Enhanced mobility of Pb in the presence of dissolved natural organic matter

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Abstract

The speciation of Pb in batch experiments and its mobility under flowing conditions in column transport experiments were investigated to study Pb behavior in a soil–water system in the presence of dissolved natural organic matter (DOM), peat humic acid (PHA) and peat fulvic acid (PFA). A sandy soil having a significant intraparticle porosity was used as the sorbing media. Batch equilibrium sorption isotherms for single components (Pb, PHA, and PFA) and for Pb in the presence of PHA and PFA were generated. Batch equilibrium experiments were also performed for both PHA and PFA to investigate Pb-DOM binding in the absence of soil. Single component (Pb, PHA, and PFA) and multicomponent (Pb-PHA and Pb-PFA) laboratory-scale column transport experiments were conducted to assess transport behavior of Pb in the presence of DOM.

Sorption isotherms indicated that the soil had a higher affinity for PHA than for PFA. However, single component column transport experiments showed that PHA was less retarded than PFA. This anomaly was attributed to the size exclusion of the larger PHA molecules from the intraparticle porosity of the media under the geochemical conditions in the column. Pb retardation predicted by equilibrium equations based upon nonlinear isotherm parameterization agreed well with observed retardation. However, equilibrium retardation equations overpredicted retardation of DOM, indicating sorption kinetic limitations (chemical and/or physical nonequilibrium), molecular size exclusion during column transport, or chemical heterogeneity of the DOM.

In multicomponent column transport experiments, Pb retardation decreased by factors of 4–8 in the presence of DOM. Multicomponent batch equilibrium experiments suggested that Pb

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mobility was governed by speciation of Pb with soluble DOM during transport. Thus, Pb eluted earlier in the presence of PHA than in the presence of PFA because PHA had a higher affinity for Pb binding than PFA. © 1997 Elsevier Science B.V.

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1. Introduction

Conventional methods for assessing contaminant migration most often rely upon modeling groundwater as a two-phase medium (immobile solid matrix and mobile solute), where the mobility of a contaminant depends, in part, upon its partitioning between the aqueous and solid phases. However, it is now well-recognized that in many systems, contaminants can migrate at a rate faster than that predicted by this approach (i.e. using the convection–dispersion equation) when a mobile colloidal phase to which contaminants partition is present (McCarthy and Zachara, 1989; McDowell-Boyer et al., 1986; Mills et al., 1991; Puls and Powell, 1992), increasing the apparent solubility of hydrophobic contaminants. This mechanism is often termed “colloid facilitated transport” (Corapcioglu and Jiang, 1993) or “cotransport” (Zachara et al., 1993). This research investigates the facilitated transport of a toxic heavy metal (Pb) with dissolved humic and fulvic acids (“natural organic matter”), naturally occurring organic colloids.

Dissolved natural organic matter (DOM) consists of humic and fulvic acids, refractory organic compounds resulting from the degradation of plant and animal detritus. DOM consists of a mixture of macromolecules, having molecular weights ranging from approximately 500 to 300 000 (Amy et al., 1992). Humic acids are typically more hydrophobic than fulvic acids (Leenheer, 1981) because of their higher density of aromatic functional groups. Both types contain as their primary reactive sites, functional groups such as hydroxyl, carboxyl, phenolic, and carbonyl substitutions (Thurman and Malcolm, 1983) which participate in the binding of heavy metals (Alberts and Giesy, 1983; Langford et al., 1983; Perdue, 1989; Pettersson et al., 1993; Stevenson, 1976).

1.1. Nonideal transport behavior of DOM

Transport of DOM has been observed on both the field (Jardine et al., 1989a; McCarthy et al., 1993) and laboratory scales. Often, DOM is highly mobile, eluting simultaneously (or closely associated) with a nonreactive tracer (Jardine et al., 1992; Dunnivant et al., 1992). However, whereas pore water breakthrough curves (i.e. those identified with a nonreactive tracer) generate nearly symmetrical plumes in laboratory column studies, breakthrough curves of DOM are seldom characterized by the Gaussian distributions predicted by the convection–dispersion equation. They often exhibit sharp breakthrough fronts and extensive tailing, indicative of a number of mechanisms, including chemical and physical nonequilibrium and sorption isotherm nonlinearity (Brusseau, 1995; Dunnivant et al., 1992).

Physical nonequilibrium (PNE) occurs when the relatively rapid transport of the solute through the primary porosity is coupled with the diffusion-limited transfer of the

solute into a secondary compartment, which may include intraparticle porosity (Brusseau, 1993). The macromolecular size of DOM may complicate the assessment of PNE via size exclusion. DOM may be excluded from binding sites in the solid which may be accessible by a traditional nonreactive tracer (i.e. $^3\text{H}_2\text{O}$ or Cl^-) or other contaminants, dampening the effects of PNE.

1.2. Cotransport of heavy metals with DOM

The enhanced breakthrough of organic contaminants has been observed in the presence of DOM and functionally similar mobile macromolecules (Kan and Tomson, 1990; Magee et al., 1991; Enfield and Bengtsson, 1988). Newman et al. (1993) reported the enhanced mobility of Cd, Cu, Cr, and Pb in laboratory soil columns by complexation with organic and inorganic hazardous waste ligands, as well as sorption to mobile, turbidity-causing colloids. In another study (Oden et al., 1993), both enhanced and inhibited transport of Cu occurred, influenced by the nature (i.e. character of binding sites) of the DOM, a function of its source. Inhibited Cu transport may have resulted from the formation of a Cu-DOM complex that was more sorbable than Cu alone. In addition, this study illustrated the influence of the contaminant upon the mobility of the DOM, noting that DOM mobility was decreased in the presence of the metal. Similar results were found in another study (Igloria and Hathhorn, 1994), where the mobility of Cd, Pb, Cu, and Zn was inhibited in the presence of DOM in a pilot-scale lysimeter. The inhibited transport was attributed to the possibility of significant sorption of DOM and DOM-metal complexes to the column media.

1.3. Evaluating nonideal cotransport with retardation factors

A retardation factor is a transport parameter which defines the apparent velocity of a retarded (sorbed) pollutant (v_p) relative to a nonreactive tracer (i.e. the velocity of the pore water, v_w). It is defined as follows:

$$R = v_w / v_p \quad (1)$$

It also defines the number of pore volumes at which the center of mass of a breakthrough front elutes at the effluent end of a column (where the center of mass of a breakthrough front of a nonreactive tracer elutes at one pore volume). The most common retardation factor is that for linear sorption:

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad (2)$$

It can be seen that R is independent of the concentration of solute and depends only upon the magnitude of the characteristic constants ρ_b (bulk density), θ (porosity), and K_d (distribution coefficient for a linear sorption isotherm).

However, R can also be defined for nonlinear isotherms, such as presented by Fetter (1993) for a Freundlich isotherm:

$$R_F = 1 + \frac{\rho_b}{\theta} N K_F C_e^{N-1} \quad (3)$$

where N and K_F are the Freundlich isotherm parameters and C_e is the soluble concentration of the solute at equilibrium. A retardation factor for a pollutant in the presence of a mobile, reactive colloidal phase was derived by Magee et al. (1991):

$$R^* = \frac{(1 + K_d^{pc} DOM + K_d^{ps} \rho_b / \theta)}{1 + \frac{K_d^{pc} DOM}{1 + K_d^{cs} \rho_b / \theta}} \quad (4)$$

where K_d^{pc} , K_d^{ps} , and K_d^{cs} represent the linear distribution coefficients between the pollutant (p), colloid (c), and solid matrix (s), and DOM represents the concentration of the dissolved colloid (e.g. dissolved organic matter). However, this formulation requires that the isotherms between the pollutant and soil, DOM and soil, and pollutant and DOM be linear, parameterized only by their individual distribution coefficients (K_d). Often, contaminant sorption does not follow linear isotherms. Thus, a retardation factor for three, nonlinearly sorbing components (colloid, contaminant, and soil), analogous to Eq. (3) and (4) is presented:

$$R_F^* = \frac{1 + (\rho_b / \theta) N_{ps} K_F^{ps} C_e^{N_{ps}-1} + N_{pc} K_F^{pc} C_e^{N_{pc}-1} DOM}{1 + \frac{N_{pc} K_F^{pc} C_e^{N_{pc}-1} DOM}{1 + (\rho_b / \theta) N_{cs} K_F^{cs} DOM^{N_{cs}-1}}} \quad (5)$$

where N_{ij} and K_F^{ij} represent the Freundlich constants describing the isotherms between constituents i and j (p, c, and s as defined above), and DOM and C_e representing the soluble concentrations of dissolved organic matter and the pollutant, respectively, at equilibrium. It should be noted that for all Freundlich exponents $N = 1$, Eq. (5) reduces to the linear isotherm retardation factor for colloidal transport (Eq. (4)).

1.4. Summary

It is important to realize that colloids can either enhance or inhibit the transport of contaminants. This degree of influence will depend upon the complex processes that govern the reactions of contaminants, colloids, and contaminant-colloid “complexes” with subsurface media. These processes include nonlinear and competitive isotherm behavior and rate-limited sorption (chemical kinetics and/or mass transfer) of the individual mobile constituents with the media, coupled with the similar reactions of colloid-contaminant complexes with the media.

The primary foci of the experiments contained herein is to illustrate the complexity of one type of colloid-contaminant-media system (Pb-DOM-soil) and to utilize observations in well-controlled batch speciation studies to explain behavior in column transport experiments. With these goals in mind, the overall motivation of this research is to contribute to the relatively young body of literature examining experimental observations of contaminant transport in the presence of mobile colloids.

2. Materials and methods

2.1. Materials

2.1.1. Soil

Bulk soil samples of Everett sand were obtained from a site near Stillwater, WA. Soil was air-dried at 20°C for two weeks prior to preparation. Particles were discretized in a muller-grinder for 30 min, washed in deionized water to remove fine particles and low-density (organic) litter, and dried at 40°C for 48 h. The 0.425–0.850 mm (mean particle diameter) size fraction was isolated in a graded sieve stack on a hammer-type shaker for 30 min. Soil was stored at 20°C under dessicated conditions.

Table 1 outlines selected chemical and physical properties of the soil. Properties of the parent material are presented elsewhere (Igloria and Hathhorn, 1994). Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis was performed on fractured and unfractured sand grains to qualitatively characterize physical and chemical surface properties and to investigate intraparticle porosity. The results from this investigation are presented elsewhere (Jordan, 1995).

2.1.2. Dissolved organic matter

Peat-extracted humic (PHA) and fulvic (PFA) acids obtained from the International Humic Substances Society (IHSS) comprised the dissolved organic matter (DOM) in this study. Stock solutions were prepared by adding 100 mg DOM to 1 L HPLC-grade deionized water and adjusted to pH 7.0 with dilute sodium hydroxide (NaOH). Stock solutions were stored at 4°C and monitored frequently for dissolved organic carbon (DOC) stability. No detectable microbial growth (evidenced by no significant change in DOC concentrations) in the stock solution was observed during its storage life (< 2 weeks). Stock solution concentrations were approximately 50 mg DOC L⁻¹. Chemical characteristics of PHA and PFA can be found in Murphy et al. (1990).

All other chemicals used in the study were of reagent grade or better. All water used in the study had a UV absorbance at 254 nm < 0.002 and DOC < 0.5 mg L⁻¹.

Table 1
Selected properties of Everett sand, 0.425–0.850 mm isolate

^a Indigenous exchangeable Pb (mg g ⁻¹)	2.5
^b Organic matter (wt.%)	0.12
^b Organic carbon (wt.%)	0.07
^b Cation exchange capacity (cmol(+) kg ⁻¹)	3
^c Theoretical surface area (m ² g ⁻¹)	0.0078
^d Measured surface area (m ² g ⁻¹)	3.54 ± 0.09
^e Specific gravity (g cm ³)	2.45 ± 0.02
^f pH	6.8 ± 0.2

^aDetermined by extraction with 1 N HNO₃ for 1 h. ^bAnalytical Sciences Laboratory, University of Idaho.

^cCalculated based on the assumption of spherical particles having a diameter of 0.63 mm. ^dMeasured by 10-point N₂ (gas) adsorption and calculated using the BET equation (Department of Earth Sciences, University of Waterloo). ^eMeasured by water displacement and vacuum air evacuation in a volumetric flask. ^fMeasured in a 1:1 (v/v) soil:water slurry after 24 h of gentle agitation on a wrist-action shaker.

2.2. Methods

2.2.1. Pb-DOM equilibration studies

Varying concentrations of lead (Pb) were added to borosilicate glass reaction flasks containing 75 mL of DOM stock (either PHA or PFA as 25 mg DOC L⁻¹) and equilibrated by gentle mixing for 24 h. The solution was adjusted to pH 7.0 with dilute NaOH at the beginning of the experiment. Following equilibration, the concentration of uncomplexed Pb was measured on the filtrate passing a 1000 molecular weight cut-off (MWCO) ultrafiltration membrane (Amicon YM-1000). Membrane pretreatment methods and quality control results are presented elsewhere (Jordan, 1995). Filter membranes (1000 MWCO) retained approximately 95% and 70% of UV-absorbing material upon filtration of stock solutions of PHA and PFA, respectively.

UV absorbance, pH, and Pb concentrations were determined on both filtered and unfiltered samples in the binding studies. In addition, linear distribution coefficients (K_d) were determined on each sample, defined as K_d (L mg⁻¹ C)

$$K_d = C_s / C_e \quad (6)$$

where C_e (mg L⁻¹) is the dissolved (uncomplexed) concentration of Pb and C_s (mg mg⁻¹ C) is the bound concentration of Pb per milligram of DOC.

2.2.2. Equilibrium sorption studies

Batch equilibrium sorption studies were performed to generate sorption isotherms for Pb and DOM onto Everett sand. In addition to Pb and DOM individually, isotherms of Pb initially equilibrated with DOM (prior to contact with soil) were developed for varying concentrations of DOM. All isotherms were developed at a constant soil concentration and varying solute concentration in 125 mL low density polyethylene (LDPE) bottles. Table 2 outlines each of the sorption isotherm experiments. All bottle points were replicated between two and five times.

Separate control experiments were performed to assess the degree of sorption of Pb and DOM onto the bottle material. Separate aqueous (no soil) 100 mL solutions (pH 7.5) with original concentrations 50 µg Pb L⁻¹ and 5 mg DOC L⁻¹ (for both PHA and PFA, individually) were brought to equilibrium on a wrist-action shaker for 48 h. Solute concentrations in aqueous phase samples were >95% of the original concentration, indicating that solute sorption onto the bottle walls was negligible.

Table 2
Summary of batch equilibrium sorption experiments

Sorbate	Soil concentration	Initial solute concentrations	Measured pH at equilibrium
Pb	10 g L ⁻¹	1–12 mg Pb L ⁻¹	6.68 ± 0.11
PHA	67 g L ⁻¹	5–25 mg DOC L ⁻¹	6.73 ± 0.18
PFA	200 g L ⁻¹	2.5–25 mg DOC L ⁻¹	6.89 ± 0.18
Pb w/PHA	10 g L ⁻¹	4 and 12 mg Pb L ⁻¹ 5 and 25 mg DOC L ⁻¹	6.77 ± 0.24
Pb w/PFA	10 g L ⁻¹	4 and 12 mg Pb L ⁻¹ 5 and 25 mg DQC L ⁻¹	6.81 ± 0.07

Soil samples were hydrated for 24 h with 50 mL of water (as 0.01 M KCl) prior to spiking with a stock solute solution. All samples were brought to equilibrium by gentle agitation on a wrist-action shaker for 48 h. Kinetics studies showed that this time was sufficient for sorption to reach 95% of equilibrium for both Pb and DOM (Jordan, 1995). All added solutions were unbuffered and adjusted to pH 7.0 with dilute NaOH. The buffering capacity of the soil resulted in a final equilibrium pH of 6.8 ± 0.2 units. The ionic strength of the solute was maintained at a relatively constant value; all solutions were prepared in a matrix of 0.01 M KCl. After equilibration with the soil, aqueous phase concentrations were determined on the centrate of a sample that had been centrifuged at 3 000 g for 20 min.

A Freundlich sorption isotherm model was parameterized for each of Pb, PHA, and PFA sorption to the soil. Sorbed concentrations (C_s , in mg kg^{-1}) are described in the Freundlich model as follows:

$$C_s = K_f C_e^N \quad (7)$$

where C_e (mg L^{-1}) is the soluble concentration at equilibrium and K_f and N are fitted parameters.

Ranges of Freundlich retardation factors (R_F) were calculated for Pb, PHA, and PFA separately (Eq. (3)), and compared with observed retardation factors integrated from the breakthrough curves of the single component column transport experiments. The Freundlich formulation (Eq. (5)) was used to predict retardation factors for Pb in the presence of DOM, and compared with those observed in the multicomponent column transport experiments. However, linear distribution coefficients (K_d) for the binding of Pb to DOM were used instead of the Freundlich model ($N_{pc} = 1$ in Eq. (5)), not only because the data could not be adequately modeled by the Freundlich isotherm, but also to simplify Eq. (5).

2.2.3. Column experiments

Transport experiments were performed in 2.5 cm (dia) $\times$ 5.7 cm (length) cylindrical soil-packed glass columns (Fig. 1). The columns were equipped with fritted glass end plates (to uniformly distribute the solute as it entered the column) clamped with Viton

Fig. 1. Column apparatus. (a) Feed solution; (b) helium injection; (c) feed pump; (d) soil column; (e) quartz flow-through cell coupled to a UV source/detector; (f) automatic fraction collector to collect samples at predetermined time intervals.

Table 3
Summary of column transport experiments

Feed soln.	Feed concentrations	
	mg Pb L ⁻¹	mg DOC L ⁻¹
PHA	n/a ^a	5.0
PFA	n/a	5.2
Pb	1.49	n/a
Pb + PHA	1.27	5.1
Kb + PFA	1.19	5.0

^aNone added to feed solution, concentration ~ 0 .

o-ring seals glass end caps. Feed was delivered by a peristaltic pump at 1.0 mL min⁻¹ (± 0.1 mL min⁻¹) through a short section of Viton tubing. Remaining tubing in the apparatus was PTFE. All feed solutions were pre-purged with helium for 24 h; during delivery of the feed, the feed reservoir was maintained under a helium atmosphere (~ 1 atm). This procedure prevented the entrainment of air into the column, maximizing water saturation of the total pore volume. DOM in the column effluent was monitored continuously for UV absorbance at 254 nm (UV₂₅₄) in a 1 mL quartz flow-through cell. Samples exiting the cell were collected by an automatic fraction collector in polycarbonate vials, acidified to pH < 2, and analyzed for Pb. Flow was monitored at predetermined intervals throughout the solute transport experiments.

Soil was packed dry in the column in 2 cm lifts, vibrating the column between lifts to ensure consolidation of the material. This packing technique produced reproducible soil bulk densities (determined gravimetrically) of 1.68 ± 0.02 g cm⁻³. Dry columns were conditioned for 48 h by feeding 0.01M KCl (adjusted to pH 7.0 with dilute NaOH) to allow the column to saturate and the effluent to achieve a stable pH and UV absorbance. After conditioning, solute feed solutions were applied as a step input and allowed to continue until complete breakthrough was approached. Various combinations of DOM and Pb in the feed (adjusted to pH 7.0 with dilute NaOH and prepared in a 0.01 M KCl matrix) were investigated in separate breakthrough experiments (Table 3). Experiments involving Pb were ended prior to complete breakthrough because of the significant retardation of Pb in the column.

Column homogeneity, dispersion, and channeling were evaluated simultaneously by analyzing the breakthrough curve (BTC) of a nonreactive tracer (³H₂O). The BTC was fitted to the convection dispersion equation to determine the dispersion coefficient and pore water velocity. These parameters were fitted using nonlinear regression analysis with the program CXTFIT (Parker and van Genuchten, 1984). These fitted and other calculated parameters are shown in Table 4. Approximate Damkohler numbers were determined by parameterization with sorption kinetics data presented elsewhere (Jordan, 1995) and provided a relative measure of transport or sorption kinetics limitations in the column studies.

2.2.4. Analytical methods

Pb samples were acidified to pH < 2 with concentrated HNO₃ prior to analysis by furnace atomic absorption spectroscopy. The influence of acidified DOM (especially

Table 4
Summary of transport parameters and column characteristics

Bulk density, ρ_b	1.68 kg L ⁻¹
Porosity, θ	0.36
Pore water velocity, v_w (for $Q = 1 \text{ mL min}^{-1}$)	0.57 cm min ⁻¹
Dispersion coefficient, D	0.052 cm ² min ⁻¹
Pore volume	10.0 mL
Average Peclet number ($= v_w L/D$)	48
Average Damkohler numbers ($= UL/v_w C$)	< 0.05

slightly coagulated PHAs) on analytical measurements of Pb was insignificant (determined by the use of standard additions) if appropriate care was taken to ensure sample homogeneity (by vigorous mixing, to disperse DOM floc) prior to injection of the sample in the graphite tube atomizer.

DOM was analyzed by measuring ultraviolet (UV) absorbance at 254 nm (UV_{254}). UV absorbance was selected over dissolved organic carbon (DOC) as an indicator of DOM because unpredictable concentrations of indigenous DOC readily desorbed from the soil upon contact with water. Initial calibration showed that UV_{254} absorbance was a reliable indicator of DOC concentrations for aqueous solutions of DOM; furthermore, there was a linear relationship between DOC and UV absorbance for the concentrations of DOC used in this study. However, the heterogeneous nature of DOM may result in the preferential retention of some of its components during filtration (in the Pb-DOM binding studies) or during contact with soil (in the batch and column studies). This preferential retention will serve to change the eluent composition of the NOM, and the correlation between DOC concentrations and UV absorbance may not be valid, as it was for the original DOM mixture. Thus, to extend this correlation's validity to the eluent mixtures, it must be assumed that desorbed indigenous DOC is a small percentage of the total soluble DOC to be quantified, and that no significant exchange of different DOC components among available soil sites are occurring during batch or column transport experiments. The feasibility of this assumption was not examined experimentally in this study. Thus, its impact upon the interpretation of the data will be addressed in Section 4.

Tritium (^3H) concentrations were quantified by liquid scintillation counting to a precision of $2s < 5\%$ (i.e. the magnitude of the confidence interval bracketed by two standard deviations was less than 5% of the mean measured value).

3. Results

3.1. Equilibrium sorption

Table 5 presents the sorption isotherm parameters for Pb, PHA, and PFA, as determined by nonlinear regression analysis. The corresponding isotherm models are shown with the experimental data for Pb (Fig. 2) and PHA/PFA (Fig. 3). As shown

Table 5
Freundlich sorption isotherm parameters

	K_f	N
Pb	788	0.298
PHA	68.3	0.602
PFA	24.7	0.445

both visually in the figures and from examination of the Freundlich exponents in Table 5, all isotherms exhibit a significant degree of nonlinearity ($N < 1$) over the concentration ranges of interest. Comparison of DOM fractions in Fig. 3 shows that the soil appears to have a higher affinity for PHA than for PFA in the dilute soil suspension.

3.2. Pb-DOM binding

Fig. 4 presents the results of the Pb-DOM binding experiment. These results indicate that PHA has a higher affinity for Pb than PFA. However, it should be noted that only 70% of UV₂₅₄-absorbing DOM was retained on the 1000-MWCO membranes in the PFA samples, compared with 94% for PHA samples. (This can be explained by the smaller size of the PFA molecules in comparison with the PHA molecules.) Thus, the PFA results likely underestimate the extent of Pb binding, since measured Pb_{free} values in the filtrate may include some complexed Pb. However, if the assumption is made that the fraction of Pb bound to DOM is independent of the molecular size of the DOM, then the DOM passing the filter contains the same fraction of Pb as the DOM retained by the filter. Thus, the error in Pb_{free} is directly proportional to the percentage of DOM passing

Fig. 2. Sorption isotherm of Pb onto Everett sand. Pb_e represents measured soluble equilibrium concentration of Pb. Pb_s represents sorbed concentration per kilogram of soil. Line indicates best-fit Freundlich isotherm model.

Fig. 3. Sorption isotherms of DOM onto Everett sand. DOC_e represents measured soluble equilibrium concentration of DOC. DOC_s represents sorbed concentration per kilogram of soil (log scale emphasizes wide range of sorbed phase concentrations). Lines indicate best-fit Freundlich isotherm models.

the filter, and a correction factor equal to the percentage of DOM retained by the filter can be applied to Pb_{free} to estimate a more realistic distribution. These corrected values are plotted in Fig. 4 with the direct observations. Even upon accounting for the inexactness of the separation method, it is apparent that PHA still has a higher affinity for Pb than PFA. All subsequent calculations were performed using the corrected values.

Fig. 4. Equilibrium binding between Pb and DOM in the absence of soil. Pb_e represents the measured uncomplexed Pb concentration passing through a 1000 MWCO ultrafiltration membrane. Pb_s represents complexed Pb concentration per milligram of C. Open symbols represent direct measurements. Filled symbols represent values corrected for small fractions of DOC passing through the membrane.

Distribution coefficients (K_d) were calculated for PHA and PFA, and were used to estimate the retardation factor of Pb in the presence of DOM (see Eq. (5)). Values of K_d (in $L\ mg^{-1}\ C$) were 2.64 ± 1.59 (s.d.) for PHA and 0.213 ± 0.076 for PFA. Calculations were performed at each corrected sample point shown in Fig. 4.

3.3. Pb sorption in the presence of DOM

Fig. 5 presents the results of experiments evaluating the equilibrium sorption to soil of Pb in the presence of DOM. It appears that the apparent solubility of Pb was enhanced in the presence of both PHA and PFA (relative to no DOM). In addition, Pb is more soluble in the presence of PFA relative to PHA, evidenced by the shift of the Pb-(PFA) isotherm lines down and to the right of the Pb-(PHA) isotherm lines, and by the lesser slope of the PFA lines. In general, these two trends are readily apparent from the data shown in Fig. 5. However, two special anomalies are apparent on close examination of the figure: the crossing of the Pb-(low PHA) and Pb-(no DOM) isotherm lines (point A), and the crossing of the DOM isotherm lines (at both low and high levels of DOM) at low equilibrium concentrations (points B_{low} and B_{high}). Point A indicates an equilibrium concentration above which Pb sorption is enhanced in the presence of low levels of PHA, reflecting a potential decrease in Pb mobility in the column. Below points B_{low} and B_{high} , Pb is more soluble in the presence of PHA than in the presence of PFA at equivalent DOC concentrations. However, above B_{low} and B_{high} , the reverse is true; in this region, Pb is more soluble in the presence of PFA than in the presence of PHA at equivalent DOC concentrations. Thus, at “low” Pb concentrations (below “B”), Pb mobility should be faster in the presence of PHA than in the presence of PFA,

Fig. 5. Equilibrium sorption of Pb in the presence of DOM. Pb_e represents measured (apparently) soluble Pb concentrations, which may include both uncomplexed Pb and Pb complexed with soluble DOM. Pb_s represents sorbed Pb concentrations per kilogram of soil. Low initial Pb concentrations were $\sim 4\ mg\ L^{-1}$; high initial Pb concentrations were $\sim 12\ mg\ L^{-1}$.

Fig. 6. Single component BTCs for PHA, PFA, and Pb. Log scale emphasizes subtle differences in initial breakthrough between PHA and PFA. Linear scale (inset) emphasizes differences in BTC tailing between PHA and PFA (Pb not shown). 3-H indicates breakthrough curve of $^3\text{H}_2\text{O}$, a nonreactive tracer.

while at “high” Pb concentration (above “B”), Pb mobility should be slower in the presence of PHA than in the presence of PFA.

3.4. Single component column experiments

Fig. 6 presents BTCs of Pb and PHA/PFA. Breakthrough was not carried out to completion in the Pb experiment because fatigue of the tubing through the feed pump resulted in unstable flow control at later times. Thus, only the data collected during steady flow is presented.

Fig. 6 shows that PHA eluted prior to PFA, and more complete breakthrough of PHA occurred earlier than PFA. Breakthrough reached 95% (in terms of relative concentration) at the termination of the PHA experiment, while breakthrough reached only 80% at the end of the PFA experiment. Replicate experiments carried out for 200 pore volumes exhibited 97% breakthrough for PHA and 92% for PFA (data not shown). PHA experiments were repeated a total of three times with no visually discernible differences in either the shape or magnitude of the BTCs. PFA experiments were repeated twice with similar results.

3.5. Single component retardation factors

A range of retardation factors were approximated by visual examination of each of the curves. Precise quantification of the retardation factor via integration of the area under the curve would have been inappropriate, since the experiments were not carried out to complete breakthrough. These estimates are superimposed upon ranges predicted using the nonlinear retardation factor equation (Eq. (3)), and are presented in Fig. 7.

Fig. 7. Predicted vs. observed retardation factors. PHA, PFA, and Pb represent single-component retardation factors estimated from the data shown in Fig. 6. Single-component predictions were made using Eq. (7). Pb-(PHA) and Pb-(PFA) represent retardation factors estimated from the data shown in Fig. 7 for Pb in the presence of DOM. Predicted values were made using Eq. (9).

Fig. 7 shows that the observed retardation factor for Pb was consistent with the predicted value. However, retardation factors for both PHA and PFA were overpredicted by Eq. (3), with the observed retardation factor for PFA falling closer to the prediction than that for PHA. It is hypothesized that overprediction of the retardation factors for DOM were a result of sorption kinetic limitations during transport. The successful prediction of the Pb retardation factor may indicate that sorption kinetic limitations are not quite as severe during Pb transport.

3.6. Multiple component column experiments

Fig. 8 presents Pb BTCs in the presence of PHA and PFA (separate experiments), compared with Pb alone (same BTC as shown in Fig. 6). BTCs of PHA and PFA were also generated during the Pb-DOM column experiments (data not shown). No visually discernible behavior was observed between DOM BTCs in the absence of Pb (Fig. 6) and in the presence of Pb (data not shown), indicating that Pb binding to DOM did not significantly alter the sorption characteristics of DOM to the soil at the observed concentrations.

Fig. 8 shows that the presence of DOM in the feed solution resulted in significantly enhanced Pb mobility. It can also be seen that Pb in the presence of PHA eluted prior to Pb in the presence of PFA.

Effluent pH was monitored in all column experiments, and ranged from 6.7 to 7.1. There was no correlation between the magnitude of effluent pH and either DOM or Pb breakthrough characteristics, indicating some degree of chemical speciation stability during transport.

Fig. 8. Pb BTCs in the presence and absence of DOM. Pb-PHA and Pb-PFA indicate Pb BTCs in the presence of PHA and PFA, respectively. Pb indicates the BTC for Pb in the absence of DOM (same BTC as shown in Fig. 6).

3.7. Multicomponent retardation factors

Estimated retardation factors for Pb in the presence of DOM are also presented in Fig. 7 and compared with those predicted based upon the multicomponent retardation factor equation (Eq. (5)). The predicted retardation factor of Pb (R_{Pb}) decreased only slightly in the presence of DOM, with Pb mobility being enhanced in the presence of PFA relative to PHA. Observed values followed the same relative trends ($R_{Pb(PFA)} < R_{Pb(PHA)} < R_{Pb}$). However, observed retardation factors of Pb in the presence of DOM were more significantly reduced (by factors of about 4–8), again, possibly resulting from sorption kinetic limitations of DOM during transport. In addition, Eq. (5), by nature of its empiricism, simply does not account for all of the fundamental, complex interactions which occur in multicomponent systems.

As seen in Eq. (5), the retardation factor for Pb in the presence of DOM depends upon both the equilibrium DOM concentration as well as the equilibrium Pb concentration. Thus, the retardation factor will vary spatially as well as temporally throughout a column as concentration breakthrough fronts migrate through the column. Further, since DOM and Pb concentration breakthrough fronts will migrate at different speeds, no single concentration of either DOM or Pb can adequately characterize R . Thus, for simplicity, $R_{Pb(PFA)}$ and $R_{Pb(PHA)}$ ranges shown in Fig. 7 represent only retardation factors calculated at a DOM concentration of 5 mg C L^{-1} . A sensitivity analysis of this model (data not shown) revealed that $R_{Pb(DOM)}$ was relatively insensitive to DOM concentration. Retardation factors varied less than 2% for equilibrium soluble DOC concentrations between 1 and 5 mg L^{-1} . This is not surprising, since DOM is far more

mobile than Pb, and its concentration breakthrough front will migrate at speeds an order of magnitude or more faster than that for dissolved Pb (see Fig. 6).

4. Discussion

The purpose of this discussion is to interpret the results of the Pb-DOM column transport experiments based upon the information presented in the batch experiments and the single component column runs. BTCs were not amenable to rigorous quantitative analysis because complete breakthrough was not observed. In addition, although equilibrium isotherm parameters were derived for single-component batch experiments, the column experiments were probably rate-limited with respect to sorption (as evidenced by batch kinetics experiments, data not shown, and the low Damkohler numbers presented in Table 4). Sorption rate limitations may also be causing the discrepancies between observed and predicted retardation factors. Currently, there are no viable models to predict multicomponent transport where sorption isotherms are nonlinear (as they are in this study), let alone ones that do the same when rate-limited sorption is affecting column transport. In light of these limitations, this discussion will focus upon a qualitative, as opposed to a quantitative, interpretation.

4.1. DOM mobility

DOM mobility in a column is dependent upon a variety of competing mechanisms, including mass transfer limitations, isotherm nonlinearity, sorption kinetics, media characteristics and pore water geochemistry, and DOM characteristics. Because of the inability to delineate these individual mechanisms in a complex system, one can only hope to approach the interpretation of the BTCs in a conjectural manner, explaining DOM mobility in a column based upon knowledge of some of these individual mechanisms (i.e. sorption isotherm, DOM characteristics). That approach is adopted here in the effort of resolving some contradictions in the sorption isotherm behavior and DOM mobility between PHA and PFA.

Based only on knowledge of the DOM sorption isotherms (Fig. 3), the following predictions might be made concerning column transport:

1. The PHA BTC should exhibit a sharper breakthrough front and less tailing relative to the PFA BTC, based upon the value of the Freundlich exponent. Fetter (1993) indicates that lower Freundlich exponents ($N < 1$) results in greater spreading of a breakthrough front.
2. PHA should be more retarded than PFA. This is not surprising, since we know that PHA, being a more aromatic molecule (Murphy et al., 1990), should be more reactive with media governed by sorption to mineral surfaces (Oden et al., 1993). In addition, PHA has been shown to be more reactive than PFA with some clay mineral surfaces (Murphy et al., 1990).

It must be kept in mind that these predictions, since they are based on observations of equilibrium sorption, are valid only if local sorptive equilibrium is established in the column.

On examination of the DOM BTCs (Fig. 6), prediction #1 is confirmed, as PFA is shown to exhibit more spreading than PHA. However, PHA elutes prior to PFA, contradicting prediction #2. Initially, it comes to mind that column transport with this soil is governed by sorption rate limitations, owing to the relatively short column residence time (< 15 min) compared to the kinetics of sorption (two days to 95% equilibrium). Thus, one would tend to assume that sorption kinetics of PHA are much slower than those of PFA, resulting in its earlier breakthrough. This is a reasonable assumption, since humic acids are larger and probably have lower diffusion coefficients than fulvic acids. Thus, if sorption rates are governed by diffusional mass transfer in the intraparticle porosity, PHA will migrate slower than PFA within the particle and elute earlier than PFA at the column effluent. However, a lower diffusion coefficient also implies a higher dispersivity (Brusseau, 1993), resulting in greater tailing of the BTC. Clearly, PHA exhibits less tailing than PFA (Fig. 6). On termination of the column experiments, DOC in the effluent of a column fed with PHA reached 97% of its influent concentration, while only 92% of the influent concentration was eluting in the PFA experiment. Thus, since PHA exhibits both a sharper breakthrough front and less tailing than that for PFA, prediction of relative behavior based solely upon molecular size, diffusion rates, and solute dispersivity should be approached with caution.

It is therefore hypothesized that, since humic acids are larger molecules than fulvic acids, greater exclusion of PHA molecules from the intraparticle porosity of the media is resulting in its enhanced transport relative to PFA. Consequently, less sites are available for PHA sorption, and it elutes earlier than PFA. Size exclusion is plausible, as evidenced by the observation of a heterogeneous intraparticle pore structure (by SEM microscopy, data not shown) and the measurement of an extremely high BET surface area (Table 1). In addition, an intraparticle diffusion model best described sorption kinetics for the uptake of a reactive solute by the soil used here (Jordan, 1995).

The most significant discrepancy with the size exclusion hypothesis is the failure to observe the effects of exclusion in the isotherm experiments. This can be explained by comparing the soil:solution ratios in the batch (67 g L^{-1}) and column (1680 g L^{-1}) experiments. Clearly, it can be seen that under column conditions, more significant quantities of exchangeable cations will dissolve from the soil (i.e. Ca, Mg), providing molecular bridges between functional groups on the DOM molecules. This will serve to increase their molecular size in higher ionic strength solutions, such as the pore water of the column. Because of the well-controlled (and probably lower) ionic strength of the solutions in the batch experiments, the extent of molecular bridging is not as severe as in the column experiments, and both PFA and PHA have more access to intraparticle binding sites.

Size exclusion results from the physical heterogeneity of NOM. In addition, chemical heterogeneity of NOM may also contribute to the observed anomalies in DOC breakthrough behavior. It is known that different molecular weight fractions of NOM possess significantly different adsorption affinities for mineral oxides, resulting in tailing of the breakthrough curve (Gu et al., 1996). In addition, chemical heterogeneity may result in the preferential early elution of certain NOM fractions: (1) less aromatic fractions of NOM may elute prior to more aromatic fractions; (2) more hydrophobic NOM components may displace more hydrophilic components from soil binding sites during trans-

port and result in the earlier elution of the hydrophilic species. Thus, although sorption kinetic limitations could contribute to the anomalous shape of the breakthrough curves, the multi-component nature of NOM may also have a significant effect on transport behavior. In fact, a recent study showed that slow, time-dependent sorption could not fully account for NOM breakthrough curve shape, indicating that the heterogeneous nature of NOM could have contributed to a nonsymmetrical breakthrough curve (McCarthy et al., 1996). The data collected herein could not be used to differentiate between the influence of kinetic limitations, size exclusion, and multi-component sorption on transport behavior. However, the data did suggest that any of these processes may have contributed to the nonsymmetric breakthrough curves that were observed. Further, it is likely that under certain system conditions, all three phenomena could collectively influence NOM transport behavior.

4.2. Relative mobility of Pb in the presence of PHA and PFA

Predicting Pb mobility in the presence of DOM requires collective consideration of the results from the batch experiments. Two scenarios arise when predicting Pb cotransport. First, Pb speciation could be governed by binding to soluble DOM. In this case, Pb mobility would be greater in the presence of PHA relative to PFA, since Pb has a higher affinity for PHA (as illustrated in the Pb-DOM binding experiments, Fig. 4). Second, Pb speciation could be governed by binding to sorbed DOM. In this case, Pb mobility would be greater in the presence of PFA (as illustrated in the DOM batch equilibrium sorption experiments, which indicate that PFA might be more mobile than PHA, Fig. 3). However, it was shown in the DOM BTCs (Fig. 6) that PHA is actually more mobile than PFA. Thus, if Pb speciation were governed by binding to sorbed DOM, Pb mobility would also be greater in the presence of PHA relative to PFA.

This is consistent with the results of the Pb-DOM column studies (Fig. 8). Of course, it does not seem readily apparent if Pb speciation is governed by soluble or sorbed DOM. The results of the Pb-DOM sorption experiments (Fig. 5) suggest some interesting mechanisms that are in competition with each other. Two trends were highlighted previously in the Results section. First, Pb solubility was enhanced in the presence of DOM relative to Pb solubility in the absence of DOM, indicating that soluble DOM is complexing sufficient Pb to prevent Pb sorption to the soil. (Alternatively, DOM and DOM-Pb complexes may be outcompeting Pb for nonspecific sorption sites on the soil.) However, it was noted that Pb solubility at higher equilibrium Pb concentrations was inhibited in the presence of low concentrations of PHA (see the point A in Fig. 5) relative to the case where no DOM was added. This behavior suggests that at low Pb concentrations, soluble PHA controls Pb speciation, keeping Pb in a more soluble species than in the “DOC = 0” case. Further, at higher Pb concentrations, the complexation capacity of the soluble PHA is approached, and Pb binds with sorbed PHA. If sorption of PHA to the soil increased the soil’s affinity for Pb, then it is not surprising that Pb sorption would actually be inhibited at higher Pb concentrations if the soil was coated with PHA.

The second general trend is that PFA enhances Pb solubility more than PHA. This

would suggest that sorbed DOM is the controlling mechanism affecting relative Pb speciation, since it was observed in the aqueous binding experiments (Fig. 6) that Pb has a higher affinity for PHA than for PFA. However, this trend is reversed at low Pb concentrations (as shown by the points labeled B_{low} and B_{high} in Fig. 5). At low concentrations, Pb solubility is greater in the presence of PHA than in the presence of PFA, suggesting that soluble DOM is controlling relative speciation. The points labeled B_i indicate the soluble equilibrium concentration at which the maximum complexing capacity of soluble DOM is being approached. Thus, these points indicate that Pb binding by sorbed DOM defines the relative degree of Pb-DOM speciation between Pb-PFA and Pb-PHA systems.

Therefore, to predict column behavior, Pb speciation over expected pore water concentration ranges must be considered. The feed solution to the column was between 1.2 and 1.3 mg Pb L⁻¹ (Table 3). Careful examination of Fig. 5 reveals that this equilibrium concentration is near B_{low} (in the presence of low DOM, which approximates the DOM concentrations in the feed solution), suggesting that the apparent solubility of Pb in the pore water of the column may have actually been higher in the presence of PHA than in the presence of PFA. This behavior would seem to occur at all Pb concentrations lower than this critical value (B_{low}), which should be representative of the pore water concentrations in the column experiment. Thus, Pb binding to aqueous DOM would dominate speciation, and Pb would be more soluble in the presence of the DOM type which has a higher affinity for Pb. Consequently, since PHA has a higher affinity for Pb than PFA, then Pb mobility should be greater in the presence of PHA than in the presence of PFA. Also, since PHA is more mobile than PFA, this relative behavior is further emphasized. Indeed, this is what occurs in the column studies, as shown in Fig. 8.

It should be noted that above this critical equilibrium concentration (B_i), as the DOM became saturated with Pb, Pb binding to sorbed DOM (and other sorption sites) would control speciation. Again, Pb would tend to favor binding to the DOM type, or fraction(s) within each type, which has a higher affinity for Pb. Thus, Pb would be more mobile in the presence of PFA relative to PHA. However, the higher affinity of PFA than PHA for the soil (evidenced in the DOM-only BTCs, Fig. 6) will introduce a competitive effect. The strength of this competition cannot be qualitatively evaluated from the batch experiments discussed above, and an a priori prediction of relative mobility in this case may be unfounded.

5. Conclusion

An experimental investigation has been performed to observe the speciation and mobility of Pb in both batch and soil-DOM-water systems. Pb transport behavior in the presence of DOM could not be qualitatively or quantitatively predicted based on information collected from single-component batch equilibrium studies. However, single component transport experiments, multi-component batch equilibrium experiments, and knowledge of DOM and media characteristics provided a conjectural basis for qualita-

tively predicting Pb transport behavior in the presence of DOM. The primary conclusions which can be drawn from this study are:

1. PHA has a higher binding affinity for Pb than does PFA.
2. The soil has a higher sorption affinity for PHA than PFA, but PHA was more mobile than PFA during the transport experiments. This anomaly was attributed primarily to the greater size exclusion of PHA than PFA under the geochemical conditions of the column experiment.
3. Based on equilibrium predictions, Pb mobility is not greatly affected by the presence of low DOM concentrations (5 mg C L^{-1}). However, because of the sorption rate limitations of DOM and/or competitive adsorption of DOM fractions during the transport experiments, Pb mobility was significantly enhanced.
4. Pb mobility is enhanced in the presence of both PHA and PFA. PHA enhanced Pb mobility more than PFA.
5. Pb mobility is dependent upon its speciation between sorbed and mobile DOM. Multicomponent batch equilibrium studies were used to predict whether sorbed or mobile DOM was controlling speciation.

The results of this study also emphasized the need to account for isotherm nonlinearity and kinetic limitations in transport models. Further, we caution against the extrapolation of data obtained in batch equilibrium experiments to transport behavior predictions, particularly under kinetic limitations during transport.

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