Appropriateness of equilibrium assumptions for determining metal distribution and transport in bacteria-bearing porous media

Benjamin F. Turner⁎, Jeremy B. Fein

Department of Civil Engineering and Geological Sciences 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, IN 46556, United States

Received 6 June 2006; received in revised form 26 February 2007; accepted 3 March 2007

Editor: D. Rickard

Abstract

The fate and transport of strongly-sorbed contaminants in aquifers is tied to the mobility of the surfaces to which they are adsorbed. Mobile particulates, including mineral colloids, natural organic matter, or microbes, can enhance the mobility of contaminants that would otherwise be adsorbed to stationary surfaces. In this study, we compare numerical transport simulations of systems involving dissolved metals and microbial suspensions with previously published experimental results. The transport simulations utilize a finite difference solute transport scheme, a colloid attachment term, and a Newton–Raphson chemical speciation solver assuming thermodynamic equilibrium in the metal distribution between solution, mobile surfaces, and stationary surfaces. While model predictions of metal breakthrough are of mixed quality, adjustment of model equilibrium constants is adequate to provide accurate fits to observed breakthrough curves. Therefore, the idealized behaviors apparent in experimental breakthrough curves indicate metal transport under equilibrium sorption conditions, and hence the assumption of chemical equilibrium used in the model is appropriate. Since flow rates in the column experiments are fast compared to most flow rates in aquifers, we conclude that the kinetics of metal redistribution are fast enough that an assumption of chemical equilibrium would be appropriate for modeling coupled solute–colloid transport in pore environments where water flow is controlled by advective transport under water velocity conditions typical for most aquifers.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Metals; Bacteria; Aquifer; Cadmium; Transport; Equilibrium

1. Introduction

Aqueous transition metal cations (e.g. Cd²⁺, Cu²⁺, Pb²⁺, Zn²⁺) adsorb strongly onto surfaces under the near-neutral pH conditions characteristic of most aquifers (Schindler et al., 1976; Stumm, 1992). In an aquifer setting, these surfaces can be either mobile (e.g. clays, organic particulates, or microbes) or stationary, so the mobility of the metal cations is closely linked to the transport behavior of the particulate surfaces. In geologic systems, a solute is redistributed among three compartments: 1) dissolved in solution; 2) adsorbed to a stationary surface; and 3) adsorbed to a mobile surface. An important consideration when characterizing or modeling metal distribution in geologic systems is whether the assumption of chemical equilibrium is justified.

A number of authors have investigated the appropriateness of various equilibrium assumptions in aquifer systems with soluble adsorbates (Goltz and Roberts,
Transport of a solute or colloids through porous medium is governed by the onedimensional advection-reaction-dispersion equation

\[
\left( \frac{\partial C}{\partial t} \right)_x = D_t \left( \frac{\partial^2 C}{\partial x^2} \right) - v \left( \frac{\partial C}{\partial x} \right)_t - \frac{\partial q}{\partial t}
\]

(1)

In this study, we must account for not only physical solute transport processes, but also transport processes affecting the bacteria, and chemical mass transfer of Cd between the solution and stationary and moving surfaces. In this section, we describe the model development by first describing the mathematical modeling of the physical transport processes. This discussion is followed by a description of the chemical equilibrium models incorporated into the transport model, and we conclude with a description of our approach to model parameterization.

2.1. Solute and colloid transport

Transport of a solute or colloids through porous medium is governed by the onedimensional advection-reaction-dispersion equation

\[
\left( \frac{\partial C}{\partial t} \right)_x = D_t \left( \frac{\partial^2 C}{\partial x^2} \right) - v \left( \frac{\partial C}{\partial x} \right)_t - \frac{\partial q}{\partial t}
\]
where \( C \) represents the concentration of a given solute or colloid, \( x \) represents position, \( D_L \) is the hydrodynamic dispersion coefficient, and \( v \) is fluid velocity. The term \( \partial q/\partial t \) is a source/sink term for the solute or colloid, representing the mass transfer between stationary surfaces and solution or suspension. The governing equation is solved in this study by the finite difference split-operator scheme, described by Appelo and Postma (1993), in which solute equilibrium reactions are calculated both after the advection step and after the dispersion step, reducing numerical dispersion (i.e. apparent dispersion produced by the solution algorithm) and the need to iterate between chemistry and transport (Parkhurst and Appelo, 1999). In the scheme, the dispersion step is executed as several mixing steps involving mixing between adjacent cells.

Deposition of colloids is governed by the following equation (substituting for the sink term in Eq. (1)):

\[
\frac{\partial C_S}{\partial t} = -C_S z_0 (1 - kC_A)
\]

(2)

where \( C_T = C_S + C_A \), and \( C_T, C_S \) and \( C_A \) are the total, suspended, and attached colloid concentrations, respectively, \( z_0 \) is the rate constant for attachment at zero surface coverage, and \( k \) is a surface blocking parameter. The equation is solved over a given time interval by substitution and integration:

\[
\int_{C_{S1}}^{C_{S2}} \frac{1}{(1-kC_T)C_S + kC_S^2} dC_S = \int_{t_1}^{t_2} -z_0 dt
\]

(3)

The solution is

\[
C_{S2} = \frac{(1-kC_T)}{e^c - k}
\]

(4)

where

\[
c = (1-kC_T)\left(z_0\Delta t + \frac{1}{1-kC_T}\ln\left(\frac{1-kC_T + kC_{S1}}{C_{S1}}\right)\right)
\]

(5)

and \( C_{S1} \) and \( C_{S2} \) are the suspended colloid concentrations at the beginning and end of the time interval, respectively. Eq. (2) is solved at each mixing step in the split-operator scheme.

2.2. Chemical equilibrium

In the experiment of Yee and Fein (2002), Cd is present either as an aqueous species, adsorbed to colloid (bacterial) surfaces (either moving or stationary), or adsorbed to stationary mineral grain surfaces. We use chemical thermodynamics, assuming the system components to be in equilibrium, to calculate the distribution of Cd between these reservoirs. We use literature values for mineral and bacterial surface site concentrations and Cd-surface stability constants to predict the distribution and transport of Cd in the simulated systems, and we compare these predictions with the experimental observations of Yee and Fein (2002). Mathematically, we solve the chemical equilibrium problem using a Newton–Raphson solver similar in principle to solvers used by MINTEQA2 (Allison et al., 1991) and PHREEQC (Parkhurst and Appelo, 1999). The solute/colloid transport algorithm keeps track of the partitioning of solute between solution, moving colloid surfaces, attached colloid surfaces, and stationary mineral grain surfaces.

The chemical speciation problem in each simulation is parameterized to correspond to the specific experimental conditions of the experiments to which the simulations are to be compared. The experiments of Yee and Fein (2002) involve aqueous Cd, the bacterial species Bacillus subtilis, and either quartz sand or ferrihydate-coated quartz sand in 0.1 M NaNO\(_3\) over the pH range 3.6 to 8.3. We use the Davies equation for calculating activity coefficients for Cd\(_{2+}\), which is appropriate for the experimental ionic strength of 0.1 M (Langmuir, 1997).

Surface acidity and adsorption of Cd to B. subtilis is described by Fein et al. (1997) using a constant capacitance model (Table 1), with Cd adsorption occurring primarily onto carboxyl and phosphoryl groups:

\[
(R–COO)H^+ \rightleftharpoons (R–COO)^- + H^+; K_1 = \frac{[\text{Cd}^{2+}]}{[\text{Cd}^{2+}][\text{Cd}^{2+}]} \frac{e^{\text{PH}/RT}}{RT} \]

(6)

\[
(R–PO_4)H^0 \rightleftharpoons (R–PO_4)^- + H^+; K_2 = \frac{[\text{Cd}^{2+}]}{[\text{Cd}^{2+}][\text{Cd}^{2+}]} \frac{e^{\text{PH}/RT}}{RT} \]

(7)

\[
(R–O)H^0 \rightleftharpoons (R–O)^- + H^+; K_3 = \frac{[\text{Cd}^{2+}]}{[\text{Cd}^{2+}][\text{Cd}^{2+}]} \frac{e^{\text{PH}/RT}}{RT} \]

(8)

\[
\text{Cd}^{2+} + (R–COO)^- \rightleftharpoons (R–COO)\text{Cd}^{2+}; K_{\text{ads1}} = \frac{[\text{Cd}^{2+}][\text{Cd}^{2+}]}{[\text{Cd}^{2+}][\text{Cd}^{2+}]} \frac{e^{\text{PH}/RT}}{RT} \]

(9)

\[
\text{Cd}^{2+} + (R–PO_4)^- \rightleftharpoons (R–PO_4)\text{Cd}^{2+}; K_{\text{ads2}} = \frac{[\text{Cd}^{2+}][\text{Cd}^{2+}]}{[\text{Cd}^{2+}][\text{Cd}^{2+}]} \frac{e^{\text{PH}/RT}}{RT} \]

(10)
Table 1
Parameters for Cd–bacteria adsorption model of Fein et al. (1997)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_1$</td>
<td>−4.82</td>
</tr>
<tr>
<td>log $K_2$</td>
<td>−6.9</td>
</tr>
<tr>
<td>log $K_3$</td>
<td>−9.4</td>
</tr>
<tr>
<td>log $K_{ads1}$</td>
<td>3.4</td>
</tr>
<tr>
<td>log $K_{ads2}$</td>
<td>5.4</td>
</tr>
<tr>
<td>(R–COO)$_{tot}$</td>
<td>$1.2 \times 10^{-4}$ mol g$^{-1}$</td>
</tr>
<tr>
<td>(R–PO$<em>4$)$</em>{tot}$</td>
<td>$4.4 \times 10^{-5}$ mol g$^{-1}$</td>
</tr>
<tr>
<td>(R–O)$_{tot}$</td>
<td>$6.2 \times 10^{-5}$ mol g$^{-1}$</td>
</tr>
<tr>
<td>Bacterial surface area</td>
<td>140 m$^2$g$^{-1}$</td>
</tr>
<tr>
<td>Capacitance</td>
<td>8.0 Fm$^{-2}$</td>
</tr>
</tbody>
</table>

aSite concentrations in mol per g of bacteria (wet weight).

where brackets indicate species concentration, and $a$ represents the activity of the subscripted species. Data used by Fein et al. (1997) to define equilibrium constant and site concentration values were collected in 0.1 M NaNO$_3$.

We test the ability of three different models to account for adsorption of Cd to silica surfaces (Table 2). Two of the models involve a two-site non-electrostatic model (Schindler et al., 1976; Brady, 1992), and the third uses a one-site double layer model (Benyahya and Garnier, 1999). The models of Schindler et al. and Brady describe Cd adsorption as follows:

$$
\text{Cd}^{2+} + (\equiv \text{Si}–\text{O})^{\text{H}}^0 \rightleftharpoons (\equiv \text{Si}–\text{O})\text{Cd}^+ + \text{H}^+; \quad (11)
$$

$$
K_{\text{SiCdl}} = \frac{\{(\equiv \text{Si}–\text{O})\text{Cd}^+\}a_{\text{H}^+}}{[\text{Cd}^{2+}]\{(\equiv \text{Si}–\text{O})^{\text{H}}^0\}}
$$

$$
\text{Cd}^{2+} + 2(\equiv \text{Si}–\text{O})^{\text{H}}^0 \rightleftharpoons (\equiv \text{Si}–\text{O})_2\text{Cd}^0 + 2\text{H}^+; \quad (12)
$$

$$
K_{\text{SiCd2}} = \frac{\{(\equiv \text{Si}–\text{O})_2\text{Cd}^0\}a_{\text{H}_2^{\text{+}}}}{[\text{Cd}^{2+}]\{(\equiv \text{Si}–\text{O})^{\text{H}}^0\}^2}
$$

where braces indicate surface species concentration in mol kg$^{-1}$. The authors also describe proton exchange with the silica with the reaction

$$
(\equiv \text{Si}–\text{O})^{\text{H}}^0 \rightleftharpoons (\equiv \text{Si}–\text{O})^- + \text{H}^+ \quad (13)
$$

subject to the mass balance constraint

$$
[(\equiv \text{Si}–\text{O})]_{\text{tot}} = [(\equiv \text{Si}–\text{O})^{\text{H}}^0] + [(\equiv \text{Si}–\text{O})^-]. \quad (14)
$$

Instead of using a conventional mass action expression, however, the authors use an empirical expression to account for the concentration of $(\equiv \text{Si}–\text{O})^-$:

$$
[(\equiv \text{Si}–\text{O})^-] = \frac{1}{a} 10^{\log \text{pH}/b+c} \quad (15)
$$

where $a$, $b$, and $c$ are empirical constants (Table 2). Schindler et al. (1976) and Brady (1992) both determined stability constants and site concentrations under conditions of 1.0 M NaClO$_4$ background electrolyte, 25 °C, using amorphous silica “Aerosil 200,” and assuming a surface potential of zero.

Although the models of Schindler et al. (1976) and Brady (1992) have been widely cited, both models exhibit important limitations that impede their application beyond the specific experimental conditions under which the models were parameterized: 1) Cd$^{2+}$ solution concentrations are used in the mass action expressions instead of activities; 2) surface species concentrations in the mass action expressions are expressed as relative to adsorbent mass rather than solution volume or mass of water; and 3) an unconventional empirical expression is used to account for $[(\equiv \text{Si}–\text{O})^-]$ rather than a conventional mass action expression. To address the first limitation and to extend the applicability of the model to the experimental conditions of Yee and Fein (2002), we convert the mass action expressions to include Cd$^{2+}$ activity rather than concentration using an activity coefficient of 0.2504 for Cd$^{2+}$ at 1.0 M calculated using the Truesdell–Jones equation. The expression of surface species concentrations as mol per g of adsorbent is particularly problematic in Eq. (12), making the expression meaningless when applied to adsorbents with different (site concentration)/(adsorbent mass) ratios than those used by Schindler et al. (1976) or Brady (1992). When the surface site concentrations are given as mol per g of adsorbent, the value of the ion activity product is effectively dependent on the specific surface area of the adsorbent, rather than on the amount of surface species available to solution. This is not problematic in Eq. (11) because the stoichiometry results in the surface species

Table 2
Parameters for Cd–silica adsorption models

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_{Si}$</td>
<td>NA</td>
<td>NA</td>
<td>−7.71</td>
</tr>
<tr>
<td>log $k_{cd1}$</td>
<td>−6.09</td>
<td>−7.0</td>
<td>−5.57</td>
</tr>
<tr>
<td>log $k_{cd2}$</td>
<td>−14.20</td>
<td>−12.8</td>
<td>NA</td>
</tr>
<tr>
<td>Corrected log $k_{cd1}$</td>
<td>−5.49</td>
<td>−6.4</td>
<td>NA</td>
</tr>
<tr>
<td>Corrected log $k_{cd2}$</td>
<td>−11.9</td>
<td>−10.5</td>
<td>NA</td>
</tr>
<tr>
<td>$(\equiv \text{Si}–\text{O})_{tot}$</td>
<td>$9.06 \times 10^{-6}$ mol m$^{-2}$</td>
<td>$7.25 \times 10^{-6}$ mol m$^{-2}$</td>
<td>$3.9 \times 10^{-6}$ mol m$^{-2}$</td>
</tr>
<tr>
<td>$a$</td>
<td>1.45</td>
<td>1.45</td>
<td>NA</td>
</tr>
<tr>
<td>$b$</td>
<td>0.1923</td>
<td>0.1930</td>
<td>NA</td>
</tr>
<tr>
<td>$c$</td>
<td>−5.349</td>
<td>−5.31</td>
<td>NA</td>
</tr>
</tbody>
</table>
concentration dimensions canceling out. However, in Eq. (12), the surface species concentration dimensions do not cancel out due to the stoichiometry of the adsorption reaction. Hence, in order to apply the model to our system, we convert the mass action expressions to forms that can be applied to systems other than the experimental systems of Schindler et al. (1976) and Brady (1992):

\[ K_{SiCd1} = \frac{[\equiv Si-O(OH)]_{aH^+}}{[\equiv Si-O(OH)]_{H^+}} \]  

\[ K_{SiCd2} = \frac{[\equiv Si-O(OH)]_{aH^+}}{[\equiv Si-O(OH)]_{H^+}} \]  

where brackets, again, represent concentrations in terms of moles of sites per L of solution. Corrected log \( K \) values are reported in Table 2. Although the practice of using dimensions of moles of sites per solid mass for surface species in mass action expressions was advocated by Stumm (1992), the practice of using site concentrations of moles of sites per to solution volume as used by Dzombak and Morel (1990) is less problematic given reaction stoichiometries as represented by Eq. (12). The unconventional method of estimating \([\equiv Si-O(OH)]\) by Schindler et al. (1976) and Brady (1992) (Eq. (15)) cannot be used in commonly used speciation calculators such as MINTEQA2 and PHREEQC. However, since we utilize a custom-built speciation solver in our transport code, we utilize this expression directly to account for \([\equiv Si-O(OH)]\) concentrations. Another limitation inherent in Eq. (15) is that \([\equiv Si-O(OH)]\) varies only with pH, regardless of the amount of Cd adsorbed. This assumption is only appropriate for systems where \([\equiv Si-O(OH)] \ll [\equiv Si-O(OH)]_{tot}\) and \([\equiv Si-O(OH)]_{2Cd} \ll [\equiv Si-O(OH)]_{tot}\) which is the case for the experimental system of Yee and Fein (2002).

Benyahya and Garnier (1999) developed their model using silica gel in a 0.05 M NaNO\(_3\) background electrolyte. Their double layer model is described as

\[ (=Si-O(OH)^+) = (=Si-O(OH)^+) + H^+; K_{Si} = \frac{[\equiv Si-O(OH)]_{aH^+}}{[\equiv Si-O(OH)]_{H^+}} \]  

\[ Cd^{2+} + (=Si-O(OH)^+) = (=Si-O(OH)^+) + H^+; \]  

\[ K_{CdSi1} = \frac{[\equiv Si-O(OH)]_{aH^+}}{[\equiv Si-O(OH)]_{H^+}} \]  

where \( F \) is Faraday’s constant, \( \Psi \) is surface potential, \( R \) is the ideal gas constant, and \( T \) is absolute temperature. Model parameters are given in Table 2.

We model the adsorption of Cd to ferrihydrite using the two-site double layer model of Dzombak and Morel (1990):

\[ (=Fe^e(OH)^+) = (=Fe^e(OH)^+) + H^+; K_{Fe1} = \frac{[\equiv Fe^e(OH)^+]_{aH^+}}{[\equiv Fe^e(OH)^+]_{H^+}} \]  

\[ (=Fe^e(OH)^+) = (=Fe^e(OH)^+) + H^+; K_{Fe2} = \frac{[\equiv Fe^e(OH)^+]_{aH^+}}{[\equiv Fe^e(OH)^+]_{H^+}} \]  

\[ (=Fe^e(OH)^+) = (=Fe^e(OH)^+) + H^+; K_{Fe3} = \frac{[\equiv Fe^e(OH)^+]_{aH^+}}{[\equiv Fe^e(OH)^+]_{H^+}} \]  

\[ (=Fe^e(OH)^+) = (=Fe^e(OH)^+) + H^+; K_{Fe4} = \frac{[\equiv Fe^e(OH)^+]_{aH^+}}{[\equiv Fe^e(OH)^+]_{H^+}} \]  

where parameters are tabulated in Table 3. Dzombak and Morel (1990) determined model parameters under varied background electrolyte strengths and using synthetic ferrihydrite.

We use the bacterial surface area and site concentrations tabulated in Table 1. Mineral surface site
concentrations are estimated using the mineral surface areas in Table 4 and site densities in Tables 2 and 3.

2.3. Parameterization of model

Transport simulation parameters (Table 4) were derived directly from reported values where possible. Based on the average breakthrough of two reported experimental conservative tracer curves, an experimental lag time of 142 s (corresponding to the travel time through tubing external to the column) was added to simulation output. Our simulated tracer breakthrough curve, using a dispersion coefficient value of 1.0 cm, is reasonably representative of the two reported curves (Fig. 1). Colloid attachment parameters $\alpha_0$ and $k$ (Table 5) were obtained for each experiment by matching simulated bacterial breakthrough curves with experimental curves. The simulated bacterial breakthrough curves reasonably represent the bacterial transport behavior (Fig. 1). Although colloid attachment parameters had to be determined through a fitting procedure using experimental results, we stress that the chemical equilibrium model parameters (Tables 1–3) were obtained directly from the literature sources cited, yielding independent predictions of the experimental systems and, thus, the comparison between calculated and observed Cd distributions is a valid and rigorous test of the assumption of chemical equilibrium that is a foundation of the modeling approach.

3. Results and discussion

In Figs. 2–5, we compare simulated Cd breakthrough curves to experimental curves in systems with and without bacteria using surface complexation models from the literature. In systems without bacteria, agreement between model-predicted Cd breakthrough and experimental observation is of mixed quality. For the quartz system (Fig. 2), there is good agreement at pH 3.6, while all models at pH 8.3 predict faster breakthrough (and less adsorption) than observed. At pH 3.6, the simulation is insensitive to adsorption model parameters since adsorption is negligible and hence Cd breakthrough is virtually conservative. At pH 8.3, the models substantially under-predict adsorption, reflecting the sensitivity of the transport simulation to adsorption model parameters for this system at this pH. For the ferrihydrite system (Fig. 3), the model predicts a slightly faster breakthrough, indicating that the speciation model significantly under-predicts adsorption of Cd. However, the shapes of model-predicted and experimental breakthrough curves are similar for the ferrihydrite system. In each abiotic system where adsorption is significant, the models under-predict adsorption.

In systems containing bacteria, the observed breakthrough of aqueous and total Cd are reasonably well predicted in both the quartz (at pH 7.6: Fig. 4) and ferrihydrite (at pH 5.7 and 6.6: Fig. 5) systems. In these systems, the observed aqueous Cd breakthrough is characterized by a retarded sinusoidal curve that

<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column and transport parameters</td>
</tr>
<tr>
<td>Mineral surface area$^a$</td>
</tr>
<tr>
<td>Mineral mass in column$^a$</td>
</tr>
<tr>
<td>Pore volume$^d$</td>
</tr>
<tr>
<td>Mineral mass per solution volume$^d$</td>
</tr>
<tr>
<td>Porosity$^d$</td>
</tr>
<tr>
<td>$D^f$</td>
</tr>
<tr>
<td>$v^f$</td>
</tr>
<tr>
<td>Experimental lag time$^g$</td>
</tr>
</tbody>
</table>

$^a$Values reported by Yee and Fein (2002).$^b$Quartz sand.$^c$Ferrihydrite-coated sand.$^d$Based on specific gravity of 2.65, and column length and diameter of 10 cm and 1 cm, respectively (pore volume = 0.25 $\pi$ · length · diameter$^2$ – $M_{\text{min}} G^{-1} \rho_w^{-1}$, where $M_{\text{min}}$ is mineral mass, $G$ is specific gravity, and $\rho_w$ is the density of water).$^e$Value fitted to experimental breakthrough curves.$^f$Based on reported flow rate of 0.035 mL s$^{-1}$.$^g$Based on experimental breakthrough curves.

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters$^a$ for colloid attachment models</td>
</tr>
<tr>
<td>System</td>
</tr>
<tr>
<td>Quartz, pH 7.6</td>
</tr>
<tr>
<td>Ferrihydrite, pH 5.7</td>
</tr>
<tr>
<td>Ferrihydrite, pH 6.6</td>
</tr>
</tbody>
</table>

$^a$Values obtained by fitting simulated bacterial breakthrough curves to observed experimental curves.

---

Fig. 1. Comparison of model simulations with experimental breakthrough curves for conservative tracer and bacteria. Solid lines represent simulations. Experimental data from Yee and Fein (2002).
plateaus at a steady-state concentration. The concentration of total Cd (aqueous Cd plus Cd adsorbed to moving cells) increases as the effluent concentration of bacteria approaches C₀. Changes in pH and mineralogy are accounted for reasonably, and relatively minor discrepancies in retardation time and/or plateau concentration likely result uncertainties in the parameters of the adsorption models. In the quartz system, the reasonable agreement between simulated and experimental breakthrough curves are due to the ability of the Cd–bacteria adsorption model of Fein et al. (1997) to predict adsorption, and the ability of the fitted colloid transport submodel to match adsorption. The Cd–quartz adsorption models are relatively insensitive to uncertainty at pH 7.6 because Cd adsorption onto Si sites is low. Discrepancy in the total Cd breakthrough curves in the quartz system between 250 and 750 s is largely due to a minor discrepancy between simulated and observed bacterial breakthrough (Fig. 1).

A sensitivity analysis of the ferrihydrite system at pH 6.6 (Fig. 6) reveals that the steady-state plateau in the concentration of dissolved Cd is controlled by adsorption to bacterial cells, and that retardation in Cd breakthrough is controlled by Cd adsorption to ferrihydrite. Since the adjustment Cd–mineral equilibrium constants affects the time of initial breakthrough of Cd (Fig. 6a), it
is apparent that retardation of breakthrough is controlled by adsorption to stationary mineral surfaces. Likewise, since the adjustment of Cd–bacteria equilibrium constants affects the steady state value of dissolved Cd (Fig. 6b), it is clear that the plateau is controlled by adsorption to bacteria. Therefore, the under-prediction of the aqueous Cd plateau in Figs. 4 and 5 is due to a slight over-prediction of Cd adsorption to the bacterial cells. The qualitative agreement between the idealized behaviors inherent in the simulations and the measured breakthrough curves indicate Cd transport under essentially equilibrium conditions. Therefore, the assumption that chemical equilibrium controls Cd distributions in the transport experiments is appropriate. The published equilibrium models of Fein et al. (1997) and Dzombak and Morel (1990) used here yield reasonably accurate predictions of Cd transport for the Cd–ferrihydrite system.

The poor prediction of Cd adsorption onto quartz in the absence of bacteria at pH 8.3 by the models of Schindler et al. (1976), Brady (1992) and Benyahya and Garnier (1999) can be explained largely by the dissimilar substrate materials (amorphous silica rather than quartz) and dissimilar ionic strengths (1.0 and 0.05 M rather than 0.1 M) used in their respective experimental studies compared with those used in the experiments by Yee and Fein (2002). Also, the Cd–silica adsorption model of Benyahya and Garnier (1999) is a one-site model that fits poorly with the data from which it was derived, resulting in an adsorption envelope with respect to pH that is much too narrow. In contrast, the two-site models of Schindler et al. (1976) and Brady (1992) fit their respective data sets very well. While the above models underpredict adsorption in the experimental system investigated here, the log $K$ values can be adjusted so that accurate predictions of the pH 8.3 abiotic quartz system are made (Fig. 7). Using these adjusted $K$ values to generate new predictions of the Cd transport behavior results in negligible differences in the predicted breakthrough curves for the abiotic quartz experiment at pH 3.6, and minimal differences in the predicted breakthrough curves for the pH 7.6 quartz experiments that contained bacteria.

Fig. 5. Comparison of model simulations with experimental breakthrough curves at (a) pH 5.7 and (b) pH 6.6 for systems involving Cd and ferrihydrite-coated quartz sand, and bacteria. Cd concentration is $7.9 \times 10^{-6}$ mol L$^{-1}$. Bacterial concentration 1.0 g L$^{-1}$. Experimental data from Yee and Fein (2002).

Fig. 6. Sensitivity of simulation output to chemical equilibrium constants for system involving Cd–ferrihydrite-coated quartz sand, and bacteria. Log $K$ values for (a) Cd–ferrihydrite and (b) Cd–bacteria adsorption mass action expressions were adjusted by the values indicated. Cd concentration is $7.9 \times 10^{-6}$ mol L$^{-1}$. Bacterial concentration 1.0 g L$^{-1}$. 
While the quantity of adsorption can be matched in this way, the shape of the breakthrough curves are dependent on the model. This effect appears to be controlled by the adsorption isotherm implied by the model (Fig. 8). The more convex shape of the isotherm implied by the Benyahya and Garnier (1999) model apparently causes adsorbed Cd to more quickly reach a steady-state concentration than the less convex isotherms, resulting in a steeper breakthrough curve than what was observed experimentally (Fig. 7).

As discussed above, the sensitivity of the Cd transport simulation to chemical equilibrium model parameters is dependent on the speciation of Cd in the system. Where the concentration of adsorbed Cd is negligible, for example, the predicted transport behavior is not sensitive to the adsorption model. According to a speciation diagram calculated for the Cd–quartz–bacteria system (Fig. 9a), adsorption of Cd to quartz is probably small at pH 7.6. Hence the transport simulation for this system is relatively insensitive to uncertainty in the Cd–quartz adsorption models at pH 7.6 in the presence of bacteria, but highly sensitive at pH 8.3 without bacteria.

The Cd–bacteria and Cd–ferrihydrite models appear to describe Cd adsorption in these systems with reasonable accuracy. In both the absence and presence of bacteria, the observed breakthrough of aqueous Cd exhibits behavior characteristic of transport under...
equilibrium conditions. Idealized equilibrium transport behavior involving the adsorption of a solute to a stationary solid, as illustrated by our simulation results, is characterized by a retardation of breakthrough followed by a sinusoidal breakthrough curve shape.

The flow rate of these experiments (74 m day$^{-1}$) is very high compared to most groundwater flow rates. If the assumption of chemical equilibrium is appropriate for experimental systems such as those examined by Yee and Fein ((2002), then it should also be appropriate for mobile pore spaces in slower moving ground water systems. The assumption of chemical equilibrium in a dynamic system greatly simplifies the modeling process. Since adsorption and desorption rates for other divalent metal cations such as Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Pb$^{2+}$ are similar to that of Cd$^{2+}$ (Jeon et al., 2003, 2004; Borrok and Fein, 2005), chemical equilibrium models are likely to yield reasonable predictions for the distributions of these metals in geologic systems as well.

4. Conclusions

Model simulations of Cd transport assuming equilibrium adsorption to bacteria and mineral surfaces were compared to previously-published experimental observations. While most models could be applied to the experimental systems as published, the models of Schindler et al. (1976) and Brady (1992) required that the mass action expression be reformulated and silica surface protonation be solved using an unconventional empirical model.

The Cd–bacteria and Cd–ferrihydrite adsorption models agreed reasonably well with the observed adsorption behaviors, with relatively minor discrepancies that are likely caused by uncertainties in equilibrium model parameters for the surface complexes present in each system. The Cd–silica adsorption models substantially underpredicted adsorption at pH 8.3 in the abiotic quartz system, resulting in poor prediction of Cd breakthrough. However, the transport model is insensitive to uncertainty in the Cd:silica adsorption model at pH 3.6 and at pH 7.6 in the presence of bacteria. Good fits to Cd breakthrough at pH 8.3 could be obtained by adjusting the log $K$ values of the Cd–silica adsorption models. The shape of breakthrough curves was found to be dependent on the isotherms implied by the adsorption models.

Regardless of the accuracy of model predictions of Cd speciation, experimental aqueous and total Cd breakthrough curves qualitatively exhibited the same patterns as our simulations which were constructed under the assumption of equilibrium adsorption. This general agreement between observation and simulation strongly suggests that transport of Cd in the experimental systems occurs under essentially equilibrium conditions. Equilibrium of adsorption reactions appears to control Cd distributions in systems with or without bacteria, using quartz or ferrihydrite substrates, and over a range of pH conditions. Our findings indicate that the assumption of chemical equilibrium is appropriate for column experiments similar to those used for comparison. Since flow rates in the column experiments (74 m day$^{-1}$) are fast compared to most flow rates in aquifers, we conclude that the kinetics of metal redistribution are fast enough that an assumption of chemical equilibrium would be appropriate for modeling coupled solute–colloid transport within mobile pore spaces in most aquifers.

Acknowledgements

Funding for this work was provided by a NSF Environmental Molecular Science Institute grant (NSF-EAR-0221966).

References


