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Adsorption and Desorption of Atrazine, Hydroxyatrazine, and S-Glutathione Atrazine on Two Soils

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Adsorption and Desorption of Atrazine, Hydroxyatrazine, and *S*-Glutathione Atrazine on Two Soils[1]

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Abstract. **Adsorption and desorption isotherms for atrazine and two metabolites, hydroxyatrazine (HA) and *S*-glutathione atrazine (GSHA), were determined by batch equilibration on Plano and Waukegan silt loam soils at two soil pH levels (Plano, 6.1 and 4.5; Waukegan, 6.1 and 4.0). Freundlich adsorption isotherms were not affected by soil type except for GSHA at pH 4.0 to 4.5. When averaged over both soils, the order of adsorption at pH 6.1 was atrazine (K_f = 3.7) < GSHA (K_f = 7.3) << HA (K_f = 25) and at pH 4.0–4.5 was atrazine (K_f = 6.1) << HA (K_f = 58) ≤ GSHA (K_f: Plano = 35; Waukegan = 78). The average slope of the adsorption isotherms ($1/n_{ads}$) was 0.81. The slopes of all desorption isotherms ($1/n_{des}$) were less than their respective $1/n_{ads}$, indicating hysteresis. Atrazine desorbed into soil solution ($1/n_{des} > 0.0$). With the exception of GSHA which desorbed from the pH 6.1 Plano silt loam ($1/n_{des}$ = 0.15), desorption of HA and GSHA from other treatments was negligible ($1/n_{des}$ = 0.0). Consequently, leaching of HA and GSHA in these and similar soils is not likely, due to high adsorption and low desorption. Nomenclature: Atrazine, 6-chloro-*N*-ethyl-*N'*-(methylethyl)-1,3,5-triazine-2,4-diamine; hydroxyatrazine, 6-hydroxy-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine; *S*-glutathione atrazine, *S*-(4-ethylamino-6-isopropylamino-*s*-triazinyl-2-)glutathione.**

Additional index words. **Freundlich isotherms, herbicide leaching.**

INTRODUCTION

Because adsorption of herbicides to soil directly or indirectly controls the fate of herbicides, including movement in soil and subsequent leaching to groundwater, there has been much research in the area. For example, atrazine sorption to soil has been widely investigated (4, 5, 6, 10, 11, 16, 17, 20, 21, 22). While it is important to understand sorption processes and mechanisms of the herbicide, it is equally as important to know the sorption mechanisms of the major metabolites. However, the soil sorption characteristics of herbicide metabolites and conjugates are not often reported.

Hydroxyatrazine (HA)[3] (Figure 1), formed from hydrolysis of atrazine with the –Cl replaced by an –OH group (1, 8, 11, 17, 18), is strongly sorbed to soil (9, 10, 17, 19, 20). Schiavon (20) has reported that HA applied at 6.7 kg ha^{-1} did not leach below 24 cm in intact outdoor soil columns. Desorption of HA from soil, however, has not been characterized.

A water-soluble metabolite of atrazine formed in plants, animals, and insects is the *S*-glutathione conjugate (8, 12, 13, 14) (Figure 1). Plants containing a specific glutathione *S*-transferase can convert atrazine to *S*-glutathione atrazine (GSHA)[3] (8, 12, 14). Other herbicides including chloroacetamides and thiocarbamates and insecticides can also be conjugated with glutathione (12, 13). Glutathione conjugate formation of atrazine was found to be the predominant detoxification mechanism in resistant corn (8) when atrazine was applied to leaves (8). Two-thirds of the applied atrazine was in a peptide conjugate form 24 h after application.

Glutathione herbicide conjugates or other peptide conjugates may enter the soil system by breakdown of incorporated plant debris. Therefore, there is a potential for atrazine transformation products to leach to ground water. Neither adsorption nor desorption of GSHA or other glutathione or peptide conjugates in soil has been characterized. The objectives of this research were to determine adsorption and subsequent desorption of atrazine, HA, and GSHA as a model peptide conjugate on two soils, each modified in the field to two soil pH levels.

MATERIALS AND METHODS

Chemicals. Atrazine solutions were prepared containing 4.0, 11.7, or 52.8 μmol L^{-1} of atrazine in 0.01 M $CaCl_2$. The atrazine solutions contained 51 kBq L^{-1} of [ring-UL-^{14}C]-atrazine. Specific activity of initial ^{14}C-atrazine was 129 MBq mmol^{-1} and final specific activity ranged from 1 kBq μmol^{-1} to 12.6 kBq μmol^{-1}.

The acid hydrolysis method for simazine (3) was adapted for hydrolysis of atrazine. Either 20.5 or 4.2 mg of atrazine with 174 kBq of ^{14}C-atrazine was dissolved in 10 ml of chloroform to which 10 ml of 6 N HCl was added, and the solution was stirred for 18 h at 40 C. The chloroform was evaporated and the remaining acid solutions were diluted to 200 ml with 0.01 M $CaCl_2$. These solutions were partitioned twice with dichloromethane to remove unreacted atrazine. The $CaCl_2$ fractions were diluted to 500 ml with additional 0.01 M $CaCl_2$ and adjusted to pH 7 with NaOH. Solutions were filtered through a 0.2-μm silver filter to remove undissolved chemical. Approximately 30% of the original added ^{14}C remained in the final 0.01 M $CaCl_2$ solutions.

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[3]Abbreviations: HA, hydroxyatrazine; GSHA, *S*-glutathione atrazine; TLC, thin-layer chromatography; LSC, liquid scintillation counting; UL, uniformly labeled.

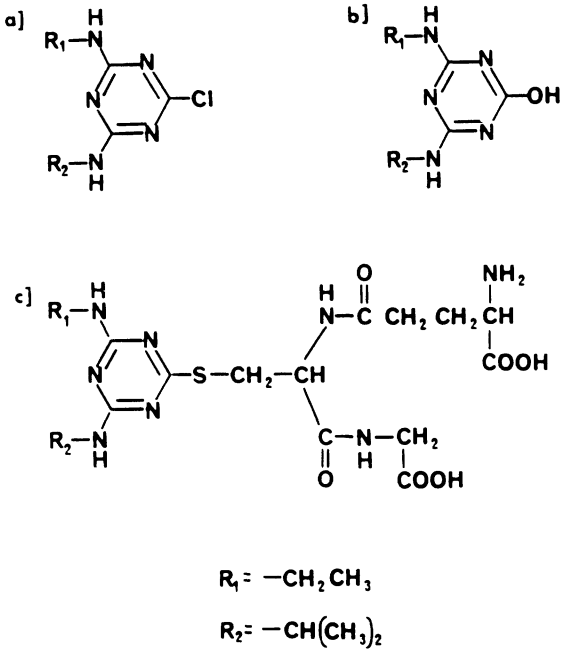

Figure 1. Structures of atrazine (a), hydroxyatrazine (b), and *S*-glutathione atrazine (c).

Purity of the solutions for ^{14}C-HA was determined by spotting 100 µl of each solution on silica gel thin-layer chromatography (TLC)[3] plates[4] which were developed to a height of 15 cm with n-butanol/acetic acid/water (11:5:4, v/v/v) and cochromatographed with an HA standard (R_f = 0.51). The R_f value for parent atrazine was 0.79. The final solutions after filtration contained 38.5, 19.3, 18.2, and 9.1 µmol L^{-1} HA in 0.01 M $CaCl_2$. Final specific activities of the HA solutions were 1.2 kBq µmol^{-1} for two higher concentrations and 7.4 kBq µmol^{-1} for the two lower concentrations.

GSHA was synthesized by a method similar to that used by Crayford and Hutson (7) for nonenzymatic synthesis of glutathione cyanazine. Either 20.3 or 5.4 mg of atrazine with 100 kBq of ^{14}C-atrazine was dissolved in 5 ml of acetone to which 200 µl of trimethylamine was added. Each solution was evaporated to dryness after 18 h at room temperature (25 C), and 600 µl of an aqueous solution containing 8.4 mg of sodium carbonate and 20.3 mg of reduced glutathione was added. These solutions were heated to 50 C, stirred for 18 h, diluted to 200 ml with 0.01 M $CaCl_2$, and partitioned twice with dichloromethane. The aqueous solutions, which contained 95% of the ^{14}C, were brought up to a volume of 500 ml with 0.01 M $CaCl_2$, adjusted to pH 7, and passed through a silver filter. The solutions were spotted on TLC plates and developed as previously described. The only ^{14}C spot had an R_f value of 0.28 that tested positive to ninhydrin, indicating the presence of amino acids. Dilutions with 0.01 M $CaCl_2$ were made to give GSHA concentrations of 9.8, 19.5, 36.3, and 72.6 µmol L^{-1}. Final specific activity for the two higher concentrations was 2.4 kBq µmol^{-1} and for the two lower concentrations was 8.9 kBq µmol^{-1}.

[4]Baker, Si. 250 F-PA (19 C) TLC plates. J. T. Baker Chem. Co., Phillipsburg, NJ.

Table 1. Mechanical and chemical characteristics of Waukegan and Plano silt loam soils.

Parameter	Characteristics	
	Waukegan	Plano
Silt, %	59	73
Clay, %	22	21
Organic carbon, g kg^{-1}	28	26
CEC, cmol kg^{-1}	21	17
pH[a], high	6.2	6.3
pH[a], low	4.1	4.7

[a]Determined in soil:0.01 M $Cacl_2$ (1:1, w/v) slurry.

Soil. Soil from the 0- to 4-cm depth of a Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, mesic Typic Hapludolls) and the 0- to 10-cm depth of a Plano silt loam (fine-silty, mixed, mesic Typic Argiudoll) was collected, air dried, and passed through a 2.0-mm sieve. Soil properties are listed in Table 1. The Waukegan soil was taken from adjacent plots at Rosemount, MN, in which two soil pH levels were produced by treating the soil each year for 7 yr with 0 or 200 kg N ha applied as $(NH_4)_2SO_4$. The Plano soil was taken from adjacent plots at Arlington, WI, in which soil pH levels were produced by differential elemental sulfur applications.

Adsorption. A 10-ml aliquot of each concentration of atrazine, HA, or GSHA was added to 10 g of each soil/pH combination in a 25-ml glass centrifuge tube. The tubes were sealed with Teflon-lined caps and mechanically shaken on a variable speed shaker at 4 excursions s^{-1} for 24 h. Time study results indicated that 98% of each chemical that was adsorbed in 24 h was adsorbed within the first 2 h and that the change in the amount of chemical adsorbed between 24 and 48 h was less than 1%. Following equilibration, each tube was centrifuged for 15 min at 10 000 rpm (ca 10 000 × *g*) and a 4-ml aliquot of supernatant was removed. The supernatant pH was determined. The amount of ^{14}C in the supernatant was determined by liquid scintillation counting techniques, with correction for quenching and background. The amount of atrazine, HA, or GSHA adsorbed to the soil was determined by the difference between that contained in soilless blanks and that in solution after soil equilibration.

All adsorption studies were run at 23 C. Duplicate samples were run for each initial concentration-soil type-pH combination. Adsorption isotherms were calculated for each chemical and soil treatment combination using the linearized form of the Freundlich equation

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

Table 2. The $K_{f\,ads}$, slope ($1/n_{ads}$), and 95% upper and lower confidence limits for atrazine, hydroxyatrazine (HA), and *S*-glutathione atrazine (GSHA) adsorption isotherms fit to the linearized form of the Freundlich equation.

Chemical	Soil	Equilibration soil pH	K_f[a]	1/n[b]	r^2
			$\mu mol^{1-1/n}\ L^{1/n}\ kg^{-1}$		
Atrazine	Plano	6.1	3.8(3.6–4.0)	0.80	0.99
		4.5	5.7(4.7–7.0)	0.81	0.99
	Waukegan	6.1	3.6(2.7–4.9)	0.85	0.99
		4.0	6.5(4.7–8.9)	0.83	0.99
HA	Plano	6.1	21.6(18.7–25.0)	0.75	0.99
		4.5	57.4(32.9–100)	0.63	0.91
	Waukegan	6.1	26.4(21.5–32.4)	0.76	0.98
		4.0	59.8(39.8–89.9)	0.65	0.92
GSHA	Plano	6.1	7.0(4.9–9.8)	0.96	0.97
		4.5	35.2(20.3–61.1)	0.79	0.93
	Waukegan	6.1	7.6(5.8–10.0)	0.97	0.98
		4.0	78.1(61.9–85.9)	0.94	0.99

[a]Numbers in parenthesis are the 95% confidence interval (CI) for K_f, the antilogs of log K_f – CI log K_f and log K_f + CI log K_f.

[b]Standard error of 1/n < 0.09.

where x/m is the μmol of chemical adsorbed per kg soil, C is μmol herbicide per L of supernatant solution after equilibration, and K_f and 1/n are empirical constants.

Desorption. Desorption studies were conducted by replacing the supernatant in the adsorption study from the initial solutions containing 11.7 μmol L^{-1} atrazine, 19.3 and 18.2 μmol L^{-1} of HA, and 36.3 and 19.5 μmol L^{-1} GSHA for each soil-pH level with 4 ml of herbicide/metabolite-free soil extract. The soil extract was the supernatant from a soil:0.01 M $CaCl_2$ (1:1, w/v) slurry which was equilibrated for 24 h and centrifuged as described above.

After the supernatant was replaced, the equilibration tubes were vibrated to disperse the soil pellet, mechanically shaken as previously described, and recentrifuged. The desorption equilibration process was repeated for three 24-h periods. Supernatant pH for each soil-soil pH-chemical combination was determined after the final chemical desorption. Desorption studies were run at 23 C using two replicates for each treatment.

The concentration of ^{14}C present in the desorption solutions was determined and the amount of herbicide/metabolite that remained adsorbed to the soil after each desorption step was calculated by subtraction. Desorption isotherms were calculated for each herbicide/metabolite concentration-soil-soil pH level treatment assuming total recovery of the herbicide/metabolite.

Atrazine/metabolite analysis. Radioactivity (^{14}C) of all solutions was determined by liquid scintillation counting (LSC)[3] techniques, with correction for quenching and background. Count rates were converted to the concentration of atrazine/metabolite in solution.

A portion of the equilibration solutions was dried and brought up to 200 μl in 0.01 M $CaCl_2$. These concentrated solutions were spotted on TLC plates and developed as previously described to determine the types of ^{14}C-compounds in solution. Standards of ^{14}C-atrazine, ^{14}C-HA, and *S*-glutathione ^{14}C-atrazine shaken in 0.01 M $CaCl_2$ for the same time as the equilibration solutions were cochromatographed on the plate with soil extracts.

Statistical analyses. Freundlich adsorption and desorption isotherm coefficients were calculated by the least squares technique using the log-transformed equilibrium data. Statistical evaluation included Bartlett's test for homogeneity of variances, comparison of slopes and elevations of the regression lines, and calculation of the 95% confidence intervals for the intercept (log K_f) and standard error of the slope (1/n).

RESULTS AND DISCUSSION

Adsorption. Adsorption of atrazine, HA, and GSHA was adequately described ($r^2 \geq 0.91$) for each soil-pH level combination by the linearized form of the Freundlich equation (Table 2, Figure 2). Atrazine adsorption was greater on the low than the high pH soils as indicated by a higher K_f value for the low pH soils. The Kf value indicates the amount of chemical sorbed to the soil when the amount in solution is

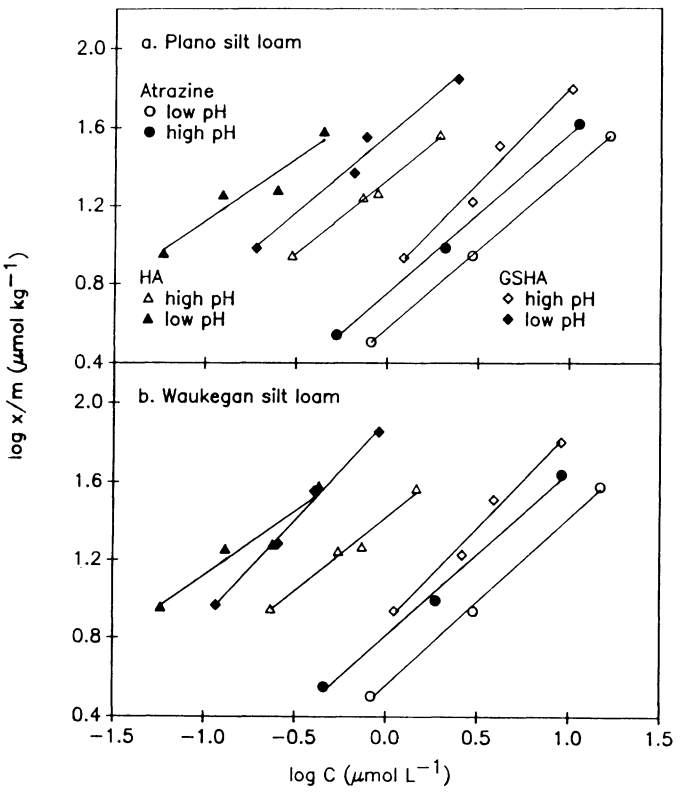

Figure 2. Adsorption isotherm for atrazine, hydroxyatrazine, and *S*-glutathione atrazine for Plano and Waukegan silt loam soils at two pH levels. The number of points used to determine the isotherm lines: for atrazine, n = 6; for HA and GSHA, n = 8.

Table 3. The $K_{f\,des}$, slope ($1/n_{des}$), and 95% upper and lower confidence limits for atrazine, hydroxyatrazine (HA), and *S*-glutathione atrazine (GSHA) desorption isotherms fit to the linearized form of the Freundlich equation.

Chemical	Initial concentration	Soil type	Equilibration soil pH	K_f[a]	$1/n$[b]	r^2
	μmol L^{-1}			μmol$^{1-1/n}$ $L^{1/n}$ kg^{-1}		
Atrazine	11.7	Plano	6.1	5.7(5.5–6.0)	0.40	0.97
			4.5	7.8(7.4–8.3)	0.29	0.88
		Waukegan	6.1	5.4(5.3–5.6)	0.43	0.98
			4.0	8.7(8.4–9.1)	0.20	0.90
HA	19.3	Plano	6.1	18.5(17.9–18.7)	0.07	0.90
			4.5	19.0(18.9–19.2)	–0.001	0.01
		Waukegan	6.1	18.5(18.4–18.5)	–0.02	0.97
			4.0	18.9(18.8–18.9)	–0.01	0.95
	18.2	Plano	6.1	17.8(17.7–18.0)	0.01	0.86
			4.5	18.6(18.6–18.7)	–0.001	0.12
		Waukegan	6.1	18.2(18.1–18.3)	0.05	0.91
			4.0	18.4(18.4–18.5)	0.01	0.88
GSHA	36.3	Plano	6.1	26.5(24.9–28.2)	0.13	0.58
			4.5	35.8(35.3–36.4)	0.04	0.42
		Waukegan	6.1	30.6(27.0–34.6)	0.04	0.91
			4.0	36.3(36.2–36.4)	0.01	0.82
	19.5	Plano	6.1	13.9(13.4–14.5)	0.17	0.88
			4.5	19.0(18.8–19.3)	0.02	0.43
		Waukegan	6.1	16.3(16.0–16.5)	0.04	0.87
			4.0	19.6(19.5–19.6)	0.01	0.93

[a]Numbers in parenthesis are the 95% confidence interval (CI) for K_f, the antilogs log K_f–CI log K_f and log K_f + CI log K_f.

[b]Standard error of $1/n < 0.09$.

1 μmol L^{-1}. Atrazine is a weak base having a pKa of 1.7 and becomes protonated as the pH decreases (16, 26), thereby increasing soil adsorption of atrazine. In a previous study, adsorption of atrazine on these soils at a pH of approximately 5.3 was intermediate to the adsorption at high and low pH's (5).

More HA than atrazine was adsorbed at both soil pH levels. The increased adsorption is evidenced by higher K_f values for HA compared to atrazine (Table 2). More HA was adsorbed at low pH levels than at the high pH levels for each soil. The pKa of HA is approximately 5.2 (23, 25). Although HA is more soluble at pH 4 than 7 (24), it is postulated that a keto form of the protonated HA species is bound to the soil at low pH (18), thus increasing HA adsorption.

GSHA adsorption was intermediate to atrazine and HA on both soils at the high pH as indicated by an intermediate K_f value. Once again, more GSHA was adsorbed on the low than the high pH soil. The low pH Waukegan soil was 0.5 pH units below the Plano low pH treatment and adsorption of GSHA was greater on the lowest pH soil. GSHA is more polar and more water soluble than atrazine (12). The glutathione portion of the conjugate may have a great influence on the chemical properties of GSHA. Glutathione is freely water soluble and the pKa of free L-glutathione is 3.6. Acid titration curves of GSHA closely followed those of free reduced *L*-glutathione (unpublished data). Greater adsorption of GSHA would be expected as the conjugate becomes protonated at the lower pH's.

The slope ($1/n_{ads}$) of the adsorption isotherm slope of the atrazine and HA was less than 1. A slope less than 1 indicated that as the initial concentration of atrazine/metabolite increased, the percentage of atrazine/metabolite adsorbed to the soil decreased. The slope of approximately 1 for GSHA on the Plano high pH soil and Waukegan soil at both pH's indicated that the percentage of GSHA adsorbed to the soil was independent of the initial solution concentration. Atrazine/metabolites in the supernatant after adsorption were confirmed to be the chemical added by TLC analyses. No transformation of the initial chemical added was observed in the supernatant.

Desorption. Desorption of atrazine and metabolites from both soils was hysteretic; i.e., $1/n_{ads}$ was greater than $1/n_{des}$. Causes of hysteresis in solute adsorption are unclear but may include nonattainment of equilibrium during desorption, formation of chemical precipitates, changes in desorption solution composition, loss of chemical due to degradation or volatilization, or irreversible binding of chemical to soil (2).

In this experiment, formation of precipitates in the adsorption solutions was avoided by adjusting the pH of the initial solutions from approximately pH 2 to pH 4 to pH 7. While solutions that contained atrazine and GSHA remained clear, HA was less soluble at pH 7 when compared to the lower pH solution. All solutions were filtered to remove nondissolved chemical. Fresh soil extract was used for desorption equilibrations to minimize changes in the composition of the desorption solution. The final pH values of the desorption solutions were similar to the adsorption solutions.

Hysteresis of atrazine adsorption-desorption isotherms has been reported (4, 6, 21). The amount of atrazine not desorbed after five 1-day soil extractions accounted for approximately 14% of the observed hysteresis in a Waukegan silt loam with a pH of 5.8 (6). Desorption of atrazine from the two soils

used in the present study was similar and pH dependent (Table 3). More atrazine was desorbed from the high compared to the low pH treatments. Greater atrazine desorption was indicated by lower $K_{f\,des}$ and higher $1/n_{des}$ compared to the low pH soils. Less atrazine desorption at the lower pH could be attributed to greater protonation and ionic bonding of the herbicide. All ^{14}C present in supernatant at the end of the desorption period cochromatographed with parent atrazine.

The slope of the HA desorption isotherm ($1/n_{des} = 0$) indicates that HA was not desorbed by soil solution extracts during the three 1-day desorption periods (Table 3). The amount of nonadsorbed HA in soil solution decreased each day; however, the decrease can be attributed to dilution of the remaining HA in the supernatant with fresh soil extract. Radioactivity in the desorption solutions was confirmed to be HA by TLC analysis. HA appeared to be irreversibly bound to the soil.

At both initial concentrations, GSHA desorbed slightly from the high pH Plano silt loam (Table 3). The average slope of the desorption isotherm was 0.15 (Table 3). Desorption from the low pH Plano soil and the two pH levels of the Waukegan silt loam was negligible ($1/n_{des} = 0$). Radioactivity in the final day's desorption supernatants could not be confirmed as GSHA due to the low amount of radioactivity remaining in solution. GSHA, a triamino acid compound, can be catabolized to di- and monoamino acid conjugates (13, 15). Ring mineralization of the ^{14}C-triazine portion of GSHA from a Waukegan silt loam at 25 C was approximately 0.2% over an 8-day period and was similar to the ^{14}C-atrazine mineralization rate in the same soil (unpublished data). However, the ^{14}C portion of the original GSHA molecule was not desorbable with soil extract.

In summary, two atrazine metabolites, HA and GSHA, were adsorbed to two silt loam soils to a greater extent than the parent atrazine. Adsorption of all three chemicals was pH dependent with higher adsorption on the low than the high pH soil. Atrazine was desorbed into soil solution over a 3-day period; however, HA and GSHA were not desorbed from the soil in most cases. These data indicate that once these metabolites are adsorbed, desorption will be very slow. The strong adsorption and low desorption characteristics indicate that HA and GSHA are not likely to leach in the soil profile.

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