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

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

Executive Summary

Atrazine use in Hawaii has declined from a high of approximately 400,000 pounds active ingredient per year in 1964 to 77,000 pounds active ingredient in 2012.

From 2000 to 2012, there were 4,800 calls to the Hawaii Poison Hotline for human pesticide exposures. One case of atrazine exposure to a worker was received by the Hawaii Poison Hotline during this time. Of the complaints made to the Hawaii Department of Agriculture (HDOA) from 2010 to October 2013 no cases of atrazine exposure were confirmed.

Environmental data for groundwater, surface water and air in Hawaii were evaluated. Extensive drinking water data for atrazine exists. Since 1993, atrazine concentrations in drinking water have not exceeded the maximum contaminant level (MCL) of 3 parts per billion. There is a downward trend in atrazine levels in drinking water throughout the state. Air sampling by the University of Hawaii (UH) on Kauai did not find detectable levels of atrazine. Limited surface water monitoring showed trace levels of atrazine on Oahu, Kauai, Maui and the Island of Hawaii. Based on this review of all available environmental data, there were no exceedances of health-based or ecological regulatory standards for atrazine.

Because little data are available on atrazine occurrence in surface waters of the State, it is not possible to assess whether ecological benchmarks for atrazine exposure are being exceeded in streams and near shore waters in Hawaii. This data gap exists because there is no regulatory program requiring surface water monitoring for pesticides, and no existing programs or funding in place within the Hawaii Department of Health (HDOH) or the HDOA to establish ongoing monitoring.

The HDOH recommends additional stream and near shore water sampling for atrazine and other commonly used pesticides to determine whether benchmarks are being exceeded. The HDOH secured limited funding and support through a partnership with the United States Geological Survey (USGS) and HDOA and intends to conduct near shore and stream sampling for a broad spectrum of currently used pesticides in the next several months. The results of the stream sampling will be made available to the legislature and public upon completion of the study.

Acknowledgements

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Acronym List

AI	Active Ingredient
AMP	atrazine monitoring program
BAT	best available technology
BHC	Benzene hexachlorides
CRP	Conservation Reserve Program
CWB	HDOH Clean Water Branch
CWS	community water systems
DDTs	dichlorodiphenyltrichlorethanes
DEA	deethylatrazine
DPR	California Department of Pesticide Regulation
DWLOC	drinking water level of comparison
EPA	Environmental Protection Agency
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GWPP	Hawaii's Groundwater Protection Program
HARC	Hawaii Agricultural Research Center
HC&S	Hawaii Commercial & Sugar Company
HDOA	Hawaii Department of Agriculture
HDOH	Hawaii Department of Health
HRS	Hawaii Revised Statutes
HSPA	Hawaii Sugar Planters Association
MCL	Maximum Contaminant Level
MOA	Memorandum of Agreement
MOS	margin of safety
NTNC	non-transient non-community systems
OPP	USEPA Office of Pesticide Programs
OW	USEPA Office of Water
PBRC	Pacific Biomedical Pacific Biomedical Research Center
ppb	parts per billion
RMPDC	Rocky Mountain Poison and Drug Center
SDWA	Safe Drinking Water Act
TMDL	Total Maximum Daily Load
USDA	United States Department of Agriculture
USGS	United States Geological Survey
WHO	World Health Organization

Introduction

House Concurrent Resolution (HCR) No. 129, H.D. 2, S.D. 1 which was adopted during the 2013 Regular Session, requested the Hawaii Department of Health (HDOH) to develop partnerships to address the potential data gaps on air, surface water, and near shore effects of atrazine. This report presents the efforts of the HDOH to develop partnerships and identify atrazine data gaps in Hawaii. Atrazine is currently under review by the Environmental Protection Agency (EPA) for human health and ecological health impacts, therefore the toxicology of atrazine is not part of this report.

The strategy HDOH used to prepare this report includes:

- Work with Hawaii Department of Agriculture (HDOA), and stakeholders in the sugar and seed crop industries to understand where and how atrazine is currently being used, and how uses and applications relate to crop types and land uses.
- Work with Kauai stakeholders, including the Kauai Council, community members, and litigants to hear their concerns about atrazine use and to gather other studies or sampling data for atrazine in Hawaii.
- Search for all available studies and environmental datasets showing testing for atrazine in Hawaii through published research and outreach to stakeholders.
- Use existing datasets from ground water, surface water and air to identify areas where atrazine has been detected and to better understand frequency of occurrences, detections and overall trends.
- Use historic atrazine detections to identify surface water sites receiving recharge from vulnerable groundwater aquifers.
- Identify all detected atrazine levels, any exceedances of water quality standards, and any land uses or study sites that show impacts.
- Work with stakeholders to determine if results provide a basis for future sampling or studies. If so, identify appropriate lead agency and funding options for future work.

To date, HDOH has engaged with the following experts and stakeholders to learn more about community pesticide concerns, pesticide usage patterns, and site selection recommendations:

- Within HDOH-Clean Water Branch, Safe Drinking Water Branch and Food and Drug Branch provided existing data.
- **Pesticides Branch, HDOA** An active partner in this study, they have provided pesticide sales and application areas data, explained pesticide labeling and Hawaii pesticide registration processes, identified trouble spots statewide and provided historical studies on pesticide use in Hawaii.

- United States Geological Survey (USGS) An active partner in this study, they have extensive sampling experience nationwide in Hawaii, unmatched analytical capabilities, existing Hawaii datasets, and technical, hydrogeologic and site selection expertise.
- **Hawaii Agricultural Research Center (HARC)** Stephanie Whalen provided information on vulnerable aquifers, detailed historical information and data on multiple atrazine studies conducted in Hawaii associated with sugarcane cultivation.
- **Representatives from Hawaii Crop Improvement Association** and individual member companies, including **Syngenta, Pioneer, Monsanto and BASF** They provided information on seed crop pest management, atrazine application practices, historic atrazine research and statewide groundwater sampling, confidential spray records (Syngenta), Integrated Pest Management Practices. Syngenta prepared a report *Atrazine Environmental Fate and Monitoring Results in Hawaii* (Appendix A).
- **Bob Boesch, Former HDOA Pesticides Branch Chief.** Bob Boesch provided historical context for regulating pesticides in groundwater in Hawaii.
- **Department of Land and Natural Resources** -Don Heacock, provided information on citizen water sampling for pesticides in Kauai.
- **Surfrider Foundation** Carl Berg from the Kauai branch and Surfrider's statewide office provided existing data and sampling site recommendations.
- Waimea Community HDOH spoke with a representative of the Kauai class action lawsuit to help us understand local community concerns about pesticide drift, off-site dust movement and use of pesticides near Waimea School.
- United States Department of Agriculture (USDA) Agricultural Statistics Service -Mark Hudson provided a helpful overview and access to a variety of Hawaii crop data and maps
- USDA Monitoring Programs Division Terry Counsell provided sampling results and explained School Water Monitoring Program that evaluated a single sample from Waimea Middle School.
- University of Hawaii Researchers -HDOH with Dr. Qing Li, University of Hawaii and Dave Penn, Water Resources Research Center about atrazine studies or ongoing research efforts by the University or its partners

What is Atrazine?

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a pre- or post-emergence herbicide used for weed control which has been registered in the US since 1958. Atrazine is one of the most widely used herbicides in the United States. Approximately 76.5 million pounds of atrazine active ingredient are used domestically each year (EPA, 2003). Annually, 75% of all field corn and 76% of all sugarcane grown are treated with atrazine. Most of atrazine applied to corn is applied pre-emergence. Currently, the heaviest atrazine uses per unit area occur in portions of Delaware, Iowa, Illinois, Indiana, Ohio, and Nebraska. Because of its widespread use

and occurrence in groundwater and surface water, atrazine has undergone extensive regulatory scrutiny.

Regulatory History

Pesticide use is regulated by both the EPA and the State of Hawaii through existing authorities under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Hawaii Pesticide Law (Chapter 149A, H). Federal law requires that before selling or distributing a pesticide in the United States, a person or company must obtain registration or license, from EPA. Under federal law, EPA's Office of Pesticide Programs is responsible for evaluating the human health and environmental risk and ensuring the safety of pesticides when properly applied. To make such determinations, EPA requires more than a 100 different scientific studies and tests from the producer of the pesticide.

Atrazine has undergone extensive regulatory scrutiny over the past 25 years (EPA, 2003). Regulatory changes over time have resulted in lower application rates, cancellation of some crop uses, worker safety provisions and setbacks to wells and surface water.

Because of groundwater concerns, EPA established a Maximum Contaminant Level (MCL) of 3 parts per billion (ppb) in the early 1990s. Also, in the early 1990s, the producers of the pesticide voluntarily instituted some risk reduction measures because of concerns about surface water and groundwater contamination. One of the measures was to classify atrazine as a restricted use pesticide. Other measures of interest to Hawaii crops include reducing application rates for corn, deletion of all uses for vegetation control on non-cropland, requiring that post-emergence application be made to corn before it reaches 12 inches in height, deleting pineapple use, and requiring setbacks from wells and surface water. In 2003, as part of the atrazine re-registration process, EPA made further changes to the atrazine label to minimize impacts to drinking water, reduce worker exposures and require surface and groundwater monitoring by the registrant in areas shown to be impacted with atrazine above EPA's level of concern. As of mid 2013, atrazine is undergoing another re-registration review.

Atrazine Use in Hawaii

Atrazine was first registered in 1958 as an herbicide. After extensive field and laboratory testing, federal and state registrations were granted in 1961 for sugarcane use. The earliest record HDOH has of pesticide usage in Hawaii is for the year 1964. The following graph depicts atrazine usage by year. Several sources were used to compile atrazine use in Hawaii. Atrazine use for the years 1964 and 1968 are from HDOA (1969), for 1977 from Pacific Biomedical Research Center (PBRC) (1982), for 1983 from HDOA (1986), for 1986 from Hawaii Sugar Planters Association (HSPA) (1987), and for 1998 from Hawaii Agriculture Research Center (HARC) (2000). Data from 2010-2012 from HDOA are atrazine sales records rather than actual usage. Total usage was not available for 1964, 1986 and 1998.

As shown in Figure 1, atrazine use fell from a high of about 400,000 pounds active ingredient per year in 1964 to 77,403 pounds active ingredient in 2012. The sugar industry was and is the largest user of atrazine in Hawaii. In the past, atrazine was also used on pineapple, vegetable crops and along highways, but at much lower levels than sugarcane. The drop in atrazine usage over time reflects the decline of sugarcane cultivation, cancellation of some uses and more restrictive label application rates.

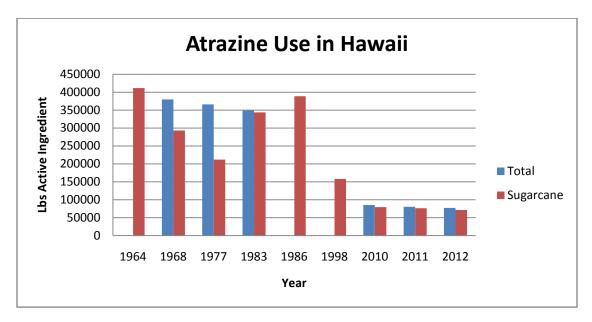


Figure 1. Atrazine use in Hawaii from HDOA, PBRC, HSPA and HARC

Sugarcane

Weeds are a major concern for Hawaii sugarcane and cause more economic loss than all other pests combined. Thus, herbicides account for almost all of the pesticides used by sugarcane growers in Hawaii. The application rates of soil applied herbicides are higher in Hawaii compared to the U.S. mainland because tropical soils have high iron oxide content and a large adsorptive surface area (HARC, 2000)

The average growth of a crop is from 22 to 26 months so only a portion of the total acreage in cane is harvested each year (HSPA, 1993-1994). From a high of 140,000 acres harvested in the mid 1930s, today one farm remains, with 34,300 total acres and 15,100 harvestable acres per year (all acres are planted, but harvested in alternate years).

Atrazine is a very important herbicide for sugarcane cultivation because it provides effective pre and post-emergent control of grasses and large-seeded broadleaves including vines. Atrazine is applied directly to the soil after the sugarcane is planted, but before the cane is large enough to shade out further growth. Up to 3 applications are made within the first four to eight months of growth (HSPA, 1987). The maximum application rate is 4 lbs. of active ingredient per application with a maximum of 10 lbs. of active ingredient per acre per year.

Use on Seed Corn

According to the USDA (2012), the acreage harvested for all seeds crops during the 2011/2012 season was expected to be 5,625 acres, down from 6,205 acres the previous year. The number of acres in active cultivation varies by year depending upon business needs. The seed crop industry currently consists of 10 farms that cultivate seed corn, soybean, wheat, sunflower and other seed crops (Loudat and Kasturi, 2013). Seed corn is estimated to account for 95% of the total value of the seed crops in 2011/2012.

Atrazine applications to corn are most often applied directly to soil as a pre-emergent herbicide. In Hawaii, corn is harvested approximately 110 days after planting. The seed corn growers in Hawaii grow three crops per year, but they are not planted within the same field each year. For example, both BASF and Syngenta grow one crop per field and don't plant again until the next year. This is because of concerns about cross contamination with different genetic varieties of corn and crop rotation to control insect pests and maintain the soil fertility. Regardless of the number of seed corn crops grown on a particular field on an annual basis, the total amount of atrazine allowed is 2.5 pounds of active ingredient per acre for a calendar year. According to the label, the total amount of atrazine applied may not exceed 2.0 pounds of active ingredient in a single application or 2.5 pounds (pre- and post-emergence combined) of active ingredient per acre per calendar year.

Current Uses 2010-2012

Atrazine is currently registered for use on corn (field and sweet); guavas; macadamia nuts; sorghum; sugarcane; range grasses for the establishment of permanent grass cover on rangelands and pastures under USDA's Conservation Reserve Program (CRP) in OK, NE, TX, and OR; wheat (where application is to wheat stubble on fallow land following wheat harvests; wheat is not the target crop); conifer forests; Christmas tree farms; sod farms; golf courses and residential lawns (Southern turfgrasses) (EPA, 2003).

As of 2012, twenty atrazine products were registered in Hawaii. From 2010 to 2012, seven of these atrazine products were used in Hawaii. Locally, all of the atrazine used in Hawaii is for agriculture. Seed corn, sugarcane, sweet corn and macadamia nuts are the only crops currently using atrazine in Hawaii.

The complete list of atrazine sales from 2010-2012 is shown in Table 1. Please note that sales records provide a reasonable, but not exact, estimate of annual usage. The average atrazine sales in the state of Hawaii for 2010-2012 are 80,912 pounds of active ingredient per year. About 94% of the atrazine sold in Hawaii is used for weed control on sugarcane. A very small fraction, 44 pounds per year is used in macadamia orchards, and 326 pounds in sweet corn production. Seed corn production accounts for 6% of the total atrazine used statewide, at an average of 4,771 pounds per year.

For the years 2010-2012, the average annual sales of atrazine on Kauai is 3,457 pounds active ingredient, representing approximately 4% of the total sales for the state during this time period, and 72% of the atrazine used on seed corn statewide. The sales results for Kauai are shown in Table 2. Table 3 summarizes the atrazine sales, application rates and harvested acres of crops using atrazine in Hawaii.

Table 1. Atrazine Sales in the State of Hawaii 2010-2012 ^a

SEEDCORN	2010	2011	2012	Average lbs a.i. ^b
AATREX NINE-0 (EPA Reg. No. 100- 585); (0.882 lbs. a.i./lb. of product)	2,175 lbs. (1,918.35)	975 lbs. (859.95)	1,350 lbs. (1,190.7)	1,323
ATRAZINE 90DF (EPA Reg. No. 66222- 37); (0.9 lbs. a.i./lb. of product)	25 lbs. (22.5)			7.5
ATRAZINE 4L (EPA Reg. No. 34704-69); (4 lbs. a.i./gal. of product)	197.5 gals. (790)	92.5 gals. (370)	397.5 gals. (1590)	916.7
AATREX 4L (EPA Reg. No. 100-497); (4 lbs. a.i./gal. of product)	105 gals. (420)	50 gals. (200)	55 gals. (220)	280
BICEP II MAGNUM (EPA Reg. No. 100- 817); (3.1 lbs. a.i./gal. of product)	441.75 gals. (1,369.425)	135 gals. (418.5)	140 gals. (434)	740.6
LUMAX SELECTIVE (EPA Reg. No. 100- 1152); (1 lb. a.i./gal. of product)	597.5 gals. (597.5)	990 gals. (990)	922.5 gals. (922.5)	836.7
ATRAZINE 4L (EPA Reg. No. 66222-36); (4 lbs. a.i./gal. of product)	60 gals. (240)	110 gals. (440)	330 gals. (1320)	666.7
TOTAL PER YEAR (in lbs. a.i.)	5,358.	3,278	5,677	4771.1

SUGARCANE	2010	2011	2012	Average lbs. a.i.
AATREX NINE-0 (EPA Reg. No. 100-	90,000 lbs.	86,725 lbs.	81,000lbs.	75,771.13
585); (0.882 lbs. a.i./lb. of product)	(79,380)	(76,491)	(71,442)	

SWEET CORN	2010	2011	2012	Average lbs. a.i.
AATREX NINE-0 (EPA Reg. No. 100-585); (0.882 lbs. a.i./lb. of product)			300 lbs. (265.)	88.3
ATRAZINE 90DF (EPA Reg. No. 66222-37); (0.9 lbs. a.i./lb. of product)	350 pounds (315)	375 pounds (338)		217.7

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ATRAZINE 4L (EPA Reg. No. 66222-36); (4 lbs. a.i./gal. of product)		5 gallons (20)	10 gallons (40)	20
TOTAL PER YEAR (in lbs. a.i.)	315	358	305	325.7
IOTALIEK TEAK (III IDS. a.i.)	515	550	303	545.1

MACADAMIA NUT	2010	2011	2012	Average lbs. a.i.
AATREX NINE-0 (EPA Reg. No. 100-585); (0.882 lbs. a.i./lb. of product)		150 lbs. (132.3)		44.1

^a Values are gross weight and in parenthesis are lbs. active ingredient. ^b AI-Active Ingredient

Table 2. Atrazine Sales for Kauai^a

	2010	2011	2012	Average lbs.
	2,175 lbs.	517.5 lbs.	1,350 lbs.	1188.4
AATREX NINE-0 (EPA Reg. No. 100-	(1,918.35)	(456.4)	(1,190.7)	
585); (0.882 lbs. a.i./lb. of product)				
	232.5 gals.	185.0 gals.	592.5gals.	1346.7
ATRAZINE 4L (EPA Reg. No. 66222-36);	(930)	(740)	(2,370)	
(4 lbs. a.i./gal. of product)				
	50 gals.	55 gals.	60 gals.	170.5
BICEP II MAGNUM (EPA Reg. No. 100-	(155)	(170.5)	(186)	
817); (3.1 lbs. a.i./gal. of product)				
	51751.	975	962.5 1.	751 7
	517.5 gals.	875 gals.	862.5 gals.	751.7
LUMAX SELECTIVE (EPA Reg. No. 100-	(517.5)	(875)	(862.5)	
1152); (1 lb. a.i./gal. of product)				
TOTAL PER YEAR (in lbs. a.i.)	3,520.85	2,241.9	4,609.2	3457

^a Values in parenthesis are lbs. active ingredient.

^b AI-Active Ingredient

Table 3. Atrazine Sales and Application Rates for Hawaii Crops

Crop	Maximum Rate per Application	Maximum Rate per Year	Acreage Harvested	Average Pounds Sold ^a
Seed Corn	2 lbs. a.i./acre	2.5 lbs. a.i./acre year	5,344 ^b	4,771
Sugarcane	4 lbs. a.i./acre	10 lbs. a.i./acre year	15,100 ^c	75,771
Sweet Corn	2 lbs. a.i./acre	2.5 lbs. a.i./acre year	400 ^c	326
Macadamia Nuts	4 lbs. a.i./acre	8 lbs. a.i./acre year	15,000 ^c	44

^aAverage pounds of atrazine (active ingredient) sold 2010-2012

^bEstimated from USDA (2012) as 95% of all seed crop acres

^c From Statistics of Hawaii Agriculture 2011 (USDA 2013a)

HDOA provided a further breakdown of the location of atrazine sales by islands, as shown on the maps in Appendix B.

Atrazine Fate and Transport

Correctly applied pesticides protect crop quality while reducing impacts from weeds and/or insect pests. However, as a result of a pesticide's chemical characteristics, toxicity, application practices and local environmental conditions at the site of application, pesticides can have impacts on non-target species. These range from unsafe exposures to farm workers or applicators who do not follow the label instructions, to inadvertent damage to crops and offsite movement of pesticides from runoff, erosion, volatilization, spray drift or migration to groundwater.

Atrazine is commonly applied to bare soil as a pre-emergent herbicide in both corn and sugar crops, and is re-applied during early crop cycles as needed until crops have established adequate cover to outcompete weeds. Atrazine is odorless, has a low vapor pressure, is not considered particularly volatile and is both persistent and mobile in surface and groundwater. Atrazine is degraded into 3 major products that bind to soil to a lesser extent than the parent product and a greater tendency to leach into groundwater.

The three major off-site transport mechanisms for atrazine are surface runoff, leaching to groundwater, and aerial transport through volatilization and drift. After the solution is applied to an agricultural field, atrazine will initially adsorb to soil particles and plant matter. In fact, one of the agricultural benefits of atrazine is the eight to ten week period of residual herbicidal activity in the soil (Shaner et al., 2010). There is a wide range of persistence in surface soils with reported half-lives ranging from 14-109 days. Degradation of atrazine by bacteria is the most important process influencing persistence in soil (Fenner et al., 2007). In addition to soil chemistry other factors such as the previous atrazine application history, presence of other pesticides, agricultural practices and tillage history can influence the degradation of atrazine. Accelerated degradation of atrazine from fields previously treated with this herbicide resulting in reduced efficiency has been shown in Hawaii and other locations (Shaner et al., 2010). Predicting the long term behavior of atrazine in soil is challenging because of the complex interaction of these different dynamic processes on degradation of pesticides. Unlike more persistent pesticides of the past, atrazine has not been found in soil from former sugarcane fields that have been out of use for several years (HDOH, 2007).

Surface Runoff

Atrazine may also be carried with eroding soil or dissolve into rainwater runoff and be transported to streams and near shore waters. As reviewed by Gish et al (2011), typical runoff losses for most herbicides are <1 to 2% of that applied. However, when a major rainfall event occurs following the application of a wettable powder formulation on a sloped field, as much as 15% of the pesticide applied can be lost through runoff.

Leaching to Groundwater

In Hawaii, leaching to groundwater is a key pathway that has the potential to introduce atrazine and other soluble chemicals into drinking water supplies, into streams through groundwater

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recharge and eventually to near shore marine waters. Atrazine that remains in the soil can dissolve into infiltrating rainwater and be carried down over time to groundwater aquifers. Within coastal zones, atrazine can leach into shallow groundwater and seep into bays, streams and near shore water. Like surface runoff, heavy rain events on bare soils treated with atrazine are likely to result in increased losses to groundwater. In groundwater, both atrazine and its major breakdown products have long half lives because they are resistant to degradation.

Atrazine is frequently detected across the US mainland, with highest incidence and concentrations in the Midwest, where water supplies for approximately 50-75% of the state populations may show ongoing detections. Currently, 30 community water systems, primarily across the Midwest, require ongoing monitoring due to exceedances of the MCL (EPA, 2013)

In partial fulfillment of EPA's re-registration requirements for atrazine, the manufacturer, Ciba-Geigy agreed to conduct groundwater monitoring in 19 states that represented the major atrazine use areas in the country. The Hawaii component of the study is described in more detail below.

Volatilization and Drift

Many pesticide complaints are due to concerns about exposure to pesticides in the air from pesticide drift. The California Department of Pesticide Regulation has prepared an informative fact sheet on pesticide drift <u>http://www.cdpr.ca.gov/docs/dept/comguide/drift_excerpt.pdf</u>. Pesticide drift is the movement of pesticides through the air away from the intended target. Scientists now recognize that almost every pesticide application produces some level of drift into nearby areas. Air monitoring around agricultural operations on the mainland has shown that pesticides can drift even when pesticide users are following federally required instructions on the label. Drift is not confined to agricultural activities and can occur when a neighbor sprays pesticides in the garden. Not all drift is harmful or illegal. The laws are designed to prevent illegal, substantial drift that occurs when applications are not done properly to prevent harm to humans and the environment.

Factors that can influence drift include temperature, wind speed, chemical nature of the pesticide, how it is applied and the application site. In general, pesticides may enter the air primarily by three main routes: 1) Droplet and vapor drift during application; 2) Post-application vapor losses from the surfaces of treated seed, soil and plants; and 3) Wind erosion of treated soil through fugitive dust. Volatile pesticides can evaporate (volatilize) into the air within hours, days or weeks after application. After introduction into the atmosphere, pesticides can be degraded, transported, and redeposited. Deposition can be either wet such as with rain or snow or dry such as gaseous sorption and particle fallout. Nonvolatile pesticides will remain in the soil and break down over time. The rate that they break down is specific to the pesticide used.

Airborne atrazine represents the most likely exposure pathway for people living near agricultural fields where it is used. However, compared to surface runoff and leaching to groundwater, volatilization of atrazine has been studied the least. With normal agricultural practices, atrazine

can be dispersed in the air due to volatilization of the applied solution from soil after application or carried away from the target area in the air as tiny droplets or "aerosol". Atrazine has been detected as far as 180 miles away from the closest application area and is commonly found in rainwater in the seasons following agricultural applications (ATSDR, 2003). Gish et al. (2011) found that 2-12% of applied atrazine was lost to volatilization after 5 days and that daytime losses were higher than nighttime losses. A previous study by Gish (2009) found that rainfall just before application increased the likelihood of volatilization and surface runoff.

Limited atrazine air monitoring exists. California Air Resources Board (2000) measured atrazine during application around the perimeter of 120 acres of sudan grass and in the ambient air about 1 to 2 miles away in a populated area. During application of atrazine, the highest sample next to the field (about 60 feet away) was 290 ng/m³. The highest level in the community monitoring site was substantially lower at 6.8 ng/m³ with over ½ of the samples below the analytical detection limit. There is no inhalation health-based screening level for atrazine, so the Air Resources Board did not assess the health significance of these findings. Notably, the California Department of Pesticide Regulation (DPR), the only state that monitors air as part of its continuous reevaluation of pesticides, does not monitor for atrazine in ambient air. California DPR monitors for 33 pesticides and 5 breakdown products based on potential health risk. Atrazine did not meet the criteria used to select high risk pesticides, which include higher use, higher volatility and higher toxicity.

Other air monitoring data as summarized in the report prepared for HDOH by Syngenta "Atrazine Environmental Fate and Monitoring Results in Hawaii" found that atrazine concentrations in Canadian agricultural regions were very low, on the order of 1 ng/m³ for vapor and 0.050 ng/m³ for particulate matter. Air monitoring in Mississippi in agricultural regions found a maximum concentration of atrazine at 2.6 ng/m³ (58% of the samples were non detectable) in the vapor form and 0.42 ng/m³ in the particulate form. Although there is no health based inhalation level for atrazine, California DPR (2012) has derived a 1 day acute screening level of 110,000 ng/m³ for simazine, a triazine herbicide like atrazine. Given the chemical similarity of these herbicides, it is reasonable to assume the levels of atrazine found in air are orders of magnitude lower (less toxic) than levels shown to cause adverse health effects. Overall, air monitoring indicates low atrazine exposure by vapor or particulate matter such as dust, in ambient air in agricultural communities using atrazine.

EPA's Definition of Drift

The potential impact of spray drift on humans and the environment is considered in the evaluations of proposed pesticides for new registration and older, existing pesticides for reregistration (EPA, 1999). EPA defines pesticide spray drift as the physical movement of a pesticide through air <u>at the time of application</u> or soon thereafter, to any site other than that intended for application (often referred to as off-target). They do not include in the definition the movement of pesticides to off-target sites caused by erosion, migration, volatility, or

contaminated soil particles that are windblown after application, unless specifically addressed on a pesticide product label with respect to drift control requirements.

Recently, however, the EPA has begun to look more closely at risks to bystanders from volatilization of pesticides. EPA has begun to explore the development of an approach for assessing inhalation exposure resulting from the field volatilization of conventional pesticides based on recommendations provided by the FIFRA Science Advisory Panel. Further information is available in docket <u>EPA-HQ-OPP-2009-0687</u> at <u>Regulations.gov</u>.

Pesticide Complaints

Pesticide complaints are handled by the HDOA and fugitive dust from agricultural fields by HDOH Clean Air Branch. Calls for acute pesticide poisoning exposures typically are made to the Hawaii Poison Hotline. A summary of calls and complaints to these agencies are summarized in the sections below.

HDOA

The HDOA is the lead agency that investigates pesticide complaints in Hawaii. Investigations involve statements from the complainant, pesticide sampling, if appropriate, and contacting the applicator to determine if pesticides were applied at the time in question. If warranted, an intensive investigation by HDOA is then conducted and suspected violations are noted for subsequent determination as to whether there has been a violation of the pesticide laws.

The role of the HDOH is to provide technical support to HDOA, the medical community and the public by providing toxicological information on the pesticides of concern.

The pesticide complaints reported to and investigated by HDOA as of October 10, 2013 are shown in Table 4. Overall there were a total of 293 statewide pesticide complaints between 2010 and 2013 with Oahu (127) and Hawaii (73) accounting for two-thirds of the total. According to HDOA, less than half of the complaints are due to agricultural activities. For complaints involving potential atrazine exposure, atrazine was not detected in any environmental samples collected during this time period.

Island	2010	2011	2012	2013	Total
Hawaii	28	13	16	16	73
Kauai	8	8	16	10	42
Maui	9	12	16	14	51
Oahu	26	29	48	24	127
Total	71	62	96	64	293

Table 4. Number of HDOA Pesticide Complaints by Year (2010-October 2013)

Dust Complaints to HDOH Clean Air Branch

HDOH Clean Air Branch investigates complaints of visible fugitive dust. Pesticides can be carried on dust particles through wind erosion and agricultural activities. Table 6 shows the agricultural dust and total dust complaints investigated by HDOH from 2010- October 2013. A total of 70 fugitive dust complaints from agriculture were made to HDOH from 2010-2013 which was 5% of the total dust complaints. In contrast to pesticide complaints made to HDOA, Kauai and Maui had the highest number of agricultural dust complaints. In the past 3 years, there have been two Notices of Violations and Order for fugitive dust violations issued by HDOH as described below.

Monsanto Company, (Kaunakakai, Molokai) was cited for causing or permitting visible fugitive dust to become airborne without taking reasonable precautions. Monsanto operates seed corn farms, and the violations were investigated after dust complaints were received by the HDOH. The Monsanto Notices of Violations and Order was issued but the case is not closed and a consent decree is being finalized.

Hawaii Commercial & Sugar Company, (HC&S)(Puunene, Maui) was cited for causing or permitting visible fugitive dust to become airborne without taking reasonable precautions and agricultural burning permit violations. Violations were discovered after dust complaints were received and a records review was conducted of their permit. HC&S operates a 36,000-acre sugarcane farm. A penalty of \$9,300 has been paid.

	Agriculture Dust	Total Dust	% Ag to Total Dust
Hawaii	4	204	2%
Kauai	35	271	13%
Maui	23	87	26%
Oahu	8	748	1%
Total	70	1,310	5%

Table 5. Fugitive Dust Complaints Reported to HDOH by Year (2010-October 2013)

Hawaii Poison Center

The Hawaii Poison Hotline, operated by the Rocky Mountain Poison and Drug Center (RMPDC) receives calls for acute poisoning exposures. Figure 2 shows the pesticide calls received by the Hawaii Poison Hotline from 2000-2012 (data provided by Dr. Al Bronstein, Medical Director of the RMPDC). The period from 2000-2001 was a period of transitioning from Kapiolani Hospital to RMPDC administration. During this period, there were 4,800 reports of human pesticide exposures, 1,910 reports of animal exposures and 548 information calls. The calls to the Hawaii Poison Hotline for pesticide exposures have decreased since 2008, a trend that is also seen for other poisoning calls to the hotline.

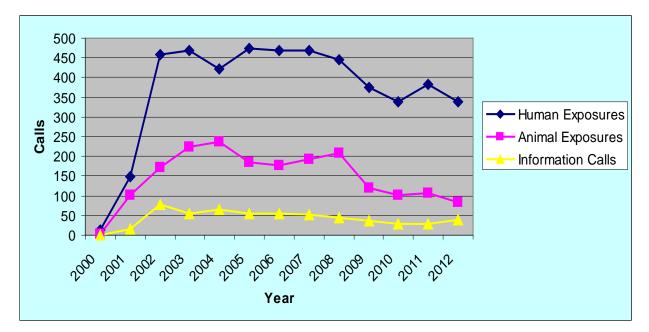


Figure 2. Hawaii Poison Calls for Pesticide Exposures 2000-2012

One case of atrazine exposure to a worker was received by the Hawaii Poison Hotline during this time. The worker was exposed dermally to atrazine and other herbicides by inadvertently entering a treated area prematurely. The health effects were considered "minor" by the Hawaii Poison Center and treated by washing the skin of the worker.

Forty-one percent of the calls involved a child 5 years old or younger, while 49 % involved an adult older than 20. Of the 4,800 human pesticide exposure calls, approximately 90% of the exposures occurred in a residence, 4.4% in the workplace and 1% in a school. The remaining 4% consisted of miscellaneous locations (i.e., other/unknown, public areas, health care facilities, and food service).

Table 6 summarizes the reason for the calls. The majority of the calls were unintentional pesticide exposures both general and environmental. Environmental exposure can include incorrect application of pesticides by the homeowner or drift from another location. Information

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on drift from agricultural fields is not readily available. Nationally, calls to poison centers for drift are small in comparison to other exposures (Dr. Al Bronstein personal communication).

Rank	Number of Exposures	%	Reason
1	2,831	59.0%	Unintentional - General
2	645	13.4%	Unintentional - Environmental
3	471	9.8%	Adverse reaction - Other
4	373	7.8%	Unintentional - Misuse
5	157	3.3%	Unintentional - Occupational

Table 6. Top 5 Reasons for Calls to the Hawaii Poison Hotline (2000-2012)

Table 7 shows the top 15 pesticides responsible for the calls. The top 5 pesticides exposure substances are insecticides, with pyrethroids comprising 22% of the calls. Pyrethroid insecticides are common general use pesticides.

Rank	Pesticide	Number Exposures	%
1	Pyrethroids	1160	22.6%
2	Other Types of Insecticide	604	11.8%
3	Borates and/or Boric Acid Pesticides	507	9.9%
4	Unknown Types of Insecticide	479	9.3%
5	Organophosphate Insecticides Alone	343	6.7%
6	Glyphosate	232	4.5%
7	Pyrethrins	230	4.5%
8	Insect Repellents with DEET	217	4.2%
9	Long-Acting Anticoagulant Rodenticides	217	4.2%
10	Sulfuryl Fluoride	142	2.8%
11	Carbamate Insecticides Alone	86	1.7%
12	Insect Repellents without DEET	83	1.6%
13	Other Types of Herbicide	75	1.5%
14	Chlorophenoxy Herbicides	49	1.0%
15	Unknown Types of Moth Repellant	47	0.9%

Table 8 lists the medical outcome of the calls. Most of the exposures resulted in either no or minor health effects. About 3% of the calls (149 cases) were judged to result in moderate health effects, 0.2% (8 cases) had major health effects and 3 exposures resulted in death.

Rank	Number Exposures	%	Medical Outcome
1	1,922	40.0%	No effect
2	1,523	31.7%	Minor effect
3	477	9.9%	Not followed, minimal clinical effects possible (no more than minor effect possible)
4	459	9.6%	Unrelated effect, the exposure was probably not responsible for the effect(s)
5	149	3.1%	Moderate effect
6	141	2.9%	Unable to follow, judged as a potentially toxic exposure
7	108	2.3%	Not followed, judged as nontoxic exposure (clinical effects not expected)
8	10	0.2%	Confirmed nonexposure
9	8	0.2%	Major effect
10	3	0.1%	Death

 Table 8. Medical Outcomes of Pesticide Exposure Calls

Discussion of Pesticide and Dust Complaints

For the period 2010 to 2012, HDOA received and investigated an annual average of about 77 pesticide complaints statewide. During the same time period, HDOH investigated about 18 dust complaints a year related to agricultural activities. None of the pesticide complaints were linked to atrazine exposures. An average of about 353 calls a year (between 2010 and 2012) was received by the Hawaii Poison Hotline for human pesticide-related complaints. One earlier case in 2006, involved atrazine exposure to a worker. Based on the calls made to the Hawaii Poison Hotline and complaints made to HDOA, the exposures related to homeowners' use of pesticides (largely general use insecticides) are far more prevalent than those from agricultural activities.

Environmental Regulations for Groundwater and Surface Water

Safe Drinking Water Act

HDOH has been authorized by EPA to administer requirements of the Safe Drinking Water Act (SDWA) in Hawaii. Hawaii's authority is found in Hawaii Revised Statutes (HRS) Chapter 340E. Hawaii's requirements for public water systems are found in Hawaii Administrative Rules, Title 11, Chapter 20, entitled "Rules Relating to Public Water Systems". State and federal

drinking water regulations require that drinking water systems be routinely tested for a large number of chemical and biological contaminants. Required testing includes 23 pesticides, including atrazine, for which the Environmental Protection Agency (EPA) has established standards known as maximum contaminant levels (MCLs). The SDWA does not require testing for breakdown products of these pesticides. Hawaii's requirements include all federal drinking water standards as well as Hawaii standards. These standards apply to all public water systems which are systems that serve 25 or more persons per day at least 60 days per year or have 15 or more service connections.

Drinking water contaminants are regulated by EPA if they meet three basic criteria. First, they must occur nationally in drinking water systems. Second, there must be adverse health effects. Third, there must be a reliable analytical method for the contaminant. On July 30, 1992, EPA national drinking water regulations took effect for a spectrum of synthetic organic chemicals including atrazine, which set MCLs, monitoring and reporting requirements for these contaminants. The MCL for atrazine was set at 3 micrograms per liter ($\mu g/l$) or parts per billion, based on the best available technology (BAT) of the time. EPA is required to consider technical and economic feasibility when setting an MCL.

Monitoring requirements for atrazine and the other contaminants were assigned to two types of public water systems known as "community" systems (CWS) (systems that serve residential populations) and "non-transient non-community" systems (NTNC) (systems that serve non-residential but constant populations such as working places). A third type of system "transient non-community" systems (systems which serve a transient population) were not required to sample for these contaminants due to the limited exposure of the service population. The monitoring requirements for atrazine are discussed under Environmental Monitoring section of the report.

State Groundwater Protection Program

Hawaii's Groundwater Protection Program (GWPP) is a non-regulatory program whose goal is to protect human health and sensitive ecosystems by protecting groundwater resources. Its focus is on water quality assessment and on developing pollution prevention and protection measures. While originally developed as a planning and coordinative activity, the GWPP has recognized the need for developing its own groundwater monitoring program for contaminants of interest or concern. Recently, the program has acquired analytical equipment to analyze for a wide variety of contaminants and is currently developing methods and capacity at the State Laboratory. The GWPP can improve the State's knowledge of the current groundwater condition in two major ways. First, with its flexibility to sample both drinking water and non-drinking water groundwater sources, HDOH will be able to confirm, track trends and better define areas of the state impacted by contaminants such as atrazine. Second, groundwater sampling can be expanded beyond the list of contaminants required for drinking water testing. It will enable the

State to sample for new contaminants of emerging concern such as new pesticides, pharmaceuticals, and other contaminants not regulated by drinking water rules.

One of the GWPP's first efforts will be to resample groundwater sources that had reported positive results for atrazine from the 1980s and 1990s and for which no subsequent monitoring has taken place.

HDOA Pesticide Regulations for Protection of Groundwater

HDOA has several rules that apply to groundwater protection. They are listed below:

HAR 4-66-32.1 Evaluation of pesticide uses

This section refers to unreasonable adverse effects for products/chemicals already being used. Of particular interest in this section is where it states that, "The head shall evaluate a licensed pesticide when unreasonable adverse effects to humans or the environment have been documented and associated with the use of that pesticide." The circumstances include public health hazard, pesticides in drinking water that are present at levels that equal or exceed 20% of the federal or state health standards or advisory, pesticides residues in food or feed that are present at levels exceeding established tolerances and several other criteria. Evaluation of the pesticide could ultimately result in no change, restriction of a use, refusal to renew a license, or cancellation or suspension of the license.

HAR 4-66-34 Applications for licensing pesticides and for approval of non-chemical pest control devices. Section (5)

"If requested by the head, the applicant for a pesticide shall provide the complete formula of the pesticide including active and inert ingredients and a description of tests and the results thereof on which claims are based, including efficacy, residue, safety and other supporting data that shows the pesticide shall perform its intended function without unreasonable adverse effects on

For new active ingredients, HDOA requests environmental fate information to determine leachability of the chemical in Hawaii soils. The potential to leach is investigated in a phased approach. If a pesticide is shown "likely to leach", a full groundwater review is required. In this case, full groundwater data is requested from the company, based on 40 CFR 158.290. After data are received, the information is forwarded on to the Water Resources Research Center at the University of Hawaii for review by a hydrologist. This review will look at specific environmental fate characteristics, the use pattern in all available products containing that active ingredient, Hawaii conditions, to determine the likelihood of leaching. At the end of this review, a determination is made to license products containing that chemical, require state restriction, or deny licensing.

<u>Hawaii Revised Statutes 149A-14 Refusal, Cancellation, or suspension of the license</u> Provides authority to refuse or cancel a pesticide should the proposed use meet certain criteria. <u>Hawaii Revised Statutes 149A-32.5 Cancellation or suspension of pesticide uses</u>. Provides authority to suspend, cancel or restrict the use of pesticides / pesticide uses if unreasonable adverse effects could result from that use.

Regulation of Atrazine in Surface Water

Except as may be required in individual NPDES permits, there are no requirements by the state or federal agencies for currently used pesticide sampling for wastewater discharges or surface runoff. Currently, there are no operations statewide that would require NPDES permits that require monitoring of currently used pesticides. HDOH Clean Water Branch does not routinely monitor for pesticides, due to funding and resource limitations. However, in the event adequate surface water data are collected that indicate a violation of water quality standards, the Clean Water Branch would be required to implement a Total Maximum Daily Load (TMDL) Study to determine whether the affected water body is a candidate for listing on the 303(D) list. Ongoing water quality studies of nutrients, sedimentation and other parameters show areas where runoff and erosion from agricultural areas have affected water quality. Relatively little data are currently available

Environmental Monitoring Data

The following is a summary of Hawaii-specific environmental monitoring data for air, surface water and groundwater.

Air Data

Between 2006-2008, several incidents involving unidentified odors caused students to be evacuated from Waimea Canyon Middle School on Kauai and seek medical attention. Waimea Canyon Middle is adjacent to Syngenta's seed fields, and it was suspected by some that pesticide drift of an odorous chemical was the cause of flu-like symptoms including dizziness, headache, nausea and throat irritation. In addition, fields next to the school contained a common plant found locally, *Cleome gynandra* or "stinkweed" which produces an objectionable odor especially after plowing. Some emergency responders considered the stinkweed the cause of the odor at the Waimea Canyon Middle School. HDOA conducted an investigation including the collection of environmental samples from the school and surrounding area and found no evidence that pesticides had been used improperly.

In response to the pesticide complaints, HDOA and Kauai County worked with the University of Hawaii to conduct air monitoring for chemicals in the ambient air in and near the school (Li et al., 2013). The study was designed to measure volatile pesticides near Waimea Canyon Middle School as well as chemicals from stinkweed. A phased approach was used where passive air monitoring initially identified (presence or absence) the volatile chemicals in air and high volume air sampling quantified the concentration during a one week time period. Passive air monitors were placed at schools around the island, including Waimea Canyon Middle School. Both indoor and outdoor passive monitors were used at Waimea Canyon Middle School. Passive

air monitoring was conducted during a period of over one year and samples were collected at approximately 4 month intervals. Twenty four pesticides and twenty nine volatile chemicals from stinkweed were analyzed. <u>Atrazine was not detected in any location</u>. Benzene hexachlorides (BHC) dichlorodiphenyltrichloroethanes (DDTs) chlorpyrifos, metalachlor, and bifenthrin were detected at Waimea Canyon Middle School while BHCs and DDT were detected at the reference locations. DDTs and BHCs were widely used historically for mosquito and other insect control and are no longer in use.

In addition, high volume sampling was conducted from February 10, 2012-February 18, 2012. Atrazine was not detected during the one week sampling period. Pesticide residues detected were the same as those measured during the passive sampling period. All levels were below health based screening levels.

Li also extracted and analyzed chemicals from the stinkweed plant and identified 29 chemicals. Those 29 chemicals were also detected in the air in a chamber that contained stinkweed plant tissues. Pilot studies were done on Maui where a field was identified that was heavily infested with stinkweed. Using high volume sampling, all 29 chemicals from the stinkweed plant were found in the air from the Maui field. Sampling on Kauai next to the school found that about ½ of the 29 chemicals were present and at lower levels than those found on Maui. One reason for the lower levels on Kauai is that the fields adjacent to the school have not been used since 2008 and the stinkweed has been plowed under and managed since then. Notably, methyl isothiocyanate (MITC), which has a pungent horseradish-like odor, was present in stinkweed plant extracts and ambient air on Kauai and Maui. MITC concentration was about 20 times higher in the air on Maui compared to air next to Waimea Canyon Middle School.

MITC is also a breakdown product of metam sodium, a restricted use pesticide that was not sold on Kauai in 2012. MITC is an infamous pesticide breakdown product because of the accidental spill of 19,500 gallons of metam sodium from a railroad tank car into the Sacramento River in 1991. Exposure of the area population to airborne MITC evolving from the river resulted in numerous visits to local healthcare facilities, largely due to complaints of eye and respiratory irritation, nausea, headache, dizziness, vomiting and shortness of breath.

HDOH obtained confidential spray records from Syngenta for the period just before and during the February 10, 2012-February 18, 2012 high volume sampling period. Atrazine was applied approximately 10 days before the sampling period on the Waimea fields.

The study by Li et al. shows that atrazine was not detected by either passive or high volume sampling during the study period. Because atrazine was not applied in the Waimea fields during the high volume sampling period, it is possible that the study missed any possible short term volatilization of this herbicide. Additionally, field 809 which was in use during the incidents of 2006-2008 is now fallow providing a buffer between pesticide spraying and the school.

As discussed in the Fate and Transport section, atrazine's vapor pressure indicates a low potential for volatilization, although under certain conditions atrazine's volatilization could be as high as 12% of the total amount applied. Air monitoring in Canada and Mississippi for atrazine found very low levels during the active agricultural season indicating that air transport is low. Furthermore, California Department of Pesticide Regulation, the only state that monitors air as part of its continuous reevaluation of pesticides, does not monitor for atrazine in air. Given that atrazine was not detected in Li's passive sampling, the low levels found in air monitoring in other areas, and that California has not chosen it as a high risk pesticide for air monitoring, HDOH believes further air monitoring for atrazine is not warranted. Although the results of Li's study cannot be used to re-create the exposure situation that resulted in medical complaints from exposure to odorous chemicals at Waimea Canyon School, it does provide an intriguing hypothesis that naturally occurring chemicals from plants have the potential at high enough concentrations to cause eye and respiratory irritation as well as other health effects.

Atrazine Residues in Food

The HDOH Food and Drug Branch samples individual lots of domestic and imported produce and analyzes them for pesticide residues to enforce the tolerances set by the U.S. Environmental Protection Agency. Samples are collected from throughout the channels of trade, including wholesale and retail outlets, distribution centers, and farmers markets. The Food and Drug Branch staff collects the samples, and delivers them to the HDOH State Laboratories Division's laboratory where all are tested with multi-residue screens capable of detecting more than 80 pesticides and breakdown products. In addition, selected samples are analyzed for other pesticides of enforcement concern.

Even though atrazine is a widely used pesticide for corn, sugarcane, macadamia nuts, sorghum, and other crops, very few atrazine residues have been found in food analyses conducted by the FDA and the USDA from 1987 to the present. Atrazine is generally applied early in the growing cycle and is not applied directly to food crops. HDOH does not currently analyze for atrazine residues in food.

Atrazine Data in Soils from Historical Sugarcane Activities

Pesticide Mixing and Loading

The most significant soil contamination in Hawai'i stems from historic pesticide mixing areas at former agricultural operations. Historically, pesticides were stored, mixed, and loaded in small, unobtrusive buildings located on old plantation lands, sometimes near the main mill; in other cases, the buildings were located on remote cane roads. As the Hawaiian sugar industry evolved, plantations consolidated and expanded. Pesticide handling operations were moved around, shared between plantations or relocated to meet changing plantation needs. As plantations began to close, many of the old structures were abandoned, ignored, and torn down. Development spread over agricultural lands with no institutional knowledge of the risks posed by these contaminated sites. The key contaminants found at the pesticide mixing areas are arsenic

and dioxin. Despite the pesticide mixing areas having the highest potential for pesticide contamination, only three pesticide mixing areas have been identified to date with atrazine concentrations in soil above the HDOH Environmental Action Level of 110 parts per billion (HDOH, 2011). The HEER Office is currently overseeing investigation and clean up of these pesticide mixing areas with significant contamination, and continues site discovery efforts to identify other historic pesticide mixing operations.

Soil in former sugarcane land

With the exception of arsenic, residual pesticides in former sugarcane fields are rarely detected above levels of potential concern. In 2007, a site assessment was completed at a former East Kapolei agricultural property that was at one time cultivated with sugarcane (HDOH, 2007). The land which is part of the Ewa Plantation was in operation for sugarcane until 1994. The property was proposed to be developed for the Kapolei Affordable Housing Project. Soil from 400 acres was sampled for dioxins and pesticides, including atrazine. Atrazine was not detected in any of the soil samples (detection limit of 55 parts per billion). This general absence of significant, residual levels of atrazine in former sugarcane fields is consistent with data from other islands (see HDOH, 2011).

Hawaii Groundwater Data

Discovery and Early Detections of Atrazine

Prior to 1993, atrazine was not routinely monitored in drinking water. The Hawaii Sugar Planters Association (HSPA) was the first to identify atrazine in groundwater and voluntarily established a monitoring program in Hawaii. At the time there was no MCL and the health advisory level was 25 ppb. I n 1983, HSPA alerted the HDOH about detectable levels of atrazine found in Kunia and Waipahu on Oahu. Subsequent groundwater sampling by HSPA in the early 1980s in areas of high agricultural use found about 40% of the sources had detectable levels of atrazine. In 1986, elevated levels were found in Pepeekeo spring and Kihalani spring on the Hamakua Coast which measured 4.1 and 2.3 ppb respectively. The monitoring found that areas of high rainfall together with permeable soils were more susceptible to atrazine groundwater contamination. Throughout the 1980s and 1990s, HSPA has been an active participant in monitoring and evaluating atrazine trends in Hawaii's groundwater.

CIBA Groundwater Study for Atrazine Re-registration

In partial fulfillment of EPA's re-registration requirements for atrazine, the manufacturer, Ciba-Geigy agreed to conduct groundwater monitoring in 19 states that represented the major atrazine use areas in the country. Hawaii's component of *The Ciba/State Groundwater Monitoring Study for Atrazine and its Major Degradation Products in the United States* began in 1992 and included active participation from the HDOA and HSPA. During the early 1990s, numerous sugar companies were still in operation and actively using atrazine. The purpose of the study was to assess the presence of atrazine and its degradate products in groundwater in areas of high atrazine use. The focus of the study was on drinking water supplies, particularly those with

hydro geologic features that increased vulnerability to contamination, but also evaluated shallow irrigation wells, and wells at different depths to better understand how and where atrazine may occur. The irrigation well data are discussed below in the section entitled, "Groundwater data from Irrigation Wells".

Atrazine concentrations in the CIBA samples did not exceed the EPA's MCL of 3 parts per billion. The MCL applies only to atrazine, and does not presently include the degradation products. To better understand the fate of atrazine in groundwater, the study also evaluated the degradation product data and found that atrazine or its breakdown products were detected in 36% of the wells at a detection limit of 0.1 ppb. The average concentration of atrazine was 0.12 ppb. The highest detected concentration of atrazine was 2.1 ppb in a spring fed drinking water well on the Hamakua Coast of the Big Island. In addition to atrazine, this well had degradation products totaling 1.4 ppb. Other wells similarly showed mixtures of atrazine and breakdown products, with some wells showing only low levels of breakdown products

USGS

As a part of the National Water Quality Assessment Program, the US Geological Survey sampled groundwater and surface waters on Oahu to better understand how land uses influence drinking water quality and the ecology of Oahu's streams (Anthony et al., 2004).

The data show that Hawaii's groundwater has continuing impacts decades after the last legal use of a number of legacy pesticides, fumigants used in pineapple fields and organochlorine pesticides associated with termite protection. Similarly, atrazine and other herbicides used in the sugar and pineapple industries remain detectable in our groundwater.

Groundwater data for herbicides and elevated concentrations of nutrients are clearly associated with current and historic agricultural uses. Atrazine was detected in groundwater beneath central Oahu, under former sugarcane lands. The USGS suggests that Oahu's central plain is particularly vulnerable to chemicals used in recharge areas over the unconfined aquifer. The wells in Honolulu however, showed few detections of contaminants, likely due to the fact that large-scale agriculture had already ceased at the time of pesticide usage. The report also evaluated pesticide detections in surface water, as described in more detail below, and concludes that both herbicides and nutrients present in groundwater can be transported into gaining streams and the near shore marine ecosystem.

USDA School Water Testing Project

In 2011, Waimea Canyon Middle School submitted a sample from a water fountain in the school to the United States Department of Agriculture (USDA) Pesticide Data Program. Atrazine and a breakdown product were found at trace concentrations below what HDOH can currently detect in its regulatory monitoring program and well below drinking water standards.

The USDA initiated the School Water Testing Program to offer schools and childcare facilities nationwide the opportunity for free testing of school drinking water. The purpose of the project

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is to collect data on the prevalence of over 100 pesticide residues at ultra-low concentrations. The study is intended to provide additional information to communities beyond what is required by the SDWA. The suite of pesticides tested includes four times as many pesticides, and their important breakdown products. The detection limits are also lower than those required for drinking water. Of the 100 pesticides tested, only atrazine and its breakdown product, desethylatrazine were found in samples collected at Waimea Canyon Middle School. The concentrations were 0.006 ppb for atrazine and 0.028 ppb for desethylatrazine, compared to the EPA's MCL for atrazine of 3 ppb. These levels detected are below the 0.050 ppb detection limit required for regulatory drinking water analyses. While beyond the scope of this report, it is important to note that there were no detections of the 98 other pesticide compounds evaluated, despite extensive current and historical agricultural uses in the aquifer recharge area.

Due to lack of federal funding, the School Water Testing Program was eliminated in early 2013. No other schools in Hawaii participated in the program.

Safe Drinking Water Program Data

Since 1993, the Safe Drinking Water Branch (SDWB) has routinely sampled community drinking water systems. The most current water quality results by water system are shown on Figure 3. All detectable levels of atrazine in the state water supply are less than or equal to 0.58 ppb, well below the MCL of 3.0 ppb.

Between 1993 and 1995, HDOH tested community drinking water systems every 3 months for atrazine. Water systems that did not detect atrazine could reduce the sample frequency for atrazine to once every three years, or twice within a one year period every three years depending on the system population. Water systems that had detectable levels of atrazine were required to sample quarterly and could reduce sampling to annual if the concentration of atrazine was reliably and consistently less than the MCL. A public water system is in violation of the atrazine standard if the running annual average of quarterly samples at any sampling point exceeds the MCL if sampling more than once annually, or if any sample exceeds the MCL if sampling less than annually.

There are currently 129 active (CWS and NTNC) systems serving a population of 1,502,575. The remainder of the population is served by transient public water systems and by non-public water systems which include individual well, stream, or rainwater catchment sources.

Since 1993, no public water system tested in Hawaii has exceeded the MCL for atrazine (quantitation limit ranged between 0.5 ppb to 0.050 ppb). Out of approximately 5,200 drinking water samples, 10% were positive for atrazine. All the detectable levels were less than or equal to 1.25 ppb. Most of those positive samples came from repeat monitoring requirements of the SDWA and do not represent 10% of the total sources tested. Maximum concentrations of atrazine in drinking water data from 1993 to present are shown in Figure 4.

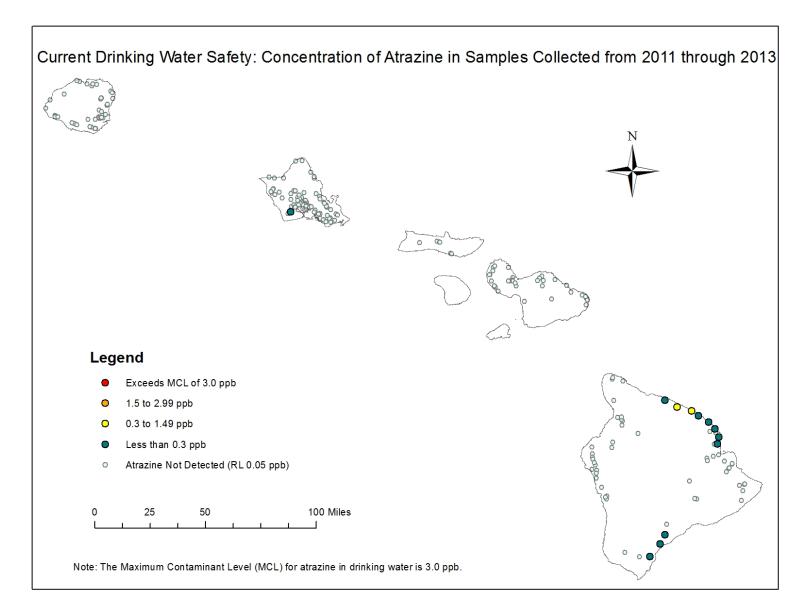


Figure 3. Current Drinking Water Safety: Atrazine in Samples Collected 2011 - 2013

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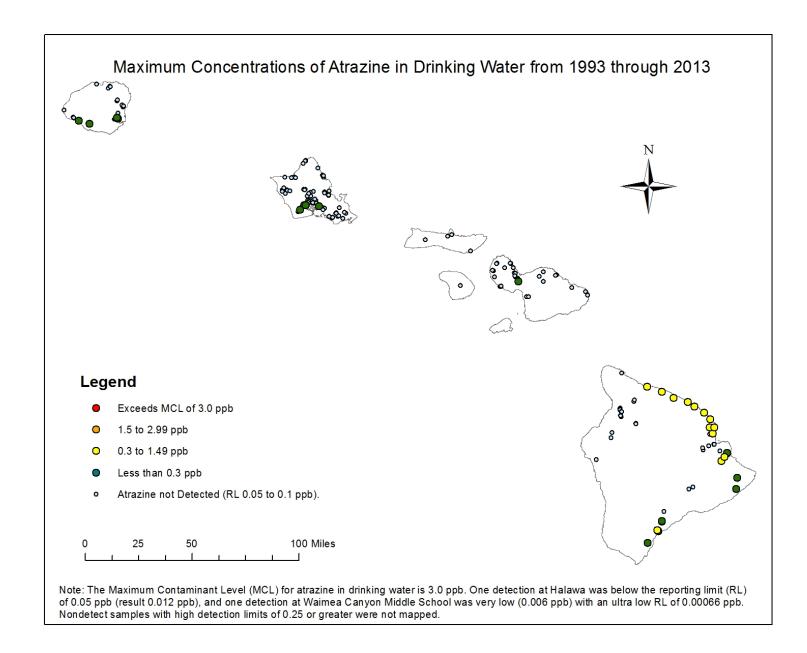


Figure 4. Maximum Concentrations of Atrazine in Regulated Drinking Water, 1993-2013

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Groundwater Data from Irrigation Wells

State and federal law do not require routine pesticide monitoring of irrigation wells. In Hawaii, no ongoing monitoring of these wells is in place, and current water quality data are not available for pesticides in irrigation wells. However, as shown on Figure 5, the research conducted by CIBA and HSPA provide a useful snapshot of historic impacts of sugarcane herbicide use on groundwater.

Irrigation wells in areas of active sugarcane cultivation were evaluated as part of the 1992-1994 CIBA study. Eight out of 14 irrigation wells sampled on Oahu had detections of atrazine or a breakdown product, and included the three wells with the highest statewide concentrations of atrazine (ranging from 0.81 ppb to 1.1 ppb), as well as the highest total atrazine plus degradation products (ranging from 1.8 to 3.1 ppb). All three of these irrigation wells were quite shallow, approximately 30 feet deep, and considered highly vulnerable to the surface infiltration of pesticides. An earlier study by HSPA reported data collected by agricultural operators between 1983 and 1986 from 8 irrigation wells in the Ewa Plain, Waipahu and Waialua on Oahu. Only one of these samples, however, an irrigation well in Waialua, had a detection of atrazine (0.6 ppb). Detection limits ranged from 0.5 to 1.0 ppb, and the sampling may have missed lower concentrations consistent with those found in the CIBA study. Detection limits were below the drinking water MCL.

Twelve irrigation wells were sampled on Maui, with detections in six wells ranging from 0.13 ppb to 0.3 ppb atrazine and 0.12 to 0.63 ppb atrazine plus degradation products. The highest detection was at a well depth of 380 ft. There were no detections of atrazine or its degradates in any of four irrigation wells sampled on Kauai during the study period. The SDWB dataset includes one additional irrigation well sampled on Kauai at Barking Sands. A single sample was taken in 1988 with a reported detection of 3.5 ppb, however, the original datasheet or other information regarding the sampling is not available. The depth and status of the well is unknown and the well was not re-sampled.

Stream and Near Shore Data

While DOH does not routinely monitor surface waters for currently used pesticides, research by USGS provides key information about pesticide incidence and movement in surface waters in Hawaii. For an overview of surface water sampling locations, please refer to Figure 6.

EPA establishes acute and chronic water quality criteria for streams and marine waters for high priority pollutants. There is currently no Acute Water Quality Criteria for atrazine, although EPA is currently proposing acute and chronic values for both freshwater streams and saltwater aquatic life in its current re-registration process for atrazine. The EPA is estimating the aquatic ecosystem level of concern as approximately 10 ppb over a 60-day period. This value is 2.5 times the highest historic detection of atrazine in groundwater, and more than 200 times the

highest detection of atrazine to date in Hawaii surface waters. For the latest information on the re-registration process see

http://www.epa.gov/oppsrrd1/reregistration/atrazine/atrazine_update.htm#current_aquatic

While early sampling in the 1970's and 1980's using detection limits up to 0.1 ppb, did not detect atrazine in Kalihi and Waikele streams on Oahu or Panaewa stream on the Island of Hawaii, subsequent 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). 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 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 and 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, 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). It's possible that trace concentrations of atrazine could be present at the other locations. Whether the atrazine is coming from current use or groundwater seepage from historical use is not known. Table 9 shows detectable atrazine levels in surface and seep sampling by HDOH and Figure 6 shows all the current and historical surface water sampling sites.

Location	Atrazine (ppb)
Unnamed Culvert at Kalapaki Beach, Kauai, HI	0.01
Nawiliwili Stream at foot bridge, Kauai, HI	0.01
Hanamaulu Beach Park, Kauai, HI	0.01
Nawiliwili Bay at mouth Nawiliwili Str, Kauai, HI	0.02
Nawiliwili Stream at altitude 18 ft., Kauai, HI	0.02
Nawiliwili Stream at Pua Loke, Kauai, HI	0.02
Black Rock Spring at Kaanapali, Maui, HI	0.04
Pua Nani Storm Drain near Lihue, Kauai, HI	0.04

Table 9. Surface and Seep Sampling HDOH 2012

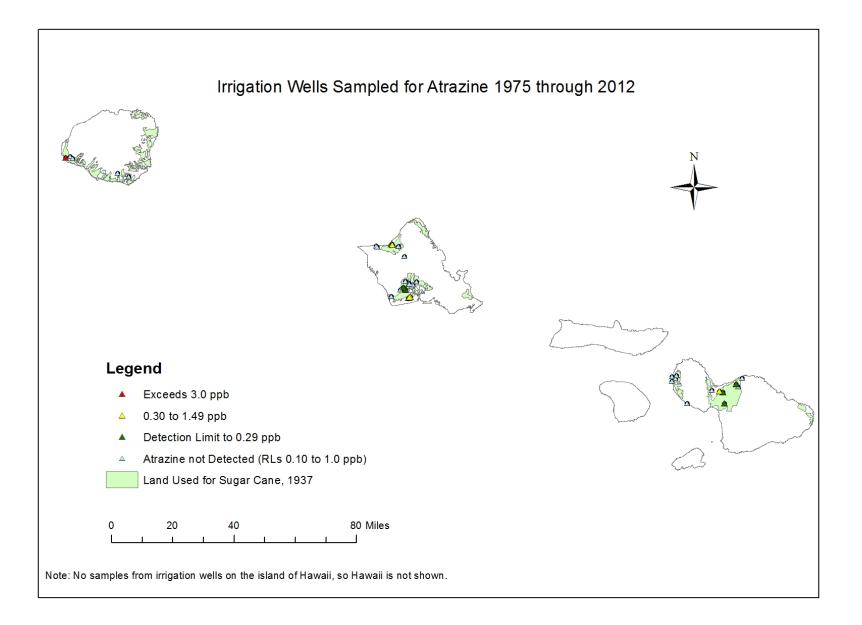


Figure 5. Irrigation Wells Sampled for Atrazine 1975-2012

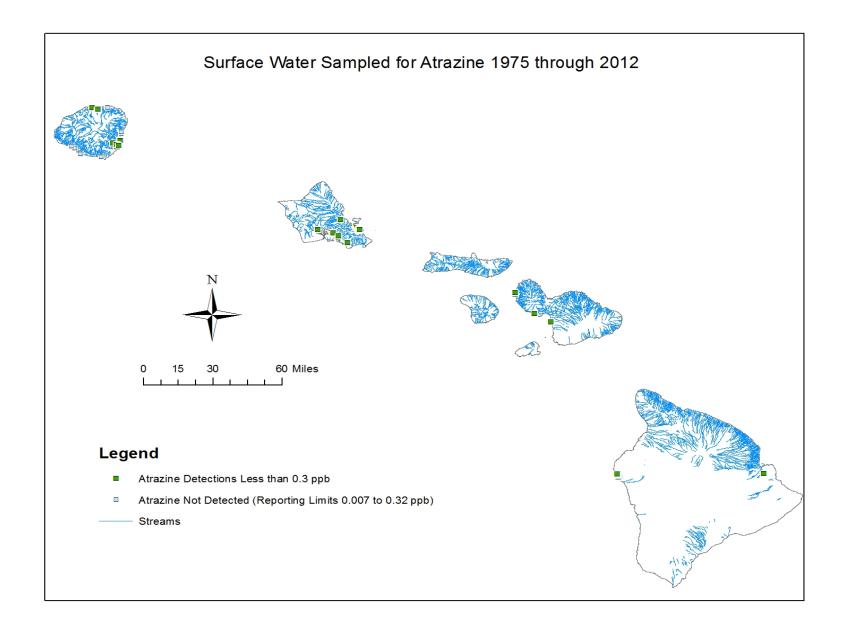


Figure 6. Surface Water Sampled for Atrazine 1975 - 2012

Interpreting the Data

Drinking Water Aquifer Vulnerability

University of Hawaii, USGS and others have intensively studied Hawaii's drinking water aquifers, and a summary of their work is beyond the scope of this report. Even from the layman's perspective, however, a review of the water quality data above shows clear connections between historical applications of atrazine in sugarcane cultivation and subsequent detections in groundwater.

There are significant differences in the patterns of groundwater contamination among islands and local hydrogeologies. Atrazine contamination of groundwater mainly has been detected within or hydraulically down gradient from areas currently or previously used for sugarcane cultivation (Figures 8-11). Areas with high rainfall, thin permeable soils, limited weathering of rocks in the unsaturated zone, shallow depths to groundwater, and high rates of atrazine use are expected to be most vulnerable to contamination.

To provide some perspective, 16 of 39 water systems on Hawaii Island have had historic detections of atrazine, compared to only 3 of 33 on Oahu, 2 of 18 on Kauai and 1 of 34 on Maui. The majority of these detections were along the Hamakua Coast on the Island of Hawaii, and suggest the particular vulnerability of spring fed water systems where the opportunity for groundwater contamination is the greatest, both as a result of shallow groundwater depths, and fractured rock substrate that may create preferential pathways to deeper water supplies. This pattern was noticed early by HSPA at both Pepeekeo and Kihalani Springs. In fact, data from 1985 to 1987 show the highest recorded values of atrazine in drinking water at Pepeekeo Spring (4.1ppb), representing the only location statewide that has ever exceeded 3 ppb, the concentration in drinking water that EPA would establish as the MCL in the early 1990s. As a result of data derived from their early sampling (Figure 7), HSPA members curtailed use of atrazine in the recharge area around Pepeekeo Spring, and the County Department of Water Supply switched to other, deeper well sources to provide drinking water to the community. (Personal communication & historic HSPA letter, S. Whalen).

Drinking water supplies on other islands show fewer detections at lower concentrations.

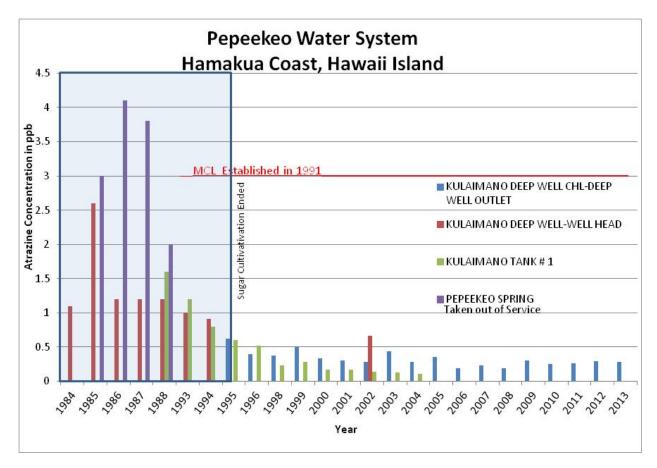


Figure 7. Pepeekeo Water System, Hamakua Coast, Hawaii Island

Atrazine Data by Island

Maps on the following pages show all atrazine sampling and detections in drinking water, irrigation and surface water by island.

On the Island of Hawaii, the sampling focus to date has been on groundwater, with very few samples taken from surface water (Figure 8). Given the USGS study on Oahu indicating movement of atrazine contaminated groundwater into Waikele Stream (Anthony et al., 2004), it is likely that atrazine from historically contaminated groundwater could be transported to surface waters at trace concentrations along the Hamakua Coast. It is important to consider, however, that the highest single concentration of atrazine measured in groundwater on the Island of Hawaii, at 4.1 ppb in 1986, is below the aquatic ecosystem level of concern currently being proposed by EPA of approximately 10 ppb over a 60-day period (see earlier reference). Ground water mixing with surface water creates additional dilution so potential concentrations in surface waters are expected to be less than the highest current detections in groundwater of 0.58 ppb. Additional surface water sampling will be conducted on Hawaii as part of the upcoming joint surface water sampling effort to measure whether and at what concentrations residual atrazine in groundwater may be reaching surface waters.

On the island of Oahu, the highest concentrations of atrazine measured were seen in 1993 in three shallow irrigation wells at the Ewa Sugar Plantation, with detections ranging from 0.81 ppb to 1.1 ppb. Drinking water data show low detections, all below 0.1 ppb, in only 3 of 33 drinking water systems: Barber's Point, Joint Base Pearl Harbor Hickam and Waipahu-Ewa-Waianae. The 1999-2001 USGS surface water data in Waikele stream demonstrates subsurface groundwater transport of trace amounts of atrazine from contaminated groundwater impacted by sugarcane cultivation into surface waters. All atrazine detections in water for Oahu can be seen on Figure 9.

The island of Maui has the only currently operating sugar plantation, which in 2012 used 93.5% of the atrazine sold statewide. Figure 10 shows all detections of atrazine in water on Maui. Historically, only one regulated drinking water well on Maui has shown detections of atrazine, with a total of two detections with a maximum concentration of 0.07 ppb in 2010 at a well in central Maui. Because the majority of sugarcane on Maui is not grown directly over drinking water aquifers, it is useful to evaluate the irrigation well data to evaluate impacts to groundwater. Data collected by HSPA in 1993-1994 show detections ranging up to 0.13 ppb to 0.3 ppb, more than ten times lower than detections on the Island of Hawaii in the same time period. No current data are available from non-drinking water sources on Maui, however, sugarcane cultivation practices have not changed. Very little surface water sampling has occurred on Maui, but samples will be collected in the coming months, as part of the joint HDOH/HDOA/USGS study.

On Kauai, as shown on Figure 11, two water systems had historic detections of atrazine in drinking water. A well in the Lihue-Kapaa water system registered a high detection of 0.28 ppb in their drinking water supply in 1986, dropping to 0.19 by 2004. The drinking water supply at the Gay & Robinson plantation in Kekaha was sampled from 1993 to 2011, with a single detection (0.081 ppb) in 2008, the last year of the sugar operation there. A sample from Waimea Valley School collected by the community and analyzed through the USDA School Water Testing Program had a detection of 0.006 ppb, well below the 0.050 detection limit used for regulatory drinking water samples. The only detection in irrigation water on Kauai was from a single irrigation well sample collected at Barking Sands in the late 1980s which measured a detection of 3.5 ppb. The status of the well is unknown and no follow up data are available. Surface water samples collected by DOH in 2012 showed trace detections of atrazine in samples from the Nawiliwili drainage.

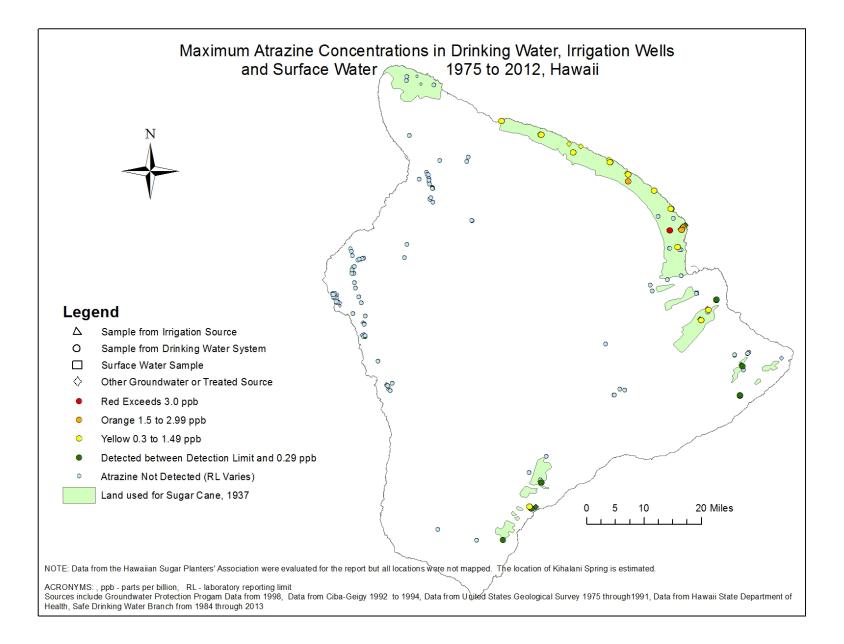


Figure 8. Hawaii Island: All Atrazine Water Quality Data 1975-2012

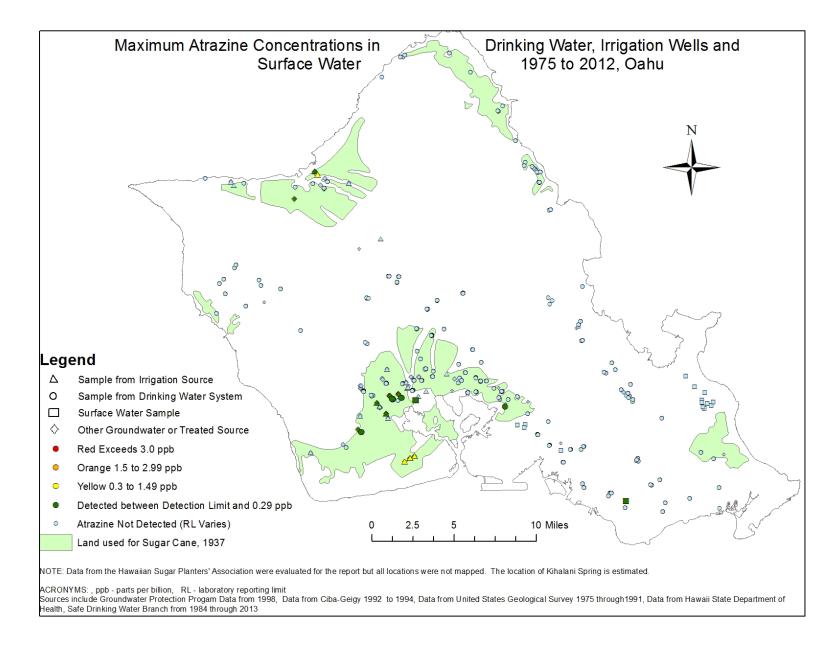


Figure 9. Oahu: All Atrazine Water Quality Data 1975-2012

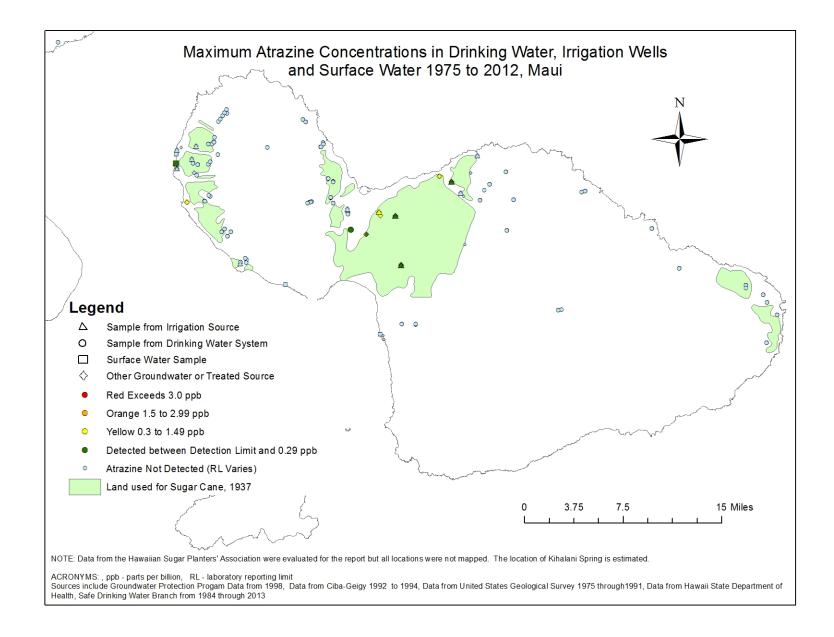


Figure 10. Maui: All Atrazine Water Quality Data 1975-2012

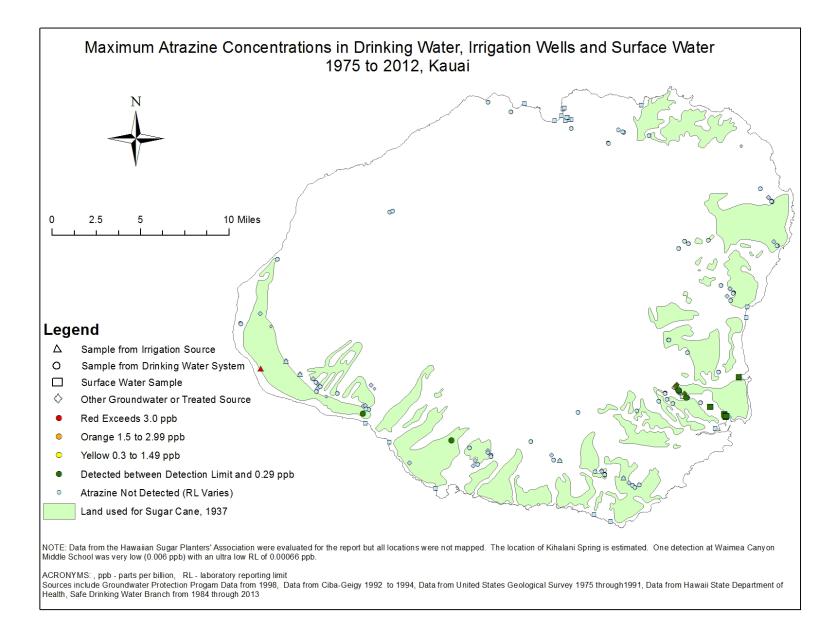


Figure 11. Kauai: All Atrazine Water Quality Data 1975-2012

Summary and Recommendations

Atrazine use in Hawaii has decreased over the years due to label restrictions and the decline of the sugar industry. Currently, the largest user in the state is the sugar industry on Maui. Early studies by HSPA detected atrazine in drinking water in areas with active sugarcane cultivation. Extensive regulatory monitoring by HDOH has shown a downward trend in atrazine in drinking water throughout the state.

Limited surface water monitoring showed trace levels of atrazine on Oahu, Kauai, Maui and the Island of Hawaii. Some of the surface water detections could be due to groundwater seepage into streams. For example, results from the 1999-2001 USGS Oahu Water Quality Study showed trace levels of atrazine in Waikele Stream under dry-season conditions likely reflecting movement of contaminated groundwater from historic agricultural activities into the stream. Storm water sampling detected atrazine much less frequently and at lower detections. Limited surface water monitoring in 2012 by HDOH showed trace levels of atrazine in several places on Kauai and one place on Maui. Additional data are needed to understand whether these detections represent current or historic uses of atrazine.

Air sampling by UH on Kauai did not find detectable levels of atrazine. Given that atrazine was not detected in UH's passive sampling, the low levels found in air monitoring in other areas nationwide, and that California has not chosen it as a high risk pesticide for air monitoring, HDOH believes further air monitoring for atrazine is not warranted.

Of the complaints made to the HDOA from 2010 to October 2013, no cases of atrazine exposure were confirmed. Out of 4,800 calls to the Hawaii Poison Hotline, one case of atrazine exposure to a worker was reported resulting in minor health effects.

Based on this review of all available environmental data, there were no exceedances of healthbased or ecological regulatory standards. After a review of drinking water, air and surface water monitoring, HDOH recommends additional stream and near shore water sampling for atrazine and other commonly used pesticides to fill identified data gaps. Limited data exist as there is no regulatory program requiring surface water monitoring. HDOH has secured limited funding through a partnership with USGS and HDOA and intends to conduct stream sampling in the next several months. The results of the stream sampling will be made available to the legislature and public upon completion of the study.

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Appendix A - Syngenta Report to HDOH



Dr. Fenix Grange Hazard Evaluation & Emergency Response Office Hawaii Dept. of Health 919 Ala Moana Blvd., Suite 206 Honolulu, HI 96816

Electronically submitted: fenix.grange@doh.hawaii.gov

Subject: Syngenta Crop Protection, LLC Statement, "Atrazine Environmental Fate and Monitoring Results in Hawaii"

Dear Dr. Grange,

Syngenta Crop Protection, LLC appreciates the opportunity to provide the attached statement entitled "*Atrazine Environmental Fate and Monitoring Results in Hawaii*". Per our understanding, House Concurrent Resolution No. 129 (House of Representatives, State of Hawaii) charges the Hawaii Department of Health (DOH) with developing partnerships to evaluate atrazine data gaps in air, soil, and water (surface, ground, near shore). To help meet that charge and at your request, we developed a summary of historical Hawaii environmental monitoring data to help determine whether additional information is needed to evaluate human health and ecological exposures and mechanisms of how atrazine moves in the environment.

We look forward to partnering with the DOH and other State of Hawaii personnel regarding the science supporting atrazine.

Sincerely,

Clint Truman, Ph.D. Technical Leader, Environmental Fate & Exposure Environmental & Product Safety (North America) Syngenta Crop Protection, LLC POB 18300 Greensboro, NC 27419

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"Bringing plant potential to life"



Atrazine Environmental Fate and Monitoring

Results in Hawaii

Introduction

Atrazine is one of the most studied chemicals in the world. Scientific studies (~7,000) conducted over the past 50 years clearly establish its safety for humans and the environment. Atrazine meets and/or exceeds the most stringent safety requirements. The United States Environmental Protection Agency (USEPA) and other respected scientific experts and government regulators, including the World Health Organization (WHO) and the Australian Pesticides and Veterinary Medicines Authority, have found atrazine to be safe at levels potentially found in the environment.

Drinking water standards are defined by the federally mandated Safe Drinking Water Act (SDWA). Maximum contaminant levels (MCLs) are health-protective values set by the USEPA Office of Water (OW), and establish a no-effect level with a margin of safety (MOS) of at least 100-fold. For atrazine, the MCL in drinking water is 3 ppb, a 70-yr lifetime average standard equivalent to a 5000-fold MOS. The MCL was established in 1991 (USEPA, 1991), and was based on a reference dose of 0.0048 mg kg⁻¹ d⁻¹ (0.005 mg kg⁻¹ d⁻¹), which is no longer used by the USEPA. In 2006, USEPA/OW established an updated reference dose of 0.018 mg kg⁻¹ d⁻¹ (0.02 mg kg⁻¹ d⁻¹) (USEPA, 2006a), 4-fold greater than that set in 1991. To date, the MCL has not been updated. In 2010, the Joint Food and Agricultural Organization/WHO revised its lifetime guideline value for atrazine in drinking water upwards 50-fold to 100 ppb for total chloro-s-triazines (TCT, atrazine parent + chloro-metabolites based on updated toxicological data and a pesticide residue assessment (WHO, 2010).

The USEPA also uses a drinking water level of comparison (DWLOC); DWLOC and MCL values are based on no-effect levels, include safety factors, and consider potential exposure durations and monitoring frequency. For TCT, DWLOC values for the 90-d (chronic) range from 12.5-68 ppb, depending on sub-population, as well as the 1-d DWLOC of 298 ppb (USEPA, 2006).

The SDWA mandates that community water systems (CWS)¹ must be monitored under State agency programs for regulated contaminants (atrazine is one of many chemicals monitored). As part of SDWA, each State must issue a notice of violation to a CWS when a contaminant exceeds the USEPA's MCL.

Surface water

Under the atrazine Memorandum of Agreement (MOA) between the USEPA Office of Pesticide Programs (OPP) and atrazine registrants, an atrazine monitoring program (AMP) is required for

¹ CWS in SDWA provide drinking water for human consumption to at least 15 service connections and provide water to the same population year around. A CWS can use multiple raw water sources: groundwater, surface water (rivers, lakes, reservoirs), or blends (both).



any CWS with annual mean SDWA concentrations of TCT in finished water equal to or greater than 2.6 ppb based on SDWA monitoring results. Since the start of AMP (2003), CWS in Hawaii have had levels below 2.6 ppb and have not met the criteria requiring monitoring via AMP.

The Hawaii DOH released data on atrazine concentrations in ~5200 drinking water samples from 268 CWS (1993-2012). Ninety three percent (93%) of the samples were non-detects; the remaining 7% were less than or equal to 1.25 ppb, which is less than half of the annual average USEPA/OW MCL. In Hawaii, no CWS has had an average annual atrazine concentration greater than 3 ppb. Also, no notice of violation has ever been issued for atrazine in any CWS in Hawaii.

Tierney et al. (2008) assessed atrazine in drinking water of CWS in 32 major atrazine use States, including Hawaii. For 5394 surface water sourced CWS in those 32 States (1993-2000), 99.9% of the CWS had atrazine concentrations less than or equal to the MCL or not detected. Majority of all atrazine samples analyzed were non-detects. Only three Midwestern CWS had individual samples greater than 3 ppb; all were obtained in raw water from an impounded reservoir, and had multi-year average atrazine concentrations ranging from 3.30-3.41 ppb.

Groundwater

In Hawaii, groundwater is the primary drinking water source. For Oahu where the vast majority of Hawaii's population resides, 95+% of all water for domestic (drinking water) and agricultural uses comes from groundwater. Because pesticides had been detected in groundwater, the Hawaii Department of Agriculture (HDOA) supported research to determine if commonly used pesticides were leaching to groundwater. Conclusions include:

- Atrazine only met the leaching criteria in the top 15-cm soil layer, and had the second lowest leaching potential (mobility) among pesticides studied;
- TCT concentrations in well water were less than 1.5 ppb, majority of which were nondetects;
- Maximum depth of movement for atrazine was only 0.33-m.

Study details supporting these conclusions from Hawaii are briefly summarized below:

Dusek et al. (2010) evaluated potential leaching of four herbicides (including atrazine), an insecticide, and a fungicide under Hawaii field conditions. Five sites were selected: three on Oahu (Poamoho, Kunia, Waimanalo); one on Kauai (Mana); and one on Maui (Kula). Of the five soils, two were Oxisols (silty clays), two were Vertisols (clay, silty clay loam), and one was an Andisol (loam). Atrazine was applied (5.41 kg ha⁻¹ a.i.) at or below the USEPA/HDOA maximum allowable rate over a season. The calculated GUS index for atrazine at the five sites ranged from 1.3-3.9; average GUS index values for 0-15, 15-30, and 60-90 cm soil depths were 2.88, 2.64, and 2.70, respectively. The GUS index is a function of half-life and K_{oc} of a given pesticide (GUS>2.8 indicate pesticides that have leaching potential). Based on GUS values, atrazine only met the leaching criteria for the top 15-cm soil layer. However, using half-life (7-14 d) and K_{oc} (40-100) values characteristic of atrazine under nontemperate environments, GUS values ranged from 2-2.4, less than the 2.8 leaching criteria. Atrazine had the second lowest leaching potential (mobility) among pesticides studied. Center of mass values for atrazine at the five sites after 600-mm of cumulative water application only averaged 18.4 cm (range 11-34 cm). Dusek et al. (2011) concluded that the rapid degradation during the 16 week study resulted in only shallow movement of atrazine in the five soil profiles studied.



Li et al. (2001) sampled 36 wells in the Islands of Hawaii (5), Kauai (5), Maui (12), and Oahu (14) from August, 1997 to January, 1998. Wells were selected based on proximity to areas where herbicides were potentially applied (land use). All reported atrazine and metabolite concentrations from samples analyzed (49) were less than 1.5 ppb (MDL=0.1 ppb). Fifteen (15) samples yielded concentrations at or above 0.1 ppb.

Alavi et al. (2007) studied five pesticides, including atrazine, in Central Oahu (Kunia) on an Oxisol. Atrazine was watered in (5-mm irrigation) just after application (~9 kg ha⁻¹ a.i.). This application rate is approximately two times the current maximum allowed rate for a sugarcane application. Maximum measured depth of movement for atrazine after 19 weeks was only 0.33-m.

In addition to specific studies conducted in Hawaii mentioned above, Syngenta has an extensive groundwater and/or drinking water monitoring database that quantifies atrazine occurrence and exposure across the U.S. For example:

Across 21 States (Hawaii to Florida; Minnesota to Texas), drinking water was sampled from groundwater sourced CWS under SDWA (1993-1998). The 14,863 water samples analyzed represent ~90% of the atrazine use area and an U.S. population-linked exposure database for this 6-yr period. Ninety seven percent (97%) of the atrazine detections were less than 3 ppb. Of the samples (3%) with atrazine concentrations above 3 ppb, no sample exceeded 7.9 ppb (well below the WHO guideline of 100 ppb). (Tierney et al., 1999).

In 2000, 438 groundwater-sourced CWS were selected to statistically represent the 14,863 water samples (Cheung et al., 2001) and analyzed for TCT. Only 3.3% of the 527 groundwater samples taken from the 438 CWS had detectable atrazine (LOQ=0.05 ppb); 5.9% had detectable chlorotriazine metabolites. Median and 95th percentile atrazine concentrations were 0.002 and 0.024 ppb, respectively; Median and 95th percentile TCT concentrations were 0.009 and 0.11 ppb, respectively; Maximum atrazine and TCT concentrations were 0.96 and 2.37 ppb, respectively. Groundwater exposure to atrazine and TCT was low in regions representing ~90% of the atrazine use in the U.S (1993-1998).

From 1992-1994, 1,505 rural drinking water wells across 19 States, including Southern U.S. States and Hawaii, were targeted for their previous positive detections of atrazine and metabolites. Wells were sited in high groundwater vulnerability areas with permeable soils and high atrazine use to represent high-end exposure scenarios. Only 7 wells (0.5%) had atrazine concentrations greater than 3 ppb. For all drinking water, 1145 wells (76.1%) had atrazine concentrations less than 0.1 ppb; 1444 wells (96+%) had atrazine concentrations less than 0.1 ppb; 1444 wells (96+%) had atrazine concentrations less than 0.1 ppb; 1444 wells (96+%) had atrazine concentrations less than 1 ppb. In a subset of wells in Hawaii, 114 samples were analyzed for atrazine and TCT (LOD=0.1 or 0.2 ppb). Only 3 (2.6%) of all atrazine samples and 9 (~8%) of all TCT samples were in the 1-2.99 ppb range. Number of atrazine and TCT samples below LOD were 77 (67.5%) and 73 (64%), respectively. Atrazine and TCT samples below 0.99 ppb were 111 (97%) and 103 (90%), respectively. (Balu & Holden, 1996).

Complimentary to Syngenta's extensive groundwater and/or drinking water monitoring database, Focazio et al. (2006) examined data from 18,827 domestic wells from State and National groundwater survey studies. Atrazine was among multiple chemicals assessed. Atrazine was detected in 24% of the 3309 wells where atrazine was analyzed, with only one well having a concentration greater than 3 ppb (5 ppb).

Similar results have been documented in southern Georgia and Brazil where soil and climatic (temperature, rainfall) conditions are more similar to those in Hawaii. In Georgia,



atrazine transport to groundwater (depth=10-m), a drinking water source, was quantified (1993-1996) (average annual rainfall + irrigation=173-cm). Average atrazine and deethylatrazine (DEA) concentrations were 0.11 and 0.57 ppb; Peak atrazine and DEA concentrations were 0.44 and 1.8 ppb (Bosch et al., 2000; Bosch & Truman, 2002).

In Brazil, Casara et al. (2012) monitored groundwater wells (1-5 m deep) (2009-2010). Atrazine concentrations (detection frequency=3%) ranged from 0.20-0.28 ppb. Nogueira et al. (2012) analyzed ~225 groundwater well samples (depth=5-140 m) (October, 2007 to May, 2008). Atrazine was not detected in groundwater in Lucas do Rio Verde. For Campo Verde, mean atrazine concentration (detection frequency=4%) was 0.70 ppb. Dores et al. (2006, 2008) analyzed 125+ water samples from irrigation and/or drinking water wells (depth=10-39 m) in September, 1998, December, 1998, and April, 1999. Median and maximum atrazine concentrations were less than 0.152 and 0.856 ppb, respectively. Lanchote et al. (2000) analyzed ~250 groundwater samples (Botucatu aquifer) from October to July (1995-1996); atrazine was not detected. In the same watershed, Cerdeira et al. (2004, 2005) collected groundwater samples (40-m deep) from October to July of each year (1996-2003); atrazine was not detected.

Near-shore (coastal) water

Jobos Bay National Estuarine Research Reserve in Puerto Rico has soil and rainfall conditions comparable to Hawaii and may be a reasonable surrogate of potential atrazine concentrations in coastal waters of Hawaii. Over a 2.5-year period (2008-2010), atrazine fate and transport was quantified in and from a 100-ha farm field adjacent to Jobos Bay. Atrazine was applied to the 100-ha field annually prior to the study. In 20 separate applications, 360 kg of atrazine was applied to the 100-ha field locations were taken between April, 2008 and November, 2010. Atrazine and DEA, were detected in only 3% of the estuary samples; no sample exceeded 0.4 ppb (Potter et al., 2013).

Atrazine in soil

Atrazine degradation is a dominant process affecting its fate. Atrazine degradation, expressed as its half-life $(t_{1/2})$, can vary depending on climate/environment (temperate vs. tropical) conditions (Table 1), especially when atrazine has repeated use. In Hawaii, atrazine was degraded ~10-fold faster in soils with a history of atrazine use $(t_{1/2} \text{ values}=0.8-1.8 \text{ d})$ compared to soils with no history of atrazine use $(t_{1/2} \text{ values}=3.4-6.8 \text{ d})$ (Shaner et al., 2010). Dusek et al. (2010) reported that atrazine had shorter $t_{1/2}$ values than those found in the literature while evaluating leaching potential of pesticides from multiple field locations throughout Hawaii.

In locations that have similar soil and climatic (temperature, rainfall) conditions to Hawaii, atrazine fate in soil was similar. In Puerto Rico, environmental conditions coupled with repeated atrazine use resulted in mean DT_{50} (time to 50% dissipation) of 2 days (Potter et al., 2013). In Georgia, atrazine $t_{1/2}$ values were ~12-d in surface soil (<100-cm). On average, 83% of the atrazine degraded 30-d after its application; by 44-d after application, all of the atrazine in the top 250-cm of soil had degraded (Bosch et al., 2000; Bosch & Truman, 2002).



Atrazine in Air and Rainfall

Based on physical-chemical properties (Table 1), atrazine transport by vapor and particulate matter (dust) is expected to be low. Atrazine concentrations in Canadian agricultural regions during the use season were on the order of 1000 and 50 pg m⁻³ for vapor and particulate matter phase, respectively (Yao et al., 2008; Hayward et al., 2010). In Mississippi (April-September, 1995), Coupe et al. (2000) reported maximum atrazine concentrations in vapor and particulate matter phases of 2.6 (n=21; median concentration=not determined; 58% non-detects) and 0.42 ng m⁻³ (n=21; median concentration=0.058 ng m⁻³; 33% non-detects), respectively. Thus, there would be low atrazine exposure via vapor or particulate matter and corresponding low risk to humans and the environment.

Based on a literature search to-date, no reported rainwater samples in Hawaii have contained atrazine. Atrazine has been reported in rainwater in multiple agricultural regions of the U.S. and in National Parks in the mid-west and western U.S., with concentrations ranging from 0.014-0.060 ppb (Mast et al., 2007; Vogel et al., 2008). Thurman and Cromwell (2000) reported that atrazine concentrations in rainfall generally ranged from 0.1-0.5 ppb, and that atrazine in rainfall was seasonal. The highest mean concentration for atrazine and DEA were 1.8 and 0.3 ppb, respectively. Coupe et al. (2000) reported maximum and median atrazine concentrations in rainfall of 0.83 and 0.02 ppb (n=16; 25% non-detects), respectively. They, along with Thurman and Cromwell (2000) and Majewski and Capel (1995) noted that atrazine occurrences tended to be seasonal. Atrazine concentrations in rainfall are not expected to contribute significantly to human or environmental exposure as they are orders of magnitude lower than the MCL.

Conclusions

Scientific data presented for Hawaii and other regions of the U.S. demonstrate that atrazine, when detected, is often detected at concentrations below the USEPA established MCL for atrazine (3 ppb). Atrazine concentrations were also one order of magnitude below the WHO LOC for TCT (100 ppb), thus posing no risk to human or environmental health.

In the 2006 re-registration of atrazine, the USEPA stated that "there is a reasonable certainty that no harm will result to the general U.S. population, infants, children, or other major identifiable subgroups of consumers from aggregate exposure (from food, drinking water, and non-occupational sources) to cumulative residues of atrazine and other chlorinated triazine pesticides." Atrazine has been used safely for 50+ years in 60+ countries.

Scientific data presented herein also shows that atrazine has been thoroughly researched. Furthermore, in the recent Registration Review (2013) for atrazine (docket EPA-HQ-OPP-2013-0266), the USEPA stated in the preliminary work plan that *"There are no remaining data gaps anticipated for the registration review of atrazine."*

Health, safety, and environment are cornerstones for Syngenta. We appreciate the opportunity to partner with the DOH and other State of Hawaii personnel, and we look forward to continued dialogue regarding the science supporting atrazine.



Respectfully,

Syngenta Crop Protection LLC

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Table 1

	Atrazine
CAS number	1912-24-9
Chemical name	2-chloro-4-ethylamino-6-isopropylamino- <i>s</i> - triazine
Molecular weight (g mole ⁻¹)	215.70
Molecular formula	C ₈ H ₁₄ N ₅ CI
Water solubility (mg L ⁻¹ @ pH 7, 22°C)	33
Vapor pressure (mm Hg @ 25°C)	2.89×10^{-7}
Henry's law constant (atm m ³ mol ⁻¹)	2.48×10^{-9}
Log K _{ow} / Log P (@ 25°C)	2.68
K _{oc} (ml g⁻¹)	40 - 394
Hydrolysis	Stable
Soil photolysis (days)	45
Aquatic photolysis (days)	335 (natural light); 1 (artificial light Hg)
Aerobic soil half-life (days)	21 - 146
Aerobic aquatic half-life (days)	41 - 237
Anaerobic aquatic half-life (days)	608
Anaerobic soil/sediment half-life (days)	58 - 547

Physical, chemical, and environmental fate characteristics for atrazine

Appendix B – Atrazine Sales Maps

