



Evaluation of bacteria-facilitated cadmium transport in gravel columns using the HYDRUS colloid-facilitated solute transport model

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[1] The colloid-facilitated solute transport model, based on HYDRUS-1D, was evaluated using the column experimental data of Pang et al. (2005) for cadmium (Cd) transport facilitated by *B. subtilis* spores or *E. coli* in saturated coarse alluvial gravels. We simulated Cd transport involving convection, dispersion, kinetic adsorption/desorption to/from the aquifer media and to/from mobile/immobile bacteria, and kinetic attachment/detachment of the bacteria to/from the aquifer media. To reduce the number of parameters to be optimized, we independently estimated Cd sorption/desorption rates to mobile bacteria from a batch study. The model described the collected experimental data reasonably well. Extensive sensitivity analysis to various reaction parameters was carried out to obtain an understanding of the relative importance of individual model parameters on model predictions. Our modeling results suggest that the rates of Cd sorption or desorption differ not only between different bacterial species but also between unattached and deposited bacteria. The results of the sensitivity analysis indicated that the Cd sorption rate to unattached bacteria had a significantly greater impact on the model results than its sorption rate to deposited bacteria. For the experimental system investigated here, model results were most sensitive to parameters describing interactions between Cd-aquifer media, bacteria-aquifer media, and Cd-mobile bacteria, and they were less sensitive to interactions between Cd-immobile bacteria and desorption rate from mobile bacteria.

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1. Introduction

[2] The classical view that strongly sorbing contaminants (i.e., heavy metals, radionuclides, some pesticides) move very slowly through soils and aquifers has been challenged recently by the evidence that their transport velocity in porous media can be from a few times up to several thousand times faster when they are adsorbed to mobile colloids [Newman et al., 1993; Grolimund et al., 1996; Saiers and Hornberger, 1996; McCarthy et al., 1998; Pang and Close, 1999; Karathanasis, 1999, 2000; Artinger et al., 2002]. Colloids (e.g., humic substances, bacteria, clays, and metal oxides) have a considerable adsorption capacity for other species present in water because of their large specific surface areas and their high concentrations in groundwater and soil-water. Colloids can be the most mobile constituent in groundwater and can thus provide a vehicle for the rapid transport of smaller, less mobile contaminants. On the other hand, colloids can be subject to straining and filtration in porous media and can thus also act as inhibitors of contaminant migration if the contaminants are adsorbed to them. Understanding this twofold role of colloids on the transport

and attenuation of contaminants has important implications for risk analysis and remediation of contaminated sites.

[3] Over the last decade, a number of computer models have been developed to simulate colloid-facilitated solute transport in porous media [Mills et al., 1991; Dunnivant et al., 1992; Corapcioglu and Jiang, 1993; Jiang and Corapcioglu, 1993; Corapcioglu and Kim, 1995; Saiers and Hornberger, 1996; van de Weerd and Leijnse, 1997]. Three-phase colloid-facilitated solute transport models (CFMs) can simultaneously simulate interactions among solutes, colloids and porous media and are superior to conventional two-phase contaminant transport models, which only address interactions between contaminants and porous media. CFMs address the coupled transport of solutes that are dissolved in the aqueous phase or adsorbed to porous media and mobile/immobile colloids, with the transport of colloids that are suspended in solution (mobile colloids) or attached to the porous media (immobile colloids). CFMs are generally based on mass balance equations of these individual components [e.g., Corapcioglu and Jiang, 1993; van de Weerd et al., 1998; Corapcioglu and Kim, 1995]. However, various assumptions and simplifications are made in different CFMs about interactions between colloids and solutes (e.g., kinetics/equilibrium, linear/nonlinear, reversible/irreversible etc), as well as the aquifer transport properties (e.g., different velocities and dispersivities of colloids and solutes). Descriptions of different assumptions in some CFMs are given by van de Weerd et al. [1998].

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[4] Colloid-facilitated solute transport has recently been incorporated into the HYDRUS-1D software package [Šimůnek *et al.*, 2006]. The existing HYDRUS-1D model is a widely used solute transport model for variably saturated porous media [e.g., *Vanderborght et al.*, 2005]. Like other CFMs, the HYDRUS CFM considers interactions among colloids, solutes, and porous media, but it also contains some features that are usually not included in other CFMs. Šimůnek *et al.* [2006] describe the major differences between the HYDRUS CFM and most other CFMs. These differences include considerations of (1) the velocity enhancement of colloids and colloid-facilitated solute transport due to size and anion exclusion (thus different pore velocities and dispersivities for colloids and solutes), (2) irreversible straining and nonlinear blocking, (3) water contents, water fluxes, and air-water interfacial areas that may change in time and space (i.e., transient variably saturated water flow), (4) the presence of the air-water interface colloids, and (5) adjustment of all kinetic rates to the number of colloids present in the system.

[5] Although the newly developed CFMs are more appropriate than conventional solute transport models in interpreting coupled solute and colloid transport in natural subsurface conditions, the models' abilities need to be evaluated using actual experimental data. Model evaluation must be an essential part of model development. In comparison with solute transport models, many more parameters are employed in CFMs and some of these parameters are difficult, if not impossible, to estimate experimentally. This significantly increases the uncertainty of parameter estimation, especially for parameters that are closely correlated. Thus, without experimental verification it is uncertain how capable and applicable these CFMs are in addressing real problems. Although a number of CFMs have been developed, model verification against experimental data is still relatively limited [Saiers, 2002].

[6] The purpose of this paper is twofold. The first objective is to evaluate the newly developed HYDRUS CFM using the column experimental data of Pang *et al.* [2005] for cadmium (Cd) transport in the presence of bacteria (*B. subtilis* spores or *E. coli*) in saturated coarse alluvial gravels. By using experimental evaluation, we aim to identify the most important processes that govern bacteria-facilitated Cd transport and the key parameters that describe these processes. The second objective is to examine whether exchange processes between liquid, solid, and colloid phases can be adequately described using linear exchange models. As part of the model evaluation, sensitivity tests were also undertaken to systematically assess the impact of model input parameters on the model's output and to provide an insight into the relative importance of individual model parameters within a complex system. Model evaluation not only assists in understanding where weaknesses in the modeling results may lie, but it also assists with data interpretation, and provides guidance for further model modifications and future experimental designs.

2. Methods

2.1. Experiments and Experimental Data

[7] Pang *et al.* [2005] conducted a series of column experiments using various concentrations of bacteria to

study Cd transport in the presence of *Bacillus subtilis* spores or *E. coli* vegetative cells under saturated conditions. A column (18 cm long, 10 cm in internal diameter) was uniformly packed with coarse gravel aquifer material (mean diameter $d_{50} = 16.69$ mm, uniformity $d_{60}/d_{10} = 53$) with a bulk density of 1.9 g/cm^3 and effective porosity of 0.27. The mean flow rate applied was $32.4 (\pm 0.4)$ mL/min. A solution containing Cd (approximately 4 mg/L) and bromide (Br) (approximately 2 mg/L), at a fixed pH value (pH = 7.0, 7.5 or 7.7 for different experiments), was first injected for about five pore volumes. *B. subtilis* spores or *E. coli* were introduced to the column together with Cd and Br for further 3.4 pore volumes. Subsequently, the column was flushed with solution-free fresh water. The experiments were conducted at room temperature ($20^\circ\text{C} \pm 1$) over 3–4 hours. Total effluent Cd concentrations, and in some experiments dissolved Cd concentrations, were analyzed. In all experiments, untreated groundwater extracted from alluvial gravel aquifers was used as the background electrolyte. The bacteria were washed with saline solution, and the solution was diluted with untreated groundwater to the required concentration before an experiment was conducted. Detailed experimental information is given by Pang *et al.* [2005].

[8] Figures 1 and 2 demonstrate that when bacterial concentrations were sufficiently high, with the introduction of either *B. subtilis* spores or *E. coli*, there were simultaneous steep rises and flat plateaus of Cd concentrations (Figures 1b, 1c, 2b and 2c), indicating that Cd was cotransported with these bacteria. In contrast, this feature was not displayed in Cd breakthrough curves (BTCs) when bacteria concentrations were low (Figures 1a and 2a). Both Figures 1 and 2 also show a relatively fast arrival, often before one pore volume, of both Br and Cd. While Br BTCs displayed a sharp rise in concentrations after the early arrival, Cd concentrations increased only gradually, indicating kinetically controlled adsorption to the aquifer material. Similarly, a gradual decrease of Cd concentrations after the maximum peak or plateau indicates kinetically controlled desorption of Cd from the aquifer material.

[9] Pang *et al.* [2005] also examined the kinetics of Cd adsorption onto *B. subtilis* spores or *E. coli* in batch experiments that were conducted in the absence of aquifer media. Bacterial solutions spiked with known masses of Cd, held in 40 mL screw top glass vials, were gently stirred continuously for three hours at room temperature ($20^\circ\text{C} \pm 1$). Bacteria-free controls with Cd only were also prepared to estimate Cd precipitation and adsorption onto the experimental apparatus. Total and dissolved Cd concentrations were analyzed. To be consistent with the column experiments, untreated groundwater was used as the background electrolyte and the bacteria used were washed with saline solution before dilution. The kinetics of Cd sorption to the bacteria is illustrated in Figure 3. While there was a sharp decrease of dissolved Cd concentrations in the solution with *B. subtilis* spores, only a small decrease of dissolved Cd concentrations was observed in the solution with *E. coli*. While Cd concentrations in the solution with *E. coli* reached a semiequilibrium state relatively quickly, sorption of Cd to *B. subtilis* spores continued for longer than three hours.

2.2. Modeling

[10] Although many complex processes (e.g., transient variably saturated water flow, irreversible straining and

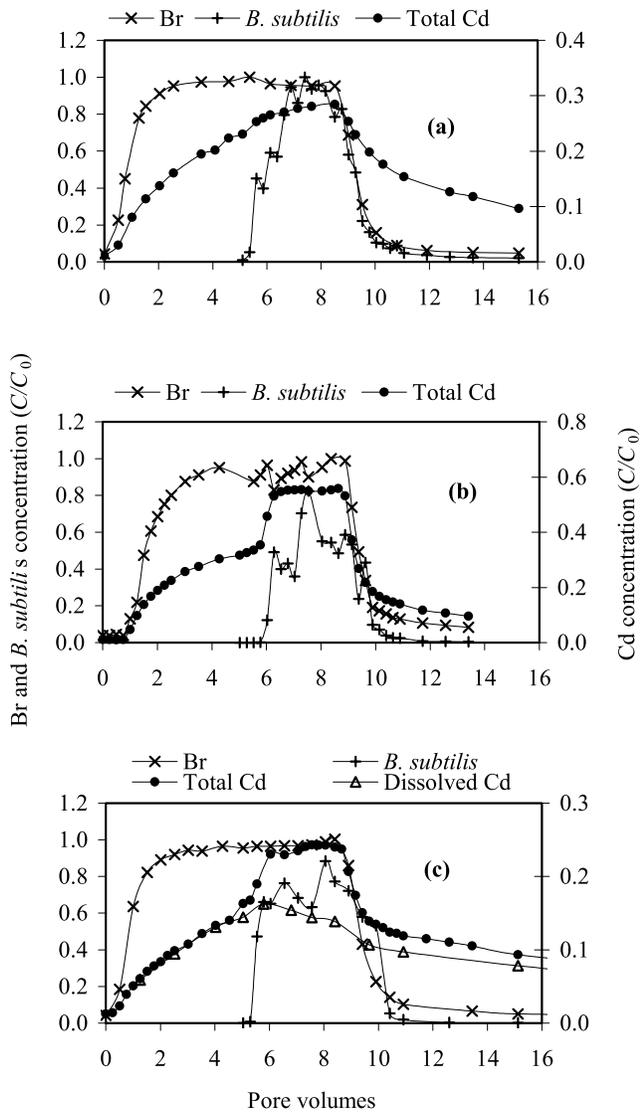


Figure 1. Cd and Br transport in the presence of *B. subtilis* spores in the column experiments of Pang *et al.* [2005] (a) *B. subtilis* $C_0 = 9 \times 10^4$ cfu/mL, pH = 7.0. (b) *B. subtilis* $C_0 = 7 \times 10^5$ cfu/mL, pH = 7.7. (c) *B. subtilis* $C_0 = 5.6 \times 10^7$ cfu/mL, pH = 7.0. *B. subtilis* spores were introduced after about 5 pore volumes injection of Cd and Br.

nonlinear blocking, air-water interface) are considered in the original HYDRUS CFM [Šimůnek *et al.*, 2006], only the simpler version of the model was needed for the relatively simple experimental system described above, which involved steady state, fully saturated flow conditions. Straining of the bacteria was considered to be negligible because the size of the largest bacteria (6 μm) was only 0.04% of the media grain diameter (16.69 mm), which is well below the 0.5% threshold for straining [Bradford *et al.*, 2004]. Inactivation of bacteria and precipitation of Cd were also considered insignificant given the short durations of experiments. Thus we have focused our attention on the kinetic behavior of Cd adsorption to bacteria and aquifer media. To describe the experimental system, the HYDRUS CFM was simplified to consider exchange processes between liquid, solid, and colloid phases using linear exchange models, which is given below.

2.2.1. Bacteria Transport

[11] Bacteria transport was described using the advection-dispersion equation coupled with the first-order attachment-detachment kinetics [e.g., Hornberger *et al.*, 1992; McCaulou *et al.*, 1994]:

$$\frac{\partial \theta_c C_c}{\partial t} + \rho \frac{\partial S_c}{\partial t} = \frac{\partial}{\partial x} \left(\theta_c D_c \frac{\partial C_c}{\partial x} \right) - \frac{\partial q_c C_c}{\partial x} \quad (1)$$

$$\rho \frac{\partial S_c}{\partial t} = \theta_c k_{ac} C_c - \rho k_{dc} S_c \quad (2)$$

where C_c is the bacteria concentration in the aqueous phase [cfu L^{-3}] (cfu is colony-forming unit, a unit indicating the number of microorganisms present in a water sample); θ_c is

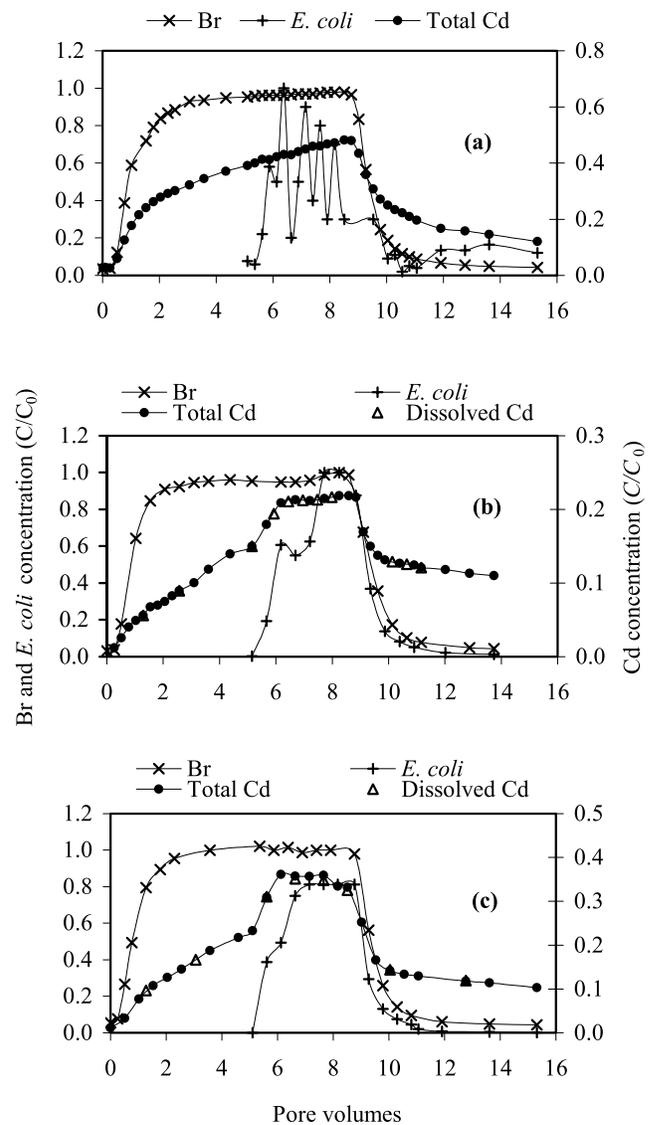


Figure 2. Cd and Br transport in the presence of *E. coli* in the column experiments of Pang *et al.* [2005]. (a) *E. coli* $C_0 = 5 \times 10^3$ cfu/mL, pH = 7.5. (b) *E. coli* $C_0 = 1.6 \times 10^5$ cfu/mL, pH = 7.0. (c) *E. coli* $C_0 = 3.7 \times 10^7$ cfu/mL, pH = 7.0. *E. coli* were introduced after about 5 pore volumes injection of Cd and Br.

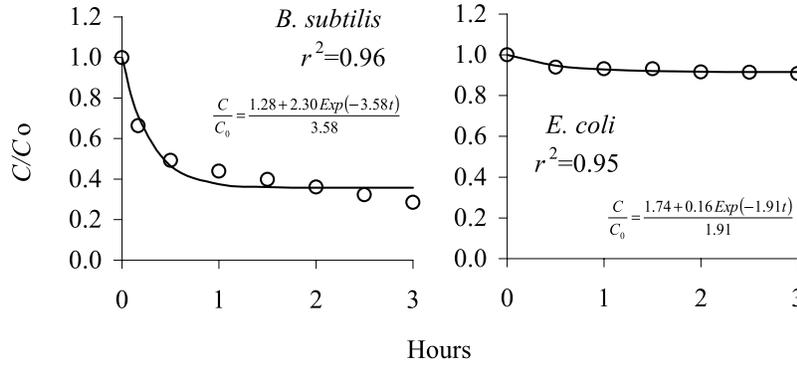


Figure 3. Results of kinetic batch study on Cd sorption to suspended bacteria. Circles are observed data, and lines are model predictions using the kinetic sorption model.

the water content accessible to bacteria [L^3L^{-3}]; S_c is the bacteria concentration attached to the aquifer media [$cfu M^{-1}$]; D_c is the dispersion coefficient for bacteria [L^2T^{-1}]; ρ is the bulk density of the aquifer material [ML^{-3}]; k_{ac} and k_{dc} are the first-order rate coefficients for bacteria attachment and detachment [T^{-1}], respectively; q_c is the water flux density for bacteria moving only in pores from which they are not excluded [LT^{-1}]; t is the time [T]; and x is the distance from the inlet [L].

[12] In comparison to solutes that are thought to travel through all pores, colloids often travel only through interconnected larger pores, with a smaller pore network. As a result of size exclusion, the aquifer pore network accessible to colloids may have smaller water content, smaller dispersion, and greater pore water velocity. The water flux density for bacteria, q_c , can be calculated from the ratio of the relative hydraulic conductivity of the entire pore space (K_{rw}) to the relative hydraulic conductivity of the bacteria accessible pores (K_{rc}), and the water flux density q_w [LT^{-1}] as follows

$$q_c = q_w \frac{K_{rc}}{K_{rw}} \quad (3)$$

2.2.2. Bacteria-Facilitated Cd Transport

[13] Transport of Cd interacting with bacteria was described by the following equation

$$\begin{aligned} \frac{\partial \theta C}{\partial t} + \rho \frac{\partial S_e}{\partial t} + \rho \frac{\partial S_k}{\partial t} + \frac{\partial \theta_c C_c S_{mc}}{\partial t} + \rho \frac{\partial S_c S_{ic}}{\partial t} \\ = \frac{\partial}{\partial x} \left(\theta D \frac{\partial C}{\partial x} \right) - \frac{\partial q_w C}{\partial x} + \frac{\partial}{\partial x} \left(\theta_c S_{mc} D_c \frac{\partial C_c}{\partial x} \right) - \frac{\partial q_c C_c S_{mc}}{\partial x} \end{aligned} \quad (4)$$

where C is the dissolved Cd concentration [ML^{-3}]; S_e and S_k are Cd concentrations sorbed instantaneously and kinetically, respectively, to the aquifer media [MM^{-1}], S_{mc} and S_{ic} are Cd concentrations sorbed to the suspended mobile bacteria and to the deposited immobile bacteria [$M cfu^{-1}$], respectively; θ is the total water content [L^3L^{-3}]; D is the dispersion coefficient [L^2T^{-1}]. Note that we used the entire water content, dispersion and water flux for Cd. Interactions between different contaminant pools in equation (4) are further expressed by a number of mass balance equations, which are given below.

2.2.2.1. Cd Sorbed to the Solid Phase

[14] Solute sorption to the aquifer material is described using the two-site sorption concept that assumes that the total sorption, S , can be divided into the kinetic and instantaneous sorption as follows:

$$S = S_e + S_k \quad (5)$$

and

$$\rho \frac{\partial S_k}{\partial t} = \omega [(1-f)K_d C - S_k] \quad (6)$$

where ω is the first-order rate constant [T^{-1}] and f is the fraction of exchange sites assumed to be in equilibrium with the solution phase (dimensionless). We have assumed that sorption S_e on the instantaneous sites is a linear process, i.e., $S_e = fK_d C$.

2.2.2.2. Cd Sorbed to Mobile and Immobile Bacteria

[15]

$$\begin{aligned} \frac{\partial \theta_c C_c S_{mc}}{\partial t} = \frac{\partial}{\partial x} \left(\theta_c S_{mc} D_c \frac{\partial C_c}{\partial x} \right) - \frac{\partial q_c C_c S_{mc}}{\partial x} + \theta \psi_m k_{amc} C \\ - \theta_c k_{dmc} C_c S_{mc} - \theta_c k_{ac} C_c S_{mc} + \rho k_{dc} S_c S_{ic} \end{aligned} \quad (7)$$

$$\rho \frac{\partial S_c S_{ic}}{\partial t} = \theta \psi_{im} k_{aic} C - \rho k_{dic} S_c S_{ic} + \theta_c k_{ac} C_c S_{mc} - \rho k_{dc} S_c S_{ic} \quad (8)$$

where k_{amc} and k_{dmc} are the rate coefficients for Cd sorption to and desorption from mobile bacteria [T^{-1}], respectively; k_{aic} and k_{dic} are the rate coefficients for Cd sorption to and desorption from immobile bacteria [T^{-1}], respectively; and parameters ψ_m and ψ_{im} are dimensionless variables that adjust the sorption rate to the changing number of mobile and immobile colloids present, respectively [Šimůnek et al., 2006]. Values of ψ_m and ψ_{im} increase from zero when there are no bacteria present to one when the number of bacteria is the same as the number (reference number) of bacteria for which k_{amc} and k_{aic} were determined. They can be larger than one if the number of bacteria is larger than this reference number. The numerical solution of the above equations has been implemented into the HYDRUS-1D CFM. Detailed information is given by Šimůnek et al. [2006].

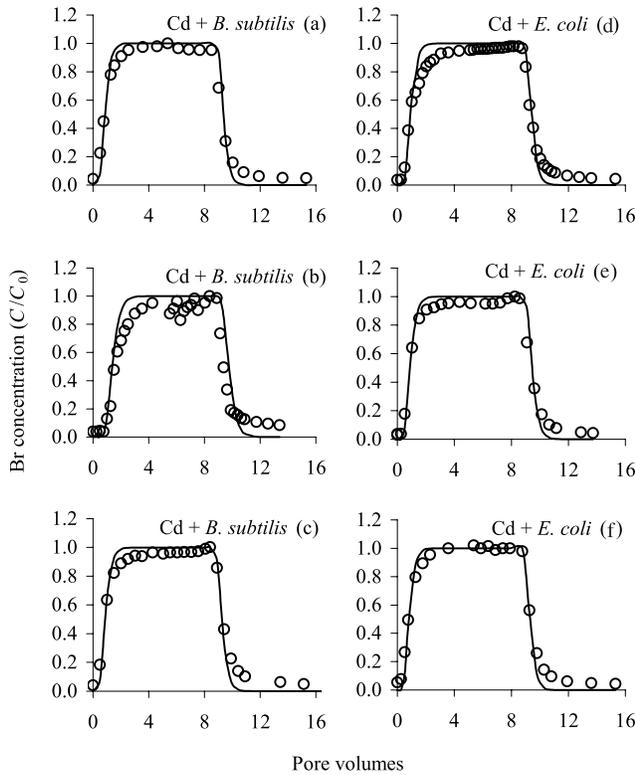


Figure 4. Observed (circles) and simulated (lines) Br concentrations using the equilibrium model. Cd + *B. subtilis* experiments: (a) $C_0 = 9 \times 10^4$ cfu/mL, pH = 7.0 (experiment a); (b) $C_0 = 7 \times 10^5$ cfu/mL, pH = 7.7 (experiment b); (c) $C_0 = 5.6 \times 10^7$ cfu/mL, pH = 7.0 (experiment c). Cd + *E. coli* experiments: (d) $C_0 = 5 \times 10^3$ cfu/mL, pH = 7.5 (experiment a); (e) $C_0 = 1.6 \times 10^5$ cfu/mL, pH = 7.0 (experiment b); (f) $C_0 = 3.7 \times 10^7$ cfu/mL, pH = 7.0 (experiment c).

2.2.3. Inverse Modeling

2.2.3.1. Batch Experimental Data

[16] Data from batch experiments carried out in the absence of aquifer material were used to derive the kinetics of Cd sorption to the mobile bacteria (k_{amc} and k_{dmc}) as the bacteria used in the batch experiments were suspended in solution. Experimental data were analyzed using an equation adopted from *Schijven and Hassanizadeh* [2000]:

$$\frac{C}{C_0} = \frac{k_{dmc} + k_{amc} \exp[-(k_{amc} + k_{dmc})t]}{k_{amc} + k_{dmc}} \quad (9)$$

in which C_0 is the initial Cd concentration [ML^{-3}]. Equation (9) was fitted to the concentration versus time data, with an aid of the least squares method using the Solver Optimizing Function that is implemented in Excel. To measure the quality of model fit, the sum of squared residuals (SSRs) and R-square (r^2) were calculated using standard statistic formula. The fitted curves are given in Figure 3.

2.2.3.2. Column Experimental Data

[17] BTCs of the conservative solute tracer Br were first analyzed to derive K_{rw} and D using the internal HYDRUS-1D optimization routine. Model-simulated and observed Br

concentrations are compared in Figure 4. Bacteria BTCs were then analyzed to estimate flow and transport properties for bacteria using the attachment and detachment model and the internal HYDRUS-1D optimization routine. In the preliminary analysis of bacteria data, K_{rc} , D_c , k_{ac} , and k_{dc} parameters were estimated independently from Br results. However, the apparent optimized D_c values were generally significantly larger than the D values estimated from Br. Since these large D_c values were considered to be an artifact and a reflection of large variations in the bacteria data, in the further analyses we neglected possible velocity enhancement of bacteria and further simulated bacteria BTCs using the same conductivity and dispersion derived from Br while optimizing only k_{ac} and k_{dc} . Because of the relatively small size of bacteria in comparison with the pore network of coarse aquifer material, the flow paths of bacteria and Br will likely be similar, resulting in the same values of mean pore velocities and dispersivities. We consider that the error in using same dispersion for bacteria and Br is relatively smaller than that using dispersion estimated from the erratic bacteria data that contains significant variations. Much smaller standard errors for the model results were obtained when assuming this simplification of the system.

[18] Finally, Cd BTCs were simulated using the bacteria-facilitated Cd transport model. The K_{rw} , D , k_{amc} , k_{dmc} , k_{ac} , and k_{dc} coefficients obtained from the analyses of the Br and bacteria BTCs and batch experiments were held constant in the simulations of bacteria-facilitated Cd transport. In addition to reducing the number of optimized parameters, the use of independently determined k_{amc} and k_{dmc} values was needed. This is because the Cd sorption rates to mobile and immobile bacteria are highly correlated ($r^2 > 0.92$) and model results would contain very high level of uncertainty if they were both optimized, as indicated by the results of some preliminary optimizations. Model simulations were first carried out to optimize the five model parameters characterizing the sorption to immobile bacteria (k_{aic} and k_{dic}) and instantaneous and kinetic sorption to the aquifer material (ω , K_d , and f). The PEST optimization package of *Doherty et al.* [1994] was used for the inverse parameter optimization. An equal weight was allocated during the optimizations to both the total and dissolved Cd concentrations observed in the effluent. As the results of optimizations constantly yielded $f = 0.01$ and $k_{dic} = 0.00$, these values were subsequently fixed. Further optimizations were carried out with fewer parameters, which significantly reduced the standard errors of the model estimations. Experimental data that did not show a significant bacteria-facilitated Cd transport were simulated by setting k_{aic} , k_{dic} , k_{amc} , and k_{dmc} equal to zero in the model, while K_d , ω and f were optimized. To measure the quality of model fit, SSRs, standard error coefficient (SE), and r^2 were calculated.

2.2.4. Sensitivity Analysis of Model Parameters

[19] To evaluate the impact of model input parameters on the model's output (the total and dissolved Cd in the effluent), a sensitivity analysis was undertaken. We focused on parameters that describe three-phase interactions. The following nine parameters, which characterize Cd sorption/desorption to/from mobile/immobile bacteria (k_{amc} , k_{dmc} , k_{aic} , k_{dic}), Cd sorption to aquifer material (f , K_d , ω), and bacteria attachment/detachment to/from the aquifer material (k_{ac} , k_{dc}), were selected for the sensitivity analysis. Cali-

Table 1. Rate Coefficients of Cd Adsorption/Desorption to/From the Suspended Bacteria Derived From the Kinetic Batch Study in the Absence of Aquifer Media

Experiment	Experimental Condition			Optimized Results				
	Bacteria C_0 , cfu/mL	Cd C_0 , mg/mL	pH	k_{ame} , h^{-1}	k_{dmc} , h^{-1}	Reversibility k_{dmc}/k_{ame}	r^2	SSRs
<i>B. subtilis</i>	9.9×10^7	0.50	7.0–7.5	2.30	1.28	0.56	0.96	0.02
<i>E. coli</i>	1.9×10^8	0.50	6.9–7.4	0.16	1.74	10.8	0.95	0.00

brated simulations were used as the baseline for comparison of the test results, with the aid of SSRs. One parameter was tested at a time while all other parameters were fixed at the calculated values. Possible ranges of parameter values were evaluated in the analysis.

3. Results and Discussion

3.1. Model Description of Experimental Data

[20] Table 1 lists the rate coefficients of Cd adsorption/desorption to/from the suspended mobile bacteria optimized applying the kinetic sorption model (equation (9)) to the data from the kinetic batch study. The kinetic sorption model appears to fit well ($r^2 = 0.95–0.96$, SSRs = 0.00–0.02) with the observed batch experimental data (Figure 3). The results show that the fraction of Cd sorbed onto *B. subtilis* spores is much greater than onto *E. coli* (Figure 3), and that the Cd sorption rate to the spores is more than one order of magnitude greater than the Cd sorption rate to *E. coli* (Table 1). The greater sorption of Cd onto *B. subtilis* spores than onto *E. coli* was also observed in the column data. As shown in Figures 1 and 2, the difference between the total and dissolved Cd effluent concentrations is significant for Cd cotransport with *B. subtilis* spores but insignificant for Cd cotransport with *E. coli*. Pang *et al.* [2005] explained this difference using the fundamentally different structural and chemical properties of cell walls of gram-positive bacteria (*B. subtilis*) and gram-negative bacteria (*E. coli*). Unlike gram-positive bacteria, the surface of the gram-negative bacterial cell could produce outer membrane vesicles. It is thought that these soluble secretion products might have chelated Cd in solution and competed with the bacterial surface for the available Cd, thereby reducing the observed degree of adsorption onto the *E. coli* cells. For a more detailed description, please refer to Pang *et al.* [2005]. The possible chelation of Cd by *E. coli* is also supported by the fact that the rate of Cd desorption from *E. coli* is one order of magnitude greater than its sorption rate (Table 1). Although sorption of Cd onto *B. subtilis* spores is also reversible, sorption rate is faster than the desorption rate (Table 1). Our observation of the reversible sorption of Cd onto the selected bacteria is consistent with findings made by others. Cd sorption was found to be fully reversible onto both *B. subtilis* [Fowle and Fein, 2000] and *E. coli* [Yee and Fein, 2001] in batch studies.

[21] Although the two bacterial species react very differently with Cd, their attachment/detachment behavior to/from the aquifer media is similar, as indicated by the k_{ac} and k_{dc} values optimized using the attachment/detachment model (Table 2). Attachment of both *B. subtilis* and *E. coli* to the aquifer media is reversible during the short time frame

of the experiments, with the attachment rate generally much greater than the detachment rate. There seems to be no clear pattern in k_{ac} and k_{dc} values with changes in bacterial concentrations and pH values. However, the optimized k_{ac} values are in a narrow interval varying by only a factor of two (with one exception) with small SE values (Table 2). Figure 5 shows that the first-order kinetic attachment/detachment model fits generally well with the observed bacteria concentrations ($r^2 = 0.71–0.94$, SSRs = 0.11–0.59), except for the erratic experimental data at low *E. coli* input concentration ($r^2 = 0.54$, SSRs = 0.98).

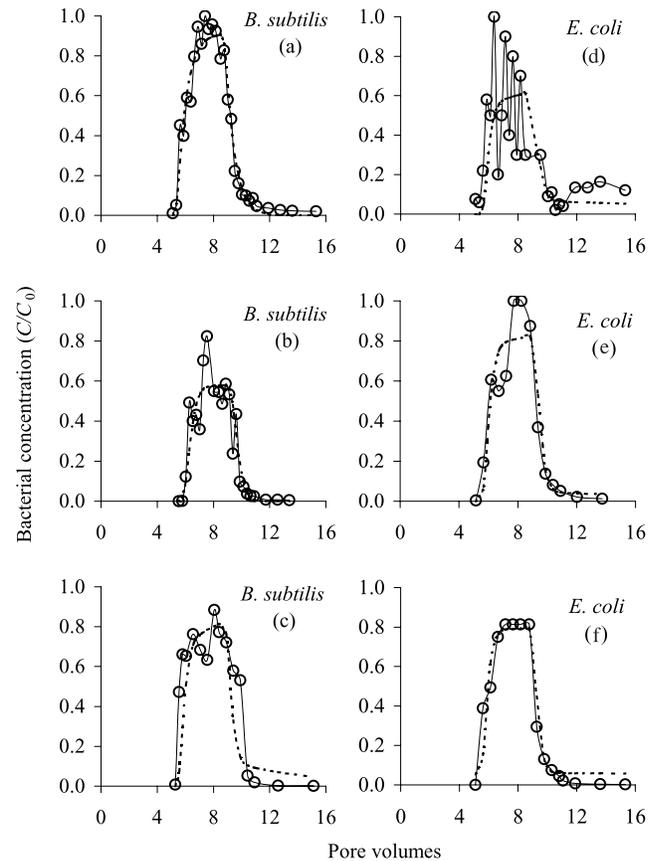


Figure 5. Observed (circles) and simulated (dashed lines) bacterial concentrations using the attachment-detachment model. Bacteria were introduced after about 5 pore volumes injection of Cd and Br. *B. subtilis*: (a) $C_0 = 9 \times 10^4$ cfu/mL, pH = 7.0 (experiment a); (b) $C_0 = 7 \times 10^5$ cfu/mL, pH = 7.7 (experiment b); (c) $C_0 = 5.6 \times 10^7$ cfu/mL, pH = 7.0 (experiment c). *E. coli*: (d) $C_0 = 5 \times 10^3$ cfu/mL, pH = 7.5 (experiment a); (e) $C_0 = 1.6 \times 10^5$ cfu/mL, pH = 7.0 (experiment b); (f) $C_0 = 3.7 \times 10^7$ cfu/mL, pH = 7.0 (experiment c).

Table 2. Rate Coefficients of Bacteria Attachment/Detachment to/From the Aquifer Media Optimized Using the Attachment/Detachment Model

Experiment	Bacteria, cfu/mL	pH	Fixed From Br Data		k_{ac} , h ⁻¹		k_{dc} , h ⁻¹		r^2	SSRs
			K_{FWS} , cm/hr	α_x , ^a cm	Value	SE	Value	SE		
Cd + <i>B. subtilis</i> (experiment a)	9.0×10^4	7.0	27.19	1.35	1.02	0.28	0.43	0.49	0.92	0.14
Cd + <i>B. subtilis</i> (experiment b)	7.0×10^5	7.7	16.71	0.90	1.96	0.26	0.00	0.19	0.83	0.27
Cd + <i>B. subtilis</i> (experiment c)	5.6×10^7	7.0	25.99	1.50	1.29	0.74	0.10	0.82	0.71	0.59
Cd + <i>E. coli</i> (experiment a)	5.0×10^3	7.5	25.08	1.31	3.11	0.80	0.36	0.44	0.54	0.98
Cd + <i>E. coli</i> (experiment b)	1.6×10^5	7.0	26.18	1.50	1.33	0.48	0.42	0.63	0.90	0.19
Cd + <i>E. coli</i> (experiment c)	3.7×10^7	7.0	28.38	1.50	1.86	0.43	0.07	0.01	0.94	0.11

^aDispersivity.

[22] Table 3 gives parameters optimized using the colloid-facilitated solute transport model. Model-simulated and observed concentrations of Cd, including both total and dissolved effluent concentrations, are compared in Figures 6 and 7. The excellent agreement between the optimized and measured BTCs suggests that the newly developed HYDRUS CFM is capable of simulating bacteria-facilitated metal transport for the experimental problem tested herein and that exchange processes between liquid, solid, and colloid phases can be adequately described using linear exchange models.

[23] The interaction of Cd with the aquifer media is described by parameters ω , f and K_d . Table 3 shows that ω and f values are similar in experiments with *E. coli* and *B. subtilis* spores and change little between experiments. This finding indicates that the Cd sorption rate to the aquifer media and the fraction of the kinetic sites are not affected by the presence of bacteria. The optimized f value is consistently close to zero, suggesting that Cd transport is a kinetic process. The K_d values do not show any particular pattern, reflecting variations of experimental conditions and uncertainty of model simulations. It is expected that similar to ω and f , K_d values should not be affected by the presence or absence of bacteria as attached bacteria would not have covered enough of the soil surface to significantly change its sorption characteristics.

[24] Bacteria-facilitated Cd transport is described by the rate coefficients of Cd adsorption and desorption to unattached and attached bacteria (k_{amc} , k_{dmc} , k_{aic} , k_{dic}). As mentioned previously, we have determined k_{amc} and k_{dmc} using the batch experimental data, and estimated k_{aic} and k_{dic} using the column experimental data. We have thus assumed that rates of k_{amc} and k_{dmc} are the same in both the batch and column systems. Results of k_{amc} and k_{dmc} have been discussed previously, here we only discuss the

results of k_{aic} and k_{dic} . During preliminary optimizations, the k_{dic} value constantly approached zero, which suggests that the sorption of Cd onto deposited bacteria is essentially irreversible.

[25] The k_{aic} value for Figures 6c and 6d is significantly greater than that for Figure 6b (Table 3), inferring a greater Cd adsorption onto deposited bacteria in Figures 6c and 6d. This may explain the more pronounced tailing in Figures 6c and 6d, in comparison with Figure 6b, as bacteria deposited to the solid matrix would act as additional sorption sites. The k_{aic} values for Figures 7b–7e are similar (Table 3), which is in agreement with the similar degree of Cd BTC tailings. The greater k_{aic} value for Figures 6c and 6d than for Figure 6b is thought to be due to an increase in the input concentration of *B. subtilis* spores providing more bacterial sorption sites for Cd. In contrast, the k_{aic} value for Figures 7d and 7e is smaller than for Figures 7b and 7c (Table 3) with an increase in *E. coli* concentration, again suggesting chelation of Cd by *E. coli*. However, the standard error of k_{aic} estimation for *E. coli* in Figures 7b and 7c is quite large (Table 3), thus the results contain a high level of uncertainty.

[26] Unlike the approach used by others [Tsezos and Bell, 1989; Corapcioglu and Kim, 1995] who assumed the same adsorption or desorption rate coefficients of a contaminant for both unattached and deposited bacteria, we assumed different rates for deposited and unattached bacteria due to a number of reasons: (1) Although unattached and deposited cells of a particular strain of bacteria have similar surface characteristics [Corapcioglu and Kim, 1995], the surface areas of deposited cells are relatively less exposed to sorption for the contaminant. (2) Nutritional state and activity of deposited and unattached bacteria may be different. Deposited bacteria might be better fed from nutrients on aquifer grain surfaces and thus may be more active metabolically for acquiring contaminants. (3) Deposited

Table 3. Transport Parameters Derived From Cd BTCs Using the Colloid-Facilitated Solute Transport Model^a

Experiment	K_d , g/mL		ω , h ⁻¹		k_{aic} , h ⁻¹		f		r^2	SSRs
	Value	SE	Value	SE	Value	SE	Value	SE		
Cd + <i>B. subtilis</i> (experiment a)	5.58	0.22	0.28	0.01	-	-	0.03	0.00	0.91	0.08
Cd + <i>B. subtilis</i> (experiment b)	2.29	0.43	0.25	0.04	18.71	5.31	0.01	-	0.93	0.16
Cd + <i>B. subtilis</i> (experiment c)	5.00	0.06	0.45	0.01	46.52	6.36	0.01	-	0.93	0.02
Cd + <i>E. coli</i> (experiment a)	2.72	0.09	0.36	0.01	-	-	0.01	0.00	0.78	0.10
Cd + <i>E. coli</i> (experiment b)	6.59	0.06	0.33	0.01	20.08	9.31	0.01	-	0.78	0.01
Cd + <i>E. coli</i> (experiment c)	4.00	0.12	0.34	0.00	16.71	4.88	0.01	-	0.87	0.16

^aHere k_{amc} and k_{dmc} were fixed at values determined from the batch experimental data. A zero k_{dic} value was fixed, as suggested from the result of preliminary optimizations.

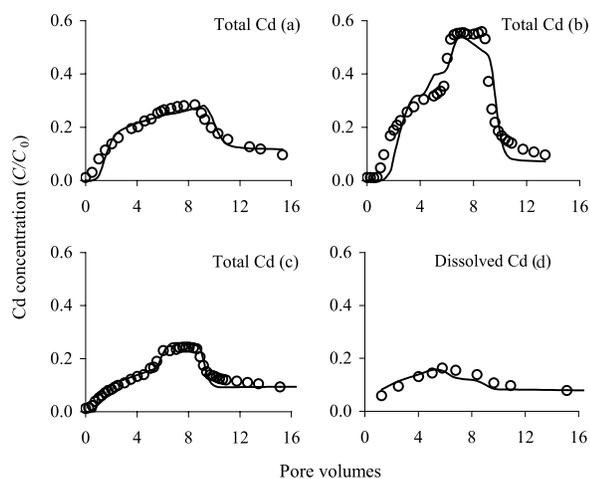


Figure 6. Observed (circles) and simulated (lines) Cd concentrations using the colloid-facilitated solute transport model for the Cd + *B. subtilis* spores experiments. (a) $C_0 = 9 \times 10^4$ cfu/mL, pH = 7.0 (experiment a). (b) $C_0 = 7 \times 10^5$ cfu/mL, pH = 7.7 (experiment b). (c and d) $C_0 = 5.6 \times 10^7$ cfu/mL, pH = 7.0 (experiment c).

bacteria cells might be surrounded by a matrix of extracellular polymers (EPS), produced by other bacterial species that naturally occur in the aquifer media. Researchers have shown that cells produce EPS to “glue” themselves to mineral surfaces [Jucker *et al.*, 1997, 1998; McWhirter *et al.*, 2002]. Bacterial EPS occur naturally in subsurface media and have well-documented metal-binding properties [Czajka *et al.*, 1997; Jensen-Spaudling *et al.*, 2004]. In contrast, unattached cells might lack EPS. (4) The chemistry in the biofilm at the mineral-water interface might be different than of the bulk water phase. Using microelectrodes to construct profiles of pH and oxygen through a biofilm at the micron scale, Haack and Warren [2003] have found a significant difference in pH and dissolved oxygen within the biofilm compared to the overlying solution.

[27] Different sorption rates to unattached and deposited bacteria seem to be evident from our inverse analyses of experimental data. In comparison with Cd sorption rates to unattached bacteria (k_{amc} in Table 1), Cd sorption rates to attached bacteria are significantly greater (k_{aic} in Table 3). However, there is a large uncertainty associated with the k_{aic} estimations since the amount of bacteria attached to the solid phase at any particular time is very small compared to the number of bacteria in the solution (Figure 5). Therefore Cd sorption to immobile bacteria is much less significant. Since sorption to the aquifer material and the mobile bacteria dominate the Cd sorption process, estimated sorption coefficients to immobile bacteria are highly uncertain. Fortunately results of the sensitivity analysis (next section) have shown that the effect of parameters k_{aic} and k_{dic} on model results is relatively insignificant compared to K_d and k_{amc} . This would offset some drawback associated with model uncertainty on k_{aic} .

[28] Nevertheless, if k_{aic} is indeed greater than k_{amc} , the most relevant explanation is the possible effects of indigenous EPS and biofilm already on the mineral surfaces, created by native microbes. It is also possible that the

degree of separation of aggregates of bacteria (“declumping”) differs between unattached and deposited bacteria, which in turn affects the extent and kinetics of their binding to Cd. We consider that the effects of change in the nutritional state of the bacteria and biofilms produced by the introduced bacteria were minimal during the short experimental durations.

[29] Although ultimately up to seven parameters (K_{rv} , D , k_{ac} , k_{dc} , ω , K_d , and k_{aic}) were fitted to experimental data, the parameter values were not fitted simultaneously, but sequentially to different sets of data. Since the dispersion and conductivity values were fitted to the Br BTC, these two parameters should be relatively well defined. Bacteria attachment, k_{ac} , and detachment, k_{dc} , coefficients were then fitted to the bacteria BTC and thus should be similarly well defined. Finally, three Cd sorption parameters characterizing Cd sorption to the solid phase (ω and K_d) and to immobile bacteria (k_{aic}) were evaluated. Note that the information about the solid phase sorption parameters is contained mainly in the first part of the BTC with the gradual increase in effluent Cd concentrations that is also not affected by the presence of bacteria. Thus with the exception of the k_{aic} parameter, other parameters should be defined reasonably well.

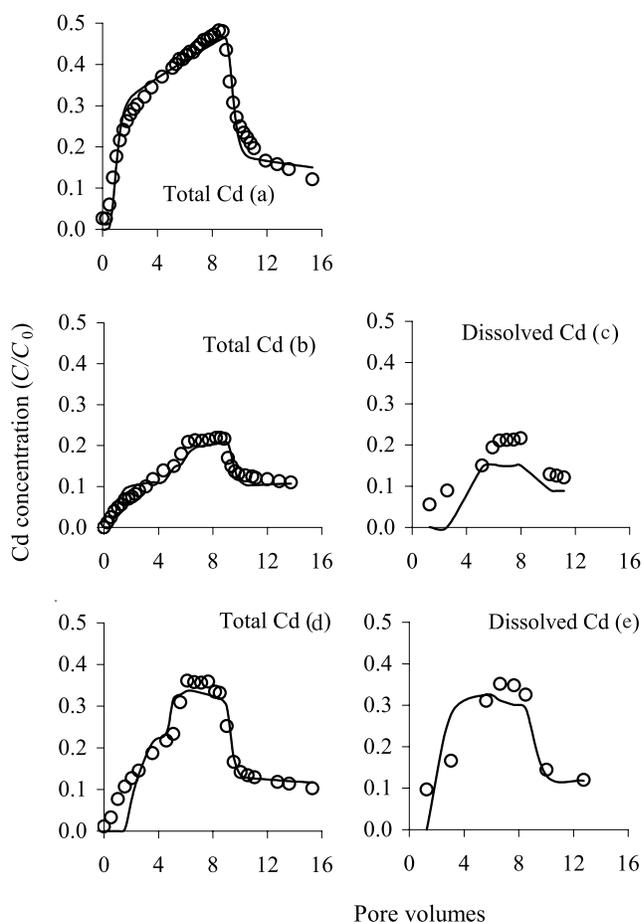


Figure 7. Observed (circles) and simulated (lines) Cd concentrations using the colloid-facilitated solute transport model for the Cd + *E. coli* experiments. (a) $C_0 = 5 \times 10^3$ cfu/mL, pH = 7.5 (experiment a). (b and c) $C_0 = 1.6 \times 10^5$ cfu/mL, pH = 7.0 (experiment b). (d and e) $C_0 = 3.7 \times 10^7$ cfu/mL, pH = 7.0 (experiment c).

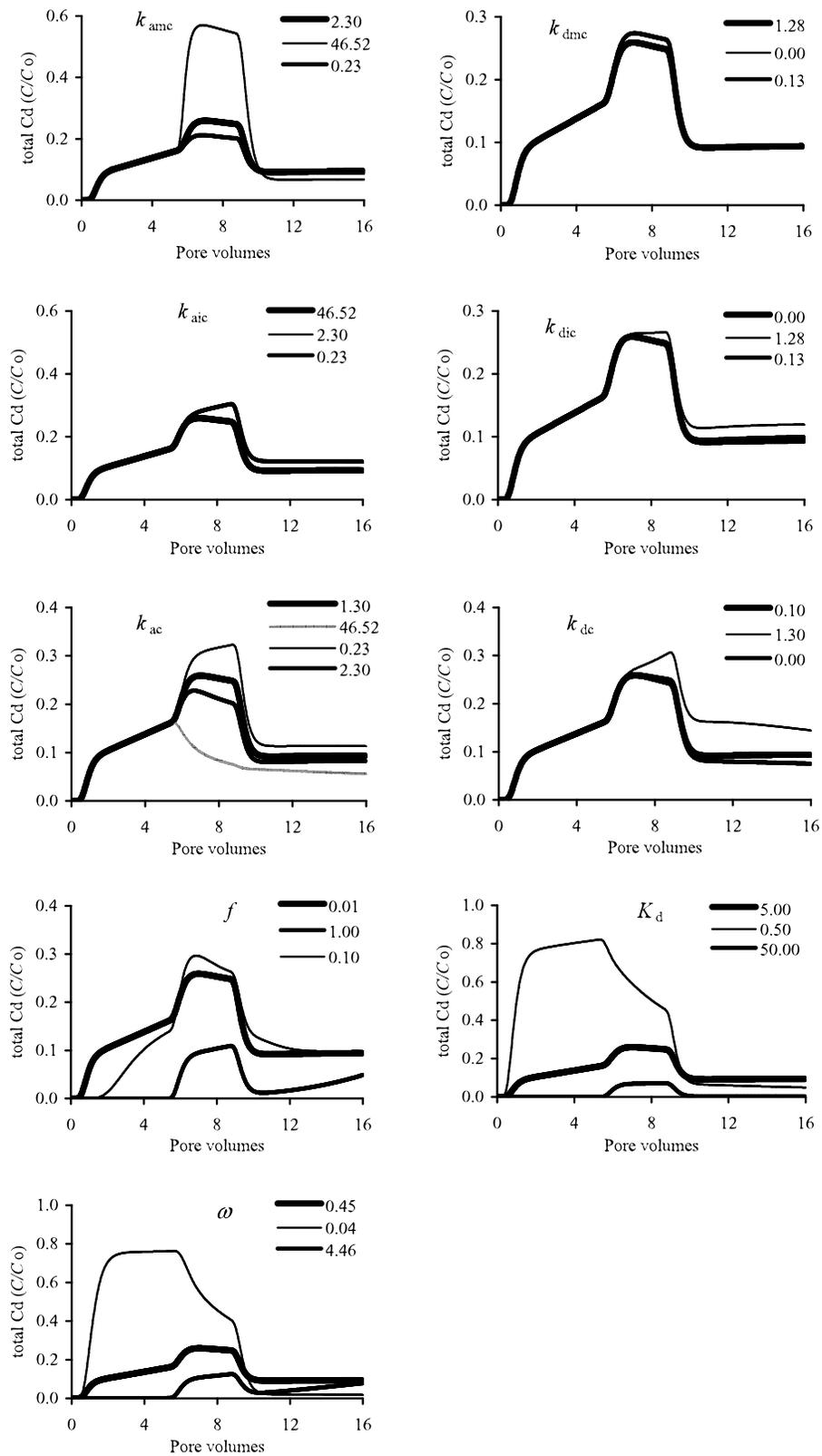


Figure 8. Effects of various reaction parameters on the total Cd concentrations in the effluent.

3.2. Sensitivity of Model Results to Selected Parameters

[30] Using Cd BTC of Figures 6c and 6d as an example, the effects of various parameters that describe three-phase interactions are shown in Figure 8 for the total Cd in the effluent (includes both dissolved Cd and Cd sorbed to mobile bacteria) and in Figure 9 for the dissolved Cd. The thickest dark line, which is the final calibrated simulation, serves as a baseline for comparison of the test results. The calibrated parameter values, their additional values used in the sensitivity analysis (Table 4) and SSRs of simulated results against the calibrated values are listed in Table 4. Results of the calibrated simulations are used as the basis for calculating SSRs in the sensitivity analysis in order to have the same number of data points at a similar time interval, while the measured data are more limited and at irregular time intervals. The possible range of parameter values is covered by the calibrated parameter values and additional values tested.

[31] Cd BTCs can be divided into three distinguish parts depending on the inflow of bacteria and solutes into the column (section 2.1): in step 1, only Cd and Br were added at the influent; in step 2, Cd, Br and bacteria were added simultaneously; in step 3 the column was flushed with freshwater without Cd, Br, or bacteria. On the basis of Figures 8 and 9, the following results are summarized and discussed.

[32] 1. As k_{amc} increases, total Cd in the effluent increases significantly in step 2 but decreases slightly in step 3, whereas dissolved Cd decreases at all times. This suggests that bacteria-facilitated Cd transport, as a result of faster adsorption of Cd onto mobile bacteria, prompts a more rapid leaching of total Cd from the system while reducing dissolved Cd concentrations. Consequently, a high k_{amc} results in less Cd staying in the system after bacteria are flushed out.

[33] 2. Higher k_{dmc} decreases the total Cd and increases the dissolved Cd during step 2, but has almost no effect on either total or dissolved Cd during step 3. This indicates that the Cd desorption rate from mobile bacteria only effects Cd concentrations during bacteria-facilitated transport and has no effect on Cd after the bacteria are flushed out.

[34] 3. Higher k_{aic} decreases both the total and dissolved Cd in the effluent at all times.

[35] 4. Higher k_{dic} increases both total and dissolved Cd at all times.

[36] 5. As k_{ac} increases, both the total and dissolved Cd decreases at all times. In contrast, as k_{dc} increases, both the total and dissolved Cd increases at all times. This is because higher bacteria attachment to the aquifer material would increase immobile bacteria mass, which in turn enhances sorption of Cd on immobile bacteria. On the other hand, higher bacteria detachment would increase mobile bacteria mass, which then promotes more Cd adsorbed onto mobile bacteria and consequently its leaching out from the system.

[37] 6. As f increases, the front of the total and dissolved Cd BTC becomes delayed and the peak of BTC is reduced. The f parameter divides the sorption sites between equilibrium and kinetic sites. While equilibrium sorption (larger f) leads to retardation of solutes, kinetic sorption leads to a gradual increase of effluent concentrations.

[38] 7. An increase in K_d or ω would reduce the total and dissolved Cd at all times, especially in steps 1 and 2, thus Cd BTC flattened. While the K_d parameter increases the equilibrium sorption (thus leads to retardation of solutes), the product of K_d and ω is proportional to the sorption rate on kinetic sites, which increases sorbed concentrations and reduces dissolved concentrations.

[39] The above section summarizes the effects of various parameters describing Cd-bacteria interaction (points 1–4), bacteria-aquifer media interaction (point 5), and Cd-aquifer interaction (points 6–7). Our points 1 and 2 are consistent with results of the sensitivity analysis by *Corapcioglu and Jiang* [1993], who used their own colloid-facilitated contaminant transport model. They also reported that the increased sorption rate of a contaminant to mobile colloids will increase the total solute flux, whereas an increase in the desorption rate of a contaminant from mobile colloids will decrease the total solute flux. Similar to point 7, *Corapcioglu and Kim* [1995] also reported that as K_d increases, the contaminant BTC flattens out. Our point 5 on the reverse effect of k_{ac} on solute concentration is also consistent with result of *Corapcioglu and Kim* [1995].

[40] The relative sensitivity of the above reaction parameters on model results could be measured by the percentage change (plus for increase and minus for decrease) in the peak Cd concentration when increasing a parameter value by tenfold. The sequence of parameters with regard to their effect on the total Cd in the effluent is as follows: K_d (−68%) > ω (−66%) > k_{ac} (−29%) > k_{amc} (+22%) > k_{dc} (+18%) > f (+15%) > k_{dmc} (−5%) > k_{dic} (+3%) > k_{aic} (−1%). The order of parameters with regard to their effect on the dissolved Cd is as follows: ω (−79%) > f (−5%) > k_{amc} (−0.43%) > k_{dmc} (+0.06%). Changes in other parameters (K_d , k_{acs} , k_{dcs} , k_{dics} , k_{aic}) have smaller or no effect on the peak dissolved Cd concentration. These general trends are also reflected in the SSRs values of the sensitivity analysis (Table 4), although SSRs do not provide a direct comparison.

[41] The above sensitivity analysis demonstrates that the bacteria-facilitated Cd transport is most sensitive to K_d , ω , k_{ac} , k_{amc} , k_{dc} and f . This suggests that for the experimental system discussed here, parameters describing Cd sorption/desorption to/from the aquifer material, bacteria attachment/detachment to/from aquifer material, and Cd sorption to mobile bacteria are the most critical parameters for the accuracy of model predications. This suggests that Cd sorption/desorption to/from the aquifer material, bacteria attachment/detachment to/from aquifer material, and Cd sorption to mobile bacteria are the most important processes that occur in our experimental system. Model results are relatively less sensitive to parameters k_{dmc} , k_{aic} and k_{dic} .

4. Conclusion

[42] The HYDRUS colloid-facilitated solute transport model, simplified to consider exchange processes between liquid, solid, and colloid phases using linear exchange models, was successfully used to describe column experimental data involving Cd transport facilitated by *B. subtilis* spores and *E. coli* in saturated gravels. The model described the observed total and dissolved Cd concentrations in the effluent reasonably well.

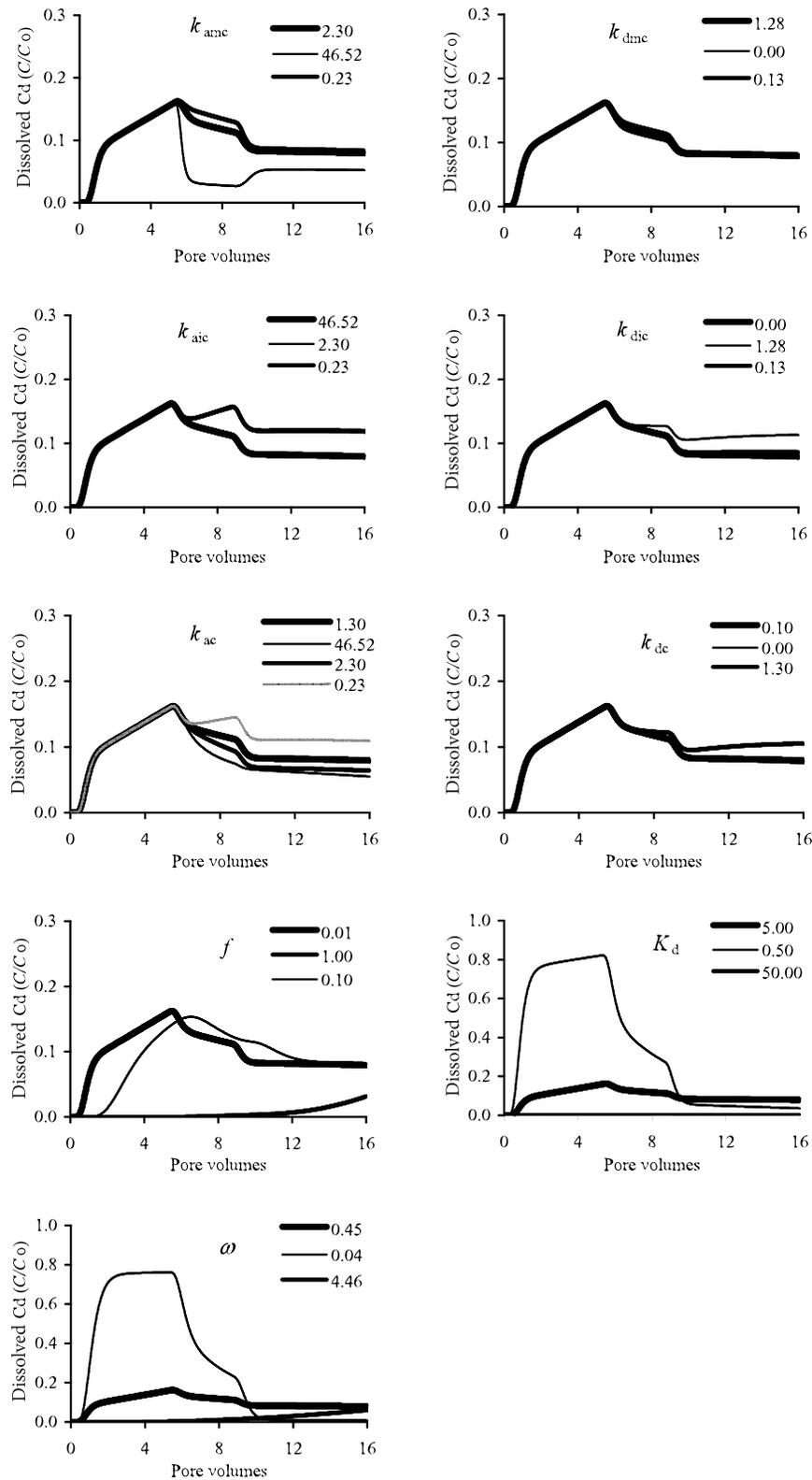


Figure 9. Effects of various reaction parameters on the dissolved Cd concentrations in the effluent.

[43] The model results suggest that the rates of Cd sorption or desorption not only differ between different bacterial species, but they also differ between unattached and deposited bacteria. Although the Cd sorption rate to

unattached bacteria was one order of magnitude greater for *B. subtilis* spores than for *E. coli*, the sorption rates of Cd to deposited spores and deposited *E. coli* did not show a significant difference. The modeling results suggest a

Table 4. Parameter Values Used in the Sensitivity Analysis and Sum of Squared Residuals in Comparison With Calibrated Values

Parameter	Units	Calibrated Value	Test Values		SSRs - Total Effluent Cd		SSRs - Dissolved Cd	
			Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
<i>Cd-Bacteria Interaction</i>								
k_{ame}	h^{-1}	2.30	0.23	46.5	0.27	12.5	0.04	1.56
k_{dme}	h^{-1}	1.28	0.00	0.13	0.03	0.03	0.01	0.01
k_{aic}	h^{-1}	46.5	0.23	2.30	0.55	0.49	0.82	0.73
k_{dic}	h^{-1}	0.00	0.13	1.28	0.01	0.29	0.02	0.47
<i>Bacteria-Aquifer Media Interaction</i>								
k_{ac}	h^{-1}	1.29	0.23	2.30	0.64	0.25	0.46	0.13
k_{dc}	h^{-1}	0.10	0.00	1.30	0.14	1.59	0.01	0.26
<i>Cd-Aquifer Media Interaction</i>								
f	-	0.01	0.10	1.00	0.90	8.03	0.83	6.75
K_d	g/mL	5.00	0.50	50.0	97.2	11.7	92.7	8.21
ω	h^{-1}	0.45	0.04	4.46	82.6	6.66	78.6	5.64

reversible sorption of Cd onto unattached bacteria and an irreversible sorption of Cd onto deposited bacteria for both species. The rate of Cd desorption from unattached *E. coli* was one order of magnitude greater than its sorption rate, which was probably caused by chelation of Cd by the outer membrane vesicles secreted by *E. coli*.

[44] Although the two bacterial species reacted very differently to Cd, their attachment/detachment characteristics to/from the aquifer media were similar, and these did not appear to be affected by their interactions with Cd. The attachment of both bacterial species to the aquifer media was reversible, and, in general, the attachment rate was much higher than the detachment rate. It also appears that Cd interactions with the aquifer media were not affected by the presence or absence of bacteria, possibly because the deposited bacteria did not cover enough of the soil surface to significantly change its sorption characteristics for the experiments discussed here. Although for the experiments discussed here bacteria-aquifer media interactions do not seem to be affected by Cd and Cd-aquifer media interactions, the results of model simulations suggest that bacterial attachment/detachment to aquifer media plays a very important role in the degree of bacteria-facilitated Cd transport as these activities significantly affect the number of mobile/immobile colloids available for Cd sorption onto them and thus alter the mobility of Cd.

[45] Compared to other optimized parameters, the rates for Cd sorption to both unattached and deposited bacteria exhibit the greatest standard errors. Although the use of independently estimated rates for Cd sorption/desorption to/from unattached bacteria from a batch study significantly narrowed the standard errors, the uncertainty of the optimized sorption rate to deposited bacteria remained quite high. Results of the sensitivity analysis indicated that the effect of the Cd sorption rate on the unattached bacteria on model results was significantly greater than its sorption rate to deposited bacteria. We have inferred some possible reasons for differences in the rate coefficients and our model results seem to support them.

[46] The model evaluation results provided some guidance for the design of future experiments. The model results are very sensitive to the parameters describing solute-solid

interaction (K_d , ω , and f); colloid-solid interaction (k_{ac} and k_{dc}) and solute mobile colloid interaction (k_{ame}). Therefore future work should focus on accurately determining these parameters. As model-optimized k_{ame} values are highly uncertain, it is recommended that this parameter be estimated from batch experiments that closely mimic the physical and biochemical conditions of the system of interest. In particular, the design of batch and column experiments need to ensure the use of the same pH and concentrations of colloids and contaminants as a slight change in these conditions may result in a significant change in the experimental results [Pang *et al.*, 2005]. Future work is also needed to closely examine the characteristics of unattached and deposited colloids, and to independently determine individual effects of different factors, including surface areas, charge, activity, EPS, chemistry of the biofilms and bulk water.

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