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Soil and Water Contamination at Pesticide Mixing and Loading Sites on Oahu, Hawaii

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Groundwater contamination by pesticides is largely attributed to non-point sources. Recent evidence suggests that point sources such as agrochemical dealerships (Mueller, 1989), pesticide mixing and loading sites (Hallberg, 1988), and pesticide applicator cleaning sites (Krueger and Seiber, 1984) may be significant sources of groundwater contamination. Point sources of pollution are more controllable than non-point sources and offer many opportunities to manage pesticide contamination.

Pineapple and sugarcane are two major agricultural commodities in Hawaii and primarily triazine herbicides are used in their production. Contamination of potable water sources in Hawaii by atrazine and de-ethylated atrazine has been reported (Hawaii State Dept. of Health, 1988). Triazine herbicides are generally extracted from soils using polar solvents with soxhlet (Xu et al., 1986), reflux (Green et al., 1977), sonication (Hill and Stobbe, 1974), and shaking (Mattson et al., 1970). Water is reported to be an essential component for quantitative recovery of weathered residues (Mattson et al., 1970). Cleanup procedures such as column chromatography on silica (Xu et al, 1986; Green et al., 1977), alumina (Hill and Stobbe, 1974; Mattson et al., 1970), and Bio-Beads$^{(R)}$ (Xu et al., 1986) are used to prolong analytical column life and improve detection limits. Both gas and liquid chromatography are used for the final analysis of triazines.

Several soil cores and water samples were taken from areas near pineapple and sugarcane pesticide mixing and loading sites and several pesticides were determined.

MATERIALS AND METHODS

The two pesticide mixing and loading sites studied are found on the island of Oahu in the saddle region between the Waianae and Koolau mountain ranges; the pineapple

Send reprint requests to CJ Miles at the above address site is located in the middle of this region (Wahiawa) and the sugarcane site is west of the Pearl Harbor area (Ewa). Wahiawa soils consist of well-drained, moderately fine textured soils developed from old alluvium derived igneous rock. The surface soil is moderately acidic silty clay approximately 30 cm thick, overlying moderately acidic to neutral silty clay subsoil approximately 120 cm thick. The underlying substratum is weathered basic igneous rock. Soil permeability is moderately rapid with slow runoff. Waipahu soils (in the Ewa area) are similar to the Wahiawa soils except the substratum is a clayey alluvium derived from the marine terrace. Also, soil permeability is moderately slow with slow to very slow runoff. The sugarcane site overlays the Honolulu-Pearl Harbor Aquifer which is an important water resource for the city of Honolulu.

Soils were collected by auger, separated into 30 cm segments, and stored frozen in plastic bags until analyzed. Percent mositure was determined by oven drying (110° C/24 hr) of duplicate 10 g samples. Fifty grams of each soil was transferred to a 500 mL roundbottom flask and water added to adjust moisture to 50%. After adding 250 mL of 4:1 ethylacetate:methanol, the sample was refluxed for 1 hour. The filtered extracts were evaporated just to dryness, dissolved in 10 mL of toluene and analyzed directly by GC/NPD. Organochlorine (OC) pesticide screening required florisil cleanup of a two mL aliquot of the sample extract according to the Pesticide Analytical Manual, section 212.4. Soils containing high concentrations of sulfur, which interfered with OC and GC/MS pesticide analysis, were also cleaned up with a tetrabutylammonium hydrogen sulfate/sodium sulfite reagent (Jensen et al., 1977). For analysis of diuron by LC, 1 ml of the toluene sample was transferred to a vial and evaporated gently with nitrogen purging. After 0.5 mL of acetonitrile was added and the sample sonicated, 0.5 mL of water was added. The sample was filtered and analyzed. Telone (cis- and trans- isomers) were extracted by distillation of 50 g soil, 10 mL hexane, and 500 mL water in a liquid-liquid extractor for 25 min. All pesticide concentrations in soils were determined on a wet basis.

To determine the extraction reproducibility of the method, five replicate extractions of a soil sample (pineapple site #1, 244-274 cm) were prepared on air-dried (11.2% moisture) and field wet (20.8% moisture) subsamples.

Well water samples were collected 2.9 km up gradient (control) and 2.5 km down gradient of the sugarcane site. The down gradient well was about 12 m deep. Water samples were collected in amber, 4 L glass bottles with

Teflon liners and refrigerated until analyzed. One liter of each water sample was extracted 3 times with methylene chloride, dried with sodium sulfate, evaporated to dryness, and redissolved in 10 mL of acetone.

Triazine herbicides in soil extracts were determined by gas chromatography (GC) using a 15m X 0.53mm, 0.88um HP-5 capillary column (Hewlett-Packard) and nitrogen-phosphorous detector (NPD) temperature programmed at 150° C for 5 min then 10° C/min to 210° C, hold 15 min then 10° C/min to 250° C, and hold 10 min. Triazine herbicides in water extracts were determined by GC/NPD using a 15m X 0.53mm, 0.83um DB-608 capillary column (J&W Scientific) at 150° C for 5 min then 5° C/min to 210° C, hold 3 min then 10° C/min to 250° C and hold 6 min. Diuron was determined by liquid chromatography (LC) using a 0.46 X 3 cm, 3 um C_{18} column (Perkin-Elmer) with a mobile phase of 40% acetonitrile in 0.01 M phosphate pH 6.2 (0.2 mL triethylamine/L) delivered at 2 mL/min and detected at 220 nm. Organochlorine pesticides were determined by GC using a 15m X 0.53mm, 0.83um DB-608 (J&W Scientific) capillary column temperature programmed from 150° C to 220° C at 5° C/min and a 15m X 0.53mm, 0.88um HP-5 capillary column temperature programmed from 150° C to 220° C at 5° C/min with an electron capture detector (ECD). Telone samples were analyzed by GC/ECD on a 25m X 0.53mm, 5 um BP-1 column (SGE Scientific) at 80° C. Gas chromatography/mass spectrometry (GC/MS) was performed with a 30m X 0.25mm, 0.25um DB-5 capillary column (J&W Scientific) temperature programmed from 50° C for 1 min then 20° C/min to 150° C then 10° C/min to 250° C and hold for 14 min. The mass spectrometer (Hewlett-Packard model 5970) was scanned from 40 to 400 amu.

RESULTS AND DISCUSSION

Diuron, ametryn, bromacil, and hexazinone were detected at the pineapple pesticide mixing and loading site (Table 1). Concentrations generally decreased with depth although there were many exceptions. Diuron, atrazine, terbacil, ametryn, and hexazinone were detected at the sugarcane pesticide mixing and loading site (Table 2). In hole #1, concentrations of atrazine and ametryn were very high and significant concentrations were observed in the deepest sample (244-274 cm). Pesticides were confirmed in representative samples by GC/MS. GC/MS analysis also showed the presence of the de-ethylated ametryn metabolite.

DDT, DDE, and DDD were detected at both sites and concentrations generally decreased with depth (Tables 1 and 2). Since detection was difficult by GC/MS (electron ionization), confirmation was achieved by two dissimilar

GC columns and GC/MS at the highest levels. Although DDT is no longer registered for use, residues from previous use are expected due to its persistance.

The percent moisture of the soil samples ranged from 14.0 to 35.7 with an average of 22.4. Comparison of the five wet (20.8% moisture) and air-dried (11.2%) soil samples showed no significant difference between the average concentrations of atrazine, ametryn, hexazinone, or diuron at the 99.5% confidence level. Percent relative standard deviations of the analyses ranged from 2.7 to 12.1 with an average of 6.1. These results suggest that the percent moisture over the range studied does not significantly affect extraction of the test pesticides. Another investigation reported that successful extraction of atrazine residues in weathered soil required water (Mattson et al., 1970). These observations are important because pesticides in field weathered samples can be more difficult to extract compared to lab fortified samples that are usually extracted shortly after spiking.

The sensitivity and selectivity of the GC/NPD method was adequate for sub-ppm determination of the nitrogeneous pesticides in soil and water. Diuron was determined by LC because of interferences caused by early elution under the GC conditions selected and irreproducibility caused by thermal degradation to the isocyanate derivative (Tamiri and Zitrin, 1987). Method detection limits of the nitrogenous pesticides in soils ranged from 0.01 to 0.06 ppm and accuracy and precision were acceptable with the exceptions of diuron and some of the organochlorines (Table 3). The precision of diuron measurements were probably affected by the transfer and reconstitution for LC analysis. Variablility in the organochlorine pesticide analyses may be the result of working close to the method detection limit and using a sample preparation scheme that is unsuitable for such a broad range of pesticides.

The well water sample approximately 2.5 km down gradient of the sugarcane mixing and loading site and 12 m deep had detectable concentrations of atrazine and ametryn and their de-ethylated metabolites (Table 4). Co-elution of de-ethylated ametryn and terbacil on the GC column used required GC/MS confirmation. A control well water sample taken 2.9 km up gradient of the site had detectable concentrations of atrazine and de-ethylated atrazine. Previously, this well and others in this area have shown detectable concentrations of atrazine. Because atrazine and ametryn are applied to fields adjacent to the wells sampled, no conclusion regarding point source contamination can be made. Further water sampling is needed to determine if the pesticide mixing and loading

Table 1. Pesticides (in ppm wet weight) found in soil cores from pineapple pesticide mixing and loading site.

depth (cm)	diuron	ametryn	bromacil	hexaz.	DDT	DDE	DDD
site #1							
0 - 8	0.06	0.12	0.29	ND	ND	ND	ND
8 - 20	0.34	0.12	0.13	ND	ND	ND	ND
61 - 91	0.23	0.06	0.23	ND	ND	ND	ND
122 - 152	ND	ND	0.09	ND	ND	ND	ND
site #2							
0 - 8	0.23	0.17	1.66	ND	0.741	0.283	0.143
8 - 20	0.22	0.15	1.59	ND	1.220	0.306	0.212
61 - 91	ND	ND	0.52	ND	0.008	ND	ND
152 - 183	ND	ND	0.15	ND	ND	ND	ND
244 - 274	ND	ND	0.08	ND	ND	ND	ND
site #3							
0 - 10	0.61	0.11	0.33	0.08	1.264	0.570	0.270
10 - 20	0.58	0.09	0.30	0.09	1.167	0.526	0.250
61 - 91	0.10	ND	0.10	0.17	0.094	0.083	0.020
152 - 183	0.33	ND	0.18	0.50	0.004	ND	ND
244 - 274	0.25	ND	0.22	0.62	ND	ND	ND

Atrazine, terbicil, fenamiphos, cis and trans-telone not detected.
hexaz. = hexazinone

Table 2. Pesticides (in ppm wet weight) found in soil cores from sugarcane pesticide mixing and loading site.

depth (cm)	diuron	atraz.	terb.	ametr.	hexaz.	DDT	DDE	DDD
site #1								
0 - 10	ND	3472	ND	17664	2.19	6.339	0.304	1.867
10 - 17	ND	1613	ND	8333	1.25	2.39	0.110	0.57
17 - 30	0.27	147.3	1.4	623.9	1.00	0.418	0.030	0.079
30 - 61	0.71	16.94	3.3	69.32	1.15	0.048	0.009	0.018
152 - 183	1.22	2.68	ND	184.8	2.08	ND	ND	ND
244 - 274	1.05	1.60	ND	53.4	1.38	ND	ND	ND
site #2								
0 - 15	1.26	6.77	3.38	19.71	0.23	0.025	0.06	0.10
61 - 91	0.08	0.03	1.43	1.59	0.10	ND	ND	ND
152 - 183	ND	0.09	0.32	2.06	0.18	ND	ND	ND
244 - 274	ND	0.80	ND	3.03	0.25	ND	ND	ND
site #3								
0 - 18	1.10	5.36	1.43	7.42	ND	ND	0.004	0.005
61 - 91	0.06	0.12	0.71	0.53	ND	ND	ND	ND
152 - 183	0.22	0.32	0.43	0.38	ND	ND	ND	ND
244 - 274	0.18	0.61	ND	0.53	0.11	ND	ND	ND

Bromacil, fenamiphos, cis and trans-telone not detected.

atraz. = atrazine; terb. = terbacil; ametr. = ametryn
hexaz. = hexazinone

Table 3. Accuracy and precision of soil analyses.

	percent recovery ± percent relative std. dev.		
pesticide	0.1 ppm[a]	1.0 ppm[b]	MDL[c]
atrazine	104 ± 7	97 ± 6	0.01
terbacil	106 ± 11	101 ± 6	0.05
ametryn	106 ± 10	97 ± 2	0.02
bromacil	102 ± 2	109 ± 11	0.05
hexazinone	117 ± 5	111 ± 3	0.02
fenamiphos	107 ± d	100 ± d	0.01
diuron	72 ± 35	68 ± 27	0.06
cis-Telone	83 ± d	102 ± d	0.02
trans-Telone	79 ± d	99 ± d	0.02
DDT	104 ± 4	76 ± 17	0.003
DDD	94 ± 24	82 ± 2	0.004
DDE	56 ± 13	61 ± 11	0.002

a = DDT 0.010 ppm; DDD 0.008 ppm; DDE 0.004 ppm spike
b = DDT 0.10 ppm; DDD 0.08 ppm; DDE 0.04 ppm spike
c = Method Detection Limit (ppm wet weight)
d = n=1

Table 4. Results of water analysis near sugarcane mixing and loading sites.

Pesticide	MDL[a]	% Rec	Exper.	Control
diuron	3.0	115	ND	ND
atrazine de-ethyl	0.1	73	1.9	0.2
atrazine	0.1	97	3.4	0.1
terbacil	1.1	98	ND	ND
ametryn de-ethyl	0.1	85	0.3	ND
ametryn	0.1	108	1.4	ND
bromacil	0.7	105	ND	ND
fenamiphos	0.5	96	ND	ND
hexazinone	0.3	92	ND	ND

a = Method Detection Limit in µg/L.

Recoveries based on duplicates (n = 2) except atrazine desethyl and ametryn desethyl (n = 1) and atrazine and ametryn (n = 3).

Compounds in experimental sample were confirmed by GC/MS of concentrated sample extract.

site is contributing significantly to non-point sources of these herbicides.

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