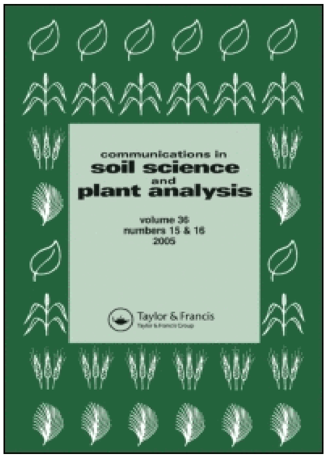

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Molybdenum Adsorption by Volcanic Italian Soils

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Abstract: Molybdenum (Mo) adsorption was investigated on five soils from the Gauro and Roccamonfina volcanoes of Campania, a southern Italian volcanic region. The soils were characterized by different degrees of development. Molybdenum adsorption exhibited a maximum near pH 4–5 and decreased with increasing pH above 5. The constant capacitance model was able to fit Mo adsorption on the soils as a function of pH. A general regression model was used to predict a Mo surface complexation constant from routinely measured soil chemical parameters. The predicted Mo constant was used to predict adsorption on the soils, thereby providing a completely independent evaluation of the ability of the model to describe Mo adsorption. The prediction equation, developed from a set of soils primarily from California, was able to predict Mo adsorption on four out of five soils from Italy, suggesting wide applicability for describing Mo adsorption by soils of diverse mineralogy and parent material.

Keywords: Andisols, constant capacitance model, molybdate, sulfate

INTRODUCTION

Molybdenum (Mo) is an essential trace element for both plant and animal nutrition. Molybdenum deficiencies have been reported for many agronomic

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crops (Murphy and Wath 1972). Molybdenum occurs in anionic form in soil solution, is readily taken up by forage plants, and can accumulate to levels detrimental to grazing ruminant animals (Reisenauer, Wath, and Hoeft 1973). Molybdenum exerts its toxic effect on ruminants by inducing a copper (Cu) deficiency that is especially pronounced in the presence of sulfur (S); this adverse effect can be mitigated by Cu supplementation (O'Connor et al. 2001). Careful quantification of soil solution Mo concentration and characterization of Mo adsorption reactions by soils are needed.

Availability of Mo to plants is affected by a variety of soil factors including solution pH, temperature, texture, clay mineralogy, oxide, and organic-matter content (Reisenauer, Walsh, and Hoeft 1973). The dominant Mo-adsorbing surfaces in soils are aluminum (Al) and iron (Fe) oxides, clay minerals, and organic matter (Goldberg, Forster, and Godfrey 1996). In volcanic ash–derived soils, allophane is also an important adsorbing surface (Wells 1956; Shoji, Nanzyo, and Dahlgren 1993). Volcanic ash–derived soils adsorbed larger amounts of Mo than soils dominated by layer silicate minerals (Theng 1971). Soils containing large amounts of amorphous aluminosilicates like allophane have a high anion exchange capacity. Statistically significant correlations were obtained between amorphous Al oxide, free Fe oxide, and allophane content and Mo adsorption for 16 Chilean volcanic soils (Gonzalez et al. 1974).

Molybdenum adsorption on soils and soil minerals increased with increasing solution pH from pH values 2 to 4, exhibited a peak near pH 4 to 5, and decreased with increasing solution pH above pH 5 (Gonzalez et al. 1974; Mikkonen and Tummavuori 1993; Goldberg, Forster, and Godfrey 1996). Ligand exchange with surface hydroxyl ions was suggested to be the mechanism of Mo adsorption on Al and Fe oxides (Ferreiro, Helmy, and de Bussetti 1985). Ligand exchange is a mechanism by which anions become specifically adsorbed. Specific adsorption of anions shifts the point of zero charge of variably charged minerals to a more acid pH value. Molybdenum adsorption lowered the point of zero charge of Al and Fe oxides and kaolinites, indicating specific adsorption (Goldberg, Forster, and Godfrey 1996).

Sulfate is abundant in most soil solutions and a potential competing anion for Mo adsorption. Prior sulfate adsorption substantially reduced Mo adsorption by Al oxide, especially at low pH (Vissenberg et al. 2000). Data on the competitive effect of sulfate on Mo adsorption by soils are contradictory. Although the presence of sulfate substantially reduced Mo adsorption on three soils from Texas (Smith, Brown, and Deuel 1987) and two biosolid-amended soils from Florida (Brinton and O'Connor 2000), no competitive effect of sulfate on Mo adsorption was found for two soils from Poland (Gorlach, Gorlach, and Compala 1969) and 16 volcanic ash–derived soils from Chile (Gonzalez et al. 1974).

Molybdenum adsorption on soils and soil minerals has been described using various surface complexation modeling approaches: constant capacitance model (Motta and Miranda 1989; Goldberg, Forster, and Godfrey 1996; Goldberg, Su, and Forster 1998; Goldberg, Lesch, and Suarez 2002), triple-layer model (Zhang and Sparks 1989; Goldberg, Su, and Forster 1998; Wu et al. 2001), and CD-MUSIC model (Bourikas, Hiemstra, and van Riemsdijk 2001). The advantage of surface complexation models over empirical adsorption models is that they define specific surface species, chemical reactions, mass balances, and charge balances and contain molecular features that can be given thermodynamic significance (Sposito 1983). In a prior study (Goldberg, Lesch, and Suarez 2002), a general regression model was developed to obtain soil Mo surface complexation constants for use in the constant capacitance model to predict Mo adsorption. The constant capacitance model parameters were obtained from easily measured soil chemical properties: cation exchange capacity, organic C content, inorganic C content, and free Fe oxide content. The prediction equations, when utilized in the constant capacitance model, provided good prediction of Mo adsorption behavior on 36 soils primarily from California. This comparison of prediction and observation resulted in a completely independent evaluation of the ability of the constant capacitance model to describe Mo adsorption. This approach avoids the necessity of performing time-consuming, detailed adsorption studies for each specific soil. Predictions of adsorption using either a monodentate or a bidentate surface configuration for Mo were of similar quality.

The objectives of the present study were 1) to determine Mo adsorption behavior on some Italian volcanic ash soils as a function of solution pH and competing sulfate concentration, 2) to evaluate the ability of the constant capacitance model to describe Mo adsorption on these soils, and 3) to test the ability of the previously developed regression model equation of Goldberg, Lesch, and Suarez (2002) to predict constant capacitance model parameters and subsequently Mo adsorption on the volcanic ash soils.

MATERIALS AND METHODS

Molybdenum adsorption was investigated on five volcanic ash soils from Campania, a southern Italian volcanic region. The soil labeled Naples is soil N 2BC1 from the Gauro volcano and has been described by Martinez Cortizas et al. (2003); the soils labeled Roccamonfina 1 to 4 are from the Roccamonfina volcano and have been described by Vacca et al. (2003). Roccamonfina 1 to 4 correspond to Pedon 7 A1, Pedon 4 2C, Pedon 1 A1, and Pedon 5 A1, respectively (Vacca et al. 2003). Morphological, physical, chemical, and mineralogical properties are described in the prior publications.

The Naples soil is developed from K-rich pyroclastic trachytic ash deposits (Astoni eruption, 3700 BP) of the Gauro volcano and is characterized by a low degree of soil development. The Roccamonfina soils are derived from trachytic ash deposits (Roccamonfina 3), alkali basaltic scoria

(Roccamonfina 2), and consolidated trachyandesitic tuffs (Roccamonfina 1 and 4). Roccamonfina 2 and 3 have andic properties, contain imogolite, and have high allophane content. In contrast, Roccamonfina 1 and 4 have weak andic properties and negligible allophane content, and pedogenesis has induced the neogenesis of crystalline clays dominated by halloysite. The Naples soil is classified as ashy, glassy, mesic Vitrandic Haploxerept, and the Roccamonfina soils are classified as medial, glassy, shallow, mesic Typic Hapludand (Roccamonfina 1); medial ferrihydritic, mesic Typic Hapludand (Roccamonfina 2); medial, amorphic, mesic Eutric Fulvudand (Roccamonfina 3); and medial, ferrihydritic, shallow, mesic Typic Hapludand (Roccamonfina 4) using the Soil Taxonomy classification (Soil Survey Staff 1999).

The soil samples range in native pH from 5.5 to 7.3. Additional soil chemical characteristics are given in Table 1. Cation exchange capacities (CEC) were determined by saturating the exchange sites with a solution of 0.4 M ammonium acetate, 0.1 M sodium chloride (NaCl), and 60% ethanol at pH 8.2 (Rhoades 1982). Surface areas were measured using ethylene glycol monoethyl ether (EGME) adsorption (Cihacek and Bremner 1979). Free Fe and Al oxides were extracted according to Coffin (1963); Al and Fe concentrations in the extracts were determined by inductively coupled plasma (ICP) emission spectrometry. Carbon contents were measured using a Full Carbon System 150 with a C coulometer[1] (UIC, Inc., Joliet, IL). Organic C contents (OC) were calculated as the difference between total C contents determined by furnace combustion at 950°C, and inorganic C (IOC) contents determined using an acidification module and heating.

Molybdenum adsorption experiments were carried out in batch systems to determine adsorption envelopes, the amount of Mo adsorbed as a function of solution pH at fixed total Mo concentration. Samples of soil (3 or 4 g) were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution for 20 h on a reciprocating shaker. The solutions contained 0.292 mmol L^{-1} Mo and had been adjusted to the desired pH range of 3 to 10 using hydrochloric acid (HCl) (1 or 4 M) or sodium hydroxide (NaOH) (1 or 4 M). Acid or base additions changed the total volumes by less then 2%. The Mo concentration was chosen to avoid Mo polymer formation in solution (Carpéni 1947). After reaction, the samples were centrifuged, and the decantates were analyzed for pH, filtered through 0.45-μm membrane filters, and analyzed for Mo concentration using ICP emission spectrometry. The competitive effect of sulfate was studied at an equimolar concentration using the same adsorption protocol. The S concentration in the supernatants was determined using ICP emission spectrometry.

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[1] Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture.

Table 1. Chemical characteristics of soils

Soils	pH (Water 1:2.5)	CEC ($\mathrm{mmol_c\ L^{-1}}$)	S ($\mathrm{km^2\ kg^{-1}}$)	IOC ($\mathrm{g\ kg^{-1}}$)	OC ($\mathrm{g\ kg^{-1}}$)	Fe ($\mathrm{g\ kg^{-1}}$)	Al ($\mathrm{g\ kg^{-1}}$)	Allophane ($\mathrm{g\ kg^{-1}}$)
Naples	7.3	85.4	0.0564	<0.01	1.2	1.88	0.325	
Roccamonfina 1	6.3	255	0.107	<0.01	47	13.4	4.77	30
Roccamonfina 2	5.5	292	0.471	0.8	14	27.9	15.0	420
Roccamonfina 3	6.7	467	0.144	0.43	95.2	14.3	9.90	170
Roccamonfina 4	6.9	278	0.141	<0.01	29.9	24.6	3.63	30

Notes: CEC = cation exchange capacity; S = surface area; IOC = inorganic carbon; OC = organic carbon.

A detailed discussion of the theory and assumptions of the constant capacitance surface complexation model is provided elsewhere (Goldberg 1992). In the present application of the model to Mo adsorption, the following surface complexation constants were considered:

$$SOH_{(s)} + H^{+}_{(aq)} \rightleftharpoons SOH^{+}_{2(s)} \tag{1}$$

$$SOH_{(s)} \rightleftharpoons SO^{-}_{(s)} + H^{+}_{(aq)} \tag{2}$$

$$SOH_{(s)} + H_2MoO_{4(aq)} \rightleftharpoons SHMoO_{4(s)} + H_2O \tag{3}$$

where $SOH_{(s)}$ represents reactive surface hydroxyl groups on oxides and aluminol groups on clay minerals in the soils. By convention, surface complexation reactions in the constant capacitance model are written starting with the completely undissociated acids; however, the model application contains the aqueous speciation reactions for Mo. Because the quality of model fit to experimental Mo adsorption data was similar for monodentate and bidentate surface species (Goldberg, Lesch, and Suarez 2002), a monodentate Mo surface configuration was used.

Equilibrium constants for the surface complexation reactions are:

$$K_{+}(\mathrm{int}) = \frac{[SOH_2^+]}{[SOH][H^+]}\exp(F\psi/RT) \tag{4}$$

$$K_{-}(\mathrm{int}) = \frac{[SO^-][H^+]}{[SOH]}\exp(-F\psi/RT) \tag{5}$$

$$K_{Mo}(\mathrm{int}) = \frac{[SHMoO_4]}{[SOH][H_2MoO_4]} \tag{6}$$

where F is the Faraday constant (C $\mathrm{mol_c^{-1}}$), ψ is the surface potential (V), R is the molar gas constant (J $\mathrm{mol^{-1}\ K^{-1}}$), T is the absolute temperature (K), and square brackets indicate concentrations (mol $\mathrm{L^{-1}}$). The exponential terms can be considered as solid-phase activity coefficients correcting for charge on the surface complexes.

Mass balance of the surface functional group is:

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SHMoO_4] \tag{7}$$

and charge balance is

$$\sigma = [SOH_2^+] - [SO^-] \tag{8}$$

where σ has units of $\mathrm{mol_c\ L^{-1}}$.

The computer code FITEQL 3.2 (Herbelin and Westall 1996) was used to fit the Mo surface complexation constant to the experimental Mo adsorption data. The FITEQL program uses a nonlinear least squares optimization routine to fit equilibrium constants to experimental data and contains the constant capacitance model of adsorption. It was also used as a chemical speciation program to evaluate predictions of Mo adsorption obtained using the regression model of Goldberg, Lesch, and Suarez (2002) to predict values of the Mo surface complexation constant from soil chemical properties. Fixed input parameter values were capacitance, $C = 1.06\ \mathrm{F\ m^{-2}}$; surface site density, $N_s = 2.31\ \mathrm{sites\ nm^{-2}}$ (recommended for natural materials by Davis and Kent 1990); protonation constant, $\log K_+ = 7.35$; and dissociation constant, $\log K_- = -8.95$ (averages of a literature compilation for various Al and Fe oxides from Goldberg and Sposito 1984) as in the prior study (Goldberg, Lesch, and Suarez 2002). Constant values of site density and capacitance are required to allow application of the prediction equation to new soils. The total number of surface functional groups for constant surface site density is obtained from the expression:

$$[SOH]_T = \frac{2.31 \times 10^{18} Sa}{N_A} \tag{9}$$

where S is the surface area ($\mathrm{m^2\ g^{-1}}$), a is the soil suspension density ($\mathrm{g\ L^{-1}}$), and N_A is Avogadro's number. The prediction equation for the monodentate Mo surface complexation constant previously developed for soils primarily from California is (Goldberg, Lesch, and Suarez 2002):

$$\begin{aligned}\log K_{Mo} = 7.81 - 0.363 \ln(CEC) + 0.219 \ln(IOC/10) \\ + 0.385 \ln(OC/10) + 0.716 \ln(Fe/10)\end{aligned} \tag{10}$$

where the units of CEC are $\mathrm{mmol_c\ kg^{-1}}$ and the units of OC, IOC, and Fe are $\mathrm{g\ kg^{-1}}$. Surface complexation constant values, $\log K_{Mo}$, were calculated for each of our soils from the chemical properties CEC, OC, IOC, and Fe and this equation. Using the predicted surface complexation constant values, Mo adsorption envelopes were in turn predicted for each soil and compared with experimentally determined adsorption values.

RESULTS AND DISCUSSION

Molybdenum adsorption as a function of solution pH was determined for five Italian volcanic ash soils, and the results are presented in Figures 1 to 5. Molybdenum adsorption was maximal in the pH range 2 to 5 and decreased rapidly with increasing pH from 5 to 8 for the four Roccamonfina soils (Figures 2 to 4). The Naples soil exhibited a shorter range of maximum adsorption from pH 2 to 4, reflecting its differing mineralogy and parent material and young state of soil development. The Roccamonfina 2 soil showed maximum adsorption extending to pH 6, the highest of any of the soils. This is may be because this soil had more than twice as much volcanic glass and allophane content than the other Roccamonfina soils (Vacca et al. 2003).

The competitive effect of the presence of sulfate on Mo adsorption is indicated in Figures 1 to 5. Except for the Roccamonfina 4 soil, the

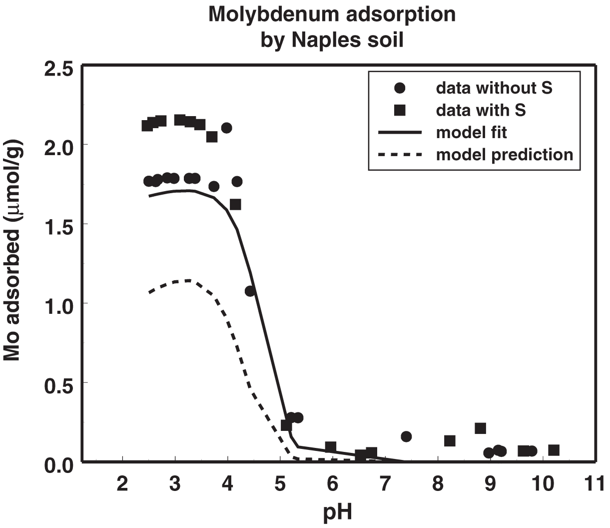

Figure 1. Molybdenum adsorption on Naples soil. Circles represent the experimental Mo adsorption data without sulfate. Squares represent the experimental Mo adsorption data in the presence of equimolar sulfate. Model fits are represented by solid lines. Model predictions are represented by dashed lines.

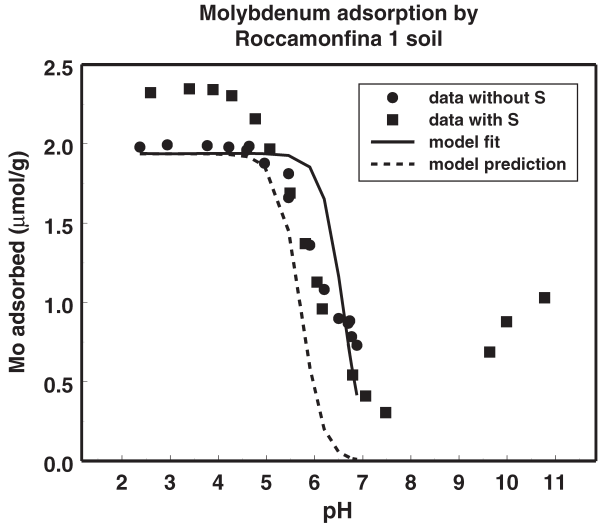

Figure 2. Molybdenum adsorption on Roccamonfina 1 soil. Circles represent the experimental Mo adsorption data without sulfate. Squares represent the experimental Mo adsorption data in the presence of equimolar sulfate. Model fits are represented by solid lines. Model predictions are represented by dashed lines.

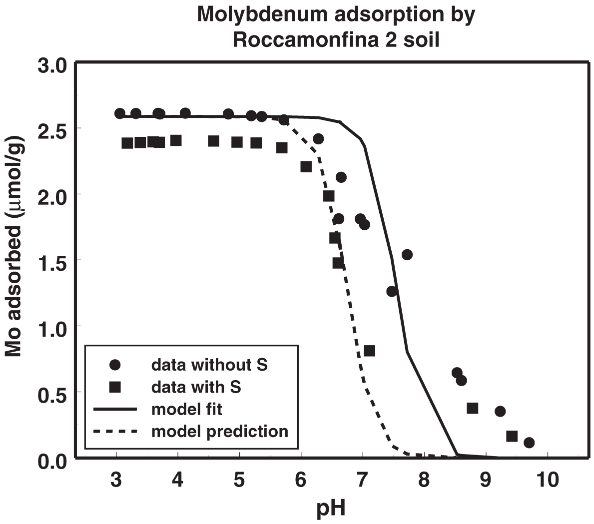

Figure 3. Molybdenum adsorption on Roccamonfina 2 soil. Circles represent the experimental Mo adsorption data without sulfate. Squares represent the experimental Mo adsorption data in the presence of equimolar sulfate. Model fits are represented by solid lines. Model predictions are represented by dashed lines.

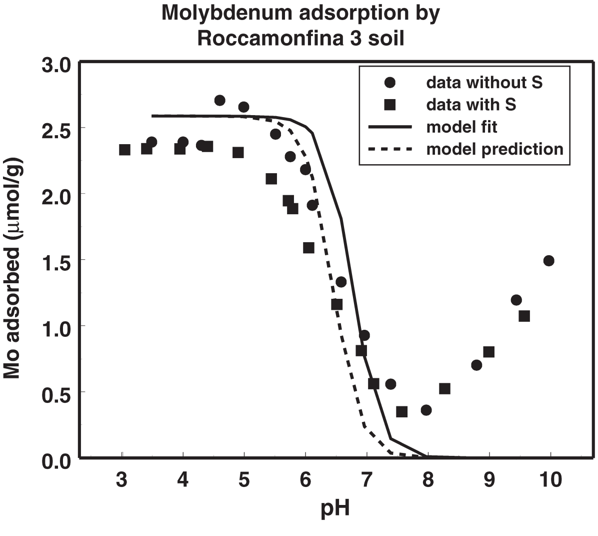

Figure 4. Molybdenum adsorption on Roccamonfina 3 soil. Circles represent the experimental Mo adsorption data without sulfate. Squares represent the experimental Mo adsorption data in the presence of equimolar sulfate. Model fits are represented by solid lines. Model predictions are represented by dashed lines.

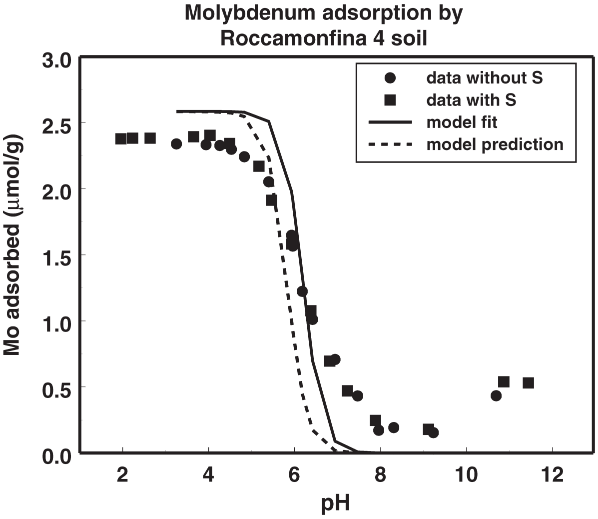

Figure 5. Molybdenum adsorption on Roccamonfina 4 soil. Circles represent the experimental Mo adsorption data without sulfate. Squares represent the experimental Mo adsorption data in the presence of equimolar sulfate. Model fits are represented by solid lines. Model predictions are represented by dashed lines.

presence of equimolar sulfate concentrations depressed Mo adsorption by about 15–20%, suggesting competition for a portion of the anion adsorbing sites.

The constant capacitance model was fit to the Mo adsorption envelopes of all of the soils using a monodentate surface configuration for adsorbed Mo. The ability of the constant capacitance model to describe Mo adsorption on the five soils is shown in Figures 1 to 5. The model was well able to describe the adsorption data. Deviations in model fit occurred only at pH values above the native pH values of the soils. In the model application, one adjustable parameter was optimized. This chemical model represents an advancement over Langmuir and Freundlich isotherm approaches that, even though they contain two empirical adjustable parameters, cannot predict changes in adsorption occurring with changes in solution pH. Table 2 provides values of the optimized surface complexation constant, log K_{Mo}(int). The average value of log $K_{Mo}(int) = 5.79 \pm 1.8$ is not statistically significantly different at the 95% level of confidence from the average value of log $K^1_{Mo}(int) = 4.84 \pm 0.88$ determined for 36 soils by Goldberg, Lesch, and Suarez (2002).

A comparison of the experimental results and the constant capacitance model predictions of Mo adsorption on the soils is presented in Figures 1 to 5. The predictions result from using the previously developed regression relation [Eq. (10)] to obtain the monodentate Mo surface complexation constant. The

Table 2. Constant capacitance model surface complexation constants

Soil	Fitted log K_{Mo}	Predicted log K_{Mo}
Naples	2.88	2.16
Roccamonfina 1	6.28	4.58
Roccamonfina 2	7.64	6.06
Roccamonfina 3	6.63	6.01
Roccamonfina 4	5.53	4.81
Average	5.79 ± 1.8	4.72 ± 1.6

Notes: K_{Mo} = Mo surface complexation constant.

ability of the model to predict the Mo adsorption data on the Roccamonfina soils (Figures 2 to 5) is very encouraging, especially because the prediction equation was determined on a set of soils primarily from California developed under different pedological conditions. The poor correspondence between experimental and predicted Mo adsorption data for the Naples soil (Figure 1) is likely due to the very low inorganic and organic C content of this soil. In our approach, the regression model [Eq. (10)] was used to obtain the surface complexation constant parameter for the constant capacitance model, which was then used to predict the soil specific Mo adsorption. This is in contrast to regression models that fit adsorption of a series of soils. The distinction is that by using the combined regression equation and the constant capacitance model, only soil chemical properties and not adsorption results are needed to predict soil-specific Mo adsorption data. Table 2 provides monodentate Mo surface complexation constants predicted by the regression model for the soils studied. The average predicted value of log $K_{Mo}(int) = 4.72 \pm 1.6$ is not statistically significantly different at the 95% level of confidence from the average fitted value of log $K_{Mo}(int) = 5.79 \pm 1.8$ or from the average predicted value of log $K^1_{Mo}(int) = 4.78 \pm 0.76$ determined for 36 soils by Goldberg Lesch, and Suarez (2002).

CONCLUSIONS

The constant capacitance model was able to fit Mo adsorption as a function of solution pH on the soils, studied. For four of the soil the constant capacitance model was able to accurately predict Mo adsorption. Prediction of Mo adsorption was not good for one soil of different mineralogy. The model predictions were obtained independent of any experimental measurement of Mo adsorption on these soils using values of easily measured soil chemical parameters. Because our model results are predictions, our approach uses zero adjustable parameters. That the prediction equation [Eq. (10)], developed from describing Mo adsorption envelopes on a set of soils primarily from California

(Goldberg, Lesch, and Suarez, 2002), was able to predict Mo adsorption on a set of volcanic ash soils from Italy is all the more encouraging. This result suggests wide applicability of the regression model prediction equation for describing Mo adsorption as a function of solution pH. Our prediction equations have been incorporated into the UNSATCHEM chemical speciation-transport model (Suarez and Simunek 1997), allowing us to simulate Mo concentrations in soil solution under diverse environmental and agricultural conditions.

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