Atrazine Adsorption and Colloid-Facilitated Transport through the Unsaturated Zone

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ABSTRACT

One explanation for unexpectedly widespread ground water contamination from atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) may be the occurrence of colloid-facilitated transport, whereby the dissolved herbicide becomes adsorbed to mobile colloids that migrate through preferential flow-paths in the soil zone and into the ground water. The objectives of this study were to determine the extent of adsorption of atrazine to bulk soil and to soil colloids and to determine the extent of colloid-facilitated transport of atrazine at a field site in Virginia during simulated rainfall events. Equilibrium batch adsorption experiments were performed over a concentration range of 0.05 to 10.0 mg atrazine L^{-1} on bulk soil samples and on colloidal suspensions of 75 mg L^{-1}, a concentration comparable with those observed at the field site. Linear partition coefficients ranged from 0.496 to 2.48 L kg^{-1} for the bulk soil and from 70.8 to 832 L kg^{-1} for the soil colloids. In the field, gravity lysimeters were installed at a depth of 25 cm below the surface of six 0.25-m^2 undisturbed plots. Mass recovery of surface-applied atrazine in the lysimeters was not significantly affected by rainfall rate and was, on average, 2.7% for plots receiving 25 mm h^{-1} simulated rainfall and 3.6% for plots receiving 50 mm h^{-1} simulated rainfall. Of the total atrazine collected in the lysimeters, the fraction that was colloid-associated ranged from 4.9 to 30% (mean of 15%), indicating that a measurable portion of mobile atrazine is transported via association with colloids.

THE presence of pesticides in ground water underlying agricultural regions raises questions about the effects on human health from long-term, chronic exposure, because ground water is the primary source of drinking water for nearly half of the population of the United States (Heath, 1984). In the first set of land-use studies in the U.S. Geological Survey's National Water Quality Assessment (NAWQA) program, one or more pesticides were found in more than 50% of the 1012 ground water sites sampled around the United States from 1993–1995 (Kolpin et al., 1998). Atrazine, the most extensively used herbicide in the country, and one of its metabolites, deethylatrazine (2-amino-4-chloro-6-isopropylamino-s-triazine), were the two most commonly detected herbicides. An understanding of the behavior of these pesticides in the environment is required for the evaluation of environmental and health risks.

Pesticide transport studies conducted to date in the field have used samples filtered prior to analysis, thus accounting for only that portion of the pesticide dissolved in solution. In at least one such study, it was

speculated that fine particles in the soil, such as clay colloids or suspended organic matter, act as "carriers" preventing adsorption of pesticides to the immobile soil matrix (Ghodrati and Jury, 1992). Colloid-facilitated transport of strongly sorbing DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was suggested by its occurrence at low levels in fractures to a depth of 1 m in a clayey glacial soil; however, such transport was not directly examined in the study (Jørgensen and Fredericia, 1992).

A growing number of studies have invoked the concept of mobile colloids acting as transport agents of other contaminants such as trace metals, radionuclides, and nonpolar organic compounds. These contaminants are typically immobile, but indications that they are moving through the soil zone and into ground water via association with mobile colloids have been found (e.g., Ryan et al., 1998; Puls and Powell, 1992; Penrose et al., 1990; McCarthy and Zachara, 1989). Colloids are defined operationally in this study as particles between 2.0 and 0.2 μm in diameter and include clays, iron and aluminum oxides, carbonates, and bacteria. Owing to their high specific surface area, colloids have a high sorptive capacity and can be excellent sorbents of low solubility, strongly sorbing contaminants.

The extent of atrazine sorption to colloids may be used as a measure of the potential for facilitated transport. One study of atrazine adsorption to colloids reported K_d values to be in the range of 39 to 13 400 L kg^{-1}, with the highest value being for montmorillonite and the lowest value for kaolinite (Gilchrist et al., 1993). Laird et al. (1992) found K_f values for atrazine from <0.01 to 1334 for soil smectites, and the values decreased with increasing surface charge density. Organic coatings on clay particles contributed 68% of the affinity of the soil clay for atrazine (Laird et al., 1994). Though these studies suggest that the potential for facilitated transport of atrazine exists, they cannot confirm that it actually occurs.

A few column studies have specifically addressed pesticide transport via association with mobile colloids. While total atrazine transport increased up to 18% when colloids were injected into soil columns, colloid-associated atrazine contributed to less than 1% of this increased transport (Seta and Karathanasis, 1997). The transport of a related s-triazine, simazine, was not found to be enhanced by the presence of organic colloids because of the compound's low K_d value of 0.168 L kg^{-1} (Spurlock and Biggar, 1990). Conversely, dispersed montmorillonite suspensions were found to transport over 50% of applied DDT through columns containing sandy loam soil (Vinten et al., 1983). Thus, it would appear that the sorptive strength of the pesticide plays a vital role in the occurrence of colloid-facilitated transport.

The objectives of the present study were to (i) determine the extent of atrazine adsorption to the immobile soil matrix vs. mobile soil colloids in an agricultural silt loam soil and (ii) examine the transport of atrazine, both dissolved and colloid-associated, in the field during simulated rainfall events of two different intensities.

METHODS

Site Description

The field site is located in the Muddy Creek watershed in Rockingham County, Virginia, in the Shenandoah Valley. The parent material in this gently sloping agricultural region is made up of sedimentary deposits of limestone, shale, and sandstone. The soil is dominated by Frederick silt loam (fine, mixed, semiactive, mesic Typic Paleudult) and Lodi silt loam (clayey, mixed, mesic Typic Hapludult), which are deep and well-drained and formed in residuum extensively weathered from limestone (Hockman et al., 1982). The average depth to ground water ranges from 0.5 m near a low-lying stream to 13 m higher in the catchment. Atrazine occurs in soil and stream water, pore fluids in the stream sediments, and shallow ground water, and it has been sporadically detected in the deeper bedrock aquifer. Concentrations range from 0 to 10 μg L^{-1} in the stream water and from 0 to 2 μg L^{-1} in the ground water (Ator et al., 1998).

Soil Characterization

Soil samples from four depths, 0 to 10, 10 to 20, 30 to 40, and 80 to 90 cm, were taken from an exposed face in a soil pit. This site was adjacent to corn (*Zea mays* L.) fields where high concentrations of atrazine were found in the shallow ground water. Grain-size analyses were carried out on each soil depth by the hydrometer method (Liu and Evett, 1984). The organic matter content of the bulk soil for each depth was determined using a Carlo–Erba carbon analyzer (CE Elantech, Lakewood, NJ), which implements a dry combustion method, after inorganic carbon had been removed with a sulfurous acid treatment (Nelson and Sommers, 1982). The organic matter content of the soil colloid suspensions used in the colloid batch equilibration experiments was determined using a Dohrmann (Cincinnati, OH) organic carbon analyzer, using ultraviolet promoted persulfate oxidation followed by infrared detection (Nelson and Sommers, 1982). Results are presented in Table 1.

Bulk Soil Batch Equilibration Experiments

Batch sorption experiments were conducted at a soil to solution ratio of 1:1 (m/v). Four atrazine solutions were prepared in 0.005 *M* NaCl, at concentrations of 10.0, 5.0, 1.0, and 0.50 mg atrazine L^{-1}, with 0.20 mg ^{14}C-ring-labeled atrazine L^{-1} (Ciba, Novartis, Greensboro, NC; radiochemical purity 98.4%, chemical purity 94.3%) being used in each. Three grams of site soil that had been air dried and sieved were placed in a 50-mL Teflon centrifuge tube (to minimize adsorption to the tube walls) with 3 mL of atrazine–NaCl solution. The batch experiments were run in triplicate for each of the four solutions. Blanks, containing the atrazine–NaCl solutions only, were run simultaneously. The tubes were placed on a shaker table and allowed to equilibrate for 24 h. The room temperature during this time was controlled at 25 ± 1°C. Following equilibration, each tube was centrifuged for 12 min at 10 000 rpm. The supernatant was then removed, and approximately 1 mL was run through a 0.2-μm pore diameter Whatman Teflon filter. The amount of ^{14}C present in the filtrate

Table 1. Grain size distribution of the soil and organic carbon content of soil and colloids taken from the field site at four depths.

Depth	>2.0 mm	Sand	Silt	Clay	OC$_{sol}$†	OC$_{colloids}$
cm				%		
0–10	0.9	23.8	40.6	34.7	2.6	13.2
10–20	3.3	33.9	29.0	33.9	1.2	5.5
30–40	7.8	29.6	33.3	29.6	1.0	4.1
80–90	27.5	37.0	15.2	20.3	0.4	2.8

† OC, organic carbon.

was quantified by liquid scintillation counting (LSC) techniques. The amount of atrazine adsorbed to the soil was the difference between the initial atrazine concentration measured in the soil-free blanks and that measured in the filtrate after equilibration.

Colloid Batch Equilibration Experiments

Colloids were generated from soil collected at each of the four depths. This was accomplished by first placing approximately 40 g of the air-dried, sieved soil in a 2-L flask containing 0.005 *M* NaCl solution and stirring vigorously with a magnetic stir bar for 1 h. This suspension was then left to sit for 1 h. The supernatant was decanted and sonicated for 10 to 15 min to break up any remaining aggregates. The mixture was then allowed to stand for 24 h; based on Stoke's Law, particles less than 2.0 μm in diameter remain in suspension during this time while any larger particles settle out (Liu and Evett, 1984). Colloids remaining in suspension were siphoned off. The colloid concentration of this suspension was determined by passing 50 mL through a preweighed 0.2-μm pore diameter Gelman (Ann Arbor, MI) filter and calculating the dry weight of the colloids retained on the filter by difference. A colloid concentration of approximately 100 mg L^{-1} was prepared by subsequent dilution.

Atrazine–colloid suspensions of 5.0, 1.0, 0.5, and 0.05 mg atrazine L^{-1} and 75 mg colloids L^{-1} in 0.005 *M* NaCl were created. Five glass vials were filled with a total of 20 mL; three contained 5 mL of concentrated atrazine solutions and 15 mL of the 100 mg L^{-1} colloidal suspensions to achieve the target atrazine concentration. The remaining two vials served as blanks, to which 15 mL of 0.005 *M* NaCl (as opposed to the colloid suspensions) were added. The experiments were run in triplicate for each of the four solutions. The vials were shaken for 24 h at 25 ± 1°C. Approximately 1 mL of each suspension was then passed through a 0.2-μm pore diameter Whatman Teflon filter to remove the colloids, and the amount of atrazine remaining in solution was quantified with liquid scintillation counting. The amount of atrazine adsorbed to the colloids was the difference between the initial atrazine concentration measured in the colloid-free blanks and that measured in the filtrate after equilibration.

Isotherm Analysis

Adsorption isotherms were calculated for the bulk soil and soil colloids at each depth. The parameters of these isotherms were obtained through fitting a linear model to the experimental data:

$$x/m = K_d C \qquad [1]$$

where x/m is weight of adsorbate divided by the weight of the sorbent, K_d is a constant adsorption coefficient, and C is the adsorbate concentration in the equilibrium solution. A relationship for the analysis of these adsorption coefficients based on the soil organic content was also determined:
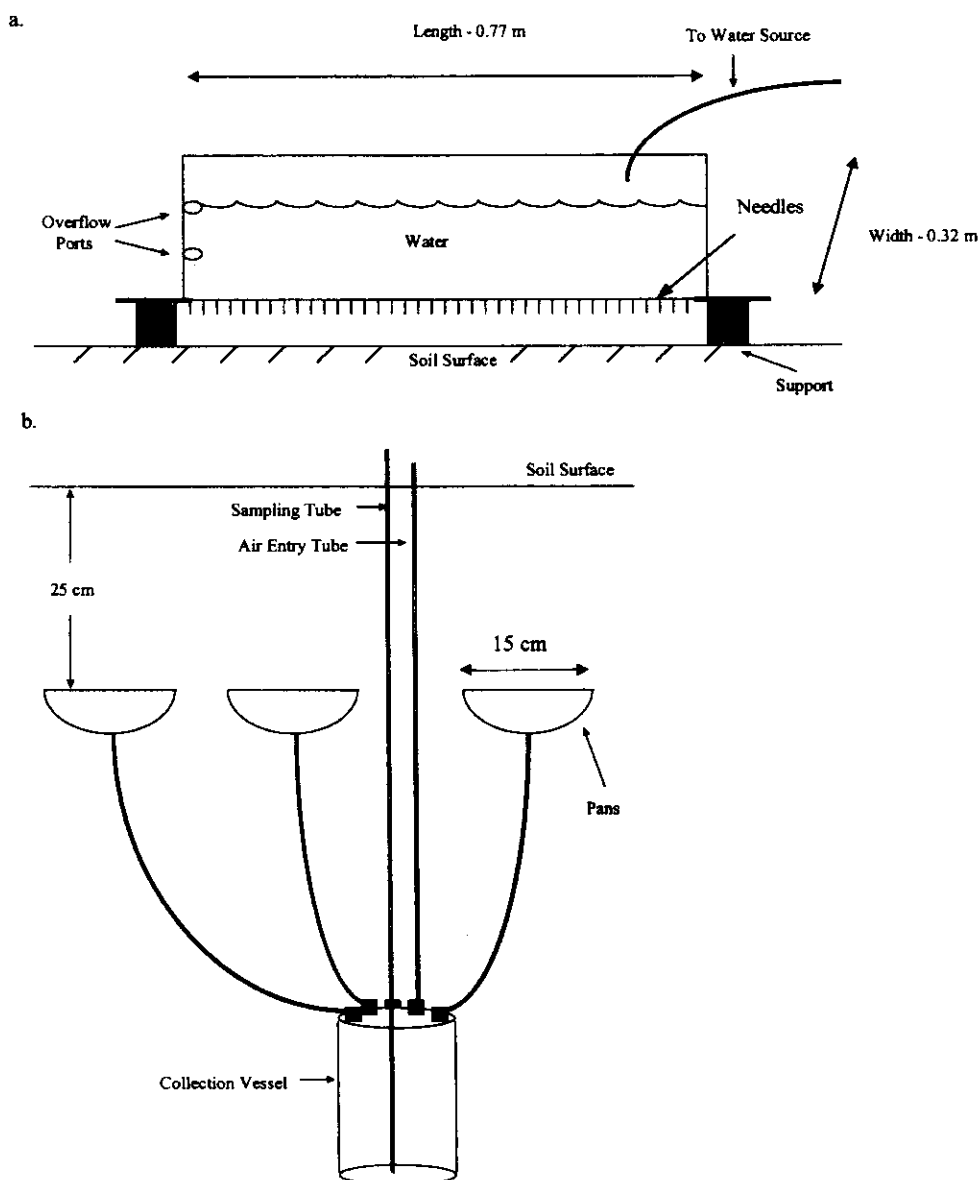
a.

b.

Fig. 1. (a) Schematic of the rainfall simulator used in the field experiments. (b) Schematic of the gravity lysimeters used in the field experiments.

$$K_{oc} = K_d/OC \qquad [2]$$

where K_{oc} is the adsorption coefficient normalized for organic content and OC is the fraction of organic carbon in the soil or soil colloids.

Table 2. Initial soil water content of field plots approximately 6 h after presaturation, just prior to the start of the rainfall simulations, measured over a depth of 25 cm.

Plot	Precipitation rate treatment	Initial soil water content
		kg kg^{-1}
2	Low	0.225
3	Low	0.182
11	Low	0.201
1	High	0.219
5	High	0.239
8	High	0.287

Field Experiments

Experimental Design

Six 0.25-m^2 plots were established along a transect adjacent to a cornfield prior to the start of the field experiments. The transect was approximately 75-m long, and the plots were located at approximately equal spacing. During the rainfall simulations, three were exposed to a high precipitation rate (50 mm h^{-1}) and three to a low rate (25 mm h^{-1}). Treatments were assigned to each plot using a random-number generator.

Rainfall Simulator and Lysimeter Design

The rainfall simulator was a drip-box design (Fig. 1a) (Sprague, 1998). Holes arranged in a 3- × 3-cm grid pattern were drilled into the bottom of a 0.77- × 0.32-m rigid plastic box. A 25-gauge 5/8 PrecisionGlide needle (Becton Dickinson, Frankling Lakes, NJ) was placed into each of the 286 drill holes
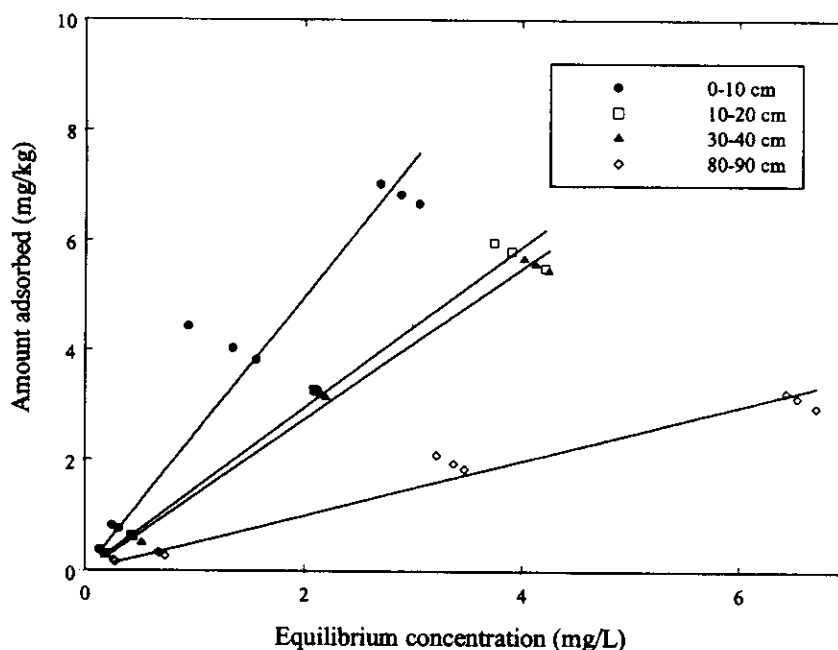
Fig. 2. Plot of isotherms for atrazine adsorption to bulk soil collected at four depths. The data shown here were obtained from experiments with a soil to solution ratio 1:1 (m/v). Lines are isotherms fitted from the data points.

and cemented with silicone sealant to create the mechanism of water delivery. "Rainfall" rate was controlled by the height of the water column in the reservoir above the needles.

Each gravity lysimeter was comprised of three "pans" and a collection vessel (Fig. 1b). The pans were constructed out of the top cylindrical portion of 15-cm diameter PVC compression caps. Attached Tygon tubing (Norton Plastics, Akron, OH) ran to a collection vessel that was made of a 30-cm length of 10-cm diameter PVC pipe fitted with dome compression caps on both ends. Three pans ran to one collection vessel. From this collection vessel, two tubes ran to the soil surface, one for air entry and one for sampling. The lysimeters were filled with 0.75-mm clean quartz sand (Unimin, Portage, WI) that had been soaked overnight in 15% HCl and rinsed with deionized water until the solution was clear. A trench was dug with a back-hoe and a lysimeter was installed into a hand-excavated cavity in the side of the trench under each undisturbed plot at a depth of 25 cm, the approximate base of the root zone. The trench was then back-filled with soil. In order to monitor soil moisture, pairs of stainless steel time domain reflectometry (TDR) rods were installed in the soil surface, 5 cm apart, to a depth of 25 cm. Time domain reflectometry is a method of relating soil-moisture levels to the propagation velocity of an electromagnetic pulse through parallel probes (Topp et al., 1982).

Rainfall-Simulation Experiments

On the day before the rainfall simulation was to take place, vegetation on the plots was trimmed to approximately 2.5 cm or less above the soil surface, taking care not to disturb the soil by removing roots. The plots were prewetted the night before the simulation was to take place by freely draining 60 L (24 cm over 0.25 m²) of 28 mg L⁻¹ NaCl through the rainfall simulator overnight (rainfall rates thus varied from 5 cm h⁻¹ to 2 cm h⁻¹ as the height of the water column progressively decreased overnight); this presaturation took approximately 8 h. The low-ionic-strength solution was prepared to approximate rainwater and was kept at a constant ionic strength

throughout the experiment to prevent colloid generation owing to changes in ionic strength. Approximately 6 h lapsed between the end of presaturation and the beginning of the rainfall simulation the next day. The rainfall simulations for each plot were run on separate days to allow the same rainfall simulator to be used for each plot.

An initial time domain reflectometry reading was taken just prior to the start of each experiment to determine the antecedent moisture level of the soil; all plots were in the range of 0.182 to 0.287 g kg⁻¹ (Table 2). Water present in the collection vessels was collected as a background sample; the atrazine concentration in the background sample was quantified and later subtracted from concentrations obtained during the rainfall simulations. Label-free atrazine was then applied as a broadcast spray at a rate of 1.5 kg ha⁻¹ using a SOLO (Newport News, VA) Portable Pump Sprayer (the ratio between the background concentration and the applied atrazine concentration was approximately 1×10^{-6}:1). The amount of atrazine applied corresponded to both a recommended rate for agricultural spraying and, given the size of the plots and the expected dilution in the soil, the maximum labeled concentrations in the batch experiments. Application of a tracer solution (50 mg L⁻¹ NaBr, 4.8×10^{-4} M NaBr) with the simulator commenced 15 min after pesticide application. After a total of 5 cm (12 L over 0.25 m²) of NaBr had been applied, 5 cm of 28 mg L⁻¹ NaCl (4.8×10^{-4} M NaCl) was applied in an effort to flush the tracer through the soil; a total of 10 cm of

Table 3. Adsorption coefficient (K_d and K_{oc}) values for atrazine sorption to bulk soil and soil colloids from four depths determined from laboratory batch experiments.

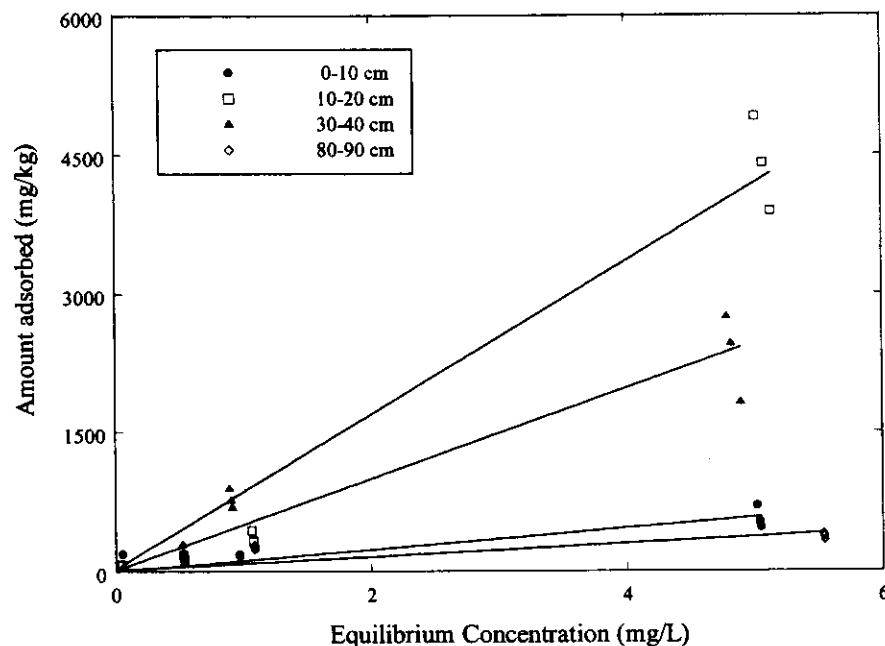| Depth	Bulk soil		Soil colloids	
	K_d	K_{oc}	K_d	K_{oc}
cm		L kg⁻¹		
0–10	2.48	95	115	870
10–20	1.47	120	832	15 000
30–40	1.38	140	491	12 000
80–90	0.496	120	70.8	2 500

Fig. 3. Plot of isotherms for atrazine adsorption to colloids generated from soils collected at four depths. The data shown here were obtained from experiments with colloid concentrations of 75 mg L^{-1}. Lines are linear isotherms fitted from the data points.

water was applied in all experiments at either 2.5 or 5 cm h^{-1}. Overland flow was not found to occur, and ponding occurred intermittently only in small, very localized areas.

The first samples were taken as soon as an adequate volume for the intended analyses had been collected in each vessel. The time to this initial collection varied for each plot. Samples were then taken at regular intervals, with the timing again depending on the plot. Samples for raw pesticide analysis were collected in glass bottles that had been burnt overnight in a 500°C oven and sample-rinsed in the field. Samples for dissolved pesticide analysis were passed through a 0.2-μm pore diameter Whatman Teflon filter (methanol- and sample-rinsed in the field), and collected in glass bottles. Colloid-associated atrazine concentrations were calculated as the difference between the unfiltered (total) and filtered (dissolved) atrazine concentrations. All samples for pesticide analysis were stored on ice. No samples could be collected any later than 15 min after water application ended, because a negligible volume was collected once the rainfall simulation had ended at all plots.

Each individual pan of the lysimeter covered an area of 182 cm^2. With three pans in each lysimeter, the total area sampled during the simulation was 0.055 m^2, or 22% of the total 0.25 m^2 plot area to which atrazine and the bromide tracer were applied. This was accounted for in subsequent calculations of mass recovery; reported values are mass recovered from the surface area of the lysimeters multiplied by 4.55, in order to extrapolate these mass recoveries to what could be expected over the total plot area.

Analyses for atrazine were performed within 3 d with enzyme-linked immunosorbent assays (Ohmicron RaPID Assays, Newton, PA; detection limit of 0.05 μg L^{-1}). The ability of this assay to detect colloid-associated atrazine was verified with a colloid–atrazine suspension of known concentration. Bromide analyses were performed with an Orion (Cambridge, MA) digital pH/mV/temperature meter in conjunction with a Corning (Medfield, MA) bromide specific ion electrode and an Orion double junction reference electrode. Because of the low ionic strength of the samples, ionic strength

adjustor (2 M KNO$_3$) was added to all samples and standards in a ratio of 1:10 (ionic strength adjustor to sample) for the bromide analysis. Colloid concentrations were determined with a spectrophotometer at a wavelength of 400 nm.

Partition coefficients for atrazine sorption to mobilized colloids from the field data were calculated using the formula:

$$K_d = \frac{\text{μg colloid-associated atrazine/kg mobilized colloids}}{\text{μg dissolved atrazine/L}}$$

[3]

and compared with the laboratory partition coefficients of atrazine sorption to colloids determined previously using Eq. [1].

Data analysis was performed using SPSS 7.5 (SPSS, 1997). A 5% probability level for significance was used for the analysis of variance (ANOVA) tests.

RESULTS AND DISCUSSION

Batch Equilibration Experiments

The K_d values for the bulk soil decreased with depth (Fig. 2) and ranged from 0.496 to 2.48 L kg^{-1} (Table 3). The K_d values for the soil-liberated colloids ranged from 70.8 to 832 L kg^{-1}, significantly higher than those

Table 4. Adsorption coefficient (K_d) values for atrazine sorption to mobilized soil colloids calculated from field experiment data.

Low precipitation rate		High precipittion rate	
Plot	K_d	Plot	K_d
	L kg^{-1}		L kg^{-1}
2	817	1	1183
3	6420	5	529
11	344	8	119
Mean	2627		610

Table 5. Mass recoveries of water, bromide, and atrazine (total, dissolved, and colloid-associated) (all reported as % of that applied at the surface) for field rainfall simulations at two rates. Each treatment was run in triplicate.

	Low precipitation rate				High precipitation rate			
	Plot 2	Plot 3	Plot 11	Mean	Plot 1	Plot 5	Plot 8	Mean
Water	25	41	33	33	19	37	50	35
Bromide	3.3	11	7.1	7.1	2.8	16	10	9.6
Total atrazine	0.43	5.8	2.0	2.7	1.6	4.4	4.6	3.6
Dissolved atrazine	0.39	4.1	1.9	2.1	1.3	3.7	4.1	3.0
Colloid-associated atrazine	0.04	1.7	0.10	0.60	0.30	0.70	0.50	0.60

found for the bulk soil. The greater adsorption here probably resulted from the higher specific surface area and organic content of the colloids relative to the bulk soil. The extent of atrazine adsorption to colloids liberated from bulk soils did not follow an easily discernible trend with depth; the highest K_d value of 832 L kg^{-1} was found at the 10- to 20-cm depth, and the lowest of 70.8 L kg^{-1} at the 80- to 90-cm depth (Fig. 3).

In order to determine the extent of the contribution of organic carbon content on adsorption, the K_d values for the bulk soil and the soil colloids were normalized to the percent organic carbon in their respective depth increments to give K_{oc} values (Table 3). Between the surface layer and the deepest layer sampled, there was an 84% decrease in the organic carbon content of the bulk soil (Table 1). The K_{oc} values for the bulk soil increased with depth and ranged from 0.95 in the 0- to 10-cm layer to 1.4 L kg^{-1} in the 30- to 40-cm layer. Similarly, a study examining atrazine adsorption to field-moist soils found that K_d values increased from 1.2 to 53 as the organic carbon content of the soil increased from 0.5 to 2.2% (Koskinen and Rochette, 1996). The

organic carbon content of the colloids decreased 79% over the profile, but the K_{oc} values for the soil colloids did not follow this trend. The highest K_{oc} value was 150 L kg^{-1} in the 10- to 20-cm layer, and the lowest was 8.7 L kg^{-1} in the 0- to 10-cm layer. Because the K_{oc} values are more scattered than the K_d values for both the bulk soil and the colloids, it is possible that the mineral components are more important than the organic carbon content for atrazine adsorption to this soil.

The K_d values for the colloids were up to three orders of magnitude higher than those for the bulk soil in this study. Additionally, the laboratory K_d values for the colloids were not significantly different from the K_d values calculated for the colloids mobilized during the field experiments (Table 4). By virtue of their size, colloids have a high surface area per unit mass, and consequently, a high adsorptive capacity. The importance of size fractions in atrazine adsorption was demonstrated by Huang et al. (1984), with the highest adsorption taking place in the 0.2- to 5-μm size fractions relative to larger sizes ranging to more than 50 μm. Atrazine is strongly adsorbed by montmorillonite (K_d values as high
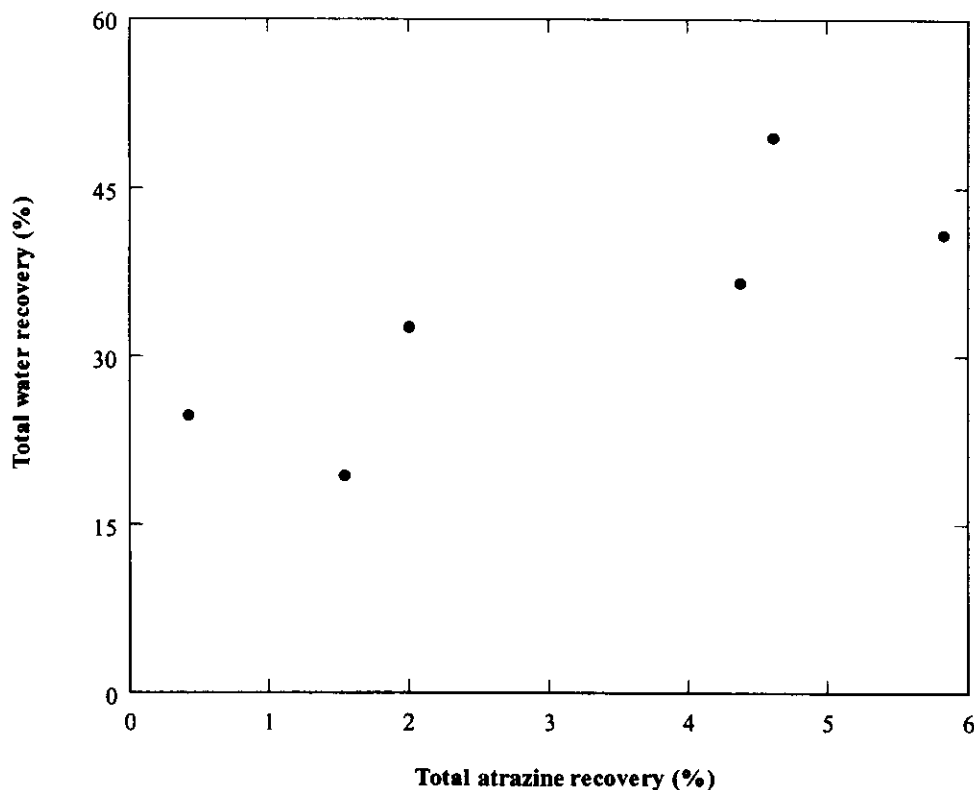
Fig. 4. Plot of total water recovered vs. total atrazine mass recovered in the six plots (Pearson's r = 0.82).
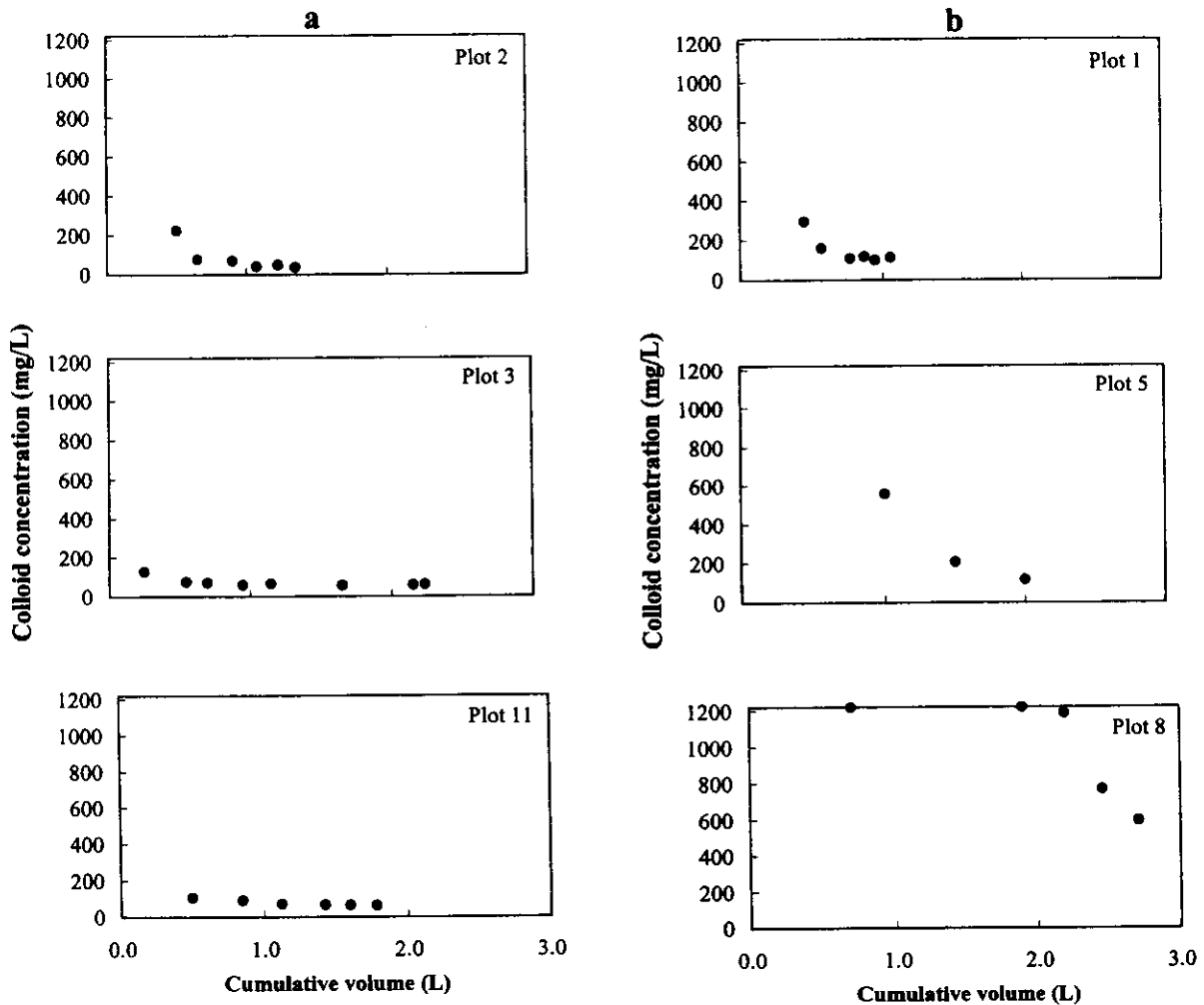
Fig. 5. (a) Colloid concentrations over the course of the field rainfall simulations for the three low-rate plots. (b) Colloid concentrations over the course of the field rainfall simulations for the three high-rate plots.

as 13 400 L kg^{-1}), by illite (247 L kg^{-1}), and to a lesser extent by kaolinite (120 L kg^{-1}) (Gilchrist et al., 1993). The K_f values for soil smectites were found to be as high as 1334 L kg^{-1} ($1/n$ = 0.70), decreasing with increasing surface-charge density (Laird et al., 1992). The soils at Muddy Creek are dominated by kaolinite and illite (Kauffman, 1998), suggesting that the effect of the high specific surface area of the colloids would be greater than that of any variation in clay mineralogy.

Field Experiments

The volume of water collected from each plot ranged from 25 to 41% (mean 33%) of the total volume applied for the low-rate plots and from 19 to 50% (mean 35%) for the high-rate plots (Table 5); the effect of precipitation rate on water recovery was not significant. These low recoveries probably resulted in part because a fraction of the applied water went in to storage in the soil to satisfy a soil moisture deficit in initially unsaturated plots and in part because water draining under unsaturated conditions bypassed the zero-tension lysimeters. The large variation in the amount of water collected during the experiments from plots at the same rainfall

rate suggested a significant amount of physical heterogeneity at the site. The effects of soil variability were much greater than differences due to variations in precipitation rate at the surface.

Total atrazine mass recovery correlated strongly with total water recovery with a Pearson's correlation coefficient of 0.82 (Fig. 4). The strong correlation with total water recovery indicates that water movement in this system explains variability in the transport of atrazine. Bromide and atrazine transport results were highly variable among replicates but not significantly affected by precipitation rate. Mass recoveries of bromide ranged from 3.3 to 11% in the low-rate plots and from 2.8 to 16% in the high-rate plots (Table 5). Total atrazine mass recoveries were low, and ranged from 0.43 to 5.8% of the surface-applied mass (Table 5). Precipitation rate has previously been found to have a significant effect on atrazine transport (e.g., Sigua et al., 1993; Edwards et al., 1992; Shipitalo et al., 1990). These studies were mainly done using soil columns. Most field studies directly considering rainfall have looked only at the relationships between timing after application and duration of the events and atrazine concentrations without con-
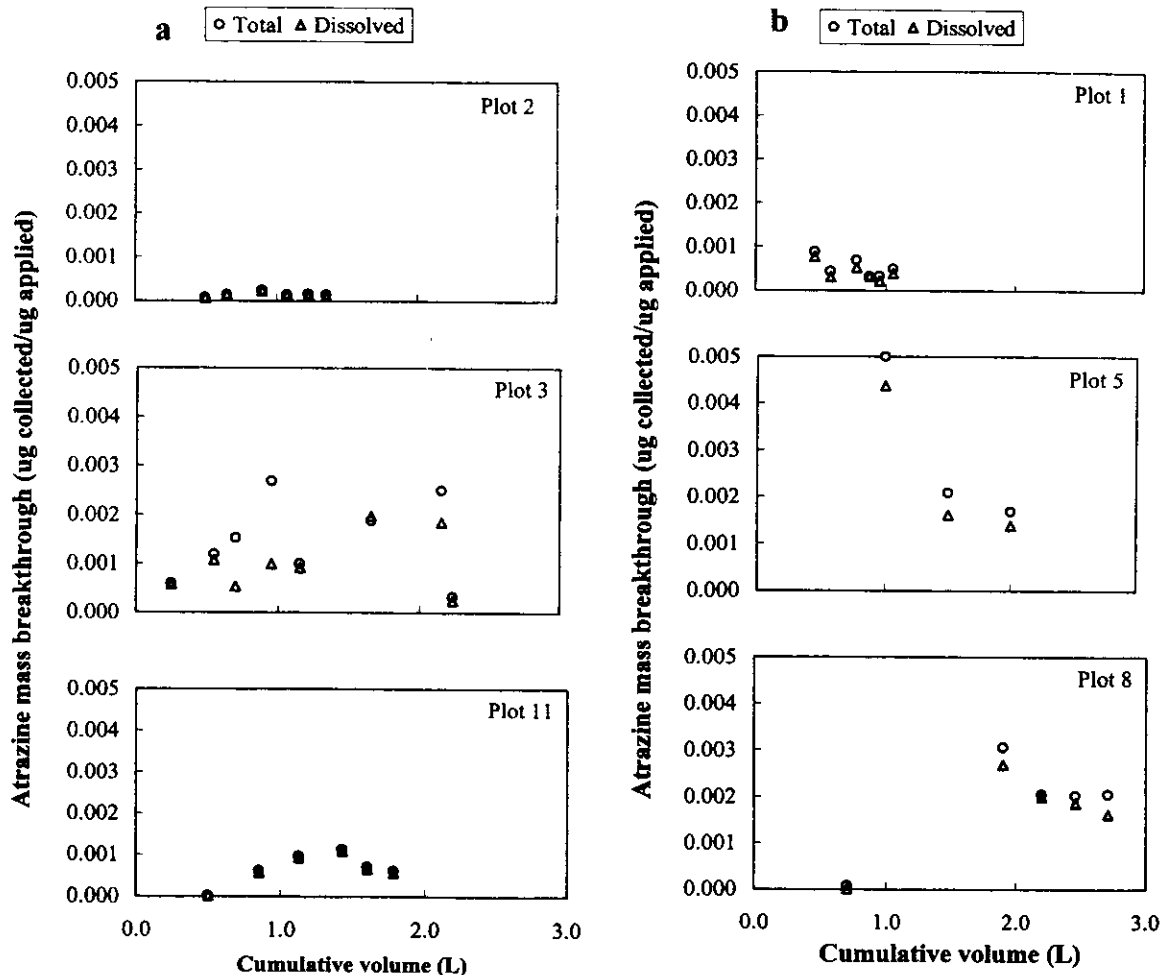
Fig. 6. (a) Atrazine breakthrough over the course of the rainfall simulations for the three low-rate plots. Circles represent total atrazine, triangles represent dissolved atrazine. The initial mass of atrazine applied to the plots was 37.5 mg and the mass of atrazine collected was the concentration of atrazine in the infiltrate multiplied by the volume of the infiltrate. (b) Atrazine breakthrough over the course of the rainfall simulations for the three high-rate plots. Circles represent total atrazine, triangles represent dissolved atrazine. The initial mass of atrazine applied to the plots was 37.5 mg and the mass of atrazine collected was the concentration of atrazine in the infiltrate multiplied by the volume of the infiltrate.

trolling precipitation rate or initial atrazine concentrations (e.g., Tindall and Vencill, 1995; Komor and Emerson, 1994; Sadeghi and Isensee, 1992). It is possible that atrazine behavior on larger field scales is not well represented by soil columns.

Colloids arrived in the lysimeters in an initial high pulse, with concentrations slowly declining through the course of the experiment (Fig. 5a,b). Possibly, colloids generated at the onset of the event were those most easily detached and represent some threshold adhesive force. Water infiltrating later in the experiment may thus not be as successful at mobilizing the remaining colloids, even with the relatively constant flow rates observed during these experiments. This pattern of colloid mobilization was also observed in a study by Kaplan et al. (1993), in which the initial water collected from reconstructed soil profiles contained a large pulse of colloids that dropped off over time. This may have resulted from either a depletion of the available colloids at the onset of infiltration or a drop in flow rate as the rainfall simulation progressed. In another study of colloid mobilization under simulated rainfall events in the field, most of the mobilization occurred early in

the experiment when flow rates were low and, overall, colloid concentrations did not correlate with flow rate (Ryan et al., 1998). The authors speculate that this lack of correlation may be attributable to the predominance of macropore flow at the site, which could quickly deplete the available supply of colloids. The occurrence of macropore flow is consistent with results from tension infiltrometry at Muddy Creek, which showed very low infiltration rates for tensions greater than 8 cm (El-Farhan et al., 1997), and with dye staining experiments for unsaturated flow on undisturbed cores from the site (Kauffman, 1998).

Peak colloid concentrations ranged from 103 to 1220 mg L^{-1} (Fig. 5a,b); timing of these peaks did not coincide with peak atrazine concentrations. Higher peak concentrations corresponded to a greater total colloid mass collected over the duration of the rainfall simulations. Total colloid mass collected ranged from 143 to 3020 mg, and these totals differed significantly for the two rainfall rates (Fig. 5a,b). When the total mass was normalized to total water volume collected over the course of the experiments, the effect from precipitation rate was no longer significant. This suggests that the average

Table 6. Mass recoveries of dissolved and colloid-associated atrazine (reported as % of total atrazine collected in the lysimeters) for field rainfall simulations at two rates. Each treatment was run in triplicate.

	Low precipitation rate				High precipitation rate			
	Plot 2	Plot 3	Plot 11	Mean	Plot 1	Plot 5	Plot 8	Mean
Dissolved atrazine	91	70	95	85	81	84	88	84
Colloid-associated atrazine	8.8	30	4.9	15	19	16	12	16

concentration of colloids mobilized during rainfall events is dependent on the amount of water moving through the soil. However, while precipitation rate significantly affected colloid mobilization, it did not affect water mass recovery. An additional effect of increased precipitation rate on colloid mobilization, but not water recovery, could be the increased shear stress imposed on soil surfaces from water infiltrating at a higher rate.

Despite the mobilization of colloids, the mass recovery of colloid-associated atrazine (as a percentage of atrazine applied at the surface) was low for all plots; on average, it was greater for the low-rate plots at 0.65% than for the high-rate plots at 0.51% (Table 5). However, the mass recovery of total atrazine was low as well. Mass recoveries of filtered (dissolved) atrazine reaching the lysimeters were always lower than recoveries of unfiltered (total) atrazine throughout the course of the experiments under either precipitation rate, as evidenced by the atrazine breakthrough curves (Fig. 6a,b). Therefore, to consider the relative contribution of colloid-associated atrazine to total atrazine movement, it is necessary to consider the mass recovery of colloid-associated atrazine as a percentage of the total atrazine actually reaching the lysimeters. Colloid-associated atrazine ranged from 4.9 to 30% of the total atrazine recovered in the lysimeters for the low-rate plots, and from 12 to 19% for the high-rate plots (Table 6). These numbers indicate that a measurable fraction of mobile atrazine is indeed transported in association with colloids.

Colloid concentrations determined turbidimetrically for the unfiltered and 0.2 μm-filtered field samples revealed that, on average, 7% of mobile colloids were left in the "filtered" samples during the experiments. As a result, the filtered fraction did not truly represent the "dissolved" phase; it may have potentially included a small fraction of the colloid-associated phase. Thus, colloid-associated pesticide concentrations reported here may be underestimates of the true concentrations.

CONCLUSIONS

The objective of this study was to quantify the role of soil colloids in atrazine transport through the unsaturated zone under different simulated rainfall intensities. Colloids isolated from the soil were found to have up to three orders of magnitude more extensive adsorption of atrazine than the bulk soil, probably a result of the higher specific surface area and organic content of the colloids. If this is conceptualized to represent the immobile soil matrix and mobile soil colloids, the potential for colloid-facilitated transport becomes apparent. The recovery of colloid-associated atrazine during rainfall

simulations in the field ranged from 4.9 to 30% of the total atrazine collected in lysimeters. This suggests that a measurable amount of total atrazine transport occurs in association with mobile colloids. The effect of precipitation rate on water, bromide, and atrazine mass recovery was not significant. Results indicated that satisfaction of a soil moisture deficit, rather than excedence of a precipitation rate threshold, was the controlling mechanism for water transport, and that this water transport explained variability in the transport of total atrazine.

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