ARSENIC PARTITIONING: MAKING PREDICTIONS USING PHREEQC

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Introduction

Arsenic species mobility in most natural waters is controlled by solid phase sorption (1,2). The literature indicates that quantitative evaluation of the sediment-water partitioning of many toxic metals, including arsenic, is best accomplished by a surface complexation approach (3,4,5). Equilibrium-condition, thermodynamics-based, numerical modeling is currently the most practical way to evaluate the competitive geochemical processes that affect the inorganic transport and toxicity of arsenic (6). It may be the only way to make predictions regarding arsenic persistence and mobility in the environment (7).

Surface complexation theories provide excellent fits to the data from laboratory experiments on arsenic sorption (8,9,10,11). There are only a small number of studies of that use attenuation by surface complexation to examine arsenic field relationships (3,12,13). The composition and concentration of the sorbing solid phase is very well known in the laboratory. This is in contrast to field studies where the composition and concentration of the sorbing solid phase(s) are unknown *a priori* and difficult to determine with either precision or accuracy. There are no published studies of how to determine the types and quantity of reactive surfaces in field samples for use in surface complexation modeling. Very little is known regarding the field application of laboratory derived surface complexation constants. No information was found in the literature on the level of error that might be expected during application of surface complexation modeling to arsenic in a field or natural setting.

We evaluated the error in estimating arsenic sorption using different conceptual models, published surface complexation constants and field data. PHREEQC (14) was used to simulate arsenic surface complexation in a small watershed with naturally high levels of arsenic and in sediments at two contaminated sites. Surface complexation mass-action coefficients were obtained from the literature in the generalized two-layer model form, or the data was refit using FITEQL or linear free energy relationships. The model fit was found very sensitive to the extraction method used. Large errors in model predictions result if the competition for sorption sites is not treated explicitly. A reasonable simulation of the observed arsenic concentrations is obtained using competitive complexation, sorption constants from the literature, detailed characterization the aqueous chemistry, solid phases occurring at field sites, and the PHREEQC model. It is apparent from our effort that small differences in the conceptual model and data collection techniques can have a large effect on the error of the simulation.

Sampling and Analysis

Data was obtained from analysis of collocated sediment and water samples from a high-arsenic watershed in Mexico and two contaminated sites in Florida. The total dissolved arsenic in Mexican waters ranged from 100 to 1100 ug/l and in the Floridian samples 10-500 ug/l. Water samples were also analyzed for a broad range of inorganic compounds. Mexico waters are silica-sodium-bicarbonate, pH 6.3-8.9 with a geothermal signature and ~1000 mg/l total dissolved solids. Floridian waters were low dissolved solids (~100 mg/l) with either a calcium-bicarbonate pH 7.0, or sodium-bicarbonate pH 5.0 character.

Arsenic analysis was by Zeeman corrected graphite furnace atomic absorption spectrophotometry (GFAA). Arsenic species separation was accomplished in the field using ion-

exchange technology. Other elements were analyzed by GFAA or flame atomic adsorption spectrophotometry. Anions were determined by ion chromatography. Arsenic sorbed to the reactive phases and bound in iron and aluminum phases was measured using microwave extraction with HNO_3 (15), the Tessier (16) method of partial extractions, amorphous phase dissolution by the method of Chao (17), and a citrate-dithionate-bicarbonate method.

Conceptual Model

We used the following general assumptions to apply equilibrium methods: 1.) The sediment-water systems were at steady state with respect to discharge, chemical flux, and chemical equilibria at the time of sampling. 2.) Known arsenic redox disequilibrium effects on total sorbed arsenic are assumed small. 3.) Arsenic attenuation in the sediments is dominantly an inorganic process and can be modeled as such, although there is up to 10% organic arsenic present and known organic solid phases that can sorb arsenic.

Preliminary modeling of saturation indices and petrographic examination of sediments indicated the presence of iron phases as goethite and ferrihydrite with less conclusive evidence for amorphous aluminum hydroxide or gibbsite. Using the values for iron and aluminum obtained for each extraction procedure, with sample-specific porosity and bulk density, four mineral assemblages (goethite, goethite and gibbsite, ferrihydrite, ferrihydrite and gibbsite) are created. Each combination of mineral surface assemblage and observed water chemistry is a conceptual model to be tested in a surface complexation framework. The difference between the modeled arsenic concentration on sediments and the arsenic observed in the extract is representative of the error in that conceptual model.

Numerical Modeling

The United States Geological Survey computer code PHREEQC version 1.6 was used for all simulations. The WATEQ4F thermodynamic database formed the core to which surface complexation parameters were added. PHREEQC was used for calculation of saturation indices, sensitivity analysis of parameters such as Eh, pH and temperature, modeling of mixing of stream water of different compositions and mechanistic, competitive, surface complexation of arsenic. The surface complexation routine used was the generalized two-layer model (6,9,14). Competition between arsenic and other anions and cations sorbing phases for the finite number of sites is allowed (11,18,19). Each mineral assemblage is allowed to come to equilibrium by simulating the flushing of many pore volumes of the observed water chemistry through the sediment-mineral surface assemblage.

Results and Conclusions

The model output was evaluated using the ratio 'R' of modeled to observed concentration of arsenic on the sediments. The choice of sorbing iron phase, goethite vs. ferrihydrite, is one of the most significant factors effecting model fit. Figure 1 presents the R-values obtained for a set of common conceptual models for 20 samples from Mexico as compared to organic carbon by loss on ignition (TOC). The main difference between modeling goethite and ferrihydrite surface complexation is that ferrihydrite has a surface area over 13 times greater than the goethite. As shown clearly in Figure 1 the overall result of selection of goethite over ferrihydrite is under prediction of the sorbed arsenic concentration by orders of magnitude.

The HNO_3 extractions with surfaces defined as ferrihydrite and gibbsite provided the best model fits for the Mexico samples. Modeling of the Florida samples that were extracted using

HNO₃ also provided reasonable fits to the observed data, but the citrate-bicarbonate-dithionate extractions provide the best fit overall. Citrate-bicarbonate-dithionate extractions were not used with the Mexico samples so direct comparison between all sites for this extraction was not possible.

Application of surface complexation modeling to three sites has taught us that field application of surface complexation modeling will rarely be successful if competition is neglected and this simplification should be avoided in

Figure 1. Model fit as a ratio of modeled to observed arsenic on sediments. R equal to unity is a perfect fit.

model conceptualization. The error of neglecting competition by common compounds such as bicarbonate or silicic acid can equal or exceed the error from inappropriate choice of mineral phases.

Our application of laboratory surface complexation parameters to three complex natural systems was successful. However, our modeling could be better tested if there were more complexation parameters available for mineral surfaces and common anions and cations, particularly carbonate-bicarbonate and silica. The continued development of field and analytical protocols to support surface complexation modeling is clearly needed.

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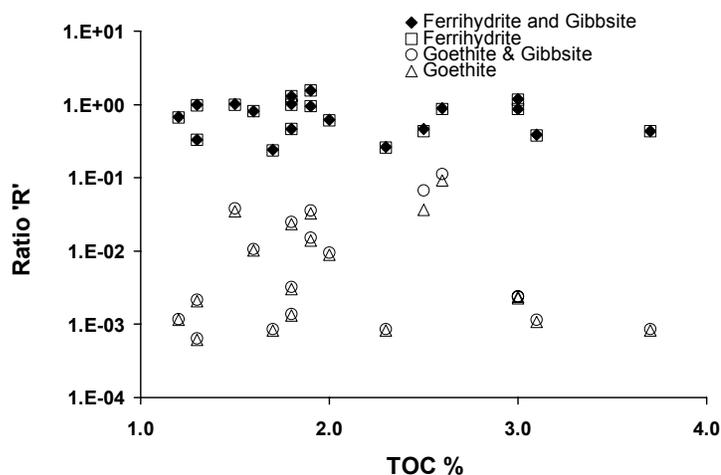
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