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How the K_d Approach Undermines Groundwater Cleanup

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Abstract

Environmental scientists have long appreciated that the distribution coefficient (the " K_d " or "constant K_d ") approach predicts the partitioning of heavy metals between sediment and groundwater inaccurately; nonetheless, transport models applied to problems of environmental protection and groundwater remediation almost invariably employ this technique. To examine the consequences of this practice, we consider transport in one dimension of Pb and other heavy metals through an aquifer containing hydrous ferric oxide, onto which heavy metals sorb strongly. We compare the predictions of models calculated using the K_d approach to those given by surface complexation theory, which is more realistic physically and chemically. The two modeling techniques give qualitatively differing results that lead to divergent cleanup strategies. The results for surface complexation theory show that water flushing is ineffective at displacing significant amounts of Pb from the sorbing surface. The effluent from such treatment contains a "tail" of small but significant levels of contamination that persists indefinitely. Subsurface zones of Pb contamination, furthermore, are largely immobile in flowing groundwater. These results stand in sharp contrast to the predictions of models constructed using the K_d approach, yet are consistent with experience in the laboratory and field.

Introduction

Contamination of groundwater and sediments by heavy metals is a widespread and persistent environmental problem worldwide. In the United States, about 64% of the roughly 1300 sites on the National Priorities List ("Superfund" sites) are contaminated with heavy metals, including lead and lead compounds, hexavalent chromium, copper, and nickel (Reisch and Beardon 1997).

Assessing the mobility of metals and radionuclides in the subsurface, furthermore, is one of the most critical tasks in engineering nuclear waste repositories. Computer models that predict how metals react chemically in groundwater flows, therefore, play an integral role in designing strategies for groundwater protection and environmental remediation.

Such reactive transport models are used routinely to assess the dangers posed by existing contamination, to design remediation schemes (e.g., to choose between pump-and-treat and "passivation" strategies), and to predict future risk posed by waste repositories and by pollution remaining after contaminated sites are cleaned up. Because sorption is in many cases the most significant chemical process affecting mobility of metals and radionuclides in the subsurface, the modeling results depend critically upon how the computer codes account for partitioning of chemical species between groundwater and the sediment surface.

Nearly all reaction transport models have used the distribution coefficient (the " K_d " or "constant K_d ") approach to describe sorption, although more sophisticated treatments such as Langmuir isotherms and surface complexation models are available (Davis and Kent 1990; Stumm 1992; Zachara and Smith 1994) and can be incorporated into transport codes (Cederberg, Street, and Leckie 1985; Jennings, Kirkner, and Thies 1982; Kent et al. 1995). The results of K_d -based models have proven in case after case to be inconsistent with laboratory and field observations (Brusseau 1994; Kohler et al. 1996). For example, whereas the models predict that fluid flushing should dislodge sorbed metals from mineral surfaces, field experience and laboratory tests show that the metals are removed only gradually. Residual contamination levels in most cases greatly exceed regulatory targets. Contrary to model predictions, furthermore, the water extracted during remediation characteristically contains a persistent "tail" of heavy metals.

The discrepancy between model prediction and experience is widely acknowledged among contaminant hydrologists, and is attributed to a variety of factors (see e.g. Brusseau 1994) that include bypassing of flow around portions of the sediment; diffusion of metals into organic matter, from which they are released slowly; and slow kinetic rates for the desorption reaction. The net effect of these factors is probably significant, and is the focus of considerable ongoing research (Ainsworth et al. 1994; Comans and Middleburg 1987; Zachara, Cowan, and Resch 1991); much of the discrepancy, nonetheless, may result simply from inadequacies inherent in the K_d approach (see e.g. Reardon 1981).

Perhaps assuming that the error introduced by the K_d approach is small compared to the uncertainty inherent in describing mass transport, hydrologists continue to use distribution coefficients routinely in their modeling. In this paper we examine the consequences of this practice quantitatively by comparing predictions of transport models calculated using the K_d approach with those made using surface complexation theory. We use as simple examples the mobility of Pb, a contaminant that has proven unresponsive in many cases to active remediation strategies, and other metals in an aquifer containing hydrous ferric oxide. Unlike previous contributions, we focus not on accuracy in describing metal partitioning, but on how the selection of an approach for describing sorption might affect the outcome of a reactive transport modeling study, and hence the choice of environmental protection and remediation strategies.

Theoretical Model

We used the XT numerical model of reactive transport, under development at the University of Illinois (Bethke 1998; Bethke in prep.) which takes account of diffusion, dispersion, and advection (Bird, Stewart, and Lightfoot 1960), as well as geochemical reaction (Bethke 1996), to simulate transport of heavy metal ions through a sorbing porous medium. Our calculations employ either

the distribution coefficient (K_d) approach or surface complexation theory (which for simple cases reduces to the Langmuir isotherm approach, as discussed later).

Distribution Coefficient (K_d) Approach

Distribution coefficients provide a simple means of describing ion sorption that can be integrated easily with mass transport equations. The resulting reactive transport equations can be solved readily by analytic or numeric methods (Javandel, Doughty, and Tsang 1984). For this reason, and because the distribution coefficients can be derived quickly from batch or column experiments (Domenico and Schwartz 1998), the approach provides the basis for nearly all of the reactive transport models that have been applied to environmental problems worldwide.

The distribution coefficient K_d (in cm^3/g) gives the ratio

$$K_d = \frac{S}{C} \quad (1)$$

of a metal ion's sorbed concentration (S , in mol/g dry sediment) to dissolved concentration (C , in mol/cm^3). The distribution coefficient may be thought of as representing the equilibrium constant for a reaction

between the dissolved (M^{++}) and sorbed ($>\text{M}^{++}$) forms of a metal. In this light, if K is the reaction's equilibrium constant, K_d may be expressed

$$K_d = K \cdot \frac{\gamma_{\text{M}^{++}}}{\gamma_{>\text{M}^{++}}} \cdot \frac{n}{(1-n)\rho_s} \quad (3)$$

where γ is a species' activity coefficient, n is porosity, and ρ_s is density (g/cm^3) of the sediment grains.

K_d theory works best for trace amounts of non-ionized, hydrophobic organic molecules (Stumm and Morgan 1996), but is too simplistic to accurately represent sorption of ionic species

within soils and sediments (Domenico and Schwartz 1998; Reardon 1981). The K_d coefficient measured for an ionic species is not meaningful in the general sense, but specific to the sediment and fluid tested. The K_d value for a metal typically varies over many orders of magnitude, depending on fluid pH and composition as well as the nature of the sediment (Davis and Kent 1990).

Surface Complexation Theory

The two-layer surface complexation model (Davis and Kent 1990; Dzombak and Morel 1990) provides a more robust and realistic description of ion sorption than the K_d approach (Kohler et al. 1996; Lichtner 1996; van der Lee 1997). According to surface complexation theory, a surface is composed of hydroxyl sites that can protonate, deprotonate, and complex according to the reactions

Here, $>\text{X}$ represents an atom exposed at the surface of the sorbing mineral, and M is a metal that can sorb. The surface site density (mol/m^2) for a sorbing surface is determined by regressing experimental data (i.e., from acid-base titrations, sorption isotherm determinations, or column experiments), as are the equilibrium constants K for each reaction (Davis et al. 1998; Dzombak and Morel 1990).

To account for electrostatic effects, the mass action constants for reactions 4-6 are multiplied by the Boltzman factor, $\exp(-\Delta z \Psi F / RT_K)$. Here, Δz is change in surface charge over the reaction, Ψ is electrical potential (volts), F is the Faraday constant (C/mol), R is the gas constant ($\text{V}\cdot\text{C}/\text{mol}\cdot\text{K}$), and T_K is absolute temperature (K). The mass action equation for reaction 6, for example, is

$$K \exp\left(-\frac{\psi F}{RT_K}\right) = \frac{m_{>XOM^+} a_{H^+}}{m_{>XOH} a_{M^{++}}} \quad (7)$$

where a and m represent activity and molal concentration. By convention, activity coefficients for the surface species are not carried; they are assumed to be approximately equal and hence cancel. From an estimate of the number of protonated, deprotonated, and complexed sites per unit area of surface, the surface charge density σ (C/m²) can be determined. The surface potential Ψ can then be calculated from σ and the solution's ionic strength. Once Ψ has been determined, the mass action equation (eq 7) for each reaction can be evaluated, giving a new species distribution and surface charge density, and then a revised surface potential. Iteration to convergence (using Newton's method, for example) gives the sorbed mass (Bethke 1996; Westall and Hohl 1980).

Among the soil solids that sorb heavy metals in oxidized subsurface environments, ferric oxides are in many cases the most significant. To calculate uptake by ferric oxides, we use here Dzombak and Morel's (Dzombak and Morel 1990) multi-site variant of the two-layer surface complexation model (Table 1). Their parameterization considers weakly and strongly sorbing sites, labeled $>(s)FeOH$ and $>(w)FeOH$, respectively; there are forty-fold more weak than strong sites.

Retardation

Models of the transport of sorbing contaminants are commonly parameterized in terms of retardation, as determined by passing a solution containing a contaminant through a column experiment. The extent to which sorption retards migration through the column is described by a retardation factor R . The retardation factor specifies how rapidly changes in the contaminant's concentration propagate in flowing groundwater, relative to a conservative solute.

For the imbibition of a sorbing solute by a pristine medium, $R = v/v_M$, where v is the average linear velocity (cm/s) of a conservative solute and v_M is the velocity of the sorbing metal. R is related to K_d by

$$R = \frac{m_{M^{++}} + m_{>M^{++}}}{m_{M^{++}}} = 1 + \frac{(1-n)\rho_s K_d}{n} \quad (8)$$

where $m_{M^{++}}$ and $m_{>M^{++}}$ are, respectively, the concentrations (molal) of the metal in dissolved and sorbed form.

Under the surface complexation approach, there is no single value for the retardation factor because the dissolved and sorbed metal concentrations are set by the mass action equation (eq 7), rather than as a simple ratio. For the case of imbibition, however, we can write

$$R \approx \frac{m_{M^{++}} + M_{>XOH}}{m_{M^{++}}} \quad (9)$$

because the metal will bind to the vast majority of the metal-sorbing sites. In this equation, $m_{M^{++}}$ is the metal concentration in the inlet fluid and $M_{>XOH}$ is the total concentration of metal-sorbing sites (whether complexed or not), which after reaction with the inlet fluid is approximately equal to $m_{>XOM^{+}}$.

Comparison of the Theories

The differences between the K_d approach and surface complexation theory can be summarized as:

- Whereas surface complexation theory is founded on balanced chemical reactions (reactions 4–6), the reaction representing the K_d approach (reaction 2) is not balanced. Reaction 2 is written incorrectly as a transformation rather than as a complexation reaction.

- Unlike surface complexation theory, there is no provision in the K_d approach for maintaining a mass balance on sorbing sites. In the K_d approach, a sediment can sorb metal ions without limit, and there is no accounting for the possibility of saturating the metal-sorbing sites, nor the effects of competition among ions (Valocchi, Street, and Roberts 1981).
- The K_d approach, unlike surface complexation theory, does not account for electrostatic effects arising from changes in charge on the sorbing surface.

It is important to identify those conditions where surface complexation theory might reduce to the K_d approach. To do so, we must assume that few of the sorbing sites complex, so that $m_{>XOH} \approx M_{>XOH}$, which is constant. We also must assume that pH and ionic strength are constant, so that a_{H^+} , σ , γ , and Ψ do not vary. We can then write

$$K_d = \frac{S}{C} = K \cdot \exp\left(-\frac{\psi F}{RT_K}\right) \cdot \frac{n}{(1-n) \rho_s} \cdot \frac{M_{>XOH} \gamma_{M^{++}}}{a_{H^+}} \quad (10)$$

from eqs 1 and 7.

This result shows why measured K_d values are specific to the sediment sample and water composition tested. The site concentration $M_{>XOH}$ differs from sediment to sediment, depending on the minerals present, their surface areas, and the extent to which their surfaces are exposed. Variables a_{H^+} , $\gamma_{M^{++}}$, and Ψ vary strongly with fluid pH, ionic strength, or both. The result also highlights an important assumption of the K_d approach: the requirement of a near-infinite supply of uncomplexed metal-sorbing sites. The surface complexation model reduces to a Langmuir isotherm (Stumm and Morgan 1996) without the need to assume an unlimited supply of sorbing sites, but with the additional restriction that a single complexation reaction (involving a single type of surface site) occurs.

Results

We simulated transport of heavy metal ions through a porous medium containing hydrous ferric oxide, assuming that the ions sorb according to surface complexation theory (Dzombak and Morel 1990). For comparison, we show analytical solutions for the K_d approach (Javandel, Doughty, and Tsang 1984), assuming the same retardation factor. The simulations begin with an imbibition leg, in which water containing 1 mmolal of a dissolved heavy metal passes into a previously uncontaminated medium, followed by an elution leg, during which the medium is flushed with clean water. The latter step is meant to represent the effects of a dilute fluid, whether introduced by a pump-and-treat operation or natural recharge, flowing through the contaminated medium.

Fluid and sorbate maintain local equilibrium at 25°C over the course of the simulation, according to the reactions in Table 1. The heavy metal reacts with the strongly sorbing sites ($>(s)\text{FeOH}$) on the ferric oxide (reaction *e*, *f*, or *g*). The number of strong sites determines the retardation factor for the simulation, as shown by eq 9. For example, if we set 1 mmolal of strong sites, then R is 2. We take a medium that is 100 m long (divided into 100 nodal blocks), contains 30% pore space ($n = .3$), and has a dispersivity of 1 m; the groundwater is a 50 mmolal NaCl solution of pH 6.

Figure 1 shows the simulation results for the transport of Pb, assuming a retardation factor of 2 (which by eq 8 is equivalent to a K_d value of $.16 \text{ cm}^3/\text{g}$). During imbibition, the ferric oxide strips the Pb from solution along a sharp reaction front. The front migrates through the medium at half the rate of groundwater flow, reflecting the retardation factor. Behind the front, fluid is rich in Pb and the metal-sorbing sites are almost entirely saturated. The simulation results differ from those predicted by the K_d approach (dashed lines) principally in the sharpness of the reaction front.

During elution, the Pb-rich fluid is flushed from the system. Pb desorbs incompletely from the ferric oxide, so that at the end of the simulation nearly all of the sorbed metal remains in place. The elution leg differs distinctly from what the K_d approach would suggest. Pb-poor water reaches the effluent in the simulation more quickly than in the K_d case because little Pb desorbs from the medium. Most significantly, whereas from the K_d approach we expect the Pb to be completely flushed from the sorbate within 3 pore volumes of elution, the surface complexation approach predicts that the sorbate will remain contaminated even if flushed many times.

Pb desorbs sparingly during elution, but the small amount released is sufficient to contaminate water flowing through the medium. The breakthrough curve (Figure 2, left) for the simulation shows a persistent tail of Pb contamination an order of magnitude higher than prescribed by U.S. drinking water standards. The K_d approach, in contrast, suggests the effluent should be potable after only a few pore volumes have been eluted. If we repeat the simulation for a larger retardation factor (and increase the duration of the imbibition leg accordingly), we obtain a similar result (Figure 2, right).

The discrepancies between predictions of the K_d and surface complexation approaches arise chiefly from the differing forms assumed for the sorption reaction (reactions 2 and 6). In the K_d approach, the ratio of dissolved to sorbed concentration is fixed. This simple relationship does not hold under surface complexation theory, however, since the concentrations of four species (Pb^{++} , H^+ , $>(\text{s})\text{FeOH}$, and $>(\text{s})\text{FeOPb}^+$) appear in the mass action equation.

Figure 3 shows how the concentrations of these species, observed at the midpoint of the medium, vary over the course of the simulation. During imbibition, arrival of water containing Pb^{++} drives the reaction

to the right, complexing nearly all of the metal-sorbing sites. The reaction has little effect on pH because the protonation reaction for the more abundant weak sites (reaction *b* in Table 1) serves to buffer the H^+ activity. During elution, the desorption reaction

need proceed only slightly to the right in order to maintain equilibrium. The reason is clear from Figure 3. By mass action, any decrease in $\log m_{Pb^{++}}$ must be compensated by an increase in $\log m_{>(s)FeOH}$ plus a decrease in $\log m_{>(s)FeOPb^+}$. Because there are so few uncomplexed sites, a small shift in the reaction causes the logarithm of the $>(s)FeOH$ concentration to rise sharply without significantly affecting the number of complexed sites.

Figure 4 shows how the equilibrium constant for the complexation reaction (reaction 6) affects the breakthrough curves predicted. For large equilibrium constants (e.g., $K = 10^6$), the breakthrough curve shows a persistent "tail" of low ($<1 \mu\text{molal}$) levels of metal contamination (Figure 4, left). In this case, the metal binds so tightly that very little is released during flushing. For lesser values of the binding constant ($K = 10^4 - 10^0$), metal concentrations in the effluent are larger and the tail becomes less persistent. When the binding constant is small ($K = 10^{-2}$), the breakthrough curve assumes a symmetrical shape characteristic of curves obtained using the K_d approach.

Figure 4 (right) shows results obtained for Cu and Ni, along with their U.S. drinking water standards, calculated using reactions *f* and *g* in Table 1. These two metals are analogous in the two-layer surface complexation model (Dzombak and Morel 1990) to Pb in that they are divalent in solution and at low concentration sorb to ferric oxide only at strong sites. Cu behaves much like Pb, but is more concentrated in the effluent because it sorbs less tightly. Because Cu is so much less toxic than Pb, however, the effluent quickly reaches potable levels. Ni, which binds less tightly

than either Pb or Cu, shows a less persistent "tail" of contamination; the effluent meets drinking water standards after about 15 pore volumes of elution.

In a final calculation (Figure 5), we consider how a zone of Pb contamination might migrate in the subsurface. One half of a pore volume of contaminated fluid enters the aquifer during the imbibition leg. Reflecting the retardation factor ($R = 2$), Pb saturates the metal-sorbing sites along one fourth of the aquifer; fluid in this zone contains Pb in the inlet concentration (1 mmolal). During the elution leg, as the fluid migrates into the uncontaminated zone, sorption strips the Pb from it. After about half a pore volume has been eluted, nearly all of the Pb has sorbed.

Because little contaminant remains in solution at this point, continued migration almost ceases; the Pb is sorbed and nearly immobile. K_d theory (Figure 5, dashed lines), in sharp contrast, predicts that dissolved concentrations in the contaminated zone remain high, according to eq 1. Contaminant, therefore, migrates freely through the aquifer at one-half the rate of ground water flow (since $R = 2$).

Discussion

When we use surface complexation theory instead of K_d 's to model Pb transport, a number of differences result:

- The aquifer is predicted to contain a contaminated zone, in which the metal sorbing sites are mostly saturated, and an uncontaminated zone which contains little Pb. The zones are separated by a sharp reaction front. K_d theory predicts sorbed metal concentrations that vary smoothly through the aquifer.
- Unlike the K_d approach, which holds the dissolved Pb concentration everywhere proportional to sorbed concentration, surface complexation theory predicts wide variation in dissolved concentration. Within the contaminated zone, where the metal-sorbing sites are largely

saturated, dissolved concentration can vary from small values upward without affecting the sorbed concentration significantly. In the simulations considered here (i.e., at pH 6), the Pb concentration in water from the contaminated zone invariably exceeds drinking water standards. The Pb content of water in the uncontaminated zone, however, is small because the metal-sorbing sites, which are largely uncomplexed, strip Pb from solution efficiently.

- Flushing the contaminated zone with fresh water displaces any water containing high levels of Pb. Continued flushing produces effluent that contains Pb in concentrations that are small but persistently in excess of drinking water standards. The flushing is ineffective at displacing sorbed Pb from the aquifer. The K_d approach, in contrast, predicts that flushing should efficiently displace sorbed and dissolved Pb, leaving the aquifer clean.
- The K_d approach predicts that a zone of Pb contamination will migrate along the direction of groundwater flow at a rate given by the retardation factor. Surface complexation theory suggests that Pb, once sorbed, is largely immobile. When water migrates from the contaminated zone, its Pb content is stripped within the uncontaminated zone by sorption. Absent a continued supply of Pb, virtually all of the contaminant becomes sorbed and hence immobile. The Pb content of water within the contaminated zone remains in excess of drinking water standards, but water elsewhere is predicted to be potable.

The calculations in this paper help make clear the extent to which the K_d approach oversimplifies a complex chemical process. The K_d approach, as a result, undermines groundwater cleanup strategies in two principal ways:

- By suggesting overly optimistic rates of contaminant displacement from sediment surfaces by non-corrosive soil flushing, or fresh recharge. The K_d -based calculation of Pb transport argues

for the potential success of active soil flushing; any residual sorbed contaminant remaining is predicted to be short-lived and easily diluted by subsequent recharge. This prediction is contrary to experience, which has shown Pb contamination to be resistant to active remediation schemes.

The surface complexation approach, on the other hand, points to a significantly more recalcitrant Pb plume that can be removed rapidly by neither non-corrosive soil flushing nor fresh recharge. Models calculated using this approach are likely to support implementation of passive approaches that focus on decreasing the mobility of Pb at the site, instead of active approaches.

- By overestimating the potential for plume advance. The K_d approach greatly exaggerates the mobility and hence potential impact of the Pb plume. One might argue that this outcome is conservative and errs on the side of human health, but this may not be true. Mobile plumes are remediated differently than immobile plumes, and applying the methods designed for one to the other risks failure. K_d -based models might call for applying soil flushing and placing monitoring wells far from the plume source. The surface complexation model, on the other hand, predicts that soil flushing will not work and that the monitoring wells might never detect Pb contamination.

In conclusion, effective remediation of subsurface contamination follows from a clear diagnosis of plume behavior. The same can be said for designing hazardous waste repositories. Where metals or radionuclides sorb, the sorption process should be described in a fashion more realistic than the K_d approach allows. The calculations presented here represent the "equilibrium limit," the state achieved in the absence of complicating chemical and physical factors (reaction

kinetics, "bypassing" of groundwater flow, diffusion of metal ions into organic matter, and so on) that influence the transport of sorbed metals; these factors should be included in reactive transport modeling, regardless of the sorption theory employed. The calculation results, nonetheless, differ from those given by the K_d approach dramatically enough to suggest alternative remediation strategies for strongly sorbing metals in the subsurface.

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Table 1
Surface Complexation Reactions Considered^a

Reaction	log <i>K</i>
(a) $>(s)FeOH + H^+ \rightleftharpoons >(s)FeOH_2^+$	7.29
(b) $>(w)FeOH + H^+ \rightleftharpoons >(w)FeOH_2^+$	7.29
(c) $>(s)FeO^- + H^+ \rightleftharpoons >(s)FeOH$	8.93
(d) $>(w)FeO^- + H^+ \rightleftharpoons >(w)FeOH$	8.93
(e) $>(s)FeOH + Pb^{++} \rightleftharpoons >(s)FeOPb^+ + H^+$	4.65
(f) $>(s)FeOH + Cu^{++} \rightleftharpoons >(s)FeOCu^+ + H^+$	2.89
(g) $>(s)FeOH + Ni^{++} \rightleftharpoons >(s)FeONi^+ + H^+$	0.37
^a From Dzombak and Morel (1990)	

Figure Captions

Figure 1. Transport at pH 6 of Pb^{++} through a medium containing hydrous ferric oxide, calculated for a retardation factor of 2 (equivalent to $K_d = .16$). A total of 30 pore volumes pass through the medium: 2 during the imbibition leg (left), and 28 during elution (right). Solid lines show predictions of surface complexation theory; dashed lines, those from the K_d approach.

Figure 2. Breakthrough curves showing Pb^{++} concentration in effluent from the medium. Plot on left shows results from simulation in Figure 1. Plot on right shows results obtained assuming a larger retardation factor ($R = 8$, equivalent to $K_d = 1.1$). Solid and dashed lines, respectively, show predictions of surface complexation and K_d theories. Horizontal lines show maximum Pb content, 15 $\mu\text{g/L}$, for drinking water in U.S.

Figure 3. Variation in concentrations of dissolved species (top) and surface species (bottom) at the midpoint of the medium, over the course of the simulation shown in Figure 1. Note that there is a one pore-volume lag before water entering the medium reaches the midpoint. By mass action (ignoring activity coefficients), the sum of the log concentrations of $>(\text{s})\text{FeOPb}^+$ and H^+ minus the log concentrations of $>(\text{s})\text{FeOH}$ and Pb^{++} must remain constant for the complexation reaction (reaction 6) to remain in equilibrium.

Figure 4. Breakthrough curves for $R = 2$ showing (left) the effect of the equilibrium constant K for the metal complexation reaction (reaction 6) on simulation results. Plot on right shows curves predicted for dissolved Ni, cupric Cu, and Pb. U.S. drinking water standards for Cu and Ni, as shown, are 1300 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$.

Figure 5. Transport at pH 6 of Pb^{++} through a sorbing aquifer ($R = 2$) in which elution begins after one-half pore volume of imbibition, before the metal-sorbing sites are saturated across the medium. Solid and dashed lines, respectively, show predictions of surface complexation and K_d theories.

Bethke & Brady, Figure 1

Bethke & Brady, Figure 2

Bethke & Brady, Figure 3

Bethke & Brady, Figure 4

Bethke & Brady, Figure 5