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In Situ Colloid Mobilization in Hanford Sediments under Unsaturated Transient Flow Conditions: Effect of Irrigation Pattern

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Colloid transport may facilitate off-site transport of radioactive wastes at the Hanford site, Washington State. In this study, column experiments were conducted to examine the effect of irrigation schedule on releases of in situ colloids from two Hanford sediments during saturated and unsaturated transient flow and its dependence on solution ionic strength, irrigation rate, and sediment texture. Results show that transient flow mobilized more colloids than steady-state flow. The number of short-term hydrological pulses was more important than total irrigation volume for increasing the amount of mobilized colloids. This effect increased with decreasing ionic strength. At an irrigation rate equal to 5% of the saturated hydraulic conductivity, a transient multipulse flow in 100 mM $NaNO_3$ was equivalent to a 50-fold reduction of ionic strength (from 100 mM to 2 mM) with a single-pulse flow in terms of their positive effects on colloid mobilization. Irrigation rate was more important for the initial release of colloids. In addition to water velocity, mechanical straining of colloids was partly responsible for the smaller colloid mobilization in the fine than in the coarse sands, although the fine sand contained much larger concentrations of colloids than the coarse sand.

Introduction

The mobility of radionuclides is currently of great concern for the quality of groundwater and vadose zone environments. Radioactive materials have leaked from underground waste tanks at the Hanford Reservation located in the southeast of Washington State. A number of studies have shown that colloid particles can potentially facilitate the subsurface transport and mobilization of radionuclides at contaminated sites (*1*−*5*). Thus, colloid movement must be considered in any long-term risk assessment and management of waste at Hanford. Hanford sediments are generally coarse and layered in structure, so limited precipitation (95−313 mm/year) can infiltrate readily and then redistribute via subsurface flows. The infiltration and recharge are largely controlled by rainfall and sediment texture (*6*). Subject to the regular pattern of local weather (wet and cool winters, and hot and dry summers) or abrupt events (e.g., thunderstorms), water flow perturbations (e.g., wetting and drying, and preferential flow) may take place in the Hanford vadose zone and effect in situ colloid mobilization by mechanisms different from those identified under steady-state flow conditions. Because Hanford colloids can be remobilized during waste leakage, when high ionic strength tank liquids (*7*) are diluted by low ionic strength pore water (*3*), the effect of solution chemistry may be superimposed upon the effect of wetting/drying events to provide colloids for transport.

Most previous studies that have examined colloid mobilization were conducted in saturated systems, and the few that considered unsaturated systems focused principally on steady-state flow conditions (*8*−*11*). Such conditions, however, do not necessarily represent natural flow regimes because the vadose zone exhibits transient unsaturated flow, which is characterized by temporal variability in water content and pore water velocity. Under natural conditions, transient flow regimes can be triggered by rainfall, irrigation, or snowmelt events interspersed by drying periods. The resulting changes in pore water saturation and flow velocity cause colloid mobilization at larger rates than those which would be predicted on the basis of steady-state flow experiments (*12*−*14*). Results of field studies demonstrate that soil colloids can be released in large concentrations during rainfall events, presumably due to hydrodynamic and chemical perturbations associated with the advancing wetting front (*12*−*16*). The field-lysimeter experiments by Kaplan et al. (*12*) found that pore water velocity and amount of dispersible colloids in the matrix had an interactive effect on effluent turbidity. However, Ryan et al. (*13*) did not observe any correlation between mobilized colloid concentrations and water flow rates in their experiments with field-installed lysimeters. El Farhan et al. (*14*) showed that transient flow could promote very rapid colloid mobilization, with the colloid pulses attributed to the passage of colloid-scavenging air−water interfaces during infiltration and drainage. Later, Worrall et al. (*15*) observed that leaching of pesticides occurred largely in the first few samples following rainfall, coinciding with the occurrence of the colloidal matter. Jarvis et al. (*16*) conducted a modeling effort to combine transient pore water flow into the traditional dual-porosity mobile−immobile models by assuming that colloid deposition in both mobile and immobile pore water follows first-order kinetics. These studies have contributed greatly to our understanding of transient colloid mobilization (*8*, *11*, *17*). However, the effect of the transient flow pattern (e.g., wetting/drying cycles) and its dependence on other factors (e.g., solution chemistry, flow velocity, and soil texture) have not been systemically examined (*18*). Our knowledge of complicated colloid−sediment interactions and our ability to predict mobilization of in situ colloids in natural subsurface environments are still quite limited.

In this study, we explore the role of transient flow in mobilizing in situ colloids from unsaturated Hanford sediments. We hypothesize that multipulse transient irrigation releases more colloids than single-pulse continuous irriga-

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TABLE 1. Summary of the in Situ Colloid Mobilization Experiments

expt no.	sand texture	flow pattern[a]	irrigation rate		solution ionic strength (mM)	initial water content (g kg^{-1})	bulk density (Mg m^{-3})	porosity[c]
			%K_s [b]	mm h^{-1}				
1	coarse	MPI-unsat	5	93.8	2	37.9	1.55	0.42
2	coarse	SPI-unsat	5	93.8	2	42.3	1.59	0.40
3	coarse	MPI-unsat	5	93.8	100	39.4	1.60	0.40
4	coarse	SPI-unsat	5	93.8	100	33.4	1.54	0.42
5	coarse	MPI-unsat	0.3	5.3	2	40.1	1.62	0.39
6	coarse	SPI-unsat	0.3	5.3	2	38.9	1.58	0.41
7	fine	MPI-unsat	9.2	4.2	2	32.0	1.40	0.45
8	coarse	SPI-sat	0.3	5.0	2	38.6	1.67	0.37
9	fine	SPI-sat	11.7	5.3	2	36.2	1.59	0.38

[a] MPI: multipulse infiltration. SPI: single-pulse infiltration. Unsat: unsaturated flow condition. Sat: saturated flow condition. [b] K_s: saturated hydraulic conductivity of sand. [c] The total porosity was calculated from bulk density of the packed columns using a particle density of 2.65 Mg m^{-3}.

tion. A series of laboratory-scale column experiments were conducted to characterize the effects of the irrigation pattern in relation to solution ionic strength, irrigation rate, and sediment texture. Relevant mechanisms are discussed based on the observations.

Materials and Methods

Porous Media. Two Hanford sediments (coarse sand and fine sand) were used as the porous media in all column experiments. The sediments, free of radionuclide contamination and representative of the material underlying the Hanford waste tanks, were collected from the ERDF pit between the Hanford 200 East and West areas at the U.S. DOE Hanford Reservation in south-central Washington State. The main minerals of the sediments include mica, illite, smectite, kaolinite, vermiculite, quartz, feldpars, and pyroxene (*19*), and the colloids consisted dominantly of smectite, kaolinite, illite, and quartz (*20*). The geometric mean diameters of the coarse sand and the fine sand grains were 797 μm and 122 μm, respectively. Additional description of the sediments is made in the Supporting Information.

Column System and Packing. The unsaturated column system used in the study consisted of a peristaltic pump, soil column, liquid sprinkler, fraction collector, vacuum source, and vacuum control valves. The column was constructed from a clear 60 cm long Schedule-40 PVC pipe (2 cm inner diameter). A nylon membrane with 20 μm pore size and −6.4 kPa air-entry value (Spectra/Mesh, Spectrum Laboratories, Inc.) was placed on the base of the column to maintain capillary pressure. To avoid possible puncture of the nylon membrane by the jagged Hanford sediments, a thin layer (<1 mm) of glass fiber was placed above the membrane prior to packing sand into the column.

To mimic the in situ soil water condition of sediments at the Hanford site (∼4 to 20% volumetric moisture) (*7*), we wetted the air-dried Hanford sands with the experimental solutions (2 mM or 100 mM $NaNO_3$) to about 4% gravimetric water content (equivalent to 6.4% volumetric water content and 16% saturation of the packed coarse sands) by gently misting a pan containing a known dry weight of sediments using a cold mist humidifier. The pan was sealed overnight to uniformly distribute the moisture within the sediment. The damp sand was then packed in the column in 2 cm increments and tapped between layers to obtain a uniform packing; care was taken to avoid drying of the sand during the packing procedure. The total soil water content of the column was calculated by weighing the packed column. The column was placed vertically between a γ-ray source and detector mounted on two computer-controlled linear actuators for monitoring the spatial and temporal distribution of soil water before and during the transient irrigation experiments (see the Supporting Information for details of in situ water content measurement). Before starting an irrigation experiment, a 10 mL syringe was used to inject 2−3 mL of deionized water, which had been deaerated for 1 h under vacuum (−50 kPa) while stirring, into a tubing on a barbed fitting at the bottom of the column to wet the nylon mesh so it could be used to control the matric potential at the base of the columns. Before beginning irrigation experiments, the initial water distribution within the column was allowed to equilibrate overnight at a constant basal tension (−5.5 kPa) by connecting the barbed fitting at the end of the column to a regulated vacuum chamber.

Transient Irrigation Experimental Design and Procedures. The effect of transient flow on colloid mobilization from the Hanford sediments was evaluated in a series of saturated and unsaturated column irrigation experiments by introducing a certain volume of an injection solution with varying solution ionic strength, irrigation rate, and infiltration frequency (a single continuous infiltration event, or multiple infiltration/drainage pulses). The infiltration solution $NaNO_3$ (pH 7) was prepared using deionized water at either 2 mM or 100 mM ionic strength. Two different irrigation rates (∼5 and ∼94 mm h^{-1}) were used, which were equivalent to 0.3% and 5% of saturated hydraulic conductivity (K_s) of the coarse sand, respectively. The 5 mm h^{-1} rate corresponded to ∼10% of the K_s of the fine sand. All experiments were conducted at room temperature (22 ± 1 °C). A summary of the experimental conditions for all of the columns is provided in Table 1. An irrigation experiment was initiated by introducing the solution into the packed column upward from the bottom (saturated experiments) or downward from the top (unsaturated experiments) of the column using a peristaltic pump. In the saturated experiments, the pump was directly connected to the bottom of the column, which was packed in the same way as for the unsaturated column. The 150 mL of effluent (∼2 pore volumes for saturated flow) was collected from the top using a fraction collector. The upward input of solution assured complete saturation of the columns during the experiments. In the unsaturated experiments, the lower boundary tension of the unsaturated column was maintained at −5.5 kPa for the entire course of the unsaturated experiments. When a desired volume of effluent had been collected, the pump was stopped, and the top of the column was covered. Drainage continued overnight under tension into the fraction collector. Hence, the unsaturated flow experiments were composed of two phases: an infiltration phase and a drainage phase. In one set of experiments (termed single-pulse infiltration), the continuous injection ceased when 150 mL of effluent from the fine sand column or 200 mL of effluent from the coarse sand column was collected, and the column was then allowed to drain overnight. In a second series of experiments (termed multipulse infiltration), the 150 or 200 mL effluent was collected

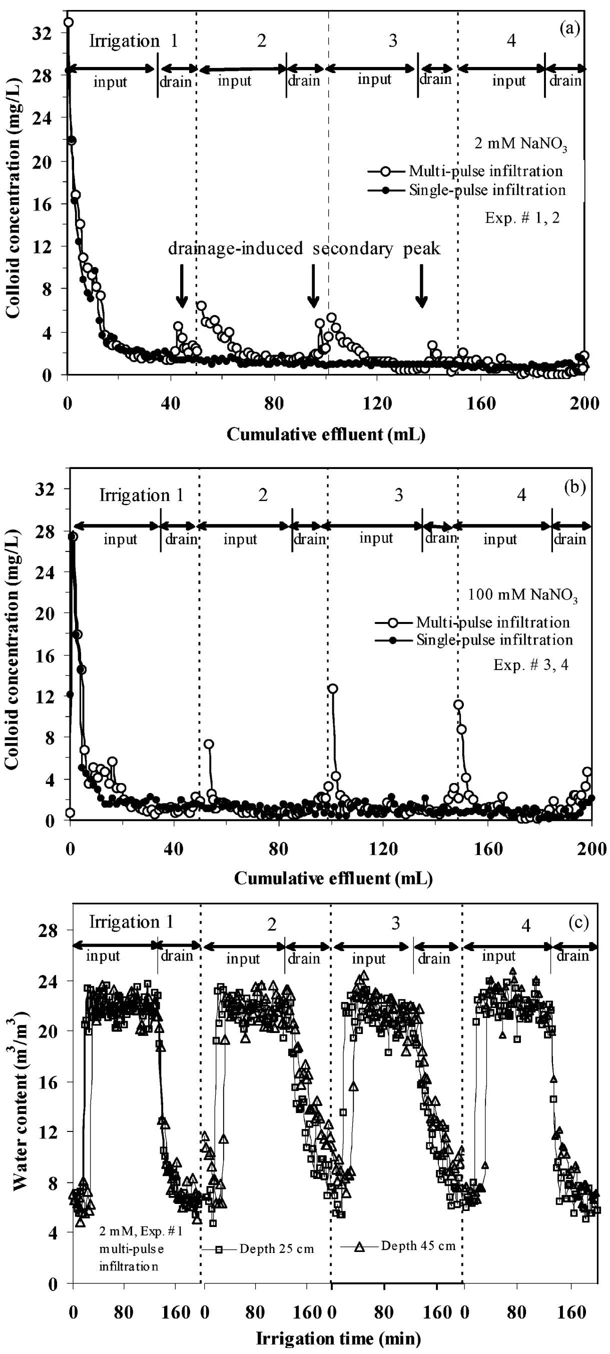

FIGURE 1. Colloid release from coarse Hanford sand as affected by flow pattern and solution ionic strength at an irrigation rate of 93.8 mm/h (5% K_s) (a and b), as well as temporal changes in sand water content (c).

in a series of three or four sequential infiltration−drainage events. Each pulse was applied as described for the single-infiltration case, except that only 50 mL of solution (~1 pore volume for unsaturated flow) was collected before the infiltration was terminated for overnight drainage under tension. Colloid concentrations were analyzed using a UV−visible spectrophotometer (see the Supporting Information for details).

Results and Discussion

Effect of Irrigation Pattern on in Situ Colloid Mobilization. Figure 1a,b compares the effects of multipulse and single-pulse infiltrations on mobilization of in situ colloids in Hanford sediments at two solution ionic strengths (2 mM and 100 mM). In both flow patterns, mobilization of the in situ colloids in each irrigation event was similar; a considerable amount of the in situ colloids was leached out of the columns along with the initial breakthrough of the injected liquid, followed by a decrease in the effluent colloid concentration to a constant low level as infiltration proceeded, and finally a secondary concentration peak near the end of the drainage phase. In the multipulse infiltration, the primary concentration peak of colloids observed for the irrigation events after the first pulse declined dramatically by more than 80%, while the constant tailing concentrations remained similar among all the infiltration pulses. Water content data (~10% in relative standard deviation) presented in Figure 1c indicates that significant colloid release took place as the water content increased during infiltration resulting in the primary peaks, and the water content decreased during drainage causing the secondary peaks, though these were relatively small and sometimes inconsistent in magnitude among the drainage events. On the basis of the primary peak concentrations observed in the unsaturated (expt nos. 1−5) and saturated (expt no. 9) experiments, we calculated the effect of a unit change in pore water saturation in the coarse sand on colloid mobilization. In the first infiltration event, a unit increase in pore water saturation caused an increase of 0.70 ± 0.07 mg/L in the effluent colloid concentration in both 2 mM and 100 mM solutions. However, in successive infiltration events, the increases decreased to 0.11 ± 0.05 mg/L and 0.23 ± 0.06 mg/L in the 2 mM and 100 mM solutions, respectively. This observed association of colloid effluent purges with hydrological pulses is consistent with the results by El-Farhan et al. (*14*), suggesting that movement of air−water interfaces, thin-film expansion, and/or fluid shear during rising (infiltration) and falling (drainage) limbs of water flux were mechanistically responsible for the observed pulses of colloid mobilization (*11*, *14*, *21*). In comparison to the small steady colloid mass flux persisting during the stable water flux (i.e., the plateau portions of the curves in Figure 1c), the primary peak concentrations (Figure 1a,b) occurring as water flux increased (i.e., the rising limb in Figure 1c) indicate that transient flow mobilized more colloids than did steady-state flow. Such an effect is further illustrated in Figure 2, in which the cumulative mass of the effluent colloids is plotted against the cumulative volume of outflow for both flow patterns. On average, the multipulse infiltration liberated ~30% more colloids than the single-pulse infiltration during the experiments, with 32 ± 11% and 32 ± 5% increases for the 2 mM and 100 mM solutions, respectively. Overall, these results suggest that the number

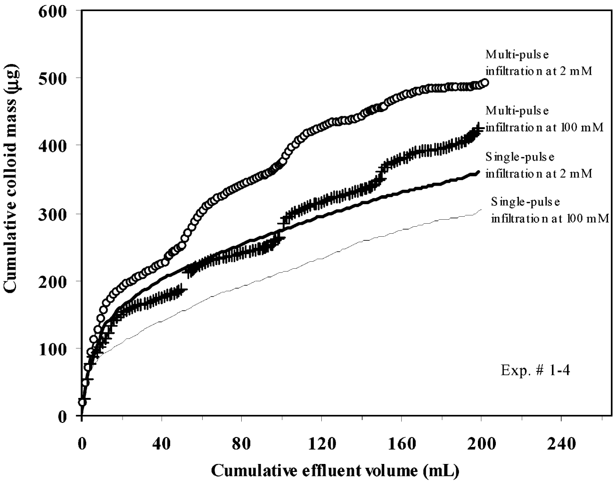

FIGURE 2. Effect of flow pattern and solution ionic strength on cumulative colloid release from coarse Hanford sand at an irrigation rate of 93.8 mm/h (5% K_s).

of irrigation pulses is more important than the total irrigation volume for increasing the total amount of colloids leached from the Hanford sediments.

The colloid release pattern shown in Figure 1 can be attributed to two sequential mechanisms: (1) physical dispersion of releasable colloids to the fluid streamlines due to loss of hydrostatic equilibrium associated with pore water and various interfaces during the transient pulses of water flux and (2) air−water interface scouring. Both the increase in soil water content during infiltration and the decrease during drainage (Figure 1c) could cause a jump of local soil water potential along with changes in pore water saturation, air−water surface area, and dimensions of corner-water ducts (*21*−*23*). As a result, colloids that were held against air−water and/or water−solid interfaces under hydrostatic conditions, or trapped in disconnected pore regions, were forced into more saturated pore spaces and mobilized by hydrodynamic shear (*12*, *14*). As water flowed downward, mobile colloids accumulated at, and moved with, the wetting or drying fronts. Ultimately, colloid movement was facilitated by the wetting/drying fronts to produce peaks of colloid mass flux. The observed larger peak concentration of colloids in the first irrigation event relative to those in successive ones is mainly attributed to the larger amount of releasable colloids present in the column prior to the first leaching. The larger effect of the multipulse infiltration on colloid mobilization than the single-pulse infiltration simply resulted from multiple disturbances (e.g., air−water interface scouring) during multipulse transient flow to the established kinetic equilibrium of colloid retention/release at a variety of interfaces including air−water, water−solid, and air−water−solid interfaces. A pulse of transient flow is similar to a "hydrological activator", which helps colloids that are persistently held at interfaces under steady-state conditions (*24*) overcome the associated "energy barrier" for release.

Dependence on Solution Ionic Strength. Figures 1 and 2 also display a significant ionic strength effect. The primary peaks of effluent colloid concentrations were larger in the 100 mM than in the 2 mM solutions in the irrigation events after the first event where the difference in peak concentrations (with a relative standard deviation (RSD) of 16%) was not significant according to the RSD of 17 ± 9% obtained from the repeated experiments of such type (see the Supporting Information). During all the irrigation events, the peak colloid concentrations decreased much more rapidly in the 100 mM than in the 2 mM solutions, leading to the increased cumulative mass of the effluent colloids in the lower ionic strength solution (Figure 2). Specifically, the decrease in solution ionic strength from 100 mM to 2 mM led to an average of an ~30% increase in the mass of mobilized colloids across the entire leaching process (i.e., increases of 31 ± 7% and 30 ± 9% during the multipulse and single-pulse infiltrations, respectively). The cumulative curves show that at the 5% K_s irrigation rate, multipulse infiltration of the 100 mM $NaNO_3$ solution was overall equivalent to a 50-fold reduction in ionic strength (from 100 mM to 2 mM) in single-pulse infiltration in terms of the positive effects of these two factors (multipulse water flux and decrease in ionic strength) on colloid mobilization.

Such effects of ionic strength during transient flow were presumably attributed to the interactive effect of air−water interface scouring, capacity limitation of colloid retention by air−water interfaces, and electrostatic interaction between colloids and mineral surfaces. Both colloids extracted from the fine and coarse Hanford sands had a net negative charge at pH 7, as indicated by the negative values of ζ potential and electrophoretic mobility (*20*). The measured ζ potentials were similar between the fine sand colloids (−35.2 ± 0.9 and −20.6 ± 0.7 mV in 2 mM and 100 mM $NaNO_3$, respectively) and the coarse sand colloids (−34.1 ± 0.7 and −21.4 ± 1.1 mV in 2 mM and 100 mM $NaNO_3$, respectively) in the same solution. The larger peak concentrations of mobilized colloids in the 100 mM than in the 2 mM solutions in successive irrigation events supports the notion of air−water interface scouring, since an increase in ionic strength reduces repulsion between the negatively charged air−water interface and like-charged mineral colloids, leading to more colloids being captured at the air−water interface in solutions with elevated ionic strengths (*11*, *25*). However, the amount of colloids retained at the air−water interface is limited by the total area of air−water surface. When the releasable colloid concentrations are large in porous media, the capacity of air−water interfaces for colloid retention could be easily reached, causing a reduced effect of ionic strength on capture and delivery of colloids by the moving air−water interfaces during transient flow. This is likely the case encountered in the first irrigation event because the sands were initially relatively rich in releasable colloids. While the larger ionic strength solution (100 mM) was favorable to colloid capture and mobilization by the mobile air−water interfaces, it decreased colloid detachment from immobile water−solid interfaces by reducing the magnitude of electric double layer repulsion between like-charged colloids and mineral grains (*26*, *27*). As a result, the larger ionic strength suppressed dispersion of colloids to fluid streamlines leading to a steeper decline of the peak effluent colloid concentrations as the infiltration approached steady-state flow conditions where motion of air−water interfaces was insignificant (Figure 1a,b).

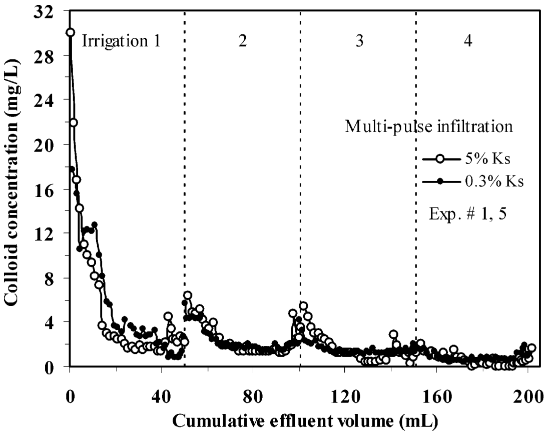

FIGURE 3. Effect of irrigation rate on the multipulse release of colloids from coarse Hanford sand in 2 mM $NaNO_3$ solution.

Effect of Irrigation Rate. Figure 3 illustrates the effect of irrigation rate on the mobilization of in situ colloids during the multipulse unsaturated flow. The initial surge of water was associated with large colloid concentrations. The primary peak concentrations of colloids were generally larger by ~66% at the large (5% K_s) than the small (0.3% K_s) irrigation rates, showing a significant flow rate effect according to the RSD of 17 ± 9% found for the first leaching event. This effect is mainly attributed to the combined influence of increased soil water content and hydrodynamic shear at the larger flow rate relative to the smaller flow rate (*27*, *28*). The measured water contents corresponding to the initial effluents were 0.16 $m^3\ m^{-3}$ (equivalent to 40% water saturation) and 0.23 $m^3\ m^{-3}$ (equivalent to 60% water saturation) for the 0.3% K_s and 5% K_s irrigation rates, respectively. It is obvious that increase in pore water saturation was greater at irrigation rates of 5% K_s (from 16% prior to the irrigation to 60%) than at 0.3% K_s (from 16% to 40%). Since pore water saturation is positively related to increases in pore water connectivity and cross-sectioned area of active flow paths, more colloids were mobilized by hydrodynamic shear as flow rate increased. Unlike the flow rate effect on colloid mobilization during the first irrigation event, the peak colloid concentrations during

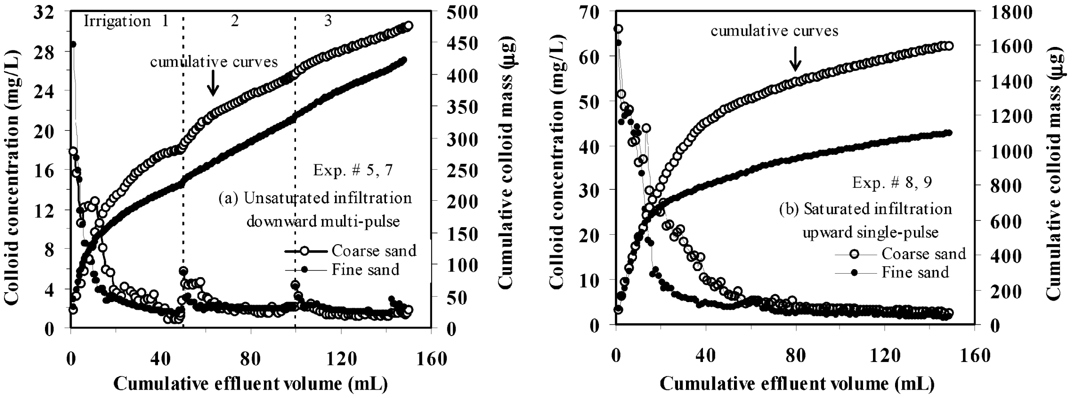

FIGURE 4. Effect of soil texture on colloid release in 2 mM $NaNO_3$ solution at a low irrigation rate of 5 mm/h. The rate is equivalent to 0.3% K_s of the coarse Hanford sand and 9.2% K_s of the fine Hanford sand. Note the scales of the *y*-axes are different between the unsaturated and saturated results.

successive events seemed not to be significantly different between the two irrigation rates because the averaged RSD of 16 ± 12% between the compared curves was not larger than the RSD of 19 ± 11% for this type of irrigation (see the Supporting Information). This lack of significance might be a result of the interactive effect of a decrease in the concentrations of mobile colloids after the first irrigation event and attainment, or exceeding, of both irrigation rates to the critical flow rate (i.e., $\leq$0.3% K_s for this study) for colloid mobilization. That is, when the flow rate exceeds the critical value, colloid mass flux is positively related to the magnitude of a particular flow rate at large colloid concentrations, while releasable colloid concentration becomes the limiting factor at small source colloid concentrations. This assumption warrants further investigation.

Effect of Soil Texture. Figure 4 illustrates in situ colloid mobilization in the fine- and coarse-textured Hanford sediments during single-pulse saturated infiltration and multipulse unsaturated infiltrations. Under both flow conditions, more colloids were released from the coarse sand than from the fine sand. This discrepancy mainly occurred in the first 60 mL elution of the saturated flow or in the first event of the multipulse unsaturated infiltration (Figure 4). Saturated conditions greatly facilitated in situ colloid release from both sands (refer to the figure provided in the Supporting Information). The averaged increases in mobilized colloid mass over the entire course of the leaching experiments were 275 ± 35% and 225 ± 52% for the coarse sand and the fine sand, respectively. The slightly different increase caused by the saturated flow relative to the unsaturated flow between the coarse and fine sands suggests a synergistic effect of the soil texture and pore water saturation. Factors leading to dependence of colloid release on soil texture may include source colloid concentration, pore water saturation, pore velocity, and pore size in the sediments. The preliminary washing experiments as described earlier show that the source concentration of in situ colloids (<2 μm) in the fine sand was ~1.2 order of magnitude higher than that in the coarse sand. During the unsaturated infiltrations with similar irrigation rates (expt nos. 5 and 7), pore water saturation increased from 10% (i.e., 0.045 $m^3\ m^{-3}$) to a steady level of 79% (i.e., 0.304 $m^3\ m^{-3}$) in the fine sand and from 16% (0.064 $m^3\ m^{-3}$) to 60% (0.233 $m^3\ m^{-3}$) in the coarse sand. The fine sand experienced a larger increase in pore water saturation and reached a larger water content than the coarse sand. According to the literature (*9, 10*) and the results described earlier, the first two factors (i.e., source colloid concentration and pore water saturation) should have caused larger effluent concentration of colloids from the fine than from the coarse sand columns. This, however, was not supported by the observed results as illustrated in Figure 4. Therefore, pore velocity and pore size within the porous media might be the factors which are responsible for the difference in colloid mobilization in the two sands. The pore velocities corresponding to the above steady water contents were 2.3 cm h^{-1} and 1.4 cm h^{-1} for the coarse sand and the fine sand columns, respectively. According to the literature (*8–11*), a larger pore velocity can increase colloid transport due to enhanced hydrodynamic shear. Hence, pore water velocity was a factor resulting in the larger colloid mass flux in the coarse sand than in the fine sand. Mechanical straining of colloids (i.e., clogging in pore channels and down-gradient throats) is likely an additional mechanism causing the different behaviors of colloid mobilization in the two sands. As studied by Bradford and co-workers using saturated transport experiments and modeling (*29–31*), colloid straining occurs in pores that are smaller than a critical size. The geometric mean diameters of pores, which were estimated using the Young–Laplace equation from the drying curves of the sand water retention, were 28.2 μm and 85.2 μm for the fine and the coarse Hanford sands, respectively (see the Supporting Information for detailed distribution curves). The ratios of grain size at 50% cumulative mass ($d_{50} = 103\ \mu$m for the fine sand, and $d_{50} = 578\ \mu$m for the coarse sand) to mean colloid sizes (d_c ranged between ~1 μm and 3 μm in the effluents from both sands) were 0.01~0.03 for the fine sand and 0.002~0.005 for the coarse sand. The d_c/d_{50} ratio for the fine sand, greater than a critical value of 0.005 as recently reported in the literature (*29–31*), suggests that mechanical straining was probably a significant mechanism responsible for the reduced mobilization of colloids in the fine sand relative to the coarse sand. This critical value partly explains the saturated results (Figure 4b), but may not apply to the unsaturated mobilization (Figure 4a), where straining can also occur in thin water films. Both experimental and theoretical studies are needed to explore the straining effect of colloid/grain size ratios on colloid retention during transient unsaturated flow, as well as the possible variations of critical size ratios with uniformity in grain size and shapes.

Colloid mobilization in natural soils involves complex interactions among many mechanisms particularly under transient unsaturated flow conditions. The results of this study suggest that a series of further investigations are needed for developing a comprehensive conceptual framework and theoretical simulation for the mechanistic description of natural colloid mobilization processes in a quantitative manner. Under natural conditions, drying/wetting cycles in shallow soils probably determine both the efficiency and the amount of colloid mobilization toward deep soils because during the period of large changes in flow rate and pore water saturation there may be movement and configuration changes of air–water interfaces. Moving air–water interfaces, and/or extension/shrinkage of water films along grain surfaces, are presumed to play a key role in exposing attached colloids to conditions for mobilization (*14*, *21*). Frequent disturbance of soil hydrological processes would thus be expected to increase the total amount of mobilized colloids. A continuous single pulse of leaching is supposed to never catch up with the effects of multiple pulses in terms of the amount of mobilized colloids on the same basis of flow volume. This is because the small effluent colloid concentrations, after the leveling off of colloid mass flux, persist in spite of the time length of the continuous single-pulse irrigation. The study presented herein may not be sufficient to elucidate all of the underlying mechanisms that might be involved in the transient mobilization of in situ colloids within heterogeneous sediments. However, it did illustrate that flow transients substantially controlled colloid mobilization in porous media and suggests that many mobilization-driving forces (e.g., capillary forces, electrostatic forces, van der Waals forces, and hydrophobic forces) may be coupled in their effects depending on the rate and area of moving air−water interfaces occurring during transient flow. From a practical perspective, the results in this study may imply that colloid transport and mobilization in deep soils might be limited or insignificant unless the water flow conditions in deep horizons are instable due to fluctuating groundwater tables or bypass flow from rainfalls.

Acknowledgments

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Supporting Information Available

Additional information on porous media, measurement errors, and data comparison between the saturated and unsaturated experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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