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Transport and Persistence of Pesticides in Alluvial Soils: I. Simazine

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ABSTRACT

Pesticide leaching is a concern in the alluvial valleys of western Washington, where high-value crops are grown in soils with water tables <3 m deep. We conducted this project to determine the long-term leaching pattern of simazine [2-chloro-4,6-bis-(ethylamino)-*s*-triazine] applied to red raspberry (*Rubus idaeus* L.) and strawberry (*Fragaria* × *ananassa* Duch.). Simazine was applied to strawberry and raspberry in paired plots at two sites. Strawberry received a split application (total 2.2 kg ha^{-1}) in August and November, and raspberry received a single 4.5 kg ha^{-1} application in November. We applied simazine yearly from 1986 to 1989, and sampled soil (to 180 cm) and shallow groundwater monthly until April 1991, and at one site again in 1994. Most of the simazine remained in the surface 15 cm of the soil or degraded, but small amounts moved downward. Preferential flow soon after application was not the main cause of downward movement. Simazine was persistent, with disappearance half lives of 128 and 175 d at the two sites the first year. Some simazine remained in the soil 4 yr after the final application. Simazine was most mobile beneath raspberry at one site. This site had finer texture and slightly more organic matter, but a lower K_d for simazine than the other site. Small amounts of simazine reached shallow groundwater beneath both crops. The observed simazine leaching peak was more asymmetric than the peak predicted by the PRZM-2 model, an indication of nonequilibrium adsorption-desorption effects on simazine movement.

TRIAZINE herbicides are well-documented groundwater contaminants (Hallberg, 1989; Ritter, 1990). Atrazine [2-chloro-4-9(ethylamino)-6-(isopropylamino)-*s*-triazine] is the second most widely used pesticide in the USA, and the one most widely reported in groundwater (Hallberg, 1989). Although simazine use is only about 5% that of atrazine, the occurrence of simazine in groundwater is still widespread (Williams et al., 1988; MacKay and Smith, 1990; Spalding et al., 1989). Although neither atrazine nor simazine are among the most widely used pesticides in Washington State, they are among the most commonly found pesticides in groundwater (Roberts and Jones, 1996; Ryker and Williamson, 1996).

Simazine and atrazine are chemically similar, differing by one methyl group in an amino side chain on the triazine ring. They both have low water solubility (3 $\mu g\ L^{-1}$ for simazine and 33 $\mu g\ L^{-1}$ for atrazine) and moderate adsorption to soil. Widely reported organic C partition coefficients (K_{oc}) are 140 L kg^{-1} for simazine and 160 L kg^{-1} for atrazine (Jury et al., 1987). Persistence in the soil is also similar for the two compounds, with typically reported half-lives of 75 d for simazine and 65 d for atrazine (Jury et al., 1987).

Field studies have shown that small amounts of pesticides can move rapidly through the soil profile, while the bulk of the pesticides remain in the surface soil (Bowman, 1989; Isensee et al., 1990; Kladivko et al., 1991). Movement often occurs after heavy rainfall or irrigation within a few days or weeks of application. Bowman (1989) and Utermann et al. (1990) suggest this leaching results from a combination of preferential flow and nonequilibrium (or time-dependent) adsorption. Preferential flow is the short-circuiting of water and solutes through soil macropores during periods of heavy rainfall or irrigation. Nonequilibrium sorption is adsorption and desorption processes that are slow compared with transport or degradation (Pignatello and Huang, 1991). Nonequilibrium sorption initially involves incomplete binding and rapid desorption, thus increasing the potential for leaching shortly after pesticide application (Utermann et al., 1990). As the pesticide becomes more strongly adsorbed over time, the potential for leaching is reduced.

In a field study with atrazine and alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-methoxymethyl acetamide), Buhler et al. (1993) did not observe elevated herbicide concentrations in tile drainage soon after application. They did see small amounts of atrazine persist in the tile drainage water for several years after the applications ceased, while the atrazine peak remained in the surface soil. This behavior may also result from a combination of nonequilibrium sorption and preferential flow. Based on laboratory column studies, Pignatello et al. (1993) hypothesized that during drier periods slow (nonequilibrium) desorption of bound pesticide could increase soluble pesticide concentrations, followed by movement deeper into the profile when rainfall or irrigation resumed. This was consistent with field observations of ethylene dibromide movement long after its use was discontinued (Pignatello et al., 1990).

Most of the reports of pesticides in groundwater come from vulnerable areas, including areas having high water tables, poor pesticide-binding capacity, and heavy rainfall or irrigation (Pionke and Glotfelty, 1989). Simazine has been used in some of the most vulnerable areas in western Washington, including the alluvial valleys that are a center of intensive agriculture. Water tables in the alluvial valleys persist within a few meters of the surface throughout the year. Surface soils are mostly silt loam and fine sandy loam in texture and contain 1.5 to 2% organic C, providing moderate binding capacity for pesticides.

Red raspberry and strawberry are two common crops in the alluvial valleys, and have different pesticide use

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patterns. Growers generally apply higher rates of pesticides to raspberry than to strawberry. Raspberry also receives more pesticides during the cooler, wetter periods of the year, when the potential for leaching is greater. Comparing the fate of pesticides applied to raspberry and strawberry can help us understand the effect of typical management practices on the risk of pesticide leaching into groundwater.

The objectives of this study were to: (i) evaluate and compare the movement, persistence, and groundwater contamination risk of simazine applied to strawberry and raspberry in alluvial soils in western Washington, and (ii) compare our results with triazine transport reported in other studies.

MATERIALS AND METHODS

Sites and Soils

The study sites were two fields that had not received simazine in recent years. They were each approximately 0.4 ha in area, and were located in the Puyallup valley of Pierce County, Washington, 60 km south of Seattle. The Puyallup valley is part of the Puget lowland of western Washington, and is a broad, glacially-carved valley filled with post-glacial alluvium and mudflows. The water table persists within 3 m of the surface throughout the valley. Land use is a mixture of fruit and vegetable crops, ornamental crops, turf production, pasture, and urban-suburban development. Mean annual precipitation is 1035 mm, falling mainly as autumn and winter rain. An average of 80% of the annual total falls between 1 October and 30 April. Summers are dry and mild (mean July temperature = 18°C) and winters are cool (mean January temperature = 4°C).

Soils at both sites developed in recent alluvium. The Site P soil is a coarse-loamy, mixed, mesic Fluventic Haploxeroll, while the somewhat wetter Site F soil is a coarse-loamy, mixed, mesic Fluvaquentic Haploxeroll. Site F is finer textured on the surface, but becomes coarser with depth. Site P is coarser textured on the surface, becoming finer with depth. A sandy substratum underlies the soils at both sites.

Soil and Environmental Data

Soil profiles were described in pits excavated adjacent to each site (Table 1). We estimated the texture of each horizon by the hydrometer method of Gee and Bauder (1986), measured pH in a 1:1 soil/water suspension, and determined organic C content using a LECO combustion carbon analyzer (Sweeney, 1989). Bulk density and −10 kPa water content were determined on undisturbed soil samples collected from each horizon (four replicates), using a double-cylinder hammer-driven core sampler (Blake and Hartge, 1986). We measured −10 kPa water contents using the undisturbed cores and a hanging column suction apparatus, and measured −1500 k Pa water on three replicate disturbed samples from each horizon using a pressure plate (Klute, 1986). Water content measurements were done for Site F only.

Table 1. Soil texture, organic C, pH, and simazine K_d by horizon.

Horizon	Lower boundary	Texture	Organic C	pH	Simazine K_d
	cm		g kg^{-1}		L kg^{-1}
		Site F			
Ap	31	Sandy loam	13	6.0	3.60
Bw1	64	Silt loam	7	6.1	4.50
Bw2	119	Silt loam	10	6.1	5.12
C	>180	Sandy loam	2	6.4	1.94
		Site P			
Ap	23	Sandy loam	15	5.9	5.42
Bw	53	Sand	2	6.3	2.70
C1	61	Sand	1	6.4	2.37
C2	81	Loamy sand	3	6.4	3.13
C3	157	Silt loam	5	6.0	4.80
C4	>180	Silty clay loam	13	5.9	8.53

Table 2. Percent of normal annual and rainy season precipitation received during the sample period (Aug. 1986–Apr. 1991).

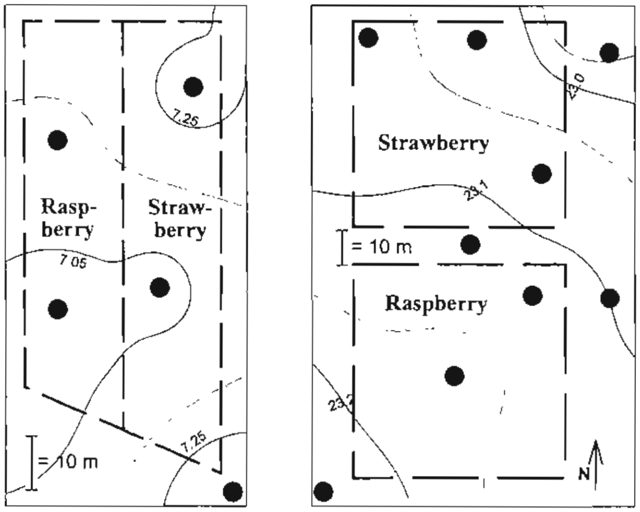
	Year†				
Precipitation	1986–1987	1987–1988	1988–1989	1989–1990	1990–1991
	% of normal				
Annual	98	82	92	109	–
1 Oct.–30 Apr.	104	81	95	111	130

† Years run from 1 Aug. to 30 July. Data is only shown through 30 April for 1990–1991.

We recorded precipitation at the WSU-Puyallup Research and Extension Center, located 0.5 km south of site P and 10 km west of site F. The study period included both wet and dry years (Table 2), with annual precipitation ranging from 850 to 1130 mm.

Pesticide Applications

We planted strawberry on one-half of each site, and red raspberry on the other half (Fig. 1). We applied simazine, metalaxyl [*N*-(2,6-dimethylphenyl-*N*-(methoxyacetyl)-alanine methyl ester], and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) to each crop, but discuss only simazine in this paper. A tractor-mounted precision sprayer applied simazine 90% DG (dispersable granules) over the entire area of each planting. Strawberry received 1.1 kg ha^{-1} simazine applications around 1 August and 1 November each year from 1986 through 1989. The August application was preceded by 13 to 25 mm of irrigation water, and followed within 1 d by a 25 mm irrigation. Raspberry received 4.5 kg ha^{-1} around 1 November each year. Application dates varied by a few days from year to year. Crop management generally followed normal practices, except (i) we maintained straw-



Site P

Site F

Fig. 1. Crops, sampling wells, and ground water gradients at sites F and P. Filled circles show locations of well pairs; contours show groundwater elevations in meters above sea level on 10 Mar. 1989.

berry as single plants by manual and mechanical removal of runners, and (ii) we mowed and removed raspberry canes each fall to ease soil sampling and pesticide applications. Surviving weeds were removed by cultivating with a rototiller, hand pulling, and occasional hand-wiping with glyphosate [*N*-(phosphonomethyl) glycine, isopropyl amine salt].

Soil Sampling

Soil sample collection began in July 1986 for strawberry and October 1986 for raspberry, before the first simazine application to each crop. We collected samples 1 and 15 d after each pesticide application, and monthly thereafter. The 1-d postapplication sampling of strawberry was done after the fields were irrigated. Monthly sampling continued through April 1991, 17 mo after the final simazine application to both crops. In March 1994 we collected a final set of samples from site F only.

Sample cores came from the following depths: 0 to 15, 15 to 30, 30 to 60, 60 to 120, and 120 to 180 cm. We used a 10.4 cm i.d. golf-course cup cutter to take the 0 to 15 cm core. To prevent surface soil from falling into the hole and contaminating deeper cores, each hole was lined with an 18-cm length of 10.4 cm i.d. PVC tube. We collected the 15 to 30 cm core using a 4.6 cm i.d. push probe, and placed a 33-cm length of 4.4 cm i.d. PVC tube in the hole as a second liner. The 30 to 60, 60 to 120, and 120 to 180 cm cores were collected using a tractor-mounted, hydraulic, soil coring machine equipped with 2.4 cm i.d. probes. A separate probe was used for each core depth.

We collected two samples of each depth from each crop at each site. Each sample was a composite of four separate cores taken from within one-half of the crop area (0.1 ha). The cores were collected from preselected random locations within the plant rows. No location was sampled more than once during the study. Following sampling, we filled the holes with pesticide-free soil of equivalent or finer texture than the field soil. During periods of high water tables, we did not sample depths completely submerged below the water table.

We screened each soil sample through a 3-mm sieve and blended it by hand or by tumbling for 5 min in a 0.028 m^3 twin shell blender. Samples that were too wet for screening and blending were first partially air dried (to approximately 100 g kg^{-1} water content) at room temperature. We froze two 100.0-g subsamples of each sample at −20°C for later analysis, and dried a third subsample at 105°C for 16 h to determine water content.

Soil Extraction and Analysis

We extracted and analyzed soil samples by the procedure of Getzin et al. (1989). In brief, samples were shake-extracted with acetone containing 10% H_2O buffered at pH 1.65. (Getzin et al. (1989) reported this buffer as pH 2, but it is actually pH 1.65). Sample cleanup was done by partitioning in CH_2Cl_2 followed by solid-phase extraction on silica gel columns. Residues were analyzed on either a Varian Model 3300 gas chromatograph or a Hewlett Packard 5890 Series II gas chromatograph equipped with a wide-bore capillary column and thermionic selective detector. Mean recovery of simazine from spiked samples was 88 ± 7% (Getzin et al., 1989). Simazine recovery from the field within 1 d of application was more variable. Mean recoveries were 100 ± 28% for simazine applied to raspberry, 90 ± 57% for simazine applied to strawberry in November, and 72 ± 29% for simazine applied to strawberry in August. Part of the variability in field recovery occurred because recoveries for all but the first year's samples were measured as the difference between simazine levels before and after application, introducing variability from both sets of measurements.

Quantification limits for simazine were 20 μg kg^{-1} soil for the 0 to 15 cm and 15 to 30 cm depths and 5 μg kg^{-1} soil for the remaining depths (Getzin et al., 1989). The 5 μg kg^{-1} level was twice the maximum baseline noise of the soil extracts. Usually, the chromatogram detected simazine at lower concentrations. The quantification limit was higher in the surface soil, because of an interfering peak that was not present in the deeper samples. Values below the quantification limit are reported as "Trace". For statistical analyses, however, we used the numerical values from the chromatograms, even when they were below the quantification limit.

We used ANOVA to determine significant differences between crops, sites, years, and interactions for simazine remaining at the end of the sampling year summed over (i) all depths (0–180 cm) and (ii) subsoil depths only (30–180 cm). Means were compared using least significant difference following a significant ($P < 0.05$) *F*-test from ANOVA. End-of-year values were the mean of four composite samples collected over the last two sampling dates before pesticide application (October and November). We calculated ANOVAs and LSDs using the GLM procedure of the Statistical Analysis System (SAS Institute, 1991).

Disappearance Rate

To estimate the disappearance rate of simazine for each site and sampling year, we first determined the simazine mass within each sample depth as the product of the simazine concentration, soil bulk density, and sample increment length. We then summed the simazine mass measured over all sample depths at each replicate each month. After converting the monthly sums to natural logarithms, we derived linear regressions for each year, assuming a single, first-order disappearance rate over the year.

The disappearance rates calculated from the regression equations are not strictly degradation half-lives, because they include all types of field losses. Also, disappearance rates after the first year are cumulative because they include simazine carryover from previous years. We estimated disappearance rates beneath raspberry only, because raspberry received a single simazine application each year, compared with two for strawberry.

Water Sampling and Analysis

At the start of the experiment in 1986 we installed five pairs of PVC groundwater sampling wells at Site P and seven pairs at Site F (Fig. 1). Each pair included a seasonal well and a permanent well. The seasonal well screens were at the approximate depth of the winter high water table (screen depth 80–150 cm at Site F and 165–235 cm at Site P). The permanent wells had screens below the depth of the summer low water table (screen depth 235–305 cm at Site F and 295–365 cm at Site P). One of the well pairs at each site was installed upgradient of the application area. In 1987, we installed two pairs of downgradient wells at Site F (Fig. 1). The downgradient well screens were all below the depth of the summer low water table (235–305 cm and 390–460 cm).

The well casings were flush-joint, threaded, 5-cm PVC monitoring pipe, with PVC wire-wound screens 70 cm in length. We placed the wells in holes dug with a hand auger or power auger drill. After filling the space around the screen with 10 to 20 mesh sand, we filled the space around the casing with bentonite grout. The well caps had 2-mm breather holes, and

Table 3. Residual simazine in soil profile before November application (mean and range of October and November pre-application analyses).

Site	Depth	1987	1988	1989	1990
	cm	Concentration μg kg⁻¹ soil			
		Raspberry			
F	0–15	626 (424–807)†	1171 (1031–1342)	2455 (2354–2509)	2034 (1665–2310)
	15–30	60 (20–89)	214 (53–508)	182 (41–411)	71 (30–106)
	30–60	16 (T–42)‡	7 (T–12)	11 (T–33)	5 (T–7)
	60–120	16 (6–26)	7 (T–14)	12 (9–16)	T (ND–10)§
	120–180	5 (T–14)	5 (T–15)	7 (T–11)	T (ND–5)
P	0–15	563 (432–673)	1048 (1026–1070)	1490 (1340–1708)	1458 (1105–1975)
	15–30	42 (6–93)	46 (44–48)	38 (14–54)	35 (16–67)
	30–60	7 (T–24)	10 (T–18)	T (T–7)	T (ND–5)
	60–120	T (T–T)	T (ND–8)	T (T–6)	ND –
	120–180	T (ND–T)	T (T–T)	T (T–T)	T (ND–8)
		Strawberry			
F	0–15	685 (561–755)†	797 (706–887)	853 (488–1137)	525 (413–634)
	15–30	21 (13–29)	54 (32–75)	34 (9–67)	17 (12–25)
	30–60	T‡ (T–6)	5 (T–7)	11 (T–20)	T (ND–T)§
	60–120	T (T–T)	T (T–T)	T (T–6)	T (ND–5)
	120–180	T (T–T)	T (T–T)	T (T–5)	ND
P	0–15	789 (697–840)	735 (731–738)	1221 (774–1539)	875 (605–1121)
	15–30	30 (5–46)	26 (26–27)	40 (24–74)	27 (9–43)
	30–60	T (T–T)	T (T–T)	T (T–T)	T (ND–9)
	60–120	T (ND–T)	T (T–T)	T (T–T)	T (ND–7)
	120–180	T (ND–T)	T (T–T)	T (T–T)	T (ND–8)

† $n = 4$ for all means except Site P, 1988, where $n = 2$. Range is in parentheses.
‡ T = Trace (<5 μg simazine/kg soil).
§ ND = Not detected.

wells were covered with plastic tarps during pesticide applications. Permanent wells were purged (minimum 1 well volume) and sampled monthly throughout the year, using a teflon bailer. Seasonal wells were purged and sampled for 1 to 4 mo during the winter, depending on the duration of high water tables. Upgradient wells were sampled always sampled first, and the bailer rinsed between wells and cleaned in the laboratory between sites. We measured water tables in the wells two to four times each month.

Water samples were stored at 4°C and transported to the Department of Agricultural Chemistry Laboratory at Oregon State University for analysis. The laboratory used a procedure to extract and analyze simazine, carbofuran, and metalaxyl, along with degradation products of carbofuran and metalaxyl. The following steps in the procedure were used to extract and analyze simazine: An 800-mL aliquot of groundwater was extracted with three successive 80-mL volumes of CH_2Cl_2. The extracts were evaporated to about 5 mL on a steam bath, and allowed to reach dryness at room temperature. The sample was transferred to a graduated 5 mL sedimentation tube, using three small rinses of warm benzene, and the volume was concentrated to 1 mL by evaporating in a stream of air. Simazine was analyzed on a Supelcowax-10 column at 225°C. Recovery of simazine from spiked samples was 99% ± 12%, and the measurement limit was 0.1 μg L^{-1}.

Model Simulations

We simulated the movement of simazine at Site F during 1986 to 1987 using the Pesticide Root Zone Model, PRZM-2 (Mullins et al., 1993). Soil inputs included the organic C data in Table 1, and bulk density and water contents from field measurements. We used weather data recorded at Puyallup, and pesticide application conditions from this study. PRZM-2 was run under freely draining conditions, because water tables were within 90 cm of the surface for only 3 wk dnring the year. PRZM-2 pesticide binding was simulated using both literature K_{oc} (140 mg L^{-1}, Jury et al., 1987) and the measured K_d values in Table 1 (Sukop and Cogger, 1992).

We ran PRZM-2 using three different degradation rates. These included a literature degradation rate (0.0092 d^{-1}) (Jury et al., 1987), and our field disappearance rate calculated for 1986 to 1987 (0.04 d^{-1}). The third rate was the literature rate with a simple adjustment for soil temperature, by estimating mean soil temperature as 13.6°C, laboratory temperature as 21.1°C and using a rate factor of 2 per 10°C temperature change. The adjusted rate was 0.0053 d^{-1}. Our field disappearance rate is not strictly a degradation rate, because it includes all forms of losses. When using the field disappearance rate we set volatilization and foliar degradation at zero, and assumed leaching and runoff to be small. Model results predicted leaching would have a negligible effect on disappearance, while runoff was <10% of disappearance. We included volatilization in the simulations using literature degradation rates.

RESULTS AND DISCUSSION

Mobility and Persistence in Soil

Most of the simazine remained in the surface 15 cm of the soil or degraded during the study. Simazine moved throughout the soil profile, but quantities leaching below 30 cm were often only trace amounts, and varied little from year to year (Table 3). The greatest amount of simazine movement occurred beneath raspberry at Site F. The simazine degraded slowly, and some persisted in the soil from year to year (Table 3). Year-end simazine levels increased significantly from 1987 to 1989 for raspberry at both sites, and for strawberry for site P. The increase was greater for raspberry, which received simazine in one large fall application each year, compared with strawberry, which received simazine in two

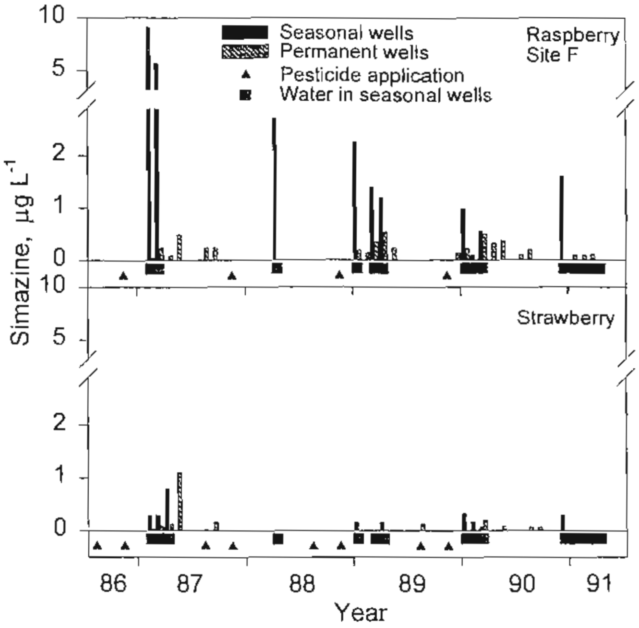


Fig. 2. Concentration of simazine in seasonal and permanent wells at site F. Vertical bars are means of simazine concentrations for each date. Boxes show months where seasonal wells contained water, and triangles show application dates.

lighter applications. The increase was confined to the 0 to 15 cm depth.

Simazine disappearance half-lives in raspberry were 128 d ($r^2 = 0.90$) at Site P and 175 d ($r^2 = 0.72$) at Site F in 1986 to 1987. Our observed half-lives are greater than typically reported values (Jury et al., 1987). This increased persistence resulted partly from the timing of application during the fall, when soil temperatures and microbial activity were declining.

By the latter part of the study, simazine was even more persistent. Disappearance half-lives calculated for 1989 to 1990 were 261 d ($r^2 = 0.49$) at site P, and 424 d ($r^2 = 0.37$) at site F. These half-lives were measured on cumulative simazine in the soil profile, and include both simazine applied in November 1989 and any residual remaining from previous years. The apparent increased persistence of simazine may result from an accumulation of less available, residual simazine remaining from earlier applications. This is consistent with the hypothesis of nonequilibrium binding reducing the long-term availability of pesticide residues to degradation. Between our final monthly sampling date of April 1991 (17 mo after last simazine application) and the post-project sample of March 1994 (52 mo after the last application), simazine measured in the soil declined by 50% beneath strawberry and 67% beneath raspberry. This suggests an even longer disappearance half-life for the residue remaining in the soil.

Simazine in Shallow Groundwater

We found small amounts of simazine in groundwater (Site F shown in Fig. 2). Trends were similar to the soil samples, with the highest levels beneath raspberry at Site F. Simazine was present in nearly all of the seasonal well samples collected beneath raspberry at Site F, and in half of the seasonal well samples collected beneath Site F strawberry (Table 4). Simazine was present in the permanent wells at Site F every year except the driest (1987–1988), but detections were less frequent than in the seasonal wells. At Site P, the permanent wells were as likely to have simazine detections as the seasonal wells, but simazine was detected in <10% of the samples at both depths (Table 4).

Simazine peaks occasionally appeared in upgradient samples from both sites. None of the other compounds analyzed in this study [carbofuran, metalaxyl, and metalaxyl acid (*N*-(2,6-dimethylphenyl-*N*-(methoxyacetyl)-alanine)] were found in the upgradient wells. At Site F, levels in the upgradient wells were lower (0.1–0.3 µg L^{-1}) than those seen beneath the plots, and frequency of detection was less. At Site P, levels were also low, but frequency of detection was similar to that beneath the plots.

The source of these upgradient detections is unclear. They could be from previous simazine use further upgradient from the sites, or the peaks may not be from simazine. Because many of the detections in the groundwater beneath Site P are low, and the source of the simazine peaks in the upgradient wells is unclear, the detections at Site P likely overestimate the actual presence of simazine in groundwater there.

Simazine levels in groundwater beneath the fields were less than the drinking water maximum contaminant level of 3 µg L^{-1}, except for a few measurements in the seasonal wells in the raspberry crop at Site F. Highest concentrations in individual seasonal wells were 17 µg L^{-1} in 1987, 4.4 µg L^{-1} in 1988, and 3.5 µg L^{-1} in 1989. Peak concentrations declined during the study. The frequency of detections seemed to be related to

Table 4. Frequency of simazine detections in sampling wells.

		No. of wells		No. of sampling dates		Sampling dates positive†		Samples positive‡	
Site	Well location	Permanent wells	Seasonal wells	Permanent wells	Seasonal wells	Permanent wells	Seasonal wells	Permanent wells	Seasonal wells
						%			
F	Raspberry	2	2	50	9	20	100	16	94
	Strawberry	3	3	50	10	14	80	8	50
	Downgradient	4	0	35	–	11	–	5	–
	Upgradient	1	1	50	9	8	33	8	33
P	Raspberry	2	2	50	11	12	9	7	5
	Strawberry	2	2	50	11	12	9	7	5
	Upgradient	1	1	50	11	4	9	4	9

† Percent of dates samples where at least one well contained detectable levels of simazine.
‡ Percent of all samples with detectable levels of simazine.

rainfall, with the most detections occurring in the wettest years (1986–1987 and 1989–1990) and the fewest during the driest year (1987–1988).

During the winter of 1990 to 1991, more than 1 yr after the last simazine application, the frequency of simazine detections decreased. We found no simazine in the seasonal wells after December 1990, the first month the seasonal wells contained water (Fig. 2). This contrasts with the consistent detection of simazine in the Site F seasonal wells the previous years. Since no fresh simazine was added in the fall of 1990, the reduced leaching may be because the previous application of simazine had become more tightly bound to the soil by nonequilibrium adsorption and less likely to leach in detectable amounts. Degradation of simazine since the last application would also reduce the amount of simazine available to leach.

The simazine found in the wells in December 1990 could be the result of the nonequilibrium desorption of small amounts of simazine during the dry season (Pignatello et al., 1993), followed by leaching with the onset of autumn rainfall. We did detect small amounts of simazine in some of the permanent wells throughout the winter of 1990 to 1991, but none in the postexperiment sampling in 1994.

Differences between Crops and Sites

Increased leaching under raspberry in this study is likely caused by the rate and timing of application to raspberry. The total simazine rate for raspberry was twice the rate used on strawberry. Furthermore, raspberry received simazine in a single application at the beginning of the leaching season, while half of the simazine used on strawberry was applied during the summer. The raspberry field would have more recently applied simazine in the soil, with less opportunity to degrade or bind more tightly to the soil by a time dependent-reaction.

Subtle differences in soils also affected leaching. Significantly more simazine moved below 30 cm at Site F, even though the upper 150 cm of soil at the site is finer textured and has higher organic C levels than the soil at Site P (Table 1). The simazine partition coefficient measured in the soils was higher in the surface soil at Site P than at Site F (Table 1), which may partly account for the differences observed between the two sites.

Simazine Distribution in the Soil

The observed movement of small amounts of simazine deep into the soil and into groundwater is consistent with preferential flow. We did not design our sampling scheme specifically to evaluate the potential for preferential flow, however. Because of spatial variability in pesticide movement, we needed more intensive sampling to be better able to detect the movement of low levels of pesticides. Even within the limitations of our sampling, we saw increased simazine levels beneath raspberry at Site F on 17 Nov. 1986, 14 d and 29 mm of rainfall after the initial pesticide application (Fig. 3a). We saw similar movement of carbofuran beneath the same site. We did not have clear evidence of simazine movement beneath raspberry at Site P until 3 mo after application (Fig. 3b), although carbofuran had moved into the 60 to 120 cm depth after 1 mo (Cogger et al., 1998).

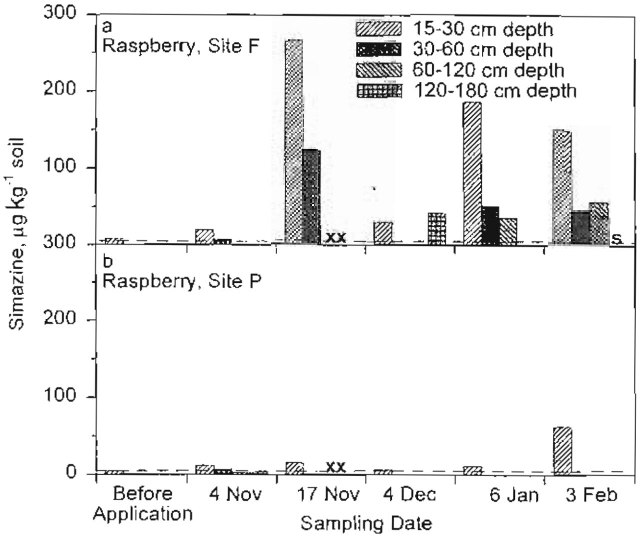


Fig. 3. Simazine movement beneath 15 cm depth in raspberry through February 1987. Dotted and dashed lines show quantification limits of 20 and 5 μg kg^{-1} soil. S indicates samples not collected because of saturated soil, and X indicates other samples not collected.

The strawberry plots received 25 mm of irrigation within hours of the initial (August 1986) pesticide application, and the soil was sampled 1 d later. Except for a spike of 30 μg kg^{-1} soil in the 15 to 30 cm depth at one replicate at Site F, we saw no evidence of simazine movement resulting from that irrigation (not shown). We did detect trace amounts of simazine below 30 cm, but levels were much less than the quantification limit of 5 μg kg^{-1} soil.

The sites received more than 200 mm of rainfall from 16 to 29 Nov. 1986, including 100 mm on 23 to 24 November, 3 wk after the fall simazine application (Fig. 4). The only evidence of substantial simazine movement from that period was a spike of 40 μg kg^{-1} soil at the 120 to 180 cm depth beneath raspberry at Site F on 4 December (Fig. 3a). This spike was more than twice any other concentration observed at that depth throughout the study. Small amounts of simazine also appeared to leach below 60 cm at Site F strawberry at the same time, although levels were less than quantification limits. Substantial leaching of carbofuran occurred during the same period, displacing the center of mass of carbofuran from the surface to the 15 to 30 cm depth or deeper (Cogger et al., 1998).

We did not detect simazine in any of the permanent well samples until March 1987, 4 mo after the November simazine application. Simazine was present in the seasonal wells beneath raspberry at Site F and beneath strawberry at both sites in January 1987, the first time the wells contained enough water to sample. In subsequent years, simazine was also present in the seasonal wells the first time they were sampled.

We could evaluate preferential flow only in 1986 to

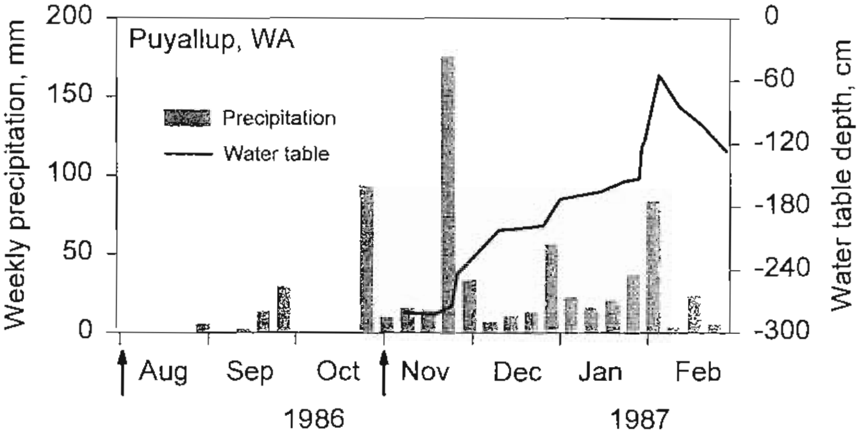


Fig. 4. Weekly precipitation measured at Puyallup, WA, August 1986 to February 1987, and water tables measured at Site F November 1986 to February 1987. Arrows note simazine application dates.

1987 (the first year of the study), because residual simazine persisted in the soil into the following years. Because of the limitations of our sampling scheme, our results are tentative. The results suggest that some preferential flow is occurring under the conditions of our study. But, preferential flow shortly after simazine application does not seem to be an important contributor of simazine to groundwater.

Nonequilibrium Sorption

Our results indicate that neither mass convection-dispersion nor preferential flow soon after application were main mechanisms of simazine leaching into the lower soil profile. Nonetheless, leaching did occur. While most of the simazine never moved below the surface 15 cm of the soil, we found small quantities throughout the profile to the 180 cm sampling depth. The subsurface simazine concentrations changed only slightly from year to year. Simazine was also present in groundwater each year, with the frequency and levels of occurrence varying with site, crop, and year.

Others have reported similar leaching patterns for atrazine (Helling et al., 1988; Buhler et al., 1993). Data reported by Gish et al. (1991) for the first 2 yr of their atrazine-leaching study also seem to fit this pattern. This pattern contrasts with the leaching behavior of carbofuran applied as part of our study (Cogger et al., 1998). Carbofuran moved as a peak by mass convection-dispersion, but largely degraded before it reached groundwater.

The simazine-leaching pattern is consistent with nonequilibrium adsorption-desorption. Movement of the desorbed material could occur by preferential flow, accounting for the low levels of simazine found throughout the profile and into groundwater. The apparent slower degradation of aged residues is also consistent with nonequilibrium adsorption.

If nonequilibrium desorption and preferential flow drive simazine leaching, this suggests that leaching to groundwater will continue after the use of these herbicides is discontinued. We found that simazine levels in groundwater did not decline until more than 1 yr after the final application. Also, groundwater levels of these herbicides are unlikely to increase much from current concentrations, because only a small portion of the herbicide is mobile at any time.

Modeling Simazine Movement

Figure 5 compares observed soil profile concentrations of simazine beneath site F raspberry with PRZM-2 simulations of simazine movement run with three sets of input conditions: literature, adjusted, and site-specific. The literature simulation uses published data for simazine degradation and adsorption, and the results underestimate the persistence of simazine, while overstimating the depth of the peak. The adjusted simulation accounts for the effect of soil temperature on degradation rate, and the results produce simazine concentrations closer to those observed. The simulation based on observed disappearance and K_d values gives the best visual fit to the data. The observed concentration profile is more asymmetric than the PRZM-2 profile, with a long leading edge moving deep into the profile, but retardation of the main part of the peak. The asymmetry is consistent with nonequilibrium adsorption-desorption. Because these models do not account for nonequilibrium processes, the model results do not show the effect of nonequilibrium on simazine movement.

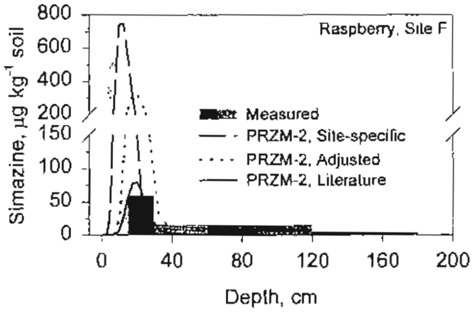


Fig. 5. Comparison of observed and simulated (PRZM-2) simazine concentrations in the soil profile at site F raspberry, 1 yr after initial application. Solid line is from simulation using literature degradation and K_{oc} values, dotted line is adjusted for soil temperature, and dashed line uses site-specific disappearance and K_d values.

Implications for Management

Our data suggest that low levels of simazine (<1 μg L^{-1}) are likely to leach to shallow groundwater under soil and management conditions typical of intensive agriculture in alluvial western Washington. Subtle differences in soils may cause significant differences in leaching. The risk of exceeding the EPA maximum contaminant level in drinking water wells appears nearly negligible, however, under these conditions. Groundwater contamination by pesticides will raise public concern, even when concentrations are well below maximum contaminant levels.

Our data also suggest that simazine levels can be reduced by adjusting the rate and timing of application. Other steps, including integrated weed management, herbicide mixtures applied at lower rates, and improved formulations such as starch encapsulation (Schreiber et al., 1993), offer promise to reduce further the leaching risk.

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