

Herbicide Contamination of Groundwater Beneath Claypan Soils in North-Central Missouri

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ABSTRACT

The impact of hydrology and site-specific soil stratigraphy on herbicide leaching are not well understood for claypan soils. The claypan is a naturally-occurring argillic soil horizon that limits percolation to groundwater. The primary objective of this study was to determine the extent of nonpoint source herbicide contamination of shallow groundwater beneath claypan soils. The secondary objective was to determine the relative importance of hydrology and land management to observed herbicide contamination of groundwater during a 5-year period. The study site was the 7250 ha Goodwater Creek Watershed in north-central Missouri. Three cropped fields with 10 yr of similar management were instrumented with 20 to 25 monitor wells each in 1991. The three fields were treated with different rates of atrazine [2-chloro-(4-ethylamino)-6-(isopropylamino)-s-triazine] and alachlor [2-chloro-2', 6'-diethyl-N-(methoxymethyl)acetanilide] and the wells were sampled quarterly from 1991 to 1996. Atrazine was detected in 7.2% of samples, with a maximum concentration of $0.12 \mu\text{g L}^{-1}$ (limit of detection, LOD = $0.02 \mu\text{g L}^{-1}$). Alachlor was detected in 0.4% of samples with a maximum concentration of $0.14 \mu\text{g L}^{-1}$ (LOD = $0.11 \mu\text{g L}^{-1}$). Site to site variability in hydrology was more important than differences in herbicide application rates, as the field treated with the least atrazine and alachlor had the most frequent detections of atrazine, the atrazine metabolite deethylatrazine [2-chloro-(4-amino)-6-(isopropylamino)-s-triazine; DEA], and the alachlor metabolite [2-[(2,6-diethylphenyl) (methoxymethyl)amino]-2-oxoethanesulfonic acid; ESA]. Groundwater recharge occurred primarily during the nongrowing season. Therefore, herbicide and metabolite leaching were limited by the extent of their degradation in the soil during the growing season. The study results demonstrate the importance of hydrologic variability, recharge timing, and chemical properties with respect to the leaching of herbicides and herbicide metabolites.

HERBICIDE transport to groundwater has been intensively studied in the 1980s and 1990s. The U.S. Environmental Protection Agency (USEPA, 1986) noted that herbicides had been detected in groundwater in numerous states. Some cases of herbicide contamination of groundwater were clearly due to point-sources (Hallberg, 1989). The extent of nonpoint source contamination of groundwater by agricultural chemicals was not known in the late 1980s. Since that time, national surveys (USEPA, 1990; Holden et al., 1992), regional surveys (Burkart and Kolpin, 1993; Richards et al., 1996), and numerous state and local studies have documented the extent of herbicide contamination of groundwater. Variation in the frequency of wells with herbicide detections between different studies may be due to whether the study focus was on public water supply or domestic wells, agricultural or urban settings, or was designed for random sampling vs. sampling

known or suspected problem areas. Differences in detection limits also impact the percentage of detections reported in different studies (Burkart and Kolpin, 1993). Barbash and Resek (1996) provide an extensive review of herbicides in groundwater.

Many factors affect groundwater vulnerability to herbicide contamination, including well characteristics, soil texture and organic matter content, aquifer type, and land management. Important well characteristics include such factors as the age, depth, diameter, and construction method (dug, driven, or drilled) of the well, and the proximity of the well to cropland, chemical mixing sites, irrigation systems, and streams. The importance of the soil to herbicide transport to groundwater is complex. Atrazine leaching was associated with sandy soils with high permeability and low organic matter (Helling and Gish, 1986). In several studies, herbicides were transported deeper in fine-grained soils than in coarse-grained soils due to preferential flow (Hallberg, 1989). Subsoil hydrology also is important, because clay layers may greatly reduce leaching (Kalkhoff et al., 1992; Masse et al., 1994). It is hard to distinguish the impact of any single factor on groundwater contamination because these factors may interact or be correlated.

The Management Systems Evaluation Areas (MSEA) Project was designed to assess farming system impact on herbicide and NO_3 concentrations in soil and aquifer systems in the Midwestern USA (Onstad et al., 1991; Ward et al., 1994). The primary objective of this study was to determine the extent of nonpoint source herbicide contamination of shallow groundwater beneath claypan soils. The claypan is a naturally-occurring argillic soil horizon that limits percolation to groundwater. The second objective was to determine the relative importance of hydrology and land management to the observed herbicide contamination on a field-scale (20–36 ha) for this soil and aquifer system. The third objective was to document temporal changes in herbicide contamination of groundwater during the 5-yr study.

MATERIALS AND METHODS

Site Description

The study site was the 7250 ha Goodwater Creek Watershed in north-central Missouri (Fig. 1). Goodwater Creek Watershed is near the southern terminus of glaciation in the dissected till plains physiographic province, which includes parts of Kansas, Nebraska, Iowa, and Missouri. This watershed is typical of the 2.8 million ha Central Claypan Region of Missouri and

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Abbreviations: LOD, limit of detection; DEA, deethylatrazine; ESA, ethane-sulfonic acid metabolite of alachlor; MSEA, Management Systems Evaluation Areas; PVC, polyvinylchloride; ELISA, enzyme-linked immunosorbent assay; GC, gas chromatography; SPE, solid phase extraction; DIA, deisopropylatrazine; MCL, maximum contaminant levels.

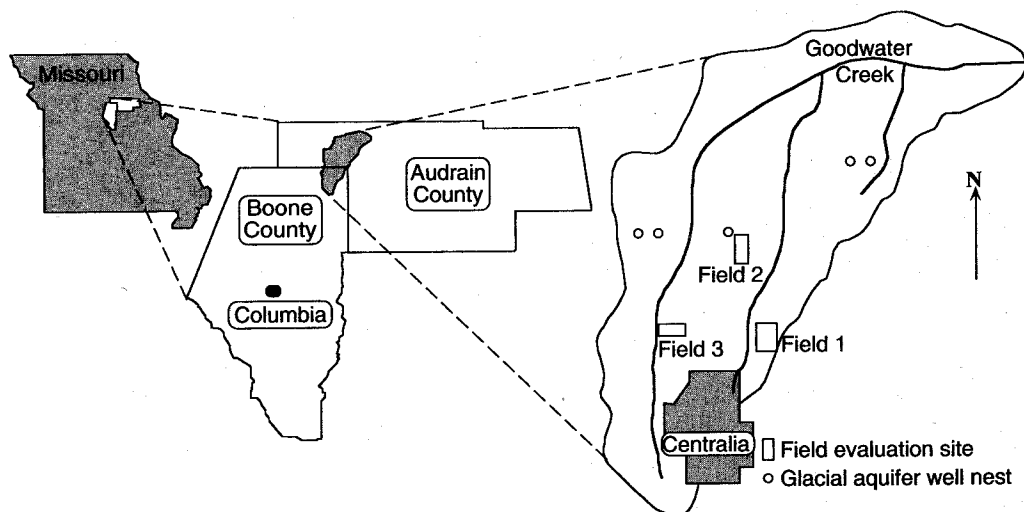


Fig. 1. Location of Goodwater Creek watershed Management Systems Evaluation Areas (MSEA), assessment fields, and glacial aquifer well nests in north-central Missouri.

Illinois (U.S. Department of Agriculture, 1981). Soils in this region have claypans, naturally occurring argillic soil horizons.

Quaternary stratigraphic relationships for north-central Missouri (Guccione, 1983) were adapted for the watershed based on core samples collected during this study (Fig. 2). Two pre-Illinoian glacial till units separated by a paleosol are found at most locations. A paleosol also is present at the top of the upper till unit. The total thickness of the glacial till is 15 m in summit landscape positions. Erosion has removed the upper or lower till units at some locations. Illinoian and Wisconsin age loess deposits that overlie the till, are about 3 m thick in summit positions and are thin or absent near the creeks. The till overlies Pennsylvanian age deposits of shale, limestone, and clay, and in some locations preglacial sediments including peat. Alluvial deposits are present near the creeks. Near the outlet of the watershed, the loess, till and Pennsylvanian deposits have been completely eroded and alluvium directly overlies the Mississippian age Burlington Limestone.

The predominant soil series in the watershed are the Putnam (Mollic Albaqualfs), Mexico (Udolic Ochraqualfs), and Leonard (Vertic Ochraqualfs) series (Natural Resources Conservation Service, 1995). These soils have an abrupt increase in clay content; the claypan formed in the Wisconsin loess by accumulation of clay in the illuvial B horizon. The claypan's low permeability restricts percolation and promotes interflow and surface runoff.

The USDA-ARS has maintained climate and surface hydrology instrumentation on the watershed since 1970. The 25 yr (1970–1994) average annual precipitation is 948.0 mm and the average annual streamflow exiting the watershed is 30.8 cm. Surface runoff accounts for 85% of the total streamflow (Alberts et al., 1995).

The impact of cropping systems on ground- and surface water quality was studied on three farm fields from 1991 to 1996 (Fig. 3). The fields were chosen because they had soils typical of the Central Claypan Region, were at topographic divides, were suitable for ground- and surface water monitoring, and had been managed similarly from 1980 to 1990. MSEA farming operations began at the fields in 1991. Detailed soil mapping on the fields was conducted by NRCS in 1991. In addition to the Putnam, Mexico, and Leonard series, two additional soil series were mapped, Adco (Albaquic Hapludalfs) and Vesser (Argiaquic Argialbolls). The Putnam, Adco, and Mexico soils are very similar hydrologically and are very slowly permeable, the Leonard is slowly permeable and the Vesser is moderately slowly permeable.

Hydrogeology and Well Drilling and Construction

The loess and glacial till have sufficient permeability and water yield for domestic use and together will be referred to as the glacial aquifer. All study wells are in the glacial aquifer,

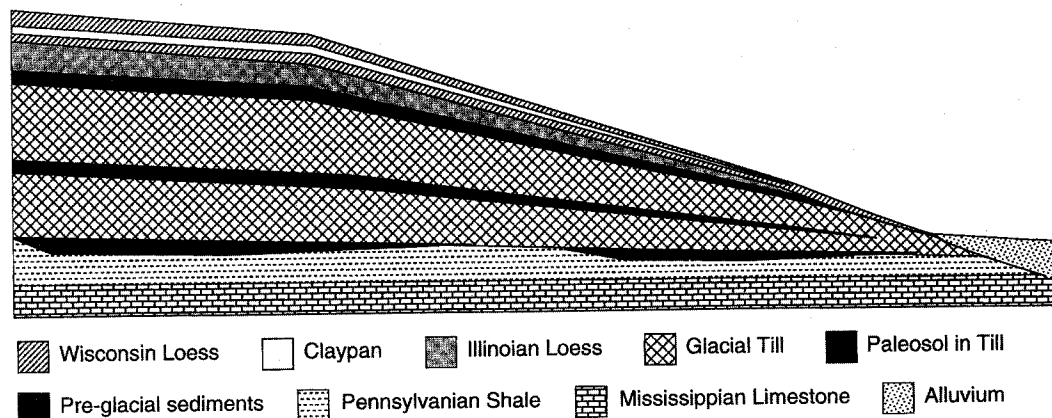


Fig. 2. Generalized cross-section and stratigraphy in Goodwater Creek watershed (not to scale).

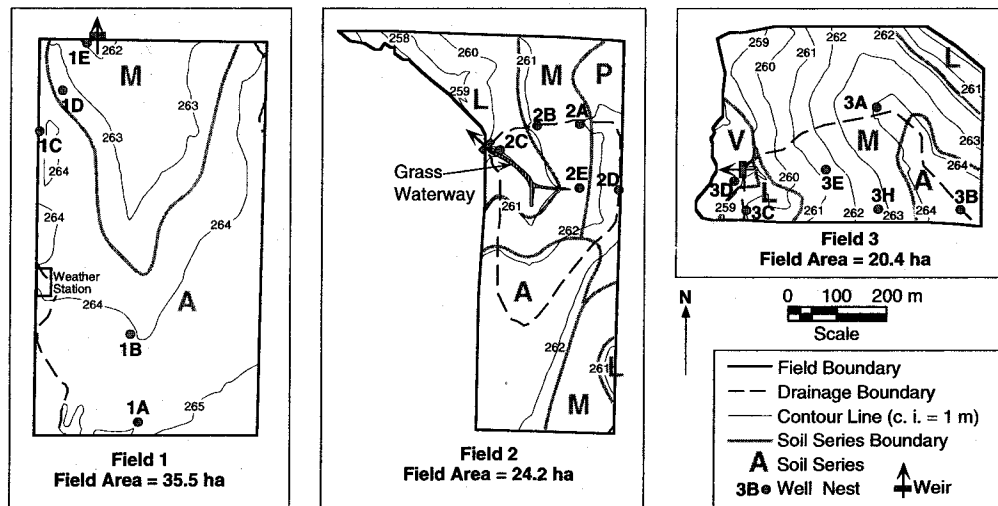


Fig. 3. Maps of Management Systems Evaluation Areas (MSEA) Fields 1, 2, and 3 showing topography (m above mean sea level), soil series, location of well nests, and surface water weirs. Soil Series: A, Adco; L, Leonard; M, Mexico; P, Putnam; and V, Vesser.

and are not subject to the groundwater–surface water interactions described by Wang and Squillace (1994) and Duncan et al. (1991). Field wells were drilled in the spring of 1991, before implementing MSEA farming systems. Each field was instrumented with five well nests, with three to five wells in each nest (Fig. 3). At least three nests per field were located within the field boundary; some nests were positioned along the field edge. Wells within in each nest were close to each other, within about 25 m² area. No herbicides were applied to the well nest area. Polyvinylchloride (PVC) wells (5.08 cm i.d.) were installed through 16.5 cm i.d. hollow-stem augers. The borehole annulus was backfilled with sand to 30 cm above the well screen, followed by 2 m of bentonite, and finally cement–bentonite grout from the top of the bentonite to the land surface. The wells installed in 1991 have 1.2 m long slotted PVC screens. Wells in each nest were screened at different depths to determine water quality differences with depth. The deepest well in each nest was screened at the bottom of the till, except the deepest wells in Nests 3B, 3C, and E (Fig. 3), which were screened in preglacial peat just below the till. Screened intervals of the shallower wells in each nest correspond to fractures, sand lenses, and color changes observed in continuous cores collected during well drilling. In 1992, 10 additional wells were installed, one at each nest where the water table was higher than the shallowest well installed in 1991 (all Field 1 Nests, 2A, 3A, 3B, 3C, E) and one at location 3H (Fig. 3), which has no deeper wells. These 10 wells are in the loess and have 0.6 m slotted PVC screens. Nineteen additional glacial aquifer wells (five well nests) were drilled in 1990 within the surrounding Goodwater Creek Watershed (Fig. 1).

Glacial till is often assumed to be low in permeability due to its clay content, however, Grisak (1975), Hendry (1982), Keller et al. (1986), and Fredericia (1990) established that the presence of fractures greatly increases glacial till permeability.

Table 1. Hydraulic conductivity of glacial aquifer strata.

Stratum	Wells no.	Hydraulic conductivity	
		Mean	Median
m s ⁻¹			
Loess	10	8.7 × 10 ⁻⁷	5.0 × 10 ⁻⁷
Glacial till	62	5.3 × 10 ⁻⁶	4.5 × 10 ⁻⁶
Paleosols in till	11	5.2 × 10 ⁻⁸	1.9 × 10 ⁻⁸

Field-measured hydraulic conductivities (K) of pre-Illinoian till in Missouri are two- to four-orders of magnitude higher than those determined on small laboratory samples (Sharp, 1984). Table 1 lists the average and median values of K for the loess, till, and paleosols, based on slug tests conducted in the MSEA wells (Heidenreich and Blanchard, 1993). The slug test data were analyzed according to the Bouwer and Rice method (Bouwer and Rice, 1976; Bouwer, 1989a,b).

The glacial aquifer hydrology is very complex. In most locations the aquifer is a water table aquifer. In some locations the upper till paleosol, lower till paleosol, or preglacial clays (Fig. 2) function as leaky confining units. The glacial till has a high permeability fracture system coupled with a low permeability, high porosity (30–40%) matrix. Flow depends on both K and the hydraulic gradient. Goodwater Creek Watershed is an area of low topographic slope and the horizontal hydraulic gradients reflect that with a range from 0.005 to 0.02. The hydraulic gradients vary spatially, seasonally, and between fields with Field 1 < Field 2 < Field 3. Within the till, vertical gradients are very small except in those locations where the lower till paleosol acts as a leaky confining unit. In general, flow within the aquifer is toward the creeks (Hesemann, 1979).

The median K value for the pre-Illinoian glacial till (Table 1) is higher than those reported for Wisconsin age till by McKay et al. (1993a, b), and the fracture porosity of the pre-Illinoian till is probably greater than the 0.003 to 0.1% calculated by McKay et al. (1993a). Making a conservative estimate of the effective porosity of the till (1%), and using the median K value, and a hydraulic gradient of 0.005 to 0.02, advective transport of solutes should be in the range of 70 to 280 m yr⁻¹. Making the same calculation for the loess using the median K value, an effective porosity of 9% (Blevins et al., 1996) and the same gradient range, the advective transport rate should be in the range of 0.8 to 3.5 m yr⁻¹. Solutes that reach the till can be transported rapidly. Surface applied chemicals must pass through the loess and upper till paleosol to reach the till. Since the K of the paleosol is more than an order of magnitude less than that of the loess, the paleosol is the limiting unit in transport to the till.

Judging by vertical hydraulic gradients between the loess and upper till, the upper till paleosol is apparently thicker and/or less permeable at Field 1 than at Field 3. The hydrogeology at Field 2 is spatially variable. The upper till paleosol acts as a confining unit at the 2A, 2B, and 2D nests, but not at

the 2C and 2E nests (Fig. 3). Flow in the loess at Field 2 is toward the grass waterway, while flow in the till is to the east. Hydrologically, the 2D nest is down-gradient despite being at the topographic high point.

Water levels within the aquifer vary significantly over time. Hydrographs of two summit position wells, 1A3 and 3A4 are shown in Fig. 4. These wells are screened in the upper till at about 6 to 7 m below land surface. The hydrographs show the general pattern of recharge from late fall to spring and significant summertime drops in water level, except for the very wet summer of 1993. The water level in well 3A4 dropped below the bottom of the loess (about 3-m depth) every summer except 1993. The water level in well 1A3 never dropped below 2 m. The loess is a silty-clay with high moisture retention, so the water level fluctuations do not represent a large flux of water.

Recharge to the glacial aquifer is by preferential flow through the claypan (Blevins et al., 1996), as the hydraulic conductivity in the absence of preferential flow pathways is very low. These preferential flow paths may be along rootlets or structural planes related to desiccation cracks (Blevins et al., 1996). Flow through the claypan primarily occurs when the topsoil is very wet and is saturated above the claypan. This condition is most commonly met from October to May. Summer and early fall rains generally eliminate any soil moisture deficit in the topsoil before flow through the claypan occurs.

The physical make-up of the aquifer with mobile water in the fractures and immobile, or less mobile water in the pore space of the matrix (unfractured till between fractures) influences solute transport. Matrix diffusion, the diffusion of solutes between fracture water and matrix water is an important transport mechanism in fractured till (Grisak and Pickens, 1980; Grisak et al., 1980). Matrix diffusion was responsible for buffering changes in nitrate concentration within the glacial aquifer (Blanchard et al., 1995).

Well Sampling

Each well was equipped with a dedicated WaTerra¹ (WaTerra Pumps, Waterloo, Ontario) hand pump, which is com-

¹ Mention of trade names or specific products is made only to provide information to the reader and does not constitute an endorsement by the University of Missouri or the USDA-ARS.

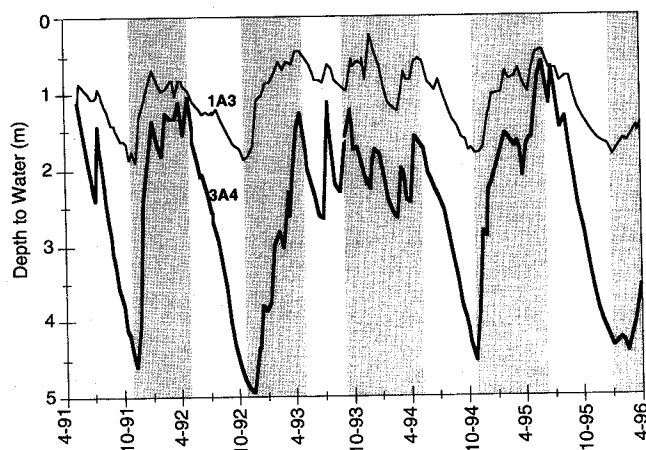


Fig. 4. Hydrographs (depth to water over time) of Management Systems Evaluation Areas (MSEA) field wells 1A3 (in Nest 1A, Fig. 3) and 3A4 (in Nest 3A, Fig. 3) from 1991 to 1996. The shaded portions of the graph are the primary recharge periods and correspond with shaded portions of Fig. 5 and 6.

posed of 1.59 cm (0.625 in) o.d. high density polyethylene tubing with a Delrin (DuPont, Wilmington, DE) plastic foot valve. Three well volumes of water were purged from each well before sample collection. Samples were collected in 900 mL amber glass bottles, placed in a cooler and transported to the laboratory at the end of the day.

Groundwater samples were collected quarterly from May 1991 to March 1996, with the exception of December 1995 (Table 2). The shallowest well in each nest was sampled quarterly. Deeper wells were sampled at least once per year. Deeper wells that had herbicide and/or metabolite detections in one quarter were sampled the following quarter.

Chemical Analyses

A total of 1137 water samples from the glacial aquifer have been collected and analyzed for herbicides. From May 1991 to September 1992, samples were screened using an Enviroguard (Millipore, Bedford, MA) enzyme-linked immunosorbent assay (ELISA) atrazine and alachlor kits (microtiter plate-based ELISA). If the ELISA analyses indicated a concentration of atrazine or alachlor $\geq 0.2 \mu\text{g L}^{-1}$, then those samples were analyzed by gas chromatography (GC). An increasing number of false positives with the alachlor kit made the screening procedure unworkable. Beginning in December 1992, all samples were analyzed by GC.

Herbicides were separated and quantified by GC using a modified version of the method of Thurman et al. (1990). The sample bottles, sample collection procedure, chemicals, reagents, and processing procedure for herbicide residue determination by GC were described earlier (Lerch et al., 1995), with the following minor differences. A volume of 200 mL of sample was extracted on C¹⁸-solid phase extraction (SPE) columns, instead of 100 mL. One milliliter of terbutylazine surrogate at $100 \mu\text{g L}^{-1}$ in methanol was added to each groundwater sample after filtration, but before SPE extraction (Nash, 1990). The terbutylazine surrogate was used to estimate herbicide recovery.

The limits of detection (LOD = three times background

Table 2. Number of samples collected from glacial aquifer wells on Management Systems Evaluation Areas (MSEA) Fields and other Goodwater Creek Watershed (Field W) wells from 1991 to 1996.

Year	Quarter	Field			
		1	2	3	W
		no. of samples collected			
1991	Fall†	20(2)	18(0)	17(1)	18(5)
	Winter†	15(1)	12(3)	15(10)	14(10)
1992	Spring†	18(7)	17(6)	16(9)	19(12)
	Summer†	24(8)	18(14)	21(15)	19(13)
	Fall†	19(8)	15(9)	17(12)	15(12)
	Winter	18	16	19	19
1993	Spring	10	16	21	19
	Summer	25	18	22	19
	Fall	20	18	22	19
	Winter	14	13	20	11
1994	Spring	15	14	22	11
	Summer	25	21	23	19
	Fall	14	17	15	12
	Winter	11	12	15	11
1995	Spring	6	8	15	6
	Summer	5	9	14	6
	Fall	5	5	6	5
1996	Spring	25	19	21	19

† Numbers in parentheses are the number of samples analyzed by gas chromatography (GC). Beginning December 1992, all samples were analyzed by GC.

Table 3. Crop rotations and herbicide management on Missouri Management Systems Evaluation Areas (MSEA) fields.

Field	Year	Crop	kg ha ⁻¹	
			Atrazine	Alachlor
1	1991	Corn	2.3	2.8
	1992	Soybean	0.0	3.4
	1993	Corn	2.3	2.8
	1994	Soybean	0.0	3.4
	1995	Grain sorghum†	2.0	2.2
2	1991	Grain sorghum	1.8	2.2
	1992	Soybean	0.0	2.8
	1993	Grain sorghum	1.8	2.2
	1994	Soybean	0.0	2.8
	1995	Grain sorghum	1.8	2.2
3	1991	Corn	0.9‡	1.1‡
	1992	Soybean	0.0	1.4‡
	1993	Wheat	0.0	0.0
	1994	Corn	2.3	3.4
	1995	Soybean	0.0	0.0

† Weather delays in 1995 forced a switch to grain sorghum.

‡ Herbicides were applied over the crop rows (about half the field) at twice the listed rate.

noise) for herbicides in groundwater samples were 0.02 $\mu\text{g L}^{-1}$ for atrazine, DEA and deisopropylatrazine [2-chloro-(4-ethylamino)-6-(amino)-s-triazine; DIA], and 0.11 $\mu\text{g L}^{-1}$ for alachlor. Herbicides were identified by comparing their retention times with standards and knowledge of what pesticides were applied to Goodwater Creek Watershed. Herbicides in selected water samples were confirmed using mass spectrometry by an external contract laboratory. Metribuzin [4-amino-6(*tert*-butyl)-3-methylthio-*as*-triazine-5(4H)-one] (LOD = 0.06 $\mu\text{g L}^{-1}$) and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide] (LOD = 0.15 $\mu\text{g L}^{-1}$) were not detected and confirmed by mass spectrometry in the study.

A quality control program was instituted with field and laboratory blanks, field duplicates, and field and laboratory spikes. Herbicide recoveries for spikes averaged 97.5% for alachlor, 98.9% for atrazine, 85% for DEA, and 45.9% for DIA. The average relative percentage of differences for groundwater field duplicates were 1.5% for alachlor, 11.8% for atrazine, 12.6% for DEA, and 11.5% for DIA from 1993 to 1996. Quality control charts of duplicate samples showed that duplicate precision was concentration dependent and increased beyond $\pm 20\%$ below 0.2 $\mu\text{g L}^{-1}$. In an external quality assurance program, the laboratory performance was satisfactory for reciprocal analysis of standard reference materials and splits with an external quality assurance laboratory.

From May 1991 to September 1992, samples were analyzed using Enviroguard alachlor ELISA kits. Baker et al. (1993) reported that false positives with alachlor ELISA kits were caused by the alachlor metabolite ESA. ESA analyses (Aga et al., 1994) conducted on 20 of the September 1992 MSEA groundwater samples at the U.S. Geological Survey Organic Geochemistry Laboratory in Lawrence, KS, confirmed that ESA was present in the samples and caused the false positives.

March 1996 samples were analyzed with an Ohmicron magnetic-particle based ELISA (Ohmicron Corp., Newton, PA).

Cross-reactivity of ESA with the Enviroguard alachlor kit, based on the concentration that causes 50% inhibition of absorbance, was 2.3 times that of alachlor (Aga et al., 1994). Although the cross-reactivity of the Ohmicron ELISA (6.0) is different from the Enviroguard ELISA (Aga et al., 1994) they are comparable for percentage of detection data. Given that the September 1992 data was confirmed as ESA and that all samples were also analyzed by GC, false alachlor detections will be called ESA detections. ESA detections are defined here as having an ELISA concentration ≥ 0.2 and alachlor concentration $< 0.11 \mu\text{g L}^{-1}$ by GC.

Farming Systems, Crop Rotations, and Herbicide Treatment

About 90% of Goodwater Creek Watershed is cropped, with about 40 and 20% of the acreage planted in soybean [*Glycine max* (L.) Merr.] and either corn (*Zea mays* L.) or sorghum [*Sorghum vulgare* (L.) Moench.], respectively (Heidenreich and Vance, 1994). Crop rotations and associated herbicide management of the three MSEA fields are listed in Table 3. Descriptions of each farming system were reported previously (Ward et al., 1994). In the 5 yr before MSEA, the fields were treated with atrazine once (1986–1988) and were never treated with alachlor.

RESULTS AND DISCUSSION

Alachlor, Atrazine, and Atrazine Metabolites

Atrazine and DEA were detected more frequently than were alachlor and DIA (Table 4). Maximum concentrations of alachlor (0.14 $\mu\text{g L}^{-1}$) and atrazine (0.12 $\mu\text{g L}^{-1}$) were well below their maximum contaminant levels (MCL) for drinking water, which are 2 and 3 $\mu\text{g L}^{-1}$, respectively (USEPA, 1995). No MCLs have been established for DEA and DIA. The percentage of detections were ranked: DEA > atrazine > DIA. This ranking matches the mobility ranking of these compounds reported by Widmer and Spalding (1995) and Kruger et al. (1996). The infrequency of DIA detections is consistent with Mills and Thurman (1994) who concluded that in soil, deethylation proceeds more quickly than deisopropylation, so that DIA is formed more slowly and degraded more quickly than DEA.

The percentage of atrazine and DEA detections must be considered in the context of this study. Samples were collected repeatedly from the 87 wells over the course of 5 yr. Eleven and 13 wells had multiple detections of atrazine and DEA, respectively (Table 4). All wells were <15 m in depth and a disproportionate number of the detections were in the loess wells (Table 5), which were

Table 4. Summary of gas chromatography (GC) analyses for atrazine, alachlor, deethylatrazine (DEA) and deisopropylatrazine (DIA) from all 87 glacial aquifer wells.

Analyte	LOD†	Time period	Total samples	Total detections	Wells with detections		Maximum concentration $\mu\text{g L}^{-1}$
					no.	Wells with 2 or more detections	
Atrazine	0.02	Sept. 1991 to Mar. 1996	945	77	37	11	0.12
Alachlor	0.11	Sept. 1991 to Mar. 1996	945	4	4	0	0.14
DEA	0.02	Sept. 1994 to Mar. 1996	281	49	27	13	0.13
DIA	0.02	Sept. 1994 to Mar. 1996	281	4	4	0	0.03

† LOD, limit of detection.

Table 5. Summary of atrazine and deethylatrazine (DEA) analyses by glacial aquifer strata.

Analyte	Stratum	Wells	Total samples	Total detections		Wells with detections	Wells with 2 or more detections
				no.			
Atrazine	Loess	11	139	27	9	5	
	Till	76	806	50	28	6	
DEA	Loess	11	54	15	9	4	
	Till	76	227	34	18	9	

screened from 2.4 to 3 m below land surface. In addition, all the atrazine and DEA detections were at low concentrations, ranging from the LOD ($0.02 \mu\text{g L}^{-1}$) to 0.12 and $0.13 \mu\text{g L}^{-1}$, respectively.

One objective of the study was to determine the influence of herbicide management on groundwater quality in the study area. The percentages of atrazine and DEA detections at the three fields and the 19 additional glacial aquifer wells throughout the Goodwater Creek Watershed are summarized (Table 6). Field 3 received the least total atrazine of the three fields (Table 3), but had the highest percentage of atrazine and DEA detections. The two well nests that had the most frequent detections of atrazine and DEA were the 3A and 3B nests, which are located at summit positions of Field 3 (Fig. 3). These nests are under the very slowly permeable Mexico and Adco soils. In contrast there were no atrazine detections and few DEA detections at the 3D nest, which is under the moderately slowly permeable Vesser soil. The herbicide use history in the fields adjacent to the watershed wells is not known. All watershed wells are screened within the glacial till. The low atrazine and DEA concentrations and the percentage of detections in these watershed wells indicate that the results from the three MSEA fields are not underestimating the degree of herbicide leaching in the watershed.

The data (Table 6) demonstrate that management differences (Table 3) at the land surface did not control the extent of groundwater contamination in this study. The most significant factors affecting groundwater contamination are hydrology, herbicide chemistry, and the timing of herbicide application. Temporal changes in the percentage of atrazine and DEA detections in the field wells illustrate these combined effects (Fig. 5).

The importance of hydrology is illustrated by the temporal distribution of atrazine and DEA detections at Field 3 (Fig. 5). Atrazine and DEA detections increased during the fall-spring groundwater recharge periods, even following years when no atrazine was applied. The

atrazine detections in 1993 and 1994 represent continuing transport of 1991 atrazine. Although atrazine was applied on 20 April 1994 (2.3 kg ha^{-1}), the frequency of atrazine detections in June 1994 and September 1994 actually declined. The highest atrazine concentration ($0.12 \mu\text{g L}^{-1}$) was detected at the shallowest well at the 3B nest (Fig. 3) in June 1994. One recharge event occurred after herbicides were applied. The atrazine concentration in the field runoff on 28 to 30 April 1994, was as high as $1500 \mu\text{g L}^{-1}$ (Alberts et al., 1995). There were no other significant recharge events until October 1994. The increasing percentage of atrazine detections in Field 3 groundwater samples between December 1994 and March 1995 corresponds with the timing of groundwater recharge and consequent transport of 1994 atrazine. The percentage of DEA detections at Field 3 rose in December 1994 at the same time as the atrazine detections. The reason that Field 3 DEA detections decreased in March 1995 while atrazine detections did not is not known.

The Field 1 and 2 results document the importance of herbicide application timing relative to groundwater recharge to explain herbicide detections in groundwater (Fig. 5). Eleven of the 13 atrazine detections at Field 1 occurred in June 1993. Atrazine was applied to Field 1 on 14 May 1993. On 17 May 1993, 32.0 mm of rainfall produced 2.0 mm of runoff containing $>300 \mu\text{g L}^{-1}$ atrazine (Alberts et al., 1995). Since most of the 17 May 1993 rainfall infiltrated, the 11 detections in the June 1993 groundwater samples probably resulted from highly contaminated soil solution that percolated to the groundwater. The volume of water reaching the water table during a recharge event is small relative to the volume stored in the aquifer. Therefore even if the recharge water was as concentrated as the surface runoff, concentrations within the aquifer could be reduced to the observed concentrations of 0.02 to $0.05 \mu\text{g L}^{-1}$ by diffusion, dispersion, sorption, and degradation. In contrast to Field 1, Field 2 was not treated with atrazine

Table 6. Summary of atrazine and deethylatrazine (DEA) analyses from glacial aquifer wells on the three Missouri Management Systems Evaluation Areas (MSEA) fields and other Goodwater Creek Watershed (Field W) monitor wells.

Analyte	Time period	Field	Wells	Total samples	Total detections		Wells with 2 or more detections	Maximum concentration
					no.			
Atrazine	Sept. 1991† to Mar. 1996	1	25	218	16	14	2	0.05
		2	20	216	6	6	0	0.10
		3	23	278	46	10	7	0.12
		W	19	233	9	7	2	0.03
DEA	Sept. 1994 to Mar. 1996	1	25	66	8	7	1	0.05
		2	20	70	7	5	2	0.12
		3	23	86	30	11	10	0.13
		W	19	59	4	4	0	0.08

† All samples analyzed by gas chromatography (GC) beginning December 1992.

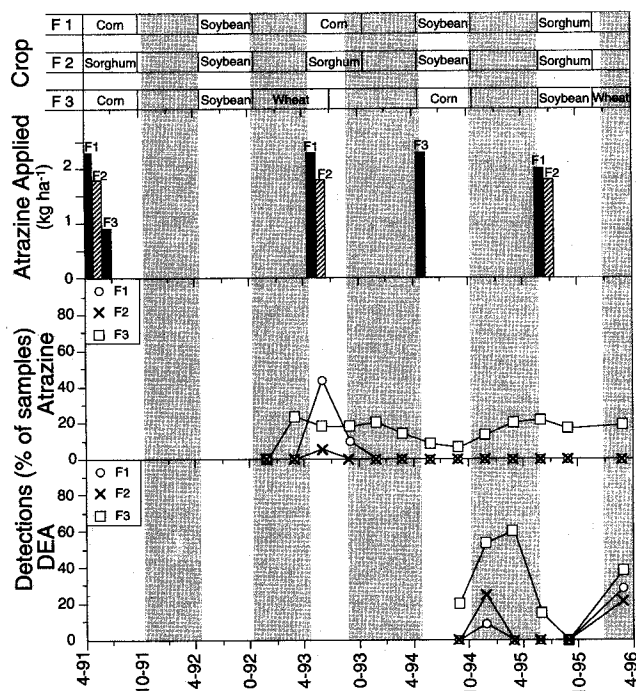


Fig. 5. Cropping history, atrazine use, and percentage of detections of atrazine and DEA from Management Systems Evaluation Areas (MSEA) fields from April 1991 to March 1996. The shaded portions of the graph correspond to the primary recharge periods shown in Fig. 5. F1, Field 1; F2, Field 2; and F3, Field 3.

until 25 May 1993, after the recharge event (Fig. 5). Only 2.0 mm of rainfall occurred between herbicide application and the June 1993 groundwater sampling at Field 2.

Other than the atrazine detections at Field 1 in June 1993, the occurrence of atrazine and DEA detections is chiefly a function of the fall-spring groundwater recharge. This suggests that preexisting sources of atrazine and DEA in the soil can be mobilized with recharge each year. To be leached through the claypan, compounds must not be tightly bound to the soil. We have no direct measure of available DEA or atrazine in the soil, however, we do have measurements of these compounds in surface water runoff from the fields. Table 7

Table 7. Average atrazine and deethylatrazine (DEA) concentrations in surface water runoff during the primary ground water recharge period (1 Oct. to 30 Apr.) from 1992 to 1996.

Field	Period	Days of runoff	Average concentration	
			Atrazine	DEA
			— $\mu\text{g L}^{-1}$ —	
1	10 Nov. 1992 to 26 Apr. 1993	24	0.06	0.13
	16 Oct. 1993 to 30 Apr. 1994	20	0.19	0.33
	20 Nov. 1994 to 27 Apr. 1995	19	0.10	0.07
	13 Nov. 1995 to 15 Nov. 1995	2	0.34	0.18
2	10 Nov. 1992 to 25 Apr. 1993	19	0.12	0.21
	16 Oct. 1993 to 30 Apr. 1994	17	0.26	0.32
	31 Oct. 1994 to 20 Apr. 1995	14	0.13	0.07
	10 Nov. 1995 to 1 Apr. 1996	6	0.32	0.20
3	10 Nov. 1992 to 25 Apr. 1993	16	0.06	0.16
	16 Oct. 1993 to 15 Apr. 1994	13	0.04	0.04
	20 Nov. 1994 to 18 Apr. 1995	14	0.45	0.97
	6 Mar. 1996 to 30 Mar. 1996	2	0.26	0.09

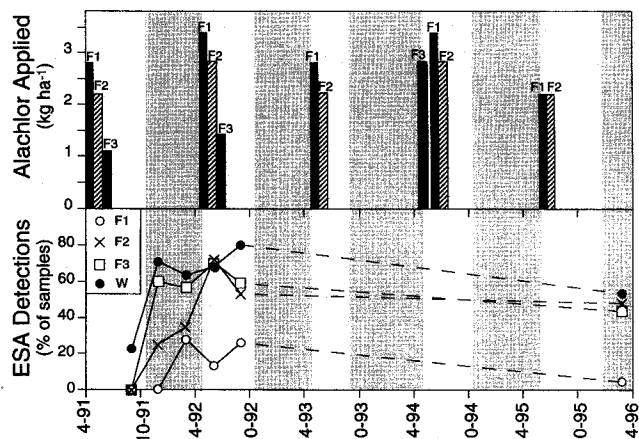


Fig. 6. Alachlor use and ESA (alachlor metabolite) detections at Management Systems Evaluation Areas (MSEA) field wells and other glacial aquifer monitor wells in Goodwater Creek Watershed. Enviroguard enzyme-linked immunosorbent assay (ELISA) used in 1991 to 1992. Ohmicron ELISA used in 1996. The shaded portions of the graph correspond to the primary recharge periods shown in Fig. 5. F1, Field 1; F2, Field 2; F3, Field 3; and W, Goodwater Creek Watershed.

lists the average concentration of atrazine and DEA in nongrowing season runoff from the MSEA fields for 1992 through 1996. The post application event on 28 to 30 April 1994, at Field 3 was not included in Table 7. Concentrations are definitely higher the first year after atrazine application; however, both DEA and atrazine were detected in the field runoff 1 yr and even 2 yr (Field 3, 1993–1994) after application. The values in Table 7 give a reasonable estimate of the concentrations available for leaching during the fall to spring recharge period. While the percentage of detections of atrazine and DEA may increase later with continued atrazine use, concentrations will probably not reach the $3 \mu\text{g L}^{-1}$ MCL for atrazine.

Ethane-Sulfonic Acid Metabolite of Alachlor

Alachlor was seldom detected in the study (Table 4). In contrast, the ethane-sulfonic acid metabolite of alachlor (ESA) was more frequently detected than atrazine, DEA, DIA, and alachlor. The temporal distribution of ESA detections for September 1991 to September 1992 and for March 1996 is summarized for the MSEA fields and other Goodwater Creek Watershed glacial aquifer wells (Fig. 6). The samples that had the four true alachlor detections were counted as ESA detections, because the ELISA concentration was at least twice that of the GC. As noted earlier, no alachlor had been used on the MSEA fields before 1991, and the history of alachlor use near the watershed wells is unknown; however, since ESA was detected in 20% of the watershed wells in September 1991, it is reasonable to assume that alachlor had been used elsewhere on the watershed. The large increase in detections between September and December 1991 coincides with fall groundwater recharge (Fig. 4). As with atrazine and DEA, Field 3 had the most ESA detections of the MSEA fields despite having been treated with the least

alachlor (Table 3). Percentage of ESA detections increased more slowly at Field 2 than at Field 3, but by June 1992, the percentage of ESA detections were similar at the two fields. Most of the Field 2 detections were at the well nests adjacent to the grass waterway (2C and 2E) and at the 2D nest, which is hydrologically down-gradient (despite being topographically upslope) from the 2E nest (Fig. 3). Field 1 had the fewest detections, despite having been treated with the most alachlor (Table 3). The fact that ESA was detected much more frequently than atrazine, DEA, DIA, and alachlor is consistent with the results of Kolpin et al. (1996) who found that ESA was the most frequently detected herbicide or herbicide metabolite in their sampling of wells throughout the midwestern USA.

The highest confirmed ESA concentration in the 20 September 1992 samples was $5.0 \mu\text{g L}^{-1}$. The more frequent detections and higher concentrations of ESA compared with the other analytes show that ESA was the analyte most likely to be transported to the groundwater and through the aquifer. Since no alachlor had been used on the MSEA fields before 1991 and ESA was the most readily transported analyte, the March 1996 samples were analyzed for ESA to trace water that had recharged the aquifer during the 5-yr study. Where alachlor use history is unknown (e.g., near the watershed wells), detection of ESA can only prove the presence of water that recharged the aquifer since 1969, when alachlor was first marketed. Samples collected in March 1996 were analyzed with an Ohmicron magnetic particle based ELISA. No ESA standards were available, so the samples were analyzed relative to alachlor standards. Actual ESA concentrations should be about six times the ELISA concentration based on ESA's cross-reactivity with the Ohmicron alachlor ELISA (Aga et al., 1994).

Boxplots of the March 1996 data show significant differences among the MSEA fields and the watershed in the ESA concentrations and frequency of detection (Fig. 7). The highest ESA concentration was in a watershed well located down-gradient from an irrigated field. The other wells in this nest also had high ESA concentrations. The high concentrations probably resulted from increased groundwater recharge due to irrigation. This does not require that recharge take place during irrigation, as irrigation water may simply be decreasing the soil moisture deficit that must be overcome before groundwater recharge occurs. ESA was more frequently detected and at higher concentrations at Fields 2 and 3 than at Field 1. The single detection at Field 1 was in the shallowest well at the 1D nest (Fig. 3). Apparently insufficient 1991 to 1996 recharge water was present for ESA to be detected ($\text{LOD} = 0.15 \mu\text{g L}^{-1}$) at the other 24 wells in Field 1.

To verify that ESA was formed at Field 1, runoff samples collected on 30 April 1996 from Fields 1 and 2 were analyzed by GC and ELISA. No alachlor was detected by GC in these samples ($\text{LOD} = 0.22$). The Ohmicron ELISA concentrations were 6.5 and $5.0 \mu\text{g L}^{-1}$ (not corrected for the cross-reactivity of ESA) for Fields 1 and 2, respectively. These high concentrations

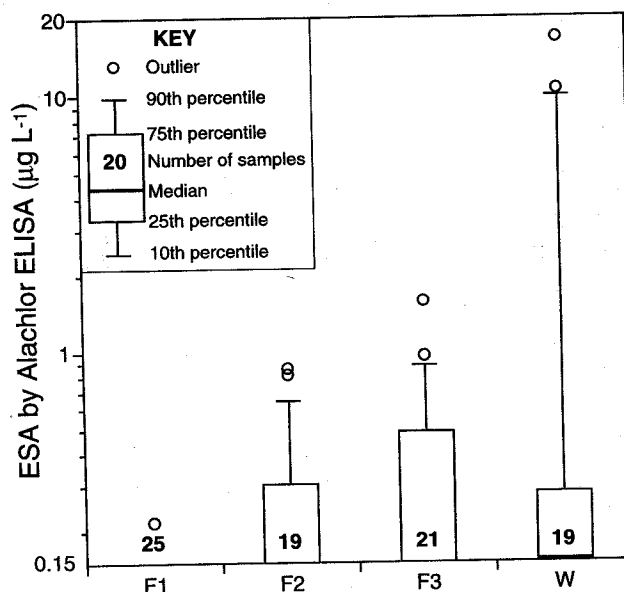


Fig. 7. Box-plots of March 1996 ESA (alachlor metabolite) concentration [by alachlor enzyme-linked immunosorbent assay (ELISA)] for Management Systems Evaluation Areas (MSEA) field wells and other glacial aquifer wells in Goodwater Creek Watershed. Concentrations not corrected for cross-reactivity of ESA with Ohmicron ELISA. F1, Field 1; F2, Field 2; F3, Field 3; and W, Goodwater Creek Watershed.

indicate not only the presence of ESA in the soil about 10 mo after the last alachlor application, but also demonstrates that ESA is more slowly degraded in the soil than are DEA and atrazine (Table 4). The fact that Field 1 had the fewest ESA detections in 1991 to 1992 and in March 1996, indicates that transport of herbicides to groundwater at this field is much less than at the other two MSEA fields.

Importance of Hydrology and Chemistry

Herbicide transport to the glacial aquifer is strongly controlled by hydrology and the chemistry of the herbicide or metabolite. No attempt was made in this study to determine if there were significant differences in herbicide sorption or degradation between the three fields. We believe that the observed differences in transport between the MSEA fields were primarily caused by spatial variations in hydrology. Field 3, which was treated with the least atrazine and alachlor, had the highest percent detections of atrazine, DEA, and ESA. Several hydrologic factors have combined to cause this. The greater topographic slope of Field 3 compared with the other fields (Fig. 3) has led to a higher hydraulic gradient and consequently faster flow within the till. The higher flow rate causes the water table to drop down through the loess and deep into the upper till paleosol. Transport of chemicals into the till is enhanced as the water table falls and the loess drains to field capacity. When the water table is within the loess, the vertical gradient between the wells screened in the loess and those in the upper till is much less at Field 3 than at Field 1. This indicates that the upper till paleosol does not retard vertical flow as significantly at Field 3

as at Field 1. Preferential flow paths within the upper till paleosol may be enhanced by wetting and drying associated with the rise and fall of the water table.

Field 1 is located at the primary divide between Goodwater Creek Watershed and the adjacent Youngs Creek Watershed, and has a broad flat summit typical of the claypan region. Field 1 also is located only a few miles from the divide between the Missouri and Mississippi Rivers. Guccione (1983) noted that there had been less erosion of the pre-Illinoian till at primary divides. The geomorphologic differences of lower topographic slope and greater preservation of the upper till paleosol probably caused the slower horizontal and vertical flow at Field 1 compared with Field 3.

Field 2 has hydrologic characteristics of both Fields 1 and 3. Herbicide and metabolite detections have primarily been in the 2C and 2E well nests. The upper till paleosol apparently retards flow less near these nests than at Nests 2A, 2B, and 2D, despite the proximity of all the nests. Another important factor may be the presence of the grass waterway. Excavation of the waterway may have removed some of the claypan and thus increased the probability of percolation. At times, water is ponded in the waterway. This increases the time available for percolation and consequent herbicide leaching, but also shows that the permeability of the bottom of the waterway is low enough for ponding to occur.

While the hydrologic variability explains differences in transport of herbicides and metabolites at the fields, it does not explain the low concentrations of DEA and atrazine that have been found, or the greater transport of ESA. These must be explained as functions of the chemistry of the compounds. A significant mass of an herbicide or herbicide metabolite will leach to the glacial aquifer only if high concentrations of the chemical are present in the soil when groundwater recharge occurs, and if the chemical is not so tightly sorbed to the soil particles that leaching is prevented. Most groundwater recharge occurs from October through April. By October, atrazine, DEA, and alachlor will have been degraded, so concentrations will be low in the soil solution. Over the course of a year, and especially over a 2- or 3-yr crop rotation, most of the recharge water will contain very low concentrations of these compounds. In contrast, the combination of mobility and stability (slower degradation) of ESA make it likely to be leached.

The concentration of any compound that reaches the water table can be reduced by several processes, including diffusion, dispersion, sorption, and degradation. While degradation will be far less than in surface soils, it can not be completely discounted (Chapelle, 1993). The combined effect of these processes in the loess will reduce the concentration that reaches the till. Flow and therefore, advective transport within the fractures of the till can be rapid; however, diffusion of solutes from the fracture to the matrix may be an important mechanism in attenuating transport.

CONCLUSIONS

Hydrologic variability between sites was more important to herbicide transport than were differences in her-

bicide application rates in this long-term study. The likelihood of a chemical leaching to groundwater depends on the recharge timing and the chemical concentration in the soil solution at the time of recharge. Herbicide or metabolite concentration in the soil solution depends on its chemical stability and mobility. ESA (an alachlor metabolite) was at higher concentrations and was more frequently detected than atrazine, DEA, DIA, and alachlor. Once formed, ESA apparently is less likely to be degraded than are the other compounds. It also is mobile because it will be transported as a poorly sorbed anion (Thurman et al., 1996). This combination of mobility and stability make ESA an excellent tracer in the hydrologic system. The concept that herbicide transport to groundwater depends on the chemical's mobility and concentration at the time of recharge is not limited to the chemicals in this study or to this study area. Chemicals that degrade before recharge, or that are tightly sorbed are unlikely to be leached. Chemicals that are in solution at the time of recharge are likely to leach. In this study area, most recharge occurred in the nongrowing season (fall-spring) when atrazine, DEA, DIA, and alachlor were significantly degraded or immobilized. In other soil and hydrologic settings, differences in recharge timing (natural or irrigation induced), sorptive capacity of the soil, and degradation rates could produce leaching of these or similar compounds. In this study area, leaching is most likely for compounds with persistence and mobility similar to ESA. Thurman et al. (1996) speculated that sulfonic acid metabolites of other chloroacetanilides may be important surfacewater contaminants. Judging by the ESA results in this study, these compounds also may be important groundwater contaminants. The groundwater quality impact of these chloroacetanilide metabolites, other herbicides, or metabolites will depend on whether their persistence and mobility are more similar to ESA or to atrazine, DIA, DEA, and alachlor.

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