

# How the $K_d$ Approach Undermines Ground Water Cleanup

by Craig M. Bethke<sup>a</sup> and Patrick V. Brady<sup>b</sup>

## 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 ground water inaccurately; nonetheless, transport models applied to problems of environmental protection and ground water 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 many 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 Pb from the sorbing surface. The effluent from such treatment contains a persistent "tail" of small but significant levels of contamination. Subsurface zones of Pb contamination, furthermore, do not migrate rapidly or far in flowing ground water. 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 ground water 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, commonly including lead and lead compounds, hexavalent chromium, zinc, cadmium, copper, mercury, and nickel (Evanko and Dzombak 1997; 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 ground water flows, therefore, play an integral role in designing strategies for ground water 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 ground water 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 and Freundlich isotherms and surface complexation models are available (Davis and Kent 1990; Stumm 1992; Zachara and Smith 1994) and can be incorporated into transport codes (Cederberget et al. 1985; Jennings et al. 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; Carriere et al. 1995; Evanko and Dzombak 1997; Kohler et al. 1996; Reed et al. 1995; Tuin and Tels 1990). 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. As is widely appreciated among hydrologists,  $K_d$ -based models calculated assuming local equilibrium do not predict "tailing" in breakthrough curves.

Figures 1 and 2 show breakthrough curves from laboratory experiments that demonstrate the phenomena of "tailing" and incomplete recovery. In the first experiment (Figure 1), a pulse of Cd-contaminated water is introduced into a soil and then flushed with dilute water (Selim et al. 1992); the results of a reactive-transport model calculated using the  $K_d$  approach is shown for comparison. The Cd, a weakly sorbing metal, appears in the effluent at a lesser concentration than expected from the  $K_d$  approach, but persists in a protracted "tail." In Figure 2, soil samples that have been previously contaminated with several solutions of Pb, a strongly sorbing metal, are flushed with tap water. In each case, the Pb in the effluent persists in a "tail" of concentrations greater than

<sup>a</sup>Corresponding author. Professor, Hydrogeology Program, Department of Geology, 1301 West Green St., Urbana, IL 61801; (217) 333-3369, fax (217) 244-4996, c-bethke@uiuc.edu

<sup>b</sup>Research Geochemist, Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185-0750; pvbalb@swcp.com

Received February 1999, accepted November 1999.

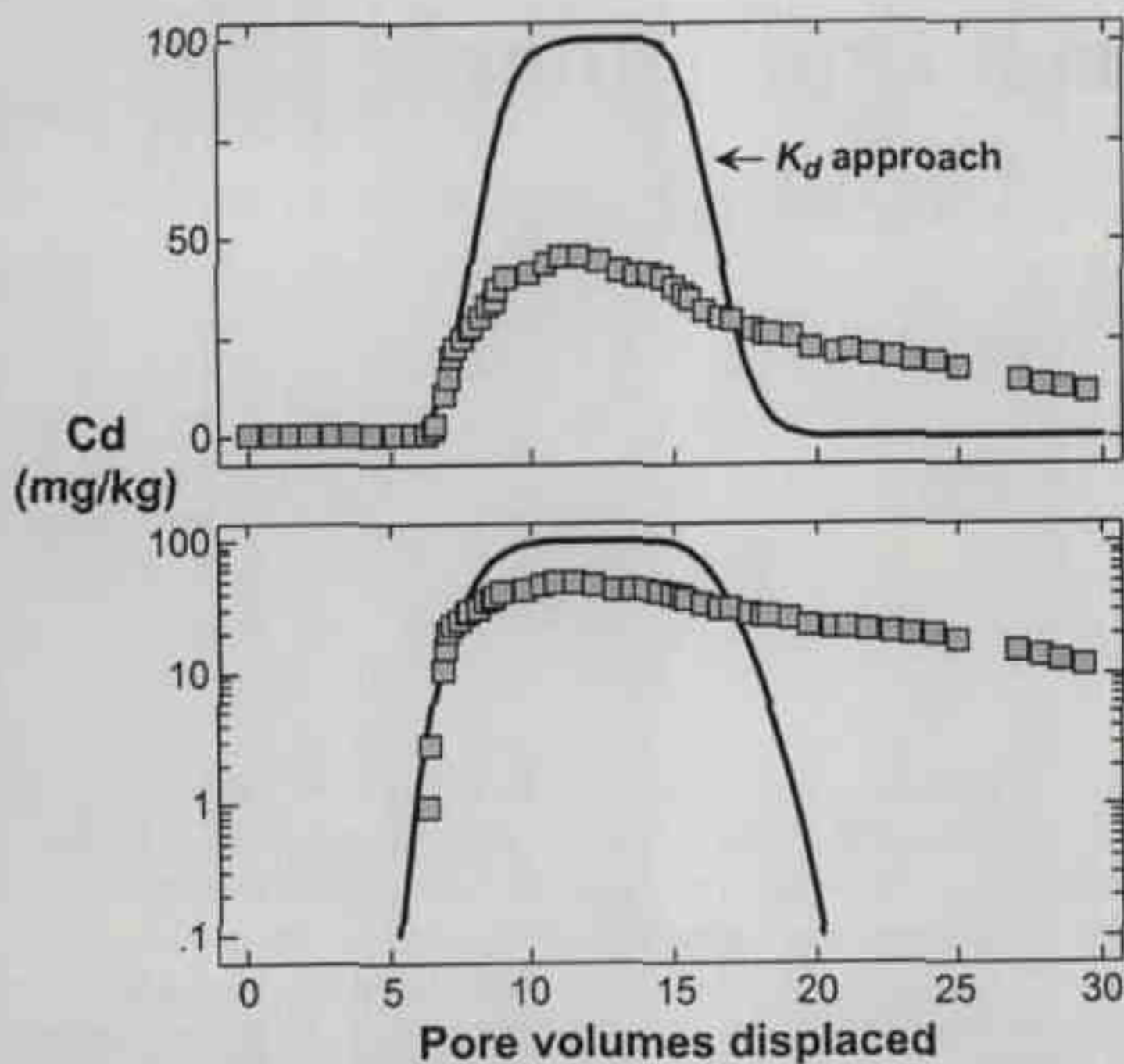


Figure 1. Observed breakthrough curve (squares, showing Cd concentration in effluent fluid) for a laboratory experiment (Selim et al. 1992) in which 8.5 pore volumes of a 100 mg/kg Cd solution are introduced into soil and then displaced with further pore volumes of dilute water. Solid line shows results of a reactive transport model corresponding to the experimental conditions, calculated using the  $K_d$  approach. Top and bottom plots show data in linear and semilogarithmic coordinates, respectively. Data show "tailing" and incomplete recovery of Cd, not predicted by the  $K_d$  approach.

1 mg/kg, orders of magnitude higher than allowed by drinking water standards. Even after the soil has been flushed about 60 times, only 0.5% to 10% of the original contamination in the experiments has been recovered. These results contradict the transport model calculated using the  $K_d$  approach, which predicts complete recovery without "tailing."

The discrepancy between model prediction and experience is widely acknowledged among contaminant hydrologists, and is attributed to a variety of factors (e.g., Brusseau 1994; Carriere et al. 1995; Reed et al. 1995; Selim et al. 1992; Tuin and Tels 1990) 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. These factors are certainly important and their net effect is likely significant; they are the focus of considerable ongoing research (Ainsworth et al. 1994; Brown et al. 1998; Comans and Middleburg 1987; Glynn and Brown 1996; Kohler et al. 1996; Payne et al. 1994; Stollenwerk 1995; Wen et al. 1998; Zachara et al. 1991). An unknown but potentially critical amount of the discrepancy, nonetheless, may result simply from inaccuracy inherent in attempting to describe chemical equilibrium using the  $K_d$  approach (e.g., Reardon 1981).

Perhaps assuming that the error introduced by the  $K_d$  approach is acceptable weighed against 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 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,

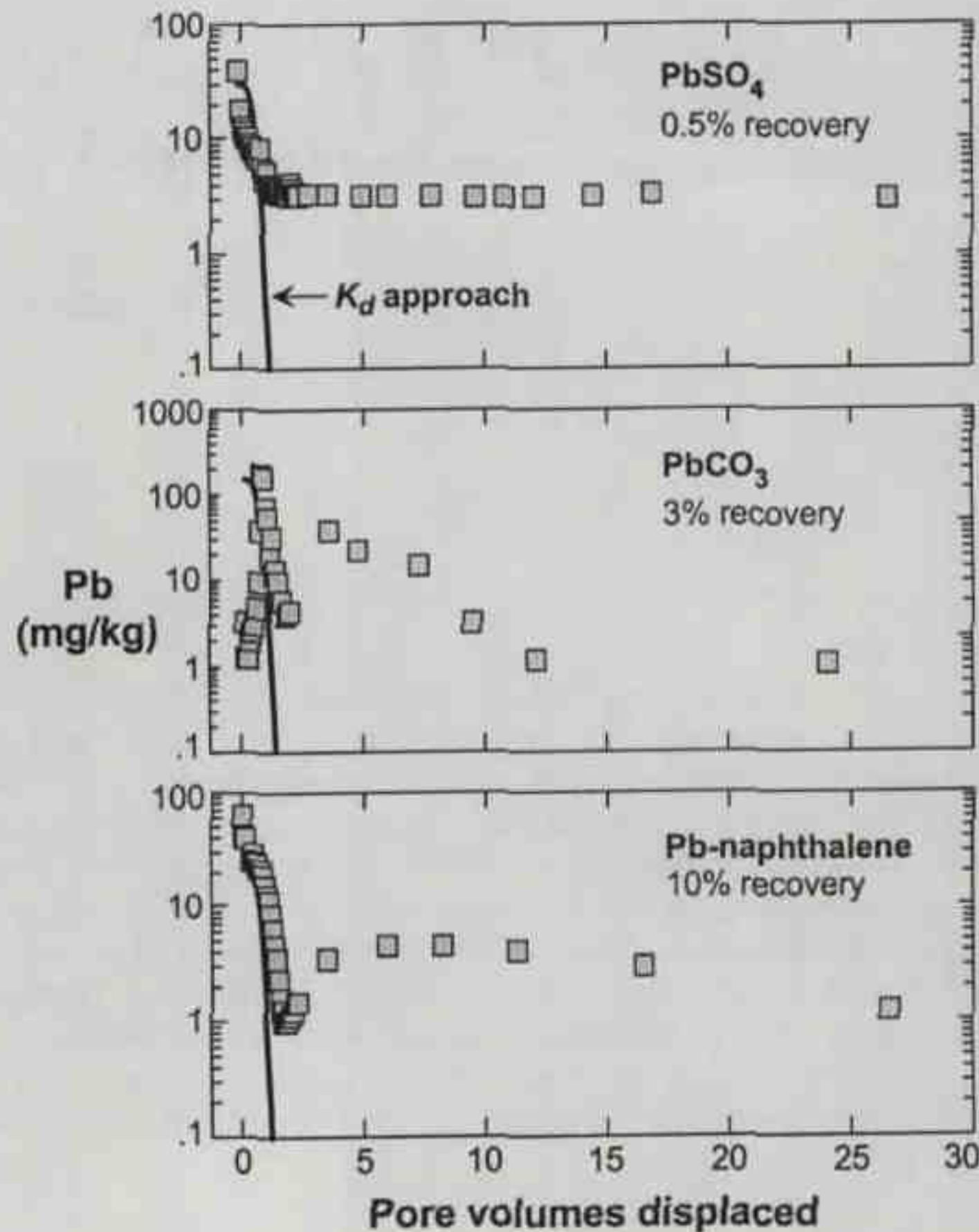


Figure 2. Observed breakthrough curves (squares) for laboratory experiments (Reed et al. 1995) in which a soil sample, previously contaminated with a  $PbSO_4$  (top),  $PbCO_3$  (middle), or  $Pb$ -naphthalene solution (bottom), is flushed with tap water. Solid lines show results of reactive transport models corresponding to the experimental conditions, calculated using the  $K_d$  approach. The fraction of the original contamination in each experiment recovered after 58 pore volumes of flushing is noted. Data show phenomena of "tailing" and incomplete recovery, which are not predicted by the  $K_d$  approach.

we focus not on accuracy in describing metal partitioning or the fitting of a particular breakthrough curve, but on how the selection of an approach for describing metal 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, developed at the University of Illinois (Bethke 1997), which takes account of diffusion, dispersion, and advection (Bird et al. 1960), as well as geochemical reaction (Bethke 1996), to simulate transport of heavy metal ions through a sorbing porous medium. Various other computer models, including PHREEQC (Parkhurst 1995), CHESS (van der Lee 1997), and HYDROGEOCHEM (Yeh and Tripathi 1990), are capable of performing the simulations shown. Our calculations assume local equilibrium and employ either the distribution coefficient ( $K_d$ ) approach or surface complexation theory.

## 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 et al. 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  $\text{cm}^3/\text{g}$ ) gives the ratio

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

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



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

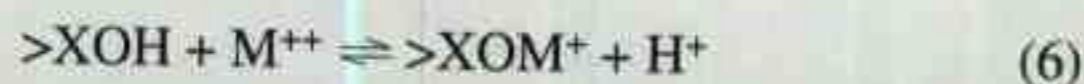
$$K_d = K \cdot \frac{\gamma_{M^{++}}}{\gamma_{>M^{++}}} \cdot \frac{n}{(1-n)\rho_s} \quad (3)$$

where  $\gamma$  is a species' activity coefficient,  $n$  is porosity, and  $\rho_s$  is density ( $\text{g}/\text{cm}^3$ ) of the sediment grains.

$K_d$  theory works best for trace amounts of nonionized, 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 is 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  $>X$  represents an atom exposed at the surface of the sorbing mineral, and  $M$  is a metal that the mineral can sorb. The surface site density ( $\text{mol}/\text{m}^2$ ) 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 through 6 are multiplied by the Boltzman factor,

$\exp(\Delta z \Psi F / RT_K)$ . Here,  $\Delta z$  is change in surface charge over the reaction,  $\Psi$  is electrical potential (volts),  $F$  is the Faraday constant ( $\text{C}/\text{mol}$ ),  $R$  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

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

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  $\sigma$  ( $\text{C}/\text{m}^2$ ) can be determined. The surface potential  $\Psi$  can then be calculated from  $\sigma$  and the solution's ionic strength. Once  $\Psi$  has been determined, the mass action equation (Equation 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) multisite variant of the two-layer surface complexation model; the complexation reactions considered in our simulations are listed in Tables 1 and 2. Their parameterization considers weakly and strongly sorbing sites, labeled  $>(w)\text{FeOH}$  and  $>(s)\text{FeOH}$ , respectively; there are 40-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 delays migration of the contaminant 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 ground water, 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 ( $\text{cm}/\text{s}$ ) of a conservative solute and  $v_M$  is the velocity of the sorbing metal.  $R$  is related to  $K_d$  by

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

where  $m_{\text{M}^{++}}$  and  $m_{>\text{M}^{++}}$  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 (Equation 7), rather than as a simple ratio. For the case of the imbibition of a strongly sorbing solute, however, we can write

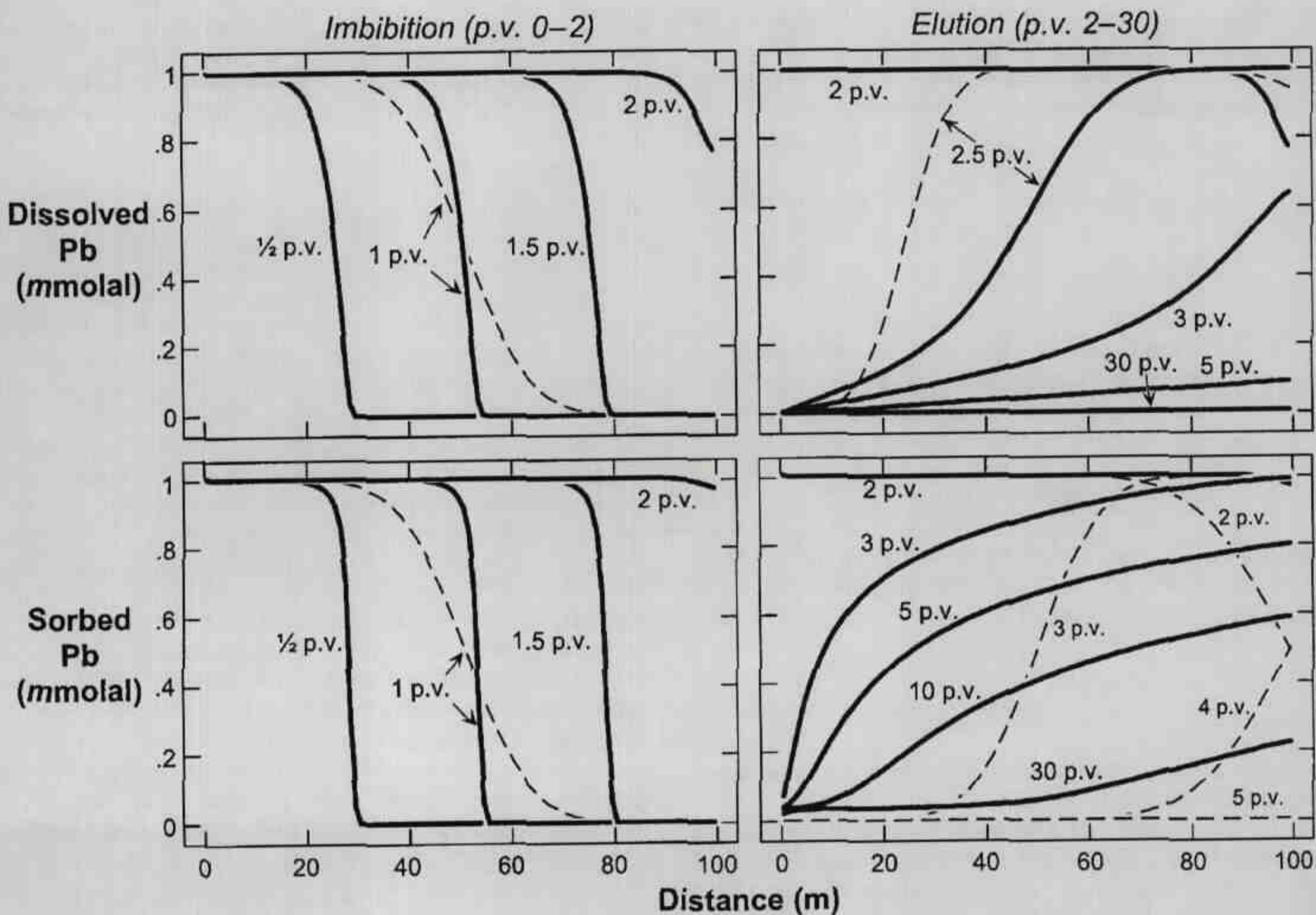


Figure 3. Transport at pH 6 of  $Pb^{++}$  by a typical ground water sample through a medium containing hydrous ferric oxide, calculated for a retardation factor of two (equivalent to  $K_d \approx .16$ ). A total of 30 pore volumes pass through the medium: two during the imbibition leg (left), and 28 during elution (right). Solid lines show predictions of surface complexation theory; dashed lines, calculations employing the  $K_d$  approach.

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

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 through 6), the reaction representing the  $K_d$  approach (reaction 2) is not balanced. Reaction 2 is written inexactly 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.

- The  $K_d$  approach, because it does not impose mass balance on sorbing sites, cannot account for the effects of competition among ions (Valocchi et al. 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  $\alpha_{H^+}$ ,  $\sigma$ ,  $\gamma$ , and  $\Psi$  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 Equations 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  $\alpha_{H^+}$ ,  $\gamma_{M^{++}}$ , and  $\Psi$  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-

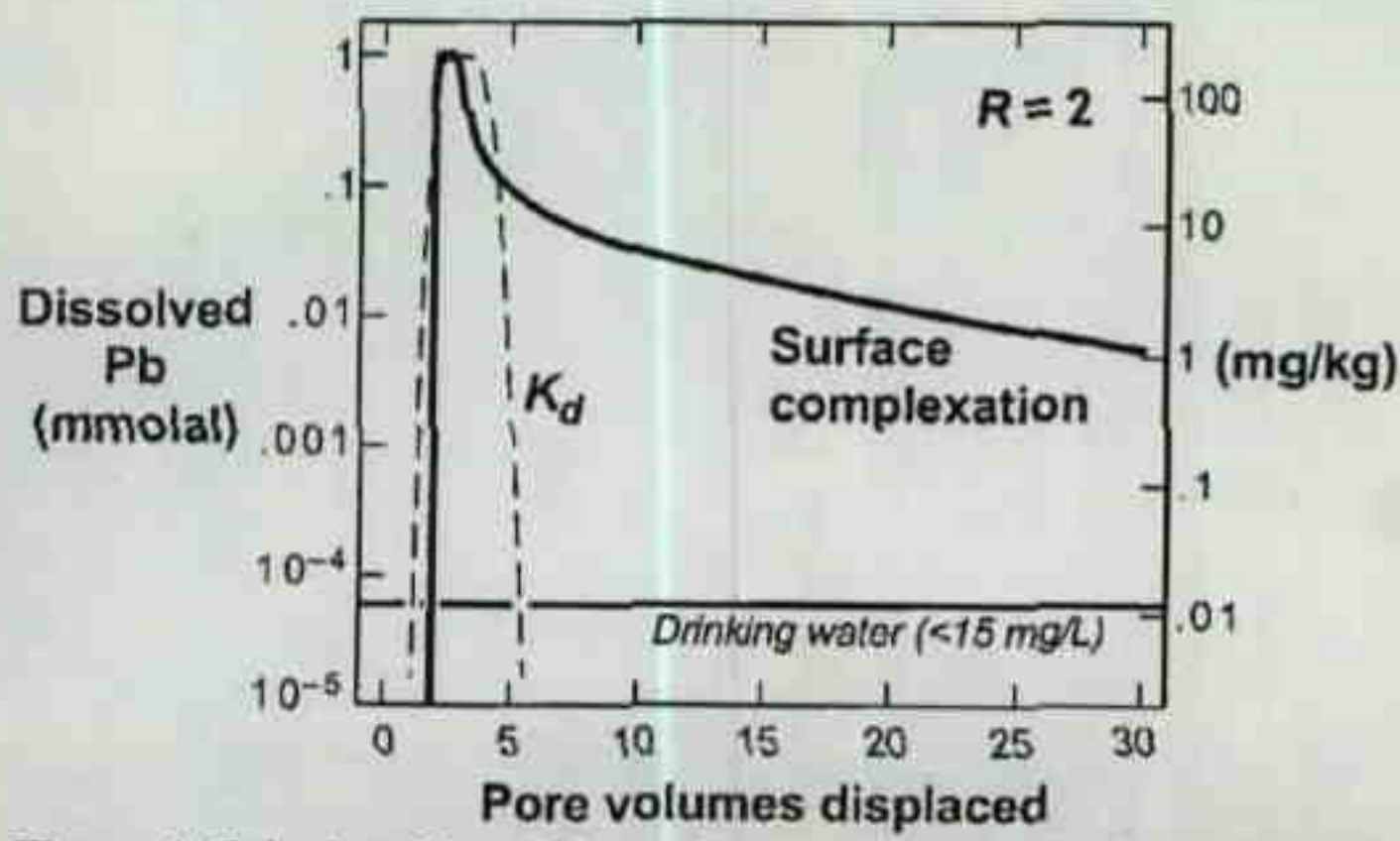


Figure 4. Calculated breakthrough curve showing  $Pb^{++}$  concentration in effluent from the medium, for simulation shown in Figure 3. Solid and dashed lines, respectively, show predictions of surface complexation and  $K_d$  theories. Horizontal line shows maximum Pb content, 15  $\mu\text{g/L}$ , for drinking water in the United States.

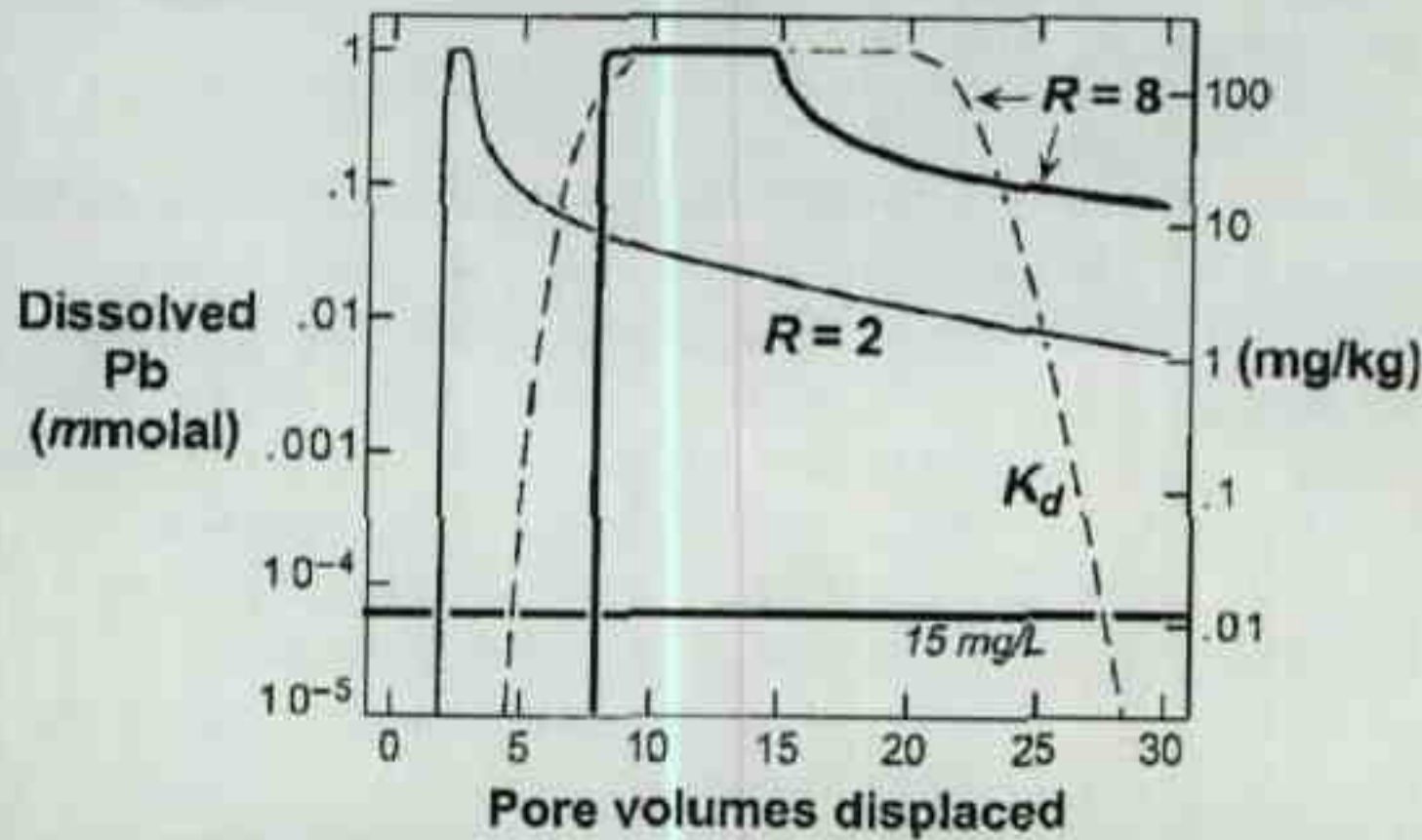


Figure 5. Breakthrough curve (solid line) for a simulation calculated assuming a larger retardation factor ( $R = 8$ , equivalent to  $K_d = 1.1$ ) than the simulation shown in Figure 4. Fine line shows curve from Figure 4, for comparison, and dashed line shows prediction of  $K_d$  approach.

**Table 1**  
Surface Complexation Reactions Considered in Simulations of Pb Transport<sup>a</sup>

| Reaction  | $\log K_{(w)}$   | $\log K_{(s)}$ |
|---|------------------|----------------|
| (a) $>\text{FeOH} + \text{H}^+ \rightleftharpoons >\text{FeOH}_2^+$   | 7.29             | 7.29           |
| (b) $>\text{FeO}^- + \text{H}^+ \rightleftharpoons >\text{FeOH}$  | 8.93             | 8.93           |
| (c) $>\text{FeOH} + \text{Ca}^{++} \rightleftharpoons >\text{FeOHCa}^{++}$                                  | —                | 4.97           |
| (d) $>\text{FeOH} + \text{Ca}^{++} \rightleftharpoons >\text{FeOCa}^+ + \text{H}^+$                         | -5.85            | —              |
| (e) $>\text{FeOH} + \text{SO}_4^{--} + \text{H}^+ \rightleftharpoons >\text{FeSO}_4^- + \text{H}_2\text{O}$ | 7.78             | —              |
| (f) $>\text{FeOH} + \text{SO}_4^{--} \rightleftharpoons >\text{FeOHSO}_4^-$                                 | 0.79             | —              |
| (g) $>\text{FeOH} + \text{Pb}^{++} \rightleftharpoons >\text{FeOPb}^+ + \text{H}^+$                         | 0.3 <sup>b</sup> | 4.65           |

<sup>a</sup>From Dzombak and Morel (1990).  
<sup>b</sup>Estimated value.

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.

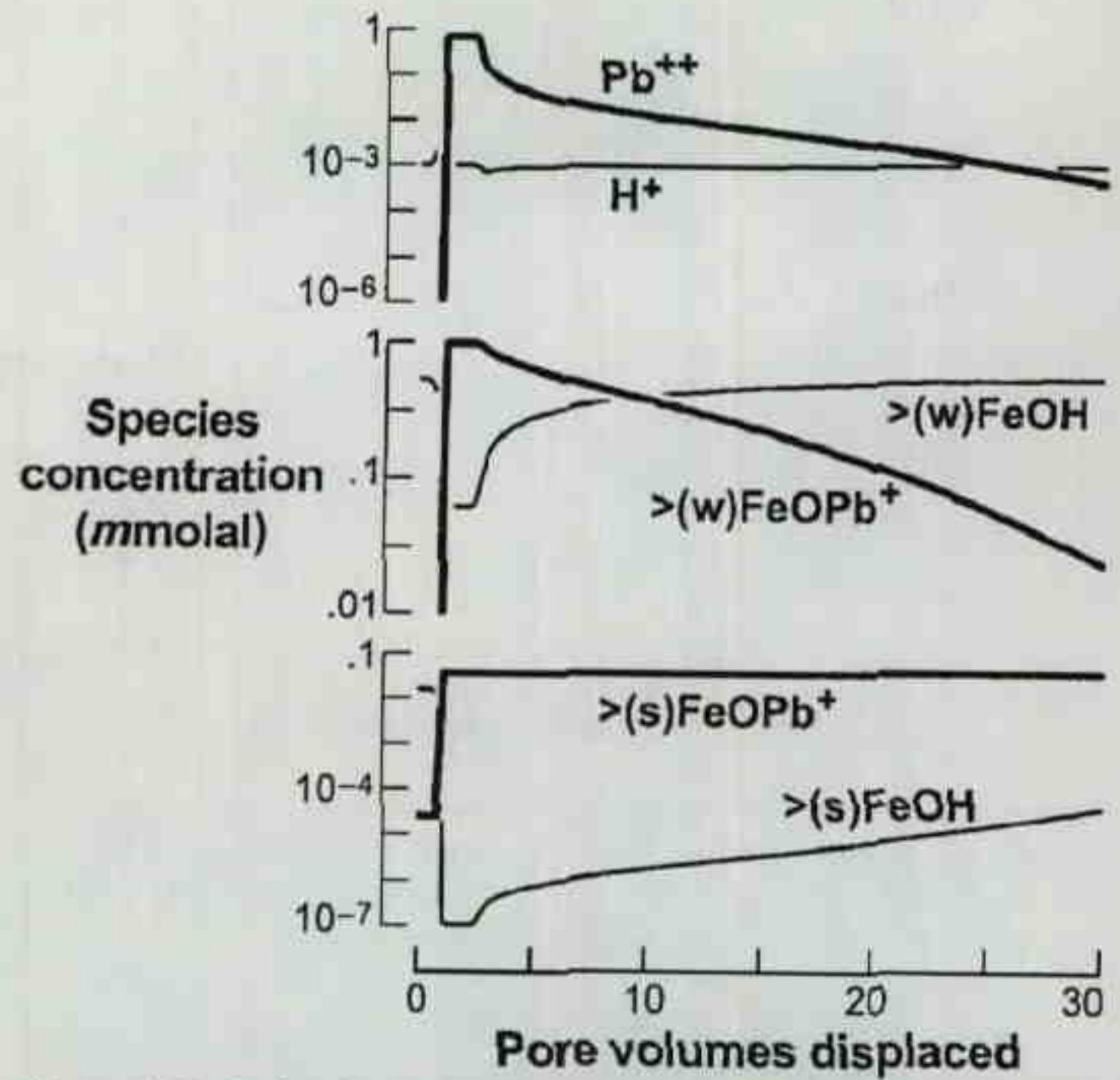


Figure 6. Variation in concentrations of some dissolved species (top plot) and surface species (middle and bottom plots) at the midpoint of the medium, over the course of the simulation shown in Figure 3. There is a one pore-volume lag before contaminant entering the medium reaches the midpoint. By mass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

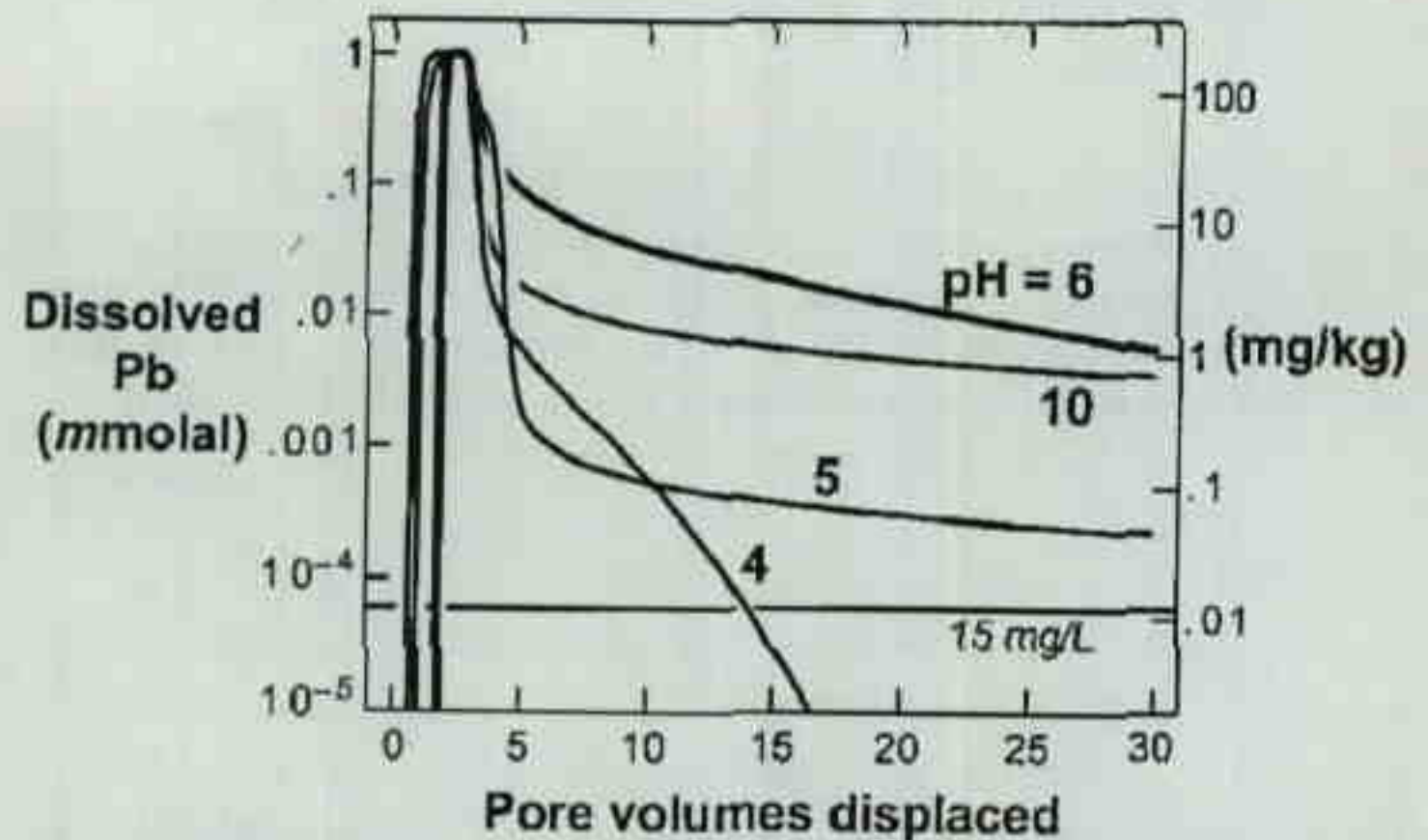


Figure 7. Effect of pH on calculated breakthrough curves for the simulation shown in Figure 3 ( $R = 2$ ).

**Table 2**  
Surface Complexation Reactions for other Metals<sup>a</sup>

| Reaction  | $\log K_{(w)}$    | $\log K_{(s)}$ |
|---|-------------------|----------------|
| (a) $>\text{FeOH} + \text{Cd}^{++} \rightleftharpoons >\text{FeOCd}^+ + \text{H}^+$ | -2.90             | 0.47           |
| (b) $>\text{FeOH} + \text{Co}^{++} \rightleftharpoons >\text{FeOC}^+ + \text{H}^+$  | -3.01             | -0.46          |
| (c) $>\text{FeOH} + \text{Cu}^{++} \rightleftharpoons >\text{FeOCu}^+ + \text{H}^+$ | 0.6 <sup>b</sup>  | 2.89           |
| (d) $>\text{FeOH} + \text{Hg}^{++} \rightleftharpoons >\text{FeOHg}^+ + \text{H}^+$ | 6.45              | 7.76           |
| (e) $>\text{FeOH} + \text{Ni}^{++} \rightleftharpoons >\text{FeONi}^+ + \text{H}^+$ | -2.5 <sup>b</sup> | 0.37           |
| (f) $>\text{FeOH} + \text{Zn}^{++} \rightleftharpoons >\text{FeOZn}^+ + \text{H}^+$ | -1.99             | 0.99           |

<sup>a</sup>From Dzombak and Morel (1990).  
<sup>b</sup>Estimated value.

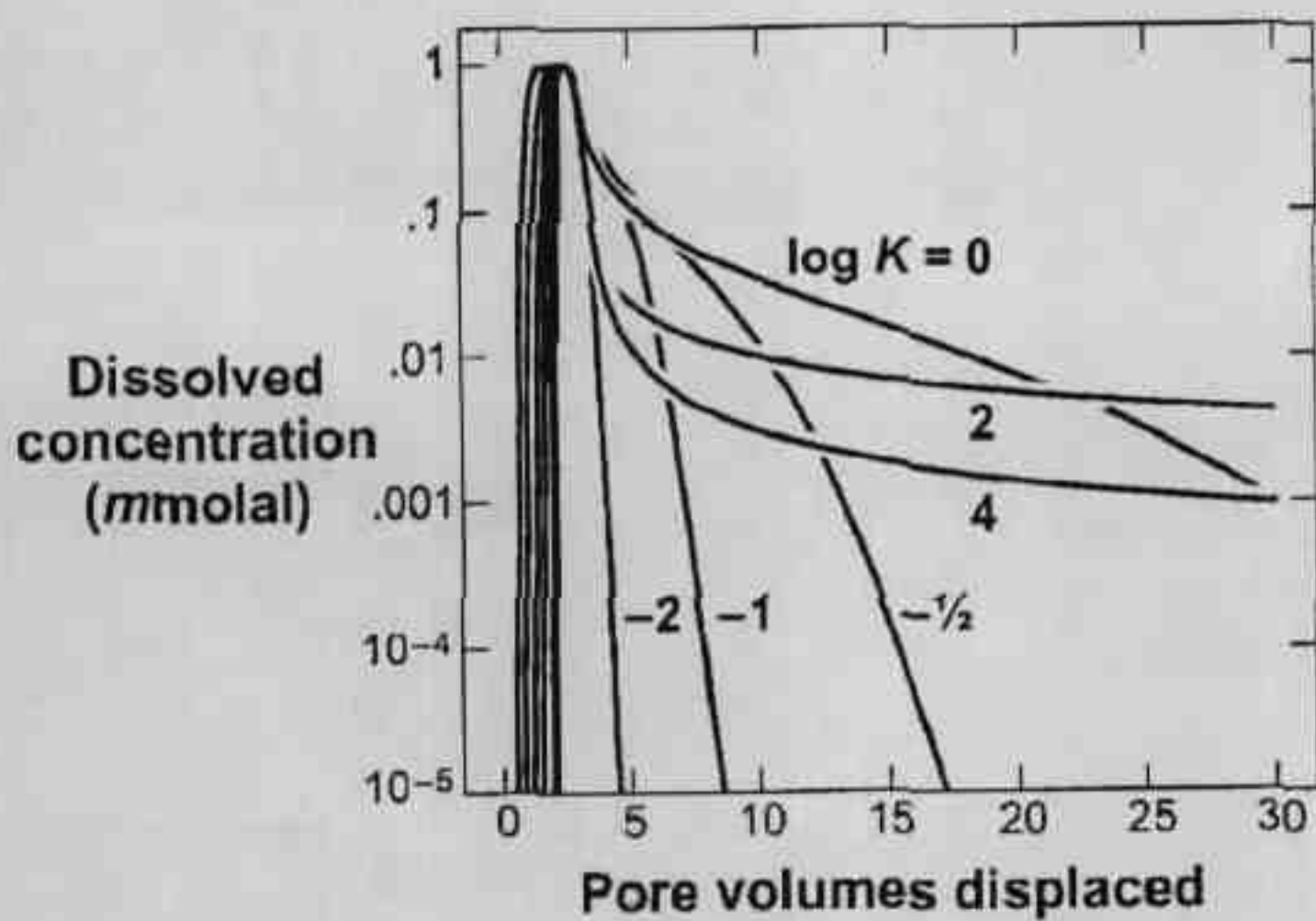


Figure 8. Effect of the equilibrium constant  $K$  for the metal complexation reaction (Equation 6) on calculated breakthrough curves for the simulation shown in Figure 3 ( $R = 2$ ). A single value of  $K$  is taken to apply to sorption at both weak and strong sites.

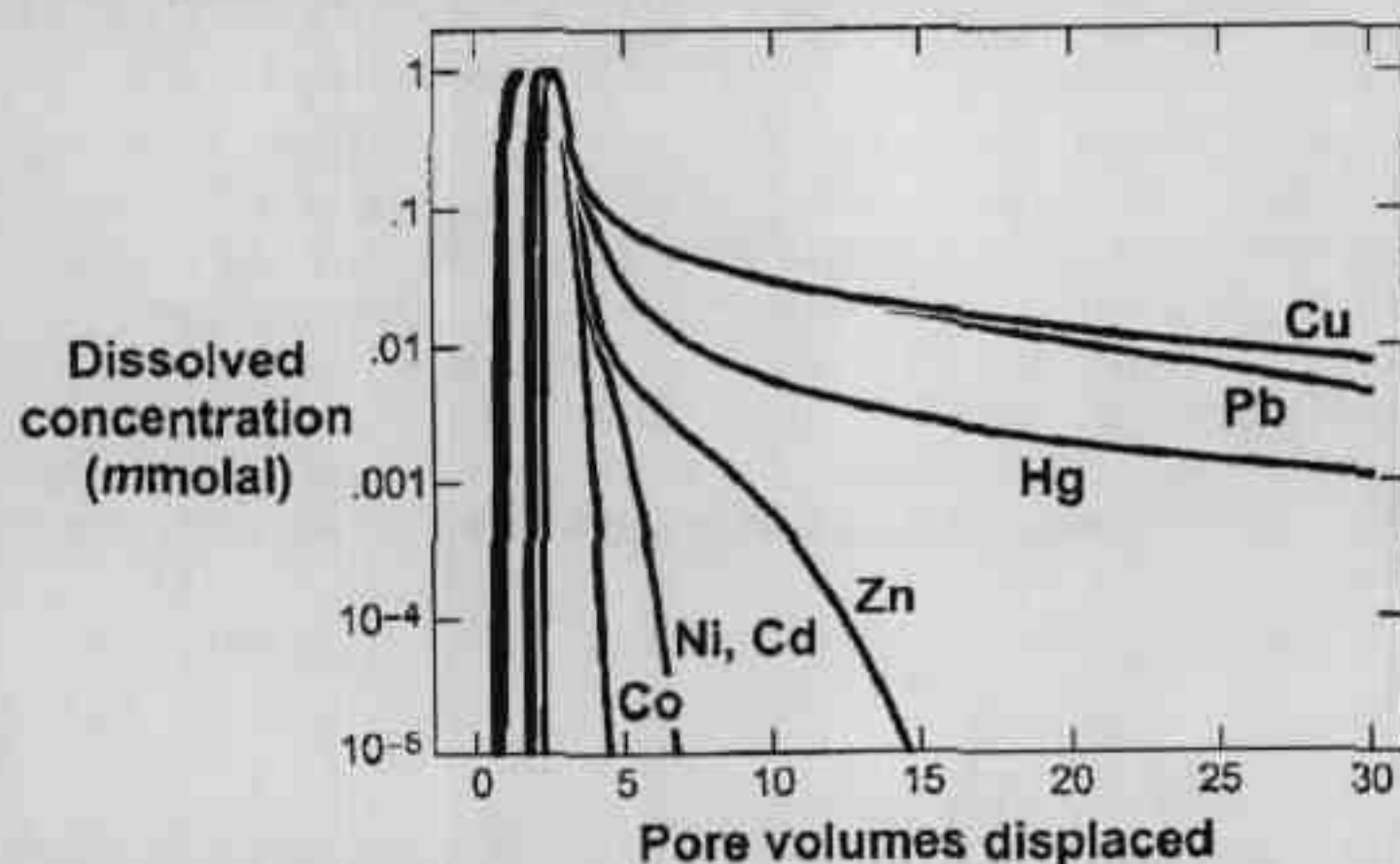


Figure 9. Calculated breakthrough curves predicted by simulations similar to that shown in Figure 3 ( $R = 2$ ) for various divalent metals: Cd, cupric Cu, Co, Hg, Ni, Pb, and Zn. Simulations assume sorption reactions and equilibrium constants shown in Table 2.

## 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 et al. 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.

The fluid is of pH 6, unless noted, and has the composition of a typical ground water sample: 30 mg/kg Ca, 20 mg/kg Na, 300 mg/kg  $\text{HCO}_3^-$ , 30 mg/kg  $\text{SO}_4^{2-}$ , and 15 mg/kg Cl. Fluid and sorbate maintain local equilibrium at 25°C over the course of the simulation, according to the reactions in Tables 1 and 2. The heavy metal reacts with the sorbing sites ( $>[w]\text{FeOH}$  and  $>[s]\text{FeOH}$ ) on the ferric oxide (reaction g in Table 1 for Pb, or the reactions in Table 2 for other metals). The number of sorbing sites determines the retardation factor for the simulation, as shown by Equation 9. For

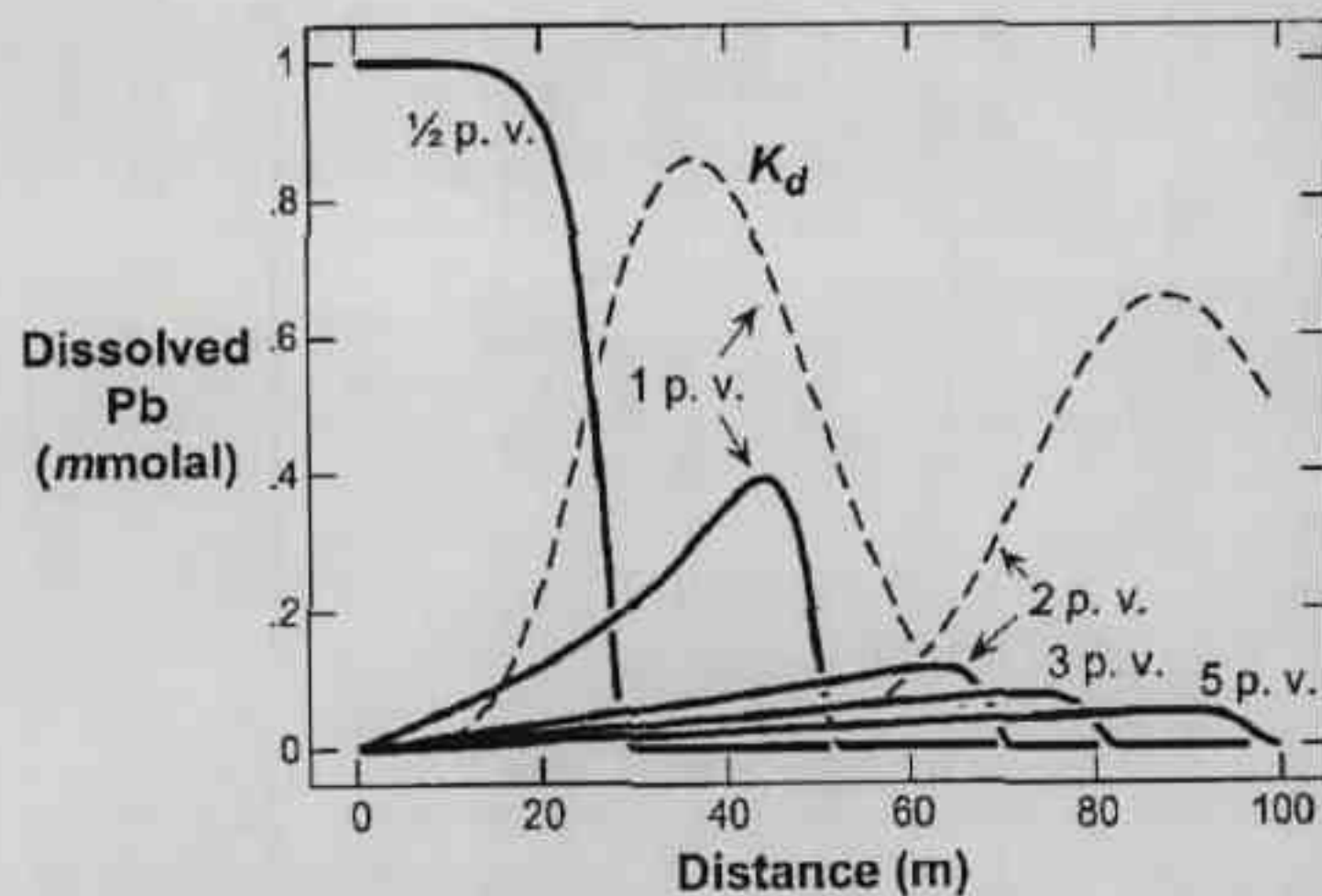


Figure 10. Transport of pH 6 of  $\text{Pb}^{2+}$  through a sorbing aquifer ( $R = 2$ ) in which elution begins after just one-half pore volume of imbibition, before the metal-sorbing sites are saturated across the medium. Solid and dashed lines, respectively, show predictions of surface complexation and  $K_d$  theories.

example, if we set 1 mmolal of sorbing 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. We do not account for the effects of sorption (i.e., "ion exchange") onto surfaces in the medium other than ferric oxide.

Figure 3 shows the simulation results for the transport of Pb, assuming an arbitrary retardation factor of 2 (which by Equation 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 at an abrupt reaction front. The front migrates through the medium at half the rate of ground water 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 the elution leg of the simulation, dissolved Pb is flushed from the system and the Pb concentration of the fluid abates, although it remains everywhere far in excess of drinking water standards. Pb desorbs gradually from the weakly sorbing sites during the flushing, whereas the strong sites remain almost completely saturated with the metal. The results of this leg differ dramatically from what the  $K_d$  approach would suggest. Whereas from the  $K_d$  approach we expect the Pb to be completely flushed from the sorbate in little more than four pore volumes of elution, the surface complexation model predicts that the sorbate, especially at its strongly sorbing sites, will remain contaminated even if flushed many times.

Pb desorbs gradually during elution, but the small amount released is sufficient to contaminate water flowing through the medium. The breakthrough curve (Figure 4) for the simulation shows a persistent tail of Pb contamination two to three orders of magnitude higher than prescribed by U.S. drinking water standards. The  $K_d$  approach, in contrast, suggests the effluent should be potable after just 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 5).

Discrepancy between predictions of the  $K_d$  and surface complexation approaches arises chiefly from the differing forms assumed for the sorption reaction (reactions 2 and 6). In the  $K_d$  approach, the

**Table 3**  
U.S. Drinking Water Standards<sup>a</sup> for Some Heavy Metals

| Metal        | mg/kg | μmolal |
|--------------|-------|--------|
| Cadmium (Cd) | .005  | .044   |
| Copper (Cu)  | 1.3   | 20.    |
| Mercury (Hg) | .002  | 0.010  |
| Nickel (Ni)  | .1    | 1.7    |
| Lead (Pb)    | .015  | .072   |

<sup>a</sup>Maximum contaminant level (MCL), as established by the U.S. Environmental Protection Agency (U.S. EPA 1995); MCL values have not been established for Co or Zn.

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 ( $Pb^{++}$ ,  $H^+$ ,  $>FeOH$ , and  $>FeOPb^+$ ) appear in the mass action equations.

Figure 6 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 reactions



for weakly and strongly sorbing sites to the right, complexing nearly all of the sites. The reaction has little effect on pH because the bicarbonate in solution serves to buffer the  $H^+$  activity. During elution, the desorption reaction



need proceed only gradually to the right in order to maintain equilibrium. The reason is clear from Figure 6. By mass action, any decrease in  $\log m_{Pb^{++}}$  must be compensated by an increase in  $\log m_{>FeOH}$  plus a decrease in  $\log m_{>FeOPb^+}$ . Because there are initially few uncomplexed sites, a small shift in the reaction causes the logarithm of the  $>(s)FeOH$  concentration to rise sharply, decreasing the number of complexed sites only gradually at first. After 30 pore volumes have been displaced, most of the weak sites but few of the strong sites have desorbed their complexed Pb.

From the form of the complexation reaction (Equation 6), we expect metal sorption to vary depending on solution pH as well as the reaction's equilibrium constant. Figure 7 shows how pH affects the breakthrough curves predicted. By Equation 6, we expect increasing the pH to favor sorption, but decreasing pH to favor displacement of sorbed metals. The results for Pb (Figure 7) show similar breakthrough curves when pH varies in the range 6 to 10. Under acidic conditions ( $pH \geq 4$ ), however, the simulations predict less pronounced "tailing" in the effluent. This result is likely of limited practical benefit because the many buffering reactions operating in most subsurface environments prevent maintaining ground water at such acidities.

Figure 8 shows how the equilibrium constant for the complexation reaction (reaction 6) affects the breakthrough curves for simulations calculated at pH 6. For simplicity, we assume here a single equilibrium constant for sorption on weakly and strongly sorbing sites. For large equilibrium constants (e.g.,  $K = 10^2$ – $10^4$ ), the breakthrough curve shows a persistent "tail" of low to moderate (1 to 10 μmolal) levels of metal contamination (Figure 8). In this case,

the metal binds tightly enough that it is released only gradually during flushing. For lesser values of the binding constant ( $K = 10^0$ – $10^{-1}$ ), the metal binds less tightly. Metal concentrations in the effluent are larger in these cases, and the tail becomes less persistent. When the binding constant is small enough ( $K \leq 10^{-2}$ ), the breakthrough curve assumes a symmetrical shape characteristic of curves obtained using the  $K_d$  approach.

Figure 9 shows results obtained for various heavy metals present in solution as divalent cations, calculated assuming the reactions and equilibrium constants shown in Table 2. Hg and cupric Cu behave much like Pb, forming persistent "tails" in excess of drinking water standards (Table 3). Zn, which binds less tightly than Pb, Hg, or Cu, shows a less persistent "tail" of contamination; the effluent is nearly devoid of this metal after about 15 pore volumes of elution. The weakly binding metals Ni, Cd, and Co do not form significant "tails" in the simulation.

In a final calculation (Figure 10), 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. As elution continues, the Pb is progressively sorbed within the aquifer, dramatically decreasing the dissolved concentration of the metal and slowing its migration.

$K_d$  theory (Figure 10, dashed lines), in contrast to surface complexation theory, predicts that dissolved concentrations in the contaminated zone remain high, decreasing only slightly due to the effects of dispersion. Contaminant, therefore, migrates freely through the aquifer in the  $K_d$  results at one-half the rate of ground water flow (since  $R = 2$ ).

## Discussion

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

- The aquifer is predicted to contain a contaminated zone, in which most of the strongly sorbing and a variable number of the weakly sorbing sites are saturated, and an uncontaminated zone that contains little sorbed Pb. The zones are separated by an abrupt 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 strongly sorbing sites are largely saturated, dissolved concentration can vary from small values upward without affecting the sorbed concentration significantly. In simulations calculated for  $pH \geq 5$ , 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, are effective at stripping Pb from solution.
- Flushing the contaminated zone with fresh water (whether during active remediation or by natural recharge) gradually displaces dissolved and sorbed Pb from the aquifer. The displaced ground water, however, contains Pb in concentrations persistently in excess of drinking water standards. The flush-

ing is ineffective at displacing sorbed Pb from the aquifer, especially from the strongly sorbing sites. The  $K_d$  approach, in contrast, predicts that flushing should efficiently displace all of the Pb, sorbed and dissolved, leaving the aquifer clean.

- The  $K_d$  approach predicts that a zone of Pb contamination will migrate along the direction of ground water flow at a rate determined by the retardation factor. Surface complexation theory suggests that the mobility of subsurface Pb contamination is limited by the aquifer's ability to sorb the metal. When water migrates from the contaminated to the uncontaminated zone, its Pb content is stripped by sorption. This process depletes the Pb content of the ground water and progressively slows the rate at which the contaminant can migrate.

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 ground water cleanup strategies in two principal ways:

- By suggesting overly optimistic rates of contaminant displacement from sediment surfaces by noncorrosive 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. Surface complexation theory, on the other hand, points to a significantly more recalcitrant Pb plume that can be removed rapidly by neither noncorrosive 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. Again, surface complexation theory suggests that the degree of soil contamination does not correlate directly to the level of ground water contamination.
- By overestimating the potential for plume advance. The  $K_d$  approach 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.

Effective remediation of subsurface contamination should follow 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 ground water 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 that the two methods suggest divergent remediation strategies for strongly sorbing metals in the subsurface.

## Concluding Remarks

An important final point to consider is whether the effort required to integrate more realistic descriptions of metal sorption into remediation efforts is worthwhile. First, the example calculations in this paper, which assume a sediment in which hydrous ferric oxide presents the only sorbing surface, are of course too simplistic to apply blindly to natural settings. General application will require descriptions of the behavior of the many varieties of real sediments and soils. Deriving a surface complexation model (or a Langmuir or Freundlich isotherm) for a given sample is by nature more complex than measuring a  $K_d$  value. Laboratory procedures for doing so exist, nonetheless, and have been applied to natural systems in a number of recent studies.

Kohler et al. (1996), for example, derived a surface complexation model for uranyl transport in a quartz sand. Using the widely applied FITEQL software (Westall and Herbelin 1994), they derived and optimized the model from the results of batch experiments and breakthrough curves taken from column experiments. Their model consisted of two site types and three complexation reactions, illustrating that a useful surface complexation model need not be overly complex. Davis et al. (1998), similarly, derived from the results of batch experiments a complexation model for Zn transport in a sandy aquifer in Cape Cod, Massachusetts. Their model contained only three adjustable parameters that needed to be regressed from the data. Such techniques could be readily applied to other field situations. Alternatively, surface complexation models for individual constituents of sediments and soils can be derived and then combined to reflect a sample's bulk composition. The latter approach, however, seems to give less accurate results than considering an individual soil or sediment sample as a whole (Davis et al. 1998).

Secondly, reactive transport models based on the  $K_d$  approach are simpler and hence easier to calculate than those employing more sophisticated sorption models. As already mentioned, however, a variety of software programs exist for performing the calculations, and most of these work well on the inexpensive and powerful personal computers available today. Given that we can expect improved software resources in the future, and even faster and less expensive computers, the computational hurdles to implementing more sophisticated simulation techniques seem minor.

Large amounts of money can be spent on a single environmental remediation project, and there is undeniably considerable direct value in protecting the environment. In this light, the additional expenditure of effort required to set up surface complexation models and to trace realistic transport simulations seems modest compared to the value of more accurate results from these simulations.

## Acknowledgments

Funding for this project was provided by a consortium of sponsors of the Hydrogeology Program at the University of Illinois: Amoco, ARCO, Chevron, Conoco, Exxon, Hewlett-Packard, Japan National Oil Corp., Lawrence Livermore, Mobil, Sandia, Silicon Graphics, Texaco, and the U.S. Geological Survey. PVB gratefully acknowledges the support of the SNL-LDRD office and the US NRC. We thank Brian Reed for supplying in numerical form the data in Figure 2. We appreciate comments by Tony Appelo, Randy Bassett, David Dzombak, Jeremy Fein, Pierre Glynn, Tom Holm, and Albert Valocchi, which improved the manuscript.

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