INFLUENCE OF SOIL COLLOIDS ON THE MIGRATION OF ATRAZINE AND ZINC THROUGH LARGE SOIL MONOLITHS

C. D. BARTON[2] and A. D. KARATHANASIS[1]*
[1] *University of Kentucky, Department of Agronomy, Lexington, KY, U.S.A.;* [2] *present address:*
Center for Forested Wetlands Research, USDA Forest Service, c/o Savannah River Ecology
Laboratory, Aiken, South Carolina, U.S.A., e-mail: barton@srel.edu, fax: (803) 725–3309
(author for correspondence, e-mail: akaratha@ca.uky.edu, fax: (859) 257–2185)*

(Received 3 October 2000; accepted 4 April 2002)

Abstract. The role of soil colloids and their potential to co-transport agrochemicals in subsurface soil environments was evaluated in a leaching experiment utilizing large soil monoliths. The monoliths were created by hydraulically driving steel pipe sections (50 cm diameter × 50 cm length) into Maury silt loam (fine, mixed, mesic Typic Paleudalf) and Loradale silt loam (fine, silty, mixed mesic Typic Argiudoll) soils. Water dispersible colloids fractionated from the Bt horizons of the above soils were spiked with 3 mg L^{-1} atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) and 10 mg L^{-1} zinc (Zn), and after a twenty-four hour equilibration were applied into the monoliths at eight hour intervals using 500 mL pulse applications. Solutions containing atrazine and Zn without added colloids were applied to separate monoliths from each soil to represent control treatments. Colloid, atrazine, and Zn recoveries in the eluent varied greatly with respect to soil type. Colloid recovery in the Loradale monoliths averaged 65.1 ± 26.5%, with maxima approaching the input level, while in the Maury monoliths the average recovery was low (5.7 ± 6.2%) and never exceeded 25% of the input level. Atrazine eluted from the two monoliths averaged 40.3 ± 12.5% (Loradale) and 29.0 ± 20.0% (Maury), with considerable enhancement in the presence of colloids, especially in the Loradale soil. In contrast, the elution of Zn averaged 3.0 ± 3.2%, in the Loradale monoliths and rarely exceeded control concentrations in the Maury monoliths, suggesting a stronger retardation of Zn over atrazine within the soil matrix, especially when colloid transport was deterred. Settling-rate experiments at varying pH and electrical conductivity (EC) values suggested that the transport of Maury colloids may have been hindered due to flocculation within the monoliths, while the Loradale colloids remained stable throughout the leaching experiment. Although the presence of colloids enhanced atrazine elution in all monoliths, the actual amount of atrazine transported bound to either colloid type was minimal, suggesting mainly physical exclusion transport processes. In contrast, stronger chemisorption of Zn to colloid surfaces than the soil matrix appeared to enhance the transport of Zn by both colloids.

Keywords: colloids, contaminant transport, heavy metals, herbicides, soil monoliths

1. Introduction

The contamination of soil and groundwater by agrochemicals is a major environmental concern. The widespread use of pesticides over the past half century has led to their detection in many hydrologic systems of the United States and other countries (Triegel and Guo, 1994). The National Water-Quality Assessment

Water, Air, and Soil Pollution **143:** 3–21, 2003.

performed during 1993–1995 in 20 major hydrologic basins of the U.S. found pesticides in 54.4% of the 1034 sites sampled (Kolpin *et al.*, 1998). Inputs of heavy metals into the terrestrial environment from fertilizers and livestock manures also pose a significant threat to groundwater quality (Förstner, 1995). Predicting the movement of such contaminants through subsurface zones has traditionally been performed with models that consider one or more mobile dissolved phases and an immobile solid phase. In this two-phase system, contaminants can migrate much slower than the rate at which groundwater flows because they tend to be adsorbed onto the immobile solid phase (Ibaraki and Sudicky, 1995). Recent evidence, however, suggests that the unaccounted mobile colloid solid phase can co-transport substantial amounts of contaminants and further contribute to groundwater quality deterioration (Ouyang *et al.*, 1996; Puls and Powell, 1992). This is due to the large surface area of colloids (10–500 m^2 g^{-1}) (Liang and McCarthy, 1995), and their high affinity for contaminant sorption and co-transport through soil macropores. In addition, colloids may migrate at rates similar to the mobile aqueous phase because solid-phase adsorption and retardation can be deterred. Consequently, predictions of contaminant transport in subsurface environments that disregard the role of dispersible mobile colloids may be significantly underestimated.

In recent years, a considerable amount of research has been performed at the University of Kentucky to characterize the stability and transportability of soil colloids, and to assess the magnitude of colloid-mediated transport of heavy metals and herbicides. From these studies it was determined that soils with extensive macroporosity induced greater transport (26%) of water-dispersible colloids, especially those with the higher surface charge (Seta and Karathanasis, 1997a). The presence of colloids enhanced the transport of atrazine by 2 to 18% (Seta and Karathanasis, 1997b), and of heavy metals (Cu and Zn) by 5 to 50-fold (Karathanasis, 1999) over that of control treatments. Colloids with high suspension pH, base saturation, CEC, OC, surface area, and electrophoretic mobility showed a greater affinity for sorption and transport of atrazine and metals (Seta and Karathanasis, 1997b; Karathanasis, 1999). Conversely, increased amounts of 1:1 clays, Fe and Al-hydroxides inhibited atrazine and metal sorption and transport. Even though the transportability of both herbicides and heavy metals increased in the presence of colloids, the primary mechanism responsible for their transport was different. Chemisorption to colloids and subsequent co-transport appears to be the dominant transport mechanism for metals (Karathanasis, 1999). In contrast, matrix-surface-site exclusion and blocking mechanisms triggered by colloid filtration and deposition within flow paths, may account for the heightened atrazine mobility (Seta and Karathanasis, 1997b).

The above findings were obtained from the use of moderately-sized, intact soil columns (13 cm diameter and 20 cm length) under continuous gravitational flow conditions in a controlled laboratory setting. However, predicting the transport and fate of contaminants in the soil subsurface environment from experiments confined to a single soil horizon may pose serious limitations. Vertical and spatial soil variability encountered under field conditions are likely to influence the movement of colloids and/or agrochemicals through both physical and chemical interactions. Also, a soil suspension moving through the soil under field conditions may contain more than one contaminant, since herbicides and fertilizers are often applied to a field within weeks from each other. Furtermore, soil saturation, temperature, and biological activity are constantly changing under field conditions. Therefore, there is a need to examine soil colloid behavior and co-transport mechanisms under a larger scale setting better approximating natural field conditions. The objectives of this study were: (i) to evaluate the role of soil colloids in co-transporting atrazine and zinc through large *in-situ* soil monoliths under field conditions; and (ii) to determine the influence of soil physicochemical properties on colloid-enhanced transport processes.

2. Materials and Methods

2.1. SOIL MONOLITHS

Undisturbed soil monoliths were prepared in the field at two sites on the University of Kentucky Agricultural Experiment Station in Lexington, KY. Soils included in the experiment were a Maury silt loam (fine, mixed, mesic Typic Paleudalf) and a Loradale silt loam (fine, silty, mixed, mesic Typic Argiudoll). Two adjacent soil monoliths per soil type were used for replication. Steel pipe sections with an inside diameter of 50 cm, wall thickness of 1 cm, and length of 1 m were used for the cores. The cylinders were beveled at one end to facilitate penetration into the soil. Cylinders were placed vertically on a prepared area in which the vegetation was removed and pushed $\approx$ 0.5 m into the soil using a 30 ton hydraulic drill rig. Bulk density measurements taken before and after the installation of cylinders in preliminary experiments suggested negligible compaction of the soil matrix. A 1.5 $\times$ 1.5 m trench was excavated with a backhoe parallel to and at a distance of 0.5 m from the row of monoliths. Soil was removed below each monolith with hand tools, thereby creating a ‘cavity’ at which the metal cylinder was visible. In this area a 52 cm diameter and 15 cm long PVC cap was installed. A male hose fitting lined with a 325 mesh (45 μm) screen was screwed into a threaded nut, which was welded into the bottom of the PVC cap. A polyethylene hose was attached to each cap and the ‘cavity’ was backfilled with soil to aid in support of the monolith.

2.2. COLLOID AND SOIL CHARACTERIZATION

Water dispersible colloids were fractionated from the Bt horizons of the Maury and Loradale soils. Extraction of colloid fractions was performed by mixing 10 g of soil with 200 mL of d-H_2O in plastic bottles, shaking for one hour, centrifuging at $\times$ 130 g (750 rpm) for 3.5 min, and collecting the suspended fraction (Seta and Karathanasis, 1997a). The concentration of the colloid fraction was determined gravimetrically. A subsample of the stock colloid was collected for characterization of physicochemical and mineralogical properties.

Physicochemical and mineralogical properties of the colloids and soils used in the experiment were determined following methods of the Natural Resources Conservation Service (NRCS) (1996). They are listed in Table I. Analyses were performed on air-dried colloid samples that had been crushed and passed through a 0.23 mm sieve. The mean diameter of fractionated colloids was measured using a Quantachrome Corporation microscan particle-size analyzer and expressed on a mass basis. Extractable bases and CEC were determined with the 1*M* ammonium acetate (NH_4OAc), pH 7.0 method (NRCS, 1996). Analysis of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}) were performed on an Instrumentation Laboratory (Franklin, MA) model S11 AA/AE spectrophotometer. Organic carbon was determined using a Leco Carbon Analyzer, Model CR-12 (Leco Corp., St. Joseph, MI). Soil pH was measured in a 1:1 soil-water suspension. Amorphous and crystalline Fe and Al were extracted with ammonium oxalate and citrate-bicarbonate-dithionate, respectively, following the procedures of Shuman (1985) and McDaniel and Buol (1991). Bulk density (BD) and particle size analysis were determined according to NRCS methods (1996), while saturated hydraulic conductivity was measured with the method of Klute and Dirksen (1986).

2.3. LEACHING EXPERIMENT

Prior to the leaching experiment, the monoliths were wetted with 5 L of d-H_2O to moisten the soil surface. The experiment was conducted under unsaturated, gravitational flow conditions in both soils. Under these conditions, a colloid-Zn-atrazine mixture was applied onto the soil monoliths in 500 ml pulses, at eight hour intervals. About 1.6 and 1.8 pore volumes were eluted from the Loradale and Maury monoliths, respectively. One of the Loradale monoliths collapsed after 1.6 pore volumes of leaching and was discontinued. Therefore, replicated data were collected up to 1.6 pore volumes for the Loradale monoliths and up to 1.8 pore volumes for the Maury monoliths. The input mixture was prepared by mixing a 300 mg L^{-1} Maury or Loradale colloid suspension with 3 mg L^{-1} reagent grade atrazine and 10 mg L^{-1} Zn. The mixture was allowed to equilibrate overnight before application to the monoliths. A solution containing 3 mg L^{-1} reagent grade atrazine and 10 mg L^{-1} Zn with no colloid was also applied in a similar fashion to another monolith at each site to represent the control treatment.

Eluents were monitored with respect to volume, colloid, atrazine, and Zn concentration, which allowed construction of breakthrough curves (BTCs). The average standard error for the above parameters associated with the replicated monoliths was $< 12\%$ for the Loradale and $< 16\%$ for the Maury monoliths. Therefore, for clarity average values are plotted and discussed in the manuscript. Eluents were also analyzed for pH, EC, Mn, Fe, and Ca to evaluate potential changes in the solid and solution phase brought on by the leaching conditions. The Mn, Fe and

Ca analyses were performed by atomic absorption spectroscopy (AAS). Colloid concentrations in the eluent were determined with a Bio-Tek multichannel (optical densitometer with fiber-optics technology; Bio-Tek Instruments, Winooski, VT) microplate reader, precalibrated with known concentrations of each colloid at 540 nm. The eluent samples were centrifuged at × 2750 g (3500 rpm) for one hour to separate the soluble Zn and atrazine fraction from the colloid-bound fraction. Supernatants were decanted into glass vials for solute analyses. The soluble Zn fraction was determined by AAS using standards of the same matrix. Due to the large number of samples and relatively high eluent atrazine concentrations ($>$ 100 μg L^{-1}), the soluble atrazine fraction was analyzed using the pyridine-alkali method (Radke *et al.*, 1966). Four mL of the aqueous atrazine solution were placed in a small glass test tube to which 1 mL of 0.25 *M* citric acid buffer and 1 mL of 70% pyridine was added. The test tube was covered with a glass marble and heated in a water bath at 90 °C for 45 min. After cooling to room temperature, 180 μL of sample was transferred to a microplate and 30 μL of 9 *N* NaOH were added. Following a minute of vortex shaking, the sample was scanned at 450 nm using the microplate reader described earlier.

For eluted samples with moderate to high colloid concentration ($>$ 25 mg L^{-1}), the colloid-bound Zn was extracted with 1 *M* HNO_3 – HCl (USEPA method 200.2, 1994) and analyzed by AAS, while the colloid-bound atrazine fraction was extracted with methanol and analyzed using an immunoassay procedure (Strategic Diagnostics Incorporated, Newark, DE), following USEPA method 4670 (1994). For eluted samples with colloid concentration $<$ 25 mg L^{-1}, the experimental and analytical uncertainty was too high to rely on direct extraction determinations. Thus, the colloid-bound Zn or atrazine fraction was calculated from adsorption isotherms generated from batch experiments. The amount of colloid-bound Zn or atazine eluted through monoliths during the leaching experiment was calculated in these situations by extrapolating the solute equilibrium concentration in the eluent to the adsorption capacity of the colloid and multiplying by the colloid concentration in the eluent.

2.4. ADSORPTION ISOTHERMS

Batch equilibrium experiments were performed using 50 mL Teflon test tubes. A 250 mg sample of air-dried colloid was added to each test tube along with 35 mL of adsorbate solution containing 0–3.0 mg L^{-1} atrazine. Samples were shaken on a reciprocating shaker for 24 h and centrifuged for 30 min at × 2750 g (3500 rpm). Supernatants were collected and measured for atrazine using the immunoassay method. Atrazine adsorption isotherms were constructed by plotting the concentration of the herbicide retained by the colloids against the equilibrium herbicide concentration in solution. The Freundlich isotherm equation was used to describe the experimental adsorption data. Atrazine adsorption isotherms were also prepared in a similar fashion for composite soil samples representing a weighted average of the entire length of each soil monolith.

Similar adsorption isotherms were also generated to evaluate Zn sorption by the soil colloids and composite soil samples. A 250 mg of air-dried colloid or soil sample was added to each test tube along with 35 ml of adsorbate metal solution containing 0–10 mg L^{-1} of Zn. After 24 h of shaking, the samples were centrifuged at × 2750 g (3500 rpm) for 30 min and the supernatants were analyzed for Zn by AAS. The Freundlich isotherm equation was also used to describe the experimental Zn adsorption data. The above procedures were repeated for the colloids using a mixture of atrazine and Zn solutions, similar to that applied in the field experiment, to examine competitive sorption processes.

2.5. COLLOID STABILITY EXPERIMENTS

The stability of colloids alone and in association with Zn and atrazine was evaluated under varying pH and EC conditions. A series of 50 mL test tubes were filled with 20 mL aliquots of either a 300 mg L^{-1} colloid suspension by itself, or a 300 mg L^{-1} colloid suspension spiked with 3 mg L^{-1} atrazine and 10 mg L^{-1} Zn. In the pH stability experiment, suspensions were adjusted in twelve pH increments ranging from 2.5 to 10.0 with HCl or KOH. A 200 μL suspension aliquot was pipetted from the 5 cm depth of each tube after 0, 1, 6, 12 and 24 h of settling time. The concentration of colloid in the pipetted suspension was evaluated with a microplate reader at 540 nm. Colloid suspensions used in the EC stability experiment were adjusted in six EC increments ranging from 50 to 1000 μS with $CaCl_2$, and were pipetted at the 5 cm depth after 0, 1, 2, 3 and 4 h of settling time. Colloid stability at each pH or EC level was expressed in terms of percent of colloid concentration remaining in suspension vs. pH or EC, respectively. The higher the percentage of colloid remaining in suspension the higher its colloid stability.

2.6. STATISTICAL ANALYSIS

Analysis of variance was used to test for differences in the breakthrough of colloids, attrazine, and zinc from the two soil types. Comparisons were determined using pooled data obtained from the first 1.6 pore volumes of collected eluent from each treatment. Analysis of variance was performed using SAS (SAS Inst., 1990). The 0.05 level of probability was used as the decision level for acceptance or rejection of statistical significance.

3. Results and Discussion

3.1. COLLOID TRANSPORT

Data from the leaching experiments were transformed into BTCs based on reduced concentration (ratio of effluent concentration to influent concentration = C/Co) versus pore volume of suspension passed through the monoliths. Over 100 one-liter samples were collected from each monolith during the leaching experiment, representing 1.6 to 1.8 pore volumes for the Loradale and Maury monoliths, respectively. Statistical analysis indicated that the samples could be averaged into groups equaling 0.2 pore volumes each with $< 10\%$ deviation from the mean. Therefore, the BTCs are plotted this way for clarity. Most breakthrough curves were irregular, indicative of the highly interactive and dynamic nature of colloids and solutes during the leaching process. The Loradale monoliths showed an initial rapid breakthrough to a C/Co value of 0.96 at 0.5 pore volumes of leaching (Figure 1). After that, colloid breakthrough declined steadily to about 0.8 C/Co at 1.2 pore volumes before dropping abruptly to 0.2 C/Co at 1.6 pore volumes. Although the high colloid breakthrough in the Loradale monoliths could have been induced by the high OC content of the Loradale soil, dislodged soil particles from the monoliths during the early stages of leaching may have inflated the colloid breakthrough values. A similar pattern of dislodged soil particles was also observed in the control Loradale monoliths that lacked colloid input. The subsequent decline in colloid elution may be the result of pore clogging and/or colloid filtration within the monoliths, as well as reduced infiltration caused by dispersion of surface soil aggregates, and development of a surface seal. Even though flow conditions remained constant, small resurgences in colloid breakthrough at approximately 1.2 and 1.6 pore volumes are attributed to partial flushing and reopening of previously clogged pores, creation of new flow paths from biological activity in the monoliths (worms, insects etc.), or changes in the chemical environment within the monolith matrix. A dye tracer application at the end of the experiment did not suggest preferential flow of colloids along the soil monolith-cylinder boundary.

Colloid transport through the Maury monoliths was greatly reduced compared to that observed in the Loradale (Figure 1). An analysis of variance between mean colloid breakthrough in the monoliths showed a significant difference ($p < 0.01$) between the two soil types. The Maury monoliths displayed essentially no colloid breakthrough ($C/Co < 0.05$) in the first 1.4 pore volumes, and only after ponding at 1.6 pore volumes it surged to about 0.15 C/Co. The physical characteristics of the Maury soil and colloid may be responsible for the observed difference between the BTCs of the two soils. The Maury soil exhibited a reduced hydraulic conductivity and a somewhat elevated bulk density immediately below the surface horizon (Table I), which may be indicative of mechanical compaction. Morphological evidence from a dye tracer indicated the presence of a weak plow pan at a depth of 15 cm in the Maury soil (Barton and Karathanasis, 2002), which may

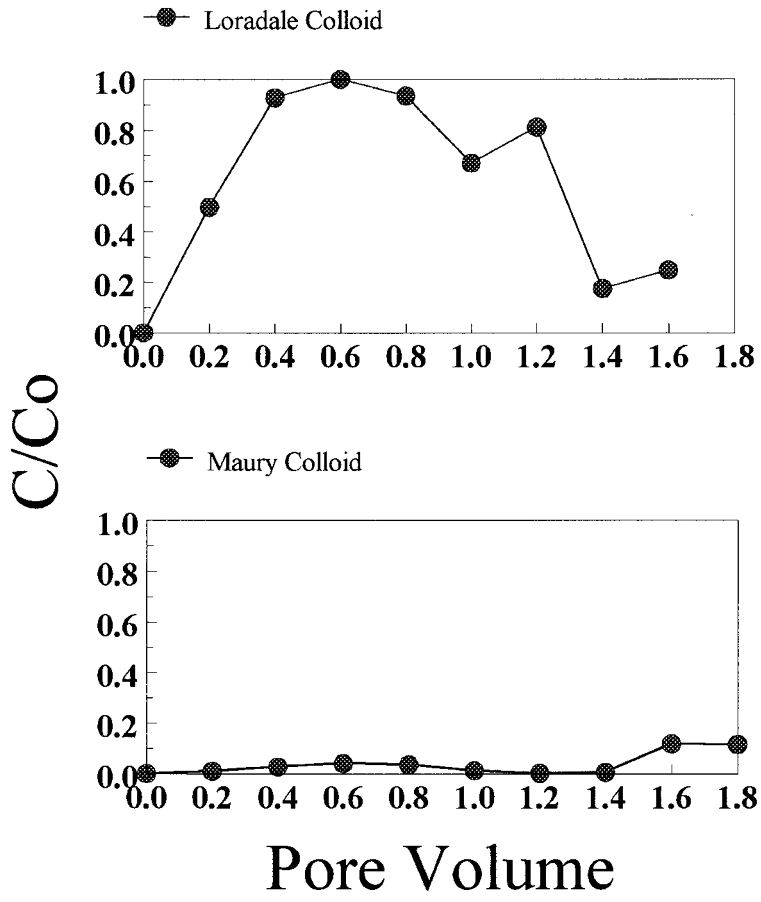

Figure 1. Breakthrough curves for Loradale and Maury colloids eluted from Loradale and Maury monoliths, respectively.

have inhibited vertical flow of colloids in the monoliths. In addition, the mean diameter of the Maury colloid was much greater than that of the Loradale (700 nm vs. 300 nm), which would make it more susceptible to filtration within the pores of the monoliths. Aggregate dispersion in the monolith's surface layer inhibited infiltration and led to pore clogging and/or colloid filtration, which further deterred the colloid breakthrough.

Other physicochemical characteristics of the Maury soil and colloid may have also contributed to the reduced colloid breakthrough. The Maury colloid contained higher Fe and Al concentrations over that of the Loradale colloid. Iron and Al often act as cementing and binding agents in soils and are known to be strong flocculants (Goldberg *et al.*, 1990). Aggregation and coagulation are promoted in the presence of Fe and Al oxides and hydroxides through an attraction between the positively charged metal and the negatively charged colloid particle (McBride, 1989). The

TABLE I

Physicochemical and mineralogical properties of soils and colloids included in the study

	Soils[b]				Colloids	
Properties[a]	Loradale (Ap)	Maury (Ap)	Loradale (Bt)	Maury (Bt)	Loradale	Maury
Clay (%)	16 ± 2.0	18 ± 0.7	28 ± 0.6	33 ± 1.0	–	–
HC (cm min^{-1})	3.1 ± 1.7	2.4 ± 1.4	0.7 ± 0.4	1.9 ± 0.5	–	–
Bulk Density (g cm^{3})	1.2 ± 0.2	1.5 ± 0.2	1.3 ± 0.1	1.4 ± 0.4	–	–
OC (%)	3.4 ± 0.05	1.7 ± 0.01	2.0 ± 0.01	0.5 ± 0.01	3.7 ± 0.02	1.0 ± 0.03
pH	5.5 ± 0.1	5.5 ± 0.2	6.0 ± 0.1	5.7 ± 0.1	6.5 ± 0.1	6.0 ± 0.2
EC (μS)[c]	17.3 ± 1.0	12.0 ± 0.4	9.4 ± 0.2	8.4 ± 0.6	4.3 ± 0.3	3.7 ± 0.1
CEC (cmol kg^{-1})	21.6 ± 0.2	15.6 ± 0.2	18.5 ± 0.1	18.1 ± 0.6	76.9 ± 2.1	45.7 ± 0.7
TEB (cmol kg^{-1})	14.9 ± 1.1	10.7 ± 0.1	13.2 ± 0.3	10.5 ± 0.4	30.8 ± 1.1	21.1 ± 0.9
Extractable Fe (mg g^{-1})	5.0 ± 0.3	3.8 ± 0.4	6.3 ± 0.6	5.2 ± 0.1	12.8 ± 0.7	15.4 ± 2.1
Extractable Al (mg g^{-1})	1.5 ± 0.4	2.3 ± 0.2	3.0 ± 0.3	2.6 ± 0.1	3.6 ± 0.5	6.5 ± 1.3
Surface Area (m^{2} g^{-1})[d]	–	–	–	–	186	190
Mean Colloid Diameter (nm)[d]	–	–	–	–	300	700
EM (μm cm v^{-1} s^{-1})[d]	–	–	–	–	–1.9	–1.4
HISM + HIV (%)[d]	–	–	–	–	44	46
Mica (%)[d]	–	–	–	–	15	10
Kaolinite (%)[d]	–	–	–	–	35	36
Quartz (%)[d]	–	–	–	–	6	8

[a] HC = hydraulic conductivity; OC = organic carbon; EC = electrical conductivity; CEC = cation exchange capacity; TEB = total exchangeable bases; EM = electrophoretic mobility; HISM = hydroxyinterlayered smectite; HIV = hydroxyinterlayered vermiculite.

[b] Average and standard deviation of duplicate samples except for HC, which represents the average of five samples.

[c] Soil EC was determined in a 1:10 soil to solution ratio, colloidal EC was determined in a 300 mg L^{-1} colloid suspension.

[d] Data from Seta and Karathanasis (1997b).

lower electrophoretic mobility, CEC and OC of the Maury colloid may have also induced instability by weakening the repulsive forces between particles (Goldberg *et al.*, 1990), and causing colloid flocculation within the Maury monolith.

The increased colloid breakthrough following surface ponding and development of saturated conditions within the column may have been the result of the detachment of deposited particles from pore surfaces due to changes in the flow velocity (Corapcioglu and Jiang, 1993). Switching from unsaturated to saturated flow conditions may alter electrical forces and double-diffuse layer conditions at the interfaces between particles, and contribute to their detachment (McDowell-Boyer *et al.*, 1986).

3.2. COLLOID STABILITY

Settling-rate experiments of the Loradale and Maury colloid suspensions performed under varying pH conditions indicated a similar behavior at pH values greater than 4.0 (Figure 2). Decreasing the pH below 4.0, however, resulted in a sharp decline in the amount of colloids that remained suspended. This decline is associated with the colloid pH_{ZPC}, where flocculation of the particles is promoted due to a reduction in the net surface potential. This condition appeared to occur at pH 3.5–4.0 in the Maury colloid and at $pH < 3.5$ with the Loradale colloid. The decrease in colloid stability over time, for both colloids, is attributed to an increased frequency of collisions and interactions between particles with elapsed time (Morrison and Boyd, 1973).

Addition of atrazine and Zn to the colloid suspensions resulted in a slight reduction in the stability of the Loradale colloid and a drastic reduction ($\sim$ 2 pH units) in the Maury colloid (Figure 3). It is likely, that the stability of the Loradale colloid was enhanced by its higher OC content. According to Kretzschmar *et al.* (1995), organic coatings promote colloid stability by steric hinderance. In addition, organic coatings may increase the pH_{ZPC} of the colloid by promoting hydrolysis and precipitation of Al and Fe oxides that had been complexed or covered with organic material (Oades, 1989).

Increases in the ionic strength of the colloid suspension, attributed to the atrazine and $ZnCl_2$ additions, may also suppress the thickness of the double-layer by reducing the electrostatic repulsive forces between the planar colloid surfaces and allowing the colloids to physically approach each other (Jekel, 1986). To examine the influence of ionic strength on colloid stability, settling-rate characteristics as affected by EC were evaluated (Figure 4). Electrical conductivity is a function of total dissolved ions, type of ions, and their potential to form charged or noncharged pairs or complexes, thus EC can be used as an estimate of ionic strength. The results showed that the stability of the Maury colloid is much more sensitive to small changes in EC. Increasing the EC of the colloid suspension to 100 μS cm^{-1} caused flocculation of the Maury colloids. In contrast, most Loradale colloid suspensions remained suspended up to 250 μS cm^{-1}. The addition of atrazine and Zn to the colloid suspension increased the EC of the Maury colloid from 3.7 to 23.4 μS cm^{-1} and that of the Loradale colloid from 4.3 to 30.1 μS cm 1. Although this elevation alone was not enough to elicit colloid flocculation, additional electrolyte inputs from the soil matrix during the leaching experiment may have further reduced colloid stability.

Eluent pH and EC in the Loradale monoliths did not change significantly during the course of the leaching experiment. Electrical conductivity remained below 100 μS cm^{-1} and pH ranged from 6.5 to 7.0, suggesting that electrochemical conditions were not conducive for flocculation and excessive colloid retention, other than natural filtration. The eluents from the Maury monoliths exhibited similar pH increases from 6.0 to 7.2, but large elevations in EC approaching 600 μS cm^{-1}.

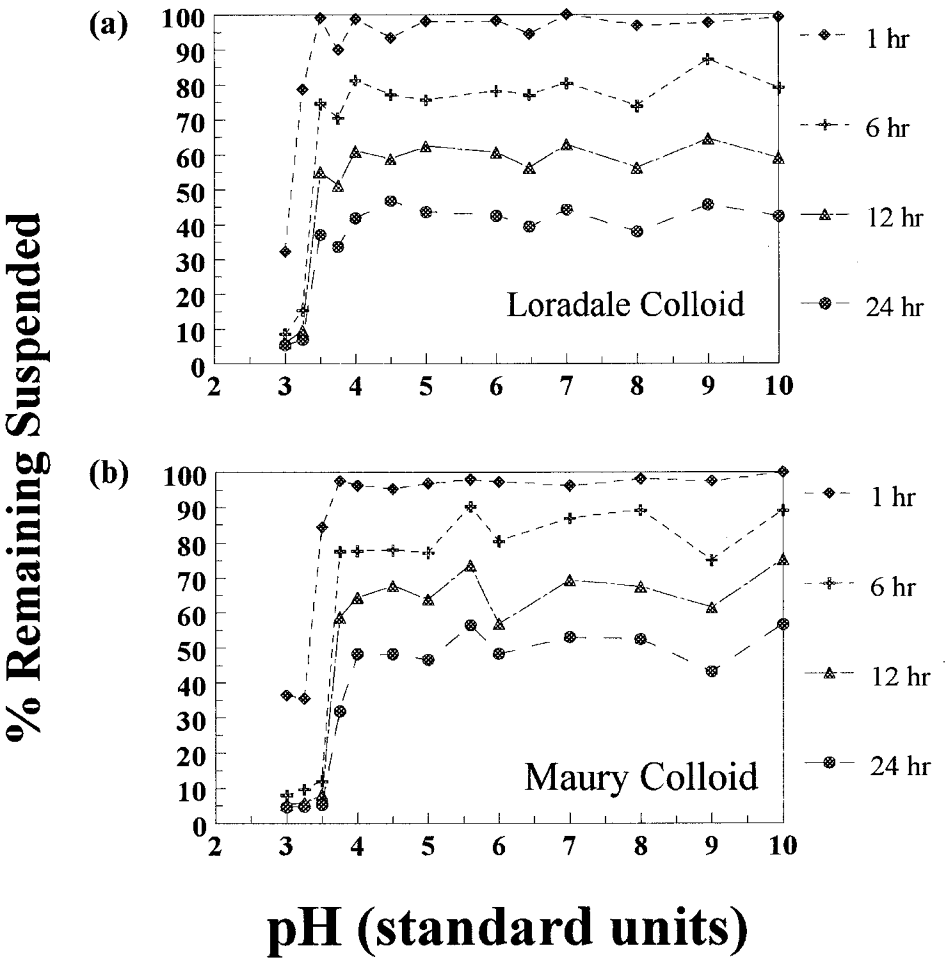

Figure 2. Settling kinetics of 300 mg L^{-1} Loradale (a), and Maury (b) colloid suspensions at various pH levels.

Although this pH change should not inhibit colloid stability (Figure 3), the overriding influence of the increase in EC was apparently enough to cause instability (Figure 4). Analysis of the eluents and visual inspection of the soils indicated that manganese concretions, which were abundant in the Maury soil, had softened and solubilized in the leaching solution. Apparently, continuous saturation of the monoliths during the leaching experiment ($\approx$ 1 month) prompted the development of reducing conditions that favored mobilization of Mn^{2+} (> 200 mg L^{-1}) increasing the ionic strength of the colloid suspension and inducing colloid flocculation.

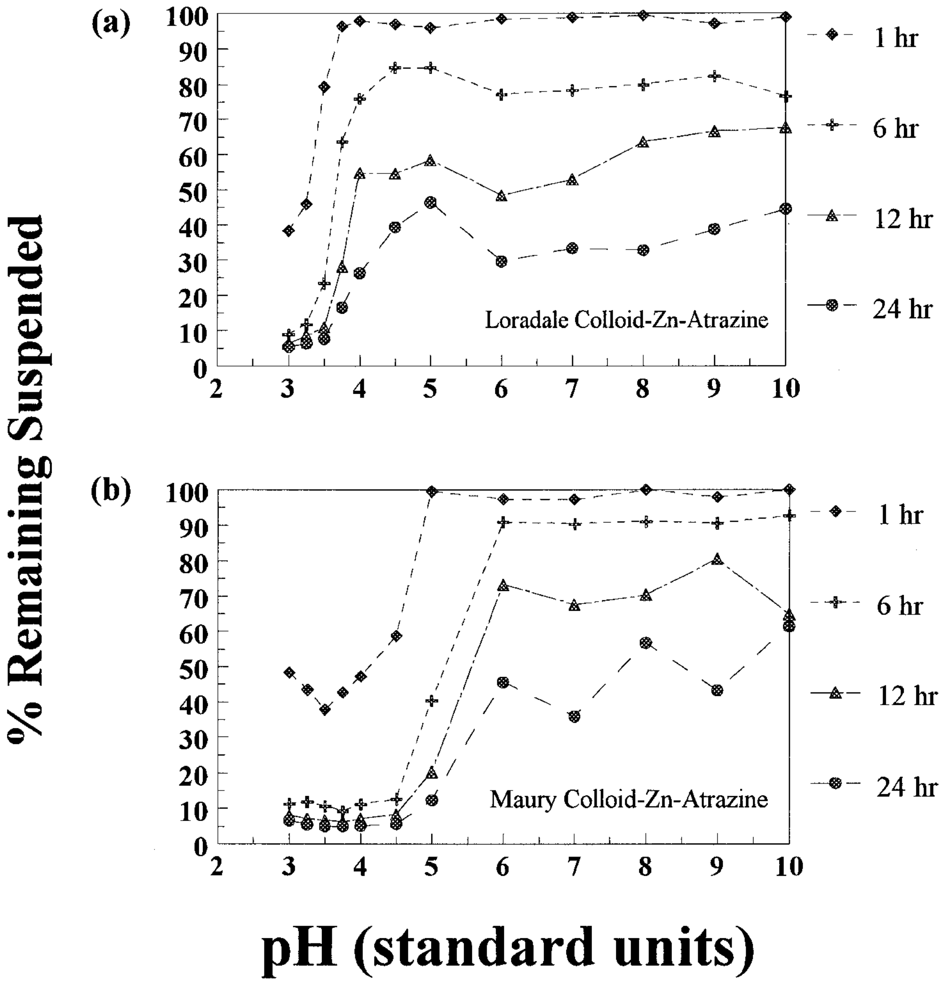

Figure 3. Settling kinetics of a suspension containing 300 mg L^{-1} Loradale (a), or Maury (b) colloid, with 10 mg L^{-1} Zn and 3 mg L^{-1} atrazine at various pH levels.

3.3. ATRAZINE TRANSPORT

Atrazine eluted in the presence of colloids is plotted as the soluble fraction and as the sum of the soluble and the extracted colloid-bound fraction. In the absence of colloids (control), atrazine exhibited a rapid breakthrough to C/Co of 0.2 in the Loradale monoliths, and remained at that level throughout the experiment (Figure 5). In spite of some fluctuation, the presence of Loradale colloids shifted the atrazine elution up to 0.6 C/Co, averaging 2 to 3 times greater concentrations than those eluted in the absence of colloids. In spite of this increase, the amount of atrazine eluted in the presence of colloids through the Loradale monoliths was not proportional to the concentration of the colloids in the eluent (Figure 1). The lack of

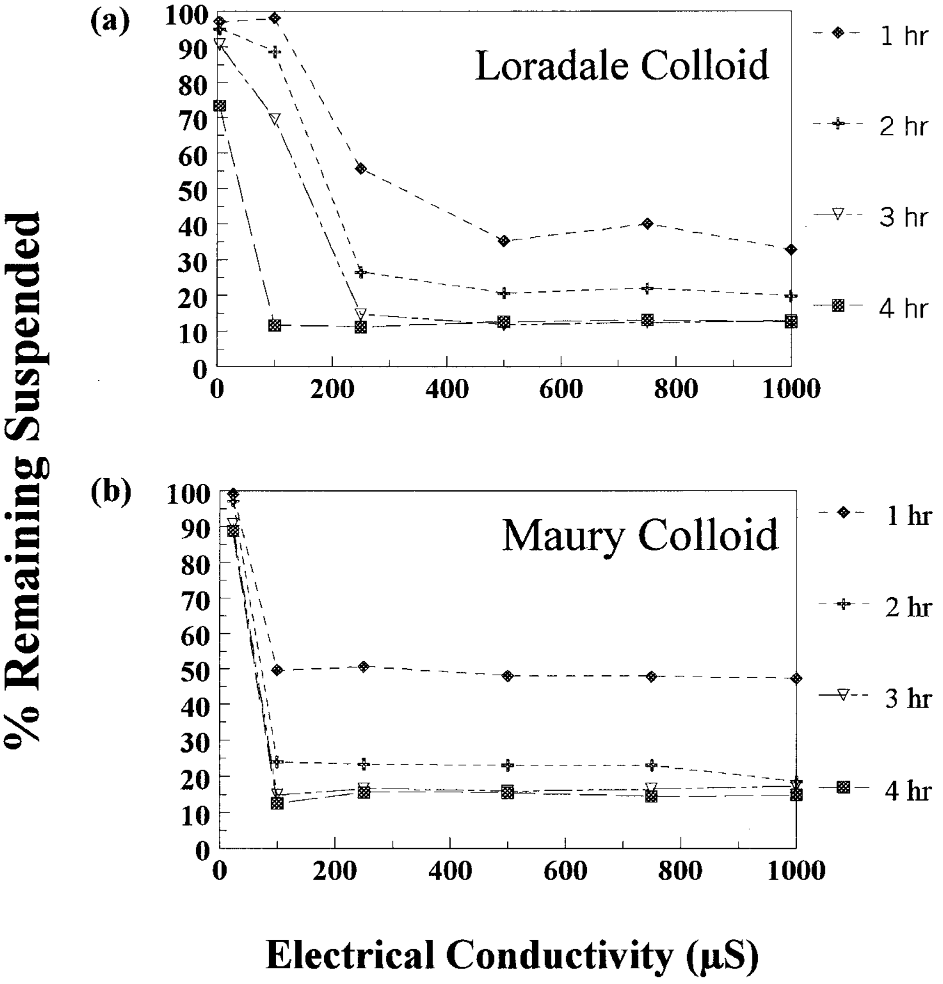

Figure 4. Settling kinetics of 300 mg L^{-1} Loradale (a), and Maury (b) colloid suspensions at various EC levels.

a better relationship between colloid and atrazine breakthrough supports the claim that some particle detachment might have occurred within the Loradale monoliths. Thus, the effect of the applied colloids on atrazine transport may have been masked by the presence of these particles in the eluents. Even though we could not distinguish the applied colloids from the detached soil particles in the eluent, we could infer their presence from their insignificant contribution to the overall load of atrazine sorbed to colloids. Also, x-ray diffractograms of the particulate material showed higher quartz levels than those present in the applied colloids, thus corroborating the contamination with detached soil particles. Extraction of atrazine from the eluted Loradale particulate material (applied colloids + detached

TABLE II

Freundlich-isotherm constants for adsorption of Zn and atrazine to colloids and soils

	K_f[a]		N[b]		r^2[a]	
Colloids	Zn	Atrazine	Zn	Atrazine	Zn	Atrazine
Loradale	4.16	3.80	0.63	0.81	0.988	0.967
Maury	3.05	2.32	0.67	0.77	0.964	0.994
Soils						
Loradale	1.42	1.81	0.52	0.44	0.995	0.999
Maury	0.94	1.42	0.47	0.57	0.981	0.996

[a] K_f = sorption capacity.
[b] N = intensity factor.
[c] number of observations for each isotherm = 6.

soil particles) showed that < 1% of the transported atrazine was bound to the solid phase. Similar results were reported by Seta and Karathanasis (1997b).

In the Maury monoliths, atrazine eluted in the absence of colloids (Figure 5) showed an irregular and gradual rise, fluctuating between 0.2 and 0.4 C/Co. The higher atrazine control breakthrough in the Maury monoliths over that observed in the Loradale monoliths may be explained by the lower sorption capacity (K_f) of the Maury soil (Table II). Atrazine elution in the presence of the Maury colloids was slightly higher than that of the control only after the elution of 1.2 pore volumes. The average breakthrough of atrazine eluted in the presence of Maury colloids was similar to that of the Loradale colloids (Figure 5). However, unlike the Loradale monoliths, the elution pattern of colloid-associated atrazine in the Maury monoliths had a much closer relationship with the colloid breakthrough (Figure 1). As it was the case with the Loradale colloids, however, atrazine extraction from the eluted Maury colloids indicated that < 1% of the overall transported atrazine load was bound to the colloid.

Since only a small amount of adsorbed atrazine was actively carried by the colloids through the soil monoliths, their contribution to the increased elution of atrazine must have been through either physical blocking of reactive sites (exclusion) or to chemical alterations that reduced the interaction of the herbicide with the soil matrix. Binding of atrazine to soluble soil organic material (humic and fulvic acids) present in the Loradale soil and colloids could result in the formation of stable soluble organic complexes, which may not be sorbed to the soil matrix (Senesi and Testini, 1982). Since the atrazine-colloid mixture was allowed to equilibrate before the leaching procedure began, formation of such organic complexes is very likely. Unfortunately, detection and/or isolation of these complexes by the method used for colloid determination was not feasible due to the masking effect of the detached

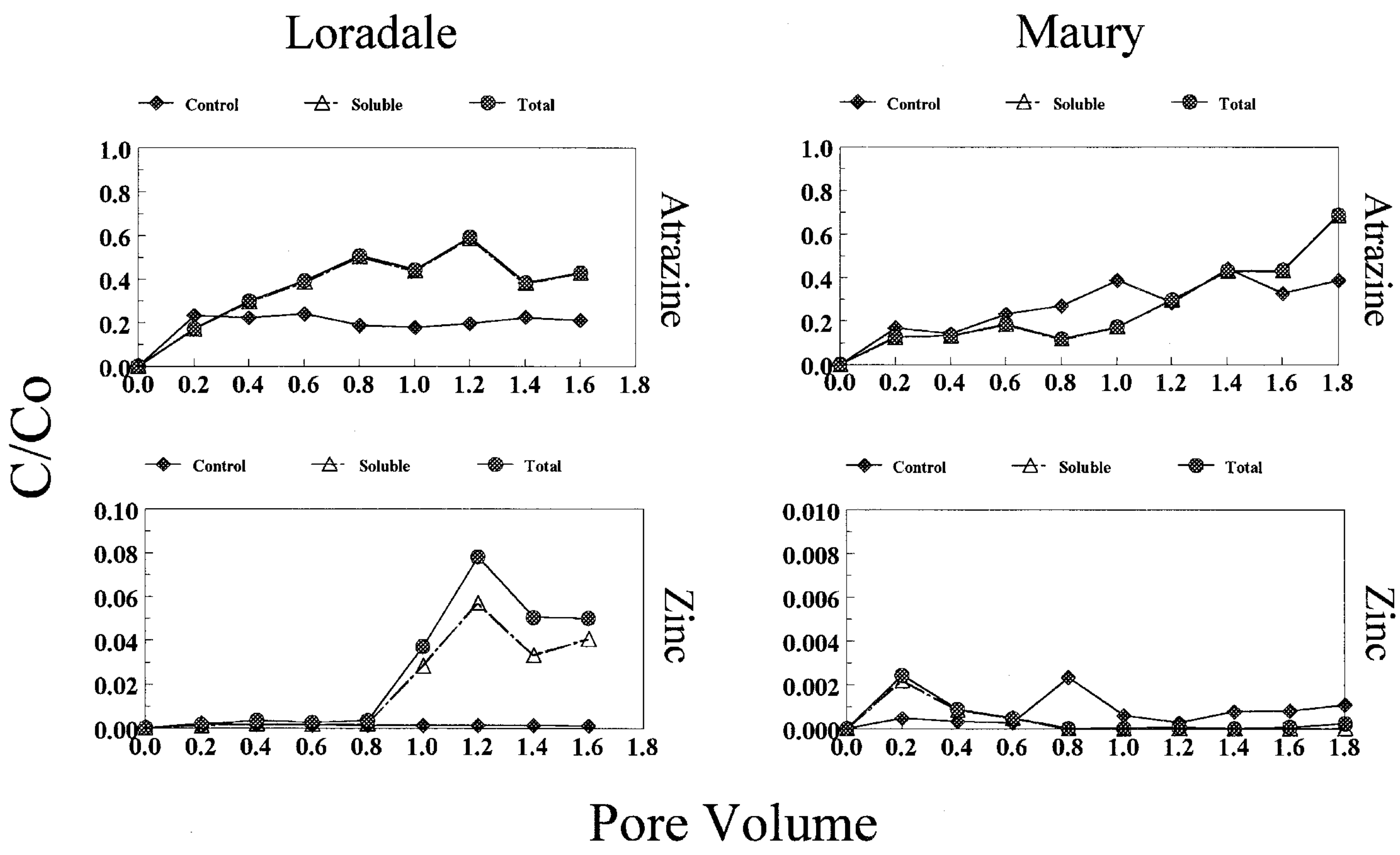

Figure 5. Breakthrough curves for atrazine (soluble and soluble + colloid-bound) and zinc (soluble and soluble + colloid-bound) eluted in the absence (control) and presence of Loradale and Maury colloids from Loradale and Maury monoliths, respectively.

soil particulate material on the applied colloids. Blocking or coating of reactive sites by retained colloids may have also enhanced atrazine transport by limiting sorption interactions within the soil matrix. The ability of transported colloids to block micropore entrances and alter the pathway of chemicals through macropores, where the velocity of flow is higher, has been documented in earlier experiments (Seta and Karathanasis, 1997b; Kretzschmar *et al.*, 1995).

3.4. ZINC TRANSPORT

In the absence of colloids (control), zinc exhibited practically no breakthrough by either soil indicating complete sorption by the soil matrix. Any observable colloid-associated Zn breakthrough from either soil was at least an order of magnitude lower than that observed for atrazine. The sorption isotherms and the lower soil Kf values for Zn compared to those for atrazine reflect these differences (Table II). The Loradale monoliths showed no colloid-associated Zn transport through the first 0.8 pore volumes (Figure 5). Afterwards, the colloid-associated Zn rose to C/Co values of 0.08 and leveled off at a value of 0.05 for the duration of the study. Once again, soil particle detachment from the monoliths likely masked the effect of the applied colloids during the initial 0.8 pore volumes of leaching. Once the detached soil particles were flushed from the monoliths in later stages of leaching, enhanzed Zn elution is believed to be the result of applied colloids. Unlike the atrazine transport, where the colloid-bound herbicide fraction was very small, the colloid bound Zn fraction exhibited increases of up to 30% over that of the soluble portion in the Loradale monoliths. In addition, the transport of Zn in the Loradale was strongly associated with the breakthrough of experimental colloids.

Chemisorption of Zn to reactive sites on the colloid and the formation of soluble organic complexes appeared to be the two primary mechanisms for metal co-transport in the Loradale soil. The high OC of the Loradale colloid provided the conditions necessary for formation of metal complexes with organic ligands (Stevenson and Fitch, 1986), and likely accounts for the observed colloid-associated soluble Zn fraction. However, the low C/Co value suggests that competitive sorption of Zn between the colloid and soil matrix may also be occurring. According to Mills *et al.* (1991), colloids can be readily stripped of adsorbed metal species by an aquifer-soil matrix to establish equilibrium between the two solid phases. Once removed of the metal, the colloid may continue to migrate through the matrix. Alternatively, physical exclusion of pore spaces and reactive sites by filtered colloids may lead to the retention of a portion of the metal-saturated colloid, while enhancing mobility of others due to a reduction in the available surface charge of the soil matrix and preferential flow through macropores (Karathanasis, 1999).

The breakthrough pattern of the Loradale colloid-associated Zn appeared different than that observed for the Maury colloid. The Maury monoliths exhibited a brief increase in colloid-associated Zn elution during the first 0.4 pore volumes over that of the control (Figure 5). Subsequently, between 0.6 and 1.8 pore volumes, the control-Zn elution was higher than the colloid-Zn elution. In contrast, the eluted Loradale colloid-associated Zn was essentially zero during the first 0.8 pore volumes, but increased drastically thereafter up to 8%. In spite of these different patterns at various stages of elution, an analysis of variance between mean Zn breakthrough during the first 1.6 pore volumes, showed no significant difference ($p < 0.05$) between the two soil types. Even though Zn exhibited a lower sorptive affinity for the Maury soil and colloids over that of the Loradale (Table II), the relative amount of soluble and colloid-bound Zn transported by the Maury colloids was smaller than that described for the Loradale. Apparently, the processes responsible for limiting colloid transport were responsible for that. Since the applied colloids were filtered in the monoliths, the colloid-associated, or sorbed, Zn was also retained. Considering that the Maury soil monoliths have a high affinity for Zn, any remaining Zn in solution is likely to be sorbed to the soil matrix.

4. Conclusions

The movement of mobile colloids and associated transport of agrochemicals in the subsurface environment of both soil types was demonstrated in this experiment. The level of co-transport was dependent upon physicochemical characteristics of the soil and the stability of the colloid within the matrix. The increased OC and CEC of the Loradale soil and colloid contributed to colloid stability and enhanced transport of atrazine and Zn over that of a control. Consistent co-transport of contaminants by the Maury colloid was somewhat inhibited by colloid instability within the soil matrix. Increased sorption affinity for the colloid surface over that of the soil matrix appeared to be the principle mechanism for the transport of Zn in association with colloid particles. In contrast, enhanced transport of atrazine in the presence of colloids may be the result of sorption to soluble organic matter and/or physical exclusion from reactive sites. The experiment provided evidence that colloids within the subsurface environment may influence the sorptive kinetics of contaminants and thus facilitate their transport to the groundwater. The results also indicated that natural or artificial elevations in ionic strength can alter the electro-chemical characteristics of the soil matrix, thereby, enhancing contaminant retardation due to colloid filtration and potential macropore sealing. The large monoliths in a field setting employed in this study provided results that, although somewhat similar, were much more variable than those obtained under laboratory conditions (Seta and Karathanasis, 1997b; Karathanasis, 1999). As such, they emphasize the importance of site- and contaminant-specific experiments for a more comprehensive understanding of colloid-facilitated and colloid-inhibited transport processes.

References

Barton, C. D. and Karathanasis, A. D.: 2002, 'A novel method for measurement and characterization of soil macroporosity', *Commun. Soil Science and Plant Analysis* **33**, 1305–1322.

Corapcioglu, M. Y. and Jiang, S.: 1993, 'Colloid-facilitated groundwater contaminant transport', *Water Resour. Res.* **29**, 2215–2226.

Förstner, U.: 1995, 'Land Contamination by Metals: Global Scope and Magnitude of Problem', in H. E. Allen, C. P. Huang, G. W. Bailey and A. R. Bowers (eds), *Metal Speciation and Contamination of Soil*, Lewis Publishers, Boca Raton, FL, U.S.A., pp. 1–33.

Goldberg, S., Kapoor, B. S. and Rhoades, J. D.: 1990, 'Effect of aluminum and iron oxides and organic matter on flocculation and dispersion of arid zone soils', *Soil Science.* **150**, 588–593.

Ibaraki, M. and Sudicky, E. A.: 1995, 'Colloid-facilitate contaminant transport in discretely fractured porous media 1. Numerical formulation and sensitivity analysis', *Water Resour. Res.* **31**, 2945–2960.

Jekel, M. R.: 1986, 'The stabilization of dispersed mineral particles by adsorption of humic substances', *Water Resour. Res.* **20**, 1543–1554.

Karathanasis, A. D.: 1999, 'Subsurface migration of Cu and Zn mediated by soil colloids', *Soil Sci. Soc. Amer. J.* **63**, 830–838.

Klute, A. and Dirksen, C.: 1986, 'Hydraulic Conductivity and Diffusivity: Laboratory Methods', in A. Klute (ed.), *Methods of Soil Analysis*, Part 1. Physical and Mineralogical Methods-Agronomy Monograph No. 9, 2nd Ed., American Society of Agronomy, Madison, WI, U.S.A., pp. 687–735.

Kolpin, D. W., Barbash, J. E. and Gilliom, R. J.: 1998, 'Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program', *Environ. Sci. Technol.* **32**, 558–566.

Kretzschmar, R., Robarge, W. P. and Amoozegar, A.: 1995, 'Influence of natural organic matter on colloid transport through saprolite', *Water Resour. Res.* **31**, 435–445.

Liang, L. and McCarthy, J. F.: 1995, 'Colloidal Transport of Metal Contaminants in Groundwater', in H. E. Allen, C. P. Huang, G. W. Bailey and A. R. Bowes (eds), *Metal Speciation and Contamination of Soil*, Lewis Publishers, Boca Raton, FL, U.S.A., pp 87–112.

McBride, M. B.: 1989, 'Surface Chemistry of Soil Minerals', in J. B. Dixon and S. B. Weed (eds), *Minerals in Soil Environments. Soil Science Society of America*, Madison, WI, U.S.A., pp. 35–88.

McDaniel, P. A. and Buol, S. W.: 1991, 'Manganese Distributions in Acid Soils of the North Carolina Piedmont', *Soil Sci. Soc. Amer. J.* **55**, 152–158.

McDowell-Boyer, L. M., Hunt, J. R. and Sitar, N.: 1986, 'Particle transport through porous media', *Water Resour. Res.* **22**, 1901–1922.

Mills, W. B., Liu, S. and Fong, F. K.: 1991, 'Literature review and model (COMET) for colloid/metal transport in porous media', *Ground Water* **29**, 199–208.

Morrison, R. T. and Boyd, R. N.: 1973, Organic Chemistry. 3rd (ed.), Allyn and Bacon, Boston, MA, U.S.A., 638 pp.

Natural Resources Conservation Service.: 1996, Soil Survey Laboratory Methods Manual. Soil Survey Investigations, Report No. 42. United States Department of Agriculture, Washington, DC, U.S.A.

Oades, J. M.: 1989, 'An Introduction to Organic Matter in Mineral Soils', in J. B. Dixon and S. B. Weed (eds), *Minerals in Soil Environments*, Soil Science Society of America, Madison, WI, U.S.A., pp. 89–160.

Ouyang, Y., Shinde, D., Mansell, R. S. and Harris, W.: 1996, 'Colloid-enhanced transport in subsurface environments: A review', *Crit. Rev. Environ. Sci. Technol.* **26**, 189–204.

Puls, R. W., and Powell, R. M.: 1992, 'Transport of inorganic colloids through natural aquifer material: Implications for contaminant transport', *Environ. Sci. Technol.* **26**, 614–621.

Radke, R. O., Armstrong, D. E. and Chesters, G.: 1966, 'Evaluation of the pyridine-alkali colorimetric meth for determination of atrazine', *J. Agricult. Food Chem.* **14**, 70–73.

SAS Institute.: 1990, SAS procedure guide, version 6, 3rd (ed.), SAS Inst., Cary, NC, 320 pp.

Senesi, N. and Testini, C.: 1982, ‘Physico-chemical investigations of interaction mechanisms between s-triazine herbicides and soil humic acids’, *Geoderma* **28**, 129–146.

Seta, A. K. and Karathanasis, A. D.: 1997a, ‘Stability and transportability of water-dispersible soil colloids’, *Soil Sci. Soc. Amer. J.* **61**, 604–611.

Seta, A. K. and Karathanasis, A. D.: 1997b, ‘Atrazine adsorption by soil colloids and co-transport through subsurface environments’, *Soil Sci. Soc. Amer. J.* **61**, 612–617.

Shuman, L. M.: 1985, ‘Fractionation method for soil microelements’, *Soil Sci.* **140**, 11–22.

Stevenson, F. J. and Fitch, A.: 1986, ‘Chemistry of Complexation of Metal Ions with Soil Solution Organics’, in P. M. Huang and M. Schnitzer (eds), *Interactions of Soil Minerals with Natural Organics and Microbes*. SSSA Special Publication No. 17. Soil Science Society America, Madison, WI, U.S.A., pp. 29–58.

Triegel, E. K. and Guo, L.: 1994, ‘Overview of the Fate of Pesticides in the Environment, Water Balance; Runoff vs. Leaching’, in R. C. Honeycutt and D. J. Schabacker (eds), *Mechanisms of Pesticide Movement into Ground Water*. Lewis Publishers, Boca Raton, FL, U.S.A., pp. 1–13.

USEPA: 1994, Methods for the determination of metals in environmental samples. EPA/600/R-94/111, Washington, DC, U.S.A. 248 pp.