2013-14 STATE WIDE PESTICIDE SAMPLING PILOT PROJECT
WATER QUALITY FINDINGS

A Joint Investigation by the Hawaii State Departments of Health and Agriculture

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PREPARED BY: STATE OF HAWAII DEPARTMENT OF HEALTH HAZARD EVALUATION AND EMERGENCY RESPONSE OFFICE

Executive Summary

Surface water samples collected from 24 sites statewide were analyzed for a total of 136 different pesticides or breakdown products. All locations had at least one pesticide detection. Only one pesticide, a historically used termiticide exceeded state and federal water regulatory limits. Five other pesticide compounds were detected at levels exceeding the most conservative EPA aquatic life benchmark. All other pesticides detected were lower than the most stringent aquatic or human health guideline value.

These findings represent a snapshot in time from a single sampling event within watersheds with multiple upstream inputs. While they provide useful information about pesticide occurrence across different land uses, they may not be representative of typical conditions or identify specific sources.

Key findings:

- Every location sampled had a trace detection of one or more pesticides; however, the majority of these represented minute concentrations that fall below state and federal benchmarks for human health and ecosystems.

- Land use significantly impacted the number and type of pesticides detected. Urban areas on Oahu showed the highest number of different pesticides.

- Oahu's urban streams had the highest number of different pesticides detected. Manoa Stream at the University of Hawaii showed 20 different pesticides and breakdown products.

- Dieldrin, a termite treatment that has been banned from sale in Hawaii since 1980, exceeded State and Federal Water Quality standards in three urban locations on Oahu.

- Fipronil detected in Manoa Stream and Waialae Iki Stream exceeded aquatic life benchmarks for freshwater invertebrates. Fipronil is an insecticide commonly used in residential settings and applied by commercial pest companies to treat soil for termites.

- Atrazine and metolachlor, two restricted use herbicides, were detected on Kauai at agricultural sites downstream of seed crop operations. One location had levels that exceed aquatic life guidelines, but remain below regulatory standards.

- The number of pesticides detected in water samples on Hawaii Island was lower than that of Kauai and Oahu.

- Atrazine, a restricted use pesticide, was the most commonly found pesticide in the study. Of the sites tested, 80 percent had atrazine detections. Only two sites, one on Kauai, and one on Maui, reflected elevated concentrations suggestive of current use of atrazine. All of the remaining detections were trace level concentrations far below state and federal benchmarks.

- The pilot study tested stream bed sediment at seven sites and found glyphosate, in all samples. Glyphosate (trade marked as Roundup) is widely used for residential, commercial, agricultural and roadside weed management.

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The DOH Clean Water Branch Water Monitoring Section led the field sampling effort, using their Oahu and outer island staff to collect and ship many samples in a short time frame. Their knowledge of sites and local conditions was critical to effective site selection and access.

The Department of Agriculture Pesticide Division provided key information needed for selection of analytical suites, knowledge of pesticide use patterns, as well as fate and transport and labeling issues. Special thanks to Avis Onaga, for her careful review of restricted and current use pesticide information presented in the report.

USGS provided training in field collection methods, tremendous logistical and technical support as well as invaluable guidance on data interpretation. Special thanks to Stephen Anthony and Marcael Jamison, and their peers in the three USGS laboratories who shared their expertise and provided specialized analytical services for this project.

Introduction

In response to growing community concerns about possible offsite impacts of currently used pesticides on local communities and ecosystems, Hawaii Department of Health (HDOH) and the Hawaii Department of Agriculture (HDOA) used agency special funds to design and implement a pilot study to sample surface waters and sediments state wide. The agencies enlisted the help of the U.S. Geological Survey (USGS) to provide state of the art analytical services and expert technical assistance. To extend the reach of the project, USGS provided additional matching funds from their Cooperative Water Program.

The short-term goal of this joint sampling effort was to gather initial data on the types and concentrations of currently used pesticides detectable in surface water and sediment associated with a variety of differing land uses. The State of Hawaii has no ongoing stream monitoring program for pesticides and consequently there is very little information available to evaluate whether current pesticide use practices are resulting in off-site movement of pesticides into state waters. The data from this pilot study will provide preliminary information on the presence or absence of pesticide residue levels in surface waters.

Previous Pesticide Studies in Hawaii

While HDOH does not routinely monitor surface waters for currently used pesticides, research conducted by USGS provides key information about pesticide incidence and movement in surface waters in Hawaii.

USGS studies on Oahu and nationwide have shown a clear pattern of detections of pesticides in surface waters associated with pesticide use in agricultural and urban settings. As part of the 1999-2001 Water Quality on the Island of Oahu study, USGS tested surface waters for 47 different pesticides in three watersheds, including Waikele, Manoa and Waihee streams to compare how different land uses affected water quality (Anthony et al., 2004)[i]. Agriculture uses a combination of restricted use and general use pesticides, where urban users typically use only general use pesticides, as they do not require special licensing or expertise. These patterns can often be seen in the chemicals present in a particular stream. In addition, pesticides can behave differently in the environment because of their chemistry. Some chemicals degrade rapidly, others dissolve readily in water, infiltrating to ground water, where they may persist for decades, and still others bind tightly to soil particles and can be transported into streams by storm runoff. To better understand offsite movement of pesticides, the USGS sampling strategy compared storm water samples and samples during dry periods ("base flow" samples). Base flow to streams at or below the groundwater table is largely supplied by groundwater, though rainfall in upper parts of the basin may also provide flow.

Waikele stream was selected because it represented both urban and agricultural inputs, and the base stream flow is provided by groundwater from aquifers known to be contaminated with low levels of atrazine and bromacil from historic sugarcane and pineapple uses. In Waikele Stream, atrazine was detected at trace levels in 90% of base flow samples and 15% of storm water samples. The highest detection in these samples was 0.007 ppb, whereas the highest detection measured in groundwater in the same area was 0.112 ppb. Bromacil and diuron, herbicides frequently used in agricultural applications and detected in area groundwater, were also commonly found at trace levels in base flow samples. Three general use insecticides and two herbicides were detected more frequently and at higher concentrations in storm water, suggesting transport through surface runoff.

In Manoa stream, three general use insecticides were also frequently detected in storm water runoff at trace levels, and one general use herbicide, prometon, was frequently detected in base flow samples. A trace level of atrazine, estimated at 0.001 ppb, was found in 1 of 27 base flow samples. The patterns of detections of general use and restricted use pesticides mirror the land use patterns of the two stream systems.

Waihee Stream, located near Kahaluu, was sampled a single time in 1999 and showed no detections of any of the analytes.

In general, USGS found that agricultural herbicides were detected in base flow originating from groundwater, indicating long term residence and subsequent subsurface transport through groundwater, as compared with insecticides that were more frequently detected in storm events, indicating movement through runoff.

In 2012, the HDOH Clean Water Branch (CWB) conducted sampling at 28 stations on Kauai and 3 stations on Maui under the EPA Monitoring Initiative. These samples were analyzed for wastewater constituents, including about 10 common pesticides, and overall, showed low concentration detections of a few contaminants. This sampling found that 8 stations, including six locations in the Nawiliwili drainage on Kauai, had trace levels of atrazine ranging from 0.01 ppb to 0.04 ppb, far below EPA's proposed aquatic level of concern of 10 ppb. The other stations sampled did not show detectable levels of atrazine; however the detection limits were substantially higher (0.16 ppb).

Pesticide Analysis

The samples were tested for the full analytical suite of currently used pesticides and their breakdown products for which there are USGS methods available. These compounds include restricted and general use herbicides, insecticides and fungicides. One hundred and thirty six different pesticides were sampled in surface water and 121 in sediment. Two laboratory methods were used for the surface water analyses, *USGS National Water Quality Laboratory Schedules 2033 and 2060*[ii]. The analytical method for sediments is from the USGS Pesticides Fate Research Group (2012)[iii]. Glyphosate was measured by the USGS Kansas Water Quality Science Center using method 0-2141-09 for water samples and USGS method LCGS in sediment.[iv]

The USGS laboratory methods used for this study measure compounds at trace levels; commonly 10 to 1,000 times lower than drinking water standards and aquatic life guidelines. Therefore, estimated concentrations are included in the results for some compounds. The methods ensure high confidence that the flagged compounds are present, but have greater uncertainty about the precise value. Using these trace values helps to better understand what compounds are entering Hawaii's waterways, and are useful to compare contaminant occurrence and distribution among land uses with differing pesticide application practices.

Figure 1 Subsampling sediment for laboratory analysis.

Sampling Design

Surface water and sediment samples were collected by HDOH personnel between December, 2013 and January, 2014 and sent to the USGS laboratories on the mainland. One liter grab samples were collected in accordance with USGS surface water sampling protocols. Sediment samples were collected following HEER guidance for multi-increment sediment sampling techniques, and handled according to USGS protocols. Quality assurance samples, including field blanks, field replicate and matrix spike samples were collected. Twenty four stream locations statewide representing four different land uses were sampled. Sediment samples were collected from seven sites to evaluate the potential for sediment to serve as a "sink" and secondary source for pesticide residues. Separate testing for the pesticide glyphosate (e.g., "Roundup") was included in this study due to community concern about use and fate of this herbicide. Analysis for glyphosate in both water and sediment was conducted on samples at seven sites, representing different land uses associated with glyphosate applications.

Figure 2: Collecting a grab sample.

The sampling effort focused on small water bodies directly adjacent to or downstream from targeted usage activities described below. At sites that did not have perennial streams, alternate locations representing local groundwater conditions were selected including anchialine pools, wetlands, lagoons that have storm overflow to the ocean, and agricultural drainage systems.

Note that this surface water sampling design cannot gather data from areas that do not have perennial surface water sources adjacent to or downstream of pesticide uses. For this reason, areas such as Molokai, Kunia, Waianae, and much of Maui's agricultural areas were not included in this study. Potential pesticide impacts to shallow groundwater in these areas could be studied in the future should resources become available to assess water quality in irrigation wells.

Figure 3 Anchialine Pond Sampling location at resort on Kona Coast.

Sampling Locations Related to Land Use

Water and sediment samples were collected from locations most likely to reflect pesticide usage and impacts. As part of the sampling plan development, HDOH worked closely with Department of Agriculture, reviewed confidential restricted use pesticide sales records for 2011-13, Good Neighbor reporting from the island of Kauai, consulted with University of Hawaii, USGS, USDA and other experts and solicited input from a wide variety of stakeholders. Sites ultimately selected for sampling are located downstream of significant agricultural activities, turf uses or urban activities. Eight sites were selected on Kauai and Oahu, six sites on the Big Island, and two sites on Maui. Printable maps can be found on the HEER website[v].

The four different land use types are listed below. However, in some cases, it was not possible to isolate a single land use.

- monoculture agriculture (relatively large tracts of land with single crops, users of restricted use pesticides)
    - 6 sites with extensive monoculture crops (seed corn, sugar, macadamia or coffee). 3 of these sites had other upstream crops or land uses.
- mixed use agriculture (small farms close together growing a variety of crops)
    - 8 sites with mixed use agriculture (wide variety of crops: vegetables, papaya, banana, sweet corn, potatoes, vegetables, herbs, taro, and ornamentals). Some sites include upstream inputs from other categories.
- turf uses (golf courses and resorts that use pesticides to maintain landscaping)
    - 6 sites with golf and resort uses. 3 sites had residential, wastewater and/or historic sugar cane cultivation.
- urban areas (these include residential pesticide uses and a wide variety of urban pesticide users, often including inputs from turf and small farms

- 4 sites that represent a mixture of residential and urban inputs. 1 of these sites, Waikele Stream on Oahu, has inputs from all categories, including small and large agriculture sites and a golf course.

Data Evaluation

The data results were compared to applicable state and federal regulatory values to evaluate whether any contaminants detected exceed levels that have been established for the protection of human health and the environment.

EPA compiles national recommended water quality criteria (AWQC)[vi] for the protection of aquatic life and human health in surface water for approximately 150 priority pollutants. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and tribes to use in adopting water quality standards. The HDOH has promulgated Hawaii State Water Quality Standards for these priority pollutants[vii].

While none of the surface waters sampled are used for drinking water, the results were also compared to drinking water standards, to provide some perspective with respect to human health. The federal drinking water standards, called Maximum Contaminant Level (MCL)[viii], are mandated by the Safe Drinking Water Act, and set by EPA's Office of Water at the "No Effect Level" with a minimum 100 fold margin of safety.

It is important to note, however, that very few drinking water or surface water standards (i.e., regulatory values) exist for currently registered pesticides; therefore, most of the values used to interpret the data results will be benchmarks and other available guidelines[ix].

In addition to comparing results to state and federal regulatory standards, detections were compared to the EPA Office of Pesticide Programs Human Health Benchmarks[x], Aquatic Life Benchmarks[xi] , and to USGS Health Based Screening Levels. In general, the strictest of these guidelines were the Aquatic Life Benchmarks. Quoting from the EPA website, these values *"are estimates of the concentrations below which pesticides are not expected to harm aquatic life."* HDOH concurs with EPA's conclusion that "*comparing a measured concentration of a pesticide in water with an aquatic life benchmark can be helpful in interpreting monitoring data, and to identify and prioritize sites and pesticides that may require further investigation.*"

Additional data for this report, including sampling location maps, data summaries and the raw data are posted on the Hazard Evaluation and Emergency Response (HEER) website[xii].

Surface Water Findings

Frequency of Pesticide Detections

Surface water samples collected from 24 sites statewide were analyzed for a total of 136 different pesticides or breakdown products. Forty two (42) pesticides or breakdown products were detected. Every location sampled had a detection of one or more pesticides. Figure 4 lists the frequency of detection of each pesticide and associated breakdown product found during sampling.

Twenty five (25) herbicides, 11 insecticides and 6 fungicides were detected in the study. Atrazine, together with its breakdown products, was the most commonly found pesticide in this study, detected in water samples at 20 of 24 locations sampled, and representing one third of all pesticide detections statewide (53 out of a total of 156 detections).

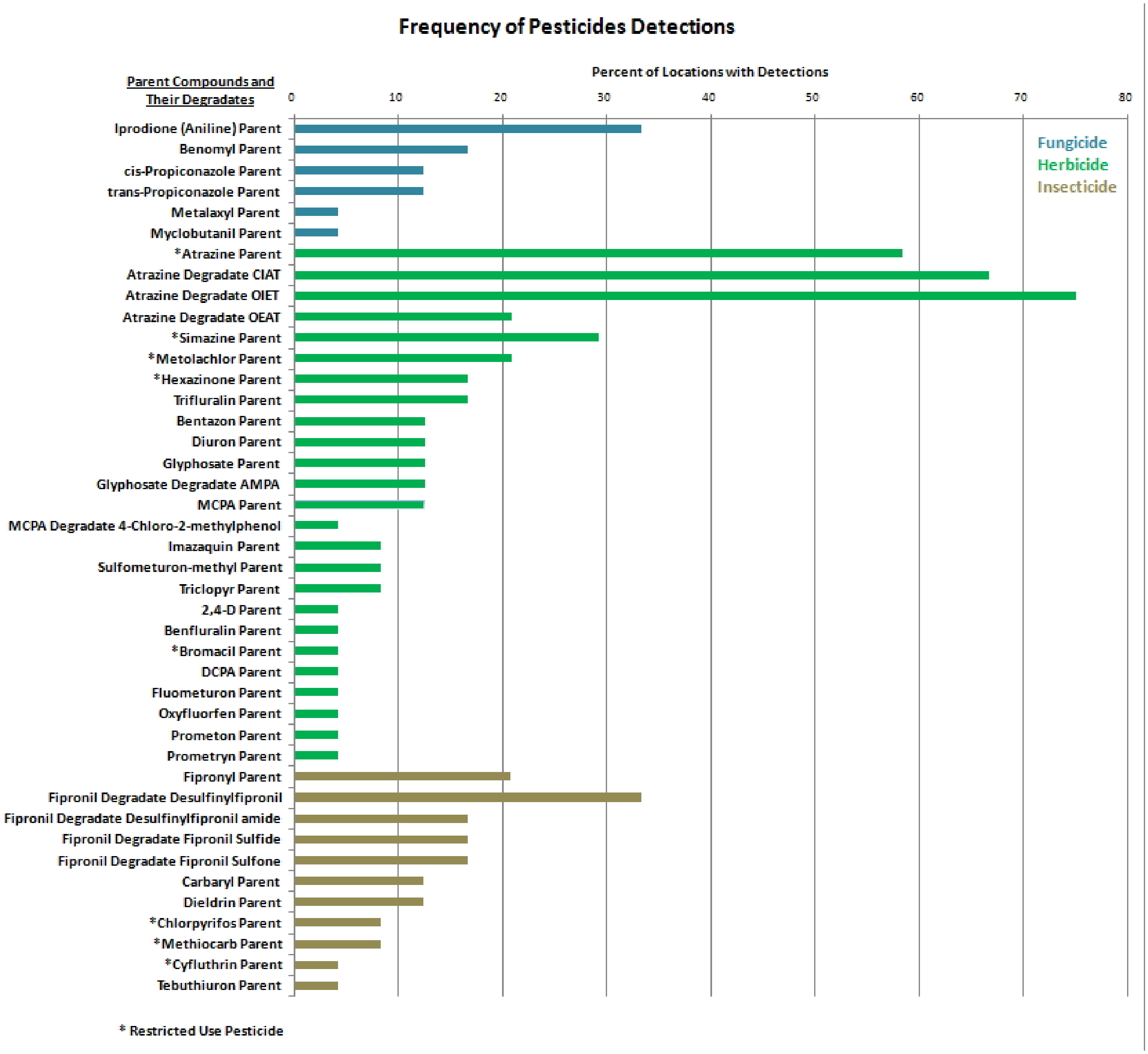

Figure 4 Percent of Locations with Detections

Pesticide Concentrations in Relation to Regulatory Limits and Benchmarks

Table 1 is a summary of the maximum concentration of each pesticide detected, the number of locations where the pesticide was detected and the number of locations where an appropriate regulatory standard or benchmark was exceeded.

Only one pesticide, a historically used termiticide exceeded state and federal water regulatory limits. Five other pesticide compounds were detected at levels exceeding the most conservative EPA aquatic life benchmark. The pesticides exceeding EPA aquatic life benchmarks include three insecticides commonly used to treat household pests like cockroaches, ants, fleas and termites and two restricted use herbicides that were detected near large monoculture agriculture operations. All other pesticides detected were lower than the most stringent aquatic or human health guideline value for the protection of human health or our ecosystem. Eighteen of those compounds were detected at concentrations more than 1,000 times lower than the most stringent aquatic or human health guideline values.

Summary of Pesticide Detections in Surface Waters
Statewide Pesticide Sampling Pilot Project

Hawaii Department of Agriculture and Hawaii Department of Health

Highest Value Above the Strictest Standard	Locations Detected	Type of pesticide	Parent or Breakdown Product	Locations Exceeding Strictest Standard	Highest Value ug/l	Strictest Standard Value ug/l	Ratio (Highest Value/Strictest Standard)	Strictest Standard Source
Dieldrin	3	Insecticide	Parent	3	0.069	0.000025	2760	Fish Consumption Hawaii WQC[4]

Highest Value Above the Strictest Benchmark	Locations Detected	Type of pesticide	Parent or Breakdown Product	Locations Exceeding Strictest Benchmark	Highest Value ug/l	Strictest Benchmark Value ug/l	Ratio (Highest Value/Strictest Benchmark)	Strictest Benchmark Source
Fipronil	5	Insecticide	Parent	3	0.026	0.011	2.364	CI OPP[2]
Atrazine*	14	Herbicide	Parent	1	2.050	1	2.05	ANVP OPP[2]
Cyfluthrin**	1	Insecticide	Parent	1	0.014	0.007	1.892	CI OPP[2]
Fipronil Sulfone	4	Insecticide	Degradate	1	0.043	0.037	1.162	CI OPP[2]
Metolachlor*	5	Herbicide	Parent	1	1.070	1	1.07	CI OPP[2]

Highest Value Between 1 and 1/10 of the Strictest Benchmark	Locations Detected	Type of pesticide	Parent or Breakdown Produce	Locations Exceeding Strictest Benchmark	Highest Value ug/l	Strictest Benchmark Value ug/l	Ratio (Highest Value/Strictest Benchmark)	Strictest Benchmark Source
Chlorpyrifos*	2	Insecticide	Parent	0	0.005	0.04	0.125	CI OPP[2]

Highest Value Between 1/10 and 1/100 of the Strictest Benchmark	Locations Detected	Type of pesticide	Parent or Breakdown Produce	Locations Exceeding Strictest Benchmark	Highest Value ug/l	Strictest Benchmark value ug/l	Ratio (Highest Value/Strictest Benchmark)	Strictest Benchmark Source
Fipronil Sulfide	4	Insecticide	Degradate	0	0.010	0.11	0.091	CI OPP[2]
Sulfometuron-methyl	2	Herbicide	Parent	0	0.025	0.48	0.052	HBSL USGS App. 3[5]
MCPA	3	Herbicide	Parent	0	0.120	2.6	0.046	Aquatic Life Guideline CAN-Interim[1]
Hydroxyatrazine (OIET)	18	Herbicide	Degradate	0	3.150	70	0.045	HBSL USGS App. 3[5]
Diuron	3	Herbicide	Parent	0	0.070	2	0.035	HBSL USGS App. 3[5]
Carbaryl	3	Insecticide	Parent	0	0.013	0.5	0.026	CI OPP[2]
Desulfinylfipronil	8	Insecticide	Degradate	0	0.009	0.59	0.015	CF OPP[2]
Fluometuron	1	Herbicide	Parent	0	0.060	4	0.015	HBSL USGS App. 3[5]
Benomyl	4	Fungicide	Parent	0	0.035	2.8	0.013	AF ECOTOX USGS App. 3[5]
Bromacil*	1	Herbicide	Parent	0	0.070	6.8	0.010	ANVP OPP[2]

1. CCME, Canadian Environmental Quality Guidelines, http://st-ts.ccme.ca/

*Hawaii Restricted Use Pesticides **Available in both Restricted Use and Non Restricted Use Formulations

2. EPA Office of Pesticide Programs Aquatic Life Benchmarks, http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks

3. EPA Basic Information about Regulated Drinking Water Contaminants and Indicators, http://water.epa.gov/drink/contaminants/basicinformation/index.cfm

4. Hawaii Water Quality Criteria, http://gen.doh.hawaii.gov/sites/har/AdmRules1/11-54.pdf

5. USGS National Water-Quality Assessment Program, http://pubs.usgs.gov/sir/2012/5045/pdf/sir20125045.pdf

Summary of Pesticide Detections in Surface Waters
Statewide Pesticide Sampling Pilot Project
Hawaii Department of Agriculture and Hawaii Department of Health

Highest Value Between 1/100 and 1/1000 of the Strictest Benchmark	Locations Detected	Type of pesticide	Parent or Breakdown Produce	Locations Exceeding Strictest Benchmark	Highest Value ug/l	Strictest Benchmark Value ug/l	Ratio (Highest Value/Strictest Benchmark)	Strictest Benchmark Source
Prometryn	1	Herbicide	Parent	0	0.008	1	0.008	ANVP OPP[2]
Simazine*	7	Herbicide	Parent	0	0.031	4	0.008	MCL EPA[3]
2,4-D	1	Herbicide	Parent	0	0.090	13.10	0.007	ANVP OPP[2]
Hexazinone*	4	Herbicide	Parent	0	0.034	7	0.005	ANVP OPP[2]
Iprodione (Aniline)	8	Fungicide	Parent	0	0.004	0.80	0.005	HBSL USGS App. 3[5]
Oxyfluorfen	1	Herbicide	Parent	0	0.001	0.29	0.003	ANVP OPP[2]
Benfluralin	1	Herbicide	Parent	0	0.002	1.9	0.0011	CF OPP[2]
Highest Value Less Than 1/1000 of Strictest Benchmark	**Locations Detected**	**Type of pesticide**	**Parent or Breakdown Produce**	**Locations Exceeding Strictest Benchmark**	**Highest Value ug/l**	**Strictest Benchmark Value ug/l**	**Ratio (Highest Value/Strictest Benchmark)**	**Strictest Benchmark Source**
Trifluralin	4	Herbicide	Parent	0	0.001	1.14	0.0009	CF OPP[2]
trans-Propiconazole	3	Fungicide	Parent	0	0.014	21	0.0007	ANVP OPP[2]
Triclopyr	2	Herbicide	Parent	0	0.060	100	0.0006	ANVP OPP[2]
Tebuthiuron	1	Herbicide	Parent	0	0.027	50	0.0005	ANVP OPP[2]
cis-Propiconazole	3	Fungicide	Parent	0	0.011	21	0.0005	ANVP OPP[2]
Methiocarb*	2	Insecticide	Parent	0	0.018	40	0.0005	HBSL USGS App. 3[5]
Glyphosate	3	Herbicide	Parent	0	0.110	700	0.000157	MCL EPA[3]
Bentazon	3	Herbicide	Parent	0	0.020	200	0.0001	HBSL USGS App. 3[5]
Metalaxyl	1	Fungicide	Parent	0	0.007	100	0.00007	CI OPP[2]
Prometon	1	Herbicide	Parent	0	0.003	98	0.000031	ANVP OPP[2]
Myclobutanil	1	Fungicide	Parent	0	0.004	200	0.000020	HBSL USGS App. 3[5]
Imazaquin	2	Herbicide	Parent	0	0.030	2000	0.000015	HBSL USGS App. 3[5]
DCPA	1	Herbicide	Parent	0	0.000	70	0.000006	HBSL USGS App. 3[5]
4-Chloro-2-methylphenol	1	Herbicide	Degradate	0	0.006	1150	0.000005	AF ECOTOX USGS App. 3[5]
AMPA	3	Herbicide	Degradate	0	0.140	249500	0.0000006	AF OPP[2]
Desulfinylfipronil amide	4	Insecticide	Degradate	0	0.022	Not Found		
Deethylatrazine	16	Herbicide	Degradate	0	0.104	Not Found		
OEAT	5	Herbicide	Degradate	0	0.060	Not Found		

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Table 1 Pesticide Detections and Benchmarks

Dieldrin exceeds water quality standards, continues to persist from historic uses of termiticides

Dieldrin was detected at two locations in Manoa Stream and in Waikele Stream. HDOH data shows that dieldrin exceeded Hawaii state water quality standards established for fish consumption of 0.000025 micrograms per liter (µg/l) at the three locations where it was detected. Dieldrin is a breakdown product of aldrin, which was widely used historically as a termiticide in soils beneath wood structures. These data are in line with earlier data from USGS showing high levels of dieldrin in sediment in Manoa Stream and are likely due to historic application of aldrin or dieldrin as a termiticide, and subsequent erosion of impacted soils into the stream. Dieldrin was not analyzed in sediments in this study but it is likely to be present.

Two commonly used household pesticides exceeded aquatic life benchmarks in Oahu's urban streams

Fipronil is a widely available insecticide used in homes for roach and flea control. Fipronil is also applied by commercial pest companies as a treatment for termites in soils around and under home foundations. Two locations in Manoa Stream and one location in Waialae Iki Stream in Kahala exceeded EPA's aquatic life benchmark of 0.011 µg/l for fipronil established for the protection of freshwater invertebrates. The Waialae Iki site also exceeded the EPA aquatic life benchmark of 0.037 µg/l for one of its breakdown products, fipronil sulfone.

A trace level detection of cyfluthrin, estimated at 0.014 µg/l, exceeded the EPA aquatic life criteria of 0.007 µg/l for the protection of freshwater invertebrates in Waikele Stream. This pyrethroid insecticide has both general and restricted use formulations, and was not detected at any other locations statewide.

Two restricted use herbicides, atrazine and metolachlor, exceeded aquatic-life benchmarks[xiii] at monoculture crop sites

One location on west Kauai, upstream of the Kikiaola Boat Harbor, had two detections of restricted use pesticides that exceed aquatic life benchmarks, but remain below regulatory standards.

Atrazine was measured at 2.05 µg/l, below the state and federal drinking water standard of 3 µg/l, and the EPA aquatic ecosystem Level of Concern of 10 ug/ l over a 60 day period[xiv]. This detection exceeds EPA's aquatic life benchmark of 1 µg/l established for the protection of freshwater algae.

Metolachlor was detected in five locations on Kauai, including four sites downstream of seed crop operations. One detection of 1.07 µg/l detected at the Kikiaola location slightly exceeded the EPA aquatic life guideline of 1.0 µg/l for protection of freshwater invertebrates. There are no U.S. regulatory standards for metolachlor in surface or drinking water. Other detections ranged from 0.040 µg/l down to the lowest detection of 0.006 µg/l measured in Wahiawa Stream. Metolachlor is an herbicide that is applied for pre-emergent control of grasses and broadleaf weeds on agricultural crop land, including corn, soybeans, sorghum and other crops, and on non-crop land for general weed control.

Widespread, trace level detections of atrazine

As discussed earlier, atrazine and its breakdown products, was the most frequently detected pesticide in the study. None of the samples exceeded state of federal water quality standards. One atrazine detection that appears to be associated with current use of atrazine on Kauai exceeded EPA's aquatic life benchmark of 1 µg/l, as discussed in the previous section. On Maui, the Kealia Pond National Wildlife Refuge (Kealia Pond NWR) had a detection of 0.182 µg/l atrazine, and may represent downstream impacts of current uses of atrazine in sugar cane and seed corn. The remaining 18 trace level detections occur on all islands across all land uses studied and are far below state and federal benchmarks. These low detections include at least three additional locations where atrazine is currently used, and generally align with areas with historic sugar cane and known concentrations in groundwater, though some detections were measured in areas where no earlier data exist.

As discussed in HDOH's November, 2013 Report to the Legislature on Atrazine Data Gaps[xv], for decades, atrazine was widely used in the sugar industry as a pre-emergent herbicide to control weeds in sugar cane fields. Drinking water monitoring statewide has shown that trace amounts of atrazine persist in groundwater in areas of historic sugar cane cultivation. Most of the locations sampled receive much of their flow from groundwater, which is likely the source for low level atrazine detections seen in this study. Atrazine is registered as a restricted use pesticide in Hawaii, so current uses cannot be ruled out at any location.

Fluometuron and benomyl, two pesticides not currently registered for use in Hawaii, detected in sampling

A confirmed detection of fluometuron, a pesticide that has never been registered for use in Hawaii, was found in Kealia Pond NWR. The source of this pesticide is unknown.

Benomyl was detected in five urban locations on Oahu, even though registration was cancelled in the early 2000's. The current detections may be a result of ongoing homeowner use of old stocks of this products, or residual concentrations in groundwater from legal uses prior to 2001.

Sediment Sampling Findings

To better understand how stream bed sediments might sequester currently used pesticides, HDOH selected 7 locations to collect stream bed sediment samples. These samples were analyzed for 121 different pesticides and breakdown products.

Glyphosate ubiquitous in stream bed sediment samples across land uses

Glyphosate, the active ingredient in Roundup, and one of its breakdown products were present at concentrations ranging from 6.8 -1,100 µg/kg (dry weight) in all seven stream bed sediment samples, and were detected in 3 of 7 paired water samples. Glyphosate is widely used across many land uses for residential, commercial, agricultural and roadside weed management. Based upon registration toxicity studies, glyphosate is labeled for weed control in aquatic environments and along banks where water contact is likely. It has a very short residence time in water and is known to bind tightly to soils and sediments.

Sediment concentrations varied between locations with detections of 1,100 µg/kg found downstream of taro fields at the Hanalei National Wildlife Refuge, and downstream of feed corn and mixed agricultural uses along Kapehu Stream on the Big Island. One site on the west side of Kauai had a detection of 800 µg/kg, down stream of seed corn crops in the agricultural drainage ditch near the Kawaiele Pump Station. Glyphosate concentrations in sediment sampled on Oahu varied between 6.8 and 9.2 µg/kg. Interestingly, the Manoa site had the highest measured concentration of glyphosate in water at 0.14 µg/l. Significant variations in hydrologic conditions between the sampling sites may account for some of the differences in concentrations of glyphosate and other pesticides detected.

Because sediment analyses for glyphosate are very new, there are no existing sediment guidelines or benchmarks. However, as a start, the glyphosate concentrations found in water samples at these same locations can be compared to US EPA's Office of Pesticides Aquatic Life benchmark of 1,800 µg/l, established for the protection of freshwater fish species. Detections in water at these three sites ranged from 0.03 -0.14 µg/l, orders of magnitude lower than the benchmark. The concentrations found in surface water were also well below the EPA's Maximum Contaminant Level (MCL) of 700 µg/l, a human health drinking water standard. As we move forward, we will be conferring closely with USGS and other glyphosate experts to develop the best available information to put the glyphosate stream bed sediment data in context.

Bed Sediment findings show few detections of other herbicides and two fungicides

Less than 5% of the 121 analytes were found in the seven sediment samples collected. Other than the glyphosate detections, there were single detections of three herbicides, two fungicides, and one historic insecticide. The other herbicides detected in sediment include atrazine, prodiamine, and oxyfluorfen. The detection of atrazine in sediments was found on the Hamakua Coast in Alia Stream, in the area overlying the aquifer that had the highest historic detections of atrazine in the state in the 1980s. The herbicide oxyfluorfen was the only pesticide detection other than glyphosate compounds at an urban location, found in Manoa Stream.

Two fungicides, azoxystrobin and propiconazole, were found in the same sample from Kapehu Stream on the Hamakua Coast of the Big Island. The paired water sample from this location also showed a trace detection of another fungicide, iprodione. DDE, a breakdown product of the historically used insecticide DDT, was detected on the west side of Kauai in the ditch by the Kawaiele Pump Station. The p'p-DDE detection of 1.1 µg/kg is below the Canadian Interim Sediment Quality Guideline of 1.42 µg/kg. Screening levels in sediment have not been established for the other detected compounds.

Discussion

Number of pesticide detections varies by land use

Urban streams on Oahu had highest number of different pesticide detections. Collectively, the four stream locations in urban Oahu had the greatest number of pesticides detected across all islands and land uses (range 11-20 detections).

Figure 5 contrasts two locations statewide that had exceedances of benchmarks, Manoa Stream at University of Hawaii on Oahu and Kikiola Ditch on Kauai's west side. The Manoa site is situated in a dense residential area, and the Kikiola site is downstream of several monoculture operations. The graph demonstrates clear differences in number, concentration and type of pesticides detected between these two different land uses.

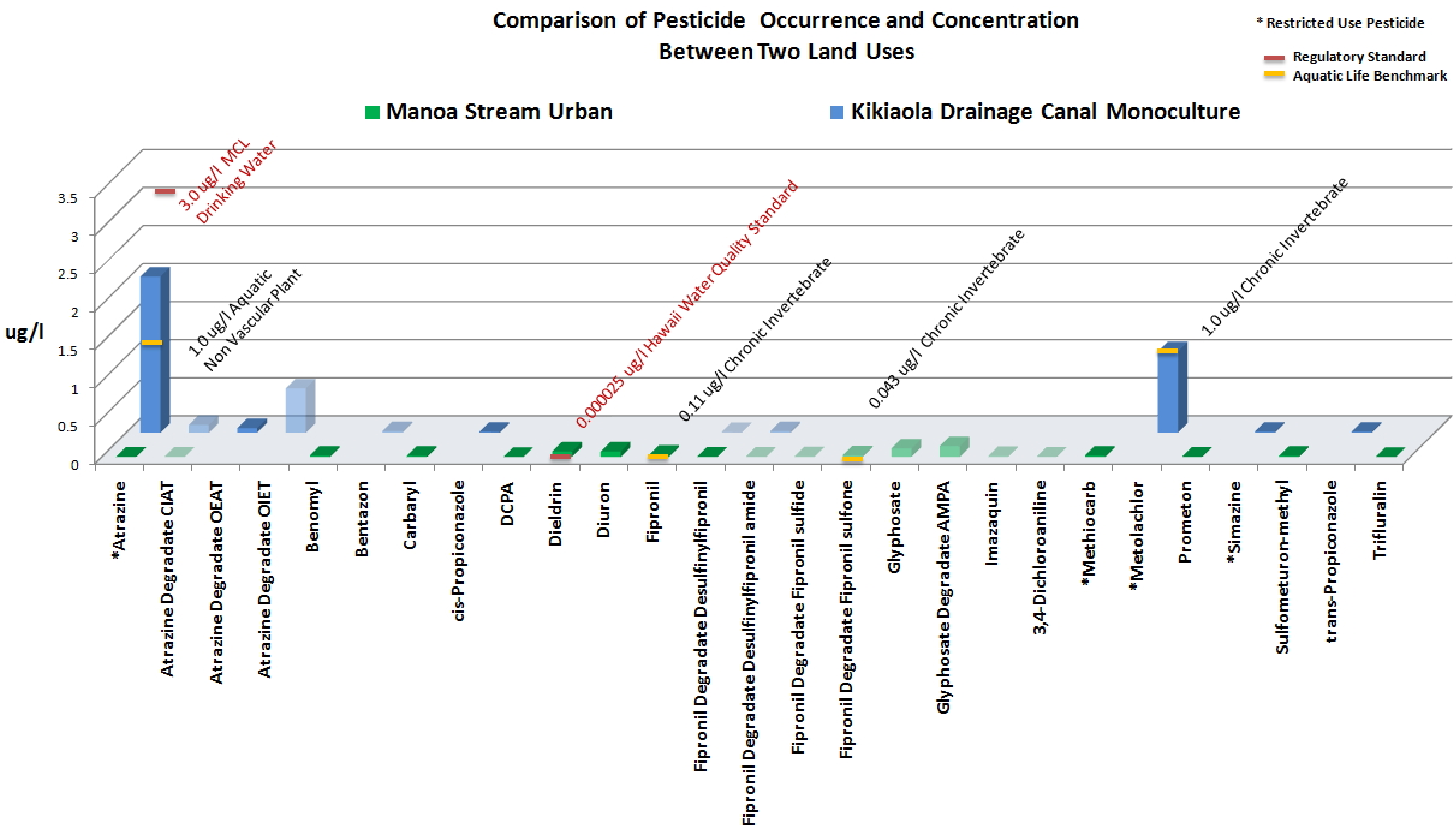

Figure 5 Comparison of Detections between Two Land Uses

Number of pesticide detections varies by island

Oahu

The Manoa Stream site at the University of Hawaii had the most individual detections in surface water state wide, with 20 different pesticides and breakdown products found in a single location. The sample from this location exceeded Hawaii's water quality standard for dieldrin (from historic use of termiticides) and EPA aquatic life benchmarks for two fipronil compounds, two insecticides commonly used in residential settings. While many of the pesticides detected are primarily for household use, traces of restricted use and an unregistered compound were found as well.

Waikele Stream showed detections of 12 different pesticides, including a broad range of restricted use herbicides and pesticides commonly used by homeowners, and historically used compounds. This location had a detection of cyfluthrin, which exceeded the EPA aquatic life benchmark.

Many of the compounds detected in Waikele and Manoa streams had been detected at the same locations by USGS in their 1999-2001 study[xvi], and are discussed in related report entitled, Ground-Water Quality and its Relation to Land Use on Oahu, Hawaii, 2000-01[xvii].

Kauai

Pesticide detections on Kauai varied widely between locations and crop types. Two sites downstream of seed corn operations on Kauai's west side each had 11 detections. One of these sites had exceedances of EPA aquatic life benchmarks for two restricted use pesticides (atrazine and metolachlor). In contrast, one location on Kauai's North Shore at Waiakalua had no detections of current pesticides, except for trace levels of atrazine and its degradates, residual evidence of former sugar cane use in that area.

Due to community concerns about pesticide usage associated with seed crops on Kauai's west side, the sampling design included three locations on drainage canals downstream of west side seed corn operations, and the Hanamaulu location that includes seed corn fields as well as a variety of mixed agricultural uses upstream. Detections at these sites were compared to reported restricted use pesticide (RUP) application under Kauai's Good Neighbor program. Five restricted use pesticides were detected at one or more of these sites, and three, atrazine, metolachlor and chlorypyrifos were reported to have been used by seed crop operators a few weeks prior to sampling. Trace concentrations of hexazinone and simazine at seed crop locations may reflect early applications or longer term residence in groundwater from earlier operations.

Chlorpyrifos, a restricted use insecticide was detected at trace levels (0.005 µg/l) at the Second Ditch location in Kekaha.

Results from Wahiawa Stream, downstream of coffee and seed crops, showed detections of atrazine, metolachlor, and two general use pesticides including iprodione, a fungicide, and the herbicide, oxyfluorfen. The coffee plantation operator reported no use of RUP pesticides during the sampling period under the Good Neighbor program. Some fields, however, are leased to seed crop operations.

Hawaii

Overall, the number of pesticides detected in water samples at the six sampling sites on the Big Island was lower than Kauai and Oahu (range 5-7 detections). All four stream locations showed levels of atrazine and its three breakdown products, consistent with historic contamination of the aquifer, but no current uses of atrazine. The three sites downstream of mixed use agriculture activities all had trace detections of simazine, a restricted use herbicide and iprodione, a fungicide.

At Honolii Stream on the Hamakua Coast of the Big Island, downstream of macadamia nut orchards, the water sample showed only one currently used pesticide in addition to trace levels of atrazine and its degradates, from former sugar cane use in that area.

Two anchialine ponds in resort areas on the Kona Coast were sampled to evaluate potential effects of pesticide use for turf management and golf courses. One location had a trace level (0.002 µg/l) detection of chlorpyrifos, an organophosphate pesticide that may be associated with insect control on the up gradient golf course.

Maui

No stream sites were sampled on Maui due to the lack of suitable perennial streams in close proximity to up gradient pesticide uses. The two surface water locations sampled are both groundwater fed, and likely receive little direct run off from upstream pesticide applications. Instead, detections at these locations may represent groundwater transport of herbicides. Atrazine and two other herbicides were detected at each site.

The Kealia Pond NWR site receives groundwater inputs from upstream sugar cane and seed corn operations. Three herbicides were detected. Atrazine and its breakdown products were detected at concentrations likely associated with current uses of atrazine. In addition, there were low level detections of two other herbicides, prometryn, and fluometuron. Prometryn is registered for general use in Hawaii. Fluometuron has not been registered for use in Hawaii.

The Kaanapali site was sampled at the mouth of a spring near Black Rock. The groundwater there has inputs from turf uses, wastewater and former sugar cane uses. Atrazine and its breakdown products were detected at low concentrations, as well as trace levels of two other herbicides, diuron and simazine.

Study Limitations

This pilot study of pesticide occurrence in surface water and sediments is limited in scope and is not adequate to describe exposure to human health and the environment. Because single grab samples were taken, data collected do not represent pesticide occurrence throughout the year, and may not capture pesticides applied outside the sampling period. Similarly, the data collected cannot be used to evaluate variability in pesticide residues found in surface water and sediments over time. Samples were not collected during high flow storm events, therefore, insecticides and other pesticides which are primarily transported to surface waters through storm runoff may not be detected. The study design did not consider pesticide application periods.

Reported concentrations of pesticides in the samples represent a snapshot in time from a small area within a watershed and may not be representative of worst-case or even typical conditions. All sites selected have multiple upstream inputs. Therefore, data collected will not conclusively identify specific source areas.

Further, water bodies and sediment conditions varied significantly between sampling sites. As an example, the photos above compare water quality conditions at the time of sampling at sites on Kauai (left) and the Big Island (right).

Next Steps

These findings and the underlying laboratory data are being made publicly available on the HDOH HEER website at **http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/pesticides**. These data will be a useful first step to bring state agencies, local governments, farmers and local communities together to learn more about the occurrence and concentration of currently used pesticides in non-target environments, and how they may relate to different land use types and current pesticide practices. Over the next few months, HDOA and HDOH will continue to analyze the data, seeking to better understand how pesticide chemistries, local conditions and differing application practices may combine to result in detections in our surface waters. We intend to seek expert assistance from USGS and other scientists, and meet with a variety of stakeholders to share ideas, identify data needs, and recommend actions, where appropriate.

[i] Anthony, S.S., Hunt, C.D., Jr., Brasher, A.M.D., Miller, L.D., Tomlinson, M.S., (2004), Water quality on the island of Oahu, Hawaii, 1999-2001: U.S. Geological Survey Circular 1239, 41 p. http://pubs.water.usgs.gov/cir1239

[ii] The National Water Quality Laboratory Schedules 2033 and 2060.
http://nwql.usgs.gov/Public/PublicQAQC/nav/S2033-PBLNK-2012.html and
http://wwwnwql.cr.usgs.gov/USGS/catalog/index.cfm?a=bs&sa=s&sap=2060&uid=

[iii] http://ca.water.usgs.gov/projects/PFRG/AnalyticalMethods.html.

[iv] http://ks.water.usgs.gov/lcgy.

[v] http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/Statewide-Pesticide-Survey

[vi] EPA Water Quality Criteria http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[vii] Hawaii Department of Health, Clean Water Branch, http://health.hawaii.gov/cwb/site-map/clean-water-branch-home-page/water-quality-standards/

[viii] EPA Drinking Water Contaminants http://water.epa.gov/drink/contaminants/

[ix] For our initial evaluation of the data, we referred to the following sources of information for information. The Appendices referred to below provide very helpful compendiums of Standards, Guidelines and Benchmarks for both Aquatic Life and Human Health. They also provide a detailed bibliography of a wide variety of state, national and international water and sediment quality guidelines. The acronyms used in our draft summary tables are referenced and well described in these Appendices.

USGS National Water-Quality Assessment Program. Prioritizing Pesticide Compounds for Analytical Methods Development, Appendix 3. Aquatic-Life and Human-Health Benchmarks Used in the Evaluation of Pesticides for Water, http://pubs.usgs.gov/sir/2012/5045/pdf/sir20125045.pdf

USGS National Water-Quality Assessment Program. Prioritizing Pesticide Compounds for Analytical Methods Development, Appendix 4. Aquatic-Life Benchmarks or Toxicity Values With Resulting Aquatic-Life Toxicity Bins and Available Sediment Benchmarks Used in the Evaluation of Pesticides for Sediment, http://pubs.usgs.gov/sir/2012/5045/pdf/sir20125045.pdf

For most current updates on individual Benchmarks, Toxicity Values and other outside reference sources, these two links are very helpful:

EPA Office of Pesticide Programs Aquatic Life Benchmarks, http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks

USGS NAWQA Pesticide National Synthesis Project, Types and Sources of Water-Quality Benchmarks for Pesticides http://water.usgs.gov/nawqa/pnsp/benchmarks/source.html#II

[x] EPA Office of Pesticide Programs Human Health Benchmarks
http://iaspub.epa.gov/apex/pesticides/f?p=HHBP:home

[xi] EPA Office of Pesticide Programs Aquatic Life Benchmarks,
http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks

[xii] http://eha-web.doh.hawaii.gov/eha-cma/Leaders/HEER/Statewide-Pesticide-Survey

[xiv] http://www.epa.gov/oppsrrd1/reregistration/atrazine/atrazine_update.htm#ewmp The EPA is currently estimating the aquatic ecosystem level of concern as approximately 10 parts per billion (ppb) for atrazine over a 60-day period. This estimate was developed using the PATI model described in EPA's issue paper that we presented to the 2009 SAP, available at www.regulations.gov in docket number EPA-HQ-OPP-2009-0104-0006.

If a watershed shows levels of atrazine above this level of concern in any two years of monitoring, atrazine registrants must initiate watershed-based management activities in concert with state or local watershed programs to reduce atrazine exposure. These remedies will be consistent with the approaches used in the EPA Office of Water's Total Maximum Daily Load (TMDL) program but are enforceable under FIFRA through the 2003 Atrazine IRED and Memorandum of Agreement.

[xv] HDOH Hazard Evaluation and Emergency Response Office, REPORT TO THE TWENTY-SEVENTH LEGISLATURE STATE OF HAWAII 2013 Pursuant to HCR 129, Requesting the Department of Health to Develop Partnerships to Address
the Data Gap on Air, Surface Water, and Near Shore Effects of Atrazine, November 2013
Available on line at: http://co.doh.hawaii.gov/sites/LegRpt/2014/Reports/1/HCR%20129F.pdf

[xvi] Anthony, S.S., Hunt, C.D., Jr., Brasher, A.M.D., Miller, L.D., Tomlinson, M.S., (2004), Water quality on the island of Oahu, Hawaii, 1999-2001: U.S. Geological Survey Circular 1239, 41 p.
http://pubs.water.usgs.gov/cir1239

[xvii]Hunt, C.D., (2004), Ground-Water Quality and its Relation to Land Use on Oahu, Hawaii, 2000-01: U.S. Geological Survey WRI Report 03-4305, 86 p. http://pubs.usgs.gov/wri/wri034305/