Table of Contents

Louisiana State University Agricultural Center, H. Rouse Caffey, Chancellor
Louisiana Agricultural Experiment Station, Kenneth W. Tipton, Vice Chancellor and Director

MOVEMENT OF ATRAZINE AND NITRATE IN SHARKEY CLAY SOIL:

EVIDENCE OF PREFERENTIAL FLOW

D. C. Johnson,[1] H. M. Selim,[1] L. Ma,[1]
L. M. Southwick,[2] and G. H. Willis[2]

Introduction

Incidence of groundwater contamination by agrichemicals in the United States and elsewhere is of concern in terms of the health effects associated with chemical contaminants present in drinking water. This relatively recent concern has resulted in numerous environmental laws regulating the use of potentially harmful chemicals involved in agricultural production. The concern over agrichemical occurrence in water supplies will continue to drive a movement toward stricter regulation and broader enforcement of environmental laws. Thus, concern about soil and water quality has led to an increased interest in understanding processes of governing the mobility and retention of applied agricultural chemicals soils.

Mississippi River alluvial soils constitute the major agricultural soils in Louisiana. Sharkey clay is a heavy textured (montmorillonitic clay type) alluvial soil characterized by shallow water tables. Sharkey clay soil is subject to extensive swelling and shrinking during periods of water infiltration and redistribution. Very little work has been done to describe the leaching behavior of agricultural chemicals in heavy textured soils. It is postulated that in such soils two major transport processes of dissolved chemicals are dominant: one is the movement through the soil matrix, and the other is a rapid by-pass flow through soil macropores or shrinking-swelling cracks (Starr and Glotfelty 1990, Utermann et al. 1990). The latter is referred to as preferential flow. In a study of pesticide movement

---

[1] Former Graduate Student, Professor, and Research Associate respectively, Department of Agronomy, Louisiana Agricultural Experiment Station, Baton Rouge, LA 70803.
[2] Scientists, USDA-ARS, Soil and Water Laboratory, Baton Rouge, LA.

to subsurface drains in a silt loam soil, Kladivko et al. (1991) found that the arrival times to subsurface drains for atrazine, cyanizine, alachlor, and carbofuran were similar. These pesticides have significantly different retention characteristics (or K_d's), however. Similar mobility of pesticides having different K_d values was attributed primarily to by-pass or preferential flow in this soil.

In Sharkey clay soils, preferential or macropore flow is perhaps the dominant water flow path to subsurface layers and ultimately to the water table. The major objectives of this study were: (1) to quantify the mobility of atrazine and nitrates in a Sharkey clay soil in the presence of a shallow water table, and (2) to determine evidence of preferential flow patterns on the mobility of agricultural chemicals in such soils.

Background

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), which has been used for more than 30 years, is one of the most widely applied herbicides in the world today. It is applied to corn, sugarcane, millet, and horticultural crops for weed control. In south central Louisiana, atrazine is applied to about half of the acreage planted to sugarcane. The applied atrazine is retained by the soil matrix and is also susceptible to movement beyond the soil root zone to the groundwater. Atrazine has been detected in groundwater samples collected from agricultural lands (Muir and Baker 1976, Helling and Gish 1986, Southwick et al. 1992). Though atrazine concentration levels in the groundwater tend to be low, long persistence suggests that degradation is slow once atrazine reaches the water table and that it is for that reason subject to accumulation in ground water (Gu et al. 1992, Goswami and Green 1971). The lifetime health advisory level for atrazine in drinking water is 3 parts per billion (ppb).

Movement of atrazine in soils is subject to biological and chemical interactions within the soil root zone as well as the physical properties of the soil. Knowledge of atrazine retention behavior including adsorption-desorption and rates of degradation (half-lives) are prerequisites for predicting the potential mobility of atrazine in soils to the water table. The classical convective-dispersive equation for the transport of dissolved chemicals in soils is

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - \frac{v}{\theta} \frac{\partial C}{\partial z} - \frac{1}{\theta} \Sigma_i \psi_i \qquad (1)$$

where C is solute concentration in solution (g/ml), is soil-water content (cm^3/cm^3), D is the hydrodynamic dispersion (cm^2/h), v is water flow velocity (Darcy's flux density) (cm/h), z is soil depth (cm), and t is time (h). The term represents rates of (irreversible) chemical or biological degradation. The retardation factor R (dimensionless) is a measure of the extent of (reversible) adsorption-desorption and directly influences the mobility of dissolved chemicals in the soil profile. For R = 1, a solute is not retained by the soil and is thus considered highly mobile and nonreactive.

The extent of pesticide retention on soils are commonly described by the Freundlich isotherm

$$S = K_f\, C^n \tag{2}$$

where S is the amount of solute retained by the soil (g g^{-1}), K_f is a partitioning coefficient between the aqueous solute and that on soil surfaces (cm^3 g^{-1}), and n is an empirical parameter. The retardation factor R can be estimated from the Freundlich isotherm such that

$$R = 1 + (\rho/\theta) n K_f\, C^{n-1} \tag{3}$$

where ρ is soil bulk density (g/cm^3). Therefore, if R or K_f and n are known, the potential mobility of a pesticide in soils can be predicted. Since n is close to one for most pesticides, a linear isotherm is often used

$$S = K_d C \tag{4}$$

where the distribution coefficient K_d replaces K_f and R is thus simplified to

$$R = 1 + (\rho/\theta) K_d \tag{5}$$

One may regard K_d as a screening parameter for estimating the extent of retention and movement of pesticides in soils. The larger the K_d value, the more retarded the pesticide. In contrast, for nonreactive chemicals, e.g., chlorides or bromides (where K_d=0), R is unity.

For most pesticides, their retention capacity is directly correlated to the amount of soil organic matter; therefore, the value often reported in the literature is for K_{oc} rather than K_d. K_{oc} represents the “soil organic carbon sorption coefficient” and is defined as $K_{oc}=K_d/f_{oc}$, where f_{oc} is the weight fraction of organic carbon present in the soil. A comprehensive listing of K_{oc} values, solubilities, and half lives for several pesticides was compiled by Wauchope et al. (1992).

Nitrate is a highly mobile nitrogen form that is subject to plant uptake and various biological transformations and can move through the soil root zone and eventually into the groundwater. Due to its anionic state, nitrate ions that move below the root zone are often regarded as a nonreactive solute with little or no retardation (i.e., K_d=0 and R=1). In addition, there is increasing evidence that high concentrations of nitrate-N in shallow aquifers underlying major agricultural regions of the U.S. is due largely to agricultural activities. Therefore, the goal of nitrogen management practices must include minimizing nitrate leaching from agricultural activities to the groundwater.

Experimental Methods

Atrazine Retention:

A study of the extent of atrazine retention by Sharkey clay soil was carried out in the laboratory. Specifically, adsorption-desorption experiments were conducted to determine the amount of atrazine retained by the soil for a wide range of concentrations. The soil used was collected from the surface (0-2 inch) from an experimental site at the St. Gabriel Research Station (St. Gabriel, LA, Iberville Parish) of the Louisiana Agricultural Experiment Station. This soil contained 61% clay, 36% silt, and 3% sand; organic matter content was 1.7%, and soil pH was 6.48 (2:1 soil:water ratio). Atrazine retention was studied using the batch method where five atrazine (input) concentrations were used (0.5, 1, 2, 4,and 10 mg/L). Radioactive atrazine (^{14}C-UL-ring-labeled) was used as a tracer to monitor the extent of retention by the Sharkey soil. Sorption was carried out using the batch method where 5 g of Sharkey soil were placed in a 40-ml Teflon centrifuge tube. Ten milliliters of atrazine solutions were added into each tube and vortex mixed. The tubes were shaken for 24 hours and then centrifuged (2000rpm for 10 min). The supernatant was decanted and collected for analysis using liquid scintillation counting. Desorption or release of atrazine was carried out following varied incubation periods (0, 1, 2, 4, 8, 12, 16, 20, 24 d). The desorption procedure was the successive dilution method. Specifically, after the solution was decanted, each desorption step included the addition of 10ml atrazine-free 0.01 N $Ca(NO_3)_2$, vortex mixing, 24 hr shaking, and decanting of the supernatant. A total of 6 desorption steps (6 days) were carried out for each incubation period.

Field Investigation:

To quantify the mobility of nitrate and atrazine in Sharkey clay soils, sugarcane plots on a site with subsurface drains were used. In 1978, subsurface drains (4-inch diameter corrugated and perforated polyethylene tubes) were installed 1 m deep and at two drain spacings (5.5 and 10.9 m). The subsurface drains of each plot directed leachate into a single sump. The land was graded to about 0.2% slope. Water was pumped from the sumps through a water meter so that cumulative flow from the drains was recorded. An automatic sampler (Isco model 2700 autosampler) was installed in each sump to sample drainage effluent from the sumps. The autosamplers collected one 50-ml sample each time the sump was filled. Frequency of sampling of effluent drainage water was dependent on the amount and time of drainage outflow. Collected drainage water samples were stored in the laboratory and later analyzed for nitrate and atrazine concentrations. In addition, in each plot suction lysimeters (made of 1-bar porous ceramic cups 5 cm in diameter, cat. # 652, Soil Moisture Equipment Corp.) cemented into 4.8-cm diameter pvc pipe, were installed in duplicates. The lysimeters were placed 100 cm apart within a row at 30, 60, 90, 120, 150, and 180 cm soil depth. Suction lysimeters are commonly used to quantify the amounts of chemicals present in the soil solution at various depths during the growing season.

Atrazine (4L) was applied at the rate of 2 kg/ha. Atrazine applications were made on June 11, 1991, December 6, 1991, and June 22, 1992 using a tractor-mounted boom sprayer. Surface soil samples were collected to determine background atrazine levels immediately prior to each application. Surface soil samples were collected frequently up to 3 months following applications. Atrazine concentrations in surface soil samples ranged from 0 to 0.39 ppb prior to application.

Nitrogen (UAN, 32% nitrogen, 50:50 urea:ammonium nitrate) was injected into the soil each spring (June 6, 1991 and May 14, 1992) at a rate of 122 kg/ha. No other fertilizer applications were made on this soil. For Sharkey soil, phosphorus or potassium fertilizer application is not commonly recommended.

Drainage water and soil (top 2.5 cm) samples were periodically collected and brought to the laboratory for analysis. Water and soil samples were extracted for atrazine, and the extracts were analyzed using gas chromatography. Water samples were also analyzed for nitrate using ion chromatography.

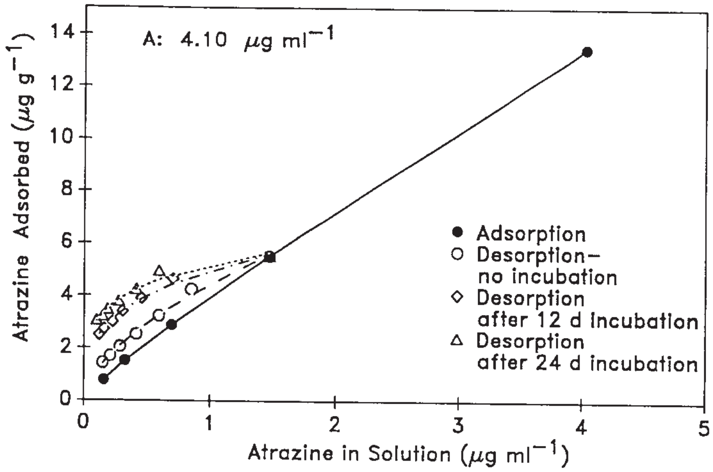
Results and Discussion

Atrazine Retention:

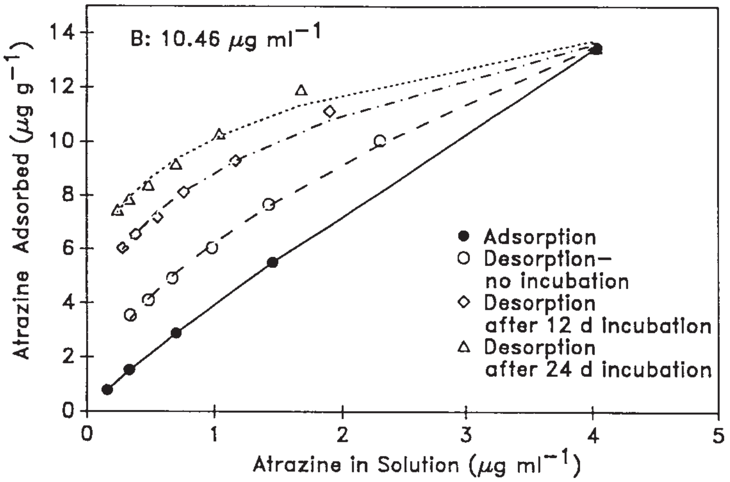
Atrazine retention (adsorption and desorption) results are shown in Fig. 1. The Freundlich model was capable of describing the adsorption isotherm (solid curve) and the family of desorption isotherms (dashed curves) at different incubation times. For adsorption, best-fit K_f was 3.963+0.031 cm^3/g, and n value was 0.877+0.007 with r^2 of 0.999. For desorption, K_f values were consistently higher (6.244 to 10.113) and n values lower (0.22 to 0.55) than that for adsorption. These results indicate that desorption isotherms deviated significantly from the adsorption

Figure 1. Atrazine adsorption and desorption isotherms for a Sharkey clay soil. Desorption isotherms (dashed curves) are for initial concentrations of (A) 4.10 g ml^{-1} and (B) 10.46 g ml^{-1}.

(1A)



(1B)

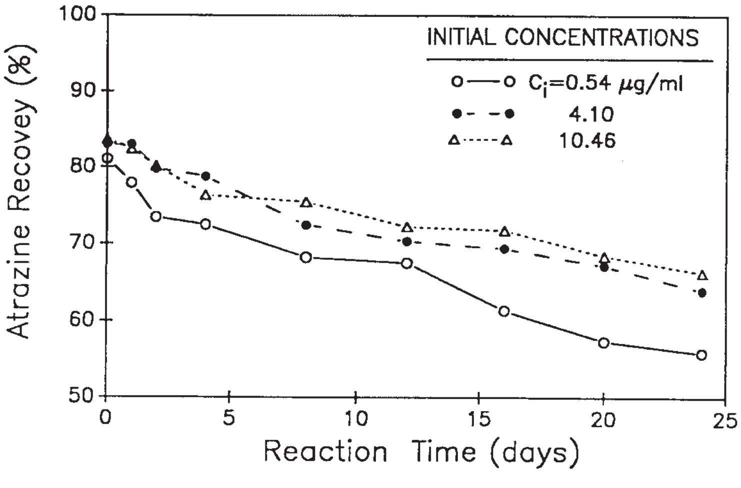


isotherm. Such a deviation is referred to as hysteresis. The extent of atrazine hysteresis was more pronounced as the incubation time increased.

An alternative approach to describing the adsorption isotherm results of Fig.1 is by use of the linear model (equation 4). Best fit K_d value was $3.421+0.105$ cm^3/g, and r^2 was 0.921. Subsequently, a value of K_{oc} of 347 cm^3/g was calculated based on organic carbon content. Wauchope et al. (1992) reported and average K_{oc} of 100 cm^3/g. The high K_{oc} value may be attributed to the high (montmorillonitic) clay content in this soil. Because of such high K_d or K_{oc}, it is expected that applied atrazine becomes strongly retained near the soil surface and is thus not susceptible to movement beyond the root zone. If we assume soil bulk density of 1.2 g/cm^3 and a soil moisture content ranging from 0.4 to 0.6 cm^3/cm^3, we estimate R values ranging from 7.8 to 11.2. For such R values, the movement of a dissolved chemical is expected to be restricted and significantly retarded compared with a nonreactive solute (R=1).

Total amount of atrazine recovered (in percent) versus incubation time for selected initial concentrations (C_is) is shown in Fig. 2 and indicates that atrazine recovery decreased with incubation time. In addition, atrazine recovery was lowest (56%) for C_i of 0.54 g ml^{-1} and highest (67%) for C_i of 10.46 g ml^{-1}. The decrease in (percent) recovery as the C_i's decreased agrees with other studies. It is conceivable that

Figure 2. Total atrazine recovery following six desorption steps versus reaction (incubation) time for three initial concentrations (C_i) of 0.54, 4.1 and 10.46 g/ml.



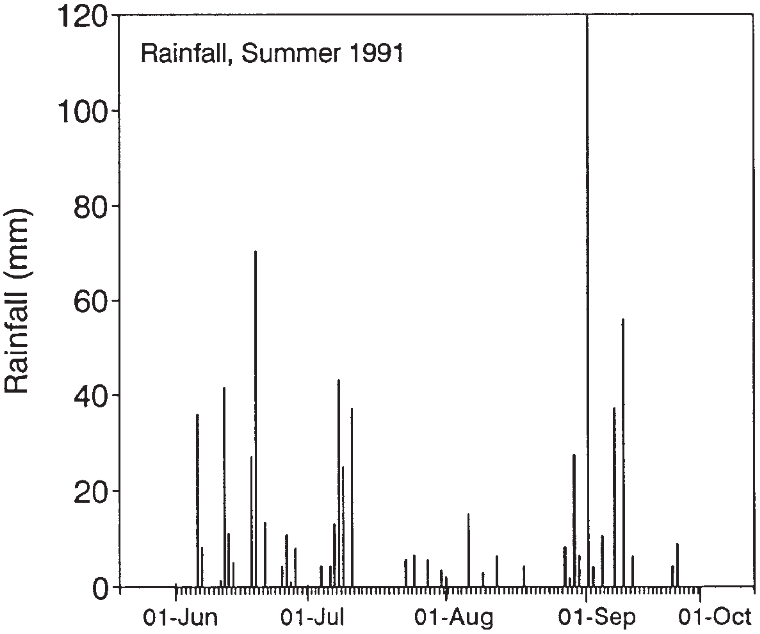
kinetic reversible and irreversible mechanisms are responsible for incomplete recovery and hysteresis, making it difficult to predict at-razine mobility in soils. Possible mechanisms include formation of atrazine-soil complexes that are not easily desorbable into solution and chemical (nonbiological) and microbial degradations. In fact, chemical degradation of atrazine by hydrolysis to hydroxyatrazine has been shown to be the primary degradation pathway by several investigators.

Atrazine in Subsurface Drainage Outflow:

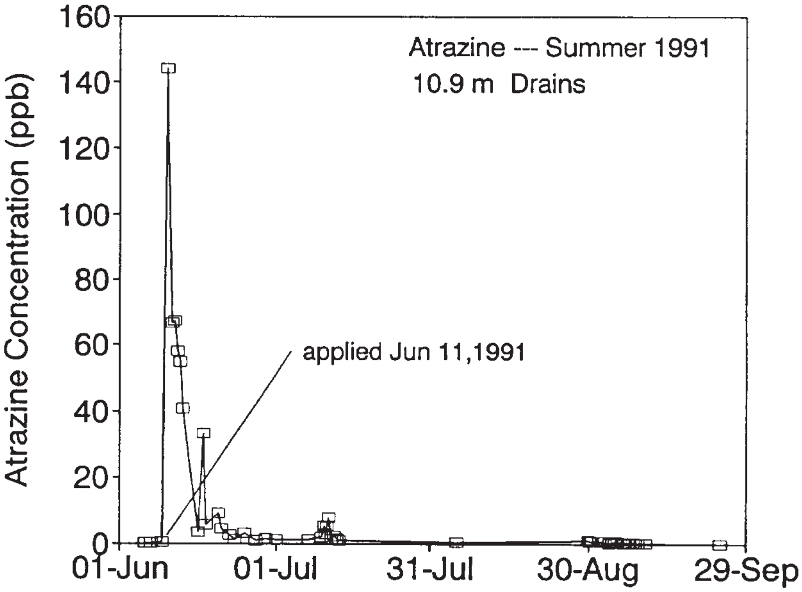
Following both summer and winter applications, atrazine exhibited a sudden elution behavior in response to the first rainfall event. The first rainfall event occurred within 1 day after atrazine was applied in the summer of 1991 (Fig. 3) and was of sufficient amount (4.2 cm) to result in a high rate of drainage outflow. Within a few hours of the onset of rain, atrazine was observed at high concentrations in drainage water. Peak concentrations were 144 and 125 ppb for the 10.9- and the 5.5-m drains,

Figure 3. (A) Rainfall distribution for summer 1991. Atrazine concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

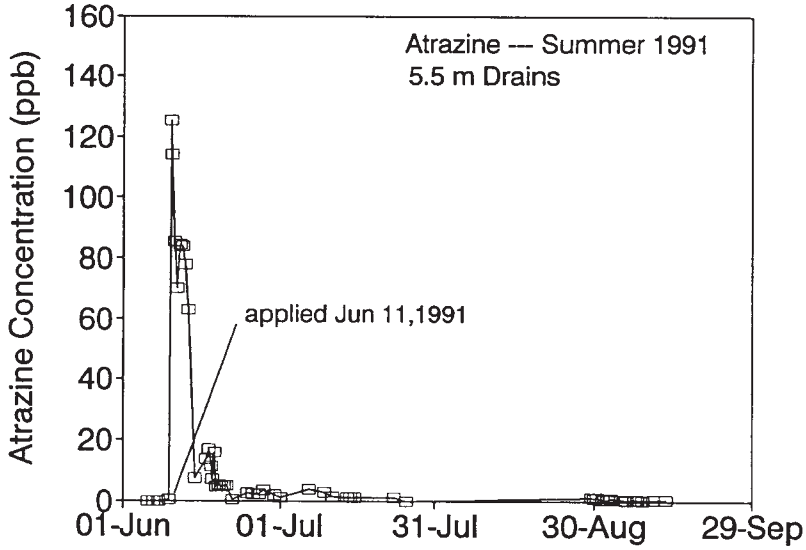
(3A)



(3B)


Atrazine --- Summer 1991
10.9 m Drains
applied Jun 11,1991
Atrazine Concentration (ppb)
160
140
120
100
80
60
40
20
0
01-Jun
01-Jul
31-Jul
30-Aug
29-Sep

(3C)


Atrazine --- Summer 1991
5.5 m Drains
applied Jun 11,1991
Atrazine Concentration (ppb)
160
140
120
100
80
60
40
20
0
01-Jun
01-Jul
31-Jul
30-Aug
29-Sep

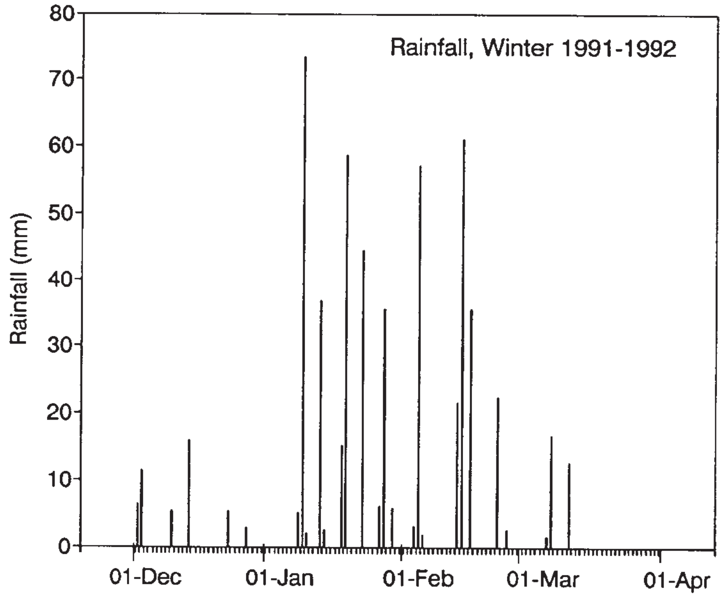
respectively (Fig.3).

During the winter sampling season, the first rainfall occurred 3 days following application (Fig. 4). The rainfall was only 0.5 cm, but sufficient to leach atrazine to the drains (16 and 1.5 ppb in the 5.5 and 10.9 m drains, respectively). A subsequent rainfall event (1.6 cm) occurred 8 days following atrazine application and resulted in leaching concentration peaks of 81 and 67 ppb for the 5.5- and 10.9-m drains, respectively.

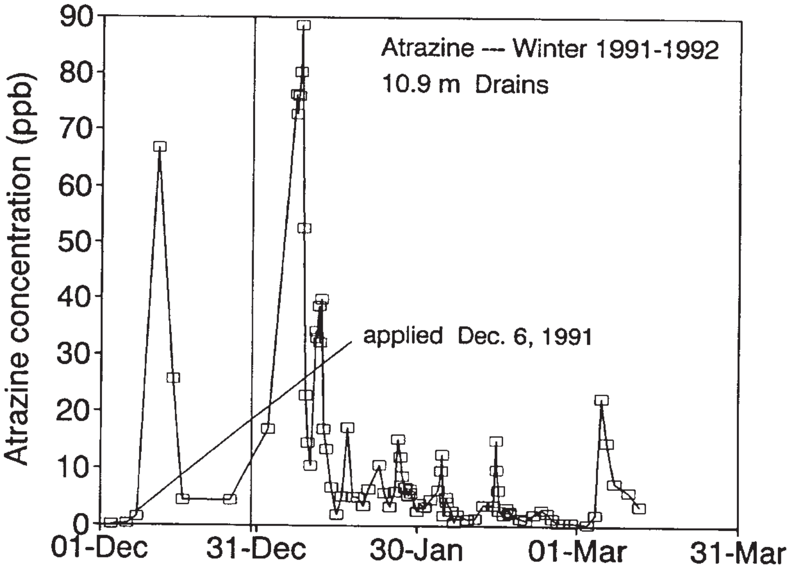
The concentration peaks corresponding to the first heavy rainfall and drainage occurring in the winter season were considerably smaller than those observed in the summer 1991 season (figs. 3 and 4). These results are consistent with findings from previously published studies that an initial, low intensity, simulated rain can move solutes into the soil matrix, thereby reducing the potential for transport in macropores during subsequent rainfall events (Shipitalo et al., 1990). During summer 1991, without an "initial low intensity storm," the first heavy rainfall produced atrazine

Figure 4. (A) Rainfall distribution for winter 1991-1992. Atrazine concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

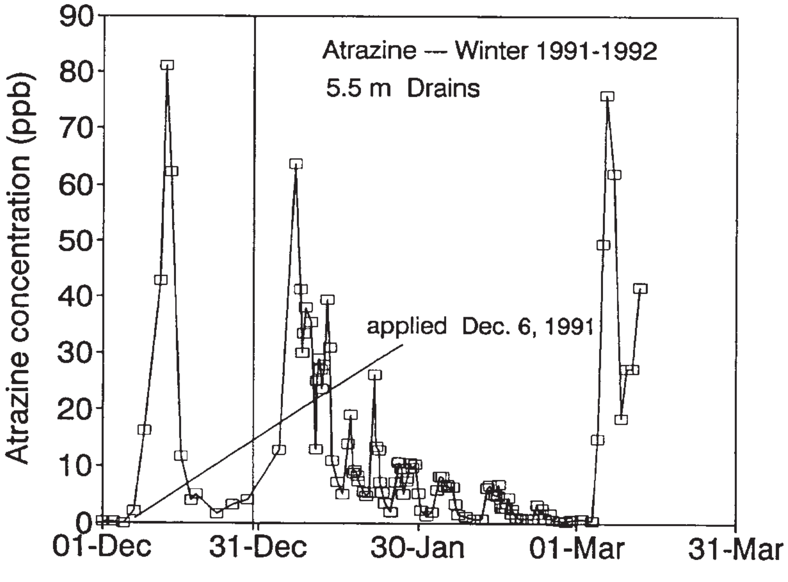
(4A)



(4B)


Atrazine --- Winter 1991-1992
10.9 m Drains
applied Dec. 6, 1991
Atrazine concentration (ppb)
0
10
20
30
40
50
60
70
80
90
01-Dec
31-Dec
30-Jan
01-Mar
31-Mar

(4C)


Atrazine --- Winter 1991-1992
5.5 m Drains
applied Dec. 6, 1991
Atrazine concentration (ppb)
0
10
20
30
40
50
60
70
80
90
01-Dec
31-Dec
30-Jan
01-Mar
31-Mar

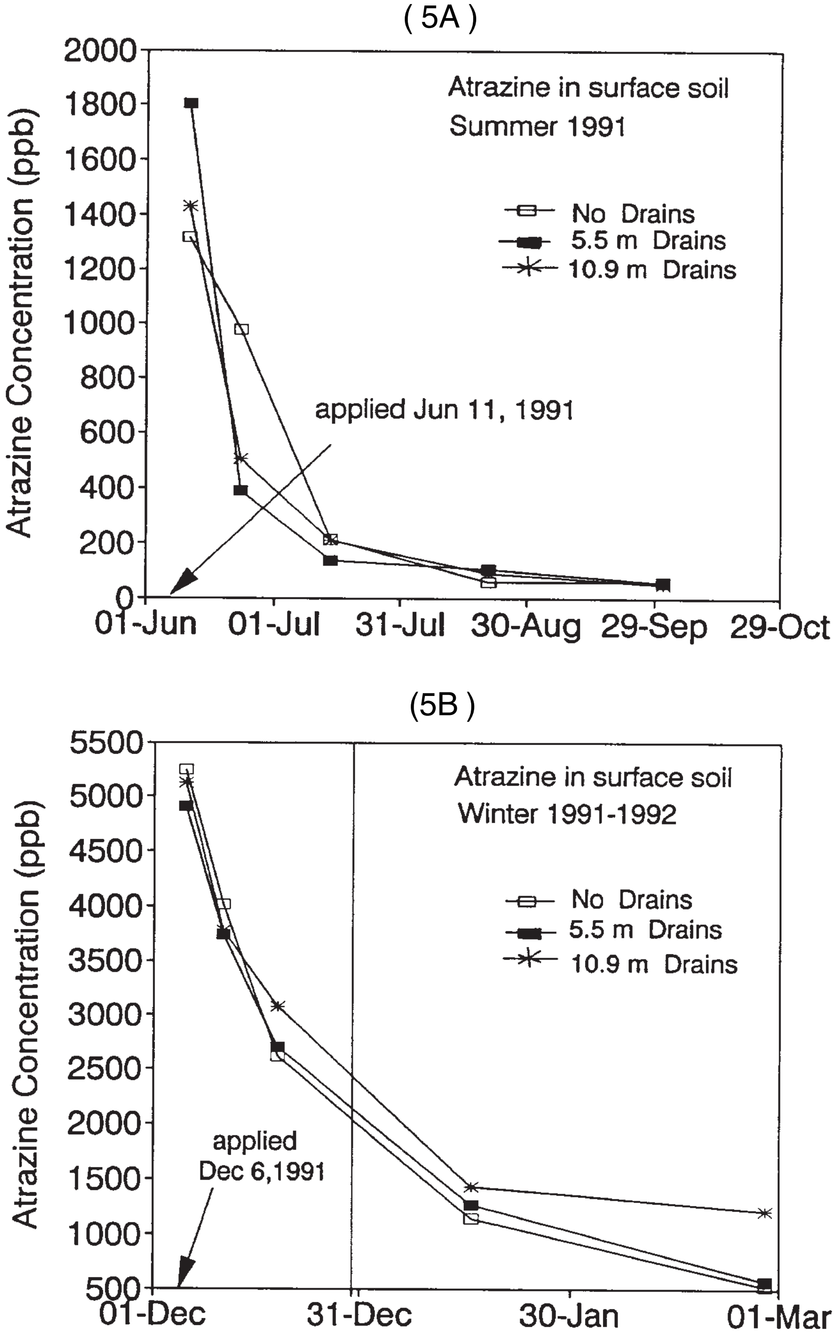
peaks averaging 135 ppb. The first heavy rainfall for the winter 1991-92 season, following an "initial low intensity storm," produced average peak concentrations of only 74 ppb. As the rate of drainage flow for the 5.5- and 10.9-m drain spacings decreased, atrazine concentrations in the effluent decreased. Subsequent rainfall events resulted in progressively smaller atrazine peaks.

Atrazine leaching patterns shown in figs. 3 and 4 were recently observed by other scientists (Kladivko et al., 1991, Everts and Kanwar, 1990). Such patterns are likely due to two major mechanisms: atrazine kinetic or nonequilibrium adsorption-desorption characteristics and preferential flow behavior. Kinetic atrazine retention is strongly supported by the retention and release results shown in figs. 1 and 2. Furthermore, at the initiation of water flow in response to a rainfall event, atrazine in the soil solution is rapidly leached through large pores and flow channels to lower soil depths and eventually to the subsurface drains. We further assume that atrazine that is sorbed or weakly retained by the soil matrix and that is strongly bound are subject to slow release or desorption to the soil solution. Kinetic behavior responsible for the slow release of atrazine results in limiting the amounts that become susceptible to downward movement in the soil profile due to subsequent rainfalls. Therefore, continued water flow during rainfall events results in a continued decrease in atrazine concentrations in drain effluent, thus minimizing potential contamination of the groundwater.

The above findings are also supported by the results of extractable atrazine present in the soil surface following both summer and winter applications (Fig. 5). Atrazine concentration in the surface 2.5 cm of soil diminished rapidly within the first 2 weeks following summer 1991 application, with an average half life of 14.4 days. For the winter application, an average half life of 21 days was observed. Differences in atrazine disappearance rates between the two seasons may not be attributable to temperature differences, since the majority of atrazine degradation occurring in soils is chemical rather than biological (Gamble and Khan 1985). These differences are probably due to the prevailing surface soil moisture and the timing and intensity of rainfall events.

In this study, the autosamplers used to collect drain outflow samples also provided sampling times for each sample, allowing comparison with rainfall recorded at the field site. Atrazine breakthrough was consistently observed to occur within 30 minutes of the onset of rain during the summer 1991 season. Such intervals were short in relation to measured hydraulic conductivity (K) of this soil. Based on data from the instantaneous profile method on this site, K values ranged from 0.01 to 3 cm/hr for the surface and 0.01 to 6 cm/hr in the subsoil (Selim et al. 1982). These K values were considered to be unrealistically high and "a direct result of water channeling through continuous shrinkage cracks." Ob-

Figure 5. Atrazine concentration in the top 2.5 cm soil during (A) summer 1991 and (B) winter 1991-1992.



served atrazine travel times to reach the drains were much shorter in comparison to estimates based on K values as high as 6 cm/hr. The rapid breakthrough of drainage is indicative of the dominance of preferential water flow in this soil.

Atrazine in Soil Solution:

Atrazine concentration at different soil depths was also measured using suction lysimeters installed at various depths in the two drained plots and in an adjacent plot without subsurface drains. Atrazine concentrations in lysimeter soil solution were much lower (maximum value of 44.63 ppb) than that in the drainage effluent (tables 1-3). The discrepancy may point to the prevalence of preferential flow in this soil. For the subsurface drains, water outflow represents both macropore (channel) and micropore (soil matrix) flows from a large area of the experimental field plot. In contrast, samples from suction lysimeters represent interstitial water within the soil matrix from a small volume surrounding the lysimeter porous cup (5.4 cm in diameter). Therefore, if the dominant pathway for chemical transport is through preferential flow, that part of soil within the influence of the lysimeter may be completely bypassed by the majority of the water flux.

Table 1--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the drained plot with 10.9-m drain spacing

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (µg/L)					
Dec. 14	-	-	-	20.96	-	8.01
Dec. 19	-	-	-	-	12.14	3.52
Dec. 26	-	-	-	-	1.3	0.59
Jan. 3		-	-	-	1.16	1.13
0.43						
Jan. 9		44.63	-	2.97	2.465	1.16
1.145						
Jan. 15	11.77	-	2	1.1	1.13	1.08
Jan. 18	4.16	-	0.67	1.53	0.69	1
Jan. 25	1.775	-	0	0.95	0	1.41
Feb. 3	-	-	-	0	0	2.26
Feb. 9	1.76	-	0	1.04	0	1.08
Feb. 17	1.33	-	0	1.21	0.51	1.71

Table 2--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the drained plot with 5.5-m drain spacing

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (μg/L)					
Dec. 14	-	-	-	2.99	23.12	5.09
Dec. 19	-	-	-	2.62	5.575	1.61
Dec. 26	-	-	-	6.55	1.33	0.945
Jan. 3		-	-	5.51	1.38	1.23
0.335						
Jan. 9		44.63	4.85	1.82	2.05	1.78
0.265						
Jan. 15	33.06	1.11	5.32	5.26	0.44	0.295
Jan. 18	2.3	1.58	2.17	1.88	0.5	0.1
Jan. 25	7.37	0.95	2.57	3.44	2.84	0.22
Feb. 3	-	-	3.54	1.95	-	0
Feb. 9	5.2	0	1.13	1.39	0.42	0
Feb. 17	9.34	-	0.975	-	0.48	0.17

Table 3--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the plot with no subsurface drains

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (μg/L)					
Dec. 14	-	-	-	20.96	33.32	3.62
Dec. 19	-	-	-	5.185	2.05	7.84
Dec. 26	-	-	-	1.98	2.58	3.36
Jan. 3		-	-	-	0.86	0.58
0						
Jan. 9		36.965	15.91	3.705	2.275	4.03
1.555						
Jan. 15	11.66	8.57	2.025	1.245	1.44	0.32
Jan. 18	4.23	1.82	0.785	0.64	0.72	0.24
Jan. 25	5.53	2.93	0.93	0.315	0.41	1.33
Feb. 3	2.33	0	0.505	0	-	0
Feb. 9	2.585	0	0.94	0.115	0	1.05
Feb. 17	3.325	0	0.62	0.34	0.39	0

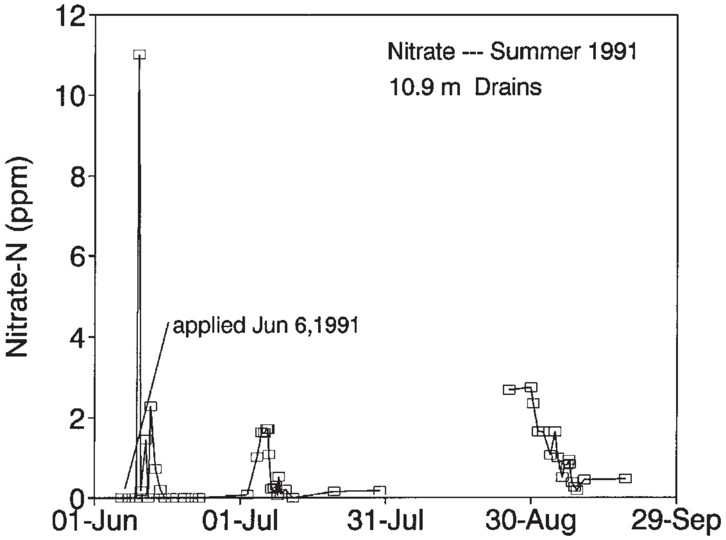
Results from lysimeters located within the fluctuating water table indicated that 3 to 10 days after application, atrazine was detected in the lysimeter samples (averaging 15 ppb at 120 cm, 28 ppb at 150 cm, and 6 ppb at 180 cm depth). The following 7-day period showed a considerable decrease in atrazine concentration within the shallow groundwater, with average values of 3.6 ppb at 120 cm, 6.6 ppb at 150 cm, and 4.3 ppb at 180 cm depth (see tables 1-3).

Nitrate in Subsurface Drainage Outflow:

The leaching behavior of nitrate during 1991 and 1992 shown in figs. 6 and 7 followed a similar pattern to that for atrazine despite the fact that nitrate is not subject to retention by the soil matrix (figs. 6 and 7). In fact, the travel time for nitrate to reach the drains was similar to that observed for atrazine. These results are not consistent with the transport equation (1) since atrazine having a large K_d is expected to be strongly retarded and with longer travel time than nitrate. Therefore, these results adds credence in support of preferential flow as the dominant transport mechanism in Sharkey soil. Kladivko et al. (1991), studying pesticide

Figure 6. Nitrate concentration versus time for summer 1991 from drained plot with (A) 10.9-m drains and (B) 5.5-cm drains.

(6A)



(6B)

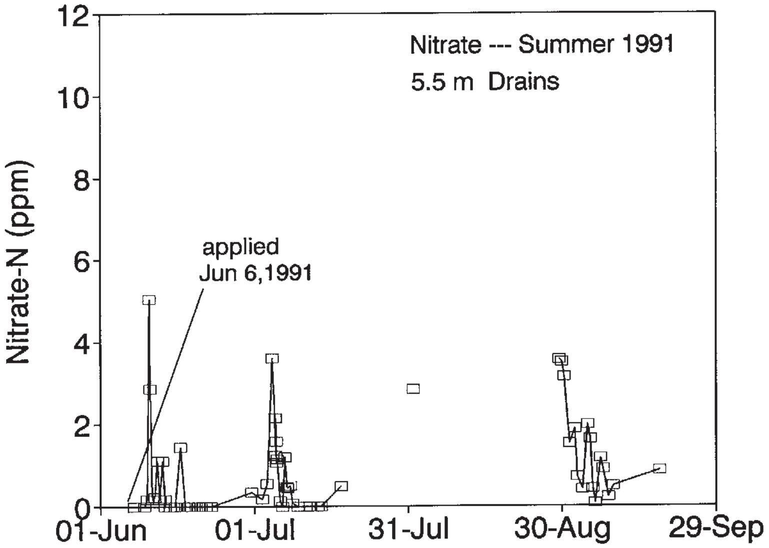
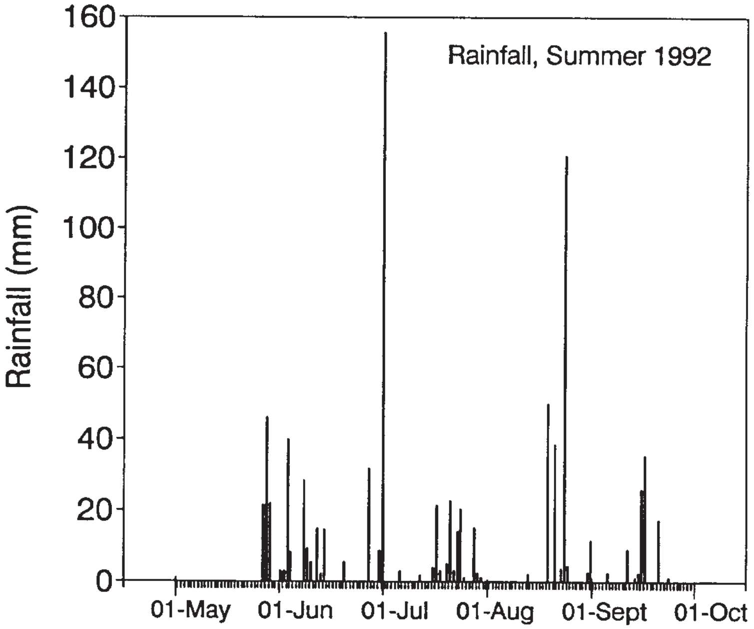
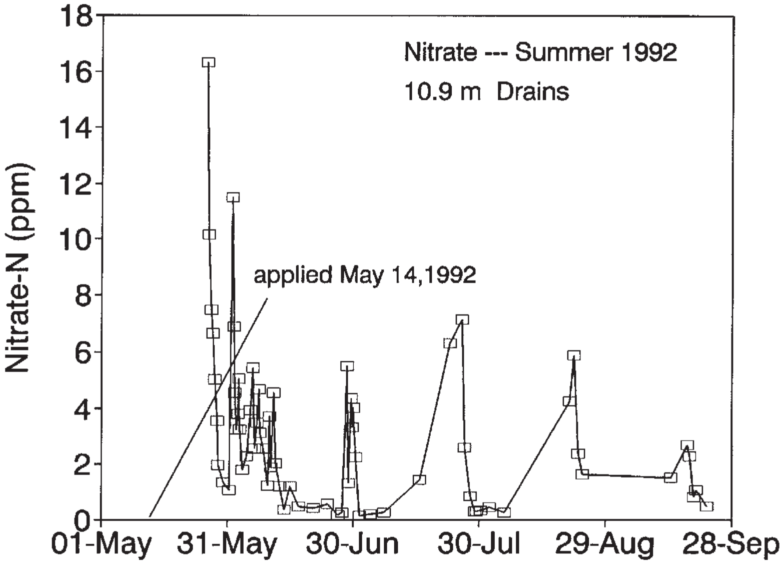


Figure 7. (A) Rainfall distribution for summer 1992. Nitrate concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

(7A)

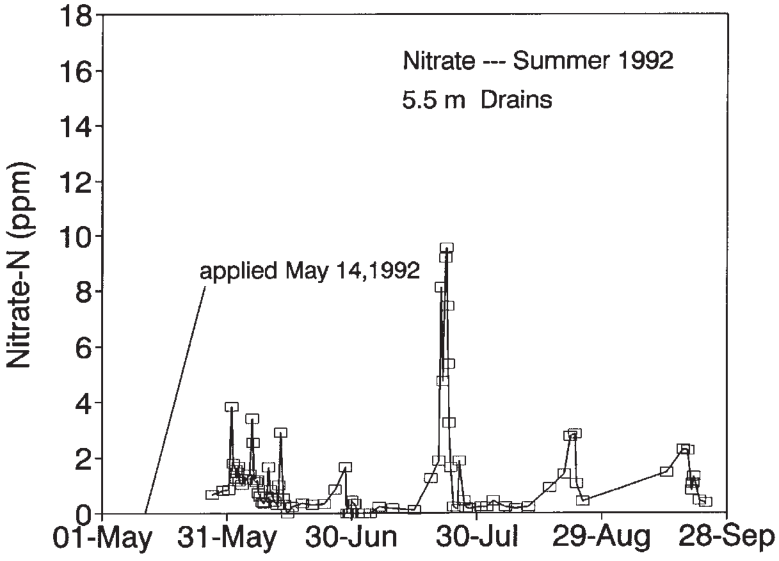


(7B)



Nitrate --- Summer 1992
10.9 m Drains
applied May 14,1992
Nitrate-N (ppm)
0
2
4
6
8
10
12
14
16
18
01-May
31-May
30-Jun
30-Jul
29-Aug
28-Sep

(7C)



Nitrate --- Summer 1992
5.5 m Drains
applied May 14,1992
Nitrate-N (ppm)
0
2
4
6
8
10
12
14
16
18
01-May
31-May
30-Jun
30-Jul
29-Aug
28-Sep

movement to subsurface drains, found that pesticides with different K_{oc} values arrived at the drains at the same time.

Consistent with atrazine results, maximum nitrate-N concentrations for both summer seasons occurred in drainage water resulting from the first substantial post-application rainfall (figs. 6 and 7). Maximum nitrate-N concentrations for 1991 were 11 ppm and 5 ppm for the 10.9- and 5.5-m drains, respectively (Fig. 6). This rainfall event occurred 5 days after fertilizer application. The first rainfall of the 1992 summer season (Fig. 7) occurred 13 days after nitrogen application and also resulted in a sudden elution of nitrate-N in the drainage with peak concentration of 17 ppm in the 10.9-m drains. The autosampler at the 5.5-m drains failed to collect samples during this initial event. For both seasons, subsequent rainfall events also resulted in the leaching of nitrate N. Concentration peaks became smaller as the season progressed, which was consistent with atrazine results. During the first summer season, nitrate concentrations of 2-3 ppm were observed in drainage outflow 84 days after nitrogen application. For the 1992 season, substantial nitrate-N was detected in drainage effluent at concentrations of 1-2 ppm more than 120 days following nitrogen application. A gap in nitrate data for August 27 through September 3 was attributed to power outage caused by Hurricane Andrew (August 26, 1992).

Summary and Conclusions

We quantified the extent of atrazine retention by Sharkey clay soil based on adsorption and desorption or release experiments. From retention results, we measured an atrazine adsorption coefficient (K_d) of 3.42 cm^3/g. This K_d value was used to calculate a K_{oc} of 347 for Sharkey soil. Atrazine adsorption-desorption were kinetic in nature. Hysteresis was observed based on deviation of atrazine adsorption data from desorption results. We also quantified the movement of atrazine and nitrate in a field site of Sharkey clay planted to sugarcane. Subsurface drains at 1 m depth provided leachate, and a series of suction lysimeters allowed sampling of soil solution. Within a few hours of the onset of rain, atrazine and nitrate were observed at high concentrations in drainage effluent. Atrazine breakthrough to the drains was consistently observed to occur within 30 minutes of the onset of rain during the summer 1991 season. Such interval was short in relation to measured soil hydraulic conductivity and indicative of the dominance of preferential water flow in this soil. The leaching behavior of nitrate during 1991 and 1992 followed a similar pattern to that atrazine despite the fact that nitrate is not subject to retention by the soil matrix. Subsequent rainfall events resulted in progressively smaller atrazine and nitrate peaks. Maximum (or peak) concentrations in drainage effluent for atrazine ranged from 60 to 80 ppb and for nitrate from 11 to 17 ppm. Despite the observed high peak concentrations, total atrazine and nitrate leaching losses, based on mass balance calculations, did not exceed 1.2 and 8% respectively.

Our findings have significant implications on management practices of sugarcane on Sharkey clay soil in south Louisiana. Concentrations of nitrate nitrogen in drainage water were below the lifetime health advisory limit in drinking water of 10 ppm. Therefore, we conclude that based on 1991 and 1992 effluent results of nitrate nitrogen, recommended fertilizer nitrogen applied to this soil did not contribute to elevated nitrogen levels of the shallow water table.

Acknowledgments

The assistance of Claire W. Harmon and Nina M. Huffstetler of the

Department of Agricultural Chemistry and Herbert Pack of the USDA-ARS Soil and Water Laboratory is greatly appreciated.

References

Everts, C.J. and R.S. Kanwar. 1990. Estimating preferential flow to a subsurface drain with tracers. Am. Soc. Agric. Eng.:451-457.

Gamble, D. S. and S. U. Khan. 1985. Atrazine hydrolysis in soils: catalysis by the acidic functional groups of fulvic acid. Can. J. Soil Sci. 65:435-443.

Goswami, K. P. and R. E. Green. 1971. Microbial degradation of the herbicide atrazine and its 2-hydroxy analog in submerged soils. Environ. Sci. Technol. 5:426-429.

Gu, J. D., D. F. Berry, R. H. Taraban, D. C. Martens, H. L. Walker, Jr. and W. J. Edmonds. 1992. Biodegradability of atrazine, cynazine, and dicamba in wetland soils. Virginia Water Resources Research Center, Bulletin 172.

Helling, C. S. and T. J. Gish. 1986. Soil characteristics affecting pesticide movement into ground water. In. Garner, W. Y. et al.

(eds) Evaluation of pesticides in ground water (ACS Symp. Series 315). American Chemical Society, Washington, DC.

Kladivko, E.J., G.E. Van Scoyoc, E.J. Monke, K. M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Qual. 20:264-270.

Muir, D. C. G. and B. E. Baker. 1976. Detection of triazine herbicides and their degradation products in tile-drain water from fields under intensive corn (maize) production. J. Agric. Food Chem. 24:122-125.

Selim, H.M.,C.E. Carter, and E.D. Aviles. 1982. Movement and retention of water in a heavy clay soil. Proc. Fourth National Drainage Symposium, ASAE Pub. No. 12-82.

Shipitalo, M.J., W.M. Edwards, W.A. Dick, and L.B. Owens. 1990. Initial storm effects on macropore transport of surface-applied chemicals in no-till soil. Soil Sci. Soc. Am. J. 54:1530-1536.

Southwick, L. M., G. H. Willis, and H. M. Selim. 1992. Leaching of atrazine from sugarcane in southern Louisiana. J. Agric. Food Chem. 40:1264-1268.

Starr, J. L. and D. E. Glotfelty. 1990. Atrazine and bromide movement through a silt loam soil. J. Environ. Qual. 19:552-558.

Utermann, J., E. J. Kladivko and W. A. Jury. 1990. Evaluating pesticide migration in tile-drained soils with a transfer function model. J. Environ. Qual. 19:707-714.

Wauchope, R.D., T. M. Buttler, A.G. Hornsby, P. W. M. Augustjin-Beckers, and H. M. Burt. 1992. The SCS/ARS/CES pesticide properties database for environmental decision making. Rev. Environm. Contamin. Toxic. 123:1-164.

FIGURE CAPTIONS

Louisiana Agricultural Experiment Station
LSU Agricultural Center
P. O. Box 25055
Baton Rouge, LA. 70894-5055

Table 1--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the drained plot with 10.9-m drain spacing

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (µg/)					
Dec. 14	-	-	-	20.96	-	8.01
Dec. 19	-	-	-	-	12.14	3.52
Dec. 26	-	-	-	-	1.3	0.59
Jan. 3		-	-	-	1.16	1.13
0.43						
Jan. 9		44.63	-	2.97	2.465	1.16
1.145						
Jan. 15	11.77	-	2	1.1	1.13	1.08
Jan. 18	4.16	-	0.67	1.53	0.69	1
Jan. 25	1.775	-	0	0.95	0	1.41
Feb. 3	-	-	-	0	0	2.26
Feb. 9	1.76	-	0	1.04	0	1.08
Feb. 17	1.33	-	0	1.21	0.51	1.71

Figure 1.Atrazine adsorption and desorption isotherms for a Sharkey clay soil. Desorption isotherms (dashed curves) are for initial concentrations of (A) 4.10 g ml^{-1} and (B) 10.46 g ml^{-1}.

Figure 2.Total atrazine recovery following six desorption steps versus reaction (incubation) time for three initial concentrations (C_i) of 0.54, 4.1 and 10.46 g/ml.

Figure 3.(A) Rainfall distribution for summer 1991. Atrazine concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

Figure 4.(A) Rainfall distribution for winter 1991-1992. Atrazine concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

Figure 5.Atrazine concentration in the top 2.5 cm soil during (A) summer 1991 and (B) winter 1991-1992.

Figure 6.(A) Nitrate concentration versus time for summer 1991 from drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

Figure 7.(A) Rainfall distribution for summer 1992. Nitrate concentration in drainage effluent from the drained plot with (B) 10.9-m drains and (C) 5.5-cm drains.

Table 2--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the drained plot with 5.5-m drain spacing

Depth cm306090120150180Sampling DateAtrazine Concentration (µg/)Dec. 14---2.9923.125.09Dec. 19---2.625.5751.61Dec. 26---6.551.330.945Jan. 3--5.511.381.230.335Jan. 944.634.851.822.051.780.265Jan. 1533.061.115.325.260.440.295Jan. 182.31.582.171.880.50.1Jan. 257.370.952.573.442.840.22Feb. 3--3.541.95-0Feb. 95.201.131.390.420Feb. 179.34-0.975-0.480.17

Table 2--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the drained plot with 5.5-m drain spacing

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (µg/)					
Dec. 14	-	-	-	2.99	23.12	5.09
Dec. 19	-	-	-	2.62	5.575	1.61
Dec. 26	-	-	-	6.55	1.33	0.945
Jan. 3		-	-	5.51	1.38	1.23
0.335						
Jan. 9		44.63	4.85	1.82	2.05	1.78
0.265						
Jan. 15	33.06	1.11	5.32	5.26	0.44	0.295
Jan. 18	2.3	1.58	2.17	1.88	0.5	0.1
Jan. 25	7.37	0.95	2.57	3.44	2.84	0.22
Feb. 3	-	-	3.54	1.95	-	0
Feb. 9	5.2	0	1.13	1.39	0.42	0
Feb. 17	9.34	-	0.975	-	0.48	0.17

Table 3--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the plot with no subsurface drains

Depth cm306090120150180Sampling DateAtrazine Concentration (µg/)Dec. 14---20.9633.323.62Dec. 19---5.1852.057.84Dec. 26---1.982.583.36Jan. 3---0.860.580Jan. 936.96515.913.7052.2754.031.555Jan. 1511.668.572.0251.2451.440.32Jan. 184.231.820.7850.640.720.24Jan. 255.532.930.930.3150.411.33Feb. 32.3300.5050-0Feb. 92.58500.940.11501.05Feb. 17
3.32500.620.340.390

Table 3--Lysimeter results of atrazine concentration in soil solution versus depth during winter 1991-92. Results are for the plot with no subsurface drains

	Depth cm					
	30	60	90	120	150	180
Sampling Date	Atrazine Concentration (µg/)					
Dec. 14	-	-	-	20.96	33.32	3.62
Dec. 19	-	-	-	5.185	2.05	7.84
Dec. 26	-	-	-	1.98	2.58	3.36
Jan. 3		-	-	-	0.86	0.58
0						
Jan. 9		36.965	15.91	3.705	2.275	4.03
1.555						
Jan. 15	11.66	8.57	2.025	1.245	1.44	0.32
Jan. 18	4.23	1.82	0.785	0.64	0.72	0.24
Jan. 25	5.53	2.93	0.93	0.315	0.41	1.33
Feb. 3	2.33	0	0.505	0	-	0
Feb. 9	2.585	0	0.94	0.115	0	1.05
Feb. 17	3.325	0	0.62	0.34	0.39	0