

Adsorption and Desorption of Atrazine, Desethylatrazine, Deisopropylatrazine, and Hydroxyatrazine in Vegetated Filter Strip and Cultivated Soil

LARRY JASON KRUTZ,^{*,†} SCOTT ALLEN SENSEMAN,[†] KEVIN JOSEPH MCINNES,[†]
 DAVID ALLEN ZUBERER,[†] AND DENNIS PATRICK TIERNEY[§]

Department of Soil and Crop Sciences, Texas Agricultural Experiment Station,
 Texas A&M University, College Station, Texas 77843-2474, and Environmental Stewardship and
 Regulatory Policy, Syngenta Crop Protection, P.O. 18300, Greensboro, North Carolina 27409

Adsorption and desorption of atrazine and its metabolites in vegetated filter strip soil (VFS) has not been evaluated, yet these data are needed to predict the transport of these compounds through the VFS. Adsorption and desorption parameters for atrazine, desethylatrazine (DEA), deisopropylatrazine (DIA), and hydroxyatrazine (HA) were compared between a cultivated Houston Black clay (CS) and an adjacent 12-year-old VFS established in a mixed stand of bermudagrass [*Cynodon dactylon* (L.) Pers.] and buffalograss [*Buchloe dactyloides* (Nutt. Engelm)]. Adsorption and desorption isotherms were determined by batch equilibrium. The evaluated chemical and physical properties of the VFS and CS were similar with the exception of a 1.7-fold increase in the organic carbon content of the VFS. Adsorption and desorption coefficients for atrazine were at least 59% higher in VFS than in CS. The adsorption coefficient for HA was 48% higher in VFS compared with CS, but desorption was not statistically different between soils. Adsorption and desorption coefficients for DEA and DIA were not statistically different between soils. The predicted order of mobility in CS is HA < atrazine = DIA = DEA. In VFS, the predicted order of mobility is HA < atrazine = DIA < DEA. These data indicate that the higher organic carbon in VFS will likely retard the transport of atrazine and HA to surface and ground waters; however, the transport rates of DEA and DIA will be similar between soils.

KEYWORDS: Vegetated filter strip; adsorption; desorption; mobility; atrazine; desethylatrazine; deisopropylatrazine; hydroxyatrazine; hysteresis

INTRODUCTION

Atrazine [2-chloro-4-(ethylamino)-6-isopropylamino-*s*-triazine] is used to control annual grasses and broadleaf weeds primarily in corn (*Zea mays* L.) and grain sorghum [*Sorghum bicolor* (L.) Moench] (1). In soil, atrazine is transformed into several products including desethylatrazine [2-amino-4-chloro-6-(isopropylamino)-*s*-triazine; DEA], deisopropylatrazine [2-amino-4-chloro-6-(ethylamino)-*s*-triazine; DIA], and hydroxyatrazine [2-hydroxy-4-(ethylamino)-6-(isopropylamino)-*s*-triazine; HA] (2) (Figure 1). The formation of DEA and DIA occurs through N-dealkylation of atrazine, a microbially mediated process (3, 4). Formation of HA occurs through both biological (5) and nonbiological (6) pathways.

Atrazine and its metabolites have been detected in surface and ground waters. The maximum concentrations in 95 Midwestern streams were 136 $\mu\text{g L}^{-1}$ for atrazine, 7.5 $\mu\text{g L}^{-1}$ for

DEA, 7.4 $\mu\text{g L}^{-1}$ for DIA, and 3.7 $\mu\text{g L}^{-1}$ for HA (7). Similar maximum concentrations for atrazine and its metabolites have been reported for the lower Mississippi River (8), various Midwestern streams (9, 10), and the Playa Lakes of West Texas (11). In groundwater, Kolpin et al. (12) reported that the maximum concentrations in 131 Iowa wells were 2.1 $\mu\text{g L}^{-1}$ for atrazine, 0.6 $\mu\text{g L}^{-1}$ for DEA, 1.1 $\mu\text{g L}^{-1}$ for DIA, and 1.3 $\mu\text{g L}^{-1}$ for HA. Similar results have been reported for near-surface aquifers of the Midwestern United States (13). Consequently, means for limiting the transport of atrazine and its metabolites from application zones are desirable.

Vegetated filter strips are bands of indigenous or planted vegetation below cultivated fields or animal production facilities that are intended to reduce the transport of sediment and agricultural chemicals. Vegetated filter strips have been reported to reduce atrazine and atrazine metabolite losses from application zones by facilitating the deposition of sediment-adsorbed compounds (14), increasing infiltration (14–23), and adsorbing compounds to vegetated filter strip grass, grass thatch, or soil surfaces (14–16, 19, 22). Although these processes reduce

* Corresponding author [e-mail lkrutz@ag.tamu.edu; telephone (979) 845-5384; fax (979) 845-0456].

[†] Texas A&M University.

[§] Syngenta Crop Protection.

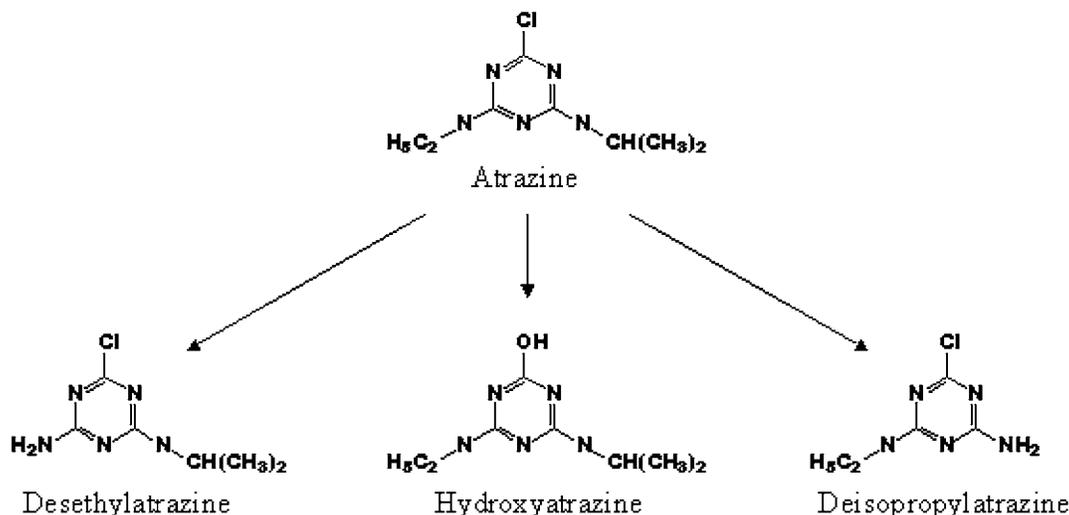


Figure 1. Chemical structures of atrazine (ATR) and its major degradation products, desethylatrazine (DEA), deisopropylatrazine (DIA), and hydroxyatrazine (HA).

runoff of atrazine and its metabolites, questions remain regarding the reversibility of the retention processes.

Vegetated filter strip soil (VFS) has been shown to accumulate greater above- and below-ground organic matter compared to adjacent cultivated soil (CS) (24–27). Organic matter significantly affects herbicide sorption, the primary process controlling pesticide mobility in soil (28). Greater adsorption of metolachlor (27), fluometuron (25, 26), and isoproturon (24) has been reported for VFS compared with CS. Similarly, greater adsorption of atrazine (29), metolachlor (29), and fluometuron (25) has been reported for bermudagrass (29) and switchgrass (25) vegetated filter strip thatch compared with CS (25, 29) and VFS (25). In these studies, metolachlor (27), isoproturon (24), and fluometuron (26) desorption coefficients were greater for VFS compared with CS.

In our previous work, buffalograss [*Buchloe dactyloides* (Nutt. Engelm)] filter strips retained dissolved-phase atrazine transported by surface runoff to a greater extent than DEA, DIA, and HA (16). Adsorption and desorption of these compounds have not been evaluated in VFS. If a herbicide is irreversibly bound to soil or if its desorption is very slow, mobility in soil is reduced. Therefore, a study was designed to compare adsorption and desorption of atrazine, DEA, DIA, and HA between VFS and CS.

MATERIALS AND METHODS

Soil. The soils evaluated in this experiment were collected from 0.6-ha watersheds constructed by the USDA-ARS in 1937 at the Blackland Research Center in Temple, TX. The soil at the site is classified as a Houston Black clay (Fine, smectitic, thermic Udic Haplusterts). In 1991, vegetated filter strips were established with a mixed stand of bermudagrass [*C. dactylon* (L.) Pers.] and buffalograss [*B. dactyloides* (Nutt. Engelm)]. Since that date, the cultivated fields directly adjacent to the filter strips have been in a corn/sorghum rotation. Soil samples were collected from the top 0–5 cm depth from the vegetated filter strip and cultivated field. The soils were air-dried and passed through a 2-mm sieve to remove roots. Particle-size distribution was determined with the hydrometer method (30). Organic carbon content was measured by combustion in a medium-temperature induction furnace (31) and corrected for total inorganic carbon (32). Soil pH (1:1) was determined as described by Thomas (33). Soil data are presented in **Table 1**.

Chemicals. Batch equilibrium experiments were conducted with ^{14}C -labeled atrazine, DEA, DIA, and HA. The specific radioactivity of atrazine was 340 MBq mmol $^{-1}$ and radiochemical purity was 98.7%. Specific radioactivity and radiochemical purity for DEA were 59 MBq

Table 1. Properties of the Vegetated Filter Strip Soil (VFS) and Cultivated (CS) Houston Black Clay

soil	sand (%)	silt (%)	clay (%)	organic carbon (%)	CEC ^a (cmol _c kg $^{-1}$)	pH
VFS	37.9	31.9	30.2	4.2	67.8	7.6
CS	36.8	29.5	33.7	2.5	62.5	7.6

^a Cation exchange capacity.

mmol $^{-1}$ and 96.8%, respectively. The specific radioactivity of DIA was 170 MBq mmol $^{-1}$, and its radiochemical purity was 97.3%. The specific radioactivity of HA was 303 MBq mmol $^{-1}$, and its radiochemical purity was 96.8%. Atrazine, DEA, and DIA parent solutions were prepared in HPLC-grade methanol. The parent solution for HA was prepared in a mixture of water/methanol/acetic acid (74.5:25:0.5 v/v). All parent solutions were diluted to 0.01, 0.05, 0.1, and 1.0 mg L $^{-1}$ batch solutions in 0.01 M CaCl $_2$ /methanol (99:1 v/v). The batch equilibrium radioactivity range was 15.6–1602 kBq L $^{-1}$.

Adsorption. Adsorption isotherms for atrazine, DEA, DIA, and HA were determined for VFS and CS using the batch equilibration technique at 24 ± 2 °C. A 5-mL aliquot of each chemical solution was added to 1 g of soil in a 50-mL glass centrifuge tube resulting in a solution-to-soil ratio of 5:1. Each concentration was replicated four times. Slurries were placed on a reciprocal shaker for 24 h and then centrifuged at 2000 × g for 20 min at 24 ± 2 °C. Three milliliters of supernatant solution was removed from each tube. One milliliter of the equilibrium supernatant solution was mixed with 10 mL of Ecolite (+) liquid scintillation cocktail. The ^{14}C content of each sample was analyzed and corrected for counting efficiency using a Beckman 6500 liquid scintillation instrument operated in the auto-disintegrations per minute mode. The amount of chemical adsorbed after each equilibration was calculated as the difference between the supernatant concentration and the amount of chemical initially added. Preliminary quality assurance steps included determining the adsorption of herbicides to glass centrifuge tubes, compound solubility at test concentrations, and equilibration time.

Desorption. Desorption isotherms were obtained from the adsorption samples in equilibrium with the largest initial concentration in solution. Three milliliters of supernatant solution was removed from the centrifuge tubes and replaced with an equal volume of 0.01 M CaCl $_2$ solution. Soil pellets were dispersed using a vortex mixer, and tubes were placed on a reciprocal shaker for 24 h at 24 ± 2 °C. Tubes were then centrifuged for 20 min at 2000 × g. One milliliter of desorption equilibrium supernatant solution was removed and mixed with 10 mL of Ecolite (+) liquid scintillation cocktail, and the ^{14}C content was quantified as described above. The sorbed concentration was calculated as the difference between the supernatant concentration and the

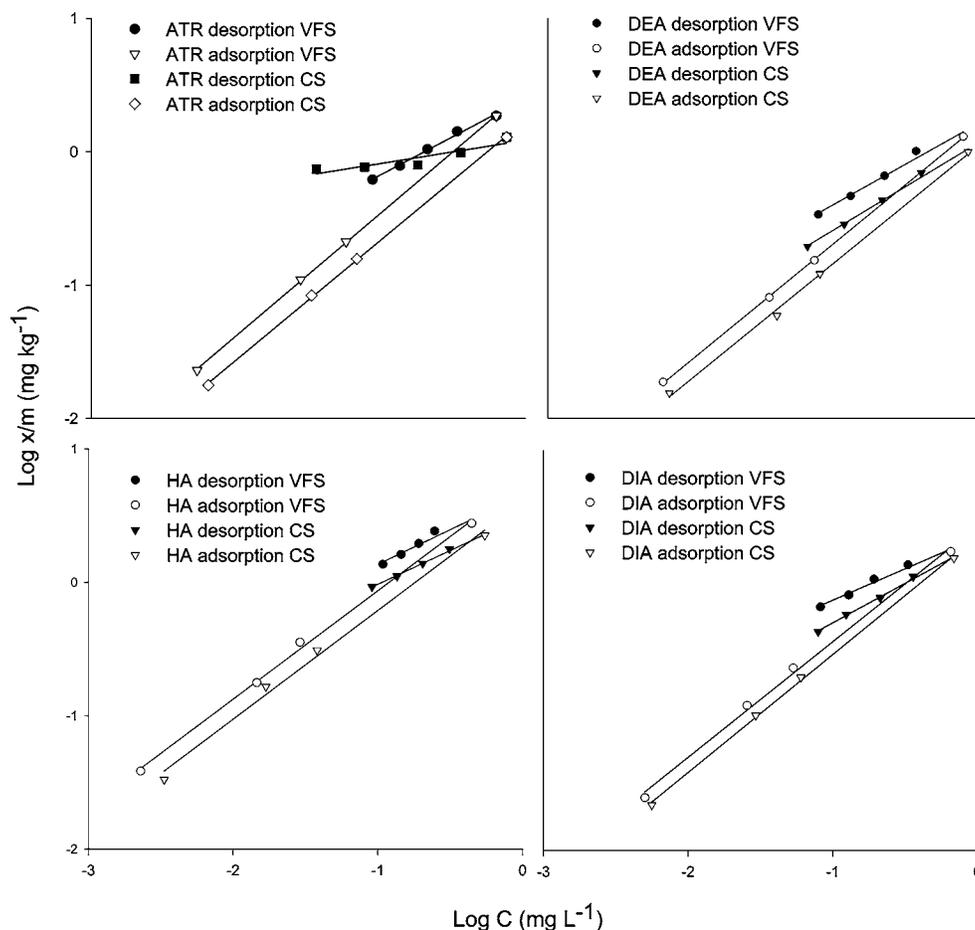


Figure 2. Adsorption–desorption isotherms for atrazine (ATR) and its major degradation products, desethylatrazine (DEA), deisopropylatrazine (DIA), and hydroxyatrazine (HA), in vegetated filter strip soil (VFS) and cultivated soil (CS).

remaining total chemical content after subtracting the amount of chemical removed. The desorption procedure was repeated three times for a total of four 24-h desorption periods.

Adsorption and desorption coefficients were calculated using the linearized form of the Freundlich equation

$$\log (x/m) = \log K_f + (1/n) \log C_e \quad (1)$$

where x/m is μg of test substance per gram of soil, C_e is μg of test substance per liter of supernatant after equilibration, and K_f and $1/n$ are empirical constants. Hereafter, $K_{f,ads}$ and $1/n_{ads}$ indicate adsorption, whereas $K_{f,des}$ and $1/n_{des}$ refer to desorption.

The adsorption distribution coefficients (K_d) were calculated as follows:

$$K_d = (x/m)/C_e \quad (2)$$

Distribution coefficients were determined at each concentration and averaged across all equilibrium concentrations to obtain a single estimate of K_d . The adsorption coefficient was normalized to the organic carbon (OC) content of the soil (K_{oc}), and hysteresis (ω) was quantified as described by Ma et al. (34):

$$K_{oc} = (K_d/\%OC) \times 100 \quad (3)$$

$$\omega = [(1/n_{ads})/(1/n_{des}) - 1] \times 100 \quad (4)$$

Statistical Analysis. Regression analysis was performed on adsorption and desorption isotherms. Ninety-five percent confidence intervals were calculated for K_f and $1/n$ values. K_d , K_{oc} , and ω were analyzed by ANOVA for a completely randomized design using SAS with treatments in a 4×2 factorial arrangement (compound \times soil). Contrasts were not orthogonal but were chosen for the objective of the

study. To control experiment-wise error, the significance of a contrast was evaluated only if the corresponding overall F test was significant ($P < 0.05$).

RESULTS AND DISCUSSION

Adsorption. Freundlich adsorption isotherms are presented in **Figure 2**. Within the range of concentrations evaluated in this experiment, the Freundlich equation adequately described atrazine, DEA, DIA, and HA adsorption to VFS and CS ($r^2 \geq 0.99$). In the VFS, $K_{f,ads}$ values decreased in the order HA (5.6 L kg^{-1}) > atrazine (2.9 L kg^{-1}) > DIA (2.7 L kg^{-1}) > DEA (1.7 L kg^{-1}) (**Table 2**). Similar trends have been reported for CS and wetland soils (35–37). In the CS, $K_{f,ads}$ values decreased in the order HA (4.0 L kg^{-1}) > DIA (2.2 L kg^{-1}) > atrazine (1.7 L kg^{-1}) > DEA (1.2 L kg^{-1}) (**Table 2**). An identical trend has been reported for sediments (38).

The $K_{f,ads}$ values for all compounds are within the range of published values. $K_{f,ads}$ values reported for atrazine include 0.2 – 4.2 L kg^{-1} (35), 3.8 – 6.5 L kg^{-1} (39), 0.4 – 3.1 L kg^{-1} (40), and 1.5 – 2.0 L kg^{-1} (37). With the exception of HA, the $K_{f,ads}$ values for DEA, DIA, and HA are consistent with those reported by Runes et al. (38): 1.5 L kg^{-1} for DEA, 3.0 L kg^{-1} for DIA, and 102.3 L kg^{-1} for HA. $K_{f,ads}$ values for DEA, DIA, and HA reported by Seybold and Mersie (37) were 0.7 – 2.0 , 1.3 – 1.8 , and 3.5 – 7.8 L kg^{-1} , respectively.

The $K_{f,ads}$ values for atrazine and HA were at least 41% higher in VFS compared with CS. Conversely, the $K_{f,ads}$ values for DEA and DIA were not significantly different between soils. In the VFS, $K_{f,ads}$ values for atrazine were 95% less than for

Table 2. Freundlich Adsorption and Desorption Parameters for Atrazine (ATR), Desethylatrazine (DEA), Deisopropylatrazine (DIA), and Hydroxyatrazine (HA) in Vegetated Filter Strip Soil (VFS) and Cultivated Soil (CS)

compd	soil	K_f ($\text{g}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$)	$1/n$	r^2
Freundlich Adsorption Parameters				
ATR	VFS	2.88 (2.552–3.258) ^a	0.92 (0.886–0.956)	0.99
	CS	1.74 (1.435–2.061)	0.90 (0.845–0.954)	0.99
DEA	VFS	1.66 (1.486–1.870)	0.89 (0.854–0.923)	0.99
	CS	1.17 (0.794–1.726)	0.88 (0.763–1.002)	0.99
DIA	VFS	2.69 (1.581–4.600)	0.87 (0.716–1.017)	0.99
	CS	2.24 (1.710–2.965)	0.88 (0.804–0.964)	0.99
HA	VFS	5.62 (3.565–8.790)	0.81 (0.703–0.922)	0.99
	CS	3.98 (1.832–8.79)	0.82 (0.613–1.017)	0.99
Freundlich Desorption Parameters				
ATR	VFS	2.51 (2.193–2.884)	0.57 (0.491–0.656)	0.99
	CS	1.23 (0.902–1.656)	0.17 (0.029–0.321)	0.83
DEA	VFS	1.70 (1.291–2.203)	0.61 (0.453–0.764)	0.98
	CS	1.20 (1.047–1.406)	0.65 (0.571–0.735)	0.99
DIA	VFS	2.24 (1.854–2.667)	0.47 (0.365–0.578)	0.99
	CS	1.99 (0.255–0.340)	0.59 (0.534–0.649)	0.99
HA	VFS	4.47 (3.076–6.577)	0.52 (0.292–0.747)	0.95
	CS	3.09 (2.825–3.388)	0.51 (0.452–0.559)	0.99

^a Numbers in parentheses are 95% confidence intervals.

Table 3. Average Values for Each Compound and Soil: Vegetated Filter Strip Soil (VFS), Cultivated Soil (CS), Atrazine (ATR), Desethylatrazine (DEA), Deisopropylatrazine (DIA), Hydroxyatrazine (HA), Soil Distribution Coefficient (K_d), Soil Distribution Coefficient Normalized for Organic Carbon (K_{oc}), and Measure of Hysteresis (ω)

compd	soil	K_d^a (L kg^{-1})	K_{oc}^a (L kg^{-1})	ω^b
ATR	VFS	3.71 (0.573) ^c	88 (13.5)	62 (12.7)
	CS	2.33 (0.436)	92 (17.2)	417 (55.7)
DEA	VFS	2.34 (0.488)	55 (11.5)	51 (25.5)
	CS	1.66 (0.390)	66 (15.4)	37 (17.1)
DIA	VFS	4.18 (0.943)	99 (22.3)	91 (17.3)
	CS	3.24 (0.645)	128 (25.5)	51 (24.7)
HA	VFS	11.85 (4.037)	280 (95.6)	63 (5.2)
	CS	8.00 (2.529)	316 (99.9)	58 (17.1)

^a $N = 16$. ^b $N = 4$. ^c Numbers in parentheses are standard errors.

HA, equal to that for DIA, and 42% greater than that for DEA. In the CS, the $K_{f,ads}$ value for atrazine was 129% less than for HA but not different from the values for DEA and DIA.

The Freundlich adsorption constant, $1/n_{ads}$, is a measure of adsorption nonlinearity. When n approaches 1, adsorption is linearly proportional to the equilibrium solution concentration, and a distribution coefficient (K_d) is more appropriate for making comparisons among treatments (37). The average $1/n_{ads}$ values for all compounds in both soils were <1 but >0.8 (Table 2). Therefore, adsorption data were assumed to be approximately linear over the concentration range evaluated. Thus, K_d values were estimated and compared between soils and compounds.

The K_d values for all compounds were within the range of published results (Table 3). Representative K_d values reported for atrazine include $0.4\text{--}14.0 \text{ L kg}^{-1}$ (35), $0.1\text{--}3.1 \text{ L kg}^{-1}$ (40), and $1.5\text{--}1.8 \text{ L kg}^{-1}$ (37). Similarly, the K_d values for DEA (1.5 L kg^{-1}), DIA (3.0 L kg^{-1}), and HA (132.0 L kg^{-1}) are consistent with those reported by Runes et al. (38). The range of K_d values reported for DEA, DIA, and HA by Seybold and Mersie (37) were $0.7\text{--}1.0$, $0.8\text{--}1.7$, and $3.1\text{--}7.9 \text{ L kg}^{-1}$, respectively.

The model F test indicated a significant difference in K_d values among compounds and soils (Table 4). Specifically, there was a compound by soil interaction. Therefore, simple effects were evaluated (Table 5). K_d values for atrazine and HA were

Table 4. P Values for Soil Distribution Coefficients (K_d), Soil Distribution Coefficient Normalized for Organic Carbon (K_{oc}), and Measure of Hysteresis (ω)

comparison	K_d^a	K_{oc}^a	ω^a
model (F test)	0.0001*	0.0001*	0.0001*
compd	0.0001*	0.0001*	0.0001*
ATR vs DEA		0.0231*	
ATR vs DIA		0.0693	
ATR vs DIA		0.0001*	
soil (VFS vs CS)	0.0001*	0.0317*	0.0001*
compd \times soil	0.0015*	0.5700	0.0001*

^a *, significant at the 0.05 probability level.

at least 48% higher in VFS compared with CS. K_d values for DEA and DIA were not different between soils (Table 5). These data indicate the greater capacity of VFS to sorb atrazine and HA compared with CS. Moreover, the results demonstrate the inability of the VFS to sorb more DEA and DIA than CS.

In this study, greater atrazine and HA sorption in the VFS compared with CS is likely attributed to higher organic matter in the VFS that arises from a lack of tillage and elevated inputs from above- and below-ground plant residues. Greater herbicide sorption to VFS compared with CS has been reported for metolachlor (27), isoproturon (24), and fluometuron (25, 26). Because herbicide sorption is generally inversely correlated with mobility, greater atrazine and HA sorption to VFS relative CS should reduce atrazine and HA transport to surface and ground waters. Conversely, enhanced retention of DEA and DIA in VFS compared with CS appears to be unlikely and may indicate that the affinity of these metabolites for the organic matter of the VFS is lower than that of the CS.

In the CS, the K_d for HA was 243% greater than that of atrazine. The K_d value for atrazine was not significantly different from those of DEA or DIA. Therefore, the predicted mobility in CS increases in the order $\text{HA} < \text{atrazine} = \text{DIA} = \text{DEA}$. Using soil thin-layer chromatography, Kruger et al. (41) predicted an identical order of mobility for one of five Iowa surface soils that were evaluated. In the VFS, the K_d value for atrazine was 219% less than that of HA, equal to that of DIA, and 55% greater than that of DEA. Thus, the predicted order of mobility in the VFS is $\text{HA} < \text{atrazine} = \text{DIA} < \text{DEA}$. Similarly, the same order of mobility was predicted for three of five Iowa surface soils evaluated (41). These results indicate that increased organic carbon in the VFS compared with CS altered the retention of atrazine metabolites relative to the parent compound. Specifically, DEA's affinity for the VFS organic matter appears to be lower than that of atrazine's. Similarly, Roy and Krapac (42) concluded that DEA has a lower affinity for organic matter than atrazine and that DEA sorption does not correlate strongly with organic carbon content.

K_d values can vary considerably among soils due to the quantities and composition of soil components. Because organic carbon is typically considered to be the primary soil component responsible for the sorption of nonionic herbicides (43), K_{oc} values are widely used to predict herbicide sorption. However, this normalization assumes that organic matter is the primary soil property controlling adsorption and that adsorption properties of organic matter are identical among soils. When these qualifications are not met, K_{oc} values can vary widely among soils (44).

The K_{oc} values for atrazine and its metabolites were calculated from eq 4 and are presented in Table 3. Our K_{oc} values are in agreement with published values. Representative K_{oc} values for atrazine include $44\text{--}102 \text{ L kg}^{-1}$ (35), 120 L kg^{-1} (38), and

Table 5. *P* Values for Simple Effects of Compound and Soil on the Hysteresis Index (ω) and the Soil Distribution Coefficient (K_d)

parameter	ω^a				K_d^a			
	VFS vs CS	ATR vs DEA	ATR vs DIA	ATR vs HA	VFS vs CS	ATR vs DEA	ATR vs DIA	ATR vs HA
compound								
ATR	0.0001*				0.0290*			
DEA	0.4631				0.2781			
DIA	0.0402*				0.1352			
HA	0.7886				0.0001*			
soil								
VFS		0.5654	0.1227	0.8511		0.0297*	0.4527	0.0001*
CS		0.0001*	0.0001*	0.0001*		0.2823	0.1472	0.0001*

^a *, significant at the 0.05 probability level.

140–234 L kg⁻¹ (37). With the exception of HA, the K_{oc} values for DEA (72 L kg⁻¹), DIA (142 L kg⁻¹), and HA (6197 L kg⁻¹) are consistent with those reported by Runes et al. (38). K_{oc} values reported for DEA, DIA, and HA by Seybold and Mersie (37) were 80–110, 128–130, and 493–609 L kg⁻¹, respectively.

The model *F* test indicated a significant difference in K_{oc} values among compounds and soils. Specifically, main effects were significant (Table 4). The K_{oc} values averaged across soils decreased in the order HA (299 L kg⁻¹) > DIA (114 L kg⁻¹) = atrazine (90 L kg⁻¹) > DEA (61 L kg⁻¹). This trend is generally in agreement with published literature and the K_d values presented in this study. However, the K_{oc} values averaged across compounds were significantly higher in the CS (151 L kg⁻¹) than in the VFS (131 L kg⁻¹). Similar results were reported for the K_{oc} values of isoproturon (24) and metolachlor (27) in VFS and CS. Thus, the K_{oc} values for all compounds are inflated in the CS, indicating that the adsorption properties of the organic matter are not identical among soils (42). In this study, relying on K_{oc} values to predict the transport of atrazine and HA would lead to an erroneous conclusion that the potential for atrazine and HA transport is higher in VFS than in CS.

Desorption. Desorption isotherms for atrazine and its metabolites are presented in Figure 2. On the basis of the coefficient of determination values, desorption isotherms for all compounds were adequately described by the Freundlich equation (Table 2). The $K_{f,des}$ values in the VFS decreased in the order HA (4.47 L kg⁻¹) > atrazine (2.51 L kg⁻¹) > DIA (2.24 L kg⁻¹) > DEA (1.70 L kg⁻¹). In the CS, the $K_{f,des}$ values decreased in the order HA (3.09 L kg⁻¹) > DIA (1.99 L kg⁻¹) > atrazine (1.23) > DEA (1.20). Ranges for $K_{f,des}$ values are consistent with those reported by Seybold and Mersie (37): 1.51–26.4 L kg⁻¹ for atrazine, 0.89–3.45 L kg⁻¹ for DEA, 1.24–6.79 L kg⁻¹ DIA, and 2.21–10.6 L kg⁻¹ for HA.

Larger $K_{f,des}$ values indicate that a greater proportion of the chemical is retained by the soil following successive desorption steps (36). The $K_{f,des}$ value for atrazine was 104% higher in VFS compared with that in CS. $K_{f,des}$ values for DEA, DIA, and HA were not different between VFS and CS. Therefore, increased levels of organic carbon in the VFS compared with CS should impede subsequent leaching and surface transport of adsorbed atrazine. However, leaching and surface transport of adsorbed DEA, DIA, and HA will presumably be equivalent between soils. Similarly, larger proportions of non-desorbable metolachlor (27), isoproturon (24) and fluometuron (25, 26) have been reported for VFS than for CS. In all cases, higher organic carbon in VFS compared with CS contributed to the increase in non-desorbable herbicide.

The Freundlich $1/n_{des}$ value describes nonlinearity in the desorption isotherm and can be used as an index of desorption intensity (45). In this experiment, the $1/n_{des}$ values are smaller than the $1/n_{ads}$ values for all chemicals, indicating hysteresis

(Table 2). The degree of hysteresis was quantified using eq 4. Our ω values are generally within the ranges reported by Seybold and Mersie (37), which were 63–223 for atrazine, 44–194 for DEA, 197–400 for DIA, and 141–355 for HA (Table 3).

The model *F* test indicated a significant difference in ω values among compounds and soils. Specifically, there was a compound by soil interaction (Table 4). Therefore, simple effects were evaluated (Table 5). The ω value for atrazine was greater in CS than in VFS, indicating a slower rate of desorption in CS than in VFS. Conversely, the ω value for DIA was higher in VFS than in CS, demonstrating that the desorption rate is slower in the VFS. The ω values for DEA and HA were not different between soils. In the VFS, ω values were not different among compounds. However, the ω value for atrazine in CS was greater than the values for DEA, DIA, and HA. Desorption hysteresis has been noted for atrazine and atrazine metabolites (36, 37, 39). A definitive explanation for hysteresis does not exist in the literature but may include nonattainment of equilibrium, precipitate formation, changes in desorption solution composition, degradation, volatilization, and irreversible binding (46).

In summary, our results corroborate previous studies regarding adsorption, desorption, and mobility of atrazine and its metabolites in agricultural soils. Under the conditions in this study, we have further determined that the order of mobility in the VFS is HA < atrazine = DIA < DEA. Moreover, atrazine adsorption and desorption parameters are significantly higher in the VFS compared with those in CS. Similarly, HA sorption is greater in the VFS compared with CS, but desorption of HA is not significantly different between soils. Therefore, the higher organic carbon content in the VFS compared with the CS may retard atrazine and HA transport to surface and ground waters. Conversely, DEA and DIA adsorption and desorption parameters are not significantly different between soils, indicating that VFS may not substantially impede the transport of DEA and DIA to surface and ground waters. In addition, using K_{oc} values to predict the mobility of atrazine and its metabolites may lead to an erroneous conclusion that the potential for the transport of these compounds is greater in VFS soil than in CS.

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