OCCURRENCE AND PERSISTENCE OF THE HERBICIDE GLYPHOSATE IN A SUBURBAN TROPICAL WATERSHED

STEVEN R. SPENGLER[1], MARVIN D. HESKETT[1], SAMUEL C. SPENGLER[2]
[1]Element Environmental, [2]United States Forest Service

ABSTRACT

Stream, streambed sediment and suspended sediment sampling for the herbicide Glyphosate was conducted in a small, 4.05-square kilometer suburban watershed on the island of Oahu, Hawaii between December 2017 and April 2020. Over this 2.5-year study period, a total of 188 stream samples (142 runoff conditions, 46 baseflow conditions), 81 streambed sediment samples, and 9 suspended sediment samples were collected and analysed for glyphosate and a subset of sediment samples were analysed for its degradation product aminomethylphosphonic acid (AMPA).

The glyphosate concentration levels measured during stormwater runoff conditions within Kawa stream were significantly higher than levels measured under groundwater dominant baseflow conditions. The mean and median glyphosate concentrations (µg/L) and the frequency of glyphosate detection (reporting limit 0.075 µg/L) measured in Kawa stream under runoff and baseflow conditions were 0.98/0.51/92% and 0.10/0.035/28%, respectively. The glyphosate concentrations measured in this small suburban tropical stream were significantly higher than mean levels measured by the USGS between 2014 and 2020 in streams that drain small urban watersheds throughout the continental United States. The glyphosate concentration levels measured in riverbed and suspended sediments in Kawa stream were generally two to three orders of magnitude higher than levels measured in stream-water.

The majority of glyphosate (>90%) was transported to Kaneohe Bay in the dissolved phase and originated from residential areas within the contributory watershed. The mean mass flux of glyphosate measured entering the near coastal environment under baseflow conditions was around 0.16 mg/min, while the mean mass flux during runoff conditions was 106 mg/min. The estimated median half-lives of glyphosate and AMPA measured in streambed sediments during this study were 4.7 and 6.2 days, respectively. This short half-life (4.7 days) along with the high-frequency (92%) of glyphosate detection in Hawaiian streams under runoff conditions illustrates the steady, unceasing input of glyphosate to Hawaiian streams.

Keywords: glyphosate, AMPA, environmental half-life, transport mechanism, streams, stream bed sediment, suspended sediment, urban mass flux.

1 DESCRIPTION OF STUDY AREA

Kawa stream is a perennial, 4.2-kilometer long stream (including a 0.6-km long tributary, Kawa Ditch) located in Kaneohe on the windward side of the island of Oahu, Hawaii. The main branch of the stream starts in the Hawaii Memorial Park cemetery and runs in a generally north/northeasterly direction through residential areas before discharging along the southern shoreline of Kaneohe Bay. Baseflow to the stream originates from small, perched groundwater seeps and springs within the watershed that range in elevation from 15 to 70 m above mean sea level. The United States Geological Survey (USGS) began continuous streamflow monitoring of Kawa stream on 9/29/2016. The mean and median streamflow measured in Kawa stream between September 2016 and July 2020 was 0.11 and 0.03 cubic meters per second (cms), respectively.

The major land uses within the 4.05 square kilometer Kawa stream watershed are single-family residential (35.5%), forest land (34%), cemetery land (11.5%), golf course (6%), school (6%), highways and streets (4%), commercial (2%) and park areas (1%) [1]. The residential portion of the watershed is known as the Pikoiloa neighborhood and has a population

ISSN: 2398-2640 (paper format), ISSN: 2398-2659 (online), http://www.witpress.com/journals
DOI: 10.2495/EI-V4-N2-141-156

of around 4 000. The houses in the watershed range in age from 20 to 80 years old and are highly sought after for their large lot sizes by Hawaiian standards (average lot size of 750 square meters). The southwestern headwaters of the watershed contain two separate cemeteries, the private Hawaiian Memorial Park and the Hawaii State Veterans Cemetery. The watershed also contains an elementary school (Kaneohe Elementary) and high school (James B. Castle High). The coastal section of the watershed contains the 18-hole Bayview Golf Course.

Urbanization of the watershed has altered the stream's natural hydrologic and hydraulic features [2]. Concrete drop structures constructed within the stream during urban development of the area reduced stream slopes and concrete channel linings stabilized the stream banks. Rainfall generated stormwater that falls on the residential portions of the watershed are conveyed to Kawa stream through a network of approximately 260 inlets (catch basins and grated inlets), 120 manholes, and nearly 13 700 linear meters of ditches, drainage pipes and box culverts [1]. The increase of impervious surfaces and installation of an efficient storm drain system during development of the residential subdivisions, cemeteries and schools within the watershed increased peak flows in the stream since storm generated runoff within the urbanized portions of the watershed can travel at greater speeds through the conveyance systems as well as through the hardened channelized sections of the stream. The resultant increased energy of flow within the stream during runoff events has led to downcutting within the unlined sections of the stream bed and undermined some of the constructed stabilizing structures within the stream [2].

Kawa stream is currently in violation of State of Hawaii water quality standards and is included in the 1998 Clean Water Act §303(d) list of impaired water bodies in the State of Hawaii. Total Maximum Daily Load (TMDL) standards, which reflect the maximum pollutant loads a waterbody (in this case, Kaneohe Bay) may receive, were previously established for nutrients (nitrogen and phosphorous) and total suspended solids (TSS) present in Kawa stream. A TMDL study of Kawa stream concluded that the nutrients leaving the watershed could enhance unwanted algae growth within the stream and Kaneohe Bay [3].

2 GLYPHOSATE PROPERTIES AND USAGE

Glyphosate and AMPA are non-volatile, polar and very soluble in water (11.6 g L^{-1}, 25 °C for glyphosate). However, these compounds strongly adsorb to soil particles, which bind them in the upper soil layer reducing their ability to leach into deeper soil layers and into groundwater [4]. Both compounds are very hydrophilic and practically insoluble in organic solvents and thus are assumed to be non-bioaccumulative in living organisms [5].

Previous half-life values measured for glyphosate range from 2 to 215 days in soils and from 2 to 91 days in waters [6]. The wide range of observed half-lives for glyphosate is a result of variable environmental conditions at the various previous study sites including soil characteristics (i.e. extent of soil-binding), pH and endogenous microbial populations and activity. Degradation of glyphosate in soils is mainly a biological process accomplished by different microorganisms, but bacteria, in particular members of the genus *Pseudomonas*, seem to be the most important [7]. The degradation product AMPA is believed to be somewhat more persistent than glyphosate in the environment, with measured half-lives in soil ranging from 60 to 240 days [8,9]. The decay of glyphosate and AMPA under laboratory conditions was fastest under warm and moist soil conditions and slowest under cold and dry conditions [10]. For instance, glyphosate was found to decay 8.4 times faster at 30^{o}C than at 5^{o}C under laboratory conditions.

Table 1: Glyphosate Use in the United States (Benbrook, 2016).

Annual glyphosate usage (1 000 kg)	1974	1982	1990	1995	2000	2005	2010	2014
Agricultural usage	363	2 268	3 359	12 465	35 699	71 481	106 941	113 347
Non-agricultural usage	272	1 270	2 402	5 679	8 980	10 025	11 357	12 037

Glyphosate is the most widely used herbicide, both in terms of mass applied and geographic distribution, in the United States. By comparison, the annual mass of the second-most used weed killer herbicide applied to agricultural crops in 2016 in the United States (atrazine) was roughly one quarter the mass of glyphosate applied. Historical usage data compiled by Benbrook [11] show that glyphosate use in the United States has increased roughly 200-fold since 1974 (Table 1). The increases in glyphosate usage in the United States and world-wide resulted mainly from widespread adoption of Roundup Ready crops that were genetically engineered to be tolerant to glyphosate in the early 1990s [12].

In the United States, it is estimated that over 12 million kilograms of glyphosate are currently used for non-agricultural purposes annually, including application by municipalities and homeowners to streets, parks, lawns, backyards and along waterways in urban and suburban settings [13,14]. The upward trend in glyphosate use has contributed to significant incremental increases in environmental loadings and human exposures to glyphosate, AMPA, and various surfactants and adjuvants used in formulating end-use glyphosate-based herbicides [11].

A previous water quality study conducted in Hawaii found widespread glyphosate contamination within surface waters and stream bed sediment on the islands of Oahu and Kauai [15]. Either glyphosate or AMPA was detected in 100% of the 32 stream bed sediment samples collected from multiple streams sampled on these two islands during this study. The present-day mean concentration levels of glyphosate measured in Hawaiian stream waters are roughly an order of magnitude higher than the next most commonly detected pesticide (the atrazine degradation product, 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine (OIET), with a mean concentration of 59 ng/l and 67% detection frequency) measured by the USGS in 32 stream waters collected on the islands of Oahu and Kauai from November 2016 to April 2017 [16]. In addition, the current mean glyphosate stream and sediment concentrations are seven and ten times higher than concentration levels of persistent organic pollutants (α-chlordane in sediment and pentachlorophenol in streams) measured in the mid-1970s on Oahu [17].

3 STUDY METHODOLOGY

Stream, suspended sediment and streambed sediment samples were collected from Kawa stream for glyphosate analysis between December 2017 and April 2020. The stream samples were also analysed for total suspended solids (TSS) and specific conductance. A total of 188 stream samples were collected in order to quantify the variation in glyphosate concentration present in the stream throughout the year under both baseflow and runoff conditions and over the duration of individual runoff events. A total of nine suspended sediment samples were collected during nine separate runoff events during this 2.5-year monitoring period. In addition, a time series of 81 increment streambed sediment samples were collected from three monitoring locations within the stream between February 2019 and April 2020. Stream and suspended sediment samples were collected at the USGS Gaging Station while the streambed sediments were collected at the Upper Dam, Lower Dam and Kawa stream Mouth sampling locations depicted in Fig. 1.

A multi-incremental sampling approach was used to collect the streambed sediments in order to produce representative temporal glyphosate concentration data. Traditional discrete sampling methodologies often produce a large variability of measured concentrations between and within individual discrete sediment samples collected at a given site. Sampling theory [18] and field experiments [19,20] have determined that a representative concentration for an analyte present in a heterogeneous matrix is best achieved by a multi-increment sampling approach which involves the collection of an adequate sample mass from an adequate number of locations within a delineated area of interest known as a Decision Unit (DU). Three DUs were established along different reaches of Kawa stream during this study which were repetitively sampled. The largest sampled DU was 250 square meters in size and established in the estuary where Kawa stream discharges into Kaneohe Bay. The two other DUs were both 20 square meters in size and were located just upstream of concrete drop structures installed to reduce the natural slope of the stream. The sampled DUs correspond to the upstream areas behind these drop structures where sediments transported in the stream tend to accumulate and the segment of stream where the stream enters the bay. A total of 50 increments of approximately 5 grams of sediment per increment were collected from each DU to create an individual

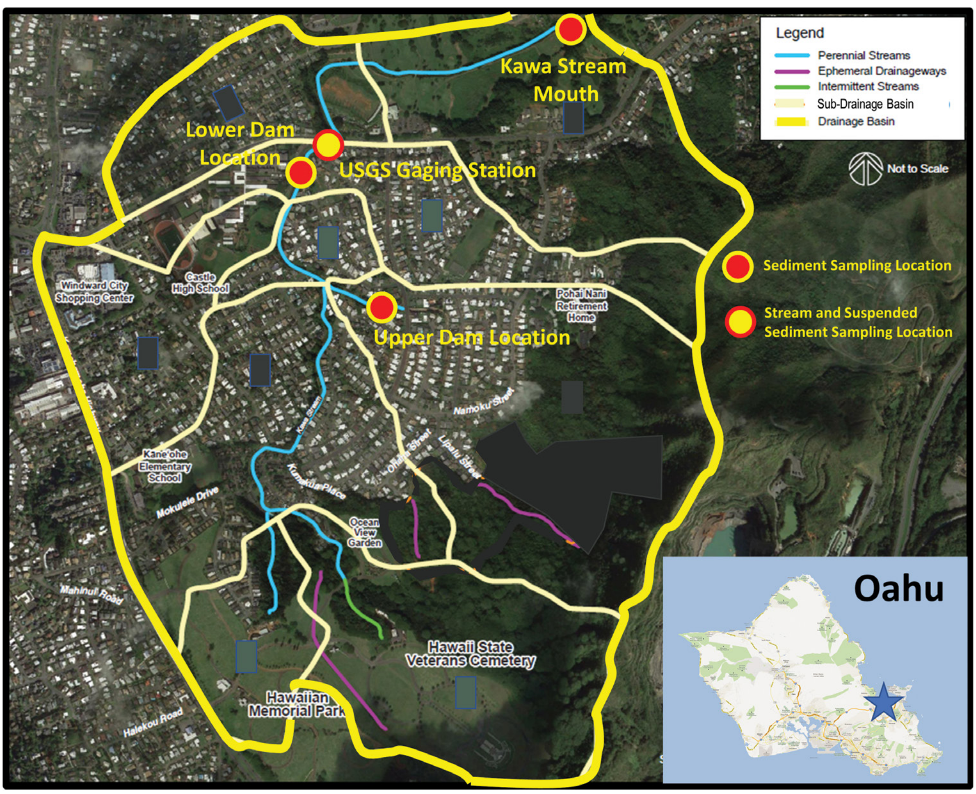

Figure 1: Kawa Watershed Kawa stream watershed and locations where stream and sediment samples were collected.

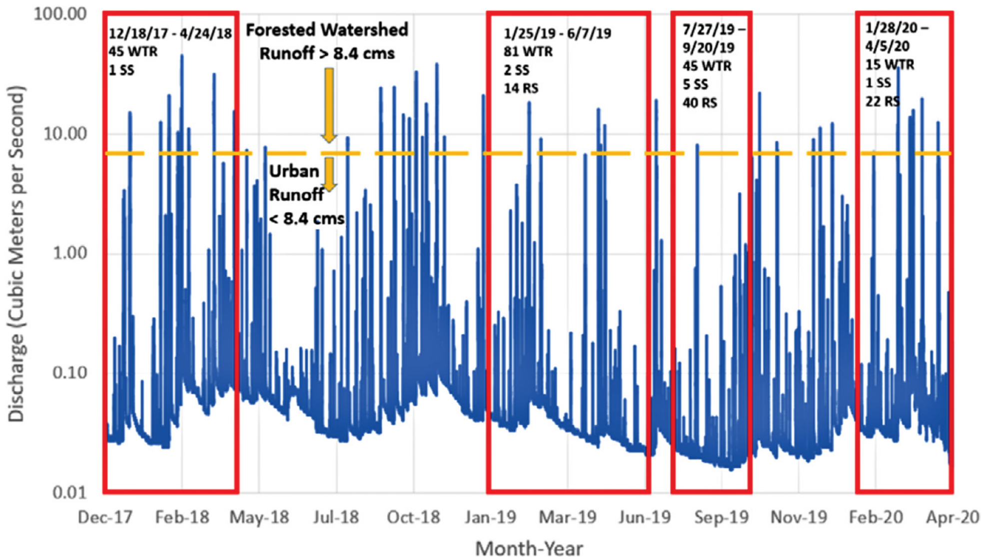

Figure 2: Kawa Stream Hydrograph Kawa stream hydrograph during study period: December 2017 to April 2020.

multi-increment sample that was then analysed for glyphosate content. An attempt was made to collect each sample from roughly the upper 1–2 cm layer of sediment present within each sampled DU. Gravel size particles (>2 mm) were removed by screening the samples prior to analysis. Suspended sediment samples were collected continuously from the stream over time periods of between 15 and 45 minutes during which time three to four coincidental stream samples were collected for glyphosate and total suspended solids analysis.

Figure 2 shows the hydrograph for Kawa stream between December 2017 and April 2020 and the four periods of time (red rectangles) when environmental samples were collected. The number of stream samples (WTR), suspended sediment samples (SS) and streambed sediment samples (RS) collected during each sampling period are also shown in this figure. The yellow dashed line shows the approximate streamflow (~8.4 cms) above which runoff from the forested watershed begins contributing to streamflow within Kawa stream. Glyphosate was not detected in three runoff samples collected from the forested portion of the watershed in early 2018.

4 STREAM, SUSPENDED SEDIMENT AND STREAMBED SEDIMENT RESULTS

Glyphosate concentrations were measured using the Abraxis Glyphosate Enzyme Linked Immunosorbent Assay (ELISA) Plate Kit. The ELISA method was used for this study since it allowed for higher frequency testing while reducing cost and time for analysis as compared to fixed laboratory methods. The Glyphosate ELISA method has a reporting limit of 0.075 and around 18 ppb for water and sediments, respectively. The sediment samples were extracted with 1 M NaOH. A total of 13 split time-series streambed sediment samples collected from the Upper Dam sampling site were submitted to Pacific Agricultural Laboratory for Glyphosate and AMPA analysis by Liquid Chromatography-Fluorescence Detection (LC-FLD). The limit of quantification for Glyphosate and AMPA in sediment with the LC-FLD method is 17 and 50 ppb, respectively. The coefficient of determination (R^2) for the glyphosate concentrations measured in the thirteen splits of sediment samples analysed by both immunoassay and LC-FLD methods was 0.66. Table 2 summarizes the glyphosate concentrations measured in suspended sediment and streambed sediments, and in stream waters under baseflow and ascending/descending runoff conditions during this study.

Stream samples collected under baseflow conditions where shallow perched groundwater was the source of streamflow typically contained undetectable or trace levels of glyphosate (28% detection frequency, 0.075 µg/L detection limit). Stream samples collected under both ascending and descending runoff conditions contained similar elevated mean glyphosate concentrations (around 1.0 part per million) and detection frequencies (around 92%). The variation in stream glyphosate concentration measured during individual runoff events suggests that glyphosate originates from both input to the stream from stormwater runoff from the surrounding residential portions of the watershed as well as from resuspension and release of glyphosate accumulated within streambed or riparian sediments deposited within and along the banks of the stream.

The highest median glyphosate concentration (724 µg/kg) was measured in the suspended sediment samples. The highest median streambed sediment concentrations were measured at the Upper Dam sampling site (573 µg/kg), which receives runoff from the surrounding residential community in the eastern portion of the watershed. The streambed sediment collected from the Lower Dam sampling site, which receives runoff from both the eastern and western portions of the watershed that contains the two cemeteries, elementary and high school, contained less than half the median glyphosate concentration (254 µg/kg) present in the sediment at the Upper Dam sampling site that receives only runoff from the eastern, residential portion of the watershed. This suggests that the residential areas within the watershed contribute higher loads of glyphosate to the stream than the cemeteries and schools within the watershed. The glyphosate concentration measured in the fine grain sediments present in the estuary where Kawa stream discharges into Kaneohe Bay are significantly lower (44 µg/kg) than levels measured in streambed sediments higher up in the watershed. This result may indicate that much of the glyphosate transported via Kawa stream discharges further out in Kaneohe Bay from the sampled DU located at the mouth of the stream during large rainfall runoff events.

Figure 3 depicts the median and range of glyphosate concentrations measured in runoff and baseflow condition stream samples, as well as the suspended sediment and streambed sediments analysed during this study. The median glyphosate concentrations measured in these media vary over five orders of magnitude. The elevated glyphosate concentrations measured in streambed sediments that accumulated at the Upper Dam site (compared to the levels measured down-stream at the Lower Dam site) suggest that the surrounding eastern residential portion of the watershed contributes the majority of the glyphosate measured within the watershed.

The mean and median concentration of glyphosate measured in Kawa Stream between 2017 and 2020, whose contributory watershed consists of residential and suburban land use, are similar to but slightly higher than glyphosate concentrations measured elsewhere on Oahu in Honouliuli Stream (mean 0.76 µg/L, median 0.22 µg/L, 54 samples collected between 2017 and 2020), which flows through the major industrial agricultural watershed on the island of Oahu, where large-scale experiments on genetically modified corn are conducted as well as diversified agriculture practiced. This illustrates the significant importance of urban and residential usage of glyphosate in the overall mass flux of this chemical within the environment.

The measured stream glyphosate concentrations are significantly lower than the U.S. Environmental Protection Agency drinking water Maximum Contaminant Level of 700 µg/L [21], and the chronic aquatic toxicity standards (1 800 µg/L) established by the State of Hawaii

Table 2: Glyphosate concentrations measured in stream and sediment samples.

Condition	# Samples	% Detect glyphosate	Median glyphosate[1]	Mean glyphosate[1]	Maximum glyphosate	Minimum Glyphosate
Stream water samples (µg/L)						
Baseflow conditions	47	27.7%	0.035	0.10	0.91	0.035
Ascending runoff conditions	93	92.5%	0.48	0.99	6.99	0.035
Descending runoff conditions	46	91.3%	0.72	0.96	6.60	0.035
Sediment samples (µg/kg)						
Suspended sediment	9	89%	724	1 056	3 934	< 97
Streambed sediment: upper dam	41	100%	573	701	4 100	51
Streambed sediment: lower dam	8	100%	254	245	418	28
Streambed sediment: stream mouth	32	31%	44	47	87	< 18

[1] Non-detect results were assigned a concentration of 0.035 ug/L.

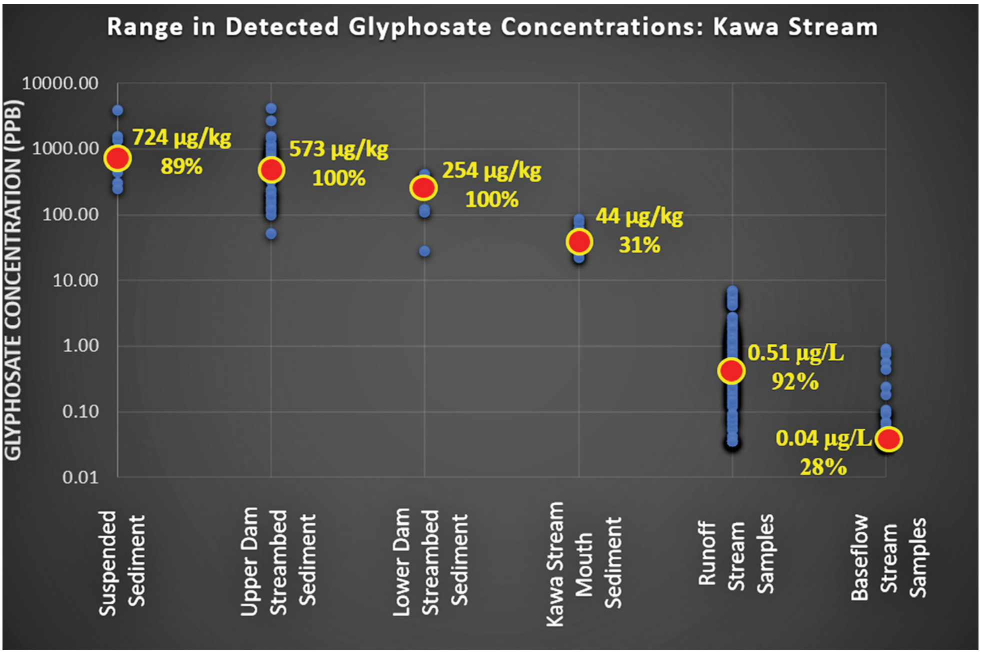

Figure 3: Median concentration and frequency of detection of glyphosate in suspended sediment, streambed sediment, runoff streamflow and baseflow streamflow.

Department of Health [22]. There are no human health or aquatic life benchmarks for AMPA. However, pesticides such as glyphosate and AMPA are often detected in the environment as chemical cocktails composed of multiple pesticides, surfactants and adjuvants. Further research is warranted on potential increased synergistic risks posed by glyphosate combined with other chemicals at the low part per billion levels commonly detected in streams.

The USGS has been conducting periodic monitoring of glyphosate and AMPA in a network of over 70 streams across the contiguous United States since the early 2000s [6,23]. The detection limit achieved by the USGS laboratory since 2009 is 20 ng/L as compared to the 75 ng/L detection limit associated with the immunoassay analysis used during this study. Table 3 compares the glyphosate concentrations measured in Kawa stream between 2017 and 2020 with glyphosate concentrations measured in small, urban watersheds in the mainland United States between 2014 and 2020 by the USGS, listed in order of median streamflow. The mean and median glyphosate concentration measured by the USGS in streams within these ten, small (<10 000 km^2) urban watersheds were 210 and 60 ng/L, respectively. By comparison, the mean and median glyphosate concentrations measured in Kawa stream were 759 and 341 ng/L, respectively, or 3.6 and 6.0 times higher. The only mainland United States stream that had similar glyphosate concentration levels as measured in Kawa stream was the Santa Ana River, which runs through the densely populated suburban metropolis surrounding Los Angeles. The elevated mean and median glyphosate concentrations measured in this small suburban Hawaiian watershed stream is likely due to three factors: (1) the small size of the Kawa watershed and the correspondingly short travel distances required for the glyphosate to enter the stream from the surrounding residential areas; (2) the extensive storm sewer

Table 3: Glyphosate levels in Hawaiian and continental United States urban watersheds.

Stream	State	Median streamflow (cms)	% Watershed developed	Number of samples	Median glyphosate (µg/L)	Mean glyphosate (µg/L)	Detect frequency
Kawa (All)	Hawaii	0.032	66.0%	186	341	759	76%
Kawa (Runoff)	Hawaii	0.032	66.0%	139	510	980	92%
Kawa (Baseflow)	Hawaii	0.032	66.0%	47	35	104	28%
Shingle	Minnesota	0.5	87.5%	128	50	95	73%
Swift	N Carolina	0.7	94.1%	128	80	173	96%
Cherry	Colorado	0.8	49.7%	135	130	343	85%
Fanno	Oregon	1.3	99.2%	126	90	135	98%
Sope	Georgia	1.4	99.1%	120	35	93	72%
Santa Ana	California	6.3	49.6%	85	320	800	99%
White Rock	Texas	2.6	97.8%	115	210	467	91%
Clinton	Michigan	8	70.8%	133	30	125	59%
Neuse	N Carolina	79	42.8%	97	50	70	79%
Chattahoochee	Georgia	111	66.2%	89	30	57	66%

system and moderately steep watershed topography within the Kawa watershed; and (3) the fact that ground treatment for weeds is required year-round in the tropical environment in Hawaii.

The instantaneous mass of dissolved phase glyphosate present in Kawa stream measured during the 2.5-year monitoring period was estimated by multiplying the measured glyphosate concentration by the streamflow volume at the time the samples containing detectable levels of glyphosate were collected. Under baseflow conditions, separate values were calculated based on just samples with detectable concentrations (13 samples) and for all baseflow samples collected (47 samples, 28% detection frequency). The mean, median and maximum glyphosate mass flux measured in Kawa stream is summarized in Table 4.

The total mass of glyphosate discharged in the dissolved phase from the Kawa watershed over the 2.5-year monitoring period was estimated to be around 4.4 kg (baseflow assumed for streamflow below 0.07 cms) when the median measured glyphosate mass flux under all baseflow and runoff conditions (0.0 and 19.9 mg/min) were applied to the 2.5-year flow data recorded by the USGS.

The annual mass of dissolved phase glyphosate discharging from Kawa stream is compared to the annual mass of glyphosate discharged from the larger, urban watersheds on the mainland United States in Table 5. The annual glyphosate mass for the mainland USGS stations was calculated by multiplying the median glyphosate concentration measured between 2014 and 2020 by the mean streamflow during this same period of time. The annual mass of glyphosate discharged from the Kawa watershed normalized to the urbanized area within the watershed is 7 to 110 times higher than the area normalized glyphosate mass flux measured in mainland streams. The contribution of glyphosate to Kawa stream per person living within the watershed is the second highest of the rivers compiled.

In addition to the dissolved phase, glyphosate is also transported out of the watershed in suspended sediment during runoff events. The percentage of glyphosate present in the suspended sediment load was measured during nine runoff events by continuously collecting suspended sediments over a 15 to 45-minute period as well as three or four contemporaneous stream samples. The total mass of suspended sediment during the sampling

Table 4: Mean, median and maximum glyphosate mass flux measured in Kawa stream.

Condition	# Samples	Mean glyphosate mass flux (mg/min)	Median glyphosate mass flux (mg/min)	Maximum glyphosate mass flux (mg/min)
Baseflow conditions (detects)	13	0.60	0.32	2.5
Baseflow conditions (all)	47	0.16	0.00	2.5
Ascending runoff conditions	86	113.6	19.0	1 006
Descending runoff conditions	42	90.3	26.4	872
All runoff conditions	128	106.0	19.9	1 006

Table 5: Annual and per capita mass of glyphosate mass discharged.

Stream	State	Annual glyphosate mass discharged (kg/year)	Annual glyphosate mass discharged per urban area (kg/year/km^2)	Total/urban watershed area (km^2)	Estimated population within watershed	Glyphosate contribution to stream per person (mg/year/person)
Kawa	**Hawaii**	**1.76**	**0.677**	**4.1/2.6**	**4 000**	**440**
Swift	N Carolina	1.76	0.034	54.4/51	25 000	70
Shingle	Minnesota	0.72	0.011	73.0/63.9	50 000	14
Sope	Georgia	1.49	0.019	80.0/79.0	30 000	50
Fanno	Oregon	3.59	0.044	81.6/80.9	60 000	60
White Rock	Texas	16.86	0.100	172/168	500 000	34
Clinton	Michigan	7.34	0.013	800/567	140 000	52
Cherry	Colorado	3.20	0.006	1 062/528	350 000	9
Santa Ana	California	63.23	0.022	5 858/2 905	1 500 000	42
Chattahoochee	Georgia	104.82	0.025	6 294/4 165	500 000	210
Neuse	N Carolina	125.00	0.042	6 972/2 984	65 000	1 923

interval was calculated by measuring the TSS concentrations in the stream samples collected. The glyphosate concentration in the composite suspended sediment collected and the concurrent stream samples were then measured by immunoassay. The percentage of glyphosate mass present in the suspended sediment compared to the mass present in the dissolved phase ranged from 1.2 to 27.7% during the nine sampled events. The mean/median percentage of glyphosate mass present in the suspended sediment versus the dissolved phase was 8.7% and 5.4%, respectively.

A total of 10 runoff samples collected during a large storm event (~2.3 inches daily rainfall on 3/15/20) were analysed for glyphosate and nutrients to provide insight to the relative amounts of suspended sediment, nutrients and glyphosate produced during a moderately large runoff event. Figure 4 shows the hydrograph for Kawa stream on 3/15/20 and the glyphosate, TSS and total nitrogen/phosphorous concentrations measured during the two periods of runoff that occurred on that day. The yellow dashed line delineates the portions of the hydrograph where runoff from the upland forested watershed contributed to streamflow. Previous sampling found that the forested portion of the watershed contributes no glyphosate but disproportionally large percentages of the suspended solids and nutrient loads that enter Kaneohe Bay during large runoff events.

The total mass of suspended solids, total nitrogen, total phosphorous, nitrate + nitrite and ammonia during the 3/15/20 runoff event was estimated to be 277,600, 2,085, 516, 142 and 19 kilograms, respectively, based upon the analytical results obtained on the ten samples collected. By comparison, the dissolved mass of glyphosate during this runoff event was estimated to be around 100 grams. The water quality data suggests that the watershed became

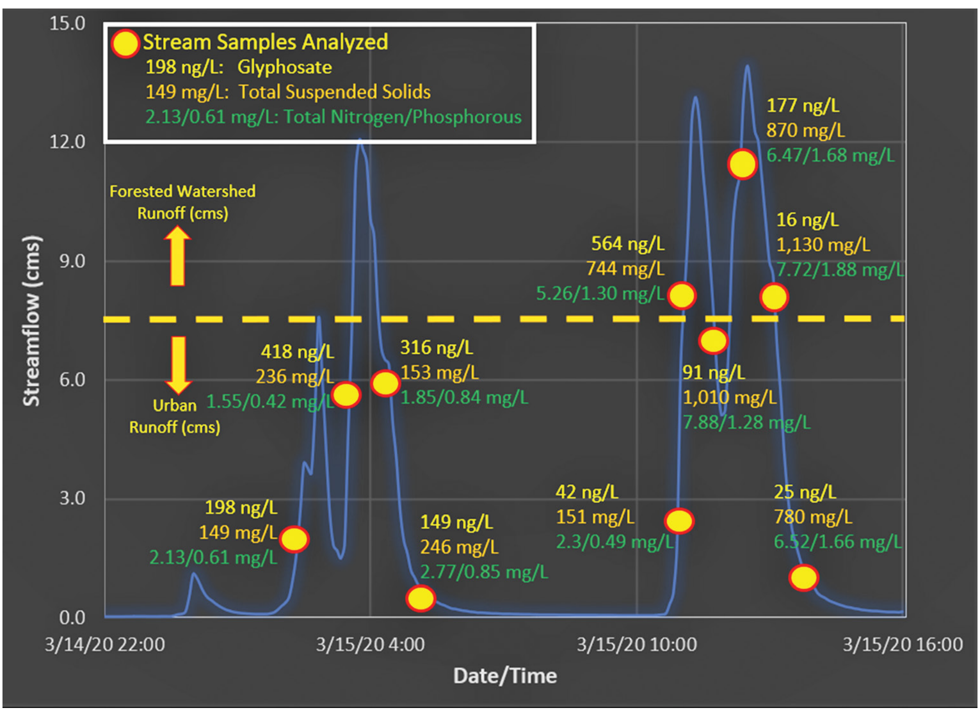

Figure 4: Variation in glyphosate, total suspended solid, nitrogen and phosphorous measured during 3/15/2020 rainfall runoff event.

almost depleted of glyphosate by around 13:00 during this storm event after 100 grams of glyphosate left the watershed since only trace levels of glyphosate were detected in the last two stream samples collected during this runoff event.

The half-life of glyphosate and AMPA in streambed sediments at the Upper Dam monitoring site was estimated by collecting a time-series of increment sediment samples from the DU established just above the concrete drop structure at this site. The decline in glyphosate and AMPA concentrations measured in the time-series of sediment samples collected during dry periods when no runoff occurred was used to derive the half-life values. It was assumed that no additional glyphosate was added to the sampled streambed sediments during these dry periods due to the near absence of glyphosate in stream samples collected under baseflow conditions.

Figure 5 plots the percentage reduction in glyphosate levels measured in sets of sediment samples collected after various durations of dry weather conditions. The degradation curves associated with half-life values of between 1 to 14 days are also shown on this figure. Measured half-lives for glyphosate in sediment ranged from 2.7 days to 7.6 days (12 measurements, median 4.7 days) while the AMPA half-lives (not plotted) ranged from 0.7 to 8.0 days (6 measurements, median 6.2 days). The median half-lives determined for glyphosate and AMPA (4.7 and 6.2 days) in stream sediments in the tropical Kawa watershed are significantly lower than typical literature values for these two compounds in soils (2–215 and 60–240 days, respectively) [6,8,9]. Despite the short persistence of glyphosate in the Hawaiian environment, the current concentration levels are seven and ten times higher than concentration levels of persistent organic pollutants (with longer half-lives on the order of years) measured in waters and sediments in the mid-1970s on the island of Oahu [15]. This attests to the significantly higher present-day mass loading of glyphosate to the Hawaiian environment than historic pesticide loading levels in urban environments.

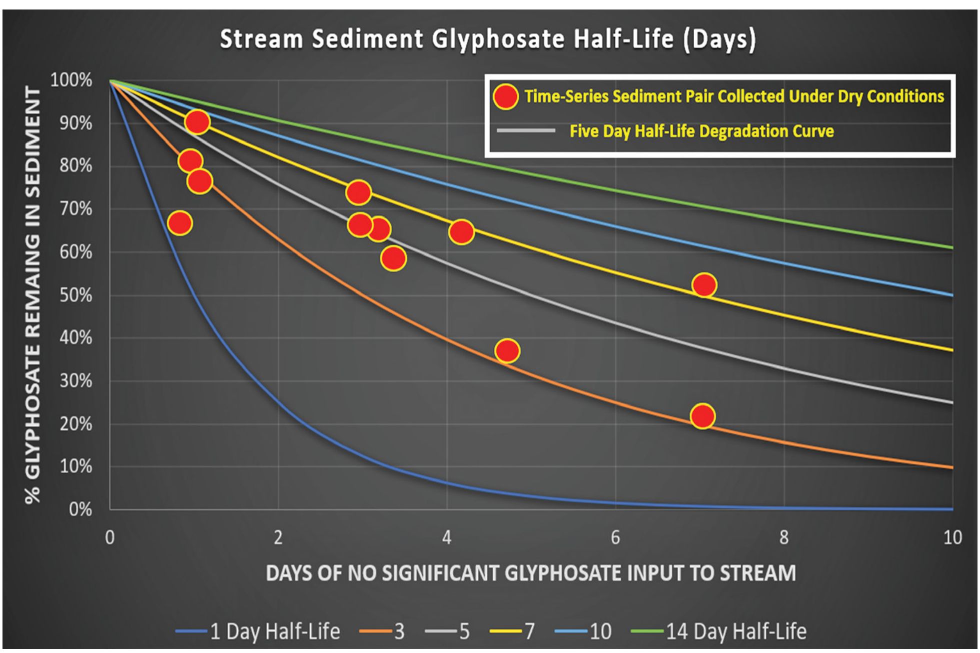

Figure 5: Range of glyphosate half-lives measured in streambed sediments.

5 CONCLUSIONS

Elevated glyphosate concentrations were measured in a stream that drains a small suburban tropical watershed in Hawaii compared to concentration levels measured in small streams in urban watersheds on the mainland United States. The present-day mean concentration of glyphosate in Hawaiian streams is an order of magnitude higher than mean concentrations levels of the next most commonly detected pesticide (the atrazine degradation product OIET, [16]) and seven and ten times higher than concentration levels of persistent organic pollutants measured in streams and sediments in the mid-1970s on Oahu [17]. Residential areas within the Kawa watershed (as opposed to golf courses, cemeteries and schools) were found to contribute the majority of glyphosate to the stream during large rainfall runoff events based on the spatial distribution of glyphosate concentrations measured in streambed sediments in Kawa stream.

The annual mass of glyphosate discharged from the Kawa watershed on Oahu normalized to the urban acreage within the watershed is 7 to 110 times higher than the area-normalized mass of glyphosate measured in mainland streams by the USGS. The small size, moderately steep topography, and extensive network of storm sewers and impervious surfaces within the watershed as well as year-round use of glyphosate for treatment of weeds likely contribute to the higher measured glyphosate fluxes in Kawa stream. The estimated mass of glyphosate (0.1 kg) discharged in Kawa stream during a well monitored runoff event on 3/15/20 was a small fraction (0.004%) of the mass of nutrients (total nitrogen and phosphorous, 2 601 kg) discharged during the same runoff event. Less than 10% of the annual glyphosate flux out of the Kawa watershed is transported in suspended sediments.

The median half-life of glyphosate and AMPA measured in streambed sediments during this study were 4.7 and 6.2 days, respectively. This short half-life combined with the ubiquitous detection of glyphosate in streams and sediments collected in Hawaiian streams during this and previous studies illustrate the unceasing nature of glyphosate input to the environment in the Hawaiian Islands. The most effective approach to reducing the mass flux of glyphosate entering the environment in the future would involve a combination of implementing governmental polices that promote reduction of nutrient, pesticide and sediment loads to urban storm drains systems and working with local health departments to provide guidance to the general public on the proper application of pesticides for homeowners.

ACKNOWLEDGEMENTS

The Pacific Islands Water Science Center (Mr. Travis Hylton) of the USGS graciously provided splits of stream samples collected by their autosampler on Kawa stream during the March 15, 2020 runoff event. The authors analysed the split samples for glyphosate while the USGS analysed the primary samples for TSS and nutrient content.

REFERENCES

[1] City and County of Honolulu. 2015. Implementation and Monitoring Plan for Kawa Stream Waste Load Allocation for the City and County of Honolulu Municipal Separate Storm Sewer System, NPDES Permit No. HI S000002, Report dated June 2015.

[2] Oceanit. 2015. Kawa Stream and Ditch Improvements Project, Kaneohe, Oahu. Draft Environmental Assessment prepared for the Department of Design and Construction, City and County of Honolulu by Oceanit Laboratories Inc. Report dated July 2015.

[3] Oceanit Laboratories, Inc. 2002. Total Maximum Daily Loads of Total Suspended Solids, Nitrogen and Phosphorous for Kawa Stream, Kaneohe, Hawaii. Report prepared March 2002 in conjunction with AECOS, Inc. and the State of Hawaii Environmental Planning Office.

[4] Yang, X.M., F. Wang, C.P.M. Bento, S. Xue, L.T. Gai, R. van Dam, H. Mol, C.J. Ritsema, V. Geissen. 2015a. Short-term transport of glyphosate with erosion in Chinese loess soil – a flume experiment. Sci. Total Environ., 512, pp. 406–414.
[5] Williams GM, Kroes R, Munro IC. 2000. Safety evaluation and risk assessment of the herbicide Roundup and its active ingredient, glyphosate, for humans. Regulatory Toxicology and Pharmacology. 31, pp. 117–165.
[6] Battaglin, W.A., Meyer, M.T., Kuivila, K.M., Dietze, J.E. 2014. Glyphosate and its degradation product AMPA occur frequently and widely in U.S. soils, surface water, groundwater and precipitation. American Water Resources Association, Am. Water Resour. Assoc. 50, 275–290.
[7] Borggaard, O.K., Gimsing, A.L. 2008. Review. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. Pest Management Science, 64:441–456 (2008)
[8] Giesy, JP, Dobson, S. and Solomon, K.R. 2000. Ecotoxicological Risk Assessment for Roundup Herbicide. Reviews of Environmental Contamination and Toxicology, 167: pp. 35–120.
[9] Bergstrom, L Borjesson, E., E. Stenstrom, J. 2011. Laboratory and lysimeter studies of glyphosate and aminomethylphosphonic acid in a sand and a clay soil. J. Environ. Qual. 40, 98–108. http://dx.doi.org/10.2134/jeq2010.0179.
[10] Bento, C.P.M., X.M. Yang, G. Gort, S. Xue, R. van Dam, P. Zomer, H.G.J. Mol, C.J. Ritsema, V. Geissen. 2016. Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. Sci. Total Environ., 572, pp. 301–311.
[11] Benbrook, C.M. 2016. Trends in glyphosate herbicide use in the United States and globally. Environ. Sci Eur. 28:3. DOI 10.1186/s12302-016-0070-0.
[12] Myers, J.P., M.N. Antoniou, B. Blumberg, L. Carroll, T. Colborn, L.G. Everett, M. Hanen, P.J. Landrigan, B.P. Lanphear, R. Mesnage, L. N. Vandenberg, F.S. vom Sall, W.V. Weishons and C.M. Benbrook. 2016. Concerns over use of Glyphosate-Based herbicides and risks associated with exposures: a consensus statement. Environmental Health, 15:19, DOI: 10.1186/s12940-016-0117-0.
[13] Hanke, I., I Wittmer, S. Bischofberger, C. Stamm, H. Singer. 2010. Relevance of urban glyphosate use for surface water quality. Chemosphere, Vol. 81, Issue 3, pp. 422–429.
[14] Tang, T., W. Boenne, N. Desmet, P. Seuntjens, J. Bronders, A. van Griensven. 2015. Quantification and characterization of glyphosate use and loss in a residential area. Science of the Total Environment 517, pp. 207–214
[15] Spengler, S.R., M.D. Heskett, J.I. Gray. 2019. Pesticide Levels in Streams and Sediments on the Islands of Oahu and Kauai, Hawaii. Int. J. Environ. Impacts, Vol. 10, No. 9, pp. 1–17.
[16] Johnson, A.G. and Kennedy, J.J., 2018, Summary of dissolved pesticide concentrations in discrete surface-water samples collected on the islands of Kauai and Oahu, Hawaii, November 2016–April 2017: U.S. Geological Survey data release, https://doi.org/10.5066/F7BG2N79.
[17] Lau, L.S. 1973. Quality of Coastal Waters, Second Annual Progress Report. Water Resources Research Center, Technical Report No. 77, September 1973.
[18] Pitard, F. F. 1993. Pierre Gy's Sampling Theory and Sampling Practice. New York: CRC Press.

[19] Brewer, R., John Peard & Marvin Heskett (2017a) A Critical Review of Discrete Soil Sample Data Reliability: Part 1 – Field Study Results, Soil and Sediment Contamination: An International Journal, 26:1, 1–22, DOI: 10.1080/15320383.2017.1244171

[20] Brewer, R., John Peard & Marvin Heskett (2017b) A Critical Review of Discrete Soil Sample Data Reliability: Part 2 – Implications, Soil and Sediment Contamination: An International Journal, 26:1, 23–44, DOI: 10.1080/15320383.2017.12441724

[21] Norman, J.E., Toccalino, P.L., Morman, S.A., 2018. Health-based screening levels for evaluating water-quality data. U.S. Geological Survey Web Page, 2d ed accessed September 23, 2019 at. https://water.usgs.gov/nawqa/HBSL doi:10.5066/F71C1TWP

[22] Hawaii Department of Health, Environmental Management Division. 2017. Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater. Hawaii Edition, https://health.hawaii.gov/heer/files/2019/11/Volume-1-HDOH-2017.pdf

[23] Medalie, N., T. Baker, M.E. Shoda, W.W. Stone, M.T. Meyer, E.G. Stets, M. Wilson. 2020. Influence of land use and region on glyphosate and aminomethylphosphonic acid in streams in the USA. Science of the Total Environment, Volume 707, March 10, 2020, 136008. https://doi.org/10.1016/j.scitotenv.2019.136008