Predicting Trace Element Adsorption by Soils Using Soil Chemical Parameters

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1 INTRODUCTION

Boron, molybdenum, and arsenic are trace elements that can be elevated in arid zone soils and waters. Boron is both an essential micronutrient element required for plant growth and toxic at elevated concentration. Crop yield losses can occur both under conditions of B deficiency and B toxicity. In arid areas, B toxicity occurs because of high levels of B in the soil solution and from additions of B via the irrigation water. Molybdenum is also an essential micronutrient element for plants and is potentially toxic especially to grazing animals. Cattle grazing on legumes on alkaline soils can be adversely affected by elevated Mo content. Molybdenum exerts its toxic effect on cattle by inducing a copper deficiency that is especially pronounced in the presence of sulfur. Arsenic is toxic to both plants and animals. Arsenic concentrations in soils and waters can become elevated as a result of application of arsenical pesticides, disposal of fly ash, mineral dissolution, mine drainage, and geothermal discharge. Agricultural drainage waters from some soils in arid regions are high in As. In oxidizing aerobic environments, the stable form of As is arsenate, As(V).

Adsorption of trace elements on soil mineral surfaces is important to managing trace element toxicity or deficiency. Availability of trace elements to plants is affected by a variety of factors including soil solution pH, soil texture, soil moisture, temperature, oxide content, carbonate content, organic matter content, and clay mineralogy. The dominant trace element adsorbing surfaces on soils are oxides, clay minerals, calcite, and organic matter. Careful quantification of soil solution trace element concentrations and characterization of trace element adsorption reactions on soil mineral surfaces is needed.

Trace element adsorption has been described using various modeling approaches including chemical models called surface complexation models, one of which is the constant capacitance model. The advantages of surface complexation models over empirical adsorption models, such as, the distribution coefficient and adsorption isotherm equations are that they define specific surface species, chemical reactions, mass balances, and charge balances. We have developed a general regression model to obtain soil B, Mo, and As(V) surface complexation constants for use in the constant capacitance model to predict adsorption of these ions. The constant capacitance model parameters are obtained from easily measured soil chemical properties: cation exchange capacity, surface area, organic carbon content, inorganic carbon content, iron oxide content, and aluminum oxide content. These are also soil properties that correlate with soil trace element adsorption capacity.

2 MATERIALS AND METHODS

Trace element adsorption was investigated using surface and subsurface samples from soils belonging to six different orders. The number of soil samples studied was 32 for B adsorption, 36 for Mo adsorption, and 49 for As(V) adsorption. The sets of soils were chosen to provide a wide range of soil chemical characteristics. Experimental methods used to determine the chemical properties are provided in Goldberg (2000).

Trace element adsorption isotherms were carried out in batch systems to determine adsorption envelopes, amount of ion adsorbed as a function of solution pH per fixed total ion concentration. Samples of soil were added to 50-mL centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution on a reciprocating shaker. This solution contained either 0.463 mmol/L B, 0.292 mmol/L Mo, or 0.02 mmol/L As(V) and had been adjusted to the desired pH range of 3 to 10 using 1 M HCl or 1 M NaOH. After reaction, the samples were centrifuged and the decantates analyzed for pH, filtered and analyzed for either B, Mo, or As concentration using inductively coupled plasma emission spectrometry.

A detailed discussion of the theory and assumptions of the constant capacitance model is provided by Goldberg (1992). Equations and input parameters for the application of the model to B, Mo, and As adsorption are listed in Goldberg et al. (2000), Goldberg et al. (2002), and Goldberg (2002), respectively.

3 RESULTS AND DISCUSSION

Boron adsorption increased with increasing solution pH, exhibited a maximum adsorption around pH 9, and decreased with further increases in solution pH (see Figure 1).
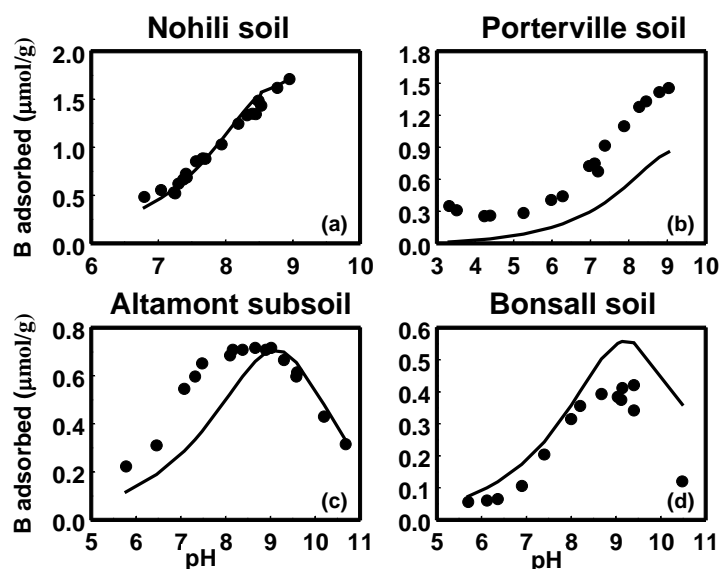

Figure 1. Prediction of B adsorption with the constant capacitance model on soils not used to obtain the prediction equations: (a) Nohili silt loam; (b) Porterville silty clay loam; (c) Altamont loam; (d) Bonsall loam. Circles represent experimental data. Model predictions are represented by solid lines.

Molybdenum adsorption was maximum in the pH range 2 to 5, decreased rapidly with increasing pH from pH 5 to 8, and was minimal above pH 9 (see Figure 2).

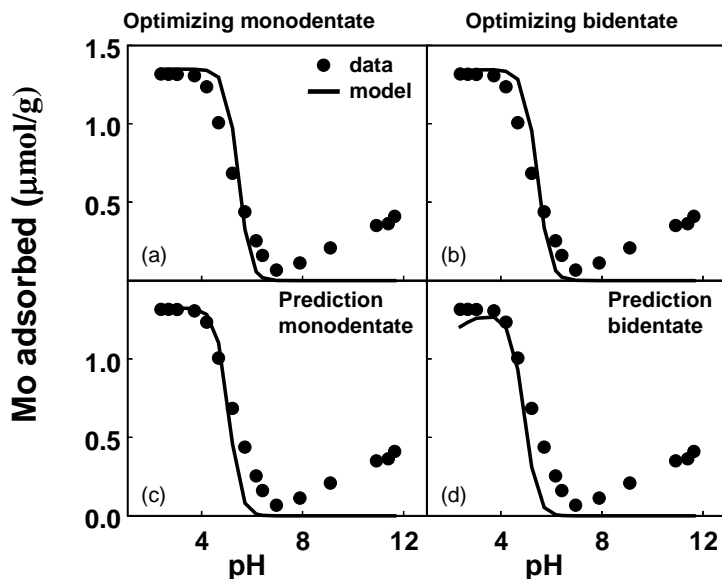**Molybdenum adsorption on Norge soil**

Figure 2.   Constant capacitance modeling of Mo adsorption on Norge soil: (a) monodentate fit; (b) bidentate fit; (c) monodentate prediction; (d) bidentate prediction. Circles represent experimental data. Model results are represented by solid lines.

Arsenate adsorption generally increased with increasing solution pH, exhibited a maximum in adsorption around pH 6 to 7, and decreased with further increases in solution pH (see Figure 3).

The constant capacitance model was fit to the trace element adsorption envelopes for all the soil samples. The quality of the model fits was universally good, as can be seen in Figures 2a and 2b for the example of Mo adsorption.

An exploratory data analysis revealed that the model surface complexation constants for all three trace elements were related to the log transformed chemical variables in a linear manner.   Therefore the following initial regression model was specified for each trace element and each surface complexation constant:

$$\ln K_i = b_{0i} + b_{1i}\ln(CEC) + b_{2i}\ln(SA) + b_{3i}\ln(OC) + b_{4i}\ln(IOC) + b_{5i}\ln(Fe) + b_{6i}\ln(Al) + \varepsilon \quad (1)$$

where the b parameters represent regression coefficients and ε the residual error component. Following   additional   statistical   analyses,   the   prediction   equations   for   the   surface complexation constants were found to be a function of: surface area, organic carbon content, inorganic carbon content, and aluminum oxide content for B adsorption; cation exchange capacity, organic carbon content, inorganic carbon content, and iron oxide content for Mo adsorption; and all six chemical properties for As(V) adsorption. The prediction equations were used to predict trace element surface complexation constants for soils that had not been used to obtain the regression model. This represents a completely independent evaluation of the ability of the constant capacitance model to predict trace element adsorption. The model predictive capability is shown in Figure 1 for B adsorption, Figure 2 for Mo adsorption, and Figure 3 for As(V) adsorption.
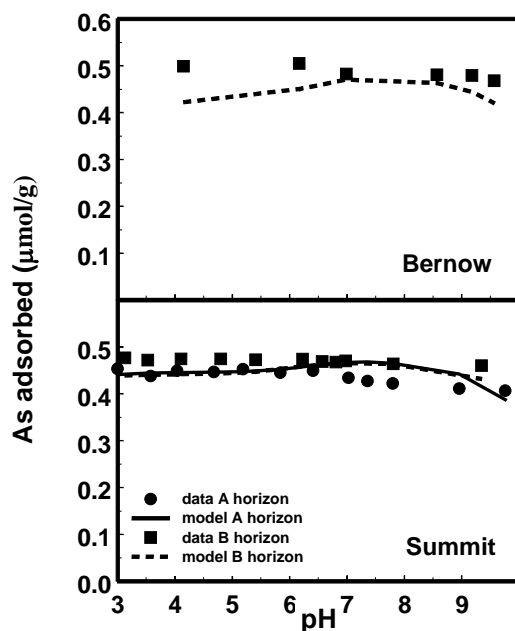
Figure 3. Prediction of As(V) adsorption with the constant capacitance model on soils not used to obtain the prediction equations. Circles represent experimental data for the A horizon. Squares represent experimental data for the B horizon. Model predictions are represented by solid lines for the A horizon and dashed lines for the B horizon.

The model was able to predict the shape of the adsorption envelopes for all three trace elements. For B adsorption, Figure 1a presents the best prediction, a quantitative representation of the data, Figure 1b shows the worst prediction, and Figures 1c and 1d present typical underprediction and overprediction, respectively. For Mo adsorption the model predictions, Figures 2c and 2d were almost as good as the model optimized fits, Figures 2a and 2b. Predictive capability of the constant capacitance model for As(V) adsorption was also good (see Figure 3).

4 CONCLUSIONS

Although prediction of trace element adsorption on some soils was only semi-quantitative, these predictions were obtained independent of any experimental measurement of trace element adsorption on these soils using values of only a few easily measured chemical parameters which are more often available. Since the model results are predictions, zero adjustable parameters are used. Incorporation of these prediction equations into chemical – speciation transport models will allow simulation of trace element concentrations under diverse agricultural and environmental conditions.

5 REFERENCES

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