



Molybdenum-phosphate retention and transport in soils



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ABSTRACT

Transport and retention experiments were carried out to quantify the mobility and sorption of molybdenum (Mo) and phosphate (P) in two different soils. Batch experiment was used to determine sorption isotherms over a wide range of concentrations for Mo and P. For both soils, sorption isotherms were nonlinear with higher affinity of P than Mo. Sorption of Mo was significantly reduced as the amount added P in solution increased. This was observed for both soils and is indicative of competitive sorption for available site. Miscible-displacement experiments were carried out using soil column where a pulse of Mo solution was introduced in each soil. Breakthrough curves (BTCs) indicated extensive sorption of Mo where as much as 50% of that applied was retained by a predominant kaolinitic soil. Subsequently, a pulse of mixed solution (of Mo and P) was introduced in each column. Results of BTCs for Mo indicated enhanced mobility of Mo in the presence of P for both soils. A five step sequential extraction procedure provided evidence that majority of applied Mo was strongly and/or irreversibly retained. A competitive transport model (CMRTM) based on the Sheindorf-Rebhun-Sheintuch (SRS) equation was capable of describing BTCs of Mo and to a lesser extent for P. Future research should focus on improvement of models that accounts for chemical mechanisms of competitive sorption.

1. Introduction

Molybdenum (Mo) is an essential trace element for both plants and animals and its estimated abundance in the soil environment is in the range of 0.05–40 mg/kg (Das et al., 2007; Aydin et al., 2012). Mo deficiencies have been widely reported for several crops in different parts of the world. Mo appears to be toxic when concentrations in plants are higher than 5 mg/kg. Addition of P could help to overcome the deficiency of Mo but may induce other deficiencies, such as Zn (Singh et al., 1988; Zhu et al., 2001). Moreover, Mo may cause significant threats to the soil and water environments and the presence of P substantially suppresses the sorption of Mo in soils. At present, the Mo-P interaction has regarded as simply two anions that tend to compete for sorption sites of the soil matrix (Xie and MacKenzie, 1991). Therefore, it is necessary to consider competitive mechanisms of Mo and P to quantify their retention, fate and transport in soils and aquifers.

Previous studies demonstrated that P strongly compete with Mo for sorption sites because Mo and P are sorbed to variable charge mineral constituents (Al-oxides, Fe-oxides, gibbsite, pyrite) (Xu et al., 2006; Goldberg, 2010) and soils (Xie and MacKenzie, 1991; Vistosso et al., 2012) via the formation of inner-sphere surface complexes through ligand exchange (Zhang and Sparks, 1989; Goldberg et al., 2002). Moreover, competition coefficients for Mo and P sorption are found to be not identical, indicating that competition between the two anions

was not symmetrical. This may be due that competitive sorption between Mo and P generally depends on a variety of chemical, physical and hydrological factors, such as surface properties of the adsorbent (Vistosso et al., 2012), ratio of Mo and P (Goldberg, 2010), solution pH (Dijkstra et al., 2009; Goldberg, 2009). Solution pH is one of the dominant factors that influence Mo and P sorption on different sites, such as oxides, clay minerals and soils. Mo adsorption increases with increasing pH up to a peak pH 4–5 and decreases with increasing at pH above 5. Likewise, P sorption significantly decreases with increasing pH (Barrow, 1984). The effect of pH on Mo adsorption is influenced by the presence of P. Xu et al., (2006) found that Mo adsorption in the absence of P is less influenced by pH under acidic conditions, but in the presence of P, Mo adsorption on goethite surfaces significantly decreases with increasing pH.

The dominant form of Mo in the soil environment under oxidized condition is Mo(VI), which readily complexes with mineral surfaces (Arai, 2010). Several studies investigated Mo adsorption by different minerals and soils based on batch equilibration methods. Mo sorption isotherms could be used as an indicator of a soil's potential to reduce Mo availability to plants (Xie and MacKenzie, 1991). The Langmuir and the Freundlich equations have been used to describe Mo sorption behavior in several soils in the absence of P. Moreover, the Sheindorf-Rebhun-Sheintuch (SRS) equation was successfully employed by Roy et al. (1986) to describe the competitive adsorption isotherms of As(V)

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and P in several soils. However, models based on competitive behavior of Mo and P in soils are rarely discussed.

Transport models describing the mobility of Mo in the environment have been sporadically reported in the past three decades. Commonly used are geochemical models, such as the PHREEQC transport model was successfully utilized to describe transport of Mo in soils (Carroll et al., 2006). Rather than geochemical models, Stollenwerk and Kipp (1990) proposed a one-dimensional solute-transport model, which was modified by four different rate mechanisms (equilibrium sorption, rate-controlled sorption, and two side-pore diffusions), to simulate Mo column-breakthrough results. These models also were adopted to simulate competitive reactions between heavy metals and P during their transport in soils and aquifers (Manning and Goldberg, 1996). In this study, we utilized an empirical rather than a geochemical approach. Specially, the SRS competitive approach was incorporated into a multireaction transport model which account for nonlinear equilibrium, reversible and irreversible kinetic reactions to describe competitive sorption between Mo and P during transport in soils.

Batch and miscible displacement experiments were carried out to investigate Mo sorption and transport behavior in two soils. The specific objectives were (i) to investigate the influence of the presence P in the soil solution on Mo transport in two soils having different physiochemical properties, and (ii) to assess the predictive capability of a multireaction (equilibrium-kinetic) model to describe the competitive sorption of Mo and P during transport in soils.

2. Materials and methods

2.1. Soils

Two surface soils from the Ap horizon (0–10 cm) of Windsor and Mahan soils were used in this study. These soils contain very little Mo and their physical, chemical, and mineralogical properties (e.g., pH, TOC, Fe and Al oxides) are given in Table 1 and detailed description of analytical methods can be found in supplementary files.

2.2. Batch experiment

The batch method was used to determine Mo and P adsorption isotherm according to the following procedure. For each soil, 3-g air-dry soil in triplicate mixed with 30-ml solution in a 40-ml Teflon

Table 1
Selected physical and chemical properties of the soils studied.

Soil	Windsor	Mahan
pH	6.11	6.10
TOC ^a (%)	2.03	1.37
CEC ^b (cmol kg ⁻¹)	2.0	7.0
Mo (mg/kg)	0.93	0.59
P (g kg ⁻¹)	0.45	0.31
K (g kg ⁻¹)	1.11	0.25
Sand ^c (%)	77	49
Silt (%)	20	20
Clay (%)	3	31
Oxalate Fe (g kg ⁻¹)	0.36	0.46
Oxalate Al (g kg ⁻¹)	0.69	0.22
CBD Fe (g kg ⁻¹)	3.68	6.07
CBD Al (g kg ⁻¹)	3.65	3.65
Clay mineralogical composition ^d	Illite (33%), Kaolinit (29%), Chlorite (15%), Smectite (12%), Quartz (10%)	Kaolinite (75–85%), Mica (5–10%), Vermiculite (5%), Interlayered, interstratified (5–10%)

^a TOC = total organic carbon.

^b CEC = cation exchange capacity.

^c Grain size distribution: sand (2.00–0.05 mm), silt (0.05–0.002 mm), and clay (< 0.002 mm).

^d Percentage of mineral present.

centrifuge tube. Reagent grade [(NH₄)₆Mo₇O₂₄] and [(NH₄)₂HPO₄] were used to prepare solutions with different Mo and P ratios. Specifically, the amount of Mo and P added, expressed as (mg/L) Mo/(mg/L) P, were 100/0, 50/0, 25/0, 10/0, 5/0, 2/0, 100/100, 100/50, 100/20, 100/10, 50/100, 20/100, 10/100, 0/200, 0/100, 0/50, 0/25, 5/10, 0/5. In order to maintain a constant ionic strength, all initial Mo and P solutions were prepared in 0.005 M KNO₃ background solution (Zhang and Selim, 2005). The mixtures were continuously shaken at 150 rpm on a reciprocal shaker. After 24 h, the suspensions were centrifuged at 5000g for 10 min and the supernatant was filtered through 0.45-μm filter papers. A 1-ml aliquot was sampled from the supernatant and subsequently acidified (0.5% HNO₃) for analysis (Gustafsson, 2003). These solution samples were then stored at +4 °C and stored before analysis. After sampling, the pH of the supernatant was measured with a standard multi-pH/mV meter and reported in Supplementary material (Fig. S1). Since the filter membrane with a 0.45 μm pore size was used to retain the soil particles, the solution samples may contain colloidal particles smaller than 0.45 μm. Concentrations of total Mo and P were analyzed using inductively coupled plasma atomic emission spectrophotometry (ICP-AES; Spectro Citros CCD, SPECTRO Analytical Instruments, Kleve, Germany).

2.3. Miscible displacement experiment

The miscible displacement method as described by Selim et al. (1987) was utilized to investigate the competitive transport of Mo and P in the two soils. Acrylic columns (10-cm in length and of 6.4-cm i.d.) were packed with air-dry soil to create uniform bulk densities and porosities. A 6.4 cm diameter filter membrane with a 0.45-μm pore size was used to retain the soil in the reaction column. Background solutions of 0.005 M KNO₃ were introduced from the bottom at a low Darcy flux with a high performance liquid chromatography piston pump to saturate the column until flow rate was stable. Approximately 10 pore volumes of 0.005 M KNO₃ was applied to each column to maintain constant ionic strength. A pulse of 100 mg/L Mo solution in 0.005 M KNO₃ then was introduced to each column. The Mo pulse was approximately 10–12 pore volumes and was then eluted by 10–12 pore volume of 0.005 M KNO₃ background solution. Subsequently, a pulse of mixed solution of 100 mg/L Mo and 100 mg/L P was applied to each column after leaching. Each mixed Mo and P pulse was also 10–12 pore volumes and was then eluted by the background solution. Column effluent was collected every 45 min using a fraction collector (Retriever II, Teledyne ISCO, Inc.). The Mo and P concentration of the collected effluent solution was measured using ICP-AES. The volume of each single ion (Mo) pulse and mixed ions (Mo and P) pulse, along with soil parameters associated with each column are given in Table 2. The pH of the effluent solution was also frequently measured during the miscible displacement experiments.

After leaching, a pulse of a tracer solution was subsequently applied to each soil column to obtain estimates for the dispersion coefficient (D). A minimum of one pore volume of tritium (³H₂O) was introduced to each column and then followed by approximately 3 pore volumes of 0.005 M KNO₃ background solution. The collected samples were analyzed using a Tri-Carb liquid scintillation β counter (Packard-3500 TR) by mixing 1-mL aliquot with 4-mL cocktail (Packard Ultima Gold) for 10 min. The classical convection dispersion equation and best-fit parameters for D and the retardation factor R were obtained from nonlinear least square optimization using CXTFIT, which is commonly utilized for describing the BTCs tritium data (Toride et al., 1995). Estimates for D values are given in Table 2 and selected tritium BTCs that represent relative concentration (C/C₀) versus pore volume (V/V₀) are shown in Fig. 1.

2.4. Distribution with soil depth

To obtain the recovery of applied Mo and P into soil column, each

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