

# Water Quality in Walnut Creek Watershed: Herbicides in Soils, Subsurface Drainage, and Groundwater

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## ABSTRACT

Herbicide transport in subsurface drainage can result in unacceptable levels of contamination in surface waters. This study assessed the extent of atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] transport to subsurface drainage and shallow groundwater. A corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] rotation was used with corn receiving banded atrazine applications of 459 g ha<sup>-1</sup> in 1992 and 561 g ha<sup>-1</sup> in 1994. Soybean were treated with metribuzin at 420 g ha<sup>-1</sup> in 1993 and 1995. Monthly flow-weighted average concentrations of atrazine in drainage water did not exceed 3 µg L<sup>-1</sup> and annual losses ranged from 0.02 to 2.16 g ha<sup>-1</sup> during the 4-yr study. Less than 3% of the groundwater samples contained atrazine concentrations exceeding the 3 µg L<sup>-1</sup> maximum contaminant level for drinking water (MCL). Atrazine was detected more frequently in groundwater beneath the lowest parts of the field, despite greater than average sorption to soils in that area. Metribuzin was also found in groundwater, but only half as frequently as atrazine. The patterns observed in subsurface drainage and groundwater reflected the persistence of atrazine and metribuzin in soil. Atrazine was detected in >90% of surface soil samples up to 23 mo after application, whereas metribuzin was rarely detected during the second year following application. Atrazine was found far more commonly than metribuzin in soil below 30 cm depth.

AGRICULTURAL PRODUCTION has been linked to contamination of surface water and groundwater with herbicides. Large-scale surveys have established that surface waters in the midwestern USA are contaminated with triazine and chloroacetanilide herbicides, with a fraction of these detections exceeding MCL concentrations (Thurman et al., 1991). Much of the midwestern farmland has subsurface drainage, which is discharged into surface waters. This route of contamination may be significant in some agricultural systems. Losses of herbicides in subsurface drainage vary extensively; between 0.6 and 60 g ha<sup>-1</sup> of atrazine were removed in drainage water in several studies (Buhler et al., 1993; Gaynor et al., 1995a; Jayachandran et al., 1994). Atrazine concentrations in subsurface drainage water exceeded the 3 µg L<sup>-1</sup> MCL in 40 and 60% of samples under conventional tillage (Gaynor et al., 1995a; Jayachandran et al., 1994). Annual losses of herbicides in subsurface drainage water can account for a significant fraction of the total herbicide loading in surface waters. Logan et al. (1994) reported mean annual concentrations from subsurface drainage exceeding the atrazine MCL. Factors that appear to control movement of herbicides into subsurface drains are the rate of herbicide application, the amount and timing of rainfall and soil

properties controlling persistence and retention of the chemical.

Herbicides have also been found in groundwater. Shallow aquifers under permeable, low-organic matter soils are vulnerable to herbicide contamination (Burkart and Kolpin, 1993), but our study area is not representative of these conditions. However, recent studies have also shown that herbicide leaching is possible in finer textured soils that are well structured (Traub-Eberhard et al., 1995). In addition, relatively few studies have examined groundwater quality beneath subsurface drains. We undertook these studies to assess the extent of herbicide leaching to a subsurface drain and to the shallow water table beneath the subsurface drain at the field scale and to assess the effects of soils and topography on processes affecting herbicide leaching and persistence. In addition, we include a comparison of the groundwater monitoring results at our field site to monitoring results from well nests throughout the entire watershed.

## MATERIALS AND METHODS

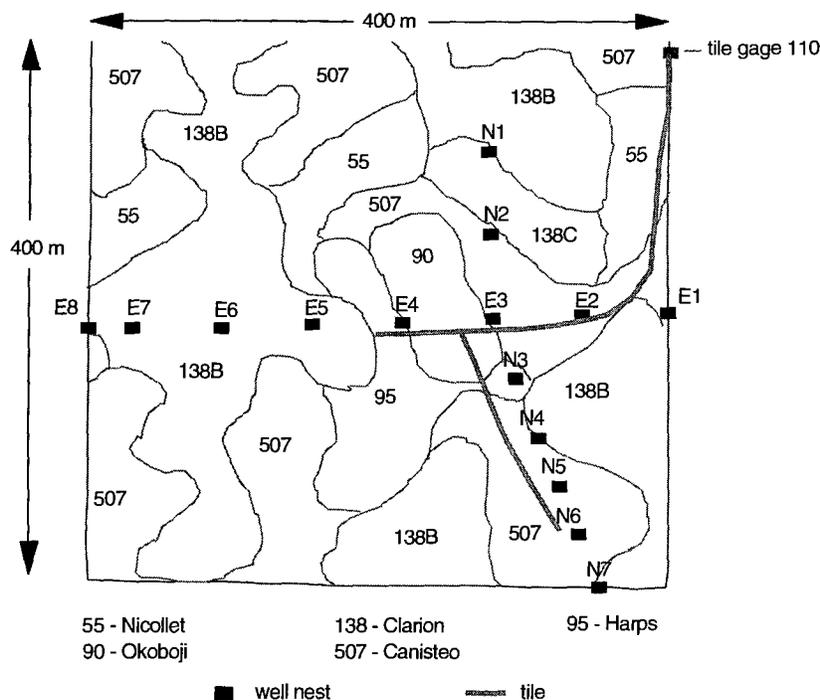
### Site Description and Sampling

The site is located in subbasin 220 in the western part of the Walnut Creek watershed, near Kelly, IA. The site contains fine-loamy, mixed, mesic soils mapped as Clarion (Typic Hapludoll), Nicollet (Aquic Hapludoll), Canisteo (Typic Haplaquoll), Harps (Typic Calciaquoll), and Okoboji (fine, montmorillonitic, mesic Cumulic Haploaquoll) series (Fig. 1). The southern half of the field contains two closed depressions (potholes) within the Canisteo, Harps, and Okoboji soils, which are the focus of this research. An intensive sampling of 6.25 ha within this site in 1992 (Cambardella et al., 1994) described soil variability. The farming practices include a corn-soybean rotation, disk tillage in the early spring, application of banded herbicides, and cultivation in spring and early summer. These practices are fairly representative of the production practices used in the watershed (Hatfield et al., 1999). In 1991, 1993, and 1995 soybean were grown and metribuzin was applied at 420 g ha<sup>-1</sup> preplant in a mixture with trifluralin, followed by a shallow disking for incorporation. In 1992 and 1994 corn was grown and a cyanazine-atrazine mixture was applied resulting in 459 g ha<sup>-1</sup> atrazine in 1992 and 561 g ha<sup>-1</sup> in 1994. These herbicides were not incorporated. These rates of application represent field averages and rates within the band are approximately twice as large.

Two transects of shallow well nests span the two potholes in the southern part of the field (Fig. 1). One transect of eight well nests extends east-west across the field and the second is on an intersecting line from a hill-top just north of the large pothole to the south fenceline (Fig. 1). Sampling wells were

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**Abbreviations:** MCL, maximum contaminant level for drinking water; DAR, deethylatrazine to atrazine ratio; SPE, solid-phase extraction column; GC/MS, gas chromatography/mass spectrometry; SIM, selective ion monitoring.



**Fig. 1.** Southern section of the study area in the Walnut Creek watershed showing soil map units digitized from the county soil survey and locations of wells. Pothole areas are generally located in the area surrounding well nests E3 and E4 and the area surrounding nest N6.

constructed by augering a 5 cm diam. hole to the proper depth, then inserting 5 cm diam. PVC Tri-Loc tubing with 0.5 mm screening. A cavity 15 cm deep and 15 cm in diameter was excavated around the top of each well and filled with a sand-cement mortar to prevent water flow from the surface. At each nest, wells with a 0.76-m screen were installed with the screen centered at 0.6, 1.5, and 2.6 m depths. The wells were sampled beginning in 1991, but some wells were not installed until 1992, and water was not in all wells at all sampling times (especially the 0.6 m depth wells). The two potholes and surrounding area (18 ha) are drained by a branching subsurface drain extending from the potholes northeast to the edge of the field where it joins a larger county subsurface drain (Fig. 1) identified as site 110 by Jaynes et al. (1999). At this junction, equipment described by Jaynes et al. (1999) was installed to measure water flow and sample water in the drain from the large pothole. Sampling was initiated on Day 344 of 1991. Samples were collected weekly (by hand) and automatically during discharge events. Following analysis, flow weighted concentrations of herbicides were calculated as described by Jaynes et al. (1999).

To determine the concentrations of herbicide in the soil profile, soil cores (2.5 cm i.d.) were taken to a depth of 120 cm at locations throughout the entire 37 ha field. Cores were contained within acetate liners and equipment was cleaned after each sampling to prevent cross-contamination. Cores were transported to the laboratory and frozen until analysis. Prior to herbicide extraction and analysis, cores were cut into segments, mixed, and a 10 g subsample weighed for extraction. Soil moisture content of additional subsamples was also determined and results are expressed on a dry weight of soil basis. In addition, 10 cm diam. soil cores were taken in 1993 at six locations, 12.5 m to either side of the east-west well transect in Clarion, Canisteo, and Okoboji soils, with two locations sampled per soil type. Total organic C and N, texture, pH and atrazine sorption coefficients were determined using methods described by Cambardella et al. (1994) on three replicate subsamples from each of the soils composited over selected depths.

Groundwater samples were also obtained from wells in 38 locations throughout the watershed on a quarterly basis starting in 1991 and continuing through 1995. At each location a nest of wells was installed at depths ranging from 0.9 to >4.6 m.

### Herbicide Analysis

Methods for the simultaneous extraction and analysis of atrazine and metribuzin were used for water and soil samples. Analytes in water samples were concentrated using solid-phase extraction (SPE) columns and analyzed by gas chromatography/mass spectrometry (GC/MS) operated in selective ion monitoring (SIM) mode as described by Hatfield et al. (1999). The quantitation limit was  $0.2 \mu\text{g L}^{-1}$  for atrazine and metribuzin and average recovery of herbicides from spiked samples was 88%.

Herbicides in soils were extracted from 10 g subsamples taken from field samples using automated methods described by Koskinen et al. (1991). Two sequential extracts using 80% methanol-water were performed and methanol was removed from the combined extracts by evaporation. The remaining aqueous solution was passed through a C-18 SPE column and eluted with ethyl acetate as described previously. Extracts were analyzed by GC as described previously with 1% of the positive detections confirmed by GC/MS. The quantitation limit for herbicides in soil was  $5 \mu\text{g kg}^{-1}$  and recoveries of herbicides from spiked samples averaged 80%. Data are presented without correction for the efficiency of recovery.

### Data Analysis

Herbicide persistence in surface soils (0–7.5 cm depth) was described by the two-compartment model of Hill and Schaalje (1985).

$$C = [C_0 \exp(-(k_s + k_r)t) + [C_0 k_p / (k_s + k_r - k_{dn})] \times [\exp(-k_{dn}t) - \exp(-(k_s + k_r)t)]$$

Two first-order rate constants describe atrazine dissipation from labile ( $k_s$ ) and nonlabile ( $k_{dn}$ ) pools. The model partitions

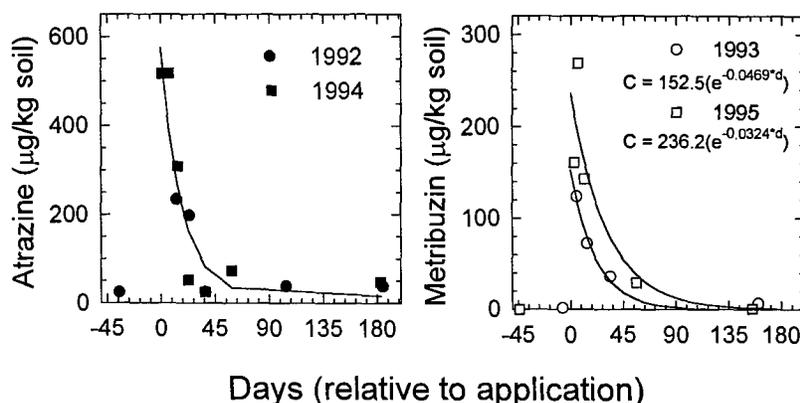


Fig. 2. Dissipation of atrazine (left) and metribuzin (right) in the surface 7.5 cm of soil under field conditions. Solid lines indicate predicted dissipation of herbicides and symbols indicate mean concentrations. Nondetects were assigned a value of zero in the calculation of the means.

herbicides into two pools which we define as follows: a readily available (labile) pool of solution phase and desorbable residues and a second pool consisting of more tightly bound or nonlabile (adsorbed, but extractable) residues. The rate constant  $k_r$  controls the transfer of atrazine from the labile pool to the nonlabile pool. Model parameters were estimated by nonlinear least squares regression (SAS version 6.03, Cary, NC) using mean herbicide concentrations in surface soil (0–7.5 cm) during the growing season following application. First-order kinetics were used to describe metribuzin dissipation using nonlinear least-squares regression procedures.

Mean and median concentrations of herbicides in groundwater samples were calculated using values of zero assigned to samples below detection limits. Trends in concentrations were determined using nonparametric one-way analysis of variance on ranks, using depth (Friedmans procedure) and soil types (Kruskal-Wallis) as class variables (Gilbert, 1987).

## RESULTS AND DISCUSSION

### Herbicide Persistence and Leaching in Soil

Atrazine dissipation in the surface 7.5 cm of soil was biphasic with rapid dissipation during the first 60 d following application followed by very slow rates of loss after 60 d (Fig. 2). The two-compartment model provided an adequate fit to the 1994 persistence data (model  $F$  significant at  $P < 0.01$ ). An initial concentration of  $575 \mu\text{g kg}^{-1}$  soil was estimated to be present immediately following application, which was slightly greater than the mean concentrations of 517 and  $518 \mu\text{g kg}^{-1}$  soil measured at 1 and 7 d after application. The model estimated values of  $0.0562 \text{ d}^{-1}$  for  $k_s$ ,  $2 \times 10^{-6} \text{ d}^{-1}$  for  $k_{dn}$  and 0.00163 for  $k_r$ . Based on the  $k_s$  parameter, atrazine in the labile pool has a half-life of 12.3 d. The rapid initial atrazine dissipation reflected the combined result of biodegradation, formation of bound (non-extractable) residues, volatilization and leaching. In 1992, more than 40% of the atrazine present in the profile at 13 d after application was leached below 7.5 cm depth. By 59 d after application, the model predicts that 46% of the remaining atrazine is in the nonlabile pool and by 183 d this percentage exceeded 99%. However, this predicted amount ( $16 \mu\text{g kg}^{-1}$  soil) is <3% of the amount estimated to be present immediately following application. Atrazine in the nonlabile pool is predicted to degrade slowly with a half-life exceeding 47 yr (based on the value of  $k_{dn} - 1 \text{ SE}$ ). We

emphasize that this estimate is based solely on the application of the model to a single year's data. The atrazine concentrations in the surface 7.5 cm soil following application in 1992 are also shown in Fig. 2, but these data were not fit with the model because we lacked measurements during the first week after application. However, the concentrations of atrazine in 1992 appear to follow a similar trend to the 1994 data.

Following atrazine application, atrazine residues in surface soil declined to concentrations generally below  $50 \mu\text{g kg}^{-1}$  soil and these residues remained stable up to 2 yr following application. The frequency of atrazine detection in the surface 7.5 cm of soil exceeded 95% over the entire period from 1991 to 1995 (Fig. 3). Long-term persistence is likely due to increases in adsorption with time, which render aged residues less bioavailable for degradation or leaching (Moorman, 1994). This is consistent with our description of atrazine behavior using the two-compartment model. After 180 d of incubation in similar soils from a nearby location, Kruger et al. (1993) reported 58% of the applied  $^{14}\text{C}$ -atrazine was present as bound (non-extractable) forms. In the field, multiple applications of atrazine over several years would create a sizable pool of non-extractable residues and the release of a small fraction of this pool as atrazine

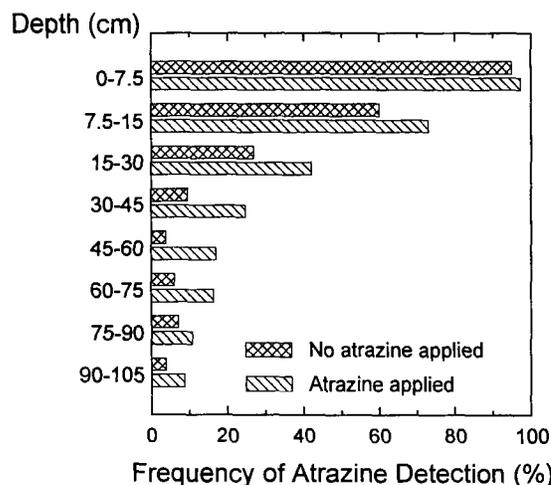


Fig. 3. Frequency of atrazine detection at different depths of sampling during 1992 and 1994 (atrazine applied) and 1991, 1993, and 1995 (no atrazine applied).

would account for the nearly constant concentrations observed in the surface soil. Formation and release of non-extractable atrazine residues back into the soil solution has been demonstrated (Capriel et al., 1985; Khan, 1991). Regardless of the exact mechanisms accounting for the long-term persistence of atrazine, these residues appear to be sufficiently available to impact subsurface drainage. In April of 1993, 11 mo after the previous application, approximately  $85 \text{ g ha}^{-1}$  of atrazine was present in the top 30 cm of soil and this quantity declined by half in the following 167 d while  $2.16 \text{ g ha}^{-1}$  of atrazine were lost in subsurface drainage.

The frequency of atrazine detection also declines with soil depth and the detection frequency in soil below 30 cm was substantially greater in years when atrazine was applied than in years without application (Fig. 3). The distributions of atrazine detections in this field were very similar to the frequency of atrazine detections at a no-till field to the north and another conservation tillage field over the years 1991, 1992, and 1993 (data not shown), suggesting that this field is fairly representative of the western watershed in general. The bulk of

the atrazine residues were found in the surface 15 cm of soil in all years. Mean concentrations of atrazine in soil deeper than 30 cm exceeded  $10 \mu\text{g kg}^{-1}$  only at sampling times within the first 30 d after application in 1992 (Fig. 4) and 1994 (Fig. 5).

The mean concentrations in Fig. 4 and 5 are our best quantitative estimates of atrazine movement in the soil profile. However, the data are highly skewed by the large numbers of samples with nondetectable residues (Fig. 3). Since values of zero were assigned to samples with non-detectable residues, the mean concentrations probably underestimate actual concentrations. The skewed distribution of data also makes conventional measures of variability meaningless, thus we have made no attempt to present standard deviations or other statistical measures, other than the frequency data in Fig. 3. Despite these problems, evidence of atrazine leaching can be seen, such as at 13 d after application in 1992, when mean concentrations generally exceeded  $15 \mu\text{g kg}^{-1}$  soil throughout the the top 75 cm of soil. In years without atrazine application such as 1993, similar trends were seen, but concentrations deep in the profile were

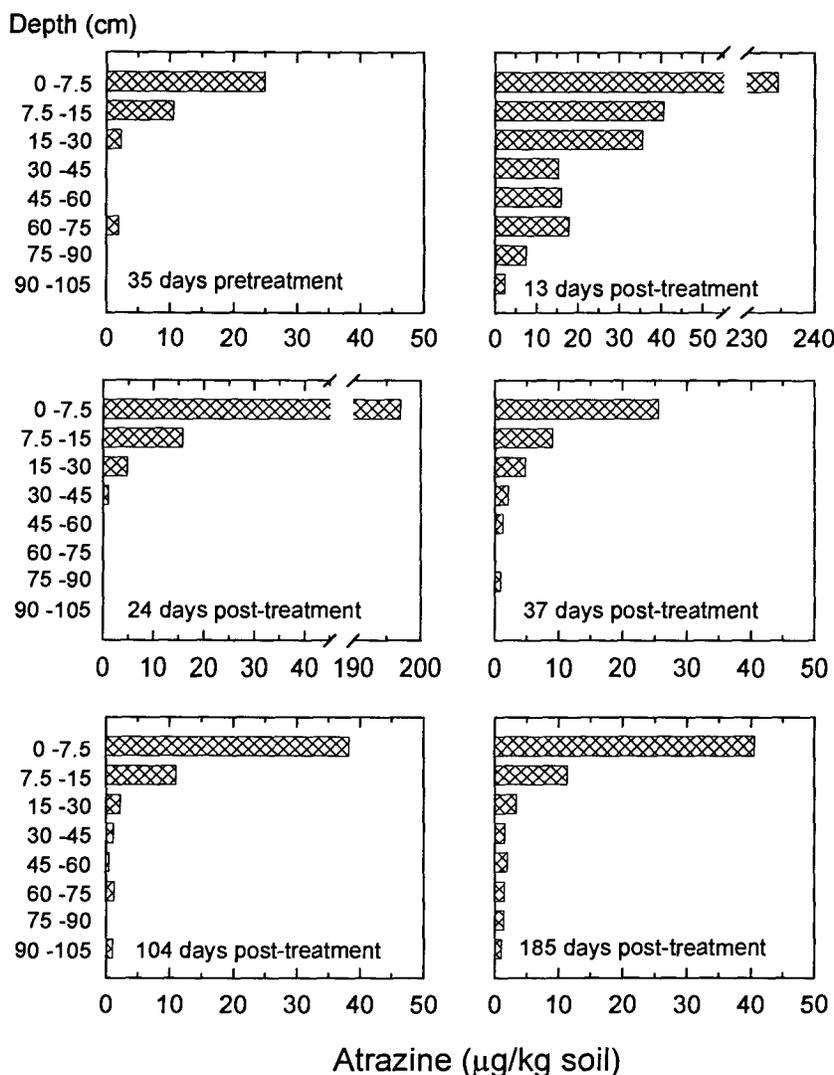


Fig. 4. Field-wide mean atrazine concentrations at different depths of soil in 1992.

greatly reduced. In 1993, average concentrations over the entire season were  $47 \mu\text{g kg}^{-1}$  in the surface 7.5 cm of soil, 15.5 at 7.5 to 15 cm, 5.5 at 15 to 30 cm depth, and  $<1.0 \mu\text{g kg}^{-1}$  below 45 cm depth.

Atrazine that leached below 15 cm depth degrades much more slowly than in surface soil. Kruger et al. (1993) measured atrazine half-lives of 69 d in soil from 30 to 65 cm depth and 231 d in the 90 to 120 cm depth in a Nicollet-Webster soil from a nearby site. In preliminary studies with sediments from our field site, the half-life of atrazine in the 140 to 210 cm depth sediments was  $>500$  d (Moorman et al., 1996). Subsurface soil (140–210 cm) from our site contained microorganisms capable of N-ethyl dealkylation, but degrader populations were estimated to be only  $1050 \text{ cells g}^{-1}$  soil,  $<25\%$  of the atrazine-degrader population in surface soil (Jayachandran et al., 1998). Microorganisms capable of degrading the triazine ring were not detected in the subsoil. Long persistence of atrazine in the subsurface soil would increase residence time and allow the slow movement of atrazine into subsurface-drainage from distant parts of the field in the year of application or in following years.

Atrazine sorption, estimated by the batch equilibrium method, is greatest in the surface soils and least in the subsurface soils, with exception of the Okoboji subsurface soil (Table 1). Sorption coefficients ( $K_d$ ) for the surface soils are very similar to the  $K_d$  values obtained from a large grid sampling previously conducted at this site (Novak et al., 1997). Atrazine sorption by Okoboji subsoil was nearly as great as that of the Clarion surface soil. The lower root zone soil and unoxidized till (320–335 cm depth) in the Clarion profile sorb atrazine only slightly, indicating that atrazine movement would be retarded only slightly relative to water or nitrate.

In contrast to atrazine, metribuzin had less long-term persistence with residual concentrations rarely detected after one growing season. Metribuzin dissipation was described by first-order kinetics (regression  $r^2 > 0.92$ ) with estimated half-lives of 15 d in 1993 and 21 d in 1995 (Fig. 2). In 1993, the first sampling was not until 5 d after application, which may have resulted in underestimation of the initial concentration. Metribuzin was not detected below 30 cm depth in any of six post-treatment samplings, except for samples taken at 34 and 160 d after treatment in 1993. Thirty-four days after treatment, metribuzin was detected as deep as 60 cm in the profile. At 160 d after treatment (2 November), metribuzin was found in concentrations averaging from  $0.35$  to  $0.93 \mu\text{g kg}^{-1}$  soil down to the 105 to 120 cm depth (data not shown). The wet conditions in 1993 did not permit core sampling until 14 d after planting, so movement immediately following application cannot be excluded. Metribuzin sorption was not measured in these soils, but other studies indicate that it is sorbed to a lesser degree than atrazine (Wauchope et al., 1992). Like atrazine, metribuzin would be more persistent in subsurface soils than in surface soils (Moorman and Harper, 1989).

## Water Quality

### Subsurface Drainage

Subsurface drainage is an important hydrologic process in the Walnut Creek watershed and in much of the glaciated areas of the Midwest. Herbicides transported in subsurface drainage contributes to the herbicide load of streams and rivers. Total yearly losses of atrazine ranged from  $0.05$  to  $2.16 \text{ g ha}^{-1}$  (Table 2), but these comprise a very small fraction of applied amounts.

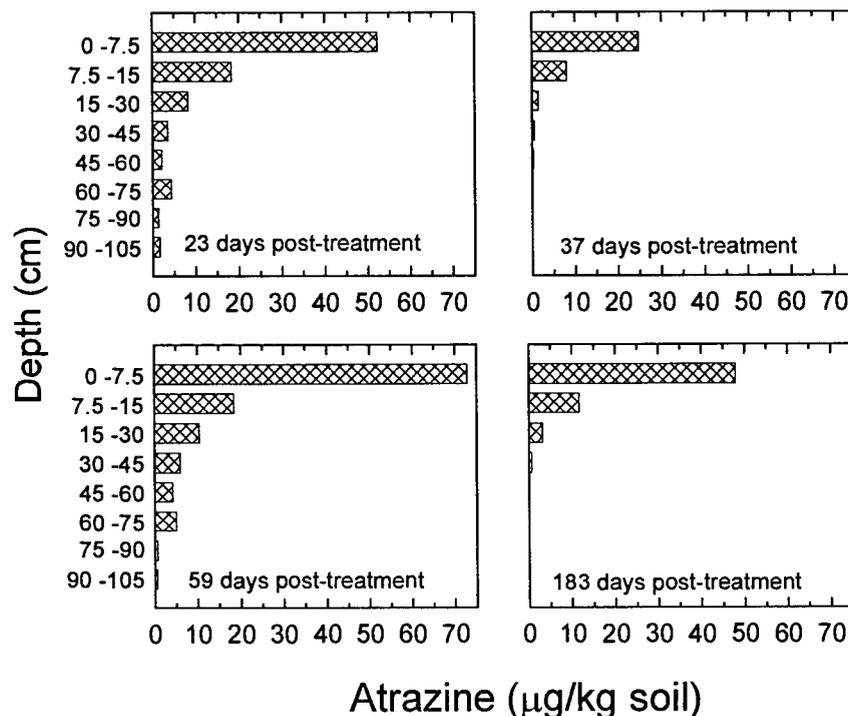


Fig. 5. Field-wide mean atrazine concentrations at different depths of soil in 1994.

**Table 1. Properties of soil within the area drained by subsurface drains.**

Soil	Depth cm	Organic C <sup>†</sup>	Sand		Clay	pH	Atrazine $K_d$ <sup>‡</sup> L/kg
			%				
Clarion (shoulder)	0-25	1.72	52	20	5.6	3.60	
	40-110	0.37	52	24	7.6	0.51	
	140-210	0.06	54	20	8.0	0.33	
	320-335	0.09	ND <sup>§</sup>	ND	7.5	0.51	
Clarion/Canisteo (backslope)	0-25	2.54	46	24	5.9	5.60	
	40-110	0.42	46	26	7.7	0.62	
	140-210	0.08	54	20	8.2	0.40	
Okoboji (depression)	0-25	5.16	28	30	6.8	16.0	
	40-110	1.29	20	36	7.2	3.20	

<sup>†</sup> Determined by oxidation methods using a Carlo-Erba C and N analyzer.

<sup>‡</sup> Adsorption coefficient determined by equilibrium techniques using methods described by Cambardella et al. (1994).

<sup>§</sup> ND = not determined.

Losses of metribuzin were generally half those of atrazine or less. On an annual basis, atrazine use and rainfall patterns appeared to be factors affecting atrazine losses in subsurface drainage (Table 2). The quantities of subsurface drainage from this site (site 110, Jaynes et al., 1999), expressed as mm, are generally similar to drainage from much larger areas within the watershed. More atrazine was lost in 1992 than in 1994 which corresponds to greater atrazine concentrations in soil at depths below 30 cm earlier in 1992 than in 1994. The smallest loss when atrazine was used occurred in 1994, when there was little subsurface drainage (Table 2). Considerable atrazine was present in drainage during 1993 and some also in 1995, when atrazine was not applied. The greatest annual loss was in 1993 when atrazine was not applied, but in a year with 58% greater precipitation than the 30 yr average (818 mm) and consequently greater leaching (Table 2). The 833 mm of discharge in 1993 resulted from the massive rainfall in spring and summer which lead to widespread flooding throughout the Midwest.

Atrazine and metribuzin concentrations in subsurface drainage also show distinct seasonal patterns (Fig. 6 and Fig. 7). Concentrations are generally greatest in the months of June, July, and August and least during the winter months. In addition to the seasonal patterns, concentrations rise and fall following individual rainfall events during the spring and summer of 1992 and 1994. The maximum atrazine concentration in any sample was 1.4  $\mu\text{g L}^{-1}$ . Monthly flow-weighted average concentra-

tions of atrazine never exceeded 1  $\mu\text{g L}^{-1}$ , which is well below the MCL values (data not shown).

The entry of herbicides into subsurface drainage water results from a combination of processes that may include direct leaching through soil and leaching in combination with lateral flow. Atrazine concentrations in subsurface drainage water increase rapidly following rainfall events and remain elevated after water flow has returned to near baseline levels before declining to atrazine concentrations typical of baseflow (Jaynes et al., 1999). The initial rise in atrazine concentrations is probably due to atrazine transport in macropore flow which is followed by atrazine transport in matrix flow. Atrazine was found in measurable quantities in soil below 30 cm throughout 1992 and up to 59 d following treatment in 1994, although the frequency of detection was low. The variation within years and between years are primarily due to rainfall events and transport in the subsoil. The distribution of atrazine in soil cores samples is infrequent at depths below 30 cm, although we cannot preclude the possibility of atrazine being present at concentrations below the 5  $\mu\text{g kg}^{-1}$  soil reporting limit for atrazine. In addition, the distribution of atrazine in samples from individual cores was often discontinuous (i.e., samples containing atrazine beneath samples containing no atrazine). These observations also support the transport of atrazine in macropore flow. Movement of herbicides and noninteracting tracers to subsurface drains within 130 min after the onset of artificial rainfall was

**Table 2. Water budget and losses of atrazine and metribuzin in subsurface drainage from an 8.9 ha field cropped with corn in 1992 and 1994 and soybean in 1993 and 1995.**

	1992	1993	1994	1995
<b>Water, mm<sup>†</sup></b>				
Precipitation	780	1290	610	700
Evapotranspiration	500	470	440	430
Subsurface drainage	240	833	63	140
Profile moisture <sup>‡</sup>	-13	8	-60	10
Ground water recharge	53	-21	167	120
<b>Atrazine, g ha<sup>-1</sup></b>				
Applied	459	0	561	0
Mass loss	0.49	2.16	0.02	0.05
Fractional loss, %	0.11	0.47 <sup>§</sup>	0.0036	0.0089 <sup>§</sup>
<b>Metribuzin, g ha<sup>-1</sup></b>				
Applied	0	420	0	420
Mass loss	0.013	1.27	0	0.029
Fractional loss, %	0.0032 <sup>§</sup>	0.30	0 <sup>§</sup>	0.0070

<sup>†</sup> Water budgets were calculated as described by Hatfield et al. (1999) using rainfall, drainage, and evapotranspiration.

<sup>‡</sup> Change in soil moisture stored in the soil profile on an annual basis.

<sup>§</sup> Expressed as a percentage of the previous year's application.

attributed to macropore flow in Okoboji soil by Czapar et al. (1994). Jayachandran et al. (1994) observed low DAR ratios early in the season in subsurface drainage water and attributed these to macropore flow. Lateral subsurface flow of water from parts of the field beneath the Clarion and Canisteo soils to the subsurface drains probably occurs in the spring and early summer, but the quantity and velocity of lateral flow are presently unknown.

Runoff from surrounding areas accumulates in the large and small potholes, where direct leaching through the soil to the subsurface drains is likely. Standing water in the potholes following runoff events was sampled and contained an average atrazine concentration of  $2.02 \mu\text{g L}^{-1}$  in the large pothole and  $9.51 \mu\text{g L}^{-1}$  in the small pothole. Average metribuzin concentrations were  $1.72$  and  $2.89 \mu\text{g L}^{-1}$  in the large pothole and small potholes, respectively. Maximum atrazine and metribuzin concen-

trations were  $313$  and  $38 \mu\text{g L}^{-1}$ , respectively. Based on observed depth of ponded waters and these concentrations, the additional loads to ponded soils would likely range from  $1$  to  $20 \text{ g ha}^{-1}$  for the herbicides. Thus, runoff results in hydrologic conditions and elevated herbicide concentrations that favor herbicide leaching to subsurface drains or groundwater: Mitigating these factors are the high quantities of organic C in the pothole (Okoboji) soils in both the surface and subsurface layers that adsorb atrazine to a greater extent than the other soils at the site (Table 1).

The atrazine was banded in 1992 and 1994, which resulted in relatively low application rates (approximately  $0.5 \text{ kg ha}^{-1}$ ). Banding coupled with rotation to soybean resulted in a farming system that had low losses of atrazine in subsurface drainage. Over the 4 yr period from 1992 through 1995, the average annual loss of atrazine was  $0.68 \text{ g ha}^{-1}$ , which was below average an-

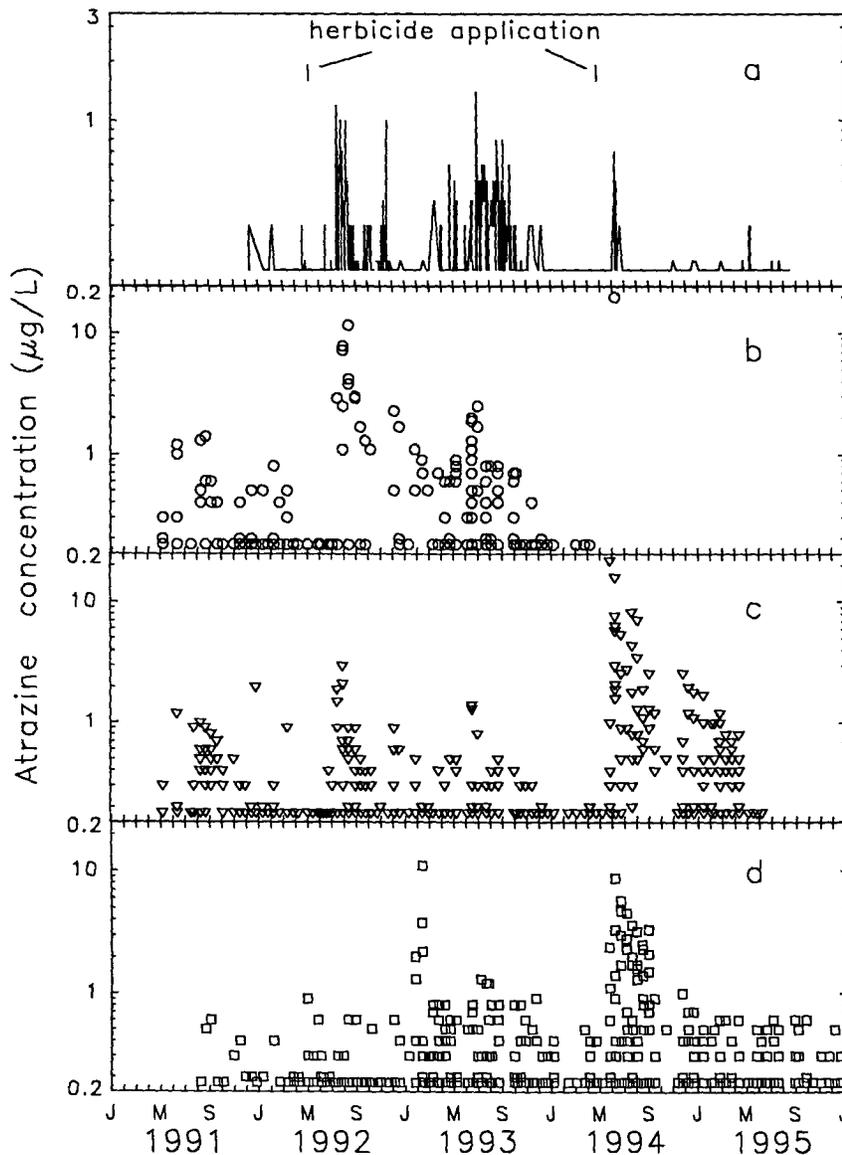


Fig. 6. Atrazine concentrations in subsurface drainage (a) and in groundwater at depths of  $0.6 \text{ m}$  (b),  $1.5 \text{ m}$  (c), and  $2.6 \text{ m}$  (d) from 1991 through 1995. Subsurface drainage was not monitored until Day 344 of 1991.

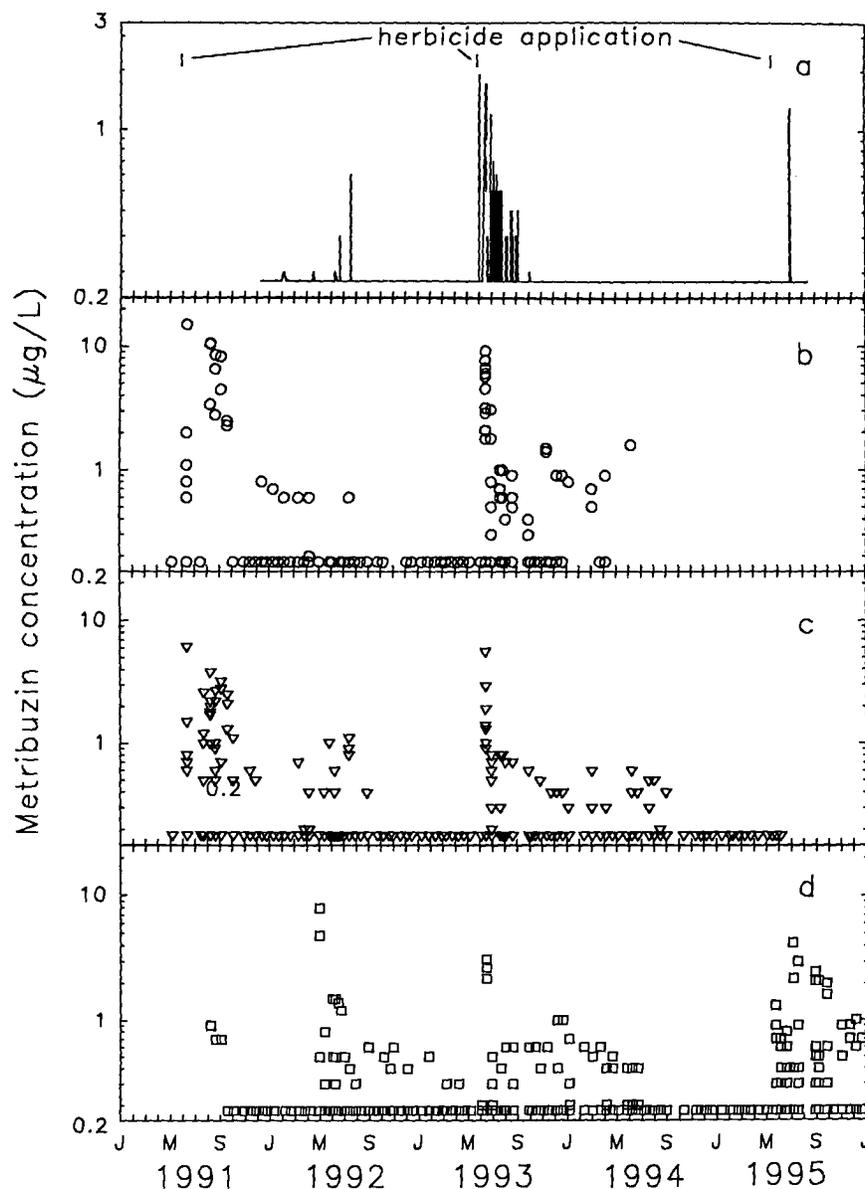


Fig. 7. Metribuzin concentrations in subsurface drainage (a) and groundwater sampled at depths of 0.6 m (b), 1.5 m (c), and 2.6 m (d) from 1991 through 1995. Subsurface drainage was not monitored until Day 344 of 1991.

nual losses from several other corn farming systems. Average annual atrazine losses from these other systems include the  $1.57 \text{ g ha}^{-1}$  during 1986 through 1988 (Buhler et al., 1993) in southern Minnesota,  $4.25 \text{ g ha}^{-1}$  at another site in central Iowa (Jayachandran et al., 1994),  $4.71 \text{ g ha}^{-1}$  in Ohio (Logan et al., 1994), and the  $26 \text{ g ha}^{-1}$  loss in drainage from field plots in Ontario (Gaynor et al., 1995a). Losses in our study were similar to the  $0.93 \text{ g ha}^{-1}$  average loss calculated from data of Masse et al. (1996). However, when total losses at our site ( $2.72 \text{ g ha}^{-1}$ ) are expressed as a percentage of applied atrazine over the same period (0.27%), the relative losses were comparable to multi-year losses at these other sites, which range from 0.04 to 1.54%. These comparisons suggest that banding and rotation are practices that reduce total atrazine loss, but it appears that this effect is primarily due to the reduction in applied herbicide.

Gaynor et al. (1995b) reported slight reductions in atrazine loss in subsurface drainage from banding at a site in Ontario. Similar comparisons were not possible for metribuzin due to lack of data, but losses of metribuzin in our study were comparable to or lower than the annual losses reported from drained plots in Ohio, which ranged from 0 to  $3.98 \text{ g ha}^{-1}$  (Logan et al., 1994).

### Groundwater

Samples were collected from wells placed in the lower part of the root zone (0.6 m depth), just beneath the root zone (1.5 m depth), and in the oxidized, late-Wisconsin till (2.6 m depth). We estimated groundwater recharge at this site using precipitation and evapotranspiration data given by Hatfield et al. (1999) and site-specific subsurface drainage and soil moisture data (Table 2). Subsurface drainage accounted for 10 to 65% of

**Table 3. Atrazine and metribuzin in shallow groundwater grouped by well depth or by location of wells within soil map units.†**

	Depth, m			Soil map unit		
	0.6	1.5	2.6	Clarion	Canisteo	Okobojo-Harps
<b>Atrazine</b>						
Mean, SD, $\mu\text{g L}^{-1}$	0.46 $\pm$ 1.6	0.29 $\pm$ 1.2	0.21 $\pm$ 0.72	0.14 $\pm$ 0.59	0.25 $\pm$ 0.94	0.51 $\pm$ 1.7
Detection frequency, %	36	28	26	13	30	45
Freq. exceeding 3 $\mu\text{g L}^{-1}$ , %	2.6	1.6	1.4	1.2	1.0	3.2
No. of observations	273	738	837	587	788	473
<b>Metribuzin</b>						
Mean, SD, $\mu\text{g L}^{-1}$	0.57 $\pm$ 1.86	0.13 $\pm$ 0.51	0.11 $\pm$ 0.47	0.10 $\pm$ 0.78	0.24 $\pm$ 1.01	0.18 $\pm$ 0.64
Detection frequency, %	21	12	13	6.7	17	17
No. of observations	274	736	842	586	801	465

† Concentrations calculated using values of zero for samples below the detection limit of 0.2  $\mu\text{g L}^{-1}$ . Median concentrations were all  $<0.2 \mu\text{g L}^{-1}$ .

precipitation and was larger than groundwater recharge of water moving past the root zone in all years, except 1994. This level of recharge resulted in slow turnover of groundwater. Eidem et al. (1999) estimated the age of the groundwater at the base of the oxidized till to be from 26 d to 1.7 yr.

Atrazine was detected in less than half of the well samples from all depths and soils (Table 3), but only a small percentage of the sample concentrations exceeded the MCL. Metribuzin was also observed but at a much lower frequency than atrazine. Wells screened at the 0.6 m depth yielded fewer samples than were obtained at the other depths due to groundwater dropping beneath this depth during the summer months. Mean atrazine concentrations declined with increasing depth ( $P = 0.05$ ) of the groundwater. The detection frequencies and fraction of samples  $>3 \mu\text{g L}^{-1}$  (MCL) also decreased with depth. The frequency of detection and mean concentrations of atrazine were greatest in groundwater beneath the Okobojo and Harps soils and least beneath the Clarion soil. Mean atrazine concentrations were generally similar in magnitude to the monthly flow-weighted atrazine concentrations in subsurface drainage water.

Metribuzin concentrations in groundwater at the 0.6 m depth were higher than at the 1.5 and 2.6 m depths (Table 3). Less than 25% of all samples contained detectable metribuzin residues, but the frequency of detection decreased with depth. Like atrazine, the frequency of detection was greatest in groundwater beneath the Harps-Okobojo soils and least under the Clarion soils. Concentrations tended to be greatest following herbicide application, with concentrations generally declining thereafter (Fig. 7). Metribuzin was detected in groundwater in both 1992 and 1995, years when atrazine was applied.

The temporal dynamics of atrazine in groundwater are compared to subsurface drainage water in Fig. 6. Like atrazine in subsurface drainage water, the concentrations in groundwater increase in response to rainfall events, particularly in 1992 and 1994, when atrazine was applied. Atrazine was also found in groundwater in 1991, 1993, and 1995 when no atrazine was applied to the field.

Despite the larger atrazine sorption coefficients in the Okobojo and Harps soils, atrazine was detected more frequently in groundwater beneath these soils (Table

3). This unexpected result may be explained by the position of these soils in the large closed depression within the field. Apparently, increased leaching through these soils is driven by runoff water or lateral water flow from other areas of the field, which overcomes any retardation effects due to herbicide sorption. The high sorption capacity of these soils probably reduces atrazine leaching into the subsurface drain by increasing the travel time, which would increase biodegradation in soil layers near the surface.

Groundwater quality within the pothole field can be compared to that measured in wells located throughout the watershed. From 1991 through 1995, 2070 samples were collected from shallow wells placed at the edges of fields. The frequency of atrazine detection and mean concentration tend to decline with depth (Table 4). However, both mean concentrations and frequency of detection of atrazine and metribuzin from the watershed-scale sample set (Table 4) were smaller than those obtained from wells within the pothole field (Table 3). The lower frequencies of detection in the watershed-scale monitoring data appears to be caused by the location of wells at edges of fields, where lateral flow is required to move herbicide into the well recharge zone. A second reason for this finding was that some wells in the watershed were not adjacent to fields where atrazine or metribuzin is applied. Concentrations of metribuzin were similar in all well depth classes. Less than 1% of

**Table 4. Concentrations of atrazine and metribuzin in shallow groundwater samples from wells within the Walnut Creek Watershed from 1991 through 1996.†**

	Depth below soil surface			
	0.9-1.5	1.5-3.0	3.0-4.6	>4.6
	m			
<b>Atrazine</b>				
Mean, $\mu\text{g L}^{-1}$	0.1	0.16	0.06	0.06
Maximum, $\mu\text{g L}^{-1}$	5.1	28.2	8.8	10.2
Detection frequency, %	10	15	4	4
No. exceeding 3 $\mu\text{g L}^{-1}$ , %	1	8	3	5
<b>Metribuzin</b>				
Mean, $\mu\text{g L}^{-1}$	0.01	0.01	0.001	0.01
Maximum, $\mu\text{g L}^{-1}$	0.4	1.4	0.5	0.9
Detection frequency, %	1	2	1	2
Observations‡	79	901	454	636

† Mean concentrations calculated using values of zero for samples with no detectable herbicides. The detection limit was 0.2  $\mu\text{g L}^{-1}$  in well water for each herbicide. Median concentrations were all  $<0.2 \mu\text{g L}^{-1}$ .

‡ Number of observations is the same for all herbicides.

all samples contained atrazine concentrations exceeding the MCL of  $3 \mu\text{g L}^{-1}$ . These results show that groundwater contamination within the Walnut Creek watershed occurs infrequently and that herbicide concentrations in shallow groundwater are not sufficiently large to serve as a source of contaminants to drinking water supplies.

## SUMMARY

In this field-scale study of a corn and soybean farming system, herbicides were lost in subsurface drainage water and to deep leaching. Atrazine concentrations in subsurface drainage and groundwater are generally well below the MCL for drinking water. Only 1.4% of the groundwater samples beneath the subsurface drains (wells at 2.6 m depth) contained  $>3 \mu\text{g L}^{-1}$  atrazine and 30% contained concentrations above the  $0.2 \mu\text{g L}^{-1}$  quantitation limit. This frequency of atrazine contamination is similar to that reported by Kolpin et al. (1995) in a survey of groundwater quality in the midwestern USA, but greater than that found in a larger number of wells at the edges of fields located throughout the watershed. More atrazine was lost in subsurface drainage at the field site than metribuzin and this appears to be related to the greater long-term persistence of atrazine in the surface and subsurface soil. The losses of atrazine from soil into drainage and groundwater are driven more by seasonal rainfall patterns than application timing or soil conditions. The greatest annual loss of atrazine and metribuzin was in 1993, even though atrazine was not applied in that year. The longer persistence of atrazine in surface and subsurface soil, compared to metribuzin, was a contributing factor in this herbicide moving into subsurface drainage and groundwater. Despite greater organic C contents and larger atrazine sorption coefficients, the Harps and Okoboji soils in the pothole areas of the field were more vulnerable to herbicide movement. Our results suggest that agricultural practices that decrease atrazine use, such as banding or rotations, will result in water quality that meets present drinking water quality standards. In addition, practices that decrease runoff and increase atrazine retention in the soil appear to have potential for decreasing herbicide losses in subsurface drainage, ultimately improving surface water quality.

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