

## Transport of molybdenum in a biosolid-amended alkaline soil

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Received 18 January 2006; received in revised form 15 March 2006; accepted 18 March 2006

Available online 3 May 2006

### Abstract

The transport of molybdenum (Mo) in a biosolid-amended, alkaline, agricultural soil was examined in the research reported herein. Batch-equilibrium and miscible-displacement experiments were conducted to examine the transport of Mo in soil with and without 10% by weight biosolid amendment. The results of geochemical modeling, conducted using PHREEQC, indicated that no mineral dissolution or precipitation reactions were expected for the system under the prevailing conditions. Sorption equilibrium coefficients ( $K_d$ ) obtained from moment analysis of the Mo breakthrough curves were similar to those calculated from the results of the batch-equilibrium experiments. Mo sorption was greater for the biosolid-amended soil ( $K_d$  of 1.3 versus 0.35). Sorption of Mo was shown to be linear, rate limited, and reversible for both unamended and amended soil. The results suggest that Mo associated with biosolid-amended soils is relatively bioavailable and mobile.

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**Keywords:** Modeling; Column; Isotherm; Sorption

### 1. Introduction

Heavy metals and trace element oxyanions, such as molybdenum (Mo), used in industrial activities are commonly discharged to waste water treatment facilities. Mo is released to the environment by wastewater discharges and land amendment of biosolids (i.e., wastewater treatment plant sludge). Mo is a necessary plant and human micronutrient (Sequi, 1973; O'Connor et al., 2001). However, it may cause copper deficiency in cattle (Elliott and Taylor, 2000; O'Connor et al., 2001), because Mo-rich soils produce vegetation (e.g., alfalfa grasses) that can be toxic to grazing animals (McBride et al., 2000). Thus, there is concern regarding the fate of Mo associated with the land application of wastewaters and biosolids.

The regulation of Mo in soil and water has not been a priority in the past due to the relatively low concentrations found in most groundwater and soils (USDOI, 1968). However, Mo has been found at elevated concentrations in the subsurface irrigation drainage of arid agricultural soils (Lemly, 1994; O'Connor et al., 2001). Little or no information currently available on Mo concentrations in the groundwater below biosolids-amended soils. New regulations for soil and water are currently being considered, and a risk analysis was recently presented for Mo in biosolids in an attempt to better inform regulators considering regulatory standards for land application of biosolids (O'Connor et al., 2001).

Retention mechanisms for metallic cations and anions include adsorption and mineral precipitation, as well as complexation with organic matter (Lindsay, 1979; McBride, 1994; Langmuir, 1997). Mo exists in soil water as a weak acid,  $\text{H}_2\text{MoO}_4$ , in acidic soils, but is likely to exist primarily as  $\text{MoO}_4^{2-}$  in systems with  $\text{pH} > 4$ . Although Mo chemistry has been studied extensively (Sequi, 1973;

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Lindsay, 1979), its environmental fate has not (O'Connor et al., 2001).

Research investigating the processes that affect the transport and fate of Mo in the environment has focused on acidic agricultural soils. Bibak and Borggaard (1994) studied the equilibrium adsorption of Mo by humic acid and aluminum and iron oxides. The authors compared the adsorption properties of individual soil components to a composite soil. The magnitude of Mo adsorbed from water with pH between 3.5 and 8 was determined for synthetic aluminum oxide, ferrihydrite, goethite, extracted humic acid, and a sandy soil. The authors found that Mo adsorbs to each of the solid phases, and that adsorption generally decreases with increasing pH (above 4). Goldberg and colleagues (Goldberg et al., 1996; Manning and Goldberg, 1996; Goldberg and Forster, 1998) examined electrostatic equilibrium adsorption of  $\text{MoO}_4$ , as a function of pH, to oxides, clay minerals, and soils. These studies found an adsorption maximum at pH 3–5 and significantly less adsorption at higher pH values (up to pH 8).

In alkaline soil conditions, Mo is generally assumed to have minimal retention by clay minerals (Goldberg and Forster, 1998) and to not readily precipitate out of solution (Lindsay, 1979). Calcium, the most common divalent cation in alkaline soils, reacts with the  $\text{MoO}_4$  anion to form a mineral precipitate (Essington, 1990). However, its solubility is relatively high, especially for soil with free carbonates and at pH values above 8 (Lindsay, 1979). Other cations that affect the complexation and precipitation of Mo include Pb, Ag, Fe, and Cu, in order of decreasing importance (Lindsay, 1979).

The processes that affect the transport and fate of Mo in alkaline agricultural soils have received minimal attention. In addition, the effect of biosolid amendment on the transport of Mo is unknown for these types of soils (O'Connor et al., 2001). There is a need for an improved understanding of the transport of Mo, specifically related to the land application of biosolids, in alkaline soils. This information is essential to understanding Mo bioavailability, to the implementation of regulations concerning the land treatment of biosolids, and to determine limiting pathways that drive risk models (O'Connor et al., 2001). The purpose of this study is to characterize the effect of biosolid-amendment on transport of Mo in a natural, alkaline, agricultural soil.

## 2. Materials and methods

### 2.1. Materials

The porous medium used in all experiments was a natural agricultural soil, classified as the Pima Loam (fine-silty, mixed, superactive, thermic, Typic Torrifuvent), collected from the University of Arizona Marana Agricultural Research Center (0–15 cm depth). Relevant properties of the soil are reported in Table 1. It contains very little Mo (Table 1). The soil was dried at 105 °C until constant weight (for approximately 48 h). The biosolid-amended soil was prepared by mixing wastewater biosolids from Merlo, New York, to 10% by weight with a portion of the soil or about 200 Mt of biosolids per hectare. The use of this high biosolids application rate was chosen to examine the possible range of behavior, because initial studies showed no significant differences in the behavior of Mo in alkaline soils with and without 1% biosolids amendment. Also, agricultural soils can receive cumulative biosolids applications of 200+ Mt over a 15–20 year period. The biosolids were air dried and then ball-milled prior to use. The biosolid was analyzed and found to contain approximately 8 mg kg<sup>-1</sup> Mo. This Mo value is similar to the national sewage survey average Mo concentration in biosolids of 9.24 mg kg<sup>-1</sup> (USEPA, 1990), which is well below the current USEPA standard (503 Rule) for biosolids land disposal (USEPA, 1994). The biosolid-amended soil was rinsed prior to use to remove mobile Mo to an effluent concentration of less than 0.05 mg l<sup>-1</sup> Mo.

The electrolyte solution used in all experiments was alkaline calcium carbonate groundwater collected from the Tucson basin regional aquifer. The composition of the groundwater is given in Table 1. The column effluent for experiments conducted with the non-amended soil varied in pH from 7.7 to 8.0, and effluent from experiments conducted with the biosolid-amended soil varied in pH from 8.1 to 8.3. Aqueous Mo solutions (9 mg l<sup>-1</sup>) were created with American Chemical Society (ACS) grade  $(\text{NH}_4)\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (mol. wt. 1235.86; J.T. Baker, Phillipsburg, NJ). A 11.3 mg l<sup>-1</sup> solution of  $\text{CaBr} \cdot x\text{H}_2\text{O}$  (mol. wt. 199.9; Aldrich Chemical Co., Inc., Milwaukee, WI) and a 120 mg l<sup>-1</sup> solution of ACS grade pentafluorobenzoic acid (PFBA; Aldrich Chemical Co., Inc., Milwaukee, WI) were used as non-reactive tracers to characterize the hydrodynamic properties of the packed columns.

Table 1  
Properties of soil and groundwater

|             | Clay (%)                              | Silt (%)                             | Sand (%)                               | TOC (%)                                | TIC (CaCO <sub>3</sub> )              | CEC (cmol kg <sup>-1</sup> )                        | Conductivity (dS m <sup>-1</sup> )                 | Fe <sub>2</sub> O <sub>3</sub> (%) | pH   | Mo (mg kg <sup>-1</sup> )                          |
|-------------|---------------------------------------|--------------------------------------|--|--|---------------------------------------|---|--|------------------------------------|------|--|
| Soil        | 23                                    | 40                                   | 37                                     | 0.80                                   | 4.70                                  | 31.00   | 1.90   | 1.5                                | 8.10 | <0.1   |
|             | Na <sup>+</sup> (mg l <sup>-1</sup> ) | K <sup>+</sup> (mg l <sup>-1</sup> ) | Ca <sup>2+</sup> (mg l <sup>-1</sup> ) | Mg <sup>2+</sup> (mg l <sup>-1</sup> ) | Cl <sup>-</sup> (mg l <sup>-1</sup> ) | SO <sub>4</sub> <sup>-2</sup> (mg l <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> ) | Conductivity (dS m <sup>-1</sup> ) | pH   | Alkalinity (mg l <sup>-1</sup> CaCO <sub>3</sub> ) |
| Groundwater | 38.0                                  | 3.0                                  | 41.0                                   | 3.5                                    | 18.0                                  | 54.0  | 8.5  | 0.4                                | 7.8  | 130.0  |

## 2.2. Batch sorption experiments

Batch experiments were conducted at 20(±2) °C to evaluate the equilibrium relationship between sorbed and aqueous phase Mo for the non-amended and the bio-solid-amended soils. Sub-samples (approximately 10 g) of the soils were placed in polypropylene vials, to which were added 10-ml aliquots of Mo solution. The solutions had five initial Mo concentrations (35.5, 9.1, 4.4, 1.9, and 0.9 mg l<sup>-1</sup>), which were selected to represent the upper range of concentrations that might be found in environmental systems. The vials were prepared in triplicate at each concentration for both soils, and blank solutions were used to confirm that no Mo was initially sorbed. The vials were shaken at 250 revolutions per minute (rpm) for 60 h, which was confirmed to be adequate for equilibration by previous batch experiments. The vials were then centrifuged at 3500 rpm for 30 min, and the supernatants were sampled and filtered using a 0.45 µm filter for analysis. The absorbed concentration was calculated from the difference between the initial and final aqueous concentrations. Statistical 95% confidence intervals (assuming a normal distribution) were calculated for the concentration data from the triplicates.

## 2.3. Miscible displacement experiments

Kontes Chromaflex (2.5 cm diameter, 5 cm long; Kontes Glass Company, Vineland, NJ) glass chromatography columns were packed to create uniform bulk densities and porosities. The gravimetric dry bulk density ( $\rho$ ) was approximately 1.49 g cm<sup>-3</sup> and the volumetric water content ( $\theta$ ) was approximately 0.5 cm<sup>3</sup> cm<sup>-3</sup>, with slight variation between experiments (Table 2). Groundwater solution was introduced from the bottom at a rate of 0.1 ml min<sup>-1</sup> with a high performance liquid chromatography piston pump to saturate the column (approximately 80 pore volumes) until the column weight was stable. All miscible-displacement experiments were conducted at 20(±2) °C. A pulse of non-reactive tracer or Mo solution was injected for several pore volumes, after which the groundwater solution was injected to elute the tracer or Mo solution from the soil column. Samples were collected from column

effluent throughout each experiment, and samples collected prior to tracer and Mo injection confirmed non-detectable background concentrations.

## 2.4. Chemical analysis

All samples for Mo and Br were acidified with concentrated nitric acid and refrigerated upon collection. MoO<sub>4</sub> and Br were analyzed using a Leeman (Hudson, NH) PS1000-UV inductively coupled plasma (ICP) spectrophotometer and a Dionex (Sunnyvale, CA) Ion Chromatograph, respectively. The lower detection limit was 0.15 mg l<sup>-1</sup> for Mo and 0.2 mg l<sup>-1</sup> for Br. The reference methods, SW-846 method 6010 for Mo and method 300 for Br, used a sequential elemental analysis emission spectrophotometer with argon plasma (USEPA, 1996). PFBA was analyzed using a Shimadzu (Kyoto, Japan) SPD-10A UV-VIS flow-through spectrophotometer with the wavelength set at 254 nm. The lower quantifiable detection limit was 1.0 mg l<sup>-1</sup>. Random duplicates and blanks were used for quality control and quantitative assurance. Experimental error associated with the analysis calculated from duplicates varied from 1% to 3%.

## 2.5. Data analysis

### 2.5.1. Moment analysis

Standard temporal moment analysis was used to calculate the mass balance and the retardation factor for all tracer experiments (e.g., Valocchi, 1985). The 0th moment (integration of eluted concentration) was compared to the measured injected mass to calculate mass recovery. The mean travel time was calculated using the normalized first moment. The ratio of the Mo and non-reactive tracer travel times was used to calculate the retardation factor.

### 2.5.2. Geochemical modeling

PHREEQC Version 2.2 (Parkhurst and Appelo, 1999), an equilibrium speciation and mineral-water mass-transfer code developed by the United States Geological Survey, was used for the calculation of aqueous complex speciation and mineral saturation indices based on the aqueous composition of the groundwater solutions used in the various

Table 2  
Conditions and results for miscible-displacement experiments (values in parentheses represent 95% confidence intervals)

| Experiment       | Tracer           | $v_o$<br>(cm h <sup>-1</sup> ) | $\rho$<br>(g cm <sup>-3</sup> ) | $\theta$<br>(-) | Recovery<br>(%) | $R$<br>(-) | $K_d$<br>(l kg <sup>-1</sup> ) | $\beta$<br>(-)  | $\omega$<br>(-) | $k_2$<br>(h <sup>-1</sup> ) |
|------------------|------------------|--------------------------------|---------------------------------|-----------------|-----------------|------------|--------------------------------|-----------------|-----------------|-----------------------------|
| Non-amended      | Bromide          | 6.9                            | 1.40                            | 0.50            | 99              | 1.0        | 0.0                            | -               | -               | -                           |
| Non-amended      | PFBA             | 6.9                            | 1.40                            | 0.50            | 99              | 1.0        | 0.0                            | -               | -               | -                           |
| Non-amended      | Mo               | 6.9                            | 1.40                            | 0.50            | 97              | 2.2        | 0.4                            | 0.7 (0.72–0.75) | 0.4 (0.32–0.46) | 0.3 (0.23–0.38)             |
| Non-amended      | PFBA (replicate) | 2.3                            | 1.55                            | 0.53            | 100             | 1.0        | 0.0                            | -               | -               | -                           |
| Non-amended      | Mo (replicate)   | 2.3                            | 1.55                            | 0.53            | 99              | 1.9        | 0.3                            | 0.8 (0.76–0.84) | 0.2 (0.11–0.34) | 0.3 (0.12–0.51)             |
| Biosolid amended | PFBA             | 2.2                            | 1.49                            | 0.55            | 102             | 1.0        | 0.0                            | -               | -               | -                           |
| Biosolid amended | Mo               | 2.2                            | 1.49                            | 0.55            | 99              | 4.6        | 1.4                            | 0.6 (0.58–0.65) | 0.5 (0.36–0.55) | 0.1 (0.08–0.15)             |
| Biosolid amended | Mo (replicate)   | 2.4                            | 1.49                            | 0.49            | 99              | 4.7        | 1.2                            | 0.5 (0.48–0.52) | 0.5 (0.43–0.52) | 0.1 (0.08–0.12)             |

Table 3  
Molybdenum reactions added to PHREEQC database

| Aqueous speciation reactions   | Equilibrium constants<br>(log $K$ ) | Refs.                      |
|--|-------------------------------------|----------------------------|
| $\text{MoO}_4^{-2} + \text{H}^+ = \text{HMoO}_4^-$   | 4.24                                | Smith and Martell (1976)   |
| $\text{MoO}_4^{-2} + 2\text{H}^+ = \text{H}_2\text{MoO}_4$                                   | 6.85                                | Kaback and Runnells (1980) |
| $\text{Ca}^{2+} + \text{MoO}_4^{-2} = \text{CaMoO}_4$  | 2.57                                | Essington (1990)           |
| $\text{Mg}^{2+} + \text{MoO}_4^{-2} = \text{MgMoO}_4$  | 3.03                                | Essington (1990)           |
| $\text{K}^+ + \text{MoO}_4^{-2} = \text{KMoO}_4^-$   | 1.29                                | Essington (1990)           |
| $\text{Na}^+ + \text{MoO}_4^{-2} = \text{NaMoO}_4^-$   | 1.66                                | Essington (1990)           |
| $3\text{H}^+ + \text{MoO}_4^{-2} = \text{MoO}_2\text{OH}^+ + \text{H}_2\text{O}$             | 7.89                                | Kaback and Runnells (1980) |
| $4\text{H}^+ + \text{MoO}_4^{-2} = \text{MoO}_2^{2+} + 2\text{H}_2\text{O}$                  | 8.34                                | Kaback and Runnells (1980) |
| $\text{MoO}_4^{-2} + \text{e}^- + 4\text{H}^+ = \text{MoO}_3^+ + 2\text{H}_2\text{O}$        | 20.95                               | Kaback and Runnells (1980) |
| $\text{MoO}_4^{-2} + 3\text{e}^- + 8\text{H}^+ = \text{Mo}^{3+} + 4\text{H}_2\text{O}$       | 29.52                               | Kaback and Runnells (1980) |
| <i>Mineral formation reactions</i>   |                                     |                            |
| Powellite $\text{Ca}^{2+} + \text{MoO}_4^{-2} = \text{CaMoO}_4(\text{s})$                    | 8.05                                | Essington (1990)           |
| <i>Adsorption reactions</i>  |                                     |                            |
| $\text{H}^+ + \text{SurfOH} = \text{SurfOH}_2^+$   | 6.3                                 | Stollenwerk (1998)         |
| $\text{H}^+ + \text{SurfsOH} = \text{SurfsOH}_2^+$   | 6.3                                 | Stollenwerk (1998)         |
| $\text{SurfOH} = \text{SurfO}^- + \text{H}^+$  | -7.1                                | Stollenwerk (1998)         |
| $\text{SurfsOH} = \text{SurfsO}^- + \text{H}^+$  | -7.1                                | Stollenwerk (1998)         |
| $\text{MoO}_4^{-2} + \text{H}^+ + \text{SurfOH} = \text{SurfMoO}_4^- + \text{H}_2\text{O}$   | 8                                   | Stollenwerk (1998)         |
| $\text{MoO}_4^{-2} + \text{H}^+ + \text{SurfsOH} = \text{SurfsMoO}_4^- + \text{H}_2\text{O}$ | 10.3                                | Stollenwerk (1998)         |
| $\text{MoO}_4^{-2} + \text{SurfOH} = \text{SurfOHMoO}_4^{-2}$                                | 1.6                                 | Stollenwerk (1998)         |
| $\text{MoO}_4^{-2} + \text{SurfsOH} = \text{SurfsOHMoO}_4^{-2}$                              | 4.2                                 | Stollenwerk (1998)         |

experiments. Chemical reactions and thermodynamic constants required for the calculations were taken from the literature (Table 3). PHREEQC was also used to predict the electrostatic adsorption of Mo based on the Gouy–Chapman, double layer electrostatic model, which was developed by Dzombak and Morel (1990) and utilized for Mo adsorption by Stollenwerk (1995, 1998). This was done assuming a set of strong sites ( $0.83 \mu\text{M g}^{-1}$ ) and a set of weak sites ( $0.02 \mu\text{M g}^{-1}$ ) were available for adsorption, with a solid-phase surface area of  $0.33 \text{ m}^2 \text{ g}^{-1}$ , which were similar to previous studies (Stollenwerk, 1998).

### 2.5.3. ADE transport modeling

The results of the miscible-displacement experiments were simulated with the widely used two-domain (also termed “two-site”), first-order non-equilibrium transport model (e.g., Cameron and Klute, 1977):

$$\beta R \frac{\partial C^*}{\partial T} + (1 - \beta)R \frac{\partial S^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C^*}{\partial Z^2} - \frac{\partial C^*}{\partial Z} \quad (1)$$

$$(1 - \beta)R \frac{\partial S^*}{\partial T} = \omega(C^* - S^*) \quad (2)$$

where

$$Z = \frac{x}{L} \quad (3)$$

$$T = \frac{v_o t}{L} \quad (4)$$

$$P = \frac{v_o L}{D} \quad (5)$$

$$C^* = \frac{C}{C_0} \quad (6)$$

$$S^* = \left( \frac{1}{(1 - F)K_d} \right) \left( \frac{S_2}{C_0} \right) \quad (7)$$

$$R = 1 + \rho K_d / \theta \quad (8)$$

$$\beta = \left( \frac{\theta + F \rho K_d}{\theta + \rho K_d} \right) \quad (9)$$

$$\omega = \left( \left( \frac{k_2 L}{v_o} \right) (1 - \beta) R \right) \quad (10)$$

and where  $C$  is the solute concentration in solution ( $\text{M l}^{-3}$ ),  $C_0$  is the solute concentration in the input solution ( $\text{M l}^{-3}$ ),  $C^*$  is the dimensionless solute concentration solution (-),  $L$  is the column length ( $L$ ),  $x$  is the transport distance ( $L$ ),  $Z$  is the dimensionless transport length (-),  $t$  is the elapsed time after injection ( $T$ ),  $T$  is the dimensionless transport time ( $T$ ),  $v_o$  is the average pore-water velocity ( $L T^{-1}$ ),  $D$  is the dispersion coefficient ( $L^2 T^{-1}$ ),  $P$  is the Peclet number (-),  $S_2$  is the sorbed concentration in the rate-limited domain,  $S^*$  is the dimensionless sorbed concentration (-),  $k_2$  is the first-order sorption rate coefficient ( $1/T$ ),  $F$  is the fraction of sorbent for which sorption is instantaneous, and  $\beta$  and  $\omega$  are the dimensionless parameters that specify the degree of non-equilibrium in the system.

CXTFIT, a non-linear least-square optimization program (van Genuchten, 1981), was used to calibrate  $P$  for the non-reactive tracer data. The dispersion coefficients obtained from analysis of the non-reactive tracer data were used to simulate the Mo data. As noted above,  $R$  values for Mo were obtained from moment analysis of the breakthrough curves. The  $\beta$  and  $\omega$  parameter values were optimized when calibrating the model to the Mo data, and

95% confidence intervals were calculated for the parameter estimates.

### 3. Results and discussion

#### 3.1. Geochemical modeling

Results from previous studies show that electrostatic adsorption occurs primarily under acidic pH ranges (Manning and Goldberg, 1996). Similar results were obtained with the PHREEQC electrostatic adsorption modeling. Fig. 1 shows that the relative concentration of total Mo in solution reaches a value of one at a pH of approximately 5, and remains at that value for higher pHs. This indicates that electrostatic adsorption has relatively little impact on Mo throughout the alkaline pH range.

The geochemical model was used to examine expected Mo speciation and chemical reactions between the soil minerals and the groundwater solution for our systems (Fig. 1). The aqueous complex speciation was calculated based on the aqueous composition of the groundwater solutions used in the experiments. The predicted speciation for Mo in the groundwater solution was 75.8%  $\text{MoO}_4^{2-}$ , 14.2%  $\text{CaMoO}_4^0$ , 5.7%  $\text{MgMoO}_4^0$ , 4.2%  $\text{NaMoO}_4^{-1}$ , and a negligible quantity of  $\text{MoO}_2^{2+}$ ,  $\text{KMnO}_4^{-1}$ ,  $\text{HMoO}_4^{-1}$ ,  $\text{H}_2\text{MoO}_4^0$ ,  $\text{MoO}_2\text{OH}^+$ ,  $\text{MoO}_2^{+1}$ , and  $\text{Mo}^{3+}$ .

Mineral saturation indices for common soil forming minerals were also calculated with the geochemical model. The groundwater in the alkaline pH range was predicted to be supersaturated with respect to calcite and aragonite, and undersaturated with respect to gypsum and  $\text{CaMoO}_4$  (powellite). These results suggest that mineral dissolution/precipitation reactions did not impact the transport of Mo in the alkaline soil system used herein.

#### 3.2. Non-reactive tracer transport

Representative measured and simulated breakthrough curves for the non-reactive tracers are shown in Fig. 2. The measured breakthrough curves are relatively symmetrical, indicating ideal transport behavior in the homogeneously packed columns. No measurable sorption was observed. Comparison of the breakthrough curves for transport in the non-amended and biosolid-amended soils indicates that the biosolid amendment did not significantly alter hydrodynamic transport behavior. The simulations produced with the transport model provided good matches to the measured data.

#### 3.3. Molybdenum sorption

The equilibrium sorption experiments were conducted to quantify sorption of Mo in the absence of physical transport processes. The results of the experiments are presented in Fig. 3. Sorption is observed to be represented well with a linear isotherm for both the non-amended and biosolid-amended soils. Note that the input concentrations used for the column experiments fall within the range employed in the batch experiments. Sorption was four times greater for the biosolid-amended soil, with a  $K_d$  value of 1.24 versus a value of 0.29 for the non-amended soil.

#### 3.4. Molybdenum transport

Measured breakthrough curves for Mo transport in the non-amended and the biosolid-amended soils are shown in Fig. 4. Transport of Mo in both soils was retarded compared to that of the non-reactive tracers. In addition, Mo exhibited greater retardation in the biosolid-amended soil,

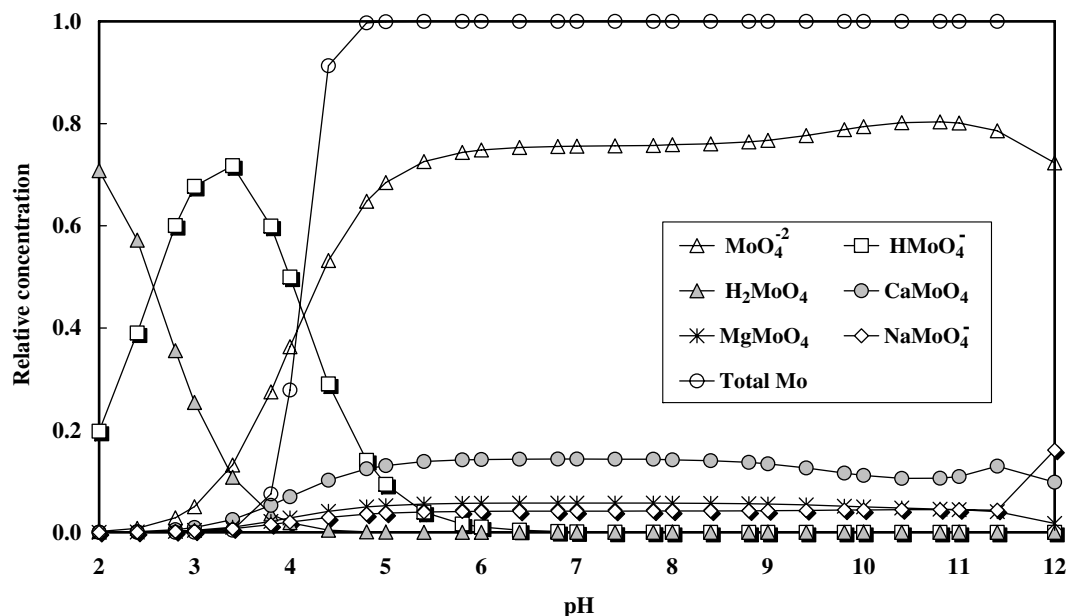


Fig. 1. PHREEQC model results for aqueous species distribution and total aqueous Mo for a range of pH values.



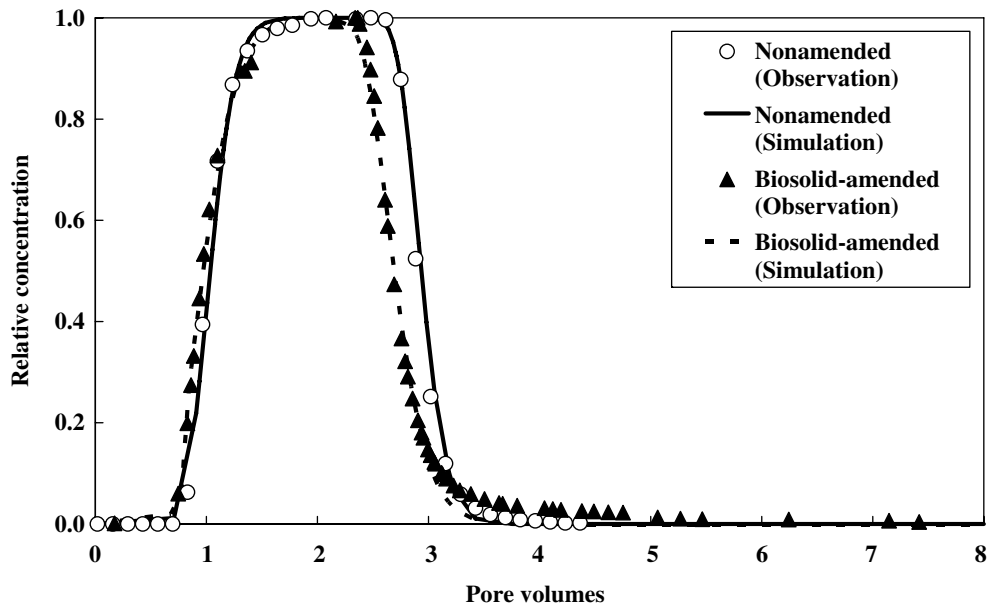


Fig. 2. Measured and simulated breakthrough curves for PFBA transport in the non-amended and biosolid-amended soils.

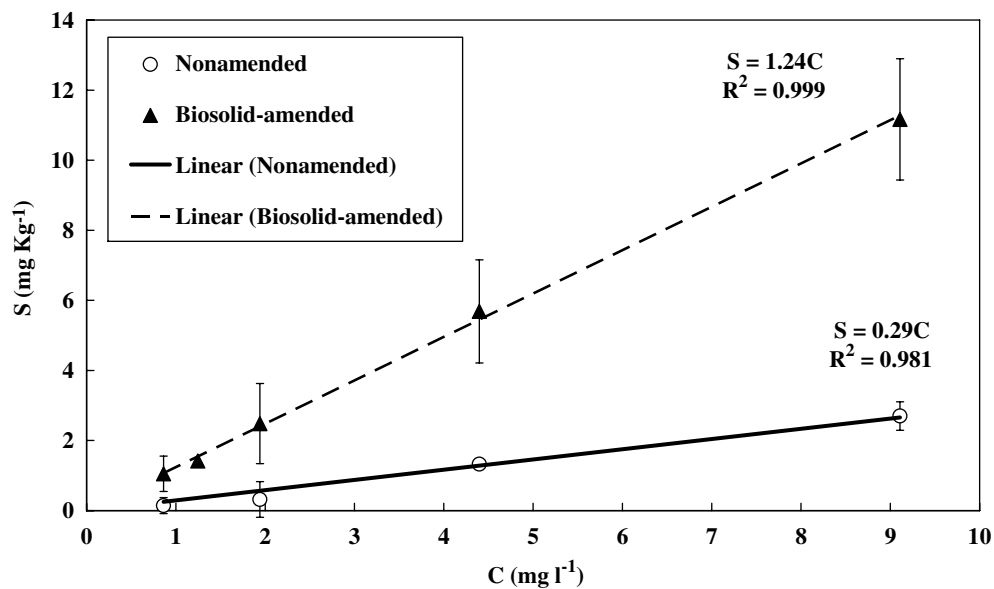


Fig. 3. Measured molybdenum isotherms and linear regressions fitted to the data. The error bars indicate the 95% confidence intervals.

with  $R$  values of 4.6 compared to values of 2.3 for the non-amended soil (see Table 2). These equate to  $K_d$  values of 1.3 and 0.35, respectively. These values are similar to the values obtained from the batch experiments. Recovery of Mo in the column effluent was 97% or greater of the mass injected, which indicates that sorption was reversible.

The Mo breakthrough curves were asymmetrical and exhibited extensive tailing (Fig. 4), in contrast to the non-reactive tracers. This suggests that rate-limited and/or non-linear sorption influenced Mo transport. As noted above, the results of the batch experiments indicated Mo

sorption is linear. Sorption linearity was further evaluated by comparing the shapes of the arrival and elution waves for each breakthrough curve (e.g., Hu and Brusseau, 1998). When non-linear sorption significantly affects transport, the arrival wave exhibits self-sharpening behavior while the elution wave exhibits spreading behavior (for concave-downward isotherms). Thus, the arrival and inverted elution waves are not coincident. The arrival and inverted elution waves are compared in Fig. 5 for Mo transport in both the non-amended and biosolid-amended soil. The coincident nature of the two sets of curves

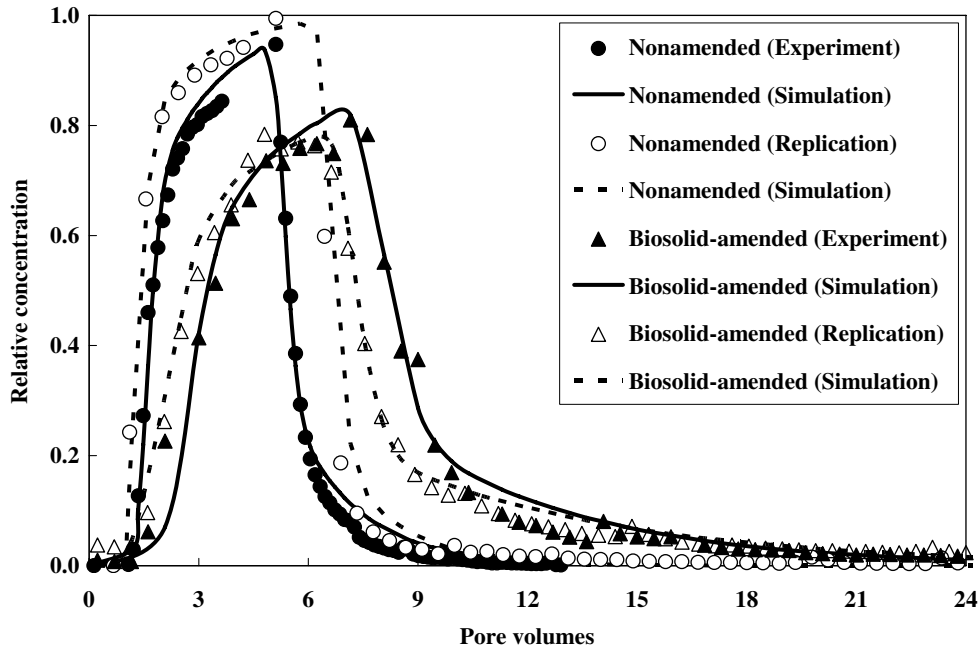


Fig. 4. Measured and simulated breakthrough curves for Mo transport in the non-amended and biosolid-amended soils.

indicates that non-linear sorption had minimal impact on transport. Thus, it appears that rate-limited sorption is responsible for the non-ideal transport observed for Mo.

The transport model coupling advective–dispersive transport with linear, rate-limited sorption was used to quantify the sorption and transport of Mo in the soils. The use of a simple two-domain, first-order mass transfer approach for the simulation of retention without explicit consideration of thermodynamic chemical processes was

supported by the results of the previously mentioned geochemical modeling and the batch experiments. The simulated breakthrough curves are compared to the measured data in Fig. 4. The model provides a good match to the measured data, suggesting that the conceptualization upon which the model was based provided a reasonable representation of Mo transport in this soil. The optimized values for  $\beta$  and  $\omega$  are presented in Table 2, along with calculated adsorption rate coefficients.

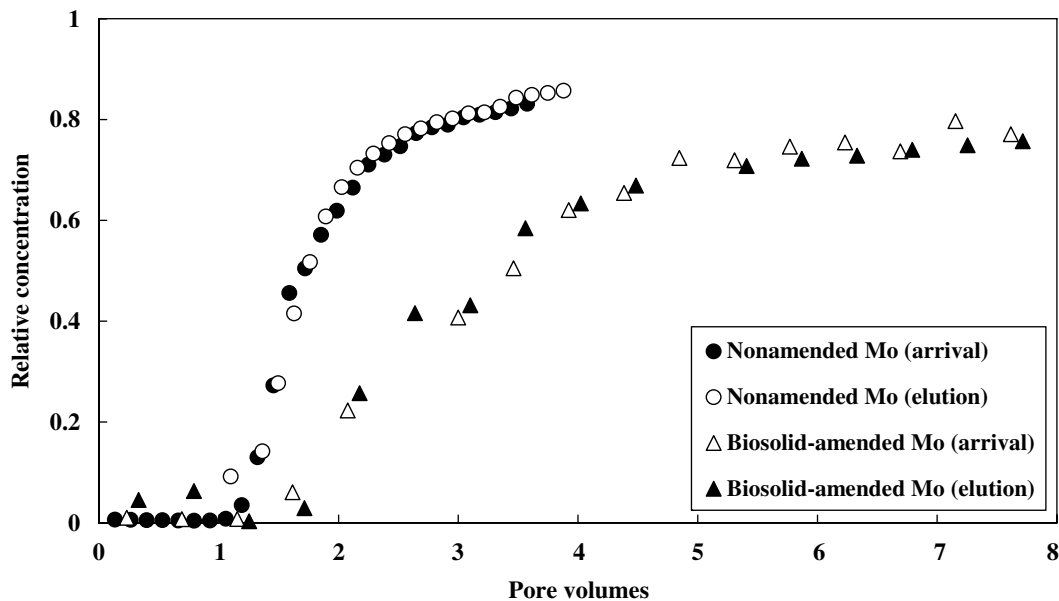


Fig. 5. Comparison of arrival and inverted elution waves for measured Mo breakthrough curves.

#### 4. Conclusion

Batch sorption and miscible-displacement experiments were used to characterize Mo sorption and transport in an alkaline soil. The biosolid-amendment of 10% by weight was selected to represent several years of cumulative agricultural soil amendments as a worse case scenario. Mo retardation was observed due to sorption in both soils, but sorption was greater for the biosolid-amended soil. The  $K_d$  values obtained from the miscible-displacement and batch experiments were similar. Sorption was shown to be linear for the relatively low concentration range used in these experiments. The results of the column experiments indicated that sorption was rate limited and reversible. However, the determination of sorption mechanism of Mo on the biosolid was beyond the scope of this investigation.

The behavior of Mo in the soil used herein may be representative of other alkaline agricultural soil systems, particularly for the thermic and hyperthermic regimes of the southwestern US deserts. Our results show that the Mo oxyanion is only temporarily retained by adsorption when applied in agricultural soils with alkaline conditions. The addition of large amounts of organic matter in the form of biosolids resulted in a factor of two increase in retardation of Mo. However, sorption remained relatively low, and was still reversible. Thus, it is unlikely that Mo from biosolids applications will accumulate in irrigated alkaline soils.

These results of this investigation support the proposed more restrictive standard of  $40 \text{ kg ha}^{-1}$  cumulative limit (O'Connor et al., 2001) since it is based on up to 5% Mo soil leaching per year, and only considers the animal feed exposure pathway of Mo. Mo leached from biosolids will tend to be bioavailable unless it becomes transported with irrigation water below the root zone, which could become a concern for groundwater. Future biosolids regulations should consider the mobility of Mo in irrigated alkaline soils in response to evolving water quality standards.

#### Acknowledgements

We would like to thank the USDA Cooperative State Research and Extension Service and NIEHS Superfund Basic Research Program for their support of this project, and Atasi Ray-Maitra for chemical analysis of the molybdenum and bromide samples.

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