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HERBICIDE MOVEMENT AND DISSIPATION AT FOUR MIDWESTERN SITES

Key Words: Atrazine dissipation, atrazine movement, alachlor dissipation, alachlor movement, ridge-tillage, nonpoint source pollution, regional management and evaluation

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ABSTRACT

This study was conducted to evaluate atrazine (2-chloro-4-ethylamino-6-isopropyl-1,3,5-triazine) and alachlor (2-chloro-N-(methoxymethyl)acetamide) dissipation and movement to shallow aquifers across the Northern Sand Plains region of the United States. Sites were located at Minnesota on a Zimmerman fine sand, North Dakota on Hecla sandy loam, South Dakota on a Brandt silty clay loam, and Wisconsin on a Sparta sand. Herbicide concentrations were determined in soil samples taken to 90 cm four times during the growing season and water samples taken from the top one m of aquifer at least once every three months. Herbicides were detected to a depth of 30 cm in Sparta sand and 90 cm in all other soils. Some aquifer samples from each site contained atrazine with the highest concentration in the aquifer beneath the Sparta sand (1.28 μg L^{-1}). Alachlor was detected only once in the aquifer at the SD site. The time to 50% atrazine dissipation (DT_{50}) in the top 15 cm of soil averaged about 21 d in Sparta and Zimmerman sands and more than 45 d for Brandt and

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Hecla soils. Atrazine DT_{50} was correlated positively with %clay and organic carbon (OC), and negatively with % fine sand. Alachlor DT_{50} ranged from 12 to 32 d for Zimmerman and Brandt soils, respectively, and was correlated negatively with %clay and OC and positively with % sand.

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropyl-1,3,5-triazine) and alachlor (2-chloro-N-(methoxy methyl)acetamide) have been widely used for weed control in corn/soybean rotations because they are relatively inexpensive and provide broad spectrum residual weed control. These herbicides and their metabolites have been found in many aquifers throughout the midwestern and north central regions of the United States (Burkart and Koplin, 1993; Juracek and Thurman, 1997; Klaseus 1988; Koplin et al., 1997; LeMasters and Doyle, 1989; Mehnert et al., 1995; Postle, 1989). Chemical contamination of wells and drinking water supplies, although not often above the United States Environmental Protection Agency (EPA) maximum contaminant levels (MCL) or long-term health advisory levels, is a continuing concern for public health officials, regulators, the United States EPA, farming communities, and the general public. Herbicide contamination of shallow aquifers directly affects agriculture's viability. In order to continue to use these efficacious, inexpensive herbicides, management techniques must be developed to minimize environmental problems and meet production goals.

Widespread herbicide application has been identified as a risk to groundwater. In 1998, 24 million kg of atrazine was used on about 70% of the United States corn crop (USDA, 1999), a considerable amount, but a 60% decrease from the 64 million kg of atrazine used in 1988 (Gianessi and Puffer, 1991). Alachlor usage in the United States in the early 1990's was about 14 million kg annually. This amount decreased to about 1.5 million kg in 1995 due to the switch from alachlor to acetochlor [(2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide]. The combined usage of these two chemicals exceeded 15 million kg in 1998 and was applied to about 30% of the corn and soybean crop (USDA, 1999).

Site characteristics influence aquifer vulnerability to herbicide contamination. Aquifers highly vulnerable to herbicide contamination are generally within a few meters of the soil surface, beneath sandy or shallow fine-textured soils, unconfined in unconsolidated material, or in areas with alluvial or karst topography (Juracek and Thurman, 1997; Klaseus, 1988; Koplin et al., 1997; LeMasters and Doyle, 1989).

Herbicide chemical properties and environmental characteristics of the site also influence an aquifer's susceptibility to contamination (Gustafson, 1989; Tillotson et al., 1995). For example, the longer a herbicide persists in the environment [measured as degradation half-life ($t_{1/2}$) or time to 50% dissipation (DT_{50})] the more herbicide is available over a longer time to move out of the root zone and into the aquifer. Also, if the herbicide is not sorbed to surface soil it may be available to leach to the aquifer. In turn, degradation and sorption are affected by climate, soil, and herbicide chemical properties (Bollag and Liu, 1990; Wolfe et al., 1990).

Individual parameters (i.e. sorption by soil type, degradation under various conditions, formulation effects etc.) that influence offsite movement have been documented extensively for atrazine and alachlor in field, greenhouse, and laboratory experiments (Koskinen and Clay, 1997). However, regional field studies seldom are conducted to evaluate common management practices on herbicide movement and dissipation although these studies provide a broader view of climate and soil type influence on these phenomena. The United States Department of Agriculture (USDA)-Management Systems Evaluation Areas (MSEA) Water Quality Initiative Northern Sand Plains project was designed to evaluate atrazine and alachlor movement and dissipation in four soil types under similar management conditions across the Northern Sand Plain Region of the midwestern United States. Common agronomic practices included corn (*Zea mays* L.)/soybean (*Glycine max* (L.) Merr.) rotation, ridge-tillage, and band applications of atrazine (corn) and alachlor (both crops). Results from individual projects have been reported previously (Albus and Knighton, 1998; Clay et al., 1998; Lamb et al., 1998; and Lowery et al., 1998). The objective of this paper is to compare and contrast the results observed across the region.

MATERIALS AND METHODS

Atrazine and alachlor movement and dissipation were monitored in a ridge-tillage management system with a corn/soybean rotation at four sites in Northern Sand Plain Region of the United States corn belt from 1991 to 1994. Specific soil characteristics, detailed plot descriptions, and agronomic management practices have been presented previously (Albus and Knighton, 1998; Clay et al., 1998; Lamb et al., 1998; and Lowery et al., 1998). Pertinent information for comparisons across sites is presented below.

Soils at the sites were a Zimmerman fine sand (mixed, frigid, Argic, Udipsamment) at Minnesota, Hecla sandy loam (sandy, mixed, frigid Oxyaquic Hapludoll) at North Dakota, Brandt silty clay loam (fine-silty, mixed, superactive, frigid Calcic Hapludoll) at South Dakota, and Sparta sand (sandy, mixed, mesic, Entic Hapludoll) at Wisconsin. Soils at Minnesota, North Dakota, and Wisconsin were sandy in texture throughout the profile (Table 1). Soil at South Dakota had a 1.5 m loess cap over sand and gravel outwash (Table 1). The saturated hydraulic conductivity, K_{sat}, for the A horizons are 12.8 cm hr^{-1} for Zimmerman fine sand (Wu et al., 1996), 0.5 cm hr^{-1} for Hecla sandy loam, 3.0 cm hr^{-1} for Brandt silty clay loam, and 27 cm hr^{-1} for Sparta sand (Wang et al., 1991). Average depth to the aquifer was 3.9, 3.3, 4.9, and 3.3 m for the Zimmerman, Hecla, Brandt, and Sparta soils, respectively.

Atrazine and alachlor sorption coefficients (K_d), measured by batch sorption techniques (Clay and Koskinen, 1990; Weber, 1995), for several horizon materials of each soil are reported in Table 1. K_{OC} values were calculated by dividing K_d by the soil organic carbon content.

TABLE 1

Location and Soil Characteristics of Four Northern Sand Plains Soils. K_ds are Partition Coefficients for Atrazine and Alachlor Determined by Batch Adsorption Techniques with the Units μmole g^{-1}. $K_{(OC)}$ Calculated by K_d/OC

							K_d		$K_{(OC)}$	
Site	Soil type	Horizon	% sand	%silt	%clay	% OC[a]	Atr	Ala	Atr	Ala
MN	Zimmerman	A	93.4	5.5	1.1	5.0	1.09[b]	0.87[a]	21.8	17.4
	Fine sand	B	95.8	3.3	0.9	3.5	1.09[b]	0.48[a]		
		C	98.2	1.2	0.6	1.0	0.37[b]	0.10[a]		
ND	Hecla sandy	A	69.2	17.6	13.2	2.2	4.66	2.01	211	91
	Loam	A2	73.3	15.0	11.7	0.6	-			
		C	75.1	15.0	9.9	0.1	-			
SD	Brandt silt	A	13.8	59.4	26.8	2.7	5.80	5.80[c]	214	214
	Loam	B	15.3	64.0	20.7	0.1	0.90	1.90[c]		
		C	85.8	8.9	5.3	0.05	0.20	0.40[c]		
WI	Sparta sand	A	95.7	2.7	0.9	0.4	0.59[d]	-	147	147[e]
		B	97.5	1.6	0.9	0.3	0.26[d]			
		C	99.7	0.1	0.2	0.01	0.02[d]			

[a] Organic carbon

[b] Rochette and Koskinen, 1996.

[c] Clay et al., 1997.

[d] Seybold et al., 1994.

[e] Assumes that alachlor sorption (not measured) is the same as atrazine sorption in this soil.

Individual plot size ranged from 0.06 ha (Sparta) to 1.8 ha (Zimmerman). Herbicides were applied as a preemergence band treatment over the row. Atrazine (4L formulation) was applied only to corn plots each year while alachlor (4E formulation) was applied to corn and soybean plots each year. Application dates ranged from April 26 to May 20 depending on site and year. Herbicide rates (based on local recommended rates) and herbicide application band width for each site are reported in Table 2. Rainfall (plus irrigation when applied) and growing degree days (GDD base 10^0C) are presented in Table 3. The GDD calculation is:

((day's high temperature + day's low temperature)/2) – 10

where the maximum high temperature is 30 and the minimum low temperature is 10.

At each site, soil samples were collected using zero contamination techniques (soil probes lined with acetate liners and probe tips methanol rinsed between samples) to minimize soil carryover and contamination between cores. Samples were taken prior to application, at application, and about 2, 5, 11, and 18 weeks after herbicide treatment (WAT). Duplicate samples were taken in the herbicide band (row) and outside the herbicide band (interrow). After collection, cores were sectioned into the 0 to 15-, 15 to 30-, 30 to 45-, 45 to 60-, 60 to 75-, and 75 to 90-cm depths and stored at -10 C until analysis.

Herbicides were extracted from soil and quantified by gas chromatography using techniques described by Sauer and Hatfield (1994) at the National Soil Tilth Laboratory (Ames, IA). QA/QC procedures included 5% duplicates, matrix blanks, and laboratory-spiked samples (Sauer and Hatfield, 1994). Recovery from soil was greater than 80% and the detection limit was 5 μg kg^{-1} for each herbicide.

Nested or multiport aquifer monitoring wells were installed at each site under each rotation. Water samples from each aquifer were taken at least once every three months to a maximum depth of 5 m below the aquifer surface. Herbicides and atrazine degradates, deethylatrazine (DEA)(6-chloro-N-1-methylethyl-1,3,5-triazine-2,4-diamine) and deisopropylatrazine (DIA) (6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine), were extracted from samples (ranging in size from 50 to 250 ml) using activated C-18 cartridges. After elution from the cartridge, chemicals were quantified using gas chromatography. Atrazine and alachlor recovery was greater than 90% with a detection limit was 0.1 μg L^{-1}. Atrazine degradate recovery ranged from 20 to 50%, therefore only presence/absence data are discussed. Hydroxy metabolites of atrazine were not included in the analysis.

Atrazine and alachlor dissipation half-lives (DT_{50}) (the net effect of degradation and transport processes) were calculated for the 0- to 15-cm depth in the banded area by site-year assuming first-order kinetics using soil herbicide concentrations from 0 to 11 WAT. Alachlor soil concentrations were averaged over data from both crop areas whereas atrazine soil concentrations were from corn only.

TABLE 2

Atrazine and Alachlor Application Rates and Band Widths Used at Each Location from 1991-1994

		Atrazine application rate				Alachlor application rate				
Site	Soil type	1991	1992	1993	1994	1991	1992	1993	1994	Band width
		kg ha^{-1}								% or row
Minnesota	Zimmerman fine sand	1.7	2.0	1.7	1.7	2.2	2.7	2.2	2.2	28
North Dakota	Hecla sandy loam	1.1	1.1	1.1	1.1	2.2	2.2	2.2	2.2	50
South Dakota	Brandt silty clay loam	1.2	0.9	1.2	0.9	2.2	2.2	2.6	2.2	33(1991), 50
Wisconsin	Sparta sand	0.8	0.8	0.3	0.3	1.7	2.8	1.7	0.7	33

TABLE 3

Growing Degree Days (GDD) and Total Water (Precipitation Plus Irrigation) from May through September 1991-1994

	GDD				Total water			
Location and soil type	1991	1992	1993	1994	1991	1992	1993	1994
	(base 10 C)				(cm)			
MN – Zimmerman fine sand	1327	1013	1019	1278	61.2	51.5	59.2	48.3
ND - Hecla sandy loam	1410	1171	1118	1328	49.5	42.4	49.9	44.6
SD – Brandt silty clay loam	1273	933	986	1131	47.5	43.6	52.1	41.1
WI – Sparta sand	1524	906	1334	1346	64.9	68.2	79.4	66.6

Gustafson (1989) combined persistence and mobility measurements to assess the potential of a chemical to leach to an aquifer. The equation is:

$$GUS = \log_{10}(t_{1/2}) * (4 - \log_{10}(K_{OC}))$$

where GUS is a groundwater ubiquity score. A score of <1.8 indicates a nonleaching chemical, a score of between 1.8 and 2.8 indicates a transition chemical, i.e. one that may leach, and a score >2.8 indicates a leaching chemical. Using the dissipation DT_{50} values instead of the $t_{1/2}$, the GUS index was calculated by herbicide, site, and year.

Analysis of covariance with appropriate F values was used to determine if differences in dissipation rates occurred between years and sites. Correlations (r) between DT_{50} and soil texture (% sand, silt, and clay) and OC were determined by year as well as across years. Correlations between DT_{50} and GDD and rainfall (plus irrigation) were determined by site across years.

RESULTS AND DISCUSSION

Climate - 1991-1994

GDD and precipitation from May to September varied between the states and years (Table 3). Two out of four years (1991 and 1994) were close to normal for GDD and precipitation based on the 30-yr average for each respective site. Both 1992 and 1993 were cooler (10 to 20% less GDD) and wetter than each site's 30-yr average.

South Dakota site had the fewest GDD in 1991, 1993, and 1994, whereas, Wisconsin had the most GDD in these same years. The warmest year based on GDD was 1991 at every site.

Wisconsin was the wettest site all four years with total water amounts (precipitation plus irrigation from May to September) ranging from about 65 to 80 cm. The North Dakota (Hecla) and South Dakota (Brandt) sites were driest with total water amounts ranging from 41 to 52 cm. The South Dakota site was not irrigated in any year, whereas about 22 cm of irrigation water was applied in 3 out of 4 years at the Wisconsin site (in 1993 only 6.3 cm was applied).

Herbicides in Soil

The highest concentrations of atrazine and alachlor were in the top 15 cm of soil in the treated area (row) (Figures 1 and 2). Herbicides moved horizontally from the band although total recovered amounts accounted for less than 10% of the amounts applied. Herbicide amounts detected below the band in the 15- to 30-cm and 30- to 90-cm depths accounted for less than 5% and 2%, respectively (data not shown). Table 4 presents the total number of samples taken per depth, the percentage of detections per depth, and the average concentration of herbicide in samples containing herbicide. For example, 21% of the samples taken from the 15- to 30-cm depth of the Sparta sand contained atrazine (average concentration of samples with detectable atrazine levels was 14.7 $\mu g\ kg^{-1}$), whereas 2% of the samples from the 30- to 90-cm depth contained atrazine (average concentration 5.9 $\mu g\ kg^{-1}$) (Table 4). Generally, the Brandt silty clay loam had the greatest

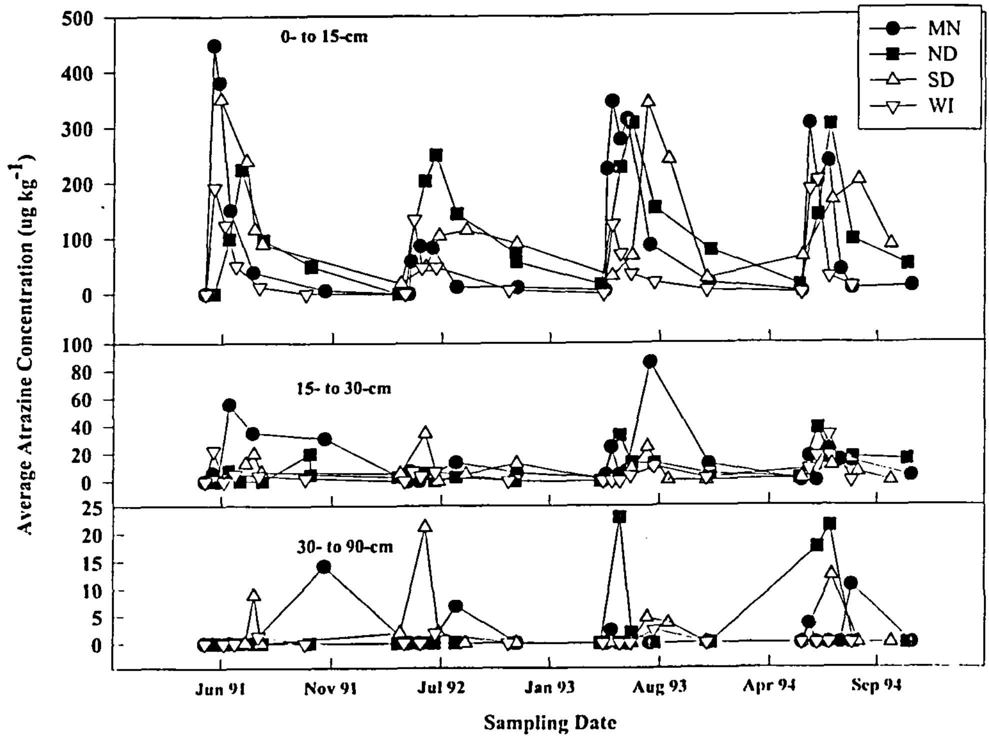

FIGURE 1
Average atrazine concentration (μg kg^{-1}) in soil cores from corn plots below the treated band area at four midwestern sites in the 0- to 15-, 15-to 30-, and 30-to 90-cm soil depths from 1991 to 1994. Samples were taken preapplication, 2, 5, 11, and 18 weeks after application. The detection limit for atrazine was 5 μg kg^{-1}.

concentrations of both herbicides at deeper depths whereas, the Sparta sand had no alachlor detections and fewest atrazine detections in the 30- to 90-cm depth under the treated area (Table 4).

Herbicides moved laterally and were detected in interrow areas (Table 4). Herbicide amounts accounted for about 3% of applied herbicide (data not shown). Drift into the interrow at the time of application or transport with water or soil particles moving from the row to the interrow may have been the major transport mechanisms (Clay et al., 1994).

In other studies, little or no herbicide has been detected in soil below the surface 0.5 m of soil when applied at rates recommended on the label. For example, at an Ohio site, neither atrazine nor alachlor were detected below the surface 15 cm of soil (Workman et al., 1995) due to low rainfall during the study period (1991 and 1992). Weed et al. (1998) reported that leaching was only a minor component of alachlor dissipation, whereas it's short half-life was the major factor controlling dissipation.

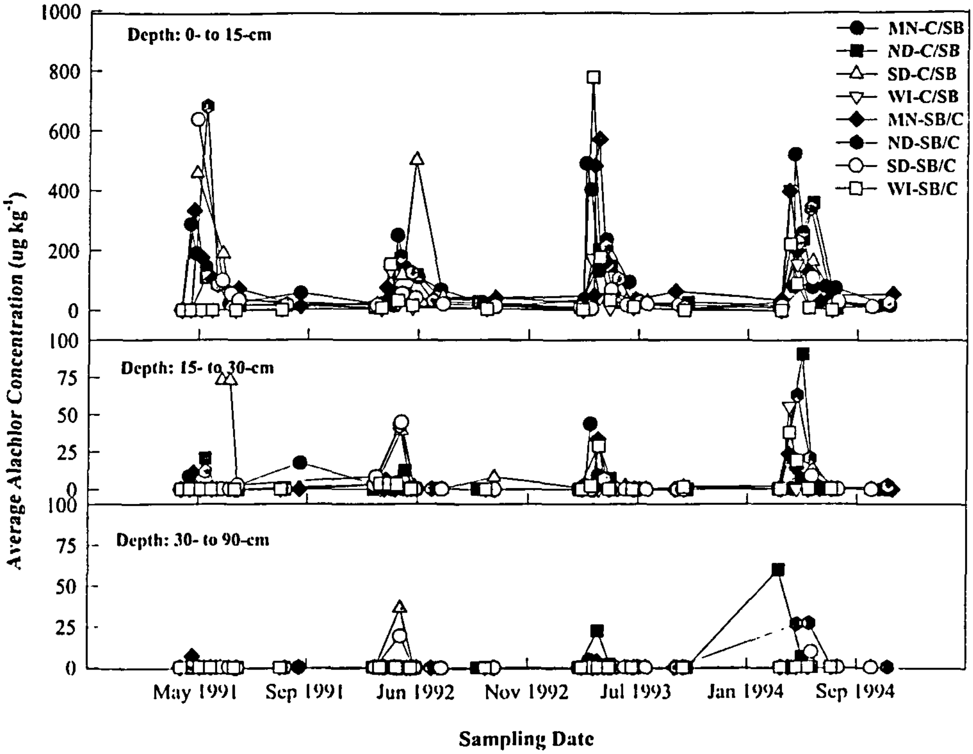

FIGURE 2

Average alachlor concentration (μg kg^{-1}) in soil cores from corn and soybean plots below the treated band area at four midwestern sites in the 0- to 15-, 15-to 30- and 30-to 90-cm soil depths from 1991 to 1994. Samples were taken preapplication, 2, 5, 11, and 18 weeks after application. The detection limit for alachlor was 5 μg kg^{-1}.

Herbicides in Aquifer Samples

Although not detected in soil at deep depths, herbicides were detected in the aquifer. This anomaly may be due to: 1) the herbicide detection limit being much lower in water than soil (0.1 μg L^{-1} versus 5 μg kg^{-1}); 2) higher recovery of herbicides from water than soil (90% versus 80% from fresh residues); 3) bound nonextractable herbicide residues on soil resulting in lower than 80% recovery; or a combination of these reasons.

Alachlor was detected only once in a South Dakota (Brandt) aquifer sample. Atrazine was detected in groundwater samples from the top 1 m of the aquifer at all four sites each year although time and amount detected varied within and between sites (Table 5). The amounts detected were always below the U.S. EPA MCL. Soil texture, time of sampling, and total water applied influenced when atrazine was detected in the aquifers. Atrazine was detected most often in summer samples (taken within the first 4 weeks after application) (Table 5) with the lowest concentration in aquifer

TABLE 4

Percentage of Detections and Mean Herbicide Concentrations of Atrazine and Alachlor in Treated and Untreated Areas Averaged Over All Sampling Periods and Years

		Atrazine				Alachlor			
		Treated		Untreated		Treated		Untreated	
Location and soil type	Depth	Detects	Conc	Detects	Conc	Detects	Conc	Detects	Conc
	cm	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}
MN – Zimmerman fine sand[a]	0-15	77	86.8	6	16	96	149	13	4.1
	15-30	56	15.1	0	0	31	13.1	0	0
	30-90	5	4.9	0	0	3	4.6	0	0
ND – Hecla sandy loam[a]	0-15	81	93.3	74	24.6	90	97.6	32	28.6
	15-30	36	15.6	6	6.8	19	34.8	4	5.8
	30-90	6	9.1	4	7.4	6	16.1	2	6.9
SD – Brandy silty clay loam[a]	0-15	98	91.6	92	39.7	93	89.9	70	87.7
	15-30	45	15	29	14.4	24	35.7	9	10.2
	30-90	13	8.3	7	6.6	9	23.9	1	18.2
WI – Sparta sand[a]	0-15	50	60.9	21	12.4	55	105	18	22.7
	15-30	21	14.7	1	5.4	11	31.9	2	8.8
	30-90	2	5.9	0	0	0	0	0	0

[a] Total number of samples per site was 52 at MN, 140 at ND, 108 at SD, and 130 at WI.

TABLE 5

Number of Detections and Average Atrazine Concentration in the Top 1m of Groundwater Sampled Quarterly, 1991-1994

		Winter		Spring		Summer		Fall	
Site- soil type	Year	Detections	Conc	Detections	Conc	Detections	Conc	Detections	Conc
		no.	μg L^{-1}	no.	μg L^{-1}	no.	μg L^{-1}	no.	μg L^{-1}
MN- Zimmerman fine sand	1991	0	--	1	0.01	1	0.01	6	0.02
	1992	5	0.01	8	0.01	0	--	0	--
	1993	5	0.01	1	0.01	3	0.01	6	0.01
	1994	7	0.02	2	0.01	3	0.01	5	0.01
ND – Hecla sandy loam	1991	0	--	0	--	0	--	0	--
	1992	0	--	0	--	0	--	0	--
	1993	0	--	2	0.31	0	--	0	--
	1994	0	--	1	0.18	1	0.07	0	--
SD – Brandt silty clay loam	1991	0	--	0	--	0	--	0	--
	1992	0	--	0	--	20	0.27	13	0.26
	1993	10	0.47	10	0.26	7	0.45	4	0.18
	1994	0	--	0	--	0	--	0	--
WI – Sparta sand	1991	0	--	2	1.06	3	1.28	2	0.49
	1992	6	0.48	11	0.26	10	0.17	7	0.17
	1993	13	0.26	8	0.18	12	0.1	0	--
	1994	0	--	0	--	0	--	0	--

samples below the Zimmerman sand and the highest concentration in aquifer samples below the Sparta sand. Atrazine degradates were detected in aquifer samples from Sparta and Zimmerman sand sites. DEA was detected more frequently than DIA.

Less herbicide was sorbed to sand than sorbed to fine-textured soil types allowing more herbicide to leach (Table 1). In addition, more water can drain through sand than clay because of higher saturated hydraulic conductivity. Cumulative drainage below the root zone of Sparta sand is about 40% of the total water input (Fermanich et al., 1996) compared to 22% of the total precipitation that recharges the aquifer below the Brandt silty clay loam (Bender[1], personal communication). Even when the rate of applied atrazine was reduced from 0.84 (1991 and 1992) to 0.28 kg ha^{-1} (1993) on the Sparta sand, atrazine was still present in many of the aquifer samples. Atrazine detections in the aquifer below the Brandt soil were unexpected because of higher clay and OC contents and higher sorbed amounts compared with these parameters at other sites. However, 16 cm of rain fell in August and September of 1992 and 24 cm of rain fell in May and June of 1993 contributing to atrazine leaching to the aquifer. Event-based sampling of the aquifer (i.e. after a rain or irrigation event) versus sampling by date can contribute to differences in chemical detections in the aquifer. For example, samples collected within 1 to 2 d after rainfall generally had more atrazine detections than samples collected later (data not shown). In a laboratory study, atrazine did not degrade readily ($t_{1/2}$>250 d) in aquifer material below the Brandt soil (Clay, unpublished data) indicating another mechanism of dissipation, most likely dilution.

Herbicide Dissipation

The dissipation rate (DT_{50}) varied by herbicide, soil type, and year (Tables 6 and 7). Dissipation can be attributed to many processes including microbial or chemical herbicide transformations, degradation, volatilization, movement from treated to untreated areas, or combinations of these and other factors.

Atrazine dissipated fastest in the Zimmerman and Sparta sands with an average DT_{50} of about 21d for the 4 years (Table 6). This DT_{50} is 10 to 12 d faster than the rate reported for atrazine on Ontario sandy soils by (Bowman 1990, 1991). The atrazine DT_{50} for the Sparta sand also was much faster than the laboratory calculated $t_{1/2}$ (which is due to only degradation/chemical transformation processes) of 72 d (Wietersen et al., 1993). Faster field dissipation rate than laboratory degradation rate may be due to rapid herbicide movement out of the sampling zone and into soil below 90-cm or into the aquifer (observed with high amounts seen in water samples).

Atrazine DT_{50} values averaged 66 d for Hecla sandy loam over the 4 years (Table 7). This rate is longer than that reported for a MN sandy loam (21 d) (Koskinen et al., 1993), but similar to a rate reported for an Australian sandy loam (62 d) (Stork, 1997). Atrazine DT_{50} for the Brandt silty clay

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[1] Alan Bender. SDSU Climatologist, Ag. Engineering, Brookings, SD.

TABLE 6

Atrazine Dissipation Rate (DT_{50}) and Groundwater Ubiquity Score (GUS) for Four Midwestern Sites

Year	MN- Zimmerman fine sand			ND – Hecla sandy loam			SD - Brandt silty clay loam			WI - Sparta sand		
	DT_{50} (d)	r^{2a}	GUS^b	DT_{50} (d)	r^{2a}	GUS^b	DT_{50} (d)	r^{2a}	GUS^b	DT_{50} (d)	r^{2a}	GUS^b
1991	19	0.96	3.4	64	0.97	5.2	39	0.86	2.7	-	-	---
1992	19	0.81	3.4	81	0.90	5.2	39	0.71	2.7	23	0.52	3.1
1993	27	0.81	3.8	85	0.99	5.2	--	-	-	30	0.59	2.5
1994	20	0.71	3.4	48	0.43	4.6	75	0.34	3.1	17	0.79	2.7
Mean	21	0.75	3.6	67	0.79	5.0	47	0.53	2.8	22	0.70	2.5

[a] r^2 is based on slope of regression line used for calculation of half-life dissipation rates. The r^2 values are significant at the 0.05 level when $r^2 > 0.65$.

[b] GUS is a groundwater ubiquity score (Gustafson, 1989). Chemicals with scores <1.8 are considered nonleaching chemicals, scores above 2.8 are considered leaching chemicals, score ≥ 1.8 and ≤ 2.8 are transition chemicals.

TABLE 7
Alachlor Dissipation Rate (DT_{50}) and Groundwater Ubiquity Score (GUS) for Four Midwestern

Sites

Year	MN- Zimmerman fine sand			ND – Hecla sandy loam			SD - Brandt silty clay loam			WI - Sparta sand		
	DT_{50}	r^{2a}	GUS^{b}	DT_{50}	r^{2a}	GUS^{b}	DT_{50}	r^{2a}	GUS^{b}	DT_{50}	r^{2a}	GUS^{b}
	(d)			(d)			(d)			(d)		
1991	34	0.51	4.2	17	0.94	2.5	17	0.93	2.1	-	-	---
1992	41	0.90	4.5	21	0.84	2.7	53	0.83	2.9	12	0.68	2.0
1993	24	0.69	3.8	16	0.98	2.5	40	0.92	2.7	15	0.59	2.2
1994	24	0.68	3.8	16	0.82	2.4	25	0.86	2.3	10	0.93	1.8
Mean	31	0.59	4.1	17	0.88	2.5	32	0.90	2.5	12	0.75	1.9

[a] r^2 is based on slope of regression line used for calculation of half-life dissipation rates. The r^2 values are significant at the 0.05 level when $r^2>0.65$.

[b] GUS is a groundwater ubiquity score (Gustafson, 1989). Chemiclas with scores <1.8 are considered nonleaching chemicals, scores above 2.8 are considered leaching chemicals, score ≥ 1.8 abd ≤ 2.8 are transition chemicals.

[c] Calculated based on the assumption that K_{oc} for alachlor = K_{oc} for atrazine.

TABLE 8

Correlation of Soil Factors with Atrazine and Alachlor Dissipation from the 0 to 15-cm Depth

	Atrazine					Alachlor				
Soil factors	1991	1992	1993	1994	Mean	1991	1992	1993	1994	Mean
% clay	0.10[a]	0.99	0.05	0.96	0.87	0.99	-0.67	-0.99	-0.99	-0.99
% silt	-0.21	0.91	-0.27	0.82	0.67	-0.94	-0.40	-0.98	-0.93	-0.90
% sand	0.12	-0.94	0.17	-0.87	-0.74	0.97	0.49	0.99	0.96	0.94
%OC	0.36	0.99	0.28	0.99	0.96	-0.98	-0.82	-0.94	-0.98	-0.99

[a] Significant at $p = 0.05$ when $r = \pm 0.88$.

loam averaged 47 d, similar to the 53 d rate reported for a clay loam soil under ridge-tillage (Gaynor et al., 1992).

When combined over soil types, atrazine DT_{50} in the top 15 cm of soil was not correlated to any measured soil parameter in 1991 and 1993 (Table 8). However, in 1992 and 1994, atrazine DT_{50} was correlated negatively with % sand, and positively correlated ($p \leq 0.05$) with % clay, silt, and OC. Atrazine DT_{50} and OC content also showed positive correlation when data were averaged over all years. The positive correlation indicates that atrazine remained in surface soil for a longer time in soils with higher clay, silt (in 2 out of 4 yr), and OC content. Atrazine dissipation was negatively correlated ($p = 0.05$) with GDD in the Zimmerman and Hecla and in the Sparta ($p = 0.1$) soils indicating faster dissipation rates in warmer years most likely due to increased microbial degradation (Walker et al., 1992 and Capri and Walker, 1993).

Slower atrazine dissipation in sandy loam and silty clay loam soils could be related to increased sorption (atrazine K_d positively correlated with % clay and OC; $r=0.84$; $p=0.1$) to surface soil or decreased microbial degradation rates in surface soil, or both. For example, when atrazine is sorbed to soil, microbial degradation decreased even in the presence of atrazine degrading microbes (Radosevich et al., 1996). Conversely, the negative correlation of atrazine dissipation with % sand may indicate greater movement out of 0- to 15-cm depth (through leaching or runoff) or faster degradation, or both.

Alachlor DT_{50} values generally were lower than those for atrazine. Alachlor mean DT_{50} values were similar among years for the Sparta and Hecla soils with mean DT_{50} values of 12 and 17 d, respectively. However, alachlor DT_{50} values were highly variable in the other two soils and ranged from about 23 (1994) to 41 (1992) d for the Zimmerman and 17 (1991) to 53 (1992) d for the Brandt. Alachlor DT_{50} and $t_{1/2}$ rates have been reported to be faster than those for atrazine. Alachlor $t_{1/2}$ values in the 0- to 30-cm soil depth have been reported as fast as 3 d (Weed et al., 1998). Alachlor DT_{50} values previously reported range from 17 (Workman et al., 1995) to 56 d (Negre et al., 1992).

The relationships between alachlor DT_{50} and soil parameters differed from those of atrazine (Table 8). When DT_{50} data were examined within a year, correlations were not significant ($p \leq 0.05$) between alachlor DT_{50} and any soil factor in 1992. However, in the other three years and across all four years, alachlor DT_{50} was correlated positively with % sand and negatively correlated with % silt, clay, and OC. The negative correlation with silt, clay, and OC indicates that as these factors increase, alachlor DT_{50} decreases. Alachlor DT_{50} also was negatively correlated ($p = 0.1$) with GDD in the Sparta and Brandt soils.

Soil herbicide concentrations did not change between 11 wk (August sampling) and 18 wk (October sampling) indicating that little dissipation or degradation occured. The biphasic dissipation phenomena for atrazine and alachlor has been reported previously (Weed et al., 1995; Gan et al., 1995; Sorenson et al., 1993, 1994, 1995; Workman and Nokes, 1998).

Groundwater ubiquity scores >2.8 for atrazine in the Zimmerman and Hecla soils all 4 years would indicate that atrazine has a high potential to leach in these soils (Table 6). In the case of the Zimmerman soil, the low K_{OC} was the factor that that caused the high GUS value. The high GUS value for the Hecla soil was due to the length of time atrazine persisted in the soil. Atrazine in the Brandt and Sparta soils would be a transition chemical (may or may not be leached). However, substituting the DT_{50} for the $t_{1/2}$, especially in the Sparta soil may be misleading. If the laboratory-derived $t_{1/2}$ of 72 d (Wietersen et al., 1993) is used in the equation then atrazine in the Sparta soil would be classified as a leaching chemical.

Alachlor, with a GUS value of about 4 in the Zimmerman sand, would be considered a leaching chemical. The GUS score of about 2.5 in the Brandt and Hecla soils indicated that alachlor would be a transition chemical. Since alachlor was only found in one aquifer sample, the GUS overestimated its leachability, especially in the Zimmerman sand. The field rate of alachlor dissipation in the Brandt soil (32 d) was similar to the laboratory derived $t_{1/2}$ (42 d) (Clay et al., 1997) and GUS scores using of these values would be similar.

Based on dissipation rates and leaching potential calculations, it is evident these herbicides applied to sandy soil types do not behave in a consistent manner. Organic matter, clay, and sand contents, and site-specific climatic conditions were variables that influenced atrazine and alachlor dissipation. Atrazine dissipation was slower than alachlor dissipation in Sparta, Brandt, and Hecla soils whereas dissipation rates were similar in the Zimmerman sand. Atrazine was found frequently in aquifer samples, although infrequently detected in soil below 30 cm. The differences between soil and aquifer results may be due to; preferential flow of the herbicide to the aquifer that is difficult to assess by soil sampling; too small a soil sample taken from lower depths to accurately detect the herbicide; leaching of the herbicide below the 90 cm sampling zone; or lower herbicide detection limit in water than soil resulting in a greater number of positive detections. Calculating the GUS index with the atrazine field dissipation rate was similar to field results at 3 out of 4 sites but overestimated the potential for alachlor to leach.

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