be insignificant. Include Category B soil in remedial actions for more heavily contaminated spill areas as practicable in order to reduce exposure (e.g., outer margins of pesticide mixing areas). Offsite reuse of soil for fill material or as final cover on a decommissioned landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions. For existing homes, consider measures to reduce daily exposure to soil (e.g., maintain lawn cover, ensure good hygiene, thoroughly wash homegrown produce, etc.). For new developments on large, former field areas, notify future homeowners of elevated levels of dioxin on the property (e.g., include in information provided to home buyers during property transactions).
Category C (>240 but ≤1,500 ng/kg)	**Moderately Impacted.** Typical of incinerator ash, burn pits, wood treatment operations that used pentachlorophenol (PCP), and the margins of heavily impacted, pesticide mixing areas associated with former sugarcane operations that used PCP. Restriction to commercial/industrial land use required with a formal restriction to the deed against sensitive land uses (e.g., residential, schools, day care, medical facilities, etc.) in the absence of significant institutional and engineered controls and HDOH approval. Use of soil as soil as intermediate (e.g., temporarily inactive portions) or interim (e.g., daily or weekly) cover at a regulated landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions. Preparation of a site-specific, *Environmental Hazard Management Plan* (EHMP) required if soil left on site for long-term management. Removal of isolated spill areas recommended when practicable in order to minimize future management and liability concerns. This includes controls to ensure no off-site dispersion (e.g., dust or surface runoff) or inadvertent excavation and reuse at properties with sensitive land uses.
Category D (>1,500 ng/kg)	**Heavily Impacted.** Typical of former pesticide mixing areas that used PCP (e.g., sugarcane operations). Remedial actions required under any land use scenario in order to reduce potential exposure. Potentially adverse health risks under both sensitive and commercial/industrial land use scenarios in the absence of significant institutional and/or engineered controls. Disposal of soil at a regulated landfill is acceptable, pending agreement by the landfill and barring hazardous waste restrictions.

ATTACHMENT 1

SUPPLEMENTAL INFORMATION ON DEVELOPMENT AND JUSTIFICATION OF UPDATED TEQ DIOXIN ACTION LEVELS

1.0 Background Information on Dioxins

Dioxins are a group of chlorinated organic molecules whose specific members, referred to as "congeners," share similar chemical structures and mechanisms of toxicity (WHO 2001, 2002, 2006). Potential sources of dioxins in Hawai'i include deposition of airborne dioxins originating from off-site sources, application of dioxin-bearing pesticides to agricultural fields, spills of concentrated dioxin-bearing pesticides (e.g., at pesticide mixing areas) and combustion of organic materials in the present of chlorine (e.g., incinerators, burn pits, fire training pits, building fires, forest fires, etc.). In agricultural areas, the primary source of dioxins in soils is believed to be associated with manufacturing impurities in certain chlorinated pesticides, such as 2,4,5-T and, in particular, pentachlorophenol. Data on the concentration of dioxins in soils outside of agricultural areas area are limited. HEER is currently conducting research to collect additional soil data in various types of settings throughout the state.

The risk to human health posed by exposure to dioxins is evaluated based on 17 specific dioxin congeners: 7 polychlorinated dibenzo-p-dioxins (PCDDs) and 10 polychlorinated dibenzofurans (PCDFs). The majority of the published literature on dioxin toxicity is limited to 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD, USEPA 2010), considered to be the most toxic of the 17 congeners studied. The World Health Organization (WHO) assigns toxicity values, referred to as "Toxicity Equivalence Factors (TEFs)," to specific congeners relative to the toxicity of TCDD (WHO 2006). The reported concentration of each congener in a sample is multiplied by its respective TEF to calculate a "Toxicity Equivalent (TEQ)" concentration. The TEQ concentrations for individual congeners are then added together to obtain a total TEQ concentration for the sample. The U.S. Environmental Protection Agency (USEPA) and HEER office recommend the use of WHO's TEFs to calculate TEQ dioxin levels for use in human health risk assessments or for comparison to risk-based action levels (USEPA 2009a, HDOH 2009a).

2.0 2008 HEER Dioxin Guidance

Soil action levels published by the HEER office in 2006 and 2008 were based on potential excess cancer risk posed by long-term, direct exposure to dioxins in soil (HDOH 2008a,b). Noncancer health risks were not specifically considered but were presumed to be less significant than cancer risks. The soil action levels were based on the USEPA Regional Screening Levels (RSLs; USEPA 2009b), adjusted to a target excess cancer risk of 10^{-4} (i.e., one in ten thousand; see Attachment 2). Action levels based on a more conservative cancer slope factor published by the Minnesota Department of Health were also developed.

Cancer slope factors published by USEPA and other agencies for dioxins are not fully accepted by the toxicology community and considered by others to be excessively conservative (e.g., Cole

et. al 2003, Hayes and Aylward 2003, NAS 2006). Confidence in the slope factors is considered to be low (see Section 4.4). A target excess cancer risk of 10^{-4} was therefore deemed appropriate (refer to Attachment 2).

The 2008 HEER action levels were used to define three categories of soil each for unrestricted (e.g., "residential") and commercial/industrial land use scenarios. Specific guidance was then presented for the management of soil in each category. The final action levels and soil categories were defined as follows:

2008 HEER TEQ Dioxin Soil Categories		
Category	**Unrestricted/Residential Land Use [1]**	**Commercial/Industrial Land Use**
Category 1 [2]	<42 ng/kg	<170 ng/kg
Category 2 [3]	42 to ≤450 ng/kg	170 to ≤1,800 ng/kg
Category 3 [3]	>450 ng/kg	>1,800 ng/kg

Notes:
1. Includes schools, day care centers, medical facilities and other related sensitive land uses.
2. Action levels based on Minnesota Department of Health cancer slope factors.
3. Action levels based on California EPA cancer slope factors.

No further action was recommended for Category 1 soils under the noted land use. Efforts to minimize exposure (e.g., lawn maintenance) were recommended for Category 2 soils if the soil was associated with widespread, trace-level dioxin contamination in former agricultural fields. Removal or capping of small isolated "hot spots" of Category 2 soils to surrounding, background levels was recommended when feasible in order to minimize exposure, but not considered necessary from a purely health-risk standpoint. Removal or capping of Category 3 soils was recommended. Long-term management of soil at commercial/industrial sites that exceeded the upper action level for unrestricted/residential land use of 450 ng/kg TEQ dioxins was recommended to ensure that the soil was not inappropriately excavated and reused offsite in the future.

3.0 Basis of 2010 Updates to Dioxin Soil Action Levels

This technical memorandum updates the 2008 soil action levels for TEQ dioxin to take into account World Health Organization (WHO) Permissible Tolerable Intake factors for potential cancer and noncancer health risks. Exposure assumptions and model parameters used to develop the earlier action levels are otherwise identical. HDOH considers the WHO factors to be more defensible (e.g., lowest uncertainty factor) and appropriate for use in Hawai‘i in comparison to alternative factors, including cancer slope factors published by USEPA and other agencies, as well as noncancer toxicity factors published by the US Agency for Toxic Substances and Disease Registry (ATSDR) and more recently by USEPA.

A discussion of alternative toxicity factors is provided for comparison. The final, updated soil action levels fall within the range of action levels that could be developed by use of the alternative toxicity factors. A detailed discussion of model equations and assumptions used to generate the action levels is provided in Attachment 2.

3.1 Use of WHO PMTI Factors to Develop Soil Action Levels

This update incorporates the use of WHO Permissible Tolerable Monthly Intake (PTMI) factors (WHO 2001, 2002) to develop alternative soil action levels for TEQ dioxins. The WHO PTMI is intended to limit the long-term, body burden of TEQ dioxins to levels that are not believed to be associated with significant cancer or noncancer health risks. WHO concluded that body burden is a more appropriate measure of potential health risks than is a traditional approach based on daily dose, although the two parameters are closely related.

In 1998 WHO published a Tolerable *Daily* Intake (TDI) range for bioavailable TEQ dioxins of 1 to 4 picograms per kilogram of body weight per day (1-4 pg/kg-day; WHO 1998). The ATSDR published an identical range of TEQ dioxin "Minimal Risk Levels" in the same year (ATSDR 1998, 2008). WHO subsequently published an updated, Permissible *Monthly* Tolerable Intake (PTMI) factor range for TEQ Dioxins of 40 to 100 pg/kg-month, after further review of available studies (WHO 2001, 2002). The PTMI of 100 pg/kg-month is based on a No Observed Effects Level (NOEL, power model) for an equivalent human monthly intake (EHMI) of 330 pg/kg per month, adjusted by safety factor of 3.2 to account for inter-individual differences in toxicokinetics among humans (rounded downward to a value of 100). The PTMI of 40 pg/kg-month is based on a Lowest Observed Effects Level (LOEL, linear model) for an equivalent human monthly intake (EHMI) of 423 pg/kg per month, adjusted by safety factor of approximately 9.6 to account for both use of a LOEL (vs NOEL) and inter-individual differences in toxicokinetics (rounded downward to a value of 40).

The WHO PTMI levels were divided by a factor of 30.4 days/month in order to generate an equivalent, tolerable *daily* intake range of 1.3 pg/kg-day to 3.3 pg/kg-day and allow their use in risk-based models for development soil action levels (see Attachment 2). WHO presents monthly, rather than daily, intake ranges to emphasize that the PMTI range is applicable to long-term exposure only, and is well below levels that could pose immediate health effects. As stated in the WHO document:

> "The PTMI is not a limit of toxicity and does not represent a boundary between safe intake and intake associated with a significant increase in body burden or risk. Long-term intakes slightly above the (upper range of the) PTMI would not necessarily result in adverse health effects but would erode the safety factor built into the calculations of the PTMI."

The more rigorous, NOEL-based PMTI of 100 pg/kg-month (3.3 pg/kg-day) was selected for calculation of final dioxin soil action levels. The adjusted factor was incorporated into the USEPA Regional Screening Level (RSL) models for noncancer health risks. This generated a soil action level 240 ng/kg for unrestricted (e.g., residential) land use and 2,800 ng/kg for commercial/industrial land use (see Attachment 2). The calculated action level for unrestricted land use was retained for use in this guidance (refer to Sections 2 and 3 in main text). As discussed in the following section, the commercial/industrial action level was reduced by a factor of 1.9 to 1,500 ng/kg in order to limit theoretical exposure to dioxins in soil to approximately

50% of the estimated dietary intake for adults (refer also to Attachment 2). The HEER office believes that the final soil action levels are appropriate and practicable for screening of dioxin-contaminated sites in Hawai‘i.

Note that the WHO PTMI assumes a 50% bioavailability of TEQ dioxins in food (see footnote to Table 14, WHO 2002). This is similar to estimates of average dioxin bioavailability in soil, as recently reviewed by the Washington Department of the Environment (Washington DOE 2007a,b). In the absence of site-specific data, further adjustment of the WHO PTMI and soil action levels presented in the main text of this guidance based on assumed dioxin bioavailability in soil is not recommended.

3.2 Comparison of Dietary Exposure

A comparison of WHO PTMI factors to typical dietary exposure to TEQ dioxins is useful in order to put potential exposure to dioxins in soil at the action levels noted in perspective. The WHO estimates the mean, dietary intake of TEQ dioxins to be 15 to 160 pg/kg-month at the 90th percentile of mean lifetime exposure (WHO 2002). This equates to a daily dietary exposure of 0.5 to 5 pg/kg-day, or up to 75 pg/day for a 15 kg child and 350 pg/day for a 70 kg adult (default body weights typically used in human health risk assessments).

As summarized in Attachment 3, dietary intake of TEQ dioxins for Pacific-Asian diets heavy in fish and vegetables is estimated to range from 66 pg/day for children (4.4 pg/kg-day for a 15 kg child) and to 102 pg/day adults (1.5 pg/kg-day for a 70 kg adult), respectively. Food of animal origin is estimated to contribute to approximately 80% of overall human exposure to dioxins (USEPA 2010). Other studies have indicated a minimal contribution of TEQ dioxins from soil with respect to dietary intake (e.g., Kimbrough et al 2010).

For comparison, the HDOH soil action level for unrestricted (e.g., residential) land use of 240 ng/kg equates to a theoretical, TEQ dioxin average daily dose of approximately 23 pg/day for a 15 kg child and 12 pg/day for a 70 kg adult (assuming a soil ingestion rate of 200 mg/day for children and 100 mg/day for adults, a bioavailability of 50% and the additional exposure factors noted in Attachment 2). This represents approximately 35% of the estimated dietary exposure for a 15 kg child (USEPA default body weight for children, as averaged for ages 1-6; refer to Attachment 2).

The HDOH soil action level for commercial/industrial land use of 2,800 ng/kg equates to a theoretical, TEQ dioxin average daily dose of approximately 96 pg/day for a 70 kg adult. This is approximately equal to the estimated dietary exposure of adults to TEQ dioxins. As an added measure of safety, however, HEER decided to reduce the soil action level to 1,500 ng/kg in order to limit the theoretical exposure to dioxins in soil to 50 pg/day or approximately 50% of the estimated dietary exposure (added safety factor of 1.9; refer to Attachment 2). Actual exposure to dioxins in soil for both children and adults is likely to be much lower than exposure predicted by the models due to the conservative nature of the exposure factors assumed in the models.

3.3 Comparison to 2009 USEPA RSLs Adjusted for Relative Bioavailability

The 2009 USEPA Regional Screening Levels (RSLs; USEPA 2009b) do not consider the relative bioavailability of dioxins in soil (i.e., relative bioavailability of dioxins in soil in comparison to bioavailability of dioxins in laboratory-based studies). Guidance published by the Washington Department of Ecology (DOE) was used to adjust the USEPA RSLs for comparison to WHO-based action levels (Washington DOE 2007a,b; see Attachment 2). Washington DOE presents the following rationale for use of a gastrointestinal absorption adjustment (bioavailability) factor in the calculation of soil screening levels for cancer risk concerns:

- Available evidence suggests that soil-bound dioxins/furans are less bioavailable than dioxins/furans used to assess the health risks from bioassays, epidemiological studies or studies used to assess the toxicity of dioxins/furans in foods and drinking water.

- Although there is uncertainty in assigning congener-specific bioavailability estimates, the available evidence suggests that the higher-chlorinated dioxin/furan congeners (hexa-, hepta-, octa-) are less well absorbed and less bioavailable than the lower-chlorinated congeners (tetra- and penta-).

- Within a range of uncertainty and variability, available evidence suggests that congener-specific differences in bioavailability should be considered when evaluating the toxicity and assessing the risks for mixtures of dioxins/furans.

Based on a review of published studies, Washington DOE (2007a) recommended a default relative bioavailability 0.7 for the tetra- and penta-chlorinated dioxin/furan congeners, and 0.4 for the less available (but usually more abundant) hexa-, hepta-, and octa-chlorinated congeners (i.e., bioavailability in soil *relative* to the bioavailability in the food used in the animal studies, estimated to be between 80% ad 90%; USEPA 2010). Final guidance published by Washington DOE recommended a weighted, relative bioavailability or gastrointestinal absorption fraction for TEQ dioxins of 0.6, based on typical mixtures of dioxin/furan congeners identified in soil (Washington DOE 2007b). This was consistent with the default, relative bioavailability of TEQ dioxins in soil recommended by a majority of other State and international agency guidance reviewed by Washington DOE. Assuming a bioavailability of dioxins in the food used in animal studies of 80% to 90%, this equates to an ultimate bioavailability of dioxins in soil of approximately 50%, similar to the bioavailability of dioxins assumed in the WHO PMTI factors (refer to Section 3.1).

An internal HEER review of dioxin/furan congener soil data from former sugarcane operations in Hawai‘i indicated an average mixture of 2% tetra- and penta- dioxin/furan congeners and 98% hexa-, hepta-, and octa- congeners, with a worst-case instance of 20% tetra- and penta-dioxin/furan congeners and 80% hexa-, hepta-, and octa- congeners. Applying Washington DOE’s approachTo dioxin data from former sugarcane fields and pesticide mixing area in Hawai‘i, HEER calculated TEQ dioxin bioavailability factors from 0.41 (average) to 0.46

(worst-case). This suggests that the default, relative bioavailability of 0.6 published by the Washington DOE is adequately for modification of the USEPA RSLs.

Modification of the 2009 USEPA RSLs for relative bioavailability applies only to the incidental ingestion portion of the soil action level models. As indicated in Attachment 2, a separate absorption factor is used for dermal exposure. Relative bioavailability is not considered for inhalation of particulates. The latter two exposure pathways are relatively minor in comparison to incidental ingestion. Adjustment of the incidental ingestion portion of the soil model to reflect a relative bioavailability 0.6 and use of a target, excess cancer risk of 10^{-4} yields modified RSLs of 650 ng/kg and 2,400 ng/kg for unrestricted/residential land use and commercial/industrial land use respectively.

The updated TEQ dioxin soil action level for unrestricted land use presented in the main text (240 ng/kg) is more conservative than the USEPA RSL adjusted for relative bioavailability and a target excess cancer risk of 10^{-4}. The updated action level for commercial/industrial land use (1,500 ng/kg) is also lower than the adjusted RSL.

3.4 Comparison to 2009 USEPA TEQ Dioxin PRGs (Draft)

USEPA recently published a draft document entitled *Recommended Interim Preliminary Remediation Goals (PRGs) for Dioxin in Soil at CERCLA and RCRA Sites* (USEPA 2009a). Although the final PRGs are similar to the updated HDOH soil action levels presented above, the HEER office considers the approach presented in this technical memorandum to be more applicable for use in Hawai‘i.

The USEPA draft guidance proposes to retract screening levels for TEQ dioxins published in 1998 for use at CERCLA and RCRA sites, including the often cited screening levels of 1 µg/kg TEQ dioxins for residential soils and 5 to 20 µg/kg for commercial/industrial soils (USEPA 1998). The HEER office had previously discounted use of these action levels in Hawai‘i, after concluding that they may not be adequately protective of human health in some circumstances.

As an alternative, the draft USEPA document proposes use of the 1998 ATSDR Minimal Risk Level (MRL) to develop TEQ dioxin soil screening levels or “Preliminary Remediation Goals” (“PRGs”). The ATSDR document presents an MRL range for TEQ dioxins of 1 to 4 pg per kilogram bodyweight per day (pg/kg-day), identical to guidance published by the World Health Organization the same year (see above). This equates to an exposure of 15 to 60 pg/day for a 15 kg child (average child bodyweight used in noncancer risk assessments) or 60 to 280 pg/day TEQ dioxins for a 70kg adult (lifetime average bodyweight used in cancer risk assessments). Exposures below these levels are assumed to not pose a significant health risk. Note that the upper limit of the ATSDR MRL range is slightly less conservative than the range proposed by WHO (WHO 2002; see above).

Using the models and exposure assumptions presented in the draft guidance with the ATSDR MRL range for TEQ dioxins of 1 to 4 pg/kg-day yields a soil screening level range of 72 to 290 ng/kg for residential land use and 850 to 3,400 ng/kg for commercial/industrial land use. This is

comparable to the range of screening levels generated by use of the WHO PTMI guidance as described above and in the main text of this document. The draft USEPA document proposed a TEQ dioxin "Preliminary Remediation Goal" (PRG) of 72 ng/kg for residential soil and 950 ng/kg for commercial/industrial, based on use of the low end of the ATSDR MRL range, or 1 pg/kg-day. These action levels do not consider the relative bioavailability of dioxins in soil (see Section 3.2). Adjusting for a relative bioavailability of 0.6 would yield correlative PRGs of 120 ng/kg and 1,600 ng/kg, respectively. While the HEER office does not disagree that soils with concentrations of TEQ dioxins below the proposed PRGs levels do not pose a significant health risk, HEER feels that the PRGs are too conservative to be useful for initial screening purposes in Hawai'i. As discussed above, the HEER office also prefers use of the more recent, WHO PTMI guidance over the 1998 ATSDR guidance.

The draft USEPA document also notes that the proposed PRGs fall within the range of screening levels that would be generated using cancer slope factors published by the USEPA in the 1980s and a risk range of 10^{-6} to 10^{-4} (e.g., 4.5 to 450 ng/kg for residential soil and 18 to 1,800 ng/kg; based on the current USEPA RSLs; USEPA 2009b). Note that identical, noncancer screening levels for TEQ dioxins were calculated as part of the 2009 USEPA RSL guidance but ultimately not selected as the final RSLs, since the screening level for cancer concerns assumes a target risk of 10^{-6}.

As discussed below, HEER prefers to focus on remediation of *localized* areas of dioxin-contaminated soil (e.g., pesticide mixing areas) to meet the surrounding area background concentrations *as practicable* on a site-by-site basis, rather than deferring to a purely risk-based soil action level. Remediation of minimally impacted soils in large, former agricultural fields to natural background concentrations (e.g., <20 ng/kg) is considered to be impracticable and, from the standpoint of risk and added health benefit, unnecessary. This is supported by consideration of dietary intake of dioxins and furans, which is estimated to exceed the hypothetical intake associated with long-term exposure to soils with concentrations of TEQ dioxins at or below the updated action levels.

3.5 Comparison to 2010 USEPA TCDD Toxicity Review (Draft)

USEPA recently released a draft review of published literature on the health effects of tetrachlordibenzonedioxin (TCDD) and related compounds (USEPA 2010). USEPA focused on two studies of human exposure to TCDD to develop a draft, noncancer reference dose. A Lowest Observed Adverse Effects Level (LOAEL) of 20 pg/kg-day exposure to TCDD was ultimately selected for development of an oral reference dose (RfD).

The selected LOAEL of 20 pg/kg-day is well above the WHO Permissible Tolerable Intake of 3.3 pg/kg-day used to develop soil action levels in this technical memorandum (refer to Section 3.2). In the draft document, however, USEPA reduces the LOAEL by an uncertainty factor of ten due to the lack of a No Observed Adverse Effects Level (NOAEL) for TCDD. The LOAEL is further reduced by a factor of three to account for human inter-individual variability, for a total uncertainty factor of thirty. The document then proposes a final, draft, TCDD reference dose of 0.7 pg/kg-day.

The selected WHO tolerable intake factor of 3.3 pg/kg-day exceeds the final RfD of 0.7 pg-kg-day selected by USEPA in it's draft document. The WHO factor falls near the low end of the RfD and LOAEL low-risk range of TCDD exposure identified in the draft review, however (0.70 pg/kg-day to 20 pg/kg-day). Adjustment of the draft USEPA RfD to take into account a reduced relative bioavailability of dioxins in soil would further reduce the difference between action levels derived by either method. For example, use of the draft RfD in the USEPA RSL models would yield soil action levels of approximately 50 ng/kg and 600 ng/kg for residential and commercial/industrial land use, respectively (refer to Attachment 2). Adjustment for a relative bioavailability of dioxins in soil of 0.6 (see Section 3.2) yields action levels of 85 ng/kg and 1,000 ng/kg, respectively.

The draft USEPA document also presents an oral slope factor range of 1.1×10^5 (mg/kg-day)$^{-1}$ to 1.6×10^6 (mg/kg-day)$^{-1}$ for possible use in cancer risk assessments, depending on the selected target risk. As discussed above, the 2009 USEPA RSLs for 2,3,7,8 dioxins is based on a slope factor of 1.3×10^5 (mg/kg-day)$^{-1}$. Use of a more conservative slope factor would (e.g., 7.8×10^5 (mg/kg-day)$^{-1}$ based on target risk of 10^{-4}) would reduce the RSL by a factor of approximately six. As discussed above, the cancer slope factors incorporate a relatively high degree of uncertainty and confidence in their use to develop meaningful soil action levels is low.

HDOH does not feel that use of an RfD or cancer slope factor that equates to an exposure below anticipated dietary intake to derive soil action levels is practical. At this time, and in consideration of the multiple lines of evidence summarized in Section 2 of the main text, HDOH considers the WHO PTMI factors to be the most technically supportable and appropriate values for development of direct-exposure soil action levels for use in Hawai‘i.

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ATTACHMENT 2

EQUATIONS AND ASSUMPTIONS FOR DERIVATION OF TEQ DIOXIN SOIL ACTION LEVELS

1.0 Introduction

A summary of models and assumptions used to develop for human health, direct-exposure concerns is presented below. For addition information on the models, refer to the USEPA document *Screening Levels for Chemical Contaminants* (USEPA 2009). See also Appendix 1 of the HEER *EHE Guidance* (HDOH 2008b).

2.0 TEQ Dioxin Toxicity Factors and Bioavailability

The WHO Permissible Tolerable Monthly Intake (PTMI) upper limit of 100 pg/(kg-month) is used to calculate noncancer soil action levels (WHO 2002). The PTMI is converted to a Permissible Tolerable *Daily* Intake (PTDI) level of 3.3 pg/(kg-day) for use in the noncancer equations. Although not necessarily applicable, a default Hazard Quotient of 1.0 is also assumed in the equations. A Cancer Slope Factor (CSF) of 1.3E+05 $(mg/kg\text{-}day)^{-1}$ and an Inhalation Unit Risk Factor (IURF) of 38 $(\mu g/m^3)^{-1}$ were selected for calculation of cancer-based soil action levels (USEPA 2009; CSF adopted from CalEPA). Action levels are based on a target excess cancer risk of 10^{-4}.

The equations incorporate an additional Gastrointestinal Absorption Factor (GIABS) to adjust for the bioavailability of dioxins and furans in soil, as necessary. A default GIABS for dioxins and furans of 0.6 is assumed for soils (Washington DOE 2007a,b). This is used to adjust the incidental ingestion exposure portion of the cancer-based action level (see Table 1 and Equations 1 and 3). An assumed bioavailability of 0.5 is directly incorporated into the WHO PTMI; further adjustment of bioavailability for exposure to soil is therefore not warranted (GIABSnc = 1; see Table 1 and Equations 2 and 4).

3.0 Soil Action Levels Models

Human exposure assumptions are summarized in Table 1. With the exceptions noted, parameter values in Table 1 were taken directly from the USEPA Regional Screening Level (RSL) guidance document (USEPA 2009). Parameter values for the construction/trench worker exposure scenario are discussed in more detail in Appendix 1. Tables 2 and 3 summarize equations and parameter values used to develop the RSL Particulate Emission Factor and physiochemical constants assumed in the models for TEQ dioxins.

Carcinogenic risks under unrestricted/residential exposure scenarios were calculated using the following age-adjusted factors. Definition of terms and default parameter values used in the equations are presented in Tables 1, 2, and 3.

1) Ingestion [(mg·yr)/kg·d)]:

$$IFS_{adj} = \frac{ED_c \ x \ IRS_c}{BW_C} + \frac{(ED_r - ED_c) \ x \ IRS_a}{BW_a}$$

2) Dermal Contact [(mg·yr)/kg·d)]:

$$SFS_{adj} = \frac{ED_c \ x \ AF_c \ x \ SA_c}{BW_C} + \frac{(ED_r - ED_c) \ x \ AF_a \ x \ IRS_a}{BW_a}$$

3) Inhalation [(m^3·yr)/kg·d)]:

$$InhF_{adj} = \frac{ED_c \ x \ IRA_c}{BW_C} + \frac{(ED_r - ED_c) \ x \ IRA_a}{BW_a}$$

Direct exposure equations for soil are summarized as follows:

Equation 1: Combined Exposures to Carcinogenic Contaminants in Residential Soil

$$C(mg/kg) = \frac{TR \ x \ AT_c}{EF_r \left[\left(\frac{IFS_{adj} \ xGIABSc \times CSF_o}{10^6 mg/kg} \right) + \left(\frac{SF_{adj} \ x \ ABS \ x \ CSF_o}{10^6 mg/kg} \right) + \left(\frac{InhF_{adj} \ x \ CSF_i}{PEF} \right) \right]}$$

Equation 2: Combined Exposures to Noncarcinogenic Contaminants in Residential Soil

$$C(mg/kg) = \frac{THQ \times BW_c \times AT_n}{EF_r \times ED_c \left[\left(\frac{1}{RfD_o} \times \frac{IRS_c \times GIABSnc}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_o} \times \frac{SA_c \times AF_c \ x \ ABS}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_i} \times \frac{IRA_c}{PEF} \right) \right]}$$

Equation 3: Combined Exposures to Carcinogenic Contaminants in Industrial Soil

$$C(mg/kg) = \frac{TR \times BW_a \times AT_c}{EF_o \times ED_o \left[\left(\frac{IRS_o \times GIABSc \times CSF_o}{10^6 mg/kg} \right) + \left(\frac{SA_a \times AF_a \times ABS \times CSF_o}{10^6 mg/kg} \right) + \left(\frac{IRA_a \times CSF_i}{PEF} \right) \right]}$$

Equation 4: Combined Exposures to Noncarcinogenic Contaminants in Industrial Soil

$$C(mg/kg) = \frac{THQ \times BW_a \times AT_n}{EF_o \times ED_o \left[\left(\frac{1}{RfD_o} \times \frac{IRS_o \times GIABSnc}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_o} \times \frac{SA_a \times AF_a \times ABS}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_i} \times \frac{IRA_a}{PEF} \right) \right]}$$

Equation 5: Derivation of Particulate Emission Factor (residential & occupational)

$$PEF\,(m^3/kg) \quad = \quad Q/C\ x\ \frac{3600s/h}{0.036\times(1-V)\,(U_m/U_t)^3\times F(x)}$$

The USEPA RSL models incorporate a Volatilization Factor (VF) for emission of volatile chemicals to outdoor air. Volatile chemicals are defined as having a Henry's Law Constant of >1.0E-05 (atm·m^3)/mol and a molecular weight of <200 g/mol. Dioxin/furan mixtures do not meet this definition. The VF term in the soil equations is therefore replaced with the Particulate Emission Factor (PEF) term for non-volatile chemicals.

4.0 Calculated Soil Action Levels

4.1 Unadjusted Action Levels

Based on the models and model assumptions described above and in Table 1, a TEQ dioxin soil action level of 240 ng/kg is generated for unrestricted (e.g., residential) land use. This action level was retained for use in the final guidance (refer to Table 1 in the main text). A preliminary soil action level of 2,800 ng/kg is generated for commercial/industrial land use. As described below, this action level was adjusted by an additional safety factor of 1.9 in order to minimize exposure to dioxins in soil to approximately 50% of the estimated dietary exposure.

4.2 Adjustment of Commercial/Industrial Soil Action Level

The HDOH soil action level for commercial/industrial land use of 2,800 ng/kg equates to a theoretical exposure to TEQ dioxins of approximately 96 pg/day for a 70 kg adult (refer to Section 3.2 in main text). This is approximately equal to the estimated dietary exposure of adults to TEQ dioxins. As an added measure of safety, however, HEER decided to reduce the soil action level to 1,500 ng/kg in order to limit the theoretical exposure to dioxins in soil to 50 pg/day or approximately 50% of the estimated dietary exposure (added safety factor of 1.9). Actual exposure to dioxins in soil for both children and adults is likely to be much lower than exposure predicted by the models due to the conservative nature of the exposure factors assumed in the models.

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TABLE 1. HUMAN EXPOSURE PARAMETER DEFINITIONS AND DEFAULT VALUES

Symbol	Definition (units)	Value	Units	References (see USEPA 2002 for full references)
CSFo	Cancer slope factor, oral	1.3E+05	$(mg/(kg{\cdot}d))^{-1}$	USEPA 2009 (references California EPA 2008)
CSFi	Cancer slope factor, inhaled	38	$(ug/m^3)^{-1}$	USEPA 2009 (references California EPA 2008)
RfDo	Reference dose, oral	3.3E-09	mg/(kg·d)	WHO 2002, see text
RfDi	Reference dose, inhaled	-	mg/(kg·d)	-
TRr/o	Target cancer risk – residential or occupational exposure scenario	1.0E-04	Unitless	HDOH, see text
THQ	Target hazard quotient	1.0	Unitless	See text
BWa	Body weight, adult	70	Kg	USEPA 2009
BWc	Body weight, child	15	Kg	USEPA 2009
ATc	Average time, cancer risk	25,550	D	USEPA 2009
ATn	Average time, noncancer risk	ED × 365	d	USEPA 2009
SAar	Exposed surface area, adult residential	5.7E+03	cm^2/d	USEPA 2009
SAaw	Exposed surface area, adult occupational	3.3E+03	cm^2/d	USEPA 2009
SAc	Exposed surface area, child	2.8E+03	cm^2/d	USEPA 2009
AFar	Adherence factor, adult residential	0.07	mg/cm^2	USEPA 2009
AFaw	Adherence factor, occupational	0.20	mg/cm^2	USEPA 2009
AFc	Adherence factor, child	0.20	mg/cm^2	USEPA 2009
ABS	Skin absorption, chemical specific	0.03	unitless	USEPA 2009
IRAa	Inhalation rate, adult	20	m^3/d	USEPA 2009
IRAc	Inhalation rate, child	10	m^3/d	USEPA 2009
IRSa	Soil ingestion, adult	100	mg/d	USEPA 2009
IRSc	Soil ingestion, child	200	mg/d	USEPA 2009
IRSo	Soil ingestion, occupational	50	mg/d	USEPA 2009
GIABSc	Gastrointestinal Absorption Adjustment Factor, cancer risk	0.6	unitless	Washington DOE 2007b, see text
GIABSnc	Gastrointestinal Absorption Adjustment Factor, noncancer risk	1.0	unitless	No adjustment; 50% dioxin bioavailability assumed in food (WHO 2002), see text
EFr	Exposure frequency, residential	350	d/yr	USEPA 2009
EFo	Exposure frequency, occupational	250	d/yr	USEPA 2009
EDr	Exposure duration, residential	30	yr	USEPA 2009
EDc	Exposure duration, child	6	yr	USEPA 2009
EDo	Exposure duration, occupational	25	yr	USEPA 2009
IFSadj	Ingestion factor, soil	114	(mg·yr)/(kg·d)	USEPA 2009
SFSadj	Skin contact factor, soil	361	(mg·yr)/(kg·d)	USEPA 2009
InhFadj	Inhalation factor	11	$(m^3{\cdot}yr)/(kg{\cdot}d)$	USEPA 2009
PEFres/oc	Particulate emission factor, residential/occupational exposure scenarios	1.32E+09	m^3/kg	USEPA 2009

Primary Reference: USEPA *Screening Levels for Chemical Contaminants* (USEPA 2009).

TABLE 2. PARTICULATE EMISSION FACTOR PARAMETER DEFINITIONS AND DEFAULT VALUES - RESIDENTIAL/OCCUPATIONAL SCENARIOS

Parameter	Definition	Default Value	Units
PEF *	Particulate emission factor	1.316E+09	m^3/kg
Q/C	Inverse of the mean concentration at the center of a 0.5-acre-square source	90.80	g/(m^2·s) per kg/m^3
V	Fraction of vegetative cover	0.5	unitless
Um	Mean annual windspeed	4.69	m/s
Ut	Equivalent threshold value of windspeed at 7 m	11.32	m/s
F(x)	Function dependent on Um/Ut derived using Cowherd (1985)	0.194	unitless

* Equivalent to an airborne dust concentration, in mg/m^3, of (1,000,000 mg / 1 kg) / PEF = 0.0007 mg/m^3.

TABLE 3. DEFAULT PHYSIOCHEMICAL PARAMETERS FOR TEQ DIOXINS (USEPA 2009)

Parameter	Default Value	Units
Molecular weight	3.56E+02	g/mol
Koc	2.57E+05	l/kg
Solubility in water	1.2E-04	mg/l
Henry's Law Constant	2.2E-06	(atm·m^3)/mol
Henry's Law Constant	9.0E-05	unitless

ATTACHMENT 3

ESTIMATED DIETARY INTAKE OF TEQ DIOXIN FOR PACIFIC-ASIAN DIETS

(see main text for full references)

Table 1. Estimated food consumption for a Pacific-Asian diet.

	Child (Ave 6mo-5yr)		Mean Population	
Food Group	**[1]Consumption (g/d)**	**Percent of Total**	**[1]Consumption (g/d)**	**Percent of Total**
Cereals & Cereal Products	**166**	**32%**	**364**	**43%**
Rice & Products	122	23%	303	58%
Corn and Products	17	3%	31	6%
Other Cereals and Products	27	5%	30	6%
Starch Roots and Tubers	**8**	**2%**	**19**	**4%**
Sugars and Syrups	**15**	**3%**	**24**	**5%**
Fats and Oils	**6**	**1%**	**18**	**3%**
Fish, Meat & Poultry	**95**	**18%**	**185**	**35%**
Fish and Products	57	11%	104	20%
Meat and Products	27	5%	61	12%
Poultry and Products	11	2%	20	4%
Eggs	**8**	2%	**13**	**2%**
Milk and Products	**179**	**34%**	**49**	**9%**
Whole Milk	158	30%	35	7%
Milk Products	21	4%	14	3%
Dried Beans, Nuts & Seeds	**4**	**1%**	**10**	**2%**
Vegetables	**13**	**2%**	**111**	**21%**
Green Leafy & Yellow	10	2%	31	6%
Other Vegetables	3	1%	80	15%
Fruits	**31**	**6%**	**54**	**10%**
Vitamin C-rich Fruits	4	1%	12	2%
Other Fruits	27	5%	42	8%
Total Food Consumption:	525		847	

	Consumption (kg/day)	
Combined Food Groups	**Child**	**Mean**
[1]Fuits & Vegetables	0.237	0.582
Dairy	0.179	0.049
[2]Meat	0.044	0.099
Fish	0.057	0.104
Eggs	0.008	0.013
Total:	0.525	0.847

1. Including cereals and cereal products, starch roots and tubers, dried beans, nuts and seeds.

2. Including fats, oil & poultry.

Reference: FNRI, 2003, The 6th National Nutrition Survey: Food, Philippine Department of Science and Technology, Nutrition and Research Institute, http://www.fnri.dost.gov.ph/index.php?option=content&task=view&id=1130

1. Raw as purchased (rice and cereals presumably dry weight).

Table 2. Estimated dietary intake of TEQ dioxins based on a typical Asian-Pacific diet (see also Table 1).

		[4]Child (6mo-5yr)			[5]Mean Population		
Food Group	**[1]TEQ Dioxins (pg/kg)**	**[2]Daily Dose (pg/d)**	**[3,4]Daily Intake (pg/Kg-d)**	**Percent TEQ Dioxins Contribution**	**[1]Daily Intake (pg/d)**	**[3,5]Daily Dose (pg/Kg-d)**	**Percent TEQ Dioxins Contribution**
Fruits and Vegetables	40	9.5	0.63	14%	23.3	0.33	23%
Dairy	100	17.9	1.19	27%	4.9	0.07	5%
Meat	130	5.7	0.38	9%	12.9	0.18	13%
Fish	560	31.9	2.13	48%	58.2	0.83	57%
Eggs	170	1.4	0.09	2%	2.2	0.03	2%
Total:		66	4.43	100%	102	1.45	100%

1. WHO, 2002, Safety Evaluation of Certain Food Additives and Contaminants: WHO Technical Report Series, Fifty-seventh report of the Joint FAO/WHO Expert Committee on Food Additives, WHO Technical Report Series 909, http://whqlibdoc.who.int/trs/WHO_TRS_909.pdf. Data for North America (vegetable data from Europe).

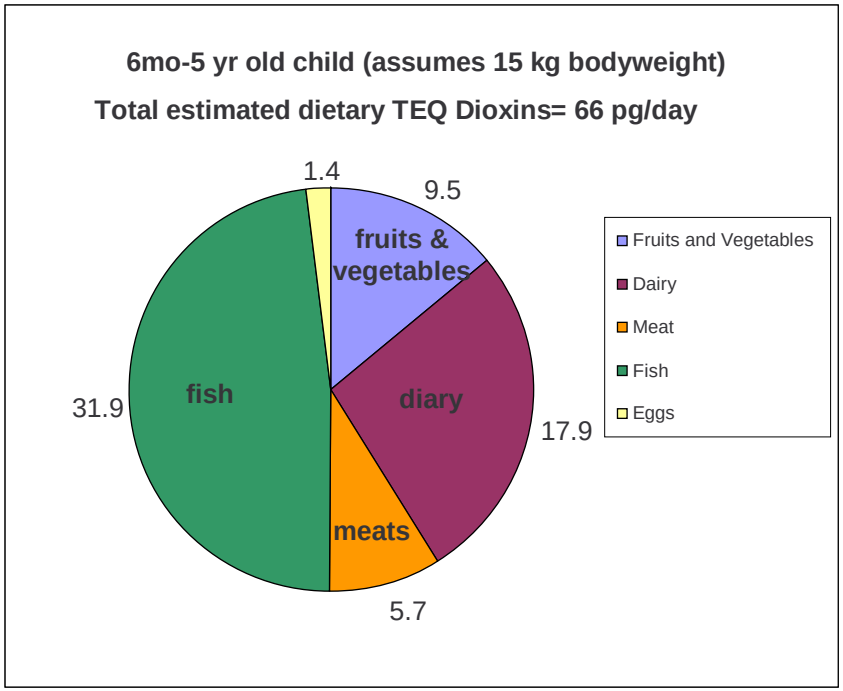
2. Calculated as: Daily Food Group Consumption (refer to Table 1; converted to kg/day) multiplied by the noted Food Group TEQ Dioxins concentration (converted to pg/kg).

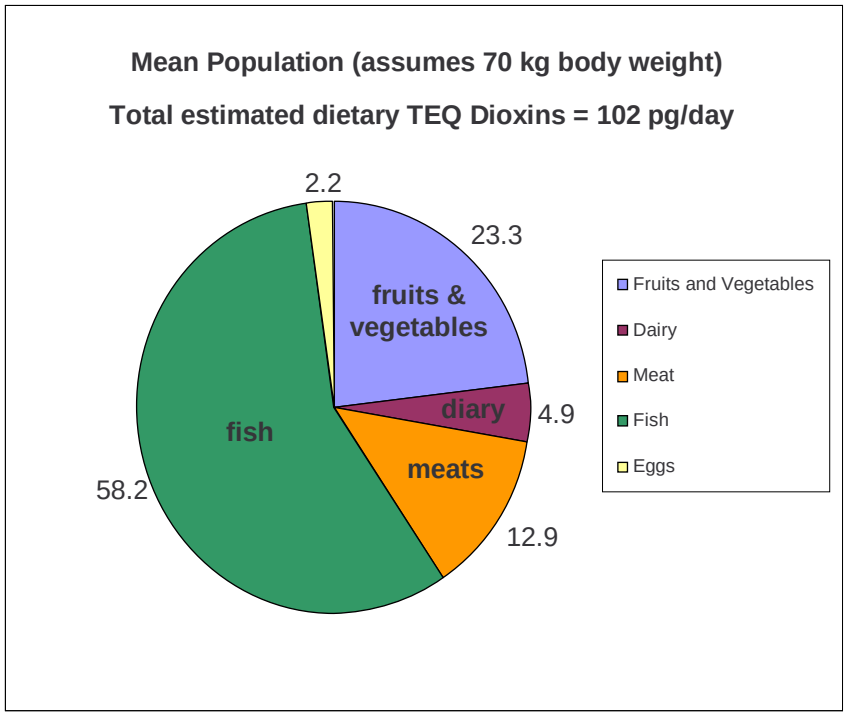
3. Calculated as: Estimated Daily Intake in pg/day divided by assumed weight in Kg.

4. Assumed Child Weight = 15 Kg (default in USEPA risk assessment guidance; e.g., USEPA 2009b).

5. Assumed Mean Population Weight =70 Kg (default in USEPA risk assessment guidance; e.g., USEPA 2009b).

Figure 1. Summary of estimated TEQ dioxin intake based on a Pacific-Asian diet [based on data reported by WHO for dioxin in food (WHO 2002)]





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In reply, please refer to:
File: EHA/HEER Office

TO: Interested Parties 2007-223-RB

FROM: Roger Brewer, Ph.D
Environmental Risk Assessment
Hazard Evaluation and Emergency Response

THROUGH: Barbara Brooks, Ph.D
Toxicologist
Hazard Evaluation and Emergency Response

DATE: April 12, 2007

SUBJECT: Use of laboratory batch tests to evaluate potential leaching of contaminants from soil (update to November 2006 technical memorandum)

Executive Summary

This technical memorandum presents the Batch Test Leaching Model (BTLM), a simple, Tier 3 approach for assessing the potential impact to groundwater posed by leaching of contaminants from vadose-zone soils. The BTLM uses site-specific soil data to evaluate contaminant mobility and estimate contaminant concentrations in soil leachate. If the contaminant is deemed sufficiently mobile, the model predicts future impacts to groundwater based on simple leachate dilution assumption. This can then be compared to target groundwater action levels appropriate for the site. An Excel spreadsheet is included to facilitate use of the model. Use of the spreadsheet model only requires input of the concentration of the contaminant in soil (in mg/kg) and the result of the batch test analysis (in µg/L). The BTLM can also be used to develop more realistic, site-specific soil action levels in lieu of the conservative, Tier 1 action levels for this concern published by HDOH. This guidance will be updated periodically as additional information and improved approaches are identified.

The guidance is most pertinent to vadose zone soils. Direct monitoring of groundwater should be carried out to evaluate leaching of contaminants in soils situated below the water table. Guidance presented in this memo does not apply to the evaluation of waste being placed in regulated landfills or to hazardous waste determinations. Evaluation of waste to be placed in landfills must be carried out under direction of the HDOH Solid and Hazardous Waste Branch.

Introduction

At a screening level, leaching of contaminants from soil is the primary environmental concern for the majority of the organic contaminants presented in the Hawai'i Department of Health (HDOH) document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater* (i.e., Tier 1 soil action levels for leaching concerns are lower than action levels for direct exposure, vapor intrusion, ecotoxicity and gross contamination concerns, HDOH 2005). Site-specific evaluation is recommended when soil action levels for leaching concerns are exceeded. In addition, action levels for metals are not provided in the document and leaching concerns must again be evaluated on a site-by-site basis. However, easy-to-use and technically sound soil leaching models that can be applied to both organic and inorganic contaminants have been lacking. The guidance presented below is intended to help address this issue.

The guidance focuses on the use of laboratory batch tests to quantify the mobility of the contaminant in soil and estimate the initial concentration of the contaminant in soil leachate. Batch tests involve placing a small amount of the soil in buffered, de-ionized water, agitating the mixture for a set period of time and measuring the fraction of the contaminant that desorbs from the soil and goes into solution. The ratio of the mass of a contaminant that remains sorbed to the mass that goes into solution, adjusted to the test method, is referred to the contaminant's "desorption coefficient" or "Kd" value.

A contaminant's Kd value is a key parameter in soil leaching models. The lower the Kd value, the greater the mobility of the contaminant in soil and the greater the leaching threat. Contaminants with Kd values less than 1.0 are considered to be highly mobile and pose a significant threat to groundwater resources. Contaminants with Kd values greater than 20 are considered to be so tightly bound to the soil that they are essentially immobile and do not pose a significant leaching concern. The strength of binding can vary among different soil types, as well as contaminant concentration and the age of the release.

Batch test data can be input into an Excel spreadsheet model ("Batch Test Leaching Model (April 2007)) that accompanies this technical memorandum to calculate Kd values for target contaminants. Use of the model only requires input of the concentration of the contaminant in soil (in mg/kg) and the results of batch test analysis (in µg/L). Additional, default parameter values in the model can be adjusted if needed but this is generally not recommended. The concentration of the contaminant in leachate hypothetically derived from the soil tested is calculated based on the Kd value determined for the contaminant. The spreadsheet then estimates the ultimate concentration of the contaminant in groundwater based on a simple groundwater/leachate mixing model. The inclusion of a more refined approach for estimating contaminant concentrations in groundwater is anticipated for future updates to this guidance.

The remainder of this guidance provides a detailed discussion of contaminant partitioning in soil, key questions to be asked in site-specific leaching models, batch test methodologies for estimation of site-specific Kd values and calculation of contaminant concentrations in soil leachate and groundwater. Equations used in the Batch Test Leaching Model are presented in Appendix 1. The use of soil gas data to estimate concentrations of volatile contaminants in leachate is also briefly introduced. A detailed understanding of these topics is not necessarily needed to use the accompanying spreadsheets and carry out a simple, site-specific evaluation of potential soil leaching concerns using batch test data. A basic understanding of contaminant fate

and transport in the subsurface is very useful, however, in determining how confident one can be in applying the results of the models to actual field conditions.

This memo updates a previous November 2006 version of the guidance and replaces text regarding use of the SPLP test presented in the May 2005 edition of the HDOH document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater"* (Volume 1, Section 3.3.3; HDOH 2005). The approach described should be considered guidance only. Alternative approaches can be proposed for specific sites. This guidance will be updated as needed in the future. Comments and suggestions are welcome at any time and should be directed to Roger Brewer of HDOH at roger.brewer@doh.hawaii.gov.

Partitioning of Contaminants in Soil

Contaminants released into soil will partition into up to four different phases in the soil matrix (Figure 1). Some of the contaminant will dissolve into the soil moisture to form leachate. Another portion will chemically bind ("sorb") to soil particles, primarily organic carbon and clay particles. If the contaminant is volatile, a portion will also partition into air-filled pore space as a vapor phase. If the total mass of the contaminant is great enough, the soil particles, soil moisture and soil vapor will become saturated and free-phase product will also be present.

In theory, the various phases of a contaminant will eventually come into equilibrium with each other. The nature of this equilibrium is controlled by the chemical properties of the contaminant, the chemistry and physical properties of the soil and the presence of other contaminants. Contaminants that readily bind to soil particles will be present primarily in the sorbed phase (e.g., PAHs, PCBs, etc.). Contaminants that are not very sorptive will accumulate in the soil moisture or soil vapor (e.g., perchlorate, chlorinated herbicides, BTEX, MTBE, solvents, etc.). Contaminants that are by nature gases will persist mainly as vapors in the air-filled pore space, especially if the soil is very dry (e.g., vinyl chloride).

In the absence of free product, the relationship between sorbed, dissolved and vapor phases of a contaminant in soil is relatively straightforward and can be described by simple partition coefficients (USEPA 2001). A contaminant's "Henry's Law Constant" is the ratio of the vapor-phase concentration of a contaminant to the dissolved-phase concentration, at equilibrium. The Henry's Law Constant is relatively constant between sites, although it may vary slightly due to differences in soil temperature and the presence of other contaminants.

A contaminants sorption coefficient, or "Kd" value, is the ratio of the sorbed-phase concentration to the dissolved-phase concentration, at equilibrium (see Figure 1). For initial screening purposes and calculation of Tier 1 soil Action Levels, Kd values for organic chemicals are estimated using published *sorption* coefficients ("koc" values) and assumptions about the organic carbon content of the soil (Kd = published koc value x assumed fraction organic carbon in soil, typically 0.1%). Generic Kd values have also been published for a limited number of metals and other inorganic contaminants, although they are considered to much less reliable than for organic compounds. In the field, however, contaminant sorption (or more specifically "desorption") coefficients can vary significantly between sites, due to differences in soil properties, the mixture of contaminants present and even the age of the release. The variability of contaminant Kd values in the field implies that this parameter should be included in site-specific evaluations of potential leaching concerns. In practice, this is rarely done.

A contaminants Henry's Law Constant and assumed (or site-specific) Kd value can be used in conjunction with assumed or know soil properties to determine how the contaminant is actually distributed in the soil. Table 1 summarizes the distribution of several common contaminants in soil as assumed in the leaching models used to generate Tier 1 action levels published but HDOH (HDOH 2005). The percent mass in each phase is calculated based rearrangement of a simple equilibrium partitioning equation presented in USEPA's *Soil Screening Guidance* (USEPA 2001, refer also to Appendix 1). Similar assumptions about contaminant partitioning in soil are made in the models used to generate the USEPA Preliminary Remediation Goals or Preliminary Remediation Goals, although this cannot be readily discerned from the equations presented in the accompanying guidance document (USEPA 2004).

As expected, contaminants such as benzo(a)pyrene and PCBs are almost entirely absorbed to soil particles (refer to Table 1). Perhaps surprising, however, is the tendency for the main mass of moderately volatile contaminants such as benzene, PCE and MTBE to be sorbed to soil particles or dissolved in soil moisture, versus being present as vapors in the soil air space. Confusion about this issue has led to over estimation (and probably over concern) of contaminant loss during sampling of soil for this group of chemicals. Compare this to contaminants that are gases and truly volatile by nature, such as vinyl chloride (see Table 1). Testing soil samples for the presence of vinyl chloride and estimating leaching concerns is probably not a worthwhile effort. The use of soil gas samples to estimate concentrations of highly volatile contaminants in soil leachate and even monitor the downward migrating vapor plumes is much more preferable. A brief introduction to this approach is provided later in this guidance and also included in the BTLM spreadsheet.

Site-Specific Evaluation of Soil Leaching Concerns

Four basic questions need to be posed when evaluating the potential for contaminants to leach from soil and impact groundwater (Figure 2):

1. "Is the contaminant potentially mobile?"

2. "What is the concentration of the contaminant in leachate in the primary source area?"

3. "What is the concentration of the contaminant in leachate at the point that the leachate reaches the top of the water table?" and

4. "What is the concentration of the contaminant in groundwater after the leachate has impacted the groundwater?"

Each of these relatively common sense and straight forward questions should be answered in a site-specific evaluation of potential soil leaching concerns. In practice, they rarely are, due in part to the "black box" nature of most soil leaching models. The guidance presented in this technical memorandum focuses on the first two of these questions, contaminant mobility and the initial concentration of the contaminant in leachate.

<u>Mobility in Soil</u>

Contaminant mobility in soil is evaluated in terms of how tightly bound the contaminant is to soil particles. From a modeling perspective, this is again described in terms of the contaminant's desorption coefficient or Kd value. Increasing Kd values reflect decreasing mobility in soil.

Figure 3 presents default, Tier 1 Kd values for several common contaminants and subdivides them in terms of relative mobility or leachability in soil (after Fetter 1993). Contaminants with a generic Kd value of less than 1.0 are considered to be highly mobile in soil, a fact that correlates well with field data and a list of common groundwater contaminants. Contaminants with a Kd value of greater than 20 in soil are considered to be essentially immobile. Not surprisingly, contaminants such as MTBE, PCE, BTEX, perchlorate and chlorinated pesticides like atrazine are predicted to be highly mobile in soil, at least at a screening level, whereas PAHs, PCBs and similar contaminants are considered to be essentially immobile. (Note that trace levels of strongly sorptive contaminants like chlordane in groundwater indicate that these contaminants can be mobile under some circumstances, especially if the leachate is migrating through unweathered bed rock.)

The ability of a contaminant to bind to soil is very much tied to the nature and concentration of the contaminant, the presence of other contaminants that may compete for prime sorption spots, the soil mineralogy and chemistry (including organic carbon and clay content) and the time elapsed since the release of the contaminant. Use of generic Kd values could in theory *under* predict how strongly bound a contaminant is to soil, especially in the presence of other contaminants or in soils with extreme pH, redox or other soil conditions. Based on (admittedly limited) data collected to date, however, generic Kd values typically used for organic contaminants tend to significantly *over* predict the potential mobility of contaminants in soils. This is especially true for organic contaminants. This makes the use of laboratory batch tests very important when Tier 1 action levels or screening levels for potential leaching concerns (based on generic Kd values) suggest that leaching concerns need to be further evaluated.

Initial Concentration in Leachate

A contaminant's Kd value is used in conjunction with it's Henry's Law Constant and assumptions about soil properties to estimate the initial concentration of a contaminant in leachate. The relatively simple equation used to perform this calculation is presented in Appendix 1 and incorporated into the accompanying spreadsheet. The proportion of the contaminant that will move into soil leachate is again mainly controlled or reflected by the contaminant's Kd value. A Kd value less than 1.0 indicates that most of the contaminant will move into soil leachate in comparison to the fraction of the contaminant that will remain sorbed to soil particles.

Concentration in Leachate at Groundwater Interface

As the leachate migrates downward, contaminant concentrations can be progressively reduced due to resorption of the contaminant to soil particles, chemical or biological degradation or volatilization into the soil air space. Estimates of contaminant concentrations in leachate at the point that the leachate reaches the groundwater interface can be made using a vadose-zone fate and transport model. This important step is not included into the BTLM at this time. The BTLM model instead very conservatively assumes that the concentration of the contaminant in leachate at the groundwater interface is equal to that in the initial source area. A more detailed evaluation of contaminant fate and transport in soil leachate (e.g., using SESOIL, VLEACH or other

vadose-zone leaching models) may be particularly useful at sites where the depth to groundwater from the base of the contaminated soil is greater than approximately ten meters and target contaminants that have default koc values greater than 1,000 cm^3/g (e.g., naphthalene), are highly degradable (e.g., TPH and BTEX), and/or are moderately or highly volatile (e.g., PCE and vinyl chloride).

Concentration in Groundwater

The concentration of a contaminant in groundwater after mixing of the leachate with the groundwater can be estimated by either dividing the concentration of the contaminant in leachate by simple dilution factor or again by use of a more rigorous fate and transport model (refer to equations in Appendix 1). The BTLM model presented relies on the former, although a more refined approach may be added in the future.

The HDOH Environmental Action Levels document (or EAL Surfer) should be referred to for target groundwater goals (HDOH 2005). Target groundwater goals will in general be the lowest of the drinking water goal (i.e., lowest of Primary and Secondary MCLs or equivalents), surface water goal (assuming potential discharge to a body of surface water, acute or chronic aquatic toxicity goal based on site location) and any other applicable goals (vapor intrusion, gross contamination, etc.).

Use of Batch Test Data To Estimate Contaminant Kd Values

Relatively simple batch test methods have been in use for decades to evaluate leaching of metals from mine tailings and estimate the mobility of pesticides sprayed on agricultural lands (USEPA 1992, 1999). The tests collectively account for a host of factors that may control binding to (sorption) and leaching of (desorption) contaminants from soil. The tests do not identify exactly how the contaminant is bound to the soil, although a review of soil properties and chemistry can shed light on this issue if needed. The most commonly used batch test method to evaluate potential leaching of contaminants from soil is the *Synthetic Precipitation Leaching Procedu*re or "SPLP" test (USEPA 1994, similar to the California "WET" test). The SPLP test is carried out as follows:

Step 1. Analyze soil sample for concentrations of target contaminants (e.g., in mg/kg)

Step 2. Run SPLP test on split sample:

- Place 100 grams soil in two liters of a de-ionized water solution (pH 5.5, 25° C),
- Remove airspace (especially for VOCs),
- Agitate 18 hours.

Step 3. Analyze extract for contaminants of concern.

Step 4. Estimate Kd by comparison of the mass of contaminant that remained sorbed to the soil to the mass of the contaminant that went into solution.

The equations used to calculate a contaminant's Kd value in soil based on batch test data are provided in Appendix 1 and incorporated into the accompanying BTLM spreadsheet. The calculated Kd value is then used to evaluate the potential mobility of the contaminant in the soil

and estimate the initial concentration of the contaminant in soil leachate and groundwater, as described in the previous section.

For batch test results that are below standard, commercial lab Method reporting Limits (MRL), Kd can be estimated using 1/2 the MRL. If the estimated Kd is less than 20, a worst-case concentration of the contaminant in groundwater can calculated as described above.

Contaminant Kd values estimated through use of batch tests apply only to the soil tested and only for the reported concentration of the contaminant in the soil. Kd values could vary with respect to contaminant concentration in the same soil type. This may need to be evaluated on a site-specific basis in cases where soil contamination is widespread and very heterogeneous.

For large areas where contaminant concentrations vary significantly and individual spill areas cannot be easily identified, it may be useful to conduct a series of batch tests and evaluate the variation in Kd with respect to contaminant concentrations in soil (keeping in mind the need to separate different soil types). Soil cleanup levels can then be developed by plotting contaminant concentration in soil versus estimated concentration in leachate, generating a regression line through the data (USEPA 1992, 1999). Soil cleanup levels can be calculated or read directly off of the graph by setting a target concentration of the contaminant in the leachate (e.g., target groundwater concentration times assumed groundwater/leachate dilution factor). An example of this approach based on perchlorate soil and SPLP data collected at a site in California is given in Figure 4. (Note that final cleanup standards varied slightly from that noted in the figure due to assumptions about representative contaminant distribution and Kd values in soil across the site.) In Hawai‘i, this approach may be especially useful in the evaluation of large, pesticide mixing areas associated with former agricultural lands.

It is important to understand that batch tests were not designed to directly estimate the concentration of a contaminant in soil leachate. Batch tests were instead designed to calculate Kd sorption or desorption coefficients, which can then be used to estimate contaminant concentrations in leachate if desired. The volume of solution used in batch test can be used to illustrate this point. A solution volume of two liters was selected primarily to help ensure that laboratory detection limits could be met, not to mimic the supposed concentration of the contaminant in actual soil leachate – as is commonly misinterpreted (USEPA 1992). If the same mass of soil (generally 100 grams) were placed in a swimming pool-size volume of solution then the resulting concentrations of target contaminants in the batch test would of course be very different. Assuming that the contaminant is not completely stripped from the soil, however, the ratio of the mass that remains sorbed to the mass that moves into solution (i.e., the Kd value) should be constant. For highly sorptive contaminants (e.g., PCBs and PAHs) and for many metals, the difference between batch test results and calculated concentration of the contaminant in leachate may indeed be very small. For less sorptive contaminants like BTEX, MTBE, perchlorate and moderately mobile pesticides, however, estimated concentrations in leachate may be an order of magnitude or more greater than the concentration reported in the batch test data. This is especially true for contaminants with Kd values less than 20 in the soil tested, where a significant fraction of the contaminant partitions into the batch test solute (e.g., >25%).

Soil Sampling Strategies

A minimum of three soil samples is generally needed to validate batch test data for each area investigated. Recording the soil type and testing for the total organic carbon content and percent clay content of the soil is also recommended. Although not directly incorporated into the BTLM, this information may prove useful in understanding the nature of contaminant binding in the soil and help direct soil cleanup actions, if needed.

For large sites with varying soil types, contaminant mixtures or release histories, it may be necessary to define multiple "decision units" and evaluate each area separately. For example, the binding capacity of sandy soils is likely to be much lower than clayey or organic-rich soils. If both soil types are present at a contaminated site, it would be prudent to treat each soil type area as a separate decision unit.

The collection and analysis of multi-increment samples (essentially very good "composite" samples) is preferred for easily identifiable spill areas or "hot spots," especially where the primary contaminants are non-volatile. Collection and field-based extraction of multi-increment samples for volatile contaminants may also feasible, although this subject is beyond the current scope of this memo. Guidance on the collection and evaluation of multi-increment samples is currently being prepared by HDOH. In the interim, and especially for cases under the formal oversight of HDOH, it is recommended that potential users of the BTLM guidance review sampling plans with the HDOH project manager prior to collection and submittal of the samples for analysis.

Use of Soil Gas Data to Evaluate Groundwater Protection Concerns

Batch tests can be used to evaluate both nonvolatile and volatile contaminants, although special care must be taken during sampling and testing of the latter (refer to USEPA 1994 SPLP method guidance). The concurrent use of soil gas data to estimate the concentration of volatile contaminants in soil leachate may also be prudent. Reasonably accurate estimations of the contaminant concentrations in soil moisture or leachate can be made by dividing the concentration of the contaminant in soil gas (converted to ug/L) by the chemical's dimensionless Henry's Law Constant (see equation in Appendix 1). A simple model based on this approach and incorporating a groundwater:leachate dilution factor is presented in Appendix 1 and included in the BTLM spreadsheet.

Cases where soil gas data may prove beneficial for evaluation of potential impacts to groundwater include: 1) sites with releases of relatively persistent, volatile chemicals that remain very dry throughout much of the year (i.e., non-irrigated areas with very low precipitation, or paved areas that overlie shallow groundwater), 2) sites known to be impacted by volatile contaminants but where specific source areas have not been identified, 3) sites where the threat to groundwater is primarily posed by downward releases of vapors from underground tanks, pipelines, etc., and 4) sites where the vulnerability and sensitivity of the first-encountered groundwater resource is very high (e.g., unconfined aquifer that is currently used as a source of drinking water). In very wet or heavily irrigated areas (e.g., groundwater recharge greater than ten inches or 25cm per year), mass loading of the contaminant to groundwater via vapor-phase

plumes is likely to be insignificant in comparison to contaminant migration via leachate. In very dry areas, however, the amount of moisture in the soils may not be sufficient to initiate the downward migration of leachate by the force of gravity. If this is the case then the model discussed above will overstate the potential threat to groundwater posed by dissolved-phase contaminants in the soil moisture.

A focus on the potential for vapor plumes to impact groundwater will be more appropriate for dry areas. Easy-to-use models that specifically evaluate the downward migration of vapor plumes to groundwater are not currently available. An evaluation of potential groundwater impact concerns may instead have to rely on long-term monitoring of soil gas in the vadose zone. Soil gas "action levels" for protection of groundwater can be developed by rearranging the Herny's Law Constant equation to solve for the concentration of the contaminant in soil vapor and setting the dissolved-phase concentration of the contaminant equal to a target groundwater or leachate goal (refer to equations in Appendix 1).

Soil gas data will be less useful for estimation of semi-volatile contaminant concentrations in leachate. This is due to the very low Henry's Law Constants for these contaminants and associated limitations on soil gas method reporting limits. As noted in Table 1 for PAHs, the overwhelming majority of the contaminant mass will also be sorbed to the soil, rather than in the soil vapor. Batch tests on representative soil samples therefore offer a better approach for the evaluation of leaching concerns related to these contaminants.

Leaching of Heavily Contaminated Soils

Soils that contain significant amounts of pure-phase or "free" product" may not be amenable to use of the Batch Test Leaching Model as described above (i.e., contaminant that is not sorbed to the soil, dissolved into the soil moisture or present as vapors in air-filled pore space). This is particularly true for soils that are heavily contaminated with petroleum. Contaminant Kd values can only be calculated if any free product present completely dissolves into the batch test solution. If free product forms in the batch test solution then analysis of solution for dissolved-phase constituents will not accurately reflect the total mass of contaminants that were stripped from the soil during the test. This will cause the model to over predict the mass of the contaminant that remained sorbed to the soil and in turn over predict the contaminants Kd value.

If the reported concentration of a contaminant in a batch test analysis exceeds 75% of the assumed solubility then it should be assumed that pure-phase contaminant product may be present in the batch test solution. In such cases, the spreadsheet model will generate a caution message and a Kd value will not be calculated. The potential mobility of the contaminant with respect to it's Kd value therefore cannot be accurately evaluated. In the spreadsheet model, the estimated concentration of contaminant in soil leachate is set to the highest of the contaminant's solubility and the reported concentration of the contaminant in the batch test analysis. Potential impacts to groundwater are estimated by dividing the assumed concentration of the contaminant in leachate by the input groundwater:leachate dilution factor. The potential downward mobility of liquid-phase free product in the soil should also be further evaluated.

Special Considerations For Petroleum-Contaminated Soils

Soils impacted by petroleum should be tested for both Total Petroleum Hydrocarbons (TPH) and target indicator compounds, including BTEX, MTBE and related fuel oxygenates and the PAHs naphthalene and methylnaphthalene (refer to Volume 1, Section 2.2.2 in HDOH EAL document, HDOH 2005). Testing for other PAHs is not necessary, due to their relative immobility in soil and low concentration in most petroleum products.

Problems related to the presence of free product in the batch test solution as discussed above could be especially pronounced for soils heavily impacted with middle distillates (diesel, jet fuel, etc.) and heavier residual fuels (waste oil, hydraulic fluid, etc.). The low solubility of these fuels in comparison to gasoline can lead to the presence of droplets of free product in soil at concentrations above only a few hundred parts-per-million (mg/kg) TPH. At high enough concentrations, this could lead to the presence of free product in the batch test solution. This will negate use of the BTLM model to calculate a Kd value for the sample tested and evaluate the potential mobility of the contaminant, as discussed in the previous section.

If the batch test results for Total Petroleum Hydrocarbons (TPH) suggest the potential presence of free product in the solution then the concentration of TPH in soil leachate should be assumed to be equal to the higher of the reported result and the assumed solubility of the targeted petroleum product. In the absence of a more site-specific review, the potential concentration of the contaminant in groundwater should be estimated by dividing the concentration in leachate but the groundwater:leachate dilution factor selected for the site. This is automatically carried out in the accompanying BTLM spreadsheet.

The presence of potentially mobile free product in the soil should also be evaluated. This can be done by comparison of TPH data for vadose-zone soil to HDOH action levels for gross contamination concerns in subsurface soils (HDOH 2005, Appendix 1). An action level of 2,000 mg/kg for gasoline contaminated soils. A somewhat higher action level 5,000 mg/kg is used for soils contaminated with either middle range petroleum distillates (e.g., diesel fuel and jet fuel) or residual fuels (motor oil, waste oil, etc.). These action levels are intended to minimize the presence of mobile free product in soil and are based on field observations and published studies (e.g, API 2000). Minimum conditions for use of the action levels in other areas include: 1) the source of the release has been eliminated, 2) grossly contaminated soil has been removed to the extent practicable (e.g., within 15 feet of the ground surface and/or to the top of bedrock) and 3) remaining contamination does not threaten nearby water supply wells or aquatic habitat (refer also to Volume 1, Section 2.2 of the HDOH 2005 EAL document).

Residual petroleum contamination in soil can be expected to naturally degrade over time. Note that impacted soil that is disturbed during future subsurface activities must also be properly managed. Continued groundwater monitoring may also be required for highly sensitive sites. Additional guidance for the long-term management of petroleum-contaminated soil (and groundwater) is currently being prepared by HDOH.

Other Limitations

Evaluation of Past Impacts to Groundwater

The approach described in this technical memorandum can only be used to predict *future* leaching of contaminants from soil and subsequent impacts to groundwater. Batch tests on residual contaminants in soil cannot necessarily be used to predict if *past* impacts to groundwater may have occurred. In part this is because the contaminants may be much more strongly bound to soil particles under current conditions than during the initial release. The possibility of past impacts to groundwater must be evaluated on a site-by-site basis, based on the nature of the contaminant released, the subsurface geology and the depth to groundwater among other factors.

Placement of Soil Below Water Table

The batch test method may not accurately mimic the placement of contaminated soil or other media below the water table for long periods of time and should not be used to predict these conditions. Long-term immersion could significantly enhance desorption of contaminants, especially if rate-limited processes such as desorption, organic carbon decay or mineral dissolution affect contaminant partitioning. Long-term immersion of the soil could increase impacts to groundwater that significantly exceed levels predicted by short-term batch tests. In the absence of a more detailed groundwater impact study, placement of contaminated soil below the water table or at a depth that is subject to future inundation by a rise in groundwater should be avoided (e.g., areas where the water table has dropped significantly due a prolonged dry period but is expected to rise again in the future). If this cannot be avoided and nearby water supply wells or aquatic habitats could be threatened, then long-term monitoring of the groundwater to verify that the contaminants are not significantly mobile is probably warranted.

Long-Term Groundwater Monitoring

Although the batch test method is believed to be very accurate, long-term groundwater monitoring may be prudent in some cases to verify the results of the evaluation. Monitoring may be especially warranted at sites where batch test data suggest that relatively high concentrations of chlorinated solvents, pesticides or other persistent contaminants can be left in place (e.g., in comparison to Tier 1 action levels for leaching concerns) but important drinking water resources are potentially threatened. Monitoring may also be needed at site where subsurface conditions could change over time and allow for increased leaching of contaminants (e.g., rising water table).

Use of Kd Values in Fate & Transport Models

Contaminant Kd values derived from batch tests cannot necessarily be incorporated into vadose-zone fate and transport models for deeper soils, even if the soil types are very similar. This is because the Kd value most likely reflects an increased difficulty in desorbing or leaching of *aged* contaminants from the tested soil. Use of the Kd value to evaluate migration of the contaminant in leachate through deeper soils not yet impacted by the initial release could over predict *resorption* to soil particles thus *under* predict potential impacts to groundwater. The use of batch tests to estimate site-specific *sorption* coefficients for contaminants in deeper soils may be practical but is beyond the current scope of this technical memorandum.

Evaluation of Solid or Hazardous Waste

Guidance presented in this memo does not apply to the evaluation of waste being placed in regulated landfills or to hazardous waste determinations. Evaluation of waste to be placed in landfills must be carried out under direction of the HDOH Solid and Hazardous Waste Branch.

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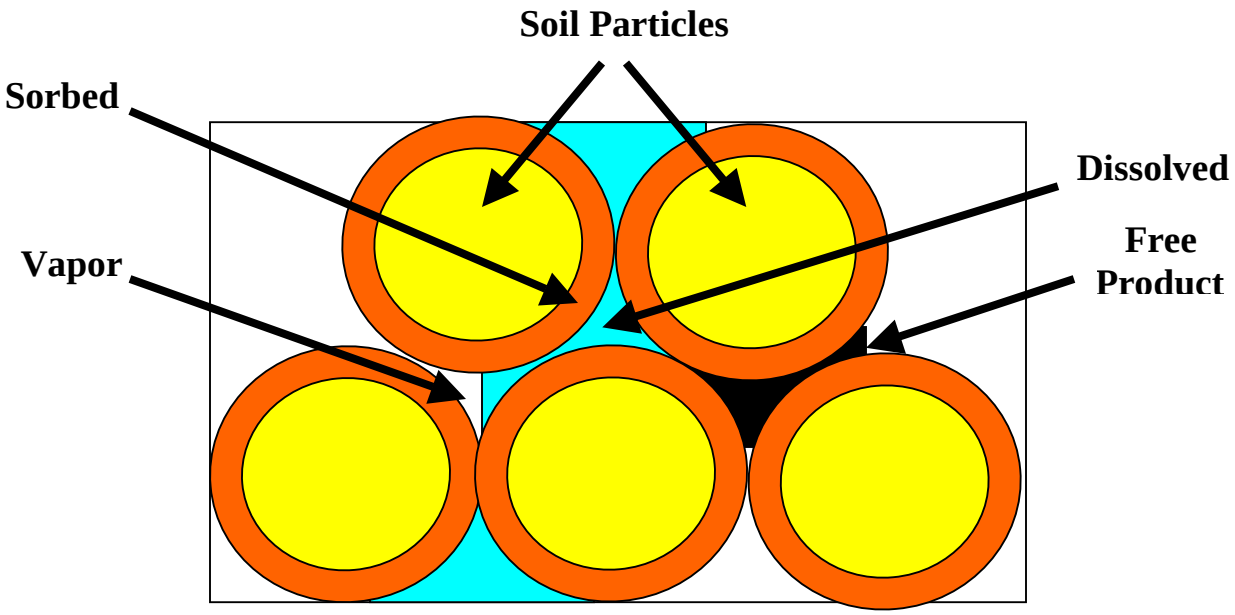
Table 1. Distribution of contaminants in soil based on contaminant properties and soil characteristics assumed in Tier 1 leaching models. Note how the fraction of the contaminant in the dissolved-phase is strongly tied to the assumed sorption coefficient or "Kd" value.

Chemical	**Default Sorption Coefficient (Kd)**	***Contaminant Phase Versus Percent Total Mass in Soil**		
		Sorbed	**Dissolved**	**Vapor**
Arsenic	29	99.9+%	0.0004%	0%
Benzo(a)pyrene	5,500	99.9+%	0.002%	0%
PCBs	33	99.7%	0.3%	0.01%
TPH	5.0	98%	1.9%	0.1%
Atrazine	0.23	70%	30%	0%
PCE	0.16	39%	25%	35%
Benzene	0.059	29%	50%	21%
MTBE	0.006	5%	91%	4%
Vinyl Chloride	0.0	5%	31%	64%

*Based on soil equilibrium partitioning equation presented in USEPA *Soil Screening Guidance* (USEPA 2001). Leachate is represented by the dissolved-phase mass of the contaminant. For organic contaminants, Tier 1 Kd value = published sorption coefficient (koc) x assumed total organic carbon content in soil of 0.1% (refer to HDOH 2005, Appendix 1, Table H). Assumes and soil moisture content of 0.10. Arsenic default Kd from USEPA *Soil Screening Guidance*.



Partition Coefficients

Kd = Sorbed Concentration/Dissolved Concentration

Henry's Law constant = Vapor Concentration/Dissolved Concentration

Figure 1. Partitioning of contaminants in soil between sorbed, dissolved and vapor phases.

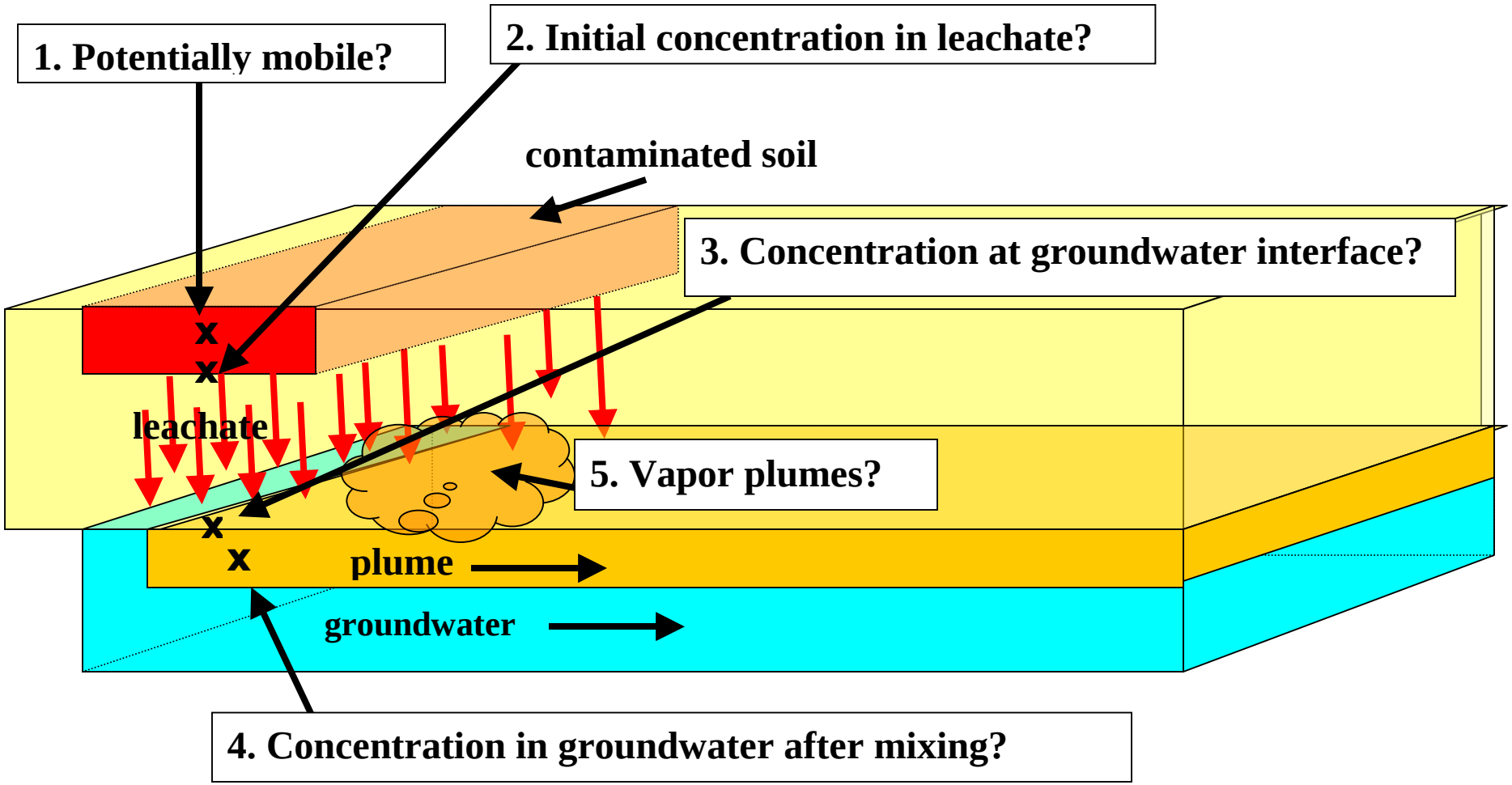


Figure 2. Basic questions that should be answered in all site-specific evaluations of soil leaching concerns. The guidance focuses on site-specific approaches to answering Questions 1 and 2, although approaches for answering the remaining questions are also provided.

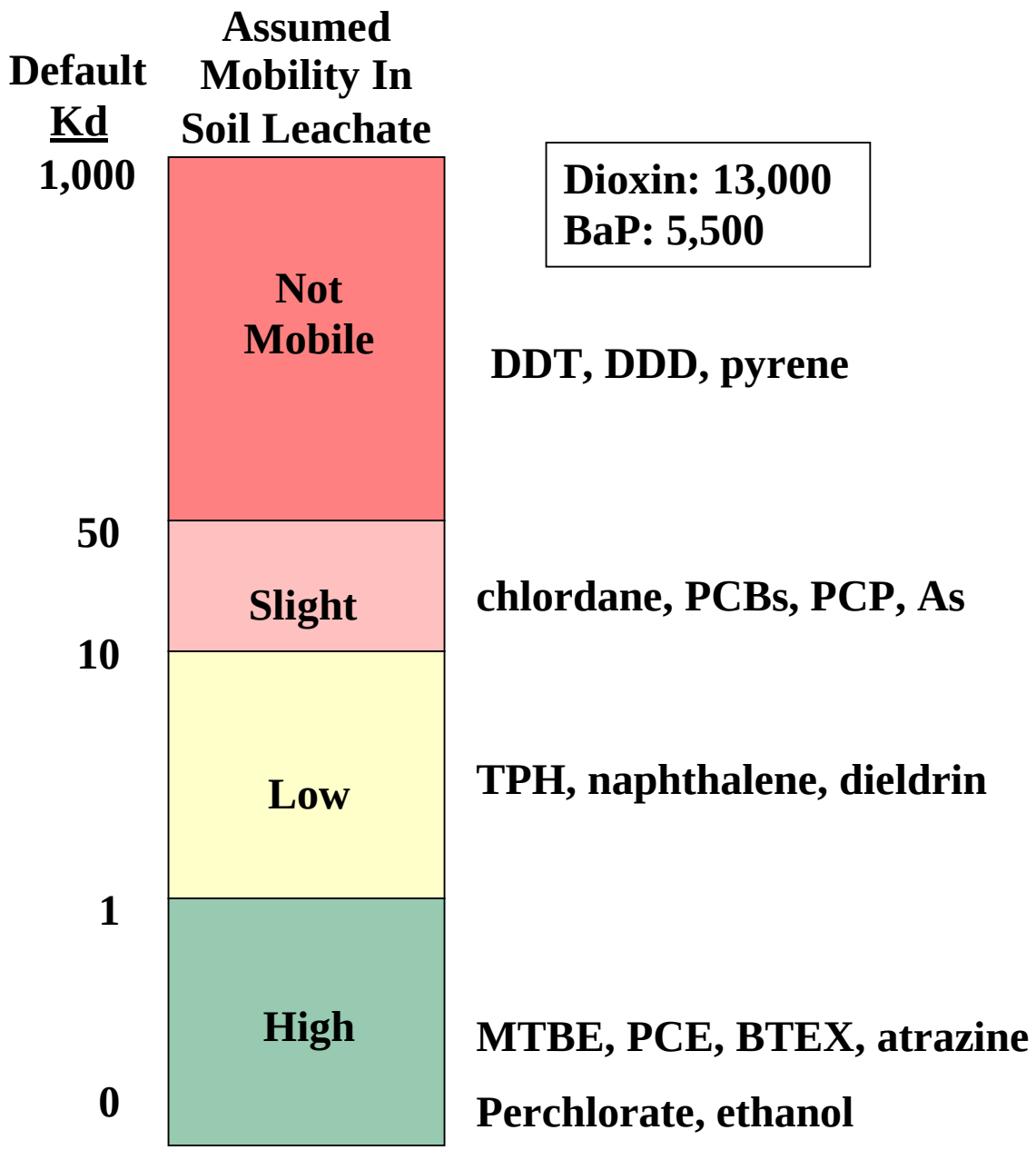


Figure 3. Assumed mobility of contaminants in soil leachate with respect to default Kd values used to develop HDOH Tier 1 soil action levels for leaching concerns. For organic contaminants, Kd values based on published koc sorption coefficients and total organic carbon content in soil of 0.1% (refer to Appendix 1 in HDOH EAL document, HDOH 2005). For arsenic, default Kd value of 29 from USEPA *Soil Screening Guidance* (USEPA 2001).

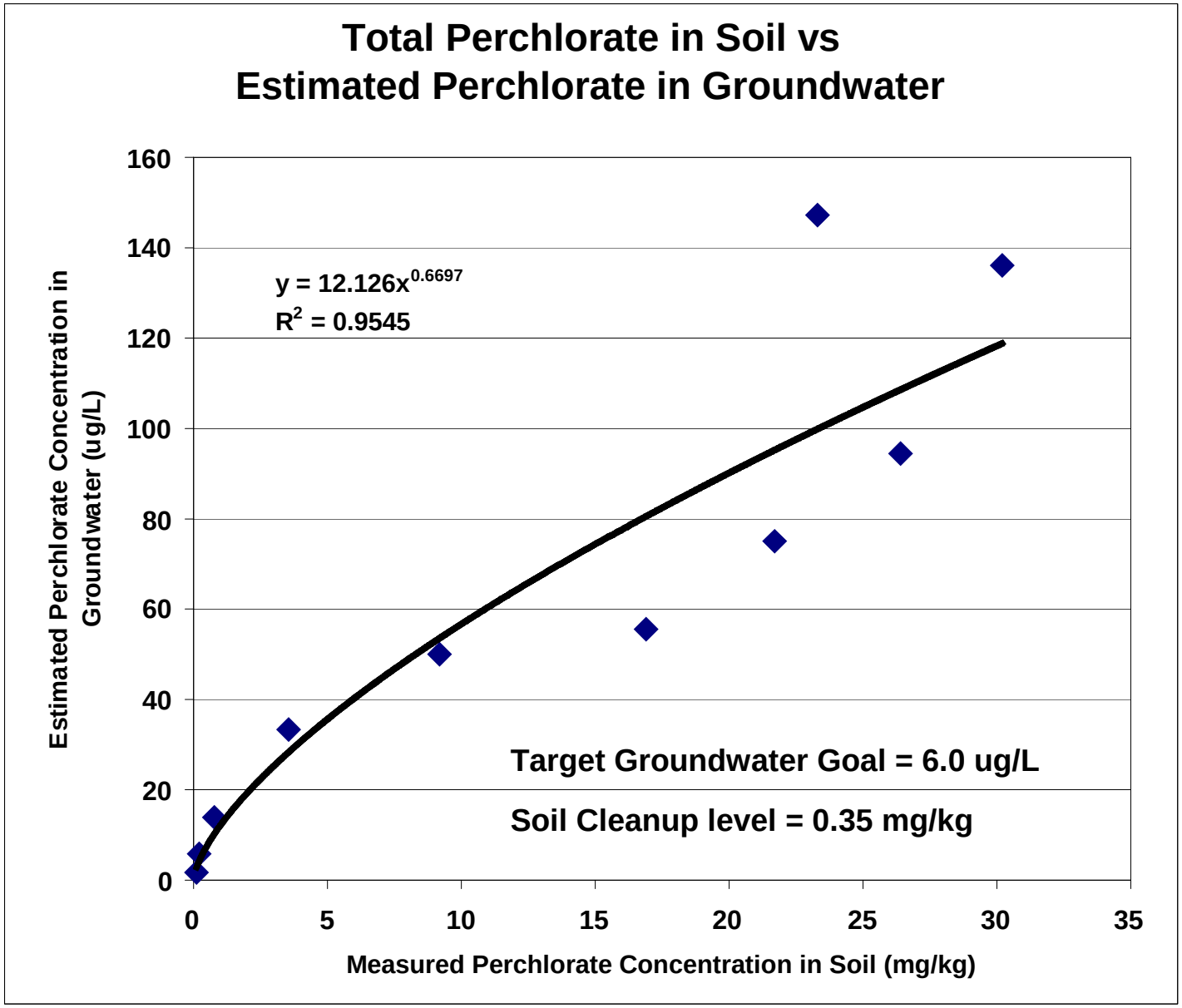


Figure 4. Example graphical calculation of soil cleanup levels based on use of multiple batch tests to estimated perchlorate desorption coefficients and correlative concentrations of perchlorate in soil leachate and groundwater at varying soil concentrations of perchlorate in soil. (For example only.)

Batch Test Leaching Model

Version: April 2007

Hawai'i Department of Health

Hazard Evaluation and Emergency Response Office

Contact: Roger Brewer (roger.brewer@doh.hawaii.gov)

-Refer to accompanying technical memorandum for background and use of this spreadsheet (HDOH 2007).
-Spreadsheet calculates Kd desorption coefficient based on input contaminant concentration in soil and Batch Test data.
-Correlative concentration of contaminant in leachate calculated based on estimated Kd value (may differ from batch test data).
-Future impacts to groundwater estimated using simple groundwater/leachate dilution factor.
-Alternative model based on soil gas data provided in accompanying worksheet.
-Possibility of past impacts to groundwater not considered and must be evaluated separately.
-Check to ensure that this is an up-to-date version of the spreadsheet.
-Password to unprotect worksheet is "EAL" (under Tools menu).

STEPS:

1. Select chemical from pulldown list (unlisted chemicals - unprotect spreadsheet and input chemical name and chemical constants).
2. Input total contaminant concentration and SPLP (or other applicable batch test) concentration.
3. Input sample properties. Use default values if sample-specific data are not available.
4. Input Batch Test method information. Default SPLP method parameter values noted.
5. Input groundwater:leachate dilution factor (DF of 1.0 = no dilution; USEPA default = 20, USEPA 2001).
6. Input target groundwater action level for comparison to model calculation of groundwater impacts (optional).
7. Spreadsheet calculates sample-specific Kd value and dissolved-phase concentration of contaminant in saturated sample.
8. Spreadsheet calculates concentration of contaminant in groundwater following impact by leachate.

Step 1: Select Contaminant (use pulldown list)	**PERCHLORATE**

Step 2: Input Sample Data	**DEFAULT**	**INPUT**
[1] Concentration in soil sample (mg/kg)	N/A	9.2E+00
[1] Concentration in Batch Test solution (ug/L)	N/A	3.7E+02
Step 3: Input Sample Properties ([5] USEPA soil defaults noted)		
Sample density (g/cm^3)	1.50	1.50
Particle density (g/cm^3)	2.65	2.65
Fraction air-filled porosity (assume saturated soil)	0.00	0.00
Step 4: Batch Test Method Data (SPLP defaults noted)		
[2] Batch Test Solution Volume (ml):	2,000	2,000
[2] Batch Test Solution Density (g/cm^3):	1.0	1.0
[2] Batch Test Sample Weight (grams)	100	100

[3] **Step 5: Input Groundwater/ Leachate Dilution Factor**	**DEFAULT**	**INPUT**
	20	20
[4] **Step 6 (optional): Input Target Groundwater Concentration (ug/L)**		5.0E+00

Model Results	
[3] Kd partition Coefficient (cm^3/g):	4.8E+00
[6] Estimated Concentration in Source Area Leachate (ug/L):	1.8E+03
[7] Estimated Concentration in Groundwater (ug/L):	9.0E+01

Chemical Constants (selected from Constants worksheet)	
Kh (atm m3/mole)	0.00E+00
Kh (dimensionless)	0.00E+00
Solubility (ug/L)	2.00E+08

Calculations:	
Sample porosity - total	0.43
Sample porosity - air-filled	0.00
Sample porosity - water-filled	0.43
Batch Test Solution Mass (grams)	2.0E+03
Batch Test Sample Mass (grams)	1.0E+02
Sample Mass:Solution Mass Ratio (gm/gm)	5.0E-02
Total Mass of Contaminant (ug)	9.2E+02
Mass Contaminant in Batch Test Solution (ug)	7.4E+02
Mass Contaminant Sorbed to Soil (ug)	1.8E+02
Concentration Sorbed (ug/kg)	1.8E+03
Batch Test Percent Solid Phase	19.3%
Batch Test Percent Dissolved Phase	80.7%
Batch Test Solid-Phase Contaminant Conc. (mg/kg)	1.8E+00
Batch Test Solution Contaminant Conc. (ug/L)	3.7E+02

Kd <20. Contaminant potentially mobile in leachate for concentration and soil type tested. Soil leaching and groundwater impact concerns must be addressed if target groundwater action level is exceeded.

Figure 5. Main page of HDOH Batch Test Leaching Model that accompanies the technical memorandum (as of April 2007).

Appendix 1
Batch Test and Soil Gas Leaching Model Equations

Batch Test Leaching Model Equations

The equations discussed below are incorporated into the Excel-based Batch Test Leaching Model that accompanies this technical memorandum. Figure 5 in the main text depicts the first page of the model (April 2007 version). The model will be updated as needed in the future.

Step 1. Calculate a partition coefficient for each chemical of potential concern.

The results of the SPLP test can be used to develop a sample-specific partition coefficient (Kd) for each chemical of potential of concern. The partition coefficient is calculated as follows (after Roy et. al, 1992; see also McClean and Bledsoe, 1992, and USEPA 1999):

$$Kd\ (L/kg) = \frac{Concentration_{sorbed}(\mu g/Kg)}{Concentration_{solution}(\mu g/L)} \qquad (1)$$

where $Concentration_{sorbed}$ is the concentration of the contaminant that remained sorbed to the soil following the batch test and $Concentration_{solution}$ is the resulting concentration of the contaminant in the batch test solution. The term Kd is commonly reported in equivalent units of (ug/g)/(ug/cm^3) or cm^3/g, based on an assumed batch test solution density of 1.0 g/cm^3.

The sorbed concentration of the contaminant is calculated as follows:

$$Concentration_{sorbed}(ug/kg) = \frac{Mass_{sorbed}(\mu g)}{Sample\ Mass\,(kg)}. \qquad (2)$$

where $Mass_{sorbed}$ is the mass of the contaminant still sorbed to the soil following the batch test. The mass of the sample called for in the SPLP batch test is 100 grams or 0.1 Kg (USEPA 1994).

The mass of the contaminant sorbed to the soil is calculated by subtracting the mass of the contaminant that went into the batch test solution from the initial, total mass of the contaminant in the soil sample:

$$Mass_{sorbed}(\mu g) = Mass_{total}(\mu g) - Mass_{solution}(\mu g) \qquad (3)$$

where $Mass_{total}$ is original, total mass of the contaminant in the soil sample and $Mass_{solution}$ is the mass of the contaminant in the batch test solution. The total mass of the contaminant in the soil sample is calculated as:

$$Mass_{total}(\mu g) = Concentration_{total}\ (mg/kg) \times \left(\frac{1{,}000\mu g}{1mg}\right) \times Sample\ Mass(kg) \qquad (4)$$

where $Concentration_{total}$ is the reported total concentration of the contaminant in the soil sample that used in the batch test (tested on a split sample). The mass of the contaminant in the batch test solution is calculated as:

$$Mass_{solution}(\mu g) = Concentration_{solution}(\mu g/L) \times Solution\,Volume(L)\,. \qquad (5)$$

The default volume of solution used in SPLP batch tests is two liters (USEPA 1994).

Note that use of the batch test method to estimate Kd values is not longer valid if the solubility limit of the contaminant is exceeded in the batch test solution (refer to section on Leaching of Heavily Contaminated Soils in the main text). Exceeding the contaminants solubility suggests that free product is present in the soil (either liquid or dry). As a precautionary measure, a cutoff of 75% the assumed contaminant solubility is used in the Batch Test Leaching Model spreadsheet to identify if free product may be present in the batch test solution. The free product acts as a second reservoir of contaminant mass that will bias the true equilibrium concentration of the contaminant in the dissolved and sorbed phases. To accurately calculate desorption coefficients, batch test analyses must be run samples with lower concentrations of the contaminant in soil.

Step 2. Estimate the concentration of the contaminant in source-area leachate.
Once the soil-specific Kd value for a target contaminant has been determined, it is relatively simple to estimate the concentration of the contaminant in the soil moisture or "leachate" within the main body of contaminated soil or the leachate "source area"). This is done by incorporating the calculated Kd into a simple equilibrium partitioning equation and assuming default (or site-specific) soil properties (after USEPA 2001):

$$C_{total} = C_{leachate} \times \left(Kd + \left(\frac{\theta_w + (\theta_a \times H')}{\rho b} \right) \right) \times \left(\frac{1mg}{1000\mu g} \right) \qquad (6)$$

where: C_{total} = Total concentration of chemical in sample (mg/kg);
$C_{leachate}$ = Dissolved-phase concentration of chemical (µg/L);
Kd = Estimated or measured partition coefficient L/kg;
$Theta_w$ = water-filled porosity (L_{water}/L_{soil});
$Theta_a$ = air-filled porosity (L_{air}/L_{soil});
H' = Henry's Law Constant at 25°C ((µg/L-vapor)/(µg/L-water)); and
p_b = Soil bulk density (Kg/L).

Table H in Appendix 1 of the HDOH EAL document provides a summary of "dimensionless" Henry's Law Constants (H') for common volatile contaminants (HDOH 2005). For the purpose of calculating Tier 1 action levels, Kd is calculated as the chemical's published organic carbon partition coefficient (koc) times the fraction organic carbon in the soil (foc). This is discussed in Appendix 1 of the HDOH Environmental Action Levels document (HDOH 2005). Note that in this equation Kd and p_b are expressed in units of L/Kg and Kg/L, respectively, rather than in equivalent units of cm^3/g and g/cm^3. A default soil density of 1.5 Kg/L and soil porosity of 43% (0.43) are typically used in Tier 1 risk assessment models (e.g., USEPA 2001, 2004).

Equation 6 can be rearranged to solve for $C_{leachate}$ as follows:

$$C_{leachate} = C_{total} \div \left(\left(Kd + \left(\frac{\theta_w + (\theta_a \times H')}{\rho b} \right) \right) \times \left(\frac{1mg}{1000\mu g} \right) \right). \quad (7)$$

This equation is incorporated into the "Batch Test Leaching Model" worksheet of the Excel file that accompanies this technical memo. The sorption coefficient should be used to estimate the dissolved-phase concentration of the contaminant in a hypothetical, saturated sample of soil at equilibrium and at the same contaminant concentration as the SPLP test. Since the soil is assumed to be fully saturated with water, the vapor-phase term of the equation "θ_a x H'" goes to zero.

Step 3. Tier 3 calculation of ultimate contaminant concentration in groundwater.

A conservative estimate of the contaminant concentration in groundwater that cuold be impacted by the leachate is made by dividing the calculated concentration of the contaminant in leachate by an assumed groundwater:leachate dilution factor (DF):

$$C_{groundwaater} = \frac{C_{leachate}}{DF} \quad (8)$$

$$DF = \frac{\text{Volume Impacted Groundwater}}{\text{Volume Leachate}}. \quad (9)$$

where: $C_{groundwater}$ = Concentration of chemical in groundwater (µg/L);
$C_{leachate}$ = Concentration of chemical in leachate (µg/L); and
DF = Groundwater/Leachate dilution factor (m^3/m^3).

This equation is incorporated into the Batch Test Leaching Model spreadsheet that accompanies this technical memo. A default DF of 20 is considered appropriate for sites less than or equal to 0.5 acres in size (USEPA 2001). A more site-specific DF factor can be calculated if needed, based on the following equation (USEPA 2001):

$$\text{Dilution Factor} = 1 + \left(\frac{K \times i \times d}{I \times L} \right) \quad (10)$$

where "K" is the aquifer hydraulic conductivity (m/year), "i" is the regional hydraulic gradient, "d" is the assuming mixing zone depth (default is two meters), "I" is the surface water infiltration rate (m/year" and "L" is the length of the contamianted soil area that is parallel to groundwater flow (m).

Note that this equation does not consider an expected reduction in contaminant concentrations as the leachat migrates downward. This component of the evalaution can be included in more site-specific evaluations as needed.

Soil Gas Leaching Model

For volatile contaminants, soil gas data offer an alternative approach for estimation of contaminant concentrations in leachate as well as a method to evaluate the threat posed to groundwater by downward migrating vapor plumes. The relationship between vapor-phase and dissolved-phase volatile chemicals under equilibrium conditions is relatively straightforward:

$$H' = \frac{Cvapor\ (ug/L)}{Cleachate\ (ug/L)}\ . \qquad (11)$$

where: H'=Henry's Law Constant at 25°C;

C_{vapor}= Vapor-phase concentration in soil gas;

$C_{leachate}$= Dissolved-phase concentration in soil pore waters.

Table H in Appendix 1 of the HDOH EAL document provides a summary of "dimensionless" Henry's Law Constants (H') for common volatile contaminants (HDOH 2005). To calculate the concentration of the contaminant in the soil moisture the equation is rearranged to solve for "$C_{leachate}$." The C_{vapor} term is also adjusted to units of ug/m3 to correspond with the units typically reported in site data:

$$Cleachate\ (ug/L) = \frac{Cvapor\ (ug/m3) \times \frac{1\ m3}{1{,}000\ L}}{H'}\ . \qquad (12)$$

Equation 8 above can be used to estimate potential impacts to groundwater with respect to soil gas-based estimates of contaminant concentrations of the in leachate.

Soil gas "action levels" for protection of groundwater can be developed by rearranging the equation to solve for C_{vapor} and setting $C_{leachate}$ equal to a target leachate goal (e.g., groundwater action level times appropriate groundwater:leachate dilution factor):

$$\text{Cvapor (ug/m3)} = \text{Cleachate (ug/L)} \times \text{H'} \times \frac{1{,}000\ \text{L}}{1\ \text{m3}} \times \text{AF} \qquad (13)$$

The term "AF" is an attenuation factor that describes the anticipated decrease in contaminant concentrations over time as the vapor migrates to and eventually impacts groundwater (e.g., via natural degradation, resorption to soil particles or migration into soil moisture). Approaches for

calculation of site-specific, vapor attenuation factors are not well established and beyond the scope of this technical memorandum.

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In reply, please refer to:
File: EHA/HEER Office
07-251 RB

May 11, 2007

TO: Interested Parties

FROM: Keith E. Kawaoka, D.Env., Program Manager
Hazard Evaluation and Emergency Response Office

SUBJECT: **Pesticides in Former Agricultural Lands and Related Areas – Updates on Investigation and Assessment (arsenic, technical chlordane, and dioxin test methodologies and action levels and field sampling strategies)**

Attached for you information is a technical report that presents guidance on the assessment of pesticides in former agricultural lands and related areas. This report serves as an addendum to the Hazard Evaluation and Emergency Response (HEER) Office document, *Screening for Environmental Concerns at Sites With Contaminated Soil and Groundwater* (May 2005).

If you have any question, place call Dr. Roger Brewer of my office at 1-808-586-4238, or contact him by email at roger.brewer@doh.hawaii.gov.

Attachment

Pesticides in Former Agricultural Lands and Related Areas
Updates on Investigation and Assessment

This technical report presents updated guidance on the investigation and assessment of residual pesticides in soils. The guidance focuses on the redevelopment of former agricultural land but is also applicable to golf courses, nurseries, military housing complexes and similar, large-scale projects involving soils that may have been treated with pesticides. Updates are provided for arsenic, chlordane and dioxin test methodologies and action levels. A basic review of multi-increment sampling strategies is also presented.

This technical report serves as an addendum to the Hawai‘i Department of Health (HDOH), Hazard Evaluation and Emergency Response (HEER) document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater* (May 2005 and updates) and other related technical reports noted below. Information presented in these technical memoranda will be incorporated into the upcoming revision of the HEER office *Technical Guidance Manual.* Comment and suggestions are welcome. Please contact Dr. Roger Brewer of HDOH at 1-808-586-4328 or roger.brewer@doh.hawaii.gov for further information.

Pesticides of Potential Concern

"Pesticides" is a general term that includes any type of chemical mixture specifically formulated to kill "pests." Pesticides commonly used in Hawai‘i include herbicides, fungicides and insecticides, the latter including termiticides and nematocides. HDOH recommends that sites where pesticides may have been regularly applied in the past be tested for residual contamination prior to redevelopment. The guidance is especially pertinent to large tracts of former agricultural land, golf courses, nurseries and military housing complexes that are being demolished and redeveloped with new homes.

In the case of former agricultural lands, contamination is likely to be heaviest in former pesticide mixing and staging areas, seed dipping areas and storage areas, although heavy contamination could occur in association with bagasse piles, settling ponds, former plantation camp areas, etc. Residual contamination in former fields has not been well documented, although HDOH is continuing to collect data for these areas. Conditions can vary dramatically from site to site.

Types of pesticides commonly used in Hawai'i include:

Pesticide Group & Related Contaminants	**Standard USEPA Laboratory Method**
Organochlorine pesticides	8081A
Organophosphorus pesticides	8041A
Chlorinated herbicides	8151A
Carbamates	8321A
Pentachlorophenol	8270
Fumigants	8260
Dioxins/furans	8280/8290
Heavy metals (primarily arsenic, lead & mercury)	various

The above list is not intended to be comprehensive, nor is it intended to represent a required list of target analytes that must be tested for in areas where pesticides were used in the past. Specific pesticides of concern should be based on a review of the historical use of the site with a focus on pesticides that may be persistent in soil above HDOH Environmental Action Levels (EALs, HDOH 2005 and updates). Soil and groundwater action levels for the majority of commonly used pesticides in Hawai‘i are included in this document. Contact the HEER office for pesticides not listed in the EAL document.

Fumigants are not likely to be persistent in shallow soils more than one year after use due to a propensity to volatilize into the atmosphere and degrade or be carried downward in leachate. Organochlorine pesticides are known to be very persistent in soils in Hawai‘i, as are arsenic and lead. Organophosphorus pesticides, chlorinated herbicides, carbamates and pentachlorophenol are more susceptible to biological and chemical breakdown over time and are more likely to be persistent in heavily contaminated, pesticide mixing areas than in fields. As of the date of the technical report, however, HDOH has not compiled adequate data to rule out the potential presence of these pesticides in former field areas above levels of concern. As discussed below, significant levels of dioxins and furans may also remain in soils even though the parent pesticide has degraded below levels of concern.

Summaries of historical pesticide use on agricultural lands are available from the Hawai‘i Department of Agriculture and other sources (e.g., Hanson 1959, 1962; HDOA 1969, 1977, 1989). The Clean Water Branch of HDOH provides a brief summary of pesticides in their NPDES guidance (HDOH 2004). A selection of pesticide-related documents can be downloaded from the HDOH EAL web page (refer to HDOH 2005).

A detailed review of pesticide use in Hawai‘i and a compilation of persistent contaminants that could accumulate in soil above levels of concern will be included in the upcoming revision to the HEER office Technical Guidance Manual (anticipated Fall 2007). Additional pesticides will be added to the current list of chemicals in the EAL lookup tables as needed.

Arsenic

HDOH recommends that the name of the soil series and a summary of the soil type be noted for samples tested for bioaccessible arsenic, including mention of the total iron and aluminum oxide content (NCRS 2007). HDOH also recommends that the fine-grained (<250µm) fraction of the soil sample that is to be tested for bioaccessible arsenic also be tested for total arsenic.

Guidance on the collection and interpretation of bioaccessible arsenic data is presented in the HDOH 2006 technical report *Soil Action Levels and Categories for Bioaccessible Arsenic* (HDOH 2006a). HDOH recommends that bioaccessible arsenic test be carried out when the total arsenic concentration in the soil exceeds 20 mg/kg (assumed upper limit for background arsenic in soil). Bioaccessible arsenic tests are used to estimate the fraction of total arsenic that could be stripped or “desorbed” from the soil following ingestion and thus made available for uptake. Arsenic that remains sorbed to the soil sample is considered to be unavailable for uptake and essentially “non-toxic.” The concentration of bioaccessible arsenic in a soil sample is calculated by dividing the mass of arsenic that moves into the batch test solution by the mass of the sample. Although not required as part of the bioaccessibility test, HDOH recommends that the concentration of total arsenic also be determined for the sample. This will help confirm the results of the test and provide insight on the range of arsenic bioaccessibility in the fine-grained fraction of contaminated soil.

The HEER Office has not developed generic bioaccessible factors for arsenic in soils in Hawai‘i and currently recommends testing on a site-by-site basis. The use of bioaccessible arsenic tests has not been formally adopted by USEPA as a substitute for bioavailable arsenic testing (i.e. in-vivo or animal testing). In lieu of formal guidance, USEPA has recommended that HDOH provide additional information to demonstrate a preponderance of evidence that the arsenic is indeed tightly bound to the soil and has very limited availability for uptake in humans. These lines of evidence include:

- *In vivo* studies that indicate very low arsenic bioavailability in soils from heavily impacted areas in Kea‘au (Exponent 2005, Roberts et al., 2006);
- The correlation of *in vivo* study results with bioaccessible arsenic data collected at the same site (e.g., Cutler 2006);
- Correlation of decreasing arsenic bioavailability with increasing iron oxide concentration (Roberts et al., 2006);
- Average iron oxide concentration in soils used for agriculture in Hawai‘i of 10-30%, well above typical soils on the US mainland (NRCS 2007);
- A lack of arsenic in groundwater underlying current and former sugar cane areas, indicating strong binding to soil and minimal leaching potential (HDOH 2006b);
- Laboratory testing at UH Manoa that demonstrated tropical soils (Andisols and Oxisols) with high levels of oxide and hydroxide mineral species have a natural ability to sequester arsenic, even over a wide pH range, making the arsenic less available to the soil solution - and therefore also estimated to be less bioaccessible through human ingestion and digestion (Cutler et al., 2006);
- Soil uptake factors for vegetables and fruits grown in arsenic-contaminated soils in the Kea‘au area are >2 orders of magnitude less than uptake factors published in scientific literature, supporting a conclusion that the arsenic is much more tightly bound to the soils than might otherwise be expected (HDOH, internal data);
- Laboratory batch test data that indicate arsenic sorption coefficients in soil greater than 500 (HDOH, internal data); and
- Use of a conservative, maximum-acceptable target risk to establish upper-bound action levels for bioaccessible arsenic in soil (HDOH 2006a).

HDOH recommends that a brief summary of the soil series associated with the subject site and sample point locations be provided with bioaccessible arsenic data (NRCVS 2007). The relationship between soil mineral characteristics and bioaccessibility is very complex and dependent on more than the metal oxide content of the soil. For example, the arsenic binding capacity of soils developed on coralline, coastal sediments is significantly less than soils developed over basalt, although these soils are rarely used for agriculture. Additional research is currently under way by the University of Hawai‘i as well as other groups.

Technical Chlordane and Other Organochlorine Pesticides

HDOH recommends that soils potentially treated with termiticides be tested for *technical chlordane* rather than individual chlordane isomers and related compounds generally found in technical chlordane. The concentration of chlordane isomers, heptachlor and heptachlor epoxide do not need to be reported. Laboratories should be directed to test for technical chlordane using USEPA Method 8081A or an equivalent method (USEPA 1996). This must be specifically requested prior

to submittal of the samples and noted on the Chain of Custody form. Laboratories should also be instructed to report any additional organochlorine pesticides that are not typically found in technical chlordane (e.g., DDT, dieldrin, endrin, etc.).

Technical chlordane is a mixture of chlordane (50-75%) and over 100 related compounds, including heptachlor and heptachlor epoxide (ATSDR 1994). Toxicity factors published by the USEPA are based on studies of technical chlordane, not individual chlordane isomers (USEPA 1997). These toxicity factors collectively take into account the full suite of compounds present in technical chlordane and are used to generate the USEPA Region IX Preliminary Remediation Goals (USEPA 2004) and HDOH Environmental Action Levels (HDOH 2005) for direct-exposure concerns. Since the quantification of technical chlordane includes chlordane, heptachlor and heptachlor epoxide, these individual compounds do not need to be reported in the analysis or evaluated separately in an Environmental Hazard ("risk") Assessment unless otherwise directed by HDOH. Doing so will cause the health risk posed by these compounds to be double counted, since it will already be included in the assessment of technical chlordane.

Tier 1 Environmental Action Levels (EALs) for technical chlordane are presented in the HDOH document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater* (HDOH 2005). Tier 1, direct-exposure action levels technical chlordane were generated using a target excess cancer risk of 10^{-6} and a noncancer hazard quotient of 1.0 (refer to Appendix 1, Tables I-1 through I-3). However, use of a target, cumulative risk of 10^{-5} is generally acceptable for evaluation of multiple contaminants under a Tier 2 or Tier 3 assessment. Since technical chlordane is actually a mixture of numerous chemicals, it is more appropriate to screen site data using Tier 2 direct-exposure action levels based on a cumulative target cancer risk of 10^{-5}. Correlative action levels for residential and commercial/industrial exposure are 16 gm/kg and 65 mg/kg, respectively. After taking into account action levels for leaching concerns, the following action levels are generated:

Tier 2 Action Levels for soil with technical chlordane only

Exposure Scenario	**Direct Exposure (mg/kg)**	**[1]Leaching (mg/kg)**	**[2]Final Tier 2 Action Level (mg/kg)**
Residential	16	15	15
Commercial/Industrial	65	15	15

1. HDOH EAL guidance document, Appendix 1, Table E-1.
2. Lowest of direct-exposure and leaching soil action level

These action levels will replace the Tier 1 action levels for technical chlordane currently presented in the HDOH EAL document (HDOH 2005). On a site-specific basis, HDOH may require calculation of cumulative cancer and noncancer health risks if contaminants not related to technical chlordane are identified in the soil above HDOH Tier 1 action levels for direct-exposure concerns. This may be necessary to assure that a cumulative cancer risk of 10^{-5} and a noncancer Hazard Index of 1.0 are not significantly exceeded. Leaching concerns posed by the additional contaminants must also be evaluated.

Refer to the HDOH technical report *Use of laboratory batch tests to evaluate potential leaching of contaminants from soil* for guidance on the site-specific evaluation of potential leaching concerns

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In reply, please refer to:
File: EHA/HEER Office

TO: Michael Miyahira 2011-649-RB
Safe Drinking Water Branch

FROM: Roger Brewer, PhD and Barbara Brooks, PhD
Environmental Hazard Evaluation
HEER Office

Through: Keith E. Kawaoka, D.Env., Program Manager
Hazard Evaluation and Emergency Response Office

DATE: January 12, 2011 (revised 2/7/11 to reflect USEPA MCL model for noncancer action levels, reduced from 33 ug/L to 20 ug/L an 11/7/11 to reflect additional groundwater data)

SUBJECT: Overview of drinking water action levels for Chromium VI

Summary
This technical memorandum presents a range of risk-based action levels for hexavalent chromium (Cr VI) in drinking water, based on published guidance and toxicity studies. The current, Maximum Contamination Level (MCL) for Total Chromium in drinking water promulgated in Hawai‘i Department of Health (HDOH) regulations is 100 µg/L, equal to the MCL published by the USEPA. The Total Chromium MCL is based on an assumption that 100% of the chromium is Cr VI.

It is anticipated that the USEPA will eventually tighten drinking water standards for Total Chromium to address updated toxicity reviews of noncancer and cancer health risks posed by Chromium VI. A summary of potential risk-based action levels for Cr VI in drinking water based on the most recent, published and draft USEPA guidance is as follows:

Target Health Effect	Cr VI Drinking Water Action Levels	Notes
***Cancer Risks:**	0.043 to 4.3 µg/L	Linear extrapolation model employed for cancer slope factor carries significant uncertainty for exposures below the current Total Chromium MCL.
Noncancer Risk	20 µg/L	Confidence in the toxicity factor used to derive the action level is medium to high.
Combined Range:	0.043 to 20 µg/L	Lower-bound and upper-bound range of risk-based action levels for Cr VI in drinking water based on current and draft USEPA

		guidelines.

*Reflects USEPA acceptable cancer risk range of 10^{-4} to 10^{-6}, include ten-fold safety factor for early life exposure.

The action levels presented above are intended to assist in the evaluation of Cr VI data for groundwater and tapwater samples to be collected by the Honolulu City and Country Board of Water Supply, as well as general groundwater investigations overseen by the Hazard Evaluation and Emergency Response (HEER) office of HDOH. **The action levels are specifically *not* intended to serve as a legally enforceable standard or requirement for municipal water suppliers**. The action level focus on potential risk to human health and do not take into account other factors that must be considered when promulgating a final drinking water MCL standard, including technical feasibility and cost of water treatment, as well as naturally occurring Cr VI in water and natural dietary exposure.

The ideal goal for Cr VI in drinking water is "zero," since Cr VI is not an essential nutrient and has been shown to be toxic over long periods of relatively high exposure. The natural occurrence of trace levels of Cr VI in our food and water, however, make this goal impractical. Naturally occurring, background Total Chromium in groundwater across the islands ranges from <2 μg/L to approximately 15 μg/L (see Table 1 in attachment). This is similar to the expected range of background Cr VI in groundwater on the mainland US. The geochemistry of the aquifers (e.g., well oxygenated and neutral pH) likewise suggests that chromium in the groundwater is likely to be dominated by Cr VI. [Followup sampling in 2011 confirmed that the majority of chromium in groundwater is Cr VI, with reported concentrations ranging from <2 ug/L to 14 ug/L. This falls within the range of risk-based, drinking water action levels for Total Chromium noted above (i.e., 0.043 ug/L to 20 ug/L). In most cases, the concentration of Cr VI falls below below USEPA's conservative, upper-bound action level of 4.3 μg/L for potential cancer risk.]

Long-term exposure to the trace levels of Cr VI likely to be naturally present in Hawaii's groundwater (i.e., based on Total Chromium levels) has not been demonstrated to pose significant health risks in epidemiological studies or laboratory studies. As discussed below, the animal studies referred to for development of the cancer-based toxicity factor relied on exposures to Cr VI in drinking water six orders of magnitude higher than the lower-bound action level (>14,300 ug/L vs 10^{-6} cancer-based action level of 0.043 ug/L, see Figure 1 of the attachment). Uncertainty in use of the cancer studies to predict long-term exposure to trace levels of Cr VI in drinking water is relatively high and the focus of much debate. Certainty in the noncancer studies and resulting action levels is much higher. Given this disparity, as well as the widespread, natural presence of trace levels Cr VI in groundwater and surface water, it is anticipated that any revision to the current MCL for Total Chromium will take natural background levels of Cr VI into account, provided that they fall within a range of risk-based action levels similar to that noted above.

Additional details are provided in the attachment to this memorandum.

(Attachment)

Overview of Chromium Occurrence, Toxicity and Drinking Water Action Levels

Chromium VI Occurrence in Nature

Chromium (Cr) is a naturally occurring element found in rocks, soil, water, animals and plants as well as volcanic dust and gases (Kotas 2000, IETEG 2005). The most common forms in the environment are metallic chromium, zero-valent chromium (Cr 0), trivalent chromium (Cr III) and hexavalent chromium (Cr VI). A fourth form of chromium, Cr V, is associated with steel making and other industrial processes but is not common in the environment.

Both Cr III and Cr VI occur naturally at trace amounts in groundwater and surface water in the presence of chromium bearing rocks, sediment or soil (IETEG 2005). The trace levels of chromium in groundwater are derived from naturally occurring chromium in the enclosing, basaltic bedrock (Sterns 1985, MacDonald et al. 1983). Background levels of total chromium in basalt can reach 2,000 mg/kg or higher (IETEG 2005). The concentration of Total Chromium in the volcanic soils of Hawai‘i typically ranges from 100 to 500+ mg/kg and can exceed 1,000 mg/kg in places (USAF 2005, USN 2006, HDOH 2008). Chromium in the soil and rock is dominated by Cr III and metallic chromium (see Kotas 2000 and IETEG 2005). Although not regularly measured, a small percentage (e.g., <15%) of the Total Chromium is likely to be Cr VI (default percentage used in past USEPA guidance).

In oxygenated water with a neutral or higher pH (pH $\geq$7), chromium is typically dominated by Cr VI, although this can vary in surface water due to various compounding factors (Kotas 2000). Between a pH of 6-7 chromium may be present as either Cr VI or Cr III. At a pH of <6 and/or under anoxic conditions, Cr III is generally dominant. Groundwater in the basaltic aquifers of the Hawai‘i typically has a pH of ranges from 7-8 (personal communication, HDOH Safe Drinking Water Branch). [Expanded sampling in 2011 confirms that Total Chromium in groundwater on the islands is dominated by Cr VI.]

Based on HDOH Safe Drinking Water Branch data from the years 2000-2010, the natural, background concentration of total chromium in the basalt aquifers of Hawai‘i ranges from <2µg/L to approximately 15 µg/L (Table 1, see also Figure 1). Total chromium was below the upper-bound, cancer-based action level for Cr VI of 4.3 µg/L in 93% to 100% of the samples collected from the Big Island, Maui and O‘ahu. Eighty-percent of the samples from Kaua‘i were below 4.3 µg/L. None of the samples exceeded the noncancer action level for Cr VI of 20 µg/L noted above. The concentration of chromium in groundwater is in general lower in areas of relatively recent and unweathered basalt (e.g., Big Island) and somewhat higher in areas of older and more intensely weathered basalt (e.g., Kauai). This is due to increased weathering and leaching of chromium and other metals from the basalt and overlying soil.

Industrial Use of Chromium and Chromium VI

Chromium is used for making steel, chrome plating, dyes and pigments as well as in leather tanning and wood preservation (IETEG 2005). Products that contain Cr(VI) include paints, pigments, inks, fungicides, and wood preservatives. Chromium VI was also used in the past as a corrosion inhibitor. The release at the PG&E site in Hinkley, California was related to the disposal of cooling tower water treated with Cr VI into unlined ponds in the 1950s and 1960s (CalEPA 2007).

The industrial use of hexavalent chromium in Hawai‘i is very limited. No significant plumes of Cr VI-contaminated groundwater have been identified. Chromium was not used as an agricultural pesticide aside from wood treatment. Leaching of chromium from treated wood and potential impacts on groundwater is considered to be insignificant. In particular, there are no known industrial sources of Cr VI in Hawai‘i that could lead to widespread contamination of groundwater.

Note that the naturally occurring level of total chromium (including Cr VI) in the groundwater of Hawai‘i, as well as other areas, is significantly lower than contamination typically associated with industrial releases of hexavalent chromium (see Figure 1). For example, the concentration of Cr VI in contaminated groundwater associated with the PG&E Chromium VI case in Hinkley, California, exceeded 3,000 µg/L in the source area (PG&E 2007). A regional, natural background level of 3.1 µg /L Cr VI in groundwater is being used to map and monitor the edge of the plume (95th percent upper threshold limit).

Dietary Exposure to Chromium

Both Cr III and Cr VI are naturally occurring in foods, although total chromium is expected to be dominated by Cr III. Dietary sources of chromium include lean meats, cheese, whole grain breads and cereal (Roussel et al. 2007). Cr III is an essential nutrient in the human diet. The follow information is provided in the USEPA Toxicological Review for chromium (USEPA 1998):

- Adults in the United States are estimated to ingest approximately 60 µg/day of chromium from food;
- The National Research Council reports a safe and adequate daily dietary intake for chromium of 50-200 µg/d, corresponding to 0.71-2.9 µg/kg/day for a 70 kg adult;
- The US Food and Drug Administration recommends a dietary Reference Daily Intake for chromium of 120 µg/d (DHHS, 1995).

The concentration of total chromium in wheat has been reported to be several hundred parts-per-billion (in Soares et al. 2010). Hexavalent chromium is generally assumed to be reduced to trivalent chromium in plants. Although data are limited, a small percentage of the Total Chromium in food is likely to be in the form of Cr VI. The relative proportion of Cr VI in foods has been reported to be up to 10% of total chromium in breads (Soares et al. 2010). If representative of foods in general, this suggests a dietary intake of Cr VI of 5 to 20 µg/day (based on NRC safe and adequate dietary intake).

Toxicology and Toxicity Factors

Chromium III is an essential nutrient and is not toxic at levels typically found in nature. Chromium VI is more water soluble, easily enters living cells and is much more toxic than Chromium III. In 2010 the USEPA published a draft, human health assessment for Cr VI (USEPA 2010a). The study is currently under peer review and public comment.

Noncancer Risks

In animal laboratory tests exposure to Cr VI has been observed to cause cellular changes to liver, small intestine and lymph nodes. A noncancer, oral Reference Dose (RfD) for Cr VI of 0.003 mg/kg-day is presented in the USEPA Integrated Risk Information System database (IRIS, USEPA 2010b) and referred to in the 2010 edition of the USEPA *Regional Screening Level* guidance (2010c). The basis of the RfD is summarized in an earlier review of Cr VI toxicity (USEPA 1998). The USEPA referred to an RfD for Cr VI of 0.005 mg/kg-day prior to the 1998 study. As discussed in a 2010 review of existing drinking water standards, this reference dose forms the basis of the current Maximum Contaminant Level (MCL) for Total Chromium (USEPA 2010d, see also next section).

Confidence in the current USEPA RfD for Cr VI of 0.003 mg/kg-day is stated in the IRIS database to be low. A composite uncertainty factor of 900 was used to generate the RfD. An alternative RfD of 0.0002 mg/kg-day was presented in a 2008 review of Cr VI toxicity published by the National Toxics Program with an associated uncertainty factor of 1,000 (USDHHS 2008). The more recent, 2010 USEPA draft, human health assessment for Cr VI proposes an RfD of 0.0009 mg/kg-day for hexavalent chromium and incorporates a composite uncertainty factor of 100 (USEPA 2010d). Confidence in the draft, revised RfD is higher than for the current RfD. This suggests that the accuracy of drinking water action levels based on the RfD will also be relatively high.

Cancer Risks

Chromium VI has been demonstrated to cause cancer of the small intestine in mice at higher doses by the oral route of exposure (USDHHS 2008). The USEPA toxicity review of Cr VI (USEPA 2010a) references an oral Cancer Slope Factor (CSF) for Cr VI of 0.5 $(mg/kg\text{-}day)^{-1}$, based on a study published by the state of New Jersey (NJDEP 2009). The study found Cr VI to be carcinogenic in cases where laboratory animals were exposed to high concentrations of Cr VI in their drinking water (>14,300 µg/L) for two years. The New Jersey CSF is also referred to in the USEPA *Regional Screening Levels* guidance to develop risk-based, soil and water screening levels (USEPA 2010c). As stated in the document supporting the New Jersey CSF, there is significant uncertainty in application of the CSF for very small doses of Cr VI over long periods of exposure (NJDEP 2009):

> "The USEPA default procedure for calculation of cancer potency that was employed herein linearly extrapolates across 5 orders of magnitude of cancer incidence from the data-based

> benchmark incidence rate (BMR) of 0.1 to estimate the dose at 1×10^{-6} (one-in-a million) cancer incidence. The shape of the dose-response function is not known below the range of the observed data, and the linear extrapolation across so large a range carries significant uncertainty."

Because Cr VI was also found to be mutagenic, USEPA guidance recommends that an additional, Age-Dependent Adjustment Factor (ADAF) be incorporated into equations for calculation of cancer-based action levels (USEPA 2010a). The USEPA Regional Screening Level for Cr VI in tap discussed in the following section incorporates an ADAF of 10.

Use in Developing Drinking Water Action Levels

The draft, 2010 USEPA noncancer RfD reflects a relatively high degree of certainty and is useful for estimation of an upper-bound action level for Cr VI. The Cancer Slope Factor for Cr VI requires significant extrapolation from high-dose animal studies for estimation of risk posed by long-term, low-dose exposures. The resulting action levels serve as very conservative, lower-bound, risk-based goals for the range of acceptable drinking water action levels. Use of the noncancer RfDs and cancer-based CSFs in published, risk-based standards and action levels for Cr VI in drinking water is discussed in the following sections.

Current USEPA Standards and Screening Levels

USEPA Drinking Water Standard

Table 1 summarizes existing drinking water standards, goals and screening levels for Total Chromium and Cr VI. The USEPA provided a review of existing drinking water standards in a 2010 notice to the Federal Register (USEPA 2010d). The current USEPA and Hawai‘i DOH drinking water standard for chromium is 100 µg/L, based on measured Total Chromium. The basis for the standard is a pre-1998, noncancer RfD for Cr VI of 0.005 mg/kg-day and a target Hazard Quotient of 1.0 (see above; USEPA 2010d). Note that this contradicts and corrects recent media statements about the lack of a drinking water standard for hexavalent chromium. The existing standard is in fact based on an assumption that 100% of the total chromium in drinking water is in fact Cr VI, as recently acknowledged in a USEPA Fact Sheet (USEPA 2011). As discussed in the 2010 USEPA review, the initial risk-based concentration for exposure to Cr VI was reduced by 30% to take into account exposure from other sources, including diet (i.e., Relative Source Contribution of 70% assumed).

The drinking water standard is based on single value for Total Chromium instead of separate standards for both Chromium III and Chromium VI due in part to the expense and difficulty in testing for Chromium VI at standard, commercial laboratories. Among other issues, water samples to be tested for Chromium VI must be delivered to the laboratory within twenty-four hours for analysis to minimize potential conversion to Chromium III after sampling. Reporting Total Chromium, and conservatively assuming that 100% of the chromium is Cr VI, is a more cost-efficient approach for regulating Cr VI in drinking water.

The USEPA concluded in their 2010 review of drinking water standards (USEPA 2010d) that the current standard for Total Chromium is still considered to be protective of human health, based on existing, published studies. When the current assessment (USEPA 2010a) is finalized, however, USEPA will review the conclusions and consider all relevant information to determine if the current standard should be revised.

Other Published Screening Levels and Goals

A non-enforceable, risk-based, tapwater screening level for Cr VI of 0.043 µg/L is published in the USEPA Regional Screening Levels (RSL) guidance (USEPA 2010c). The screening level is based on the New Jersey CSF of 0.5 $(mg/kg\text{-}day)^{-1}$, discussed above and a target excess cancer risk of 10^{-6} (one-in-a-million). The screening level also incorporates an age-sensitivity safety factor of "10" in order to take into account potential mutagenic effects posed to young children by Cr VI. A noncancer-based tapwater screening level for Cr VI of 110 µg/L is also presented in the USEPA RSL guidance, based on the current IRIS RfD of 0.003 mg/kg-day presented in the USEPA IRIS database and a target Hazard Quotient of 1.0. Although not yet incorporated into the USEPA RSLs, use of the revised, draft RfD for Cr VI of 0.0009 mg/kg-day (USEPA 2010a) would reduce the noncancer-based tapwater screening level from 110 µg/L to 33 µg/L. Incorporation of the updated RfD in the model used to develop the current drinking water standard of 100 ug/L would lower the standard to approximately 20 ug/L (assumes 30% additional dietary source of Cr VI).

The California's Office of Environmental Health Hazard Assessment (OEHHA) has proposed a draft, non-enforceable, Public Health Goal (PHG) of 0.02 µg/L for Cr VI in drinking water (CalEPA 2010). The PHG is based on the New Jersey CSF of 0.5 (mg/kg-day)-1, a one-in-a-million carcinogenic health risk and a slightly modified approach for the inclusion of age-dependent adjustment factors in the risk equations in comparison to the USEPA tapwater RSL. The California PHG document also recommends a noncancer-based PHG of 2 µg/L, based on the RfD of 0.0002 mg/kg-day presented in the 2008 NTP report referenced above (USDHHS 2008). The NTP RfD incorporates a relatively high uncertainty factor (composite UF = 1,000) in comparison to the RfD of 0.0009 mg/kg-day and subsequently proposed in the draft, USEPA review of Cr VI toxicity (composite UF = 100).

Comparison of Action Levels to Natural Background

A summary of the range of potential health-based action levels for Cr VI in drinking water is provided in the table of the main text and noted on Figure 1. Although data are limited, the geochemistry of the island aquifers (e.g., well oxygenated and neutral pH) suggests that chromium in the groundwater is likely to be dominated by Cr VI. Assuming this is the case, the naturally occurring concentration of Cr VI in groundwater across the islands falls within the range of risk-based, drinking water action levels for Total Chromium noted above. In most cases, the concentration of Cr VI is likewise anticipated to fall at or below USEPA's conservative,

upper-bound action level of 4.3 µg/L for potential cancer risk. Long-term exposure to the trace levels of Cr VI likely to be naturally present in Hawaii's groundwater (i.e., based on Total Chromium levels) have not been demonstrated to pose significant health risks in epidemiological studies or laboratory studies.

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Island	*Total Number of Samples	Number of Samples Within Noted Range of Total Chromium (µg/L)					Maximum Reported Total Chromium (µg/L)
		≤2.0	>2.0-4.3	>4.3-10	>10-20	>20	
Big Island	424	322	88	14	0	0	8
Maui	304	269	35	0	0	0	4
O'ahu	695	488	161	29	17	0	14
Kauai	308	110	134	61	3	0	11

*Includes multiple samples from some sampling points, mixed pre- and post wellhead data.

Island	*Total Number of Samples	Number of Samples Within Noted Range of Total Chromium (µg/L)					Maximum Reported Total Chromium (µg/L)
		<2.0	>2.0-4.3	>4.3-10	>10-20	>20	
Big Island	424	76%	21%	3%	0%	0%	8
Maui	304	88%	12%	0%	0%	0%	4
O'ahu	695	70%	23%	4%	2%	0%	14
Kauai	308	36%	44%	20%	1%	0%	11

Table 1. Summary of Total Chromium in groundwater in Hawai'i (2001-2010).

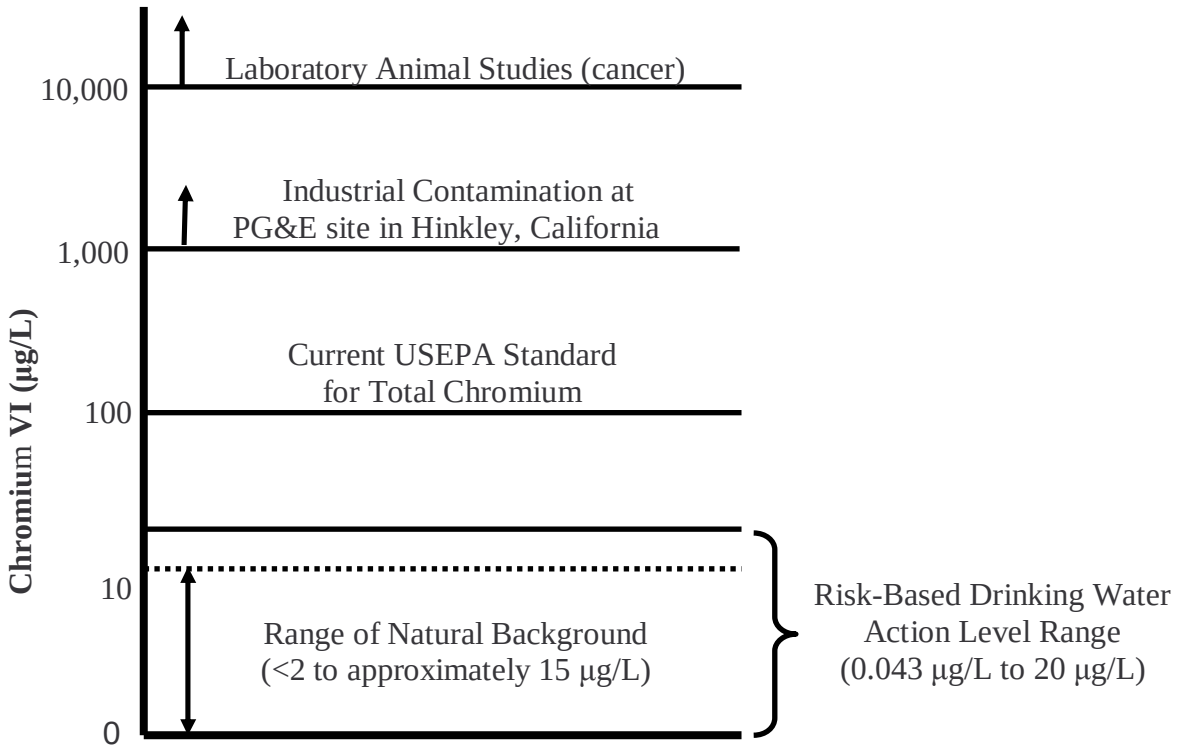

Figure 1. Comparison of natural background Total Chromium in groundwater across Hawai‘i to risk-based range of drinking water action levels and other criteria.

APPENDIX 9

UPDATES TO 2009 EHE GUIDANCE

Hawai'i DOH
Fall 2011

Hawai'i DOH
Fall 2011

NEIL ABERCROMBIE
GOVERNOR OF HAWAII

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In reply, please refer to:
File: EHA/HEER Office

2011-716-RB

December 2011

To: Interested Parties

From: Roger Brewer, Ph.D., Environmental Risk Assessor, HEER

Subject: *Screening for Environmental Hazards at Site with Contaminated Soil and Groundwater*, Fall 2011 Updates [Revised January 2012, see Note #9 in the attachment]

This technical memorandum summarizes updates to Environmental Action Levels (EALs) published by the Hazard Evaluation and Emergency Response (HEER) office of the Hawai‘i Department of Health (HDOH). The background and development of the EALs is described in the HEER office guidance *Screening for Environmental Hazards at Site with Contaminated Soil and Groundwater* (“EHE” guidance; HDOH 2011). The Fall 2011 updates replace and take precedence over earlier editions of the EALs.

A detailed review of revisions to the 2009 EALs is provided in the attachment to this memorandum and in the appendices of the updated EHE guidance. Significant revisions to the EALs include:

- Soil action levels presented in EAL Surfer for **dioxins** revised to reflect June 2010 updates (HDOH 2010a);
- Reference to October 2010 update of categories for **arsenic-**contaminated soil added to Surfer notes box (HDOH 2010b);
- Soil action levels for **aldrin and dieldrin** revised to reflect higher confidence in noncancer studies and common co-occurrence in termiticide-treated soil in the absence of other chemicals (final Tier 1 soil action levels increased);
- Target noncancer Hazard Quotient for **thallium** adjusted to 1.0 to help take into account natural background presence of thallium in soil;
- Inhalation toxicity factor (Reference Concentration) and target risk for **“TPH” in indoor air and soil gas** revised based on soil gas study carried out by HEER office (increased TPH soil gas action level for vapor intrusion hazards);
- **Physiochemical constants** for chemicals updated to reflect change in USEPA Regional Screening Level guidance (HDOH EALs not significantly affected);
- **Sorption coefficient** used to define “low-mobility chemicals” revised downward from 30,000 cm^3/g to 5,000 cm^3/g (final Tier 1 action levels for several **PAHs** and **organochlorine pesticides** increased to more appropriately reflect direct-exposure action level, rather than leaching based action level);

- Alternate Volatilization Factor (estimates vapor emissions from soil) that takes into account poor air flow in trenches used to calculate **VOC soil action levels for trench and construction workers** (USEPA 2002, see Appendix 2). Reduced previous action levels by a factor of approximately four.
- Updates to **background metals in soils** added (see Appendix 1, Section 7);
- Soil ecotoxicity action levels eliminated (increase in action levels for some **metals** to reflect direct exposure action levels, rather than generic, ecotoxicity based action levels);
- Aquatic (and associated groundwater) **acute toxicity action levels for PAHs** updated to reflect generic action level for PAHs (increased some groundwater action levels).
- Additional discussion on development of **Tier 1 vs Site-Specific Soil Action Levels** provided (Volume 1, Section 4.1);
- Additional discussion of site-specific evaluation of **leaching of contaminants from soil** (Volume 1, Section 4.3.3 and Appendix 1, Section 4.4);
- Additional discussion on distinguishing **background levels of VOCs in indoor air** from vapor intrusion added (Volume 1, Section 4.5);
- Expanded discussion of **vapor intrusion models and action levels** included in Appendix 1, Chapter 2;
- HDOH technical memorandum discussing the natural occurrence of **hexavalent chromium in groundwater** added to Appendix 8;
- Note regarding the presence of apparently natural, **background lead in caprock sediment groundwater** above action levels added to Volume 1, Section 4.3);
- **EAL Surfer** updated.

A summary of the more significant changes to the 2009 Tier 1 EALs is provided in Table 1 (organochlorine pesticides), Table 2 (metals) and Table 3 (Total Petroleum Hydrocarbons in soil gas). Groundwater action levels were not affected in this update of the EALs. These updates reflect site-specific studies carried out in Hawai‘i by HEER staff and environmental consultants since publication of the 2009 EHE guidance. This includes reviews of toxicity factors, soil batch tests for evaluation of leaching hazards, carbon range soil gas data from petroleum-contaminated sites and background metal concentrations in soils. Separate reports on background metals in soils and the measurement, chemistry and toxicity of petroleum vapors in soil gas are to be published separately by the HEER office.

The EHE document and associated EALs will be revised and updated on a regular basis. Comments and suggestions from the general public are welcome at any time. Updates will be posted to the HDOH EHE website and notification sent to persons on the EHE mailing list. Workshops to present and discuss the EALs will also be held periodically. To provide comments or be included on the mailing list for updates and workshop announcements, please contact:

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Fall 2011

Table 1. Updates to Tier 1 EALs for Organochlorine Pesticides (2009 EAL noted in parentheses).

Chemical	Groundwater IS a Potential Source of Drinking Water (mg/kg)		Groundwater is Not a Potential Source of Drinking Water (mg/kg)	
	Surface Water <150m	**Surface Water >150m**	**Surface Water <150m**	**Surface Water >150m**
ACENAPHTHENE	120 (20)	120 (20)	120 (23)	140 (140)
ALDRIN	0.92 (0.029)	0.92 (0.029)	0.92 (0.029)	0.92 (0.029)
ANTHRACENE	4.3 (2.5)	4.3 (2.5)	4.3 (2.5)	4.3 (2.5)
BIPHENYL, 1,1-	10 (0.52)	10 (0.52)	10 (5.2)	10 (5.2)
DIELDRIN	1.5 (0.003)	1.5 (0.007)	1.5 (0.003)	1.5 (0.03)
ENDOSULFAN	18 (0.032)	18 (0.12)	18 (0.032)	18 (0.12)
ENDRIN	3.7 (0.004)	3.7 (0.06)	3.7 (0.004)	3.7 (0.06)
FLUORENE	100 (7.3)	130 (130)	100 (7.3)	130 (130)
HEPTACHLOR EPOXIDE	0.053 (0.003)	0.053 (0.046)	0.053 (0.003)	0.053 (0.046)
PHENANTHRENE	69 (11)	69 (18)	69 (11)	69 (18)
TRIFLURALIN	24 (14)	24 (14)	54 (32)	54 (32)

Table 2. Updates to Tier 1 EALs for Metals.

Chemical	Residential			Commercial/Industrial		
	2009 (mg/kg)	**2011 (mg/kg)**	**2011 Basis**	**2009 (mg/kg)**	**2011 (mg/kg)**	**2011 Basis**
ANTIMONY	6.3	6.3	DE	40	82	DE
ARSENIC (total)	20	*24	BG	20	*24	BG
BARIUM	750	1,000	GC	1,500	2,500	GC
BERYLLIUM	4.0	31	DE	8.0	150	DE
CADMIUM	12	14	DE	12	120	BG
CHROMIUM (Total)	500	*1,100	BG	500	*1,100	BG
CHROMIUM III	750	*1,100	BG	750	*1,100	BG
CHROMIUM VI	8.0	29	DE	8.0	480	DE
COBALT	40	180	DE	80	180	DE
COPPER	230	626	DE	230	2,500	DE
LEAD	200	200	DE	800	800	DE
MERCURY	4.7	4.7	DE	10	61	DE
MOLYBDENUM	40	78	DE	40	1,000	DE
NICKEL	150	760	DE	150	870	DE
SELENIUM	10	78	DE	10	1,000	DE
SILVER	20	78	DE	40	1,000	DE
THALLIUM	1.0	0.78	DE	13	10	DE
VANADIUM	110	*770	BG	200	1,000	DE
ZINC	600	1,000	GC	600	2,500	GC

DE: Direct Exposure; BG: Background; GC: Gross Contamination. *Estimated Upper Bound of naturally occurring metal in volcanic soils. Natural background concentration may be higher in some areas. Thallium action level may be below natural background in some areas (likely to be natural background if detected and no known, past releases of thallium salts at site). Background metals likely to be lower in carbonate-rich, coast sediments and soils. Compare soil data for vanadium directly to direct-exposure action levels if a release of one or more of these metals is known to have occurred in carbonate-rich, coastal soils.

Table 3. Updates to TPH soil gas action levels.

Chemical	Reference Concentration (ug/m^3)		Soil Gas Action Level (ug/m^3)			
			2009		2011	
	2009	2011	Residential	Commercial/ Industrial	Residential	Commercial/ Industrial
TPH(gasolines)	50	126	26,000	73,000	130,000	370,000
TPH(middle distillates)	110	126	57,000	160,000	130,000	370,000

TPH = Total Petroleum Hydrocarbons; middle distillates includes diesel fuels.

ATTACMENT

Technical Overview of Fall 2011 Updates to 2009 HDOH/HEER Tier 1 EALs

HDOH 2011, *Screening for Environmental Hazards at Sites with Contaminated Soil and Groundwater* (December 2011), Hawai'i Department of Health, Hazard Evaluation and Emergency Response, http://hawaii.gov/health/environmental/hazard/index.html

1. Adjustment of target risk and soil action levels for aldrin and dieldrin. Soil action levels for aldrin and dieldrin revised to reflect higher confidence in noncancer studies. Updated action levels are noted in Table 1 of the cover memo. Aldrin was sometimes used as an alternative to Technical Chlordane as a termiticide for treatment of soil around and under wooden structures. Dieldrin is a breakdown product of aldrin. The target noncancer Hazard Quotient for each chemical was adjusted to 0.5, based on the common co-occurrence in termiticide-treated soil in the absence of other chemicals and a target, cumulative Hazard Index of 1.0. The target cancer risk was adjusted upwards to 10^{-4}.

Cumulative risk should be evaluated if other contaminants are identified in the soil at concentrations that approach or exceed their respective, direct-exposure action levels (e.g., Technical Chlordane). Lead in the soil around structures (e.g., from lead-based paint) should be evaluated separately.

2. Residential Soil Action Level for Lead. The 2009 Tier 1 soil action levels for lead in residential soils ("Unrestricted" land use) was 200 mg/kg. This was based on a published, plant toxicity screening level in soil (see Appendix 1, Table A and B series in 2009 document). An action level of 400 mg/kg was presented in the document for residential, direct-exposure hazards. This action level was based on a "Preliminary Remediation Goal (PRG)" (more recently referred to as the "Regional Screening Level (RSL)") published by the USEPA in the 1990s and still presented in their 2011 RSL guidance (USEPA 2011a).

The USEPA PRG/RSL is intended to reflect a maximum, target lead blood level in children of 10 ug/dl. Recent USEPA guidance recommends that this target level be reduced to 5 ug/dl (USEPA 2011b). In order to reflect this change, the residential direct-exposure soil action level for lead in this update of the HEER EHE guidance has been reduced from 400 mg/kg to 200 mg/kg. This is intended to serves as an interim action level until such time that the USEPA PRG for lead in soil is formally updated. Note that the final Tier 1 soil action level for lead remains unchanged at 200 mg/kg, even though the 2009 soil ecotoxicity action level for lead of 200 mg/kg has been dropped (see note Number 5). The commercial/industrial soil action level for lead of 800 mg/kg was not changed (based on USEPA commercial/industrial PRG/RSL).

3. Update of chemical sorption coefficients. Sorption coefficients (koc) presented in Appendix 1, Table H of the EHE guidance were updated to reflect revisions to generic koc values used in the June 2011 edition of the USEPA Regional Screening Levels guidance (USEPA 2011a). Coefficients used in the 2009 EALs were based on an earlier edition of the same guidance. Sorption coefficients are included in models used to generate soil action levels for direct exposure, vapor intrusion and leaching hazards. The updates to the sorption coefficients resulted in only minor changes to the soil action levels.

4. Default sorption coefficient (koc) used to define "low mobility" chemicals in soil leaching models reduced from 30,000 cm^3/g to 5,000 cm^3/g. Sorption coefficients (koc) are use to estimate how strongly a chemical will bind to organic carbon in soil and are key components of soil leaching models. Chemicals with low sorption coefficients, like MTBE (11 cm^3/g) and PCE (95 cm^3/g), are highly mobile and a significant proportion of the chemical will preferentially dissolve into pore water and leachate, posing a potential threat to underlying groundwater. Published koc values are multiplied by the assumed organic carbon content of the soil to calculate an adjusted, "Kd" coeffiecient for modeling (e.g., Kd = koc x 0.2% organic carbon). Chemicals with high sorption coefficients, like PCBs (131,000 cm^3/g) and chlordane (87,000 cm^3/g), will become tightly bound to soil particles and relatively immobile in soil. These chemicals do not pose significant risk to groundwater unless pure product manages to reach the water table.

The approach used to develop soil action levels for potential leaching hazards is discussed in Appendix 1 of the EHE guidance. A generic algorithm is used to develop action levels for chemicals with an assumed moderate to high mobility. Chemicals with a sorption coefficient greater than 30,000 gm/cm^3 were considered to be very low mobility and not a significant threat to groundwater. Leaching based soil action levels were set at that chemicals theoretical saturation limit in soil (i.e., the maximum amount of the chemical that could be sorbed onto soil particles or dissolved in pore water before free product began to appear).

In 2007 the HEER office published guidance on the use of laboratory "batch tests" to more accurately evaluate the leachability of chemicals in soil on a site-specific basis (HDOH 2007). The specific batch test used is referred to as the Synthetic Precipitation Leaching Procedure or "SPLP" test. The test can be used to directly measure the Kd sorption coefficient (or more accurately a *desorption* coefficient) for a chemical in the soil rather than relying on generic factors and assumed soil properties, as is done for the soil action levels.

Since 2007 time batch test data have consistently indicated that aged-chemicals in soil are much less mobile and pose a much lower threat to groundwater than the generic sorption coefficient and associated action levels would otherwise suggest. A significant number of batch test have in particular been carried out on soil contaminated with organochlorine pesticides, such as chlordane, dieldrin and aldrin. These tests suggest that the published sorption coefficients and generic leaching model used *over predict* contaminant mobility and potential impacts to groundwater by at least an order of magnitude.

Examples of default versus measured sorption coefficients from studies in Hawai'i are provided below (measured as "Kd," see HDOH 2007). A Kd value greater than 20 indicates that the chemical is essentially "immobile."

Chemical	**[1]Published Koc Value (cm^3/g)**	**[2]Modeled Kd Value (cm^3/g)**	**[3]Measured Kd Value (cm^3/g)**
Assumed Moderate- to High-Mobility Chemicals			
[4]Ametryn	450	0.45	30
[4]Atrazine	230	0.23	6.9
[6]Benzene	170	0.17	8.4 to 203
[7]Dieldrin	11,000	11	650-690

[4]Diuron	136	0.14	86
[4]Trifluralin	9,680	9.7	5,000
Assumed Low-Mobility Chemicals			
[7]Aldrin	106,000	106	5,800-6,600
[5]Arsenic	(not applicable)	29?	2,100 to 19,000
[8]Chlordane	87,000	87	4,200-7,800
[4]Dioxins	257,000	257	10,000-51,000

1. Default koc value used in leaching models (from USEPA 2011a); refer to EHE guidance Appendix 1, Table H (HDOH 2011).
2. Calculated Kd used in EAL soil leaching model = koc x assumed Total Organic Carbon fraction of 0.001.
3. Based on results of SPLP batch test for soil samples collected at the noted site (HDOH 2007).
4. *Site Investigation Report and Environmental Hazard Evaluation, East Kapolei II Pesticide Mixing and Loading Site,* Enviroservices & Training Center, LLC, March 2010.
5. *Remedial Alternatives Analysis & Response Action Report*, Former Ka‘u Agribusiness, ASCI-ERM, November 2008. Leaching based soil action levels for arsenic not included in EHE guidance; site-specific batch test data required. Noted Kd from USEPA SSL and RSL guidance (USEPA 1996, 2011a).
6. *Remedial Investigation Report, Former GASCO Facility*, Weston Solutions, April 1, 2009.
7. *Results of Leachability Testing for Organochlorine Pesticides in Soil using the Synthetic Precipitation Leaching Procedure, Earhart I-4 Neighborhood, Hickam Air Force Base, Hawai‘i*, Tetra Tech, December 18, 2009.
8. *Removal Action Plan and Environmental Hazard Evaluation, Ironwoods at Kailua,* Tetra Tech EM, Inc., July 18, 2011 (draft).

As can been seen from the table, soil action levels calculated using generic sorption coefficients and assumed Kd values tend to significantly over predict the mobility of the chemical in soil. Although not routinely measured, organic carbon in the soils is typically 1% or less and does not by itself explain the increased Kd value. The higher Kd value is instead most likely associated with secondary sorption onto or diffusion into clays, as well as an increased difficulty in *desorption* of an aged chemical in soil from organic carbon.

Based on soil SPLP batch test data collected in Hawai‘I, the default sorption coefficient (koc) used to define "low mobility" chemicals in soil leaching models was reduced from 30,000 cm^3/g to 5,000 cm^3/g. The theoretical soil saturation concentration is then used as the default leaching based soil action level for potential leaching hazards for all chemicals with a published koc that exceeds this value. This has proven to be a useful approach to verifying the leachability of presumed low-mobility chemicals in soil. This significantly increased the leaching based action levels for several chemicals, especially PAHs and organochlorine pesticides. Chemicals affected include: Acenaphthene, Anthracene, 1,1 Biphenyl, Endosulfan, Endrin, Fluorene, Heptachlor, Heptachlor Expoxide, Phenanthrene, Trifluralin. The following table summarizes the changes in the 2009 versus 2011 action levels (2009 action level noted in parentheses):

	Groundwater IS a Potential Source of Drinking Water		**Groundwater is Not a Potential Source of Drinking Water**	
***Chemical**	**Surface Water <150m**	**Surface Water >150m**	**Surface Water <150m**	**Surface Water >150m**
ACENAPHTHENE	120 (20)	120 (20)	120 (23)	170 (200)
ANTHRACENE	4.3 (2.5)	4.3 (2.5)	4.3 (2.5)	4.3 (2.5)
BIPHENYL, 1,1-	210 (0.52)	210 (0.52)	210 (5.2)	210 (5.2)
DIELDRIN	30 (0.003)	30 (0.007)	30 (0.003)	30 (1.2)
ENDOSULFAN	18 (0.032)	18 (0.12)	18 (0.032)	18 (0.12)
ENDRIN	30 (0.004)	30 (0.07)	30 (0.004)	30 (0.07)

FLUORENE	100 (7.3)	370 (460)	100 (7.3)	460 (560)
HEPTACHLOR EPOXIDE	12 (0.003)	12 (0.046)	12 (0.003)	12 (0.046)
PHENANTHRENE	69 (11)	69 (18)	69 (11)	69 (18)
TRIFLURALIN	24 (14)	24 (14)	54 (32)	54 (32)

*Chemicals listed in the EHE guidance with a koc value between 5,000 and 30,000 cm^3/g . *Reduction* of some action levels (e.g., fluorine) reflects a significant *reduction* of the published koc value used in the model, based on updates to the USEPA RSLs. This offset use of the alternative saturation model.

These changes are reflected in Table 1 in main technical memorandum. Note that a lower action level in Table 1 than presented above reflects use of the direct-exposure action level over leaching based action level for final, Tier 1 EAL. The above table only summarized changes to leaching based soil action levels, while Table 1 comprehensively summarizes changes to all categories of action levels and presents the lowest. Site-specific SPLP batch tests are recommended in cases where the saturation level is exceeded (see HDOH 2007).

5. Naturally occurring, background levels of metals in soil updated. The HEER office undertook a review of background concentrations of metals in soil in 2011 (to be published in late 2011 or early 2012). The estimated Upper Bound concentration of metals in volcanic soils was incorporated into Appendix 1 of the EHE guidance for consideration in selection of final, Tier 1 EALs. Updated action levels are noted in Table 2 of the cover memo. Target noncancer Hazard Quotient for **thallium** adjusted to 1.0 to help take into account natural background and lack of available soil data.

The Background Threshold Value noted in Table 2 reflects the maximum-reported concentration of the metal in the samples compiled for the study. *Higher* concentrations are possible in volcanic soils due to localized, metal-rich volcanic deposits or due to testing of small aliquots of discrete soil samples with non-representative nuggets of metal-rich, iron hydroxides. Background metals are likely to be *lower* in carbonate-rich, coast sediments and soils. Compare soil data for nickel, thallium and vanadium directly to direct-exposure action levels if a release of one or more of these metals is known to have occurred in carbonate-rich, coastal soils.

Naturally occurring trace metals in the volcanic and caprock soils of Hawai‘i are not significantly bioavailable and do not pose a risk to human health. Similar trace metals are used in the production of steel and other alloys. With perhaps the exception of lead, these trace metals *will not be released to soil in a bioavailable form* upon use or even degradation (e.g., rusting) of metallic objects (e.g., tanks, heavy equipment, etc.). Toxicity factors and associated, risk-based soil action levels are likewise based on soluble, highly bioavailable forms of these metals (e.g., thallium salts). *The soil action levels do not apply to metals in soil likely to be associated with natural background or degraded, metallic objects.*

6. Soil ecotoxicity action levels discontinued. The use of generic, published soil action levels for terrestrial ecotoxicity has always been a contentious issue, due to site-specific differences in soil type and more importantly pertinent, ecological receptors. An internal HEER review also indicated that naturally occurring concentrations of metals in the iron-rich, volcanic soils of Hawai‘i often exceed generic, ecotoxicity soil screening levels developed for use in soils more typical of granitic, continental geologic settings (to be published in 2011or 2012). In Hawai’i these metals are tightly bound to soil particles (e.g., iron hydroxides) and not significantly toxic.

This negates the use of generic screening levels developed outside of the state. Site-specific assessment will instead be required in rare cases where a sensitive ecohabit is present.

7. Childhood Adjustment Factor deleted from vapor intrusion models. Earlier editions of the USEPA Residential Preliminary Remediation Goals (PRGs, 2004 and earlier) included a "Childhood Adjustment Factor" of 0.791 for indoor air PRGs (carcinogens only; reduced initially calculated goal by approximately 20%). This adjustment factor was incorporated into HEER EAL models used to generate indoor air, soil gas, soil and groundwater action levels for vapor intrusion (not shown in Appendix 2 Indoor Air action level equations). Use of the adjustment factor was discontinued in post-2004 updates of the USEPA PRGs due to the already conservative nature of the model assumptions (now referred to as Regional Screening Levels; see USEPA 2011a). Eliminating the adjustment factor increased indoor air, soil gas, soil and groundwater residential action levels by approximately 20% in the Fall 2011 update of the EHE guidance.

8. Tapwater risk-based action levels corrected to only consider inhalation of vapors during showering for volatile chemicals (action levels not significantly affected).

9. Noncancer RfC for TPH revised based on carbon range data for soil gas samples collected at petroleum release sites (same RfC used for both gasolines and middle distillates). Target noncancer Hazard Quotient revised to 1.0, based on overwhelming predominance of non-BTEX/PAH, "TPH" compounds in petroleum vapors. TPH soil gas action levels significantly increased. Refer to Appendix 1, Chapter 6 of the EHE/EAL guidance document for details. [Note: Risk-based action levels for TPH were revised in January 2012 to correct an error in calculation of the carbon range-weighted TPH toxicity factors. See Chapter 6 of Appendix 1.]

The HEER office is currently reviewing laboratory analytical methods for reporting TPH in soil gas. Field methods for the collection of soil gas samples presented in the HEER office Technical Guidance Manual will also be updated in 2012.

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