MOBILIZATION AND LEACHING OF NATURAL AND WATER DISPERSIBLE COLLOIDS IN AGGREGATED VOLCANIC ASH SOIL COLUMNS

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ABSTRACT

Colloid-facilitated transport enhances migration of strongly sorbing compounds (e.g., radionuclides, phosphorus, heavy metals) in soil and groundwater. Mobilization, transport and deposition of soil colloids are the underlying processes governing colloid-facilitated contaminant transport. Although significant progress has been made in simulating mobilization and transport/deposition of model colloids in different collector systems, it may be inadequate for the prediction of natural colloidal behavior in the subsurface. This study quantifies the leaching of natural volcanic ash soil colloids (NC) as well as the simultaneous transport of applied water dispersible soil colloids (WDC) in aggregated volcanic ash soil columns. Two water-saturated soil columns were irrigated with artificial irrigation water (AIW) at an intensity of 80 mm/hr for 60 hours. Two additional columns were irrigated at the same intensity, but a colloidal suspension of 5 mg/L was applied after 20 hours for a period of 20 hours. Effluent colloid concentrations were measured in each experiment. HYDRUS-1D was used for the simulation and estimation of colloid transport parameters. The results clearly showed different kinetics for applied colloid transport and natural colloid leaching. Transport of applied WDC followed first-order attachment kinetics, while the two-site equilibrium/kinetic model with equal fractions of equilibrium and kinetic sites best described the leaching of NC. Coupling these best model approaches well predicted the simultaneous leaching of natural and applied colloids, hereby providing a useful tool for the design of colloid-based in-situ soil remediation systems.

Key words: chemical non-equilibrium, column experiment, leaching, soil colloids, two-site equilibrium/kinetic model, volcanic ash soil, water dispersible colloids (IGC: D4/E7)

INTRODUCTION

Naturally occurring particles of colloidal dimensions (i.e., diameter less than few micrometers) are ubiquitous in subsurface environments. They have a wide variety of inorganic, organic and microbiological origins including layer silicates, sesquioxides (Fe- and Al- oxyhydroxides), mineral precipitates, humic materials, microemulsions of non-aqueous phase liquids and microorganisms including viruses and bacteria (McCarthy and Zachara, 1989; de Jonge et al., 2004a). Under favorable geochemical conditions, such colloid-sized materials can remain suspended for a long time in soil pore waters without coagulation or precipitation and hence constitute another mobile phase in soil-water systems. Owing to the extensive specific surface area with mostly high surface charge densities (predominantly electronegative), mobile colloids are highly reactive in the subsurface and hence can facilitate rapid transport of potentially harmful contaminants.

Naturally occurring colloids have been found to play an instrumental role in the translocation of strongly sorbing chemicals (so-called colloid-facilitated contaminant transport) such as radionuclides (Kersting et al., 1999), pesticides (Vinten et al., 1983; de Jonge et al., 1998), phosphorus (Motoshita et al., 2003; de Jonge et al., 2004b), heavy metals (Amrhein et al., 1993; Karathanasis, 1999), organic substances (de Jonge et al., 2002; Totsche et al., 2006), and pathogens (Tufenkji et al., 2004) into groundwater.

The colloidal particles facilitating the chemical transport are either applied to the soil (for example, during precipitation runoff and subsequent particle infiltration or during application of animal slurries or sewage sludge) or mobilized inside the soil profile. Of the different sources of mobile colloidal particles in soils and groundwater aquifers mentioned, in-situ release of particles is the most common (Kretzschmar et al., 1999). Physical perturbation in the hydraulic system is known to be one
of the primary causes of in-situ colloid generation (Ryan and Elimelech, 1996). For example, following a rapid rainfall event, the high raindrop impacts (on the ground surface) and hydrodynamic shear (on the pore walls by infiltrating rainwater) can cause extensive release of colloids from soil matrices. Significant changes in the hydrogeochemistry of aquifer systems (for example, infiltration of rainwater of low ionic strength or high pH) have also been recognized as key processes in mobilizing natural colloids (Ryan and Elimelech, 1996; Laegdsmand et al., 2007; Shiratori et al., 2007).

The mobilized colloids are transported with infiltrating rainwater and are en route intercepted by the collector surfaces resulting in subsequent colloid deposition. Colloid attachment and colloid straining are the two key mechanisms by which colloids are deposited in porous media. Colloid attachment occurs due to the net interaction (i.e., summation of van der Waals forces and electrostatic double-layer forces) between colloidal and grain surfaces (DeNovio et al., 2004). Colloid straining, on the other hand, is the entrapment of colloids in pore throats and at grain-grain junctions which are too small to allow particle passage (Bradford et al., 2002).

Despite extensive research on colloid transport, the lack of knowledge on the processes governing colloid release, transport and deposition in natural subsurface environments demands further research for more reliable predictions on colloid transport and hence colloid-facilitated contaminant transport. Although significant progress has been achieved in simulating model colloid transport in collector systems, it may be inadequate for accurate predictions of natural colloid transport (Grollmund et al., 1998). As a result, although the compelling evidences available today are enough to raise concerns, colloid and colloid-facilitated contaminant transport has not received due attention in recent risk assessment tools (e.g., Risk Based Corrective Action (RBCA) in ASTM, 2000).

Most of the previous colloid transport studies concerning soil colloid leaching have used extracted water dispersible soil colloids to simulate natural colloid leaching, assuming they follow the same transport kinetics due to the presumably similar physicochemical characteristics. This study attempts to investigate leaching, transport and deposition of both natural colloids and applied water dispersible colloids in saturated, soil-packed columns under steady irrigation intensity. The numerical simulations invoke two chemical nonequilibrium models, a two-site equilibrium/kinetic model and a one-site kinetic model, in order to compare transport kinetics of two colloid types. We also propose a conceptual mechanism to describe the leaching of natural soil colloids.

**NUMERICAL MODELING**

Following the implicit analogy to solute transport, typical colloid transport models invoke the Convection-Dispersion Equation (CDE) with slight modifications to account for colloid deposition as follows:

\[ \frac{\partial \rho c}{\partial t} + \frac{\partial \rho c}{\partial z} = D \left( \frac{\partial^2 c}{\partial z^2} \right) - \frac{\partial qc}{\partial z} \]  

(1)

where \( c [\text{mL}^{-1}] \) is the aqueous phase colloid concentration, \( \rho [\text{mM}^{-1}] \) is the solid phase colloid concentration, \( \rho [\text{ML}^{-1}] \) is soil bulk density, \( \theta [\text{L}] \) is the colloid accessible water content, \( D [\text{L}^2\text{T}^{-1}] \) is the hydrodynamic dispersion coefficient, \( q [\text{LT}^{-1}] \) is the volumetric flux density of the colloids, and the independent variables \( t [\text{T}] \) and \( z [\text{L}] \) are, respectively, temporal and spatial dimensions. The CDE with modifications has been used in many previous studies related to colloid transport in order to account for both physical and chemical nonequilibrium conditions (e.g., Kjaergaard et al., 2004a, b).

Chemical sorption models have been widely used to describe mass transfer between the aqueous phase and the solid phase. Of these, the simple chemical equilibrium

Fig. 1. Conceptual models for colloid transport based on chemical sorption/desorption. Chemical equilibrium model (a) and chemical nonequilibrium models consisting of one kinetic site model (b), two-site equilibrium/kinetic model (c), and two-site kinetic model (d), which, if the two sites are identical, simplifies to one-site kinetic model (e). In the plots, \( C \) is the aqueous phase colloid concentration, \( K_s \) is distribution coefficient, \( S^r \) is sorbed concentration in equilibrium with aqueous phase concentration, \( S^r \), \( S^r \), \( S^r \) are kinetically sorbed concentrations in corresponding sites, \( S^r \) is sorbed concentration that would be reached at equilibrium following kinetic mass transfer, \( f \) is fraction of sorption sites in equilibrium with aqueous phase concentration, \( \alpha \) is first-order mass transfer coefficient, \( k_{11}, k_{12}, k_{21}, k_{22}, k_{11}, k_{12} \) are, respectively, first-order attachment and first-order detachment coefficients for the corresponding sites. (Modified from Šimůnek and van Genuchten, 2008)
model (Fig. 1(a)) assumes instantaneous, reversible sorption, such that the sorbed concentration, \( s^r [\text{mM}^{-1}] \), is all the time uniquely and algebraically related to the aqueous phase concentration, \( c \) (van Genuchten and Wagenet, 1989). If the sorption process is linear, this leads to:

\[
s^r = K_d c
\]

where \( K_d [\text{M}^{-1} \text{L}^3] \) is the distribution coefficient.

Due to the inherent physicochemical heterogeneities at different facets of the collector-colloidal surfaces, however, colloid sorption is not always an essentially reversible and instantaneous process. The concept of chemical non-equilibrium arises when the total sorption, or a fraction of it, is considered to be time-dependent (kinetic) rather than instantaneous. The one kinetic site model (Fig. 1(b)) assumes that the sorption on all the sites is controlled by a single kinetic rate law (Singh et al., 1992). The first-order reversible kinetic equation with a linear isotherm can be written as:

\[
\frac{\partial s^k}{\partial t} = \alpha (s^e - s^k)
\]

\[
s^k = K_d c
\]

where \( \alpha [\text{T}^{-1}] \) is the first-order rate coefficient, \( s^k [\text{mM}^{-1}] \) is the sorbed colloid concentration at kinetic sites, and \( s^e [\text{mM}^{-1}] \) is the sorbed colloid concentration that would be reached at equilibrium with the liquid phase. It is noted that although the mass transfer occurs kinetically between solid and aqueous phases, the overall mass transfer is governed by the equilibrium concentration. Hence, the mass transfer ceases as the equilibrium is reached between the two phases.

The two-site equilibrium/kinetic sorption concept presumes that the total sorption site consists of two fractions, whereon the \( f \) fraction of the sites, the sorption \( s^r [\text{mM}^{-1}] \) is instantaneous, while the sorption on the other fraction \( s^k [\text{mM}^{-1}] \) follows first-order (equilibrium-bound) kinetics (Fig. 1(c)). The system of equations describing the two-site equilibrium/kinetic model can be given by (Šimůnek and van Genuchten, 2008a):

\[
s = s^r + s^k
\]

\[
s = f K_d c
\]

\[
\frac{\partial s^k}{\partial t} = \alpha (s^e - s^k)
\]

\[
s^k = (1 - f) K_d c
\]

The two-site kinetic model (Fig. 1(d)), on the other hand, divides total sorption sites into two different fractions of kinetic sorption sites, \( s^r_1 [\text{mM}^{-1}] \) and \( s^r_2 [\text{mM}^{-1}] \), as described by following equations (Šimůnek and van Genuchten, 2008a):

\[
s = s^r_1 + s^r_2
\]

\[
\rho \frac{\partial s^r_1}{\partial t} = k_{d1} \theta c - k_{d1} \rho s^r_1
\]

\[
\rho \frac{\partial s^r_2}{\partial t} = k_{d2} \theta c - k_{d2} \rho s^r_2
\]

where \( k_{d1} [\text{T}^{-1}] \) and \( k_{d2} [\text{T}^{-1}] \) are attachment coefficients for the first and second fractions of kinetic sorption sites, respectively, while \( k_{d1} [\text{T}^{-1}] \) and \( k_{d2} [\text{T}^{-1}] \) are, respectively, detachment coefficients for the first and second fractions of kinetic sorption sites. Due to its ability to symbolize two different kinetic processes, the two-site kinetic model is often used to describe colloid attachment and colloid straining in colloid transport modeling studies (Bradford et al., 2004). If both sites have identical rate coefficients, the two-site kinetic model simplifies to the well known one-site kinetic model (Fig. 1(e)):

\[
s = s^k
\]

\[
\rho \frac{\partial s^k}{\partial t} = k_a \theta c - k_d \rho s^k
\]

where \( k_a [\text{T}^{-1}] \) and \( k_d [\text{T}^{-1}] \) are first-order attachment and detachment coefficients, respectively. Considering the analogy of mass transfer (Eqs. (3) and (6)), correlations among transport parameters could be derived theoretically (Šimůnek and van Genuchten, 2008a). Conceptually, however, each model is supposed to function uniquely.

The HYDRUS-1D computer code (Šimůnek and van Genuchten, 2008b), which simulates water, heat and multiple solute movements in one-dimensional porous media was employed in this study. The program enables the use of nonequilibrium solute transport models which were found to be applicable to describe colloid transport/retention kinetics as well (Bradford et al., 2004; Šimůnek and van Genuchten, 2008a). The code is coupled to a nonlinear least squares optimization routine based on the Levenberg-Marquardt algorithm (Marquardt, 1963) to facilitate inverse estimation of transport parameters from experimental data.

**MATERIALS AND METHODS**

**Soil Material**

Nishi-Tokyo loam, an aggregated volcanic ash soil, was sampled at a depth of 0–10 cm from a cultivated land at Field Production Science Center, the University of Tokyo (UP FPSC), Japan to be used as the porous media in all soil columns. The physicochemical properties of the soil are listed in Table 1. The fraction of soil below 2 mm was sieved out prior to its use for column packing.

**Feed and Colloidal Solutions**

Artificial irrigation water (AIW) was used as the feed solution in all column experiments. The AIW, which had a composition (0.085 mM NaCl + 0.015 mM CaCl₂) close to that of natural rainwater (Motoshita et al., 2003), was assumed to mimic the flow of natural rainwater. In order to prepare water dispersible colloidal solutions, AIW and Nishi-Tokyo loam soil were mixed in a 1:8 (w/w) ratio followed by 24 hours shaking and resting undisturbed for another 24 hours for particle settling. The water dispersible colloidal fraction having a Stoke’s diameter of less than 2 μm was then siphoned from the supernatant and finally filtered by a 1-μm filter (GF/B filter, Whatman®) to be used in the experiments. Table 2 lists the character-
Table 1. Soil physical characteristics

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth m</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>Organic matter</th>
<th>Soil mineral density g cm⁻³</th>
<th>pH</th>
<th>EC mS/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nishi-Tokyo loam</td>
<td>0.0–0.1</td>
<td>8.7</td>
<td>39.8</td>
<td>51.5</td>
<td>7.8 – 9.2</td>
<td>2.68</td>
<td>6.5</td>
<td>5.8–6.5</td>
</tr>
</tbody>
</table>

Table 2. Characteristics of artificial irrigation water and colloidal solution at natural pH

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>EC mSm⁻¹</th>
<th>Colloid Concentration mgL⁻¹</th>
<th>Dissolved Organic Carbon mgL⁻¹</th>
<th>ζ-Potential (pH = 6 – 7) mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial irrigation water†</td>
<td>6.5</td>
<td>2.1–2.3</td>
<td>—</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Colloidal solution</td>
<td>6.5</td>
<td>2.5–5.8</td>
<td>4.8–7.1</td>
<td>0.42–2.33</td>
<td>−12–−14</td>
</tr>
</tbody>
</table>

† 0.085 mM NaCl+0.015 mM CaCl₂
‡ ζ-potential was estimated using electrophoresis

Characteristics of both AIW and the colloidal solution.

Turbidity of the influent and effluent colloidal solutions was measured using a portable turbidimeter (2100P, HACH). Electrophoresis was used to characterize the electrokinetic properties of the colloidal solution. The electrophoretic mobility measurements were performed at 25°C using a Zetameter (Model 502, Nihon Rufuto) and converted to zeta potentials using the Smoluchowski equation.

Column Experiments

The sampled Nishi-Tokyo loam soil was carefully packed in a column (4.9 cm diameter, 10 cm high) incrementally in 1-cm layers to a bulk density of 0.62 g/cm³. During packing, the water level was always maintained above that of the layer being packed (referred to as wet-packing) in order to ensure complete saturation and each layer was gently stirred to remove any entrapped air bubbles before proceeding to the next layer. Two 1-cm layers of glass beads were placed at the top and bottom of the column for three purposes: to level irregularities at the soil surface, to ensure a uniform distribution of applied solution across the cross section, and to prevent mobilization of colloids due to raindrop impact. A perforated stainless steel filter of 1-mm pore size was placed at the bottom of the column to prevent any loss of fine soil particles. A schematic of the column experimental set-up is shown in Fig. 2.

In the first two column experiments (Expt. A and Expt. B), the columns were irrigated with AIW at an intensity of 80 mm/hr by means of a peristaltic pump for a period of 60 hours. In the next two column experiments (Expt. C and Expt. D), the same irrigation intensity was used to sequentially apply two different solutions. AIW was first applied for a 20-hour period and switched to a pulse of 5 mg/L colloidal suspension and continued for another 20 hours, followed by another session of AIW for the remaining 20 hours. The concentration of applied colloid suspension (5 mg/L) was selected in such a way that it was consistent with the maximum concentration resulting from natural colloid leaching under the same irrigation intensity. The application sequence of solutions in column experiments is given in Table 3. Effluent turbidity, pH and electrical conductivity (EC) were monitored periodically in all column experiments. An observed linear relationship between colloid turbidity (expressed in Nephelometric Turbidity Units, NTU) and corresponding colloid concentration (mg/L) was used to estimate colloid concentration from measured turbidity. The initial in-situ colloid concentrations in Expt. A and Expt. B were estimated by integrating the breakthrough and breakdown curves.

Fig. 2. Schematics of the apparatus for column experiments

Table 3. The applied sequence of solutions in column experiments

<table>
<thead>
<tr>
<th>Experiment (Expt.)</th>
<th>Sequence of Solutions†</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>AIW (60 hours)</td>
</tr>
<tr>
<td>B</td>
<td>AIW (60 hours)</td>
</tr>
<tr>
<td>C</td>
<td>AIW (20 hours) CS (20 hours) AIW (20 hours)</td>
</tr>
<tr>
<td>D</td>
<td>AIW (20 hours) CS (20 hours) AIW (20 hours)</td>
</tr>
</tbody>
</table>

† AIW: Artificial irrigation water, CS: Colloidal solution
RESULTS AND DISCUSSION

Characteristics of a Colloidal Solution and Colloid Stability

Characteristics of a colloidal system have a significant impact on colloid stability and hence colloid transportability in porous media. Fluctuations in electrolytic pH, for example, can significantly change colloid stability (Tombácz et al., 1990; Shiratori et al., 2007). As illustrated in Fig. 3(a), soil colloids exhibited high stability at high pH values and showed a sharp decline with decreasing pH. This observation can be attributed to the increased mutual repulsion among colloids at high pH as a result of an increased amphoteric (pH-dependent) charge due to deprotonation at colloid surfaces. The observed decrease in $\zeta$-potential with increasing pH (Fig. 3(b)) revealed the increase of net negative surface charge (and hence increased mutual repulsion), which corroborates the previous observation. As the coagulation progressed the $\zeta$-potential showed a significant increase at low pH (Fig. 3(b)) due to charge neutralization. Near and above neutral pH ($pH = 6.8$), however, the $\zeta$-potential was largely negative and remained unchanged even after 48 hours, exhibiting a high colloid stability. In this study, the colloidal system was therefore maintained at near-neutral pH during the column experiments.

Leaching of Natural Soil Colloids

The natural soil colloids, predominantly generated as a result of dispersion from soil aggregates, started leaching from the soil-packed column when the feed solution was applied (Fig. 4(a)). Since colloid transport is often presumed to follow first-order kinetics (McGechan et al., 2002), we first attempted to describe the observed colloid leaching with a one-site kinetic model (Fig. 1(e)). The observed and simulated results (Expt. A) are illustrated in Fig. 4(a). The simulated profile failed to mimic the observed breakthrough curve, suggesting that the leaching of natural colloids does not essentially follow first-order kinetics. A simple sensitivity analysis on the reaction parameters (Figs. 4(b) and (c)) further revealed the inappropriateness of using a pure first-order kinetic approach to describe the observed natural colloid leaching behavior.

The applicability of a two-site equilibrium/kinetic model (Fig. 1(c)) was, therefore, examined next. Figure 5(a) illustrates simulation results using a two-site equilibrium/kinetic model with three different equilibrium site fractions. Of these, the model with equal fractions of equilibrium and kinetic sorption sites (i.e., $f = 0.5$) described well both the observed breakthrough (profile with rising concentration) and breakdown (profile with receding concentration) curves. It should be noted that in the above analysis the hydrodynamic colloid dispersivity ($l$) was set at an assumed value of 1 cm as a sensitivity analysis on colloid dispersivity proved that it had negligible impact on the simulation results (not shown).

The foregoing discussion, therefore, leads to the conclusion that natural colloid leaching is more a combined equilibrium and kinetic process rather than a pure kinetic process. In order to distinguish the different roles the equilibrium and kinetic sorption sites play, a sensitivity analysis on the two reaction parameters ($K_d$ and $\alpha$) was performed. The analysis revealed that varying $\alpha$ with $K_d$ unchanged incurred significant fluctuations to the breakdown curve (Fig. 5(b)). For the same $\alpha$ with varying $K_d$, on the other hand, the resulting breakdown curve remained virtually unchanged with significant changes to the breakthrough curve (Fig. 5(c)). From these results, together with the previous observations from one-site model predictions, we can conclude that the initial colloid breakthrough is primarily an instantaneous process with colloids mobilizing from equilibrium sites, whereas the subsequent breakthrough with extended tailing is mainly controlled by first-order mass transfer kinetics.

The results of the numerical analysis on the basis of the chemical nonequilibrium approach can be used to invoke the following explanation on the conceptual mechanisms behind the release of naturally occurring soil colloids from aggregated soils. Prior to irrigation, the soil-packed

![Fig. 3. Effect of electrolytic pH on (a) colloid stability with time and (b) $\zeta$-potential initially and after 48 hours](image-url)
columns were kept saturated for a few hours during which water dispersible soil colloids from equilibrium sorption sites would have been released into interstitial pore water in order to maintain equilibrium with the solid phase. With the applied irrigation water, these readily available colloids appeared as the ‘first flush’, exhibiting an instantaneous breakthrough. As the irrigation proceeded, the release of colloids from equilibrium sites steadily increased giving a concentration peak in the breakthrough curve. The potential equilibrium sites, however, gradually depleted exposing the interior surfaces of soil grains to which soil colloids are not loosely bound. The mobilization of colloids then became a time-dependent process since the water dispersible colloids from intra-aggregate pore water have to traverse rather tortuous pathways (presumably controlled by diffusion) to make their way out, as reflected by the observed breakdown curve with an extended tailing.

**Transport of Applied Water Dispersible Soil Colloids**

Figure 6(a) illustrates the breakthrough and breakdown curves of total water dispersible colloids (Expt. C) together with the natural colloid leaching profile in Expt. B. Assuming the mutual interactions between applied water dispersible colloids and natural colloids are negligible and the leaching of natural colloids and transport of applied colloids occurred independently, the breakthrough and breakdown curves for applied water dispersible colloids (i.e., total colloids minus natural colloids) were obtained for the four possible combinations (Fig. 6(b)) (we further assumed here the reproducibility of results for both total and natural colloids).

Breakthrough and breakdown curves of applied colloids had two distinct features in that they seemed to reach a plateau before breakdown occurred, and, in contrast to the natural colloids, the applied colloids did not exhibit any tailing effect.

Since both natural colloids and applied water dispersible colloids are derived from the same soil type, the physicochemical characteristics of the two colloid types are essentially identical. The first attempt to model applied colloid transport, therefore, was with the two-site equilibrium/kinetic model, using the same reaction parameters ($K_d$ and $\alpha$) that we used to model natural colloid leaching. As can be seen from Fig. 6(b), the predicted curves (dotted line) significantly differed from the observed curves, meaning that, despite their similarity in properties, the two colloid types do not follow the same kinetics. Further, the predictions of the two-site equilibrium/kinetic model based on optimized $K_d$ and $\alpha$...
Fig. 5. (a) Observed natural colloid breakthrough and breakdown profiles (Expt. A) against two-site equilibrium/kinetic model (Eq. (4)) predictions for three different equilibrium site fractions ($f = 0.1, 0.5$ and $0.8$). Sensitivity analyses for the selected equilibrium site fraction with $f = 0.5$ on the (b) mass transfer coefficient ($\alpha$) and (c) distribution coefficient ($K_d$).

values (shown in Fig. 6(b), thin line) also proved to be unsuccessful, suggesting that the two-site equilibrium/kinetic model does not correctly describe the applied colloid transport process.

The one-site kinetic model here seemed to perform very well as the model predictions (Fig. 6(b), thick line) showed a good agreement with the observed results ($r^2 = 0.94$). The fitted detachment coefficient was observed to be negligibly small and hence transport of applied colloids could be explained simply with an attachment coefficient. This implies that the transport of applied colloids follows first-order kinetics. The estimated attachment coefficient here is, in effect, a lump parameter representing colloid retention due to adsorption of colloids onto grain surfaces as well as straining of colloids at narrow pore throats. Table 4 summarizes the transport and reaction parameters resulting from the simulations.

The simulated breakthrough and breakdown curves for both natural and applied colloid leaching (Expt. A through Expt. D) have been compared with observed data in Fig. 7. The figure clearly illustrates that the model resulting from coupling best model approaches for infiltration and leaching of applied colloids and mobilization and leaching of natural soil colloids could accurately describe the combined leaching of applied and natural colloids. This observation, in particular, is of great importance for the development and modeling of in-situ soil remediation systems based on applied colloids used for cleaning-up of contaminated sites. The new approach is particularly applicable for removing strongly sorbing pollutants (for example, polycyclic aromatic hydrocarbons (PAH) at coal tar-contaminated sites), the fate of which is predominantly controlled by nonequilibrium conditions and are highly facilitated by mobile colloids (Totsche et al., 2006, 2007).

CONCLUSIONS

The pH of the electrolytic solution has a significant influence on the stability of natural soil colloid systems. At higher pH values soil colloids exhibited higher stability against coagulation/flocculation due to the increased electrostatic repulsion.

Two different kinetics were observed for natural soil colloid leaching and applied water dispersible soil colloid transport in saturated columns packed with aggregated
Table 4. Transport and reaction parameters used for the simulations of column experiments

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters for water transport</td>
<td>Saturated volumetric water content, cm³ cm⁻³</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>Dry bulk density, g cm⁻³</td>
<td>0.62</td>
</tr>
<tr>
<td>Parameters for natural colloid leaching</td>
<td>Initial sorbed phase concentration, mg mg⁻¹</td>
<td>3.73 × 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>Fraction of equilibrium sorption sites</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Equilibrium distribution coefficient, cm² g⁻¹</td>
<td>21.9 (Expt. A) and 20.9 (Expt. B)</td>
</tr>
<tr>
<td></td>
<td>First-order rate coefficient, h⁻¹</td>
<td>0.0214 (Expt. A) and 0.0220 (Expt. B)</td>
</tr>
<tr>
<td>Parameters for applied colloid transport</td>
<td>Initial sorbed phase concentration, mg mg⁻¹</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>First-order attachment coefficient, h⁻¹</td>
<td>0.781</td>
</tr>
<tr>
<td></td>
<td>First-order detachment coefficient, h⁻¹</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Percent recovered mass of colloids</td>
<td>47 – 53%</td>
</tr>
</tbody>
</table>

Nishi-Tokyo loam soil under steady irrigation. Transport of applied water dispersible colloids followed simple first-order attachment kinetics. However, a two-site chemical nonequilibrium model with equal fractions of equilibrium and kinetic sites was better for describing the leaching of natural soil colloids. The two kinetic models, when combined, can accurately predict combined leaching of applied and natural colloids, hence providing a useful tool for the modeling of colloid-mediated clean-up of contaminated sites. The numerical analysis further revealed that the release of colloids from equilibrium sites yielded the initial breakthrough, while the subsequent breakdown with tailing reflected the release from kinetic sorption sites. The proposed conceptual mechanism assumes that with the onset of irrigation, water dispersible soil colloids instantaneously mobilize into interstitial pores from the equilibrium sites giving rise to a steady breakthrough and subsequently, with the depletion of potential equilibrium sites, a time-dependent (diffusion-limited) process dominated the colloid release and transport from the intra-aggregate pore water as reflected by the long-tailed breakdown curve.

This study clearly differentiates between the kinetics of applied colloid transport and natural colloid leaching, hence questioning the applicability of extracted colloids, used in many previous colloid transport studies, to mimic subsurface migration of natural colloids. Additional experiments covering different colloid and porous media systems, however, are warranted to further confirm these observations.

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**NOTATION**

- $c$: aqueous phase colloid concentration [mL$^{-1}$]
- $\rho$: soil bulk density [ML$^{-3}$]
- $\theta$: colloid accessible water content [-]
- $D$: hydrodynamic dispersion coefficient [L$^2$T$^{-1}$]
- $q$: volumetric flux density of the colloids [LT$^{-1}$]
- $t$: time [T]
- $z$: spatial coordinates [L]
- $K_d$: distribution coefficient for colloids [M$^{-1}$L$^3$]
- $f$: fraction of sites in equilibrium with aqueous phase concentration [-]
- $\alpha$: first-order rate coefficient [T$^{-1}$]
- $s$: solid phase colloid concentration [mM$^{-1}$]
- $s'$: sorbed colloid concentration in equilibrium with aqueous phase colloid concentration [mM$^{-1}$]
- $s_2'$: sorbed concentration that would be reached at equilibrium with the liquid phase following kinetic mass transfer [mM$^{-1}$]
- $s_2^k$: sorbed colloid concentration at kinetic sorption sites [mM$^{-1}$]
- $s_1^k$: sorbed colloid concentration at the first fraction of kinetic sorption sites [mM$^{-1}$]
- $s_2^k$: sorbed colloid concentration at the second fraction of kinetic sorption sites [mM$^{-1}$]
- $k_d$: colloid detachment coefficient of kinetic sorption sites [T$^{-1}$]
- $k_a$: colloid attachment coefficient of first fraction of kinetic sorption sites [T$^{-1}$]
- $k_{d1}$: colloid detachment coefficient of first fraction of kinetic sorption sites [T$^{-1}$]
- $k_{a1}$: colloid attachment coefficient of second fraction of kinetic sorption sites [T$^{-1}$]
- $k_{d2}$: colloid detachment coefficient of second fraction of kinetic sorption sites [T$^{-1}$]

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