EVALUATION OF ATRAZINE BINDING TO SURFACE SOILS

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ABSTRACT

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), one of the most widely used agro-chemicals in the Midwestern United States, has appeared in surface waters at levels above the maximum contaminant level of 3 µg/L. Although atrazine is relatively mobile in soil-water systems, it can associate with a variety of soil components. Our study focused on atrazine interactions with two surface soils from the Hillsdale Reservoir Basin in eastern Kansas. One soil was collected from an agricultural field (3.4% SOM), while the other was obtained from an adjacent forested area (6.2% SOM). U-ring-^{14}C-labeled atrazine was used in sterile bottle-point adsorption experiments with synthetic "surface water" to create adsorption isotherms. The distribution of "bound" atrazine was then determined by "surface water" extractions (quickly desorbed), ethyl acetate extractions (slowly desorbed), and alkali extractions (humic and fulvic acid bound). Atrazine remaining on each soil component after extraction was determined by combusting the soil at 925°C and counting the $^{14}CO_2$ on a liquid scintillation counter. At least 70% of the initially sorbed atrazine was quickly desorbed, and soil type did not have a significant effect on atrazine distribution. The presence of the soil enzyme, horseradish peroxidase, was determined to have little effect on the nature and extent of atrazine binding.

Key words: atrazine, sorption, desorption, soil organic matter, enzyme

INTRODUCTION

Agricultural chemicals, while often benefiting farming productivity, can have detrimental environmental effects when applied improperly. Herbicides, such as atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), are frequently detected in ground and surface waters (Koplin et al., 1997; Miller et al., 2000; Pereira and Rostad, 1990). Several factors affect adsorption and desorption of herbicides from soils, including physico-chemical characteristics of the soil and the herbicide, surface acidity, temperature, electric potential of the clay surface, and nature of the herbicide formulation (presence of surfactants, etc.) (Bailey and White, 1970). Several recent studies have focused on the role of soil organic matter (SOM) in the overall fate of agricultural chemicals (Barriuso and Koskinen, 1996; Barriuso et al., 1992a; Capriel et al., 1985; Kaloušková,

1987; Piccolo et al., 1998; Saint-Fort and Visser, 1988; Xing et al., 1996; Wang et al., 1992). This paper evaluates the distribution of adsorbed atrazine among the fulvic acid, humic acid, and humin components of SOM associated with two Kansas surface soils. A sorption-enhancing process, engineered humification, was also investigated.

BACKGROUND

Atrazine, despite being banned in most European countries, is the most widely used herbicide in the United States and is registered in more than 70 countries worldwide (Kauffmann et al., 2000). It has been used since 1958 as a pre- and post-emergent herbicide to control broad-leafed weeds in the production of corn and sorghum (Jones et al., 1982). Once absorbed though the roots of the target species, atrazine is translocated to the

leaves and apical meristem, where photosynthesis is inhibited, causing chlorosis and death of the weed (Donnelly et al., 1993). Corn and other crops are able to take up atrazine, but decompose it enzymatically before herbicidal effects occur (Wu, 1980). While atrazine is only moderately persistent in the environment, with a half-life of one to twelve months, appearance in surface waters raises concern due to its possible health hazards (Bouquard et al., 1997). Atrazine is a probable human carcinogen, and its current EPA maximum contaminant level (MCL) in drinking water is 3.0 µg/L. In addition, atrazine has recently been reported to have long-term reproductive and endocrine-disrupting effects (Tugulea et al., 1998). Additional properties of atrazine are listed in Table 1.

Recent attention has focused on atrazine loadings in the Hillsdale Reservoir in northeast Kansas. A 1997 USGS study revealed significantly higher concentrations of triazine pesticides in water samples taken downstream of the reservoir when compared to upstream samples (Putnam, 1997). Such findings indicate herbicide storage, rather than an expected dilution effect. Since the reservoir is only 92,160 acres in size, and no significant climate change is expected, it is believed that the herbicides are being shielded from biodegradation, possibly through sorption to natural organic matter. While parallel studies are examining sediment and water samples from the reservoir, the objective of this research is to characterize atrazine behavior at the point of application: Hillsdale Basin soils.

Once atrazine has been applied to soils, it has the ability to associate with various soil components, including soil organic matter. Adsorption isotherms, such as the Freundlich isotherm, are often used to describe the overall

Table 1. Physical and chemical properties of atrazine.
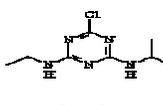
Structure	Atrazine
Application Rate (lb/acre ai [b])[a]	1-2
Aqueous Solubility (mg/L)[a]	33
log K_{ow}[a]	2.68
Melting Point (°C)[a]	175-177
Vapor Pressure (mPa, 25°C)[a]	0.038
Henry's Law Constant (Pa-m³/mol, 25 °C)[a]	2.5×10^{-4}
pK$_a$ (20°C)[a]	1.68
MCL (µg/L)[c]	3.0

[a]Source: Capel et al., 1999
[b]ai = active ingredient
[c]Source: Acero et al., 2000

sorption characteristics of a particular soil at equilibrium with a range of contaminant concentrations. The Freundlich model is described by the equation:

$$q_e = K_F C_e^n \text{ or } \log q_e = n \log C_e + \log K_F$$

where q_e and C_e represent the solid- and aqueous-phase equilibrium concentrations of the target chemical, respectively. The Freundlich constant K_F is a measure of the sorption capacity of the sorbent. The Freundlich n measures sorption linearity, which is related to the heterogeneity of sorption site energy. Both K_F and n are dependent upon the physical and chemical properties of the sorbate and sorbent.

Adsorption of atrazine to various soils, clay minerals, and soil organic matter has been widely researched. In general, SOM becomes an important factor with atrazine adsorption in soils with high SOM contents $(> 6\%)$ (Shea, 1989). Barriuso et al. (1992b) examined atrazine sorption to two Brazilian oxisols and concluded that SOM was the most important factor effecting atrazine adsorption. Xing et al. (1996) examined the role of SOM more specifically by examining competitive sorption between atrazine and other organic compounds to various sorbents. While the study demonstrated competitive sorption between atrazine and s-triazine analogs, it also provided evidence for non-linear or dual-mode sorption of atrazine to peat and humic acid particles. Piccolo et al. (1998) found that the type of SOM plays an important role in atrazine adsorption. Studies using ^{13}C-NMR indicated that aliphatic groups in humic substances may contribute more to

atrazine binding than aromatic groups. Atrazine adsorption to humic acid was higher than adsorption to montmorillonite in a study by Celis et al. (1997); however, several studies reveal notable atrazine associations with clay minerals. Roy and Krapac (1994) found that atrazine sorption to low organic carbon sand, till, and alluvial samples conformed to linear isotherms. In addition, for eight of the ten adsorbents studied, atrazine adsorption was not proportional to the organic carbon content, indicating mineral surface interactions. Other studies also indicate that clay minerals can contribute to the physical adsorption of atrazine, particularly when SOM content is low (Brown and White, 1969; Laird et al., 1994).

While adsorption is an important mechanism to examine, desorption is equally significant, since it is directly related to herbicide runoff and leaching that leads to surface water and aquifer contamination, respectively. Barriuso et al. (1994) found that atrazine adsorption was generally reversible for smectities, suggesting weak van der Waals forces or hydrogen bonds between the atrazine molecules and the clay surfaces. For soil samples, particularly those high in SOM, however, adsorption is typically less reversible. Many researchers have found that atrazine exhibits hysteresis effects, i.e. less herbicide desorbs than is predicted by adsorption isotherms. Hysteresis reflects the portion of contaminant that is very strongly or irreversibly bound to the soil or SOM, and has been recently described by the hysteresis index:

Hysteresis Index, $HI = \dfrac{q_e^d - q_e^a}{q_e^a}\Big|_{T, C_e}$

where q_e^a and q_e^d are solid-phase solute concentrations for the adsorption and desorption experiments, respectively, and T and C_e specify conditions of constant temperature and residual aqueous-phase concentration (Huang and Weber, 1997). Several studies have confirmed hysteretic characteristics of atrazine, with degrees of hysteresis varying with soil type and SOM content (Ma et al., 1993; Clay and Koskinen, 1990; Roy and Krapac, 1994).

The adsorption and desorption of atrazine has considerable effects on its biodegradation and ultimate fate in surface soils. Barriuso et al. (1997) found that SOM content affects atrazine biodegradation; as increasing amounts of compost were added to soils, the formation of bound residues increased and atrazine mineralization decreased significantly. Capriel et al. (1985) analyzed soil samples that were sprayed with ^{14}C-labeled atrazine nine years earlier and found that approximately 50% of the radioactivity remained. Furthermore, 90% of the ^{14}C was present in organic materials, present as parent atrazine as well as metabolites. Such results indicate that soil organic matter plays an important role in the overall bioavailability of atrazine. While there has been widespread research on atrazine interactions with soil and soil organic matter, results are very case-specific, and available information is unable to explain the scenario at the Hillsdale Reservoir. Therefore, the goal of this study is to develop a specific understanding of atrazine associations with Hillsdale Basin surface soils and soil organic matter.

PROCEDURES

Soils

Two soils were collected near the city of Gardner in Johnson County, Kansas. The site, which is north of the Hillsdale Basin, drains into the reservoir. One soil was collected from an agricultural field (SOM = 3.4%, pH = 6.1), while the other was obtained from an adjacent forested area (SOM = 6.2%, pH = 6.9). Both soils belong to the Woodson Series (silty loam). Additional soil characteristics are shown in Table 2. The two soils were selected due to their varying organic matter content and type, while having similar parent materials, pH, and

Table 2. Properties of two Hillsdale Reservoir Basin soils.

Type	Agricultural Soil Woodson (silty loam)	Forest Soil Woodson (silty loam)
Organic Matter Content	3.4%	6.2%
pH	6.1	6.9
Texture Composition	32% sand 52% silt 16% clay	38% sand 52% silt 10% clay
Cation Exchange Capacity (CEC)	19.8 meq/100 g	23.7 meq/100 g

texture composition. In addition, atrazine had not been applied to the site for approximately a year and a half.

Upon collection, soils were air-dried and passed through 1-mm and 500-mm sieves. Each soil was split into smaller representative fractions using the coning and quartering method. Before soils were used, spore-forming bacteria were neutralized using a sequential autoclaving/incubating procedure, where the soils were incubated twice for 24 hours and autoclaved three times for 50 minutes. Soils were then stored in the dark in glass jars at 0°C.

Chemicals

To enhance atrazine tracking and detection limits, U-ring-^{14}C-labeled atrazine was used. The chemical was purchased from Sigma Aldrich and had a specific activity of 18 µCi/ µmol. Known volumes of radioactive atrazine were added to non-radioactive solutions of atrazine (Supelco) in synthetic surface water. Radioactive and non-radioactive atrazine were used without further purification, and stock solutions were prepared in acetone. The synthetic surface water consisted of 500 mg/L sodium azide (Fisher Scientific) in distilled water to ensure sterile conditions. Horseradish peroxidase (Type II, RZ: 1.9) was purchased from Sigma Chemicals and used without further purification. Radioactivity remaining in solution during bottle-point adsorption experiments was enumerated as disintegrations per minute (dpm) using a Beckman 6500 liquid scintillation counter (LSC) with quench and luminescence corrections. Radioactivity remaining on the soils was determined by combustion at 925°C, using an OX-500 R.J.Harvey Bio-Oxidizer and counting the $^{14}CO_2$ produced on the liquid scintillation counter.

Adsorption-Desorption Experiments

Sorption-desorption experiments were conducted in centrifuge tubes at five sorbate concentrations spanning three orders of magnitude. The initial atrazine concentrations were 0.25, 1.0, 2.5, 10.0, and 25.0 µM. Preliminary experiments determined that a solid/liquid ratio of 0.175 sorbed a desired 30-70% of added atrazine. Other preliminary experiments showed negligible increase in atrazine sorption after seven days of contact for the selected solid/ liquid ratio; therefore atrazine adsorption experiments were allowed a seven-day equili- bration period.

Adsorption experiments were conducted in completely mixed batch reactors (CMBRs) consisting of 10 mL glass centrifuge tubes closed with open-closure phenolic caps, sealed with Teflon-lined silicone septa. Tubes were first filled with 1.5 grams of soil, and then approximately 8.5 mLs solution containing radioactive and non-labeled atrazine was added with minimal headspace. Nine replicate CMBRs were used for each initial atrazine concentration. Two controls containing no soil were used to determine atrazine losses. The tubes were vigorously mixed with a Vortex- mixer, sealed with Teflon tape to minimize losses, and then placed on a custom-design vertical tumbler for seven days at 25 ± 1°C. At the end of the equilibration period, the tubes were centrifuged at 2200 rpm for 45 minutes to separate the solid and liquid phases. A 250-µL

aliquot was removed from each tube and transferred into a scintillation vial containing 5 mL scintillation fluid (ScintSafe Plus 50%, Fisher Scientific). The vials were then gently mixed and allowed to sit overnight to minimize chemiluminescence before LSC analysis. Adsorption data was fitted to the Freundlich model.

After the adsorption data was collected, the remaining atrazine solution was removed with a pipette, and replaced with clean synthetic surface water for sequential "fill-and-draw" desorptions described by Bhandari et al. (1997). The tubes containing clean surface water were re-capped and placed on the tumbler overnight for atrazine desorption. The next day, the tubes were centrifuged and the supernatant was analyzed as previously discussed for desorbed atrazine on an LSC. The liquid was then removed, and the procedure was repeated until atrazine concentrations fell below the detection limit (typically after seven desorptions). After all of the water-extractable atrazine was removed, three of the replicates were immediately combusted to determine the amount of atrazine remaining on the soil as $^{14}CO_2$. The atrazine removed with synthetic surface water was operationally defined as "quickly desorbed" atrazine.

After surface water desorptions, "fill-and-draw" desorptions were repeated using a 4:1 v/v ratio of ethyl acetate and water. This particular solvent mixture was chosen based on recent literature comparing solvent efficiency for atrazine extraction from soil (Laabs et al., 1999). After one extraction, the slowly desorb-ing atrazine was removed and counted on an LSC as previously discussed. An additional extraction removed non-detectable concentrations of atrazine. After the two extractions, three of the remaining six replicates were immediately combusted and the "slowly desorbed" atrazine was quantified from the $^{14}CO_2$ on a LSC.

Humic Acid-, Fulvic Acid-, and Soil/Humin-Bound Atrazine

After water and solvent desorptions, the remaining three samples were alkali-extracted under a nitrogen atmosphere with 0.1 N sodium hydroxide (Fisher Scientific) to remove humic and fulvic acids. Each day, the tubes were removed from the tumbler, centrifuged at 2400 rpm for 45 minutes, and the supernatant transferred into separate tubes. Fresh sodium hydroxide was added and the procedure was repeated until the supernatant became clear in color, and negligible humic or fulvic acids remained in the soil. After eight to ten alkali extractions, the remaining soil was dried and combusted to determine the atrazine that remained bound to the soil/humin.

To separate the humic acid from the fulvic acid, a few drops of concentrated sulfuric acid were added to the remaining supernatant samples to precipitate the humic acid. The samples were then centrifuged at 1200 rpm for 60 minutes and the supernatant fulvic acid was removed. The remaining humic acid was immediately combusted and the bound atrazine, measured as $^{14}CO_2$, was counted on an LSC. The fulvic acid was too dilute for direct LSC analysis, so fulvic acid-bound atrazine was
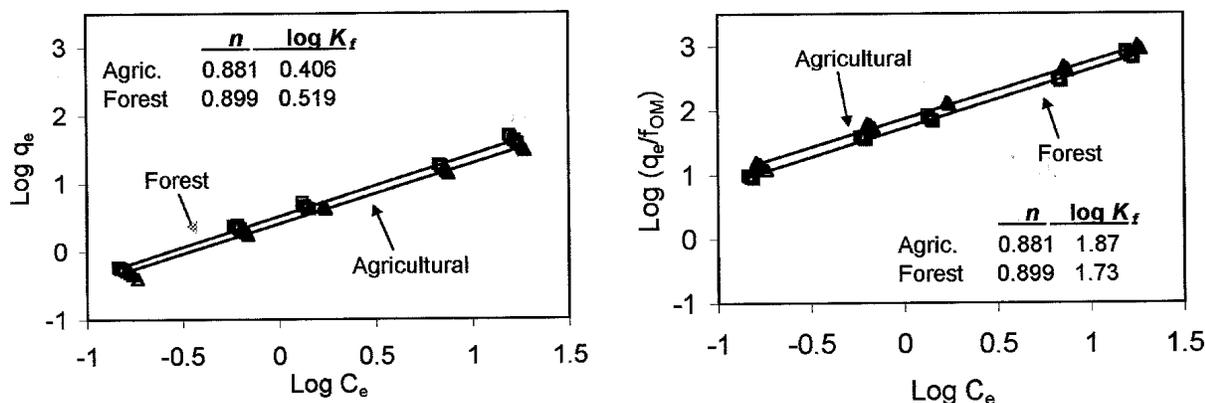
Figure 1. Adsorption of atrazine to two Hillsdale Basin soils displayed as a Freundlich isotherm (left), and a Freundlich isotherm adjusted for SOM content (right).

determined by mass balance since losses would be large during concentration.

RESULTS AND DISCUSSION

Adsorption Isotherms

The adsorption isotherms for both the agricultural and forest soils were near linear, with Freundlich n values of 0.88 and 0.90, respectively (Figure 1, left). Values of $n < 1$ are indicative of adsorption by heterogeneous media where high energy sites are occupied first, followed by adsorption at lower energy sites, while linear isotherms ($n = 1$) indicate simple partitioning into the amorphous SOM (Weber and DiGiano, 1996). The higher n value for the forest soil reflects a larger presence of young amorphous SOM, when compared to the agricultural soil. Figure 1 (left) also indicates that the forest soil has a slightly higher adsorption capacity (0.52) than the agricultural soil (0.41).

While the forest soil appears to have a slightly higher adsorption capacity than the agricultural soil, the trend reverses when SOM content is accounted for (Figure 1, right). The

forest soil, which has SOM content of 6.2%, had a lower sorption capacity per unit SOM content than the agricultural soil, which has 3.4% SOM content. This is likely related to the type of organic matter present; forest soil is likely to contain more young, amorphous organic matter, thus explaining the relatively higher Freundlich n value. Since forest soil receives a constant supply of dead leaf litter that is rich in oxygen, forest SOM has a higher proportion of partially degraded, amorphous biopolymers. Agricultural soil does not receive a constant input of fresh organic material; therefore, agricultural SOM is more degraded and relatively older. The amorphous SOM associated with the forest soil has a lower adsorption capacity than the older, more crystalline SOM that is present in the agricultural soil. However, it is important to note that the two soils, while containing different amounts and types of SOM, also contain slightly different clay contents (16% for the agricultural soil, 10% for the forest soil). This may be important to consider, especially for the agricultural soil, since atrazine-clay
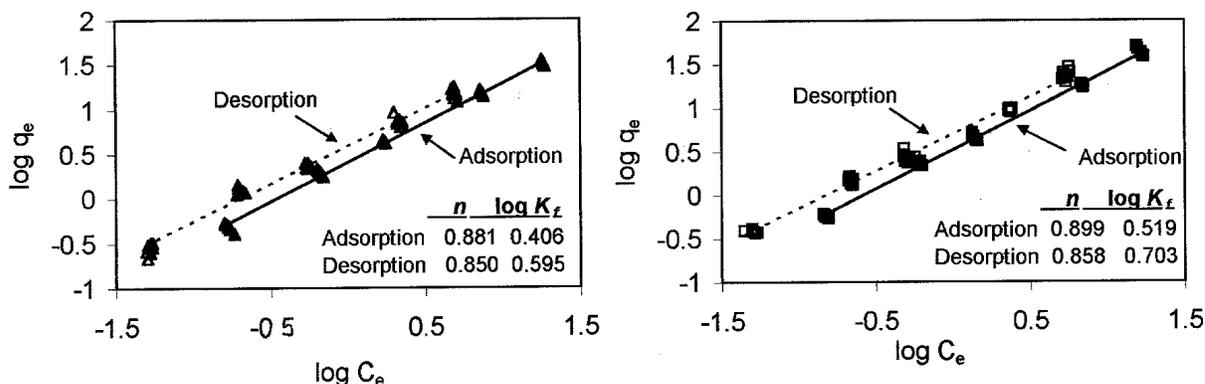
Figure 2. Adsorption and desorption of atrazine to Hillsdale Basin agricultural soil (left) and forest soil (right).

associations have been reported to be important with soils that contain less than 6% SOM (Shea, 1989). In general, the adsorption characteristics for the two soils were relatively similar.

Desorption of atrazine from the two Hillsdale soils was also very similar. Figure 2 shows the adsorption and desorption data for both of the soils. It is important to note that the desorption data represents only the first desorption from the sequential fill/draw procedure. Hysteresis indices (HIs), which were calculated at $C_e = 1$ mM, were 0.55 for the agricultural soil, and 0.53 for the forest soil. The HI values, which are low and not significantly different for the two soils, are indicative of the relatively young, amorphous nature of the SOM. Huang and Weber (1997) examined the adsorption and desorption of phenanthrene with materials having a range of O/C atomic ratios (higher O/C ratios correspond to geologically younger, less degraded SOM). Results showed that as the ratio of oxygen to carbon decreased, HI values increased and Freundlich n values decreased, nearly proportionally. As adsorption becomes more site-specific in more geologically aged

materials such as kerogens, desorption becomes more hysteretic, i.e. molecules that are adsorbed within the amorphous "rubbery" SOM matrix are more easily removed than had they been adsorbed to a more crystalline "glassy" matrix. Both the agricultural and forest soils exhibited near linear adsorption and were therefore associated with younger SOM having a high O/C ratio.

Atrazine Distribution

Although the two soils have slightly different SOM contents and type, the distribution of adsorbed atrazine within the two soils was quite similar. Table 3 summarizes the distribution of the adsorbed atrazine for each data point on the Freundlich isotherm previously discussed. Results are expressed in both μmol/kg and percent of the total adsorbed atrazine. At all concentrations for both soils, over 70% of the adsorbed atrazine was quickly desorbed with synthetic surface water. The trends in atrazine distribution can be more easily interpreted from an area plot (Figure 3), where initial atrazine concentrations between the experimental values

are interpolated. For both soils, the percent of bound atrazine (soil/humin-, humic acid- and fulvic acid-bound) increased relatively proportionally to increases in initial atrazine concentration, i.e. as C_o increased an order of magnitude, the total bound atrazine also increased approximately an order of magnitude. This is likely due to a concentration gradient effect; at higher concentrations, more atrazine molecules are forced into the micropores associated with SOM and mineral domains, where they are less easily desorbed. The unusual increase in quickly desorbed atrazine at the 10 µM con-

centration for the agricultural soil is likely due to experimental error.

Another point of interest in the data is the greater association of atrazine with fulvic acid than with humic acid. Barriuso and Koskinen (1996) have suggested that fulvic acids play an active role in the immobilization of herbicides; however, with increasing time, the proportion of bound residues associated with humic acids and humin increases. While a seven-day equilibration period was determined to be appropriate for overall atrazine adsorption, a longer equilibration period may possibly increase the humic

Table 3. Atrazine distribution in Hillsdale Basin agricultural and forest soil.

		Distribution of Adsorbed Atrazine (µmol/kg) [% of initially adsorbed]				
		0.25 µM	1.0 µM	2.5 µM	10.0 µM	25.0 µM
Agricultural Soil	[a]Quickly Desorbed	0.349 [72.1]	1.44 [73.4]	3.22 [74.8]	12.3 [83.7]	22.9 [72.6]
	[b]Slowly Desorbed	0.089 [18.4]	0.320 [16.3]	0.596 [13.8]	0.444 [3.02]	3.56 [11.3]
	Humic Acid Bound	0.013 [2.69]	0.045 [2.30]	0.091 [2.11]	0.437 [2.97]	0.901 [4.18]
	Fulvic Acid Bound	0.017 [3.51]	0.099 [5.05]	0.169 [3.92]	1.05 [7.15]	2.69 [8.53]
	Soil/Humin Bound	0.016 [3.30]	0.057 [2.91]	0.230 [5.34]	0.459 [3.12]	1.49 [4.72]
Forest Soil	[a]Quickly Desorbed	0.409 [71.6]	1.65 [72.9]	3.53 [78.0]	13.7 [77.2]	31.2 [73.9]
	[b]Slowly Desorbed	0.104 [18.2]	0.363 [16.1]	0.455 [10.0]	1.71 [9.63]	4.05 [9.60]
	Humic Acid Bound	0.013 [2.28]	0.066 [2.92]	0.126 [2.79]	0.578 [3.25]	1.28 [3.03]
	Fulvic Acid Bound	0.023 [4.03]	0.081 [3.58]	0.224 [4.95]	0.804 [4.53]	2.66 [6.30]
	Soil/Humin Bound	0.022 [3.85]	0.101 [4.47]	0.189 [4.18]	0.958 [5.39]	3.01 [7.13]

[a]Quickly Desorbed = removed with synthetic surface water
[b]Slowly Desorbed = extracted with 4:1 ethylacetate = synthetic surface water
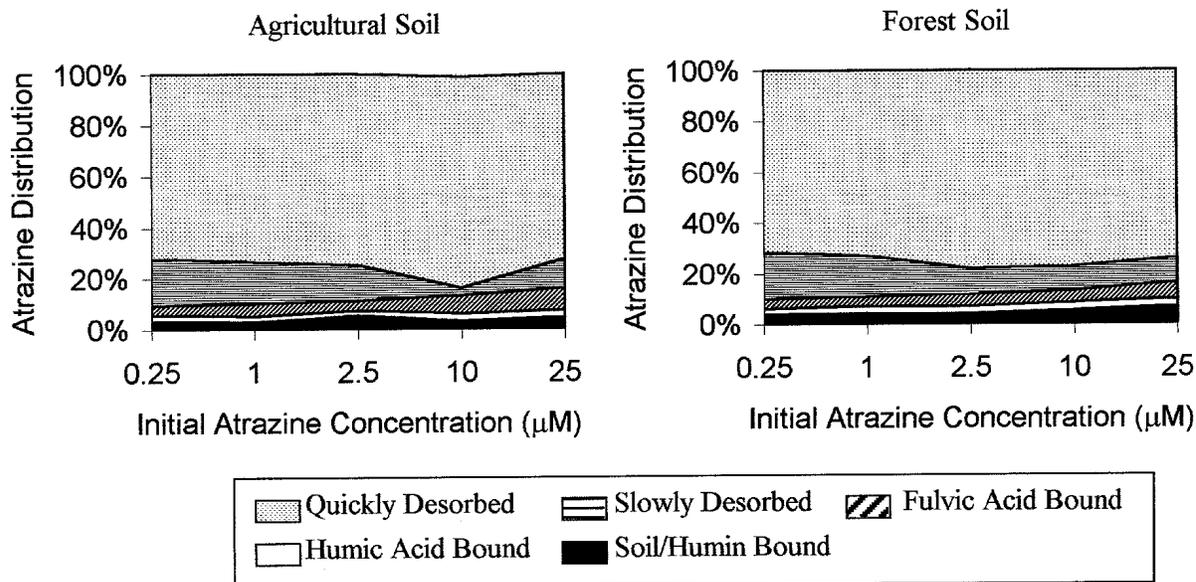
Figure 3. The effect of C_O on atrazine distribution in Hillsdale Basin agricultural soil (left), and forest soil (right).

acid fraction of bound atrazine. In addition, the interaction of humic acids with atrazine is also strongly dependent upon pH. Kalousková (1987) found that atrazine adsorption to humic acid increased as pH decreased within the range of 6.1 to 2.6. The pH of the soil/synthetic surface water slurry for this research was 5.95 for the agricultural soil and 5.96 for the forest soil. Had the pH been lower, it is likely that more atrazine would have been present in the humic acid fraction. Finally, traditional alkali separation techniques, such as the one used, are harsh and may decrease the amount of atrazine associated with humic acid. As pH is raised under alkali conditions, humic acid swells and becomes more open in structure. This may allow atrazine molecules entrapped in a folded humic acid structure to desorb more readily as the macromolecule opens up, thus being accounted for in the fulvic acid fraction.

Peroxidase Enzyme Study

The addition of enzymes to enhance adsorption of phenolic compounds is becoming an increasingly researched topic (Bhandari et al., 1997; 1998; 1999; Bollag, 1992). Soil enzymes such as peroxidases, laccases, and polyphenol oxidases are able to catalyze oxidative coupling reactions that can result in the formation of covalent bonds between phenolic compounds and humic material, i.e. enhancing irreversible adsorption. The results from a batch equilibrium study with horseradish peroxidase indicated that adsorption of parent atrazine to Hillsdale soils was not influenced by enzyme addition. Figure 4 shows adsorption data for a single atrazine concentration (10 μM), atrazine plus enzyme and H_2O_2, and atrazine plus H_2O_2 (control). It is important to note the Figure 4 is not an isotherm; data variations represent small differences in test tube volume. While it ap-
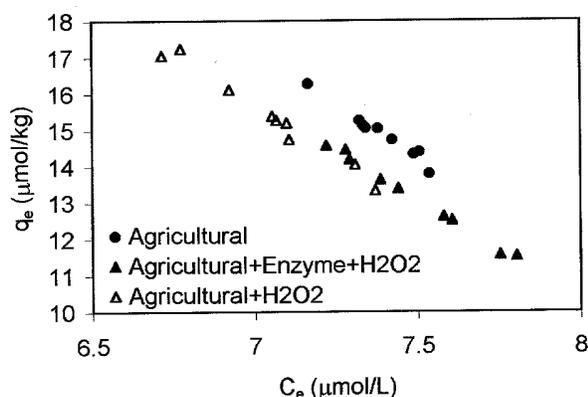
Figure 4. The effect of peroxidase enzyme on atrazine adsorption to Hillsdale Basin agricultural soils (10 μM initial aqueous atrazine concentration).

pears that enzyme addition actually decreased adsorption, the same effect was noted with the H_2O_2 control. This is believed to be the result of partial chemical oxidation, perhaps via a Fenton reaction, of atrazine by the H_2O_2 that caused the herbicide to become slightly less hydrophobic. While engineered humification appears to be ineffective for parent atrazine, future work is needed to determine if there are any effects on adsorption of hydroxyatrazine, a common phenolic degradation product.

CONCLUSIONS

The purpose of this paper was to present and discuss the results of an ongoing investigation to describe the role of soil organic matter in the fate and transport of atrazine in the Hillsdale Reservoir Basin. Specifically, studies with Hillsdale agricultural and surface soils produced the following results:

- Atrazine adsorption was non linear for both agricultural and forest Hillsdale Basin soils at concentrations ranging from 0.25 μM to 25 μM. Freundlich n values were 0.88 and 0.90 for agricultural and forest soils, respectively, and log K_f values were 0.41 and 0.52.

- When SOM content was accounted for, the agricultural soil manifested a slightly higher adsorption capacity than the forest soil. Differences in SOM type or clay content are possible causes for this observation.

- Hysteresis was observed for both soils; hysteresis indices were 0.55 for the agricultural soil and 0.53 for the forest soil.

- Soil type did not have a significant effect on atrazine distribution.

- As atrazine concentrations increased, "bound" atrazine also increased proportionally. However, for all concentrations, over 70% of the initially adsorbed atrazine was quickly desorbed with synthetic surface water.

- More atrazine was associated with the fulvic acid fraction of the SOM, rather than with the humic acid fraction.

- Engineered humification, or the use of enzymes to enhance adsorption, is not applicable for parent atrazine.

REFERENCES

Acero, J.L., K. Stemmler, and U.Von Gunter, 2000. Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment, Environ. Sci. Technol., 34, pp. 591-597.

Bailey, G.W., and J.L. White, 1970. Factors Influencing the Adsorption, Desorption, and Movement of Pesticides in Soil, Residue Review, 32, pp. 29-92.

Barriuso, E., and W.C. Koskinen, 1996. Incorporating Nonextractable Atrazine Residues into Soil Size Fractions as a Function of Time, Soil Sci. Soc. Am. J., 60, pp. 150-157.

Barriuso, E., D.A. Laird, W.C. Koskinen, and R.H. Dowdy, 1994. Atrazine Desorption from Smectities, Soil Sci. Soc. Amer. J., 1994, pp. 1632-1638.

Barriuso, E., U. Baer, and R. Calvet, 1992a. Dissolved Organic Matter and Adsorption-Desorption of Dimefuron, Atrazine, and Carbetamide by Soils, J. Environ. Qual., 21, pp. 359-367.

Barriuso, E.,C.H. Feller, R. Calvet, and C. Cerri, 1992b. Sorption of Atrazine, Terbutyrn, and 2,4-D Herbicides in Two Brazilian Oxisols, Geoderma, 53, pp. 155-167.

Barriuso, E., S. Houot, and C. Serra-Wittling, 1997. Influence of Compost Addition to Soil on the Behaviour of Herbicides, Pestic. Sci., 49, pp. 65-75.

Bhandari, A., J.T. Novak, W.D. Burgos, and D.F. Berry, 1997. Irreversible Binding of Chlorophenols to Soil and Its Impact on Bioavailability, J. Environ. Engrg.,ASCE, 123, pp.506-513.

Bhandari, A., A. Orlov, and W.J. Weber Jr., 1998. Engineering the Immobilization of Couplable Organics in Soils and the Subsurface, Proceedings of the 13th Annual Conference on Hazardous Waste Research, pp. 251-261.

Bhandari, A., and I. Cho, 1999. Peroxidase Mediated Binding of Phenols to Soils, Proceedings of the 14th Annual Conference on Hazardous Waste Research, pp.27-40.

Bollog, J.-M., 1992. Decontaminating Soils with Enzymes, Environ. Sci. Technol., 26, pp. 1876-1881.

Bouquard, C., J. Ouazzani, J. -C. Promé, Y. Michel-Briand, and P. Plésiat, 1997. Dechlorination of Atrazine by a *Rhizobium* sp. Isolate, Appl. and Environ. Microbiol., 63, pp. 862-866.

Brown, C.B., and J.L. White, 1969. Reactions of 12 s-Triazines with Soil Clays, Soil Sci. Soc. Amer. Proc., 33, pp. 863-867.

Capel, P.D., A.H. Spexet, and S.J. Larson, 1999. Occurrence and Behavior of the Herbicide Prometon in the Hydrologic System, Environ. Sci. Technol., 33, pp. 674-680.

Carpriel, P., A. Haisch, and S.U. Khan, 1985. Distribution and Nature of Bound (Nonextractable) Residues of Atrazine in a Mineral Soil Nine Years after the Herbicide Application, J. Agric. Food Chem., 33, pp. 567-569.

Celis, R., J. Cornejo, Hermosín, and W. C. Koskinen, 1997. Sorption-Desorption of Atrazine and Simazine by Model Soil Colloidal Components, Soil Sci. Soc. Am. J., 61, pp. 436-443.

Clay, S.A., and W.C. Koskinen, 1990. Characterization of Alachlor and Atrazine Desorption from Soils, Weed Sci., 38, pp. 74-80.

Donnelly, P.K., J.A. Entry, and D.L. Crawford, 1993. Degradation of Atrazine and 2,4-Dichlorophenoxyacetic Acid by Mycorrhizal Fungi at Three Nitrogen Concentrations In Vitro, Appl. and Environ. Microbiol., 59, pp. 2642-2647.

Huang, W., and W.J. Weber, Jr., 1997. A Distributed Reactivity Model for Sorption by Soils and Sediments. 10. Relationships Between Desorption, Hysteresis, and the Chemical Characteristics of Organic Domains, Environ. Sci. Technol., 31, pp. 2562-2569.

Jones, T.W., W.M. Kemp, J.C. Stevenson, and J.C. Means, 1982. Degradation of Atrazine in Estuarine Water/Sediment Systems in Soils, J. Environ. Qual., 11, pp. 632-638.

Kalousková, N., 1987. Interaction of Humic Acids with Atrazine, J. Environ. Sci. Health, B22(1), pp. 113-123.

Kauffmann, C., O. Shoseyov, E. Shpigel, E.A. Bayer, R. Lamed, Y. Shoham, and R.T. Mandelbaum, 2000. Novel Methodology for Enzymatic Removal of Atrazine from Water by CBD-Fusion Protein Immobilized on Cellulose, Environ. Sci. Technol., 34, pp. 1292-1296.

Koplin, D.W., S.J. Kalkhoff, D.A. Goolsby, D.A. Sneck-Fahrer, and E.M. Thurman, 1997. Occurrence of Selected Herbicides and Herbicide Degradation Products in Iowa's Ground Water, 1995, Ground Water, 35, pp. 679-688.

Laabs, V., W. Amelung, and W. Zech, 1999. Multi-Residue Analysis of Corn and Soybean Pesticides in Brazilian Oxisols Using Gas Chromatography and Mass Selective Detection, J. Environ. Qual., 28, pp. 1778-1786.

Laird, D.A., P.Y. Yen, W.C. Koskinen, T.R. Steinheimer, and R.H. Dowdy, 1994. Sorption of Atrazine on Clay Components, Environ. Sci. Technol., 28, pp. 1054-1061.

Ma, L., L.M. Southwick, G.H. Willis, and H. Magdi Selim, 1993. Hysteretic Characteristics of Atrazine Adsorption Desorption by a Sharkey Soil, Weed Sci.,41, pp. 627-633.

Miller, S.M., C.W. Sweet, J.V. DePinto, and K.C. Hornbuckle, 2000. Atrazine and Nutrients in Precipitation: Results from the Lake Michigan Mass Balance Study, Environ. Sci. Technol., 34, pp. 55-61.

Pereira, W.E., and C.E. Rostad, 1990. Occurrence, Distributions, and Transport of Herbicides and Their Degradation Products in the Lower Mississippi River and Its Tributaries, Environ. Sci. Technol., 24, pp.1400-1406.

Piccolo, A., P. Conte, I. Scheunert, and M. Paci., 1998. Atrazine Interactions with Soil Humic Substances of Different Molecular Structure, J. Environ. Qual., 27, pp. 1324-1333.

Putnam, J.E., 1997. Occurrence of Phosphorus, Other Nutrients, and Triazine Herbicides in Water from the Hillsdale Lake Basin, Northeast Kansas, May 1994 through May 1995, USGS Water-Resources Investigations Report 97-4019.

Roy, W.R., and I.G. Krapac, 1994. Adsorption and Desorption of Atrazine and Deethylatrazine by Low Organic Carbon Geologic Materials, J. Environ. Qual., 23, pp. 549-556.

Saint-Fort, R., and S.A. Visser, 1988. Study of the Interactions Between Atrazine, Diazinon and Lindane with Humic Substances of Various Molecular Weights, J. Environ. Sci. Health, A23(6), pp. 613-624.

Shea, P.J., 1989. Role of Humified Organic Matter in Herbicide Adsorption, Weed Technol., 3, pp. 190-197.

Tugulea, A-M., L.P. Sarna, and G.R.B. Webster. 1998. Solid Phase Microextraction (SPME) of the Herbicide Atrazine in Aqueous Soil Suspensions, Intern. J. Environ. Anal. Chem., 68, pp. 137-153.

Xing, B., J.J. Pignatello, and B. Gigliotti, 1996. Competitive Sorption Between Atrazine and Other Organic Compounds in Soils and Model Sorbents, Environ. Sci. Technol., 30, pp. 2432-2440.

Wang, Z., D.S. Gamble, and C.H. Langford, 1992. Interaction of Atrazine with Laurentian Soil, Environ. Sci. Technol., 26, pp. 560-565.

Weber, Jr., W.J., and F. A. DiGiano, 1996. Process Dynamics in Environmental Systems, John Wiley & Sons, Inc., New York.

Wu, T.L, 1980. Dissipation of the Herbicides Atrazine and Alachlor in a Maryland Corn Field, J. Environ. Qual., 9, pp. 459-465.