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ATRAZINE AND ALACHLOR DISSIPATION RATES FROM FIELD EXPERIMENTS

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ABSTRACT. *Chemical transport is being monitored in the root zone of three agricultural management systems at the Ohio Management Systems Evaluation Area (OMSEA). Atrazine and alachlor concentration data from soil cores taken to a depth of 0.9 m and partitioned into the increments of 0.0 to 0.15, 0.15 to 0.3, 0.45 to 0.6, and 0.75 to 0.9 m show the herbicides remained in the top 0.15 m of the profile during the 1991 and 1992 growing seasons. The slow movement of herbicides was partly due to below normal rainfall during the period. Since the herbicides have not been transported out of the soil profile, dissipation rates could be determined from the field observations.*

The data collected follow first-order kinetics in the dissipation of atrazine during the 1991 and 1992 growing season and of alachlor during the 1991 growing season for the two- to three-month period following chemical application. The computed rate constant, k, was 0.02 d^{-1} and half-life, $t_{1/2}$, was 35 days for atrazine for both years. A rate constant of 0.04 d^{-1} and half-life of 17 days were computed for alachlor. The degradation rates became slower with residence time in the soil as a result of decreased availability from sorption/binding in the soil. **Keywords.** *Atrazine, Alachlor, MSEA, Degradation, Transport.*

The Ohio Management Systems Evaluation Area (OMSEA) is one of five MSEA sites funded as part of the 1989 Presidential Water Quality Initiative (Ward et al., 1994). The other four project sites are located in Iowa, Minnesota, Missouri, and Nebraska. The goal of the MSEA program is to develop research and education programs that evaluate the productivity, profitability, and resulting water quality of established and alternative agricultural management systems. The Midwest was chosen as the target area for the MSEA program because it produces 80% of the nation's corn and soybeans and is a primary user of fertilizers and pesticides.

The OMSEA is located on the 260-ha Vanmeter farm in Pike County, Ohio. The site overlies the Scioto River Alluvial Valley Aquifer which was formed when fluvial and glacial-fluvial materials were deposited in the preglacial valley of the Teays River to a depth of 25 m. Silt loams (fluventic hapludolls) are the predominant soils in the valley. These soils extend to a depth of 1 to 3 m and overlie sand and gravel that make up the alluvial valley aquifer.

A primary focus of the OMSEA project is the evaluation of chemical movement through the soil profile. The chemicals of interest include atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide], metribuzin (4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one), and nitrogen. The management systems studied are a continuous corn system, a corn-soybean rotation, and a corn-soybean-wheat/vetch rotation. Atrazine was applied to the corn phase in all treatments. Alachlor was applied to the corn and soybean phases of all treatments and metribuzin was applied to the soybean phase of the treatments.

One of the objectives of the OMSEA chemical movement study is the persistence of agricultural chemicals in the root zone under field conditions. Atrazine has been studied extensively since its development in the late 1950s. Roeth et al. (1969) found the dissipation of atrazine to be a function of temperature, water content, and soil depth in a silty clay loam and a silt loam soil. In addition, they found atrazine to degrade two to three times faster in topsoil than in subsoil. Hall (1974) reported that 72% of atrazine was dissipated within one month of application in Pennsylvania soils. Approximately 12% of the atrazine remained in the soil five months after application. Harris et al. (1969) studied atrazine dissipation at three depths (3, 9, and 15 in.) in 12 soils and found dissipation to be a function of soil depth and temperature. Hurle and Walker (1980) described many of the factors that control the persistence of atrazine and other chemicals in

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soils including soil type, pH, chemical formulation, and adsorption.

Alachlor has been found to be less persistent than atrazine in soil profiles (Buhler et al., 1993). In their tests of drain tile outflow, alachlor was found in only 2% of samples whereas atrazine was detected in 97% of the samples taken in a six-year period. Eshel (1969) showed that alachlor could be leached in sand, sandy loam, or clay loam soils in a test where 5 cm of water was added to the soil surface of columns. Leaching was not shown in clay soils.

Dissipation of herbicides is often described by first-order kinetics (Hurle and Walker, 1980). The equation for a first-order reaction is:

$$C = C_0 e^{-kt} \quad (1)$$

where

C = concentration (mass/mass or vol/vol) after time t

C_0 = initial concentration

k = rate constant ($time^{-1}$)

The slope of a plot of logarithm of concentration against time should result in a straight line with a slope equal to the rate constant (Hurle and Walker, 1980). If the chemical dissipation truly follows first-order kinetics then the reaction is independent of initial concentration and a half life of the chemical, $t_{1/2}$, can be defined as:

$$t_{1/2} = \frac{0.6932}{k} \quad (2)$$

Guth et al. (1976) stated that field evaluations of half-life generally result in lower estimates than do laboratory determinations. This is thought to be due to the use of laboratory soils that are less biologically active.

The half-life is a common parameter used to compare dissipation rates of chemicals and is important in most models that simulate chemical transport. The GLEAMS and CREAMS models (Leonard and Knisel, 1989; Knisel, 1980) are examples of chemical transport models that use a constant value of half life for a chemical. Walker (1978) and Nicholls et al. (1982) found good agreement between observed and measured chemical concentrations with models that allowed the rate constant to be determined as a function of soil temperature and soil water content.

Soil samples have been taken at regular intervals since the start of data collection activities in 1991 at the OMSEA. The purpose of this article is to present data on the persistence and dissipation of atrazine and alachlor in these soils over the two-year period, 1991 to 1992. These data represent baseline information about the behavior of agricultural chemicals in the soils at the research site before OMSEA management systems were fully developed. The data were used to determine a rate constant for these chemicals at the research site.

Procedure

The research site includes three large plots (10 ha) used for the evaluation of the three agricultural management systems on groundwater quality (Workman et al., 1991). Adjacent to the large plots are 18 small plots (0.4 ha) consisting of three replicates of each phase of the three management systems [continuous corn (C-C), corn-soybean (C-S or S-C), and corn-soybean-wheat (C-S-W, S-W-C, or W-C-S)]. The plots were assigned one of the six phases randomly within each of the three blocks of replicates. Pesticides were applied in early May of both years with the application rates presented in table 1. Pesticides were applied in a 0.25-m strip over the row in the corn-soybean-wheat rotation beginning in 1992, and were applied over the entire surface (broadcast) in the other rotations.

The tillage system for the continuous corn plots was chisel plow, disk, and harrow. The corn phase of the corn-soybean rotation was chisel plowed, disked, and harrowed in 1991 and was no-tilled into the soybean stubble in 1992. The soybean phase of the C-S rotation used the chisel plow, disk, and harrow tillage treatment for both years. The corn-soybean-wheat rotation was planted with the ridge-till system. The ridge-till system included two row cultivations throughout the vegetative period for corn and soybeans. The ridges were constructed in the fall of 1990. Farming operations were initiated in the spring of 1991.

To facilitate the selection of sampling locations, a grid was superimposed over the plots. A 30-m grid was used in the 10-ha plots and a 7.6-m grid was used in the 0.4-ha plots. Each grid point was numbered in a serpentine pattern. Three subsamples were removed from each plot during each sampling event. In order for the three sampling locations to be evenly distributed over the field, cluster sampling was used. The total number of grid points (55 for the replicate plots) was divided by the number of subsamples (three) to determine the number of grid points needed between each sample in a cluster (18 points in the replicate plots). The first sampling point was randomly selected, then the other two sampling points for a given sampling event were obtained by advancing along the serpentine pattern a predetermined number of points (18 and 36 points for the replicate plots). The clusters were sampled without replacement in each year. The large plots were sampled similarly, except different clustering algorithms were required.

Soil cores were taken from all plots approximately every two weeks during the growing season and monthly during the nongrowing season from within the row. The cores (22 mm in diameter) extended to a depth of 0.9 m and were encased in an acetate liner. The samples were stored in a freezer until processing. The cores were sectioned into intervals of 0.0 to 0.15, 0.15 to 0.3, 0.45 to 0.6, and 0.75 to 0.9 m, frozen, and shipped via overnight mail to the National Soil Tilth Laboratory (NSTL) in Ames, Iowa.

A robotics system was used at the NSTL to perform the extraction procedure. The procedure included centrifuging

Table 1. Application rates in kilograms of active ingredient per hectare (kg ai/ha) of atrazine and alachlor applied to the research plots in 1991 and 1992. Chemicals were banded over the row in the corn-soybean-wheat plots in 1992

Phase	Rotation	Atrazine 1991	Atrazine 1992	Alachlor 1991	Alachlor 1992
Corn	C-C	3.4	3.4	2.8	2.8
Corn	C-S & S-C	3.4	1.7	2.8	2.8
Soybean	C-S & S-C	0.0	0.0	2.8	2.8
Corn	C-S-W, S-W-C, & W-C-S	1.7	0.22	2.8	0.34
Soybean	C-S-W, S-W-C, & W-C-S	0.0	0.0	2.8	0.93
Wheat	C-S-W, S-W-C, & W-C-S	0.0	0.0	0.0	0.0

10 g of soil and 20 mL of extraction solvent for 10 min. The centrifuging was repeated after 14 mL of extraction solvent was added to the solution. The solution was evaporated and transferred to a C-18 cartridge activated with 2 mL of methanol followed by 2 mL of water. The herbicides were eluted with 2 mL of ethyl acetate containing terbuthylazine as an internal standard. The samples were analyzed with a gas chromatograph (Koskinen et al. 1991). The chemical concentrations were reported in micrograms of chemical per kilogram of soil (μg/kg). The detection limit was 5 μg/kg for atrazine and alachlor.

The surface horizons of the soils at the OMSEA site can be grouped into the textural classes of silt loam, silty clay loam, and sandy loam. A Level I soil survey conducted by the USDA-Soil Conservation Service during the first year of the project identified eight distinct soils in the research plots. The surface 0.3 m of the profile contained approximately 1.6% organic carbon, 24% clay, 55% silt, and 21% sand for the Huntington soil (fluventic hapludoll) and 1.3% organic carbon, 15% clay, 42% silt, and 43% sand for the Rossburg soil (fluventic hapludoll). These two soils were present over more than 50% of the treated area.

Figure 1 shows the monthly rainfall totals for 1991 and 1992 measured at the site and the long-term average rainfall totals based on 30 yrs of record at a nearby gage (Fisher et al., 1992). May, June, and July of 1991 were much drier and warmer than normal. The average maximum temperature during this period was 29.1° C and the average minimum was 15° C. The months of May and June of 1992 were near normal in rainfall totals. The July rainfall total of 181 mm for 1992 was 62 mm greater than the long-term average. Two rainfall events (10 July – 43.5 mm and 24 July – 58.2 mm) accounted for most of the total. The average maximum temperature for May, June, and July of 1992 was 25.1° C and the average minimum was 15° C. September and October rainfall totals were lower than the long-term average for both years. Overall, the rainfall totals for 1991 and 1992 were lower than normal.

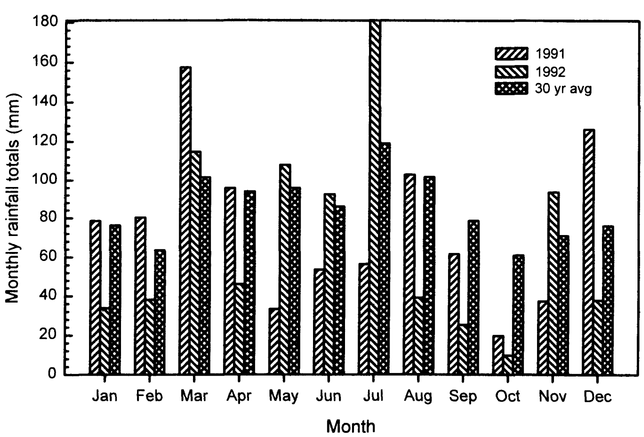

Figure 1–Monthly rainfall totals (mm) for 1991 and 1992 observed at the Ohio MSEA site. Long-term average rainfall totals are presented from 30 years of recorded data at Waverly, Ohio.

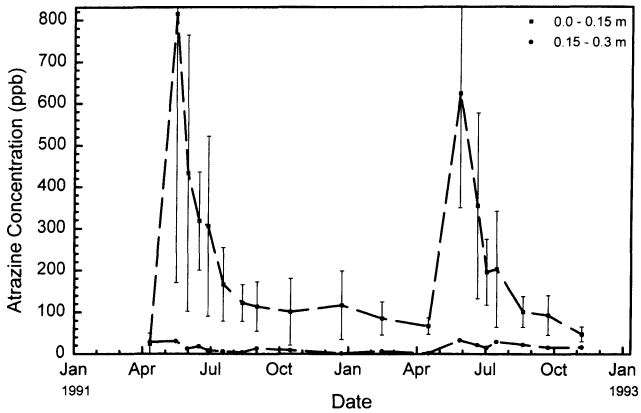

Figure 2–Mean atrazine concentration (μg/kg) in the 0.0 to 0.15 and 0.15 to 0.3 m depth increments for 1991 and 1992 in the continuous corn management system. Error bars represent the 95% confidence interval for the population mean at each sampling event.

Results and Discussion

Figure 2 shows the distribution of atrazine with depth in the continuous corn system and is typical of the depth distribution found for the other five phases. Error bars representing the 0.95 confidence interval for the population mean have been added to the 0.0- to 0.15-m data. Each data point represents the mean of 9 to 12 samples taken during a sampling event. All data points (except the initial baseline sampling event) show a statistically significant difference in atrazine concentration between the depths of 0.0 to 0.15 and 0.15 to 0.30 m at the 0.95 (most at 0.99) confidence level. Lines that describe atrazine concentrations at the depths of 0.45 to 0.6 m and 0.75 to 0.9 m fall below the line shown for the 0.15 to 0.3 m depth. Atrazine was applied to the continuous corn plots at a rate of 3.4 kg ai/ha in 1991 which would result in a concentration of approximately 1600 μg/kg of atrazine in the 0.0 to 0.15 m portion of the profile assuming no losses and uniform mixing in a soil with a bulk density of 1.4 g/cm^3. Volatilization, uneven application of the herbicide, and incomplete mixing of the sample reduce the ability to precisely determine the herbicide concentration in the soil. The herbicide was applied at planting (2 May 1991) and the first sampling date after planting was on 14 May 1991.

It is noteworthy that atrazine was routinely detected in the soybean-wheat plots at an average concentration of 5 to 8 μg/kg although no atrazine had been applied since 1989. The residual atrazine concentration remaining in the top layer of the soil over the winter (September 1991 to April 1992) was approximately 100 μg/kg in the continuous corn system. The residual level was approximately 50 μg/kg in the corn phases of the corn-soybean and corn-soybean-wheat rotations. First-order kinetics (eq. 1) would have predicted lower concentrations of herbicide to have remained in the profile during this period. Pignatello and Huang (1991) have discussed the possibility that herbicides diffuse into the soil matrix (termed slowly reversible fraction) and become less accessible with time. The 5 to 8 μg/kg of atrazine observed in the 0 to 0.15 m increment of the soil profile at the start of the experiment supports the presence of a slowly reversible fraction in the soil.

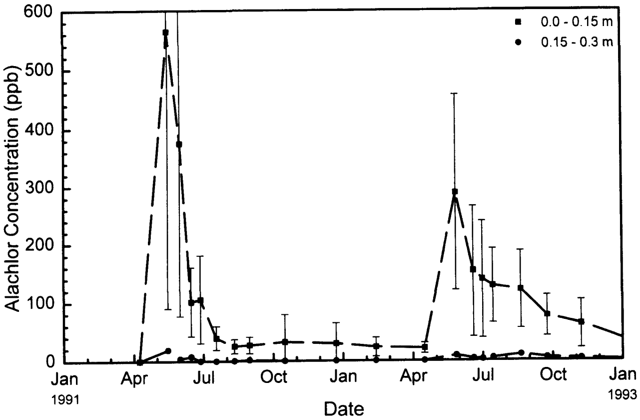

Figure 3–Mean alachlor concentration (μg/kg) in the 0.0 to 0.15 and 0.15 to 0.3 m depth increments for 1991 and 1992 in the continuous corn management system. Error bars represent the 95% confidence interval for the population mean at each sampling event.

Figure 3 shows the alachlor concentration measured in the continuous corn system during 1991 and 1992 and is typical of the results found in the other plots. Error bars representing the 0.95 confidence interval for the population mean have been added to the 0.0 to 0.15 m data. Most data points (except the initial sampling event) show a statistically significant difference in alachlor concentration between the depths of 0.0 to 0.15 and 0.15 to 0.30 m. The 1991 decay curves are very similar for all treatments. The 1992 decay curves differed in shape from the 1991 curves, however, a similar pattern was exhibited between treatments. The 1992 data resulted in a much more gradual dissipation of alachlor from the soil profile.

The chemical dissipation data from each phase of the management systems were modeled with the first-order kinetics equation (eq. 1). As described earlier, the slope of the line of a plot of natural logarithm of normalized concentration versus time is the negative of the rate constant, k. The computed rate constant, the associated half-life, and the R^2 of the line (forced through the origin) are presented in table 2 for each of the concentration-time curves fitted to data measured in 1991 and 1992. Equation 1 was only applied to the decay portion of the curve (usually the first 150 days or 7 sampling events after application) since both the atrazine and alachlor data decayed to a residual value after which first-order kinetics were not valid.

Rate constants averaged 0.02 d^{-1} for atrazine decay curves that had an R^2 greater than 0.95. The rate constants for these three curves were statistically equivalent at a significance level of 0.05. The corresponding half-life was 35 days. This is less than the half-life of 60 days that is typically reported for atrazine (Knisel, 1980). Nicholls et al. (1982) found a rate constant of 0.015 d^{-1} which is a half-life of 47 days in laboratory tests of atrazine dissipation. Walker (1978) measured atrazine half-life as a function of temperature and water content and found values that ranged from 16.5 days in a warm environment (30° C) to 209 days in a cold environment (5° C). An average half-life of atrazine for a temperature of 25° C was 27 days for 4 water contents ranging from 3.7 to 12.6%. The average maximum temperature for the period May through July was 29° C in 1991 and 25° C in 1992. The average minimum temperature for both years was 15° C. The decay curve for the corn phase of the corn-soybean system was dominated by a few very high observations that resulted in a higher predicted half life and a poorer fit to the exponential decay model.

The average value for the rate constant for alachlor was 0.04 d^{-1} for the 1991 curves with an R^2 greater than 0.95. The associated half-life was 17 days. This compares favorably to the reported half-life of 15 days (Knisel, 1980) in the literature. Four of the five decay curves in 1991 fit the assumption of first-order kinetics well with the exception of the decay curve for the corn phase of the corn-soybean system. There was no evidence that the slope differed at a significance level of 0.05. All decay curves measured in 1992 had longer half lives and lower R^2 values

Table 2. Rate constant, k (d^{-1}), and half-life, $t_{1/2}$(d), for the decay curves of atrazine and alachlor computed from soil cores taken during 1991 and 1992

	Atrazine 1991				Atrazine 1992			
Rotation	Crop	k	$t_{1/2}$	R^2	Crop	k	$t_{1/2}$	R^2
C-C	Corn	0.022	31	0.97	Corn	0.018	38	0.96
C-S	Corn	*	*	*	Soybean			
S-C	Soybean				Corn	0.013	54	0.88
C-S-W	Corn	0.019	36	0.98	Soybean			
S-W-C	Soybean				Wheat			
W-C-S	Wheat				Corn	0.015	45	0.88

	Alachlor 1991				Alachlor 1992			
Rotation	Crop	k	$t_{1/2}$	R^2	Crop	k	$t_{1/2}$	R^2
C-C	Corn	0.035	20	0.98	Corn	0.011	63	0.93
C-S	Corn	0.017	41	0.76	Soybean	0.018	38	0.95
S-C	Soybean	0.043	16	0.96	Corn	0.009	77	0.85
C-S-W	Corn	0.039	18	0.97	Soybean	0.021	33	0.88
S-W-C	Soybean	0.047	15	0.97	Wheat			
W-C-S	Wheat				Corn	0.017	41	0.65

* Data do not exhibit a peak concentration for the analysis.

than those measured in 1991. The slower dissipation of alachlor at the OMSEA in 1992 can be seen in figure 3.

Conclusions

The herbicides atrazine and alachlor have moved slowly through the soil profile at the OMSEA site during the 1991 and 1992 growing seasons. Chemical data from soil cores taken to depth of 0.9 m and partitioned into the increments of 0.0 to 0.15, 0.15 to 0.3, 0.45 to 0.6, and 0.75 to 0.9 m have shown that the herbicides have remained in the top 0.15 m of the profile. Neither year represented wet soil conditions that would have enhanced chemical leaching. Two possible leaching events occurred in July of 1992; however, no significant downward movement of the herbicides was observed. In addition, the chemicals seem to adsorb to the soil since the residual level of atrazine remained relatively high during the winter (50 to 100 μg/kg).

The data were shown to follow first-order kinetics in the dissipation response of atrazine during the 1991 and 1992 growing season and for alachlor during the 1991 growing season for the first 100 days following chemical application. The computed rate constant, k, and half-life, $t_{1/2}$ was 0.02 d^{-1} and 35 days for atrazine, respectively. A rate constant of 0.04 d^{-1} and half-life of 17 days were computed for alachlor. The five alachlor concentration-time curves for the 1992 growing season had longer measured half lives than the same plots in 1991.

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