PESTICIDE LEVELS IN STREAMS AND SEDIMENTS ON THE ISLANDS OF OAHU AND KAUAI, HAWAII

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ABSTRACT

A survey water quality study was conducted between 2014 and 2017 to investigate the presence and concentration of pesticides in the nearshore marine environments on the islands of Oahu and Kauai. On Kauai, a total of 32 surface water and 16 sediment samples were collected from four streams and one irrigation ditch over multiple sampling events. On Oahu, a total of 27 surface water and 16 sediment samples were collected from six streams on the leeward side of the island over multiple sampling events, typically under baseflow conditions. The samples were analysed for 197 compounds spanning eight chemical classes of pesticides. Five herbicide (glyphosate, metolachlor, atrazine, imazapyr and MCPA) and one insecticide (imidacloprid) compounds were detected in the surface water samples collected. Seven insecticide (imidacloprid, carbaryl, chlordane, *p*,*p*′-DDD, *p*,*p*′-DDE, *p*,*p*′-DDT and dieldrin), five herbicide [glyphosate, aminomethylphosphonic acid (AMPA), diuron, DCPMU and pendimethalin] and one fungicide (azoxystrobin) compound were detected in the stream bed sediments collected. Detected pesticides spanned the pesticide class list, with seven of the eight classes of pesticides tested discovered. This study found widespread, low level contamination by both legacy and currently used pesticides in nearshore waters and river bed sediments on the islands of Oahu and Kauai.

Based on the pesticide data obtained during the study, five streams on the island of Oahu (two leeward and three windward streams) were selected for additional high-frequency sampling for the broad-spectrum herbicide glyphosate (Roundup), due to this compound's prevalence and the elevated concentration levels (compared to other pesticides) measured. These five streams flow through watersheds dominated by agricultural, residential and mixed-use land use and were sampled under both baseflow and storm conditions.

The pervasiveness and overall concentration levels of glyphosate detected are greater than any other pesticide currently or historically present in Hawaiian streams. Glyphosate was detected in 95% of stream samples collected during storm events (59 samples, 798 ng/L median, 1,308 ng/L mean detects) and 60% of stream samples collected under baseflow conditions (103 samples, 152 ng/L median, 462 ng/L mean detects), respectively (detection limit = 50 ng/L). In addition, either glyphosate or its degradation product AMPA was detected in 100% of the stream bed sediment samples collected on Oahu and Kauai during the study. The higher glyphosate concentrations in measured stream samples collected under storm versus baseflow conditions is believed to result from the release of adsorbed glyphosate present in stream-bed sediments as they become re-suspended during the rapid rises in stream volumes that characterize Hawaiian stream during runoff events.

The mean glyphosate concentration measured in streams that drain urban and mixed-use areas (1,020 and 1,050 ng/L, respectively) was slightly higher than concentration levels measured in streams that drain agricultural areas (760 ng/L). Glyphosate was detected more frequently in stream samples collected from agricultural areas than from urban and mixed-use areas (82%, 69% and 63% detection rates, respectively). The mean glyphosate concentrations measured during this study in stream waters and their associated bed sediments are more than 7 and 10 times higher than the maximum mean detect concentration of the most prevalent persistent organic pollutants (α-chlordane in sediment and pentachlorophenol in stream and bay waters) measured in waters and sediments in urban and mixed-use areas on Oahu in the mid-1970s.

Keywords: glyphosate, Hawaii, pesticides, streams, stream bed sediment, suspended sediment.

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1 INTRODUCTION

There are increasing community concerns about the potentially damaging human health and ecological impacts from exposure to chemical pesticides in the nearshore environments of the Hawaiian Islands. The intensive historical use of herbicides in Hawaii, year-round cultivation practices, prevalence of subterranean termites and proximity of agricultural and residential lands to streams enhance the possibility of pesticide transport to Hawaiian streams. Starting in the early 1970s, water quality studies conducted by the Water Resources Research Center (WRRC) [1,2,3], United States Geological Survey (USGS) [4,5] and the State Department of Health [6] have detected widespread, low-levels of pesticide contamination within groundwater and surface waters in the State of Hawaii.

Crop production within the State of Hawaii has dropped approximately two-thirds from 350,830 to 113,030 acres since 1980 with the large-scale closure of sugarcane and pineapple plantations [7]. In 2015, a total of 22,354 and 21,310 acres of land were being used to grow crops on the islands of Oahu and Kauai, respectively. On Oahu, diversified crops (9,865 acres), seed production (7,333 acres) and pineapple (3,414 acres) were the three largest types of agriculture. On Kauai, seed production (13,299 acres), coffee (3,788 acres) and commercial forestry (3,788 acres) represented the dominant agricultural usages of land [7].

In 2013, a total of 590,000 kg of Restricted Use Pesticides (RUP) were sold in Hawaii, with 36% of the total being used for urban and structural purposes to treat termites and 32% for agricultural purposes [8]. In 2017, the total mass of reported RUP used on the island of Kauai was 23,500 kg while a total of 397,500 kg were used on the island of Oahu [9]. Public pressure led to the recent passage of Senate Bill 3095 in June 2018 banning the use of the insecticide chlorpyrifos and the spraying of any pesticide within 100 feet of schools during normal school hours.

The objectives of this study included evaluating the occurrence and distribution of current-use and legacy pesticides in streams and sediments which drain watersheds containing urban (8 sites), agricultural (6 sites) and mixed-use (both agricultural and urban) (3 sites) land use on the islands of Oahu and Kauai. The portion of the study conducted from November 2014 to January 2018 focused on sampling streams under low-flow conditions for a broad spectrum of pesticides. Follow-on high-frequency sampling of five streams on the island of Oahu for the herbicide glyphosate was conducted between December 2017 and April 2018 under both low-flow and storm conditions.

2 PREVIOUS STUDIES

The WRRC conducted sampling of streams, bay waters, and stream and bay sediments for chlorinated pesticides in the mid-1970s as part of surveys of the quality of coastal waters on Oahu [1,2,3]. The principal areas sampled were Maunalua (urban) and Kahana (rural) Bays [1] and three drainage subareas (Kaneohe (urban), Waihee (mixed) and Waikane (rural) within Kaneohe Bay [2,3]. Low part per trillion levels of *p*,*p*′-DDT, chlordane, dieldrin and pentachlorophenol (PCP) were commonly detected in both stream and bay waters. These studies found that sediment and water samples collected near urban areas have higher concentration levels of pesticides than those collected in rural areas and that samples collected near the mouths of streams have higher levels of pesticides than sampling locations further out in the bay. Bottom muds and sediments were found to contain 3–4 orders of magnitude higher concentrations of these chlorinated pesticides than were detected in the water column of the sampled streams and bay waters.

The USGS began periodic sampling and analysis of Hawaiian streams and sediments for pesticides in the late 1970s. The data generated is accessible online through their National Water Information System Web interface. The USGS tested surface waters for pesticides between 1999 and 2001 under both baseflow and storm runoff conditions from three streams (Waikele, Manoa, and Waihee) on the island of Oahu as part of the National Water-Quality Assessment program [4]. Herbicides were generally detected in streams more frequently during base flow and insecticides generally detected more frequently in storm runoff.

The State of Hawaii Department of Health collected surface water samples from 24 sites statewide for pesticide analysis between December 2013 and January 2014 [6]. Glyphosate was detected in water samples collected from three of the seven sampling sites: Manoa stream on Oahu, a taro patch in Hanalei, Kauai and in an agricultural ditch located in the Mana Plain on Kauai. Co-located sediment samples were collected from all seven stream sampling sites during this study; glyphosate and its degradation product (aminomethylphosphonic acid; AMPA) were detected at concentrations ranging from 6.8 to 1,100 µg/kg in all seven samples. The USGS sampled 32 streams on Oahu and Kauai in 2016 and analysed these water samples for 225 current-use pesticide compounds, but not glyphosate or AMPA [5].

The data generated during these previous studies document the persistence of certain chlorinated pesticides in the Hawaiian environment. For instance, dieldrin was phased out of use as a termiticide in Hawaii by 1988 in favour of less persistent compounds [10]. A total of 19 stream samples collected from Kaneohe Stream measured persistent low levels of dieldrin between 20 and 50 ng/L from 1989 to 1999 while 26 stream samples collected between 1999 and 2013 from Manoa Stream consistently detected dieldrin at levels between 15 and 77 ng/L.

3 SURVEY PESTICIDE STUDY METHODOLOGY

The sampled areas on the islands of Oahu and Kauai had the following features: (1) surface water bodies discharging to the ocean that were potentially impacted by inland agricultural, urban or recreational activities and (2) areas where recreational users (surfers, boaters, beach-users, fishermen) may be impacted by runoff. Stream water samples were collected up to four times from near the mouths of streams where previous studies had detected the highest concentration levels of pesticides [3]. Stream bed sediment samples were also collected over four rounds of sampling throughout the survey period.

Approximately, 80% of the population in the Hawaiian Islands lives on the island of Oahu; agricultural activity is more prevalent on the island of Kauai. This is reflected by the types of land use in the contributory watersheds sampled on each island: Kauai (4 agricultural and 2 mixed use areas) and Oahu (3 urban, 4 mixed use and 3 agricultural areas) (Fig. 1).

3.1 Sample Collection

An incremental sampling method (ISM) was used to collect both water and sediment samples. A representative decision unit (DU) was delineated at each sampling site that was determined to be representative of discharge to the marine environment. Stream water samples were collected into a 1 L US DH-81 sampler in a linear fashion across the lateral extent of the stream and vertically from the stream surface to the depth of the stream at the time of sampling. The individual stream increments collected from the DU were combined into a churn constructed of non-reactive material to make one overall sample of suitable volume to

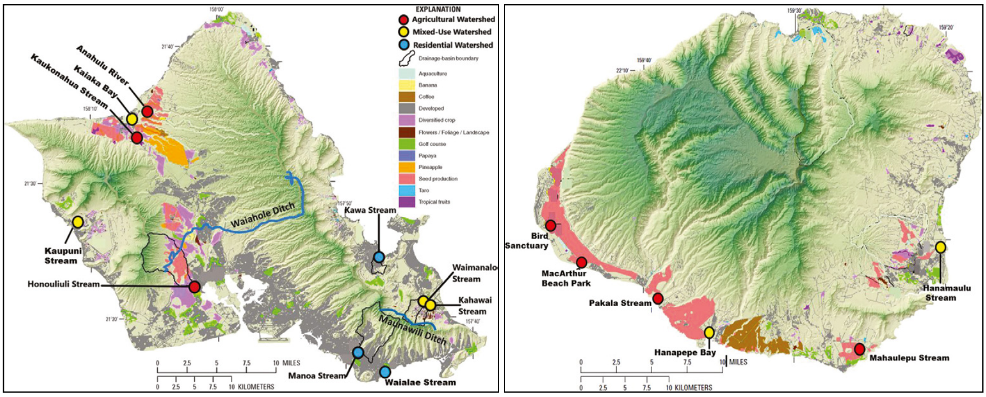

Figure 1: Maps of Oahu and Kauai showing stream sampling locations and land use [5].

conduct the various pesticide analyses. The combined sample volume was then subsampled into individual sample jars for analysis. The general water chemistry of the stream samples (conductivity, pH, oxygen reduction potential, dissolved oxygen, turbidity, and temperature) was measured using a calibrated field metre (YSI Pro Plus or Hydrolab Multi-Meter). A total of 27 water samples were collected on Oahu (7 screening-only samples, 4 laboratory-only samples, and 16 combined screening/laboratory samples); a total of 32 water samples were collected on Kauai (16 screening-only samples and 16 combined screening/laboratory samples). All but two of the stream samples (Kaupuni Stream on 8/24/15 and Manoa Stream on 8/26/15) were collected under low-flow conditions.

Stream bed sediment samples were collected from within the same DUs as the water samples. Sediment samples were collected using an ISM, with increments placed into a stainless-steel bowl for mixing prior to being subsampled into individual sampling jars for analysis. Sufficient increments, at least 30, were collected from the DU to amass at least 500 grams of sediment sample material at each site. The size of the increments varied depending on the amount/depth of the sediment present within the DU. Sediment increments were typically collected down to depths of between one to up to six inches beneath the surface of the river bed. A total of 16 stream bed sediment samples were collected from streams on both the islands of Oahu and Kauai for laboratory analysis. Sediment samples were packaged and transported to a certified commercial analytical laboratory for analysis.

3.2 Laboratory Analysis

The samples collected during this study were analysed for a total of 197 pesticide compounds. The stream water and sediment samples were analysed according to the following methods: Chlorinated Herbicides by SW-846 Method 8151A; Multi-Residue Pesticides Profile by SW-846 Methods 8081B Modified, 8141B Modified, 8270D Modified, and 8321B Modified (combined test); Imidazolinone Herbicides by American Cyanamid; Sulfonylurea Herbicides by DuPont Method; Glyphosate by SW-846 Method 547 (Liquid Chromatography/Fluorescence Detector); and Paraquat by SW-846 Method 549. The primary laboratory for this project was Pacific Agricultural Laboratory located in Portland, Oregon. Additional analytical services (high resolution glyphosate analysis) were provided by Vista Analytical Laboratory located in El Dorado Hills, California.

3.3 ELISA Analysis

Enzyme-linked immunosorbent assay (ELISA) test kits manufactured by Abraxsis were used to measure the concentration of atrazine, metolachlor, and glyphosate in the collected stream samples [11]. The detection limits for these pesticides were 50, 58, and 50 ng/L, respectively. For quantification of glyphosate, a six-point calibration curve (0, 75, 500, 750, 1000 and 4,000 ng/L) was constructed with two replicates with a blank measured as zero for comparison. A quality control solution containing 750 ng/L glyphosate was included in each analytical run.

Correlation sampling was performed to determine if the ELISA results were comparable to data generated by the analytical laboratory. Eleven surface water samples were split: one set of samples was analysed for glyphosate, atrazine and metolachlor using the ELISA field kits while the other set was sent to a commercial analytical laboratory for analysis by high performance liquid chromatography (glyphosate), liquid chromatography with tandem mass spectrometry (atrazine), and by gas chromatography (metolachlor).

3.4 High Frequency Glyphosate Sampling

The prevalence of glyphosate in stream and sediment samples detected during the regional study led to additional high frequency sampling of five streams on Oahu for glyphosate content between December 2017 and April 2018 [13]. A number of discrete rainfall runoff events were sampled in streams draining two urban (Manoa and Kawa), one agricultural (Honouliuli), and two mixed-use (Waimanalo and Kahawai) watersheds located on both the windward and leeward sides of Oahu. This high frequency sampling of individual runoff events was conducted to gain a better understanding of variations in glyphosate concentration and glyphosate load that occur within Hawaiian streams throughout runoff events. In addition, a number of samples were collected under groundwater dominated baseflow conditions from each stream to allow a comparison of glyphosate concentrations present under runoff and baseflow stream conditions. Glyphosate and AMPA concentrations were also measured in suspended sediments during three separate sampled runoff events at Kawa, Waimanalo, and Honouliuli streams. The mass of glyphosate measured in suspended sediments collected over a 30-min collection period within these three streams ranged from 11% to 23% of the dissolved phase mass measured in the stream waters during the same 30-min time period.

4 SURVEY PESTICIDE STUDY RESULTS

The commercial laboratories analysed the collected surface water and sediment samples for 197 pesticide compounds that fall within the following eight major classes of chemicals: organophosphorus and organosulfur pesticides, halogenated pesticides, organonitrogen pesticides, phenylurea herbicides, carbamate pesticides, chlorinated herbicides, imidazolinone herbicides, sulfonylurea herbicides, and paraquat (in water only).

4.1 Surface Water Pesticide Results

Surface water sampling consisted of both screening samples (using ELISA) and primary laboratory analytical samples. Five herbicide and one insecticide compounds were identified at detectable levels in surface water on Oahu and/or Kauai during this study (Table 1). The compounds detected were glyphosate (organophosphorus herbicide), metolachlor, atrazine

Table 1: Surface water results – Oahu and Kauai.

Analyte	Date	Metola-chlor	Atrazine	Glypho-sate	Imazapyr	MCPA	Imida-cloprid
Units	m/d/y	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Method		ELISA	ELISA	ELISA	Lab	Lab	Lab
			Oahu				
Anahulu River	2/19/15	<100	<50	<75	<20	<80	<60
	5/29/15	<58	<50	<75	NA	NA	NA
	9/1/15	<100	<50	<75	<20	<80	<60
Honouliuli Stream	2/19/15	<100	<50	1,600	<20	<80	<60
	5/29/15	198	<50	>4,000	NA	NA	NA
	9/1/15	77j	116	401	<20	<80	<60
	5/31/16	<100	<50	504	<20	<80	<60
	12/19/16	<100	<50	558	<20	<80	<60
	2/8/17	NA	NA	NA	<20	<80	200
Kaiaka Bay, Upstream	5/31/16	<100	<50	<75	34	<80	<60
	2/19/16	<100	<50	93	<20	<80	<60
	2/8/17	NA	NA	NA	<20	<80	200
Kaukonahua	5/29/15	<58	<50	255	NA	NA	NA
Kaupuni Stream	2/19/15	<100	<50	130	<20	<80	<60
	5/29/15	<58	<50	92	NA	NA	NA
	8/24/15	87J	125	>4,000	NA	NA	NA
	5/31/16	<100	<50	206	<20	<80	<60
	12/19/16	<100	<50	<75	<20	<80	<60
	2/8/17	NA	NA	NA	<20	<80	160
Manoa Stream	2/19/15	<100	<50	<75	<20	<80	<60
	5/29/15	<58	69	272	NA	NA	NA
	8/26/15	74J	151	130	<20	<80	<60
	9/1/15	<100	<50	<75	<20	<80	<60
	5/31/16	56J	>5,000	<75	<20	<80	<60
	12/19/16	<100	<50	92	<20	<80	<60
	2/8/17	NA	NA	NA	<20	<80	<60
Waialae		NA	NA	1,510	<20	<80	<60
			Kauai				
Bird Sanctuary	3/9/16	77J	38J	209	NA	NA	NA
Hanamaulu Stream	2/23/15	<100	<50	640	<20	<80	<60
	7/23/15	<58	<50	<75	NA	NA	NA

Table 1: *Continued*

Analyte	Date	Metola-chlor	Atrazine	Glypho-sate	Imazapyr	MCPA	Imida-cloprid
Hanamaulu Stream at Mouth	9/10/15	162	74	<75	<20	<80	<60
	3/9/16	<100	<50	49J	NA	NA	NA
	6/12/16	<100	<50	46J	<20	<80	<60
	12/14/16	<100	<50	<75	<20	<80	<60
Hanapepe Bay Discharge	11/17/14	<100	<50	330	NA	NA	NA
	2/23/15	<100	<50	165	<20	<80	<60
	7/23/15	<100	<50	>4,000	NA	NA	NA
	9/10/15	<100	<50	<75	<20	<80	<60
	3/9/16	<100	<50	146	NA	NA	NA
Hanapepe River	3/9/16	<100	<50	<75	NA	NA	NA
	6/12/16	<100	<50	93	<20	<80	<60
	12/14/16	<100	<50	<75	34	<80	<60
Kaupuni Stream	11/17/14	<58	<50	80	NA	NA	NA
	11/17/14	<100	<50	<75	NA	NA	NA
	2/23/15	<100	<50	<75	<20	<80	<60
	7/23/15	<58	<50	<75	NA	NA	NA
	9/10/15	<100	<50	124	<20	<80	<60
	3/9/16	93J	26J	158	NA	NA	NA
	3/9/16	156	<50	137	NA	NA	NA
	6/12/16	184	<50	307	<20	<80	<60
	12/14/16	<100	<50	221	<20	460	<60
Mahaulepu Stream	11/17/14	<100	10	80	NA	NA	NA
	2/23/15	<100	69	272	<20	<80	<60
	7/23/15	<58	151	130	NA	NA	NA
	9/10/15	<100	<50	<75	<20	<80	<60
	3/9/16	58J	24J	<75	NA	NA	NA
Mahaulepu Stream at mouth	6/12/16	<100	<50	67J	<20	<80	<60
	12/14/16	<100	<50	145	<20	<80	<60
Pakala Stream	3/6/16	226	<50	<75	NA	NA	NA

NA = not analysed; J = estimated value.

and MCPA (chlorinated herbicides), imazapyr (imidazolinone herbicide), and imidacloprid (organonitrogen insecticide). The chlorinated herbicide MCPA was not detected in surface waters on the island of Oahu while the organonitrogen insecticide imidacloprid was not detected on the island of Kauai.

4.2 Stream Bed Sediment Pesticide Results

A total of 13 different pesticides (5 herbicides, 7 insecticides, 1 fungicide) were detected in 25 of the 32 stream bed sediment samples collected from stream bed sediments on Oahu and Kauai. The compounds detected were glyphosate and AMPA (organophosphorus herbicides), azoxystrobin (organonitrogen fungicide), carbaryl (carbamate insecticide), chlordane, *p*,*p*′-DDD, *p*,*p*′-DDE, *p*,*p*′-DDT and dieldrin (halogenated insecticides), diuron and DCPMU (phenylurea herbicides), pendimethalin (organonitrogen herbicide) and imidacloprid (organonitrogen insecticide). The only pesticides detected in the riverbed sediments on Kauai were the herbicides glyphosate, its degradation product AMPA, and the insecticide carbaryl. On Oahu, 10 of the 13 pesticides detected statewide were found in stream bed sediments collected from Honouliuli Stream. The legacy insecticides chlordane and dieldrin as well as the herbicides glyphosate and AMPA were detected in Manoa stream. Table 2 contains the data for the most commonly detected pesticides in stream bed sediments. In addition to these detections, carbaryl was detected in two duplicate samples collected from Mahaulepu stream (0.011 mg/kg). Chlordane was detected in sediments from Manoa stream collected on 9/1/15 (0.19 mg/kg) and 5/31/16 (0.15 mg/kg). Diuron (the parent of DCPMU) was detected in Honouliuli Stream sediment collected on 2/19/15 (0.0083 mg/kg) and 5/31/16 (0.0069 mg/kg). The compound *p*,*p*′-DDE was detected in Honouliuli Stream sediments on 2/19/15 (0.13 mg/kg), on 9/1/15 (0.041 mg/kg) and on 5/31/16 (0.060 mg/kg) while *p*,*p*′-DDD was detected in sediments from this stream on 5/31/16 (0.0071 mg/kg). Imidacloprid was detected in Honouliuli Stream on 9/1/15 (0.018 mg/kg). Pendimethalin was detected in Honouliuli Stream on 2/19/15 (0.077 mg/kg).

4.3 Results from High Frequency Glyphosate Sampling

The median and mean concentration and detection frequency of glyphosate measured in the five streams of Oahu that were sampled multiple times under storm and baseflow conditions are summarized in Table 3.

The mean glyphosate concentration measured in stream water sampled from urban and mixed-use watersheds during the survey water quality and high frequency studies was somewhat higher than the mean level measured in streams from agricultural watersheds (1,050, 1,020 and 760 ng/L mean detect in mixed-use, urban, and agricultural areas, respectively). The median glyphosate concentration measured in stream water sampled from urban watersheds was higher than the median levels measured in streams from agricultural and mixed-use watersheds (440, 260 and 240 ng/L median detect in mixed-use, urban, and agricultural areas). The frequency of glyphosate detection was greatest in stream samples collected from agricultural areas followed by urban and mixed-use areas (82%, 69% and 63% detection frequency). The mean and median glyphosate concentrations measured in the same streams were much higher during elevated stream flow conditions than under dry, baseflow conditions when groundwater input to the streams dominated (Table 3).

4.4 Quality Assurance/Quality Control

Five of the eleven pairs of stream water samples analysed at both the laboratory and using ELISA provided detectable results for glyphosate by both methods while atrazine and metolachlor were not detected in any of the paired laboratory samples. The paired ELISA/laboratory

Table 2: Stream sediment sample results – Oahu and Kauai.

Analyte	Date	Glyphosate	AMPA	Azoxystrobin	DCPMU	*p,p′*-DDT	Dieldrin
Units	m/d/y	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Method		Lab	Lab	Lab	Lab	Lab	Lab
Oahu							
Anahulu River	2/19/15	<0.017	0.018	<0.007	<0.007	0.100	<0.027
	2/19/15	<0.017	0.029	<0.007	<0.007	<0.027	<0.027
	2/19/15	<0.017	0.027	<0.007	<0.007	<0.027	<0.027
Honouliuli Stream	2/9/15	0.67	0.54	0.010	0.026	<0.027	<0.027
	9/1/15	3.1	1.8	0.016	0.024	<0.027	<0.027
	5/31/16	5.5	6.9	0.012	0.031	0.009	<0.027
	12/19/16	1.2	1.4	0.009	0.020	<0.027	<0.027
Kaiaka Bay	5/31/16	<0.017	0.02	<0.007	<0.007	<0.027	<0.027
Kaupuni Stream	2/19/15	<0.017	0.03	<0.007	<0.007	<0.027	<0.027
	9/1/15	<0.017	0.024	<0.007	<0.007	<0.027	<0.027
Manoa Stream	2/19/15	0.033	0.068	<0.007	<0.007	<0.027	<0.027
	9/1/15	<0.017	0.13	<0.007	<0.007	<0.027	0.032
	5/31/16	0.90	3.5	<0.007	<0.007	<0.027	ND
	12/19/16	0.16	0.23	<0.007	<0.007	<0.027	ND
Kauai							
Hanamaulu	2/23/15	<0.017	0.018	<0.007	<0.007	<0.027	<0.027
Hanapepe Bay	2/23/15	0.033	0.041	<0.007	<0.007	<0.027	<0.027
	9/10/15	0.61	0.61	<0.007	<0.007	<0.027	<0.027
	9/10/15	0.61	0.61	<0.007	<0.007	<0.027	<0.027
	6/12/16	1.3	1.0	<0.007	<0.007	<0.027	<0.027
	12/14/16	0.046	0.11	<0.007	<0.007	<0.027	<0.027
MacArthur Beach Park	9/10/15	0.13	0.072	<0.007	<0.007	<0.027	<0.027
	9/10/15	0.13	0.072	<0.007	<0.007	<0.027	<0.027
Mahaulepu Stream	9/10/15	0.10	0.10	<0.007	<0.007	<0.027	<0.027
	2/23/15	0.14	0.12	<0.007	<0.007	<0.027	<0.027

glyphosate results (in ng/L) were as follows: 504/584, 558/280, 206/91, 1,510/1,520, and 67J/14J. The correlation coefficient determined for these paired samples was $R^2 = 0.95$, which indicates a strong correlation between the results obtained using the laboratory analytical method and the ELISA immunoassay method. A similar strong correlation (0.96) between immunoassay and laboratory results was obtained in a recent study of glyphosate levels in dairy cow urine [12].

Table 3: Glyphosate concentrations measured in storm and baseflow stream samples.

Location	Land use	Stream glyphosate data				
		Median detect (ng/L)[1]	Mean detect (ng/L)[1]	Detect range (ng/L)	Detect frequency[1]	Sample count
Storm samples (rainfall runoff dominant streamflow)						
Manoa	Residential	5,080	3,775	56–8,420	83%	6
Kahawai	Mixed use	2,808	2,379	1,287–2,930	100%	5
Honouliuli	Agricultural	1,181	1,417	469–4,000	100%	11
Kawa	Residential	488	726	75–1,836	93%	27
Waimanalo	Mixed use	368	576	130–1,816	100%	8
Baseflow samples (groundwater dominant streamflow)						
Manoa	Residential	123	155	69–272	63%	8
Kahawai	Mixed use	203	207	48 J–400	75%	4
Honouliuli	Agricultural	144	576	48 J–4,000	100%	15
Kawa	Residential	66	344	<50–910	20%	15
Waimanalo	Mixed use	171	171	134–208	33%	6

[1]Detection limit = 50 ng/L.

Four of the samples analysed for atrazine using both methods yielded ELISA atrazine concentrations above the laboratory detection limit (60 ng/L). Abraxis states their atrazine assay will detect atrazine and related triazines to different degrees [11]. Thus, it is likely that the ELISA atrazine values reported in Table 1 reflect the concentration of both atrazine and its various degradation products, such as 2-hydroxyatrazine (OIET), deispropylatrazine (CEAT), and deethylatrazine (CIAT), which have been detected in Hawaiian streams at higher concentrations than the parent compound during recent studies [5].

5 DISCUSSION

A total of five herbicide compounds (glyphosate, metolachlor, atrazine, imazapyr, and MCPA) and one insecticide compound (imidacloprid) were detected in Hawaiian stream water during the survey water quality study conducted between 2015 and 2018. Table 4 compares the range in detected concentrations, mean and median of detected concentrations and frequency of detection of these pesticide compounds with concentration levels and detection frequencies measured during previous studies. Different detection limits achieved during different studies can impact the rate of detection as well as the calculated mean and median of detected pesticide concentrations. The detection limits achieved by the commercial laboratories used during this study were somewhat higher than the detection limits achieved by the USGS National Water Quality Laboratory in Colorado during the 2013–2014 and the 2016–2017 water quality studies listed in the table [5,6].

As previously discussed, the atrazine concentrations measured using ELISA during this study are likely higher than the actual atrazine levels present since this method also detects other triazine compounds such as the various atrazine degradation compounds commonly present in Hawaiian streams [5]. The concentration levels of metolachlor, MCPA, and imidacloprid measured in Hawaiian streams during this study are generally consistent with levels measured during two other recent water quality studies [5,6]. The maximum glyphosate

Table 4: Comparison of historic pesticide concentrations measured in Hawaiian streams.

Pesticide	Years	Detected range (ng/L)	Detect limit (ng/L)	Detection rate	# of sample	Median/ mean detect (ng/L)	Source
Atrazine	94–97	NA	50	0%	11	<50	USGS database
Atrazine	99–01	1–7	1	27%	56	6/5	[5]
Atrazine	13–14	4–2,050	4–8	44%	18	8/264	[7]
Atrazine	16–17	3E–10	6.8	9%	32	6/6	[6]
Atrazine	14–16	10E–6,000	50	19%	54	74/535	Current study
Metolachlor	93–97	NA	50	0%	8	<50	USGS database
Metolachlor	99–01	NA	2–13	0%	56	<13	[5]
Metolachlor	13–14	6E–1,070	12	67%	18	6/219	[7]
Metolachlor	16–17	134–369	9	6%	32	152/152	[6]
Metolachlor	14–16	56E–226	58	22%	54	90/121	Current study
MCPA	99–01	20E	24	8%	60	20/20	[5]
MCPA	13–14	20E–120	40	23%	13	20/53	[7]
MCPA	16–17	271–647	95	14%	28	291/375	[6]
MCPA	14–16	460	80	3%	36	460/460	Current study
Imidacloprid	99–01	100–200	7–100	9%	22	150/150	[5]
Imidacloprid	13–14	<80	80	0%	14	<80	[7]
Imidacloprid	16–17	9E–4,940	16	41%	32	39/464	[6]
Imidacloprid	14–16	160–200	60	6%	36	180/180	Current study
Glyphosate	13–14	30–110	20	43%	7	30/57	[7]
Glyphosate	14–18	48E–8,420	50	73%	162	319/864	Current study

concentrations measured in streams during this study are significantly higher than the levels measured in the previous HDOH study [6]. This difference likely reflects the greater number of samples analysed for glyphosate in this study (155 versus 7 samples) and the fact that stream samples were collected under both baseflow and stormflow conditions during this study as opposed to just baseflow conditions sampled during the HDOH study.

The ubiquity and abundance of glyphosate and its degradation product AMPA in Hawaiian streams and sediments relative to historic concentration levels of other persistent organic pollutants (POPs) can be seen by the data tabulated in Table 5. This table compiles the pesticide data generated for nearshore stream and sediment samples collected by researchers from the WRRC in the early to mid-1970s during two studies conducted in the relatively new urban community of Hawaii Kai (Maunalua Bay) and from watersheds that contribute runoff to Kaneohe Bay, which contain a mixture of urban, agricultural and mixed-use areas [1,2,3]. In order to be more comparable to the nearshore stream and sediment data collected during this study, bay water and sediment samples collected during these studies from offshore locations within Kaneohe and Maunalua Bays as well as stream samples collected from inland portions of the watersheds were excluded from the calculations compiled in Table 5.

Unfortunately, the data for chlordane, dieldrin, and DDT obtained during this study in stream and sediment samples is difficult to compare to the mid-1970s data because of the significantly higher detection limits achieved by the commercial laboratory compared to the detection levels reported by the researchers at WRRC [2] (120–600 ng/L versus 1–10 ng/L).

The mean detected concentration of glyphosate currently present in Hawaiian streams is over seven times higher than the mean detected concentration of PCP and over 100 times higher than the mean detected concentrations of chlordane, dieldrin, and DDT present in Oahu streams in the mid-1970s. The mean concentration of glyphosate in sediments is also over 10 times higher than the mean detected concentration of chlordane and over one hundred times higher than the mean concentration of dieldrin, DDT, and PCP present in sediments in the mid-1970s. It is likely that AMPA is also present in Hawaiian streams at roughly similar concentration levels as Glyphosate (its parent compound). The average ratio of glyphosate to AMPA concentration measured in the sixteen sediment samples where both compounds were detected was 1.02. Previous studies have attributed the high detection frequency of glyphosate in streams to its high solubility and persistent applications in agricultural and urban settings for weed control along roadsides and ditches as well as ubiquitous household use [14]. The addition of surfactants and other adjuvants to glyphosate formulations may also increase glyphosate's mobility in the environment. Glyphosate and AMPA also enter the marine environment in the suspended sediment load during runoff events. It is estimated that between 10% and 18% of the total glyphosate load is present in suspended sediment during runoff events [13].

Figure 2 compares the range in glyphosate concentrations detected during the current study with the range in concentrations of the four most commonly detected pesticides during the recent USGS water quality study of 32 streams on the islands of Oahu and Kauai [15]. The samples collected during the USGS study were analysed for 225 current-use pesticide compounds (109 pesticides and 116 pesticide degradants) but not for Glyphosate or AMPA.

Two of the four most commonly detected pesticides during the USGS study were degradation products of herbicides used in Hawaii, OIET (atrazine) and DCPMU (diuron). The other two most commonly detected pesticides were the insecticides Imidacloprid and Fipronil. As is the case for glyphosate, generally higher concentration levels of these herbicides and insecticides were detected under high-flow conditions in the sampled streams. The detection limit for glyphosate (50 ng/L) during this study was significantly higher than the detection limits achieved for these four pesticide compounds by the USGS laboratory (4–16 ng/L). Despite this elevated detection limit, the detection frequency for glyphosate in Hawaiian streams was still very high under both high and low flow conditions. As can be seen in Fig. 2, the range in glyphosate concentrations measured in Hawaii streams under both high and low flow conditions are generally an order of magnitude higher than the four next most commonly detected pesticides observed during the USGS study. The ubiquity of glyphosate in the Hawaiian environment is demonstrated by the fact that glyphosate and/or its degradation product AMPA was detected in every river bed sediment collected during this study and the previous HDOH study [6] and in surface water collected from seventeen of eighteen streams sampled during this study.

Table 5: Comparison of mid-1970 POPs and present glyphosate/AMPA concentrations.

Matrix	Sample	Chlordane	Dieldrin	DDT	PCP	Glyphosate	AMPA
Current study (2014–2018): mean/median detected values (detection frequency)							
Water (ng/L)	36	<600/<600 (0%)	<120/<120 (0%)	<120/<120 (0%)	NA	864/319[1] (73%)	NA
Sediment (ng/kg)	25	170,000/ 170,000 (8%)	32,000/ 32,000 (4%)	54,500/ 54,500 (8%)	NA	916,375/ 385,000 (67%)	727,875/ 105,000 (100%)
Kaneohe Bay [3,4]: mean/median detected values (detection frequency)							
Water (ng/L)	64	4.8/2.8 (100%)	3.2/1.5 (95%)	5.9/3.8 (86%)	116/80 (95%)	NA	NA
Sediment (ng/kg)	6	88,083/38,950 (100%)	5,142/2,350 (100%)	8,267/ 6,000 (83%)	6,900/5,050 (100%)	NA	NA
Maunalua Bay [2]: mean/median detected values (detection frequency)							
Water (ng/L)	19	2.4/2.5 (47%)	1.9/2.0 (58%)	1.4/1.0 (79%)	9.0/7.5 (75%)	NA	NA
Sediment (ng/kg)	32	2,156/794 (97%)	795/399 (91%)	2,501/1,407 (97%)	2,560/1,420 (100%)	NA	NA

[1]Median stream glyphosate concentration based on 118 detected concentrations (162 samples analysed).

NA = not analysed.

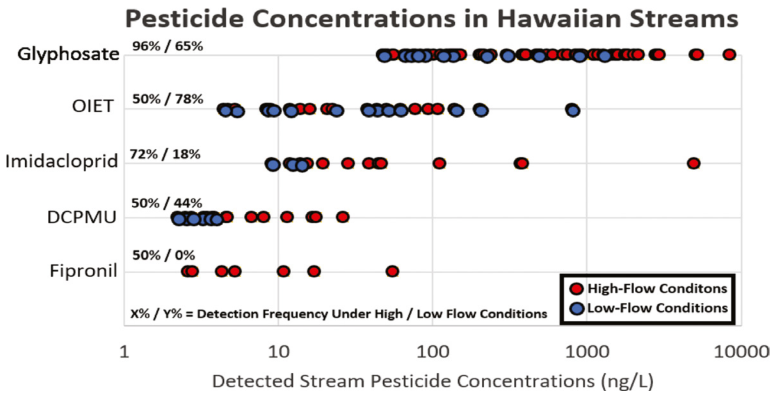

Figure 2: Concentration levels of most common pesticides detected in Hawaiian streams.

In order to put the pesticide concentrations detected in Hawaiian streams and sediments during this study in perspective, Fig. 3 plots the mean glyphosate concentration (in parts per billion [ppb]) measured in various environmental media in Hawaii along with glyphosate concentration levels detected in human urine in the United States [15], beer and wine [16], honey on the island of Kauai [17] and various oat-based breakfast foods [18]. The graph includes information on the mean and standard error of glyphosate concentrations measured, the number of samples collected (n), and the frequency of detection below each data point. The mean concentration of glyphosate detected in human urine (3.1 ppb) is more than twice the mean concentration level of glyphosate detected in Hawaiian streams under high flow conditions (1.3 ppb) while beer and wine (6.9 and 9.3 ppb) contain between five to seven times the mean stream concentration level. The mean glyphosate concentration levels measured in honey (115 ppb) and oat-based cereals (305 ppb) are broadly similar to the mean glyphosate concentration levels measured in stream bed sediments (268 ppb).

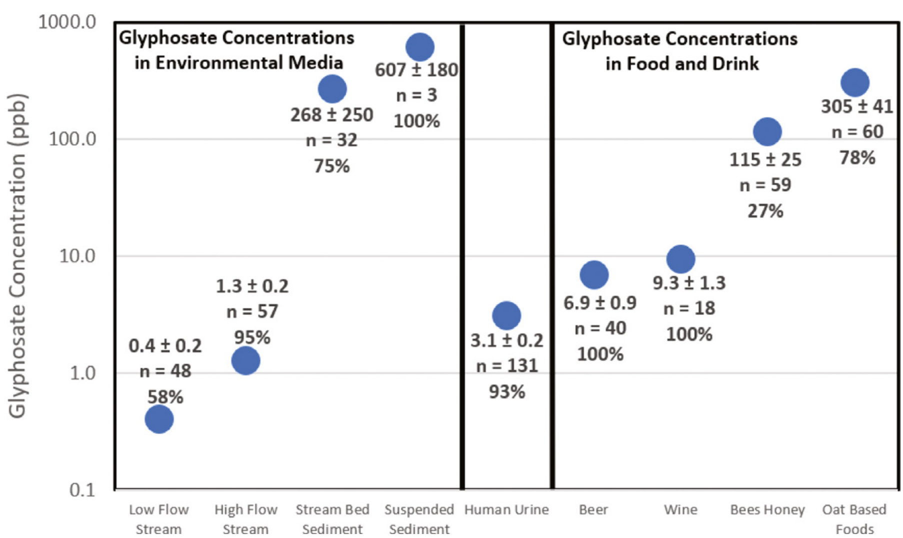

Figure 3: Glyphosate concentration in environmental media, food, drink and urine.

A rough estimate of the annual glyphosate loading to the marine environment on Oahu can be made using recent estimates of average daily rainfall runoff developed for the island of Oahu (264.77 million gallons per day) [19]. Unlike other pesticides, glyphosate was seen in runoff emanating from sampled watersheds from all around the island regardless of land use during this study. If one assumes that the average glyphosate concentration measured during this study under storm runoff conditions (1,308 ng/L) is representative for the island as a whole, an average daily flux of roughly 1.3 kg of glyphosate is estimated to enter the marine environment on Oahu. The daily load of AMPA to the marine environment is likely similar. This rough estimate does not count the smaller amounts of glyphosate and AMPA that enter the marine environment under baseflow conditions. On Oahu, the vast majority of suspended sediment transport and to a lesser extent rainfall runoff occurs during individual, large storm events. Monitoring conducted over a 3-year period in the Waikele watershed in central Oahu by the USGS found that more than 90% of the suspended-sediment yield over the 3-year period and 12% of annual streamflow from this watershed occurred during a single 9-h duration storm event on 11 December 2008 [20]. A recent study in Australia demonstrated that glyphosate is moderately persistent in the marine water under low light conditions (47-day half-life) and is highly persistent in the dark (315-day half-life) [21]. Little degradation would be expected during the typical flood plumes created during large storm events, which could potentially deliver a significant mass of dissolved and sediment-bound glyphosate and AMPA into the marine environment on Oahu far from shore.

6 CONCLUSIONS

This survey water quality study found widespread, low-levels of pesticide contamination within surface waters and stream bed sediment on the islands of Oahu and Kauai. Five herbicide and one insecticide compound currently used in Hawaii were detected in the stream samples collected. Seven insecticides, five herbicide and one fungicide compound that are both legacy and currently used pesticides were detected in the stream bed sediment samples analysed. The herbicide glyphosate and/or its degradation product AMPA were detected in every sediment sample collected and in all but one of the eighteen streams monitored on the islands of Oahu and Kauai over a 3-year period. The present-day mean detected concentration levels of glyphosate are roughly an order of magnitude higher than the next most commonly detected currently used pesticide present in Hawaiian streams (imidacloprid) and seven and ten times higher than concentration levels of POPs measured in streams and streambed sediments in the mid-1970s on the island of Oahu.

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