



# On the critical salt concentrations for particle detachment in homogeneous sand and heterogeneous Hanford sediments

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## Abstract

One of the mechanisms for sudden particle release is a decrease in groundwater salt concentration to below the critical salt concentration (CSC), where repulsion forces between fine particles and matrix surfaces exceed binding forces. In this paper, an attempt was made to determine the CSC with both batch and column experiments. Two types of sediments were tested: (a) homogeneous quartz sand and (b) mineralogically heterogeneous sediment, taken from the Hanford formation in southeast Washington. Stepwise decreasing concentrations of NaNO<sub>3</sub> solution were applied until fine particles were released from the sediments and the CSC was determined. Two methods were used to minimize the interference of particle release due to physical forces (shear stress) in the batch experiments: (a) postexperimental correction for mechanical effects, and (b) minimization of shear stress on the sediments during the experiment. CSCs from batch experiments were compared to those obtained from column experiments. It was found that both the amount of particles released and the CSC were an order of magnitude higher for the Hanford sediment than for the Sand. Moreover, particle detachment above the CSC was observed for the Hanford sediment. This suggests that the concept of sharp CSCs could be problematic in natural heterogeneous sediments where fine particles may mobilize at salt concentrations significantly above the CSC, thus unexpectedly enhancing colloid-facilitated transport of contaminants.

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## 1. Introduction

Understanding colloidal transport in the subsurface is essential for assessing the migration of contami-

nants with low solubility, such as radionuclides and hydrophobic organic compounds. Numerous studies have shown that mobile colloids and fine particulate matter are abundant in the subsurface and may facilitate the transport of contaminants that have a high affinity for their surfaces, beyond that predicted by aqueous-phase transport models (e.g., Kersting et al., 1999; Kretzschmar et al., 1999; McCarthy and

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Zachara, 1989; McDowell-Boyer et al., 1986; Ryan and Elimelech, 1996; Saiers and Hornberger, 1999; Weisbrod et al., 1996). However, the specific conditions necessary for detachment and mobilization of fine particles are still an area of active research (Khilar and Fogler, 1998; Kretzschmar et al., 1999; Mohan et al., 1999).

Researchers from many disciplines are increasingly focusing their attention on the causes and consequences of particle release. At high flow rates, particle release may occur due to the hydraulic shear stress on larger particles (Kaplan et al., 1993; Khilar and Fogler, 1998; Ochi and Vernoux, 1998; Sharma et al., 1992). In natural subsurface flow, where flow rates are generally low, particle release is more likely to occur due to changes in soil solution/groundwater chemistry (Kaplan et al., 1993; Khilar and Fogler, 1984, 1998). Changes in pH or in ionic strength may modify the balance between the forces at the particle–grain interface and result in particle detachment (Khilar and Fogler, 1998; Kretzschmar et al., 1999). This phenomenon and its implications have been observed and studied in many different environments and under different circumstances such as clogging of coastal aquifers (Goldenberg et al., 1984), formation damage during oil exploitation (Khilar and Fogler, 1984; Kia et al., 1987; Mohan et al., 1999), decreasing soil hydraulic conductivity in soils irrigated with sodic waters (Frenkel et al., 1978; Pupisky and Shainberg, 1979), groundwater turbidity caused by artificial recharge (Nightingale and Bianchi, 1977), and contaminant transport (e.g., Grolimund et al., 1998; Puls and Powell, 1992; Saiers and Hornberger, 1999).

This study focuses specifically on critical salt concentrations (CSCs), taken here to be the threshold in salinity, below which fine particles are released from matrix surfaces. CSCs can be of importance at waste deposits such as the Hanford Site in southeast Washington. At this site, single-shelled tanks filled with highly radioactive waste had been leaking into the Hanford formation for many years. The leaking waste solution included an extremely high concentration of salts ( $>5$  M  $\text{Na}^+$ ) as well as radionuclides, other toxic metals, and some organic compounds (Gephart and Lundgren, 1998; GJPO, 1996). While migrating in the vadose zone, these hypersaline solutions (brines) can be diluted dramatically by mixing

with either the permeating solution or condensed water vapor, osmotically derived from the surrounding native sediment (Weisbrod et al., 2003). Once the native fine particles detach from the sediments, they can either enhance radionuclide migration (e.g., Flury et al., 2002) or settle within fine layers, reducing the formation's permeability (Blume et al., 2002). Thus, the CSC values at which fine particles may be mobilized are of particular interest in the Hanford sediments.

CSCs have traditionally been determined through column experiments in which solutions of stepwise decreasing salt concentrations are applied to the media until particles are released (Goldenberg et al., 1984; Khilar and Fogler, 1984). Batch experiments are usually used to determine critical coagulation concentrations (CCCs), i.e., the concentration at which particles coagulate and settle (e.g., Hesterberg and Page, 1990a,b). Media chosen for these experiments are often either glass beads or acid-cleaned silica sand with artificial colloids attached to their surfaces (Amirtharajah and Raveendran, 1993; Nocito-Gobel and Tobiason, 1996; Roy and Dzombak, 1996; Yan et al., 1995), or cores of Berea sandstone, due to their importance to the oil industry (Khilar and Fogler, 1998).

CSCs not only differ from sediment to sediment, but they are also dependent on valence and size of the solubilized salt's cation (Khilar and Fogler, 1984). The most commonly applied salt in experiments determining CSC is NaCl, a monovalent dispersive salt (Table 1). Khilar and Fogler (1984) determined CSCs of Berea sandstone for a number of other salts. For the monovalent salts, which usually generate higher particle release, CSCs ranged from 0.006 M for CsCl to 0.07 M for NaCl and LiCl. The CSCs can

Table 1  
Collection of  $\text{Na}^+$ -critical salt concentrations (CSCs) found in the literature

Authors	Matrix used	CSC ( $\text{Na}^+$ , M)
Khilar and Fogler (1984)	Berea sandstone	0.07
Kia et al. (1987)	Berea sandstone	0.03–0.04
Grolimund et al. (1998)	Silty loam soil	0.2
Quirk and Schofield (1955)	Silty loam soil	0.25
Mohan and Fogler (1997)	Stevens sandstone	0.25

Note that the value reported for Grolimund et al. (1998) was the critical deposition concentration, which is marked by a sudden decrease in deposition rate.

be placed in the following order from high to low, depending on the cation in the salt solution:  $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Cs}^+$  (Khilar and Fogler, 1984). Divalent salts, such as  $\text{Ca}^{2+}$ , show almost no particle release and their CSC is less than 0.0001 M.

Swelling clays, such as montmorillonite, can also induce migration of colloidal particles. This refers to the dislocation of neighboring fine particles as a result of the sudden expansion of swelling clays (see Mohan and Fogler, 1997 for details). This sudden expansion is attributed to a specific salt concentration, which can also be called the CSC. For example, the CSC for Stevens sandstone, which contains swelling clays, was found to be an order of magnitude higher than CSC values for Berea sandstone, which does not contain them (Mohan and Fogler, 1997).

In this study, an attempt was made to determine CSCs using batch experiments as well as column experiments. Batch experiments may be cheaper, simpler, and less time-consuming than column experiments, allowing for more exhaustive screening of CSCs by soil and salt. Batch experiments have been used in many cases to determine critical flocculation/coagulation concentrations (CFCs/CCCs) of natural colloids and clays (Hesterberg and Page, 1990a,b; Kaplan et al., 1996; Miller et al., 1990), as well as the amounts and mineralogical and chemical characteristics of water- and sodium-dispersible colloids in a variety of soils (Seta and Karathanasis, 1996). The CSC was identified in both Hanford sediment (hereafter “HS”) and homogeneous iron oxide-coated quartz sand (hereafter “Sand”). These two sediments represent the two extremes in terms of sediment composition: one (Sand) represents an almost ideal system (chemically and physically homogeneous), while the other (HS) represents a heterogeneous system with complex mineral assemblages, more typical of many natural environments.

## 2. Materials and methods

### 2.1. Sediments and solutions

Batch and column experiments were carried out with two types of sediments: (i) a clean 40:50 (0.3–0.42 mm) quartz sand (Accusand<sup>®</sup>, Unimim, Le Sueur, MN), and (ii) a natural sediment taken from

the Hanford formation in southeastern Washington. The almost pure quartz sand was chosen for its chemical and physical homogeneity and its known composition and properties (Schroth et al., 1996). The sediment from the Hanford formation was chosen for the potential importance of colloidal release from these sediments at the Hanford Site. Samples used in this study were obtained 3 m below the surface in the 200E Area of the Hanford Site, about 1 km from one of the tank farms.

As this paper focuses on the detachment of fine particles originally attached to the sediment grain surfaces (rather than mobilization of the fine fraction and accumulated dust particles), the naturally existing fine fraction within the HS was removed by sieving. Only the coarser sand fraction was used (>0.42 and <2 mm). The sediment was also washed several times with water to eliminate excess dust particles. It should be noted that this sediment pretreatment is likely to change the absolute amount of particle release. A relatively large amount of gravel-size particles is included in the HS and a huge amount of dust is accumulated in the upper part of the soil profile. These two ends (in terms of size) were screened out from the sediments. Without this pretreatment, a few gravel-size grains could completely bias determinations of particle detachment and dust could bias the turbidity measurements of the effluent. Note that this pretreatment is common practice in studies focusing on colloidal detachment from sediments (e.g., Flury et al., 2002; Zhuang et al., 2003). Under natural conditions, the total amount of mobilized particles is thus very likely to be considerably higher than that observed during the experiments described here.  $\text{NaNO}_3$ , the major salt in the wastes leaking from the Hanford tanks, was used for these experiments in solutions with a range of concentrations, from 5 mol/l (approximating the leaked solution concentrations) down to about 0.001 mol/l. De-ionized water was used for dilution purposes. All experiments were conducted at room temperature (20–23 °C). pH values of the inflow solutions ranged from 6.0 to 6.4.

Chemical compositions of both sediments were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin and Elmer<sup>®</sup> Optima 3000). Mineralogical composition of the Hanford sediment and of the particles detached from the HS and Sand was determined by X-ray analysis.

Sediment samples were hand-ground to a fine powder using a diamondite mortar and pestle. The powders were then analyzed with a computer-assisted Philips XRD 3100 X-ray diffractometer utilizing monochromatic Cu K $\alpha$  radiation (40 kV, 35 mA; quartz reference intensity = 37,500 counts/s). The approximate volume of clay in the suspended fraction was estimated using intensity relations of known clay–quartz–feldspar mixtures. The samples of particles released from the HS and Sand column experiments were analyzed without further grinding as they were generally <20  $\mu\text{m}$ . Following the initial analysis, the fine particles were resuspended and allowed to settle for 5 min. The suspended portion was concentrated by centrifuging for 10 min at 10,000 rpm using a Sorval RC-5B refrigerated centrifuge. These concentrated fine particles can be expected to consist of the <5  $\mu\text{m}$  component of the original dispersed particles. A sample of this material was then prepared for X-ray diffraction (XRD) analysis.

Particle-size distributions for the released particles were determined by sequential filtration of a 10-ml solution through a Millipore<sup>®</sup> Swinnex-25 filtration device using Nuclepore<sup>®</sup> polycarbonate membrane filters with pore sizes of 10, 8, 5, 2, 0.4, and 0.1  $\mu\text{m}$ . The use of six pore sizes and thin membranes minimized membrane clogging. Nevertheless, it should be noted that this method is not absolutely accurate as particles smaller than the pore size can be retained on the membrane. Absorbance of light (directly correlated with turbidity) was measured using absorbance spectrometry after each filtration step to estimate the amount of particles in each size class. This method provides merely an estimate as not only particle concentration but also particle size and shape can have an effect on the absorbance of light (Hiemenz and Rajagopalan, 1997; Skoog et al., 1996). The electrophoretic mobility of several suspensions of the released fine particles was measured with a Malvern<sup>®</sup> Zetasizer 3000 HS. Surface charges of the sediments were not measured. Nevertheless, it is well known that quartz as well as most of the HS minerals are negatively charged at the pH values present in our experiments. The heterogeneity of the HS [and thus different points of zero charge (PZC) for each mineralogical component] limits the ability to obtain a single charge value. Moreover, the zeta potential of the mineralogical components of the sediments varies

dramatically in different solute concentrations (e.g., Ochi and Vernoux, 1998). The pH was determined with pHydrion<sup>®</sup> paper strips.

## 2.2. Experimental procedures

### 2.2.1. Batch experiments

*2.2.1.1. Method 1.* Twenty grams of Sand or 2.5 g of the HS, respectively, was placed in capped 45 ml polypropylene containers and then mixed with 20 ml of highly concentrated saline solution (>1 mol/l NaNO<sub>3</sub>) by shaking at 150 rpm (lowest setting) for 1 h on an Eberbach platform shaker. Particle concentration and NaNO<sub>3</sub> concentration of the supernatant were determined at the end of this process. For these analyses, the supernatant was sampled immediately after shaking (about 1 cm from top of fluid level), when particles are assumed to be uniformly dispersed. Light absorption of all samples was measured spectrophotometrically with a Bausch and Lomb<sup>®</sup> Spectronic 21 at 600 nm and converted to particle concentration using a calibration curve. Particles obtained from detachment experiments were oven-dried, weighed and resuspended, and a linear correlation was found for both sediments between the light absorption values and the particle concentration (g/l) of the detached particles from 0.05 to 1 mg/ml. NaNO<sub>3</sub> concentration was determined from electrical conductivity (EC), which was measured with a GLA<sup>®</sup> Instant EC Salinity Drop Tester. A calibration curve between EC and NaNO<sub>3</sub> concentration was obtained from 0 to 5 mol/l. In the case of the HS, the amount of sediment per sample was reduced to 2.5 g to keep the light absorption values within the measuring range of the spectrophotometer. After taking these measurements, the supernatant was removed. New solution with lower salinity was added to the sediment sample and put on the shaker for 1 h before measuring EC and light absorption again. The process was repeated several times while decreasing the ionic strength of each newly added solution stepwise from 1.2 down to 0.002 mol/l (the resulting concentrations were 1.2, 0.41, 0.16, 0.08, 0.03, 0.015, 0.002 and 1.17, 0.4, 0.23, 0.17, 0.11, 0.06, 0.003 mol/l for Sand and HS, respectively). The high variance in released amounts of fine particles due to sample-to-sample variability was avoided with this experimental method because

the series of salt concentrations is applied to the same sediment sample rather than to a new sample for each concentration. This decreases the effect of sample-to-sample variability within a single series. The concentration of released particles at each step decreases with increasing number of increments as a result of dilution. Consequently, it was necessary to limit the number of steps in order to remain above the measuring limit of the spectrophotometer. Each series usually consisted of five repetitions.

Two methods were used to address the possibility of mechanical particle release due to shear stress (resulting from the shaking procedure). For the first set of experiments, mechanical release was determined in a separate experiment where the sample was agitated continuously while salinity was kept constant, high above the CSC (at  $\sim 1 \pm 0.17$  mol/l). Chemical release (induced by changes in solution chemistry) is assumed to be zero at these high salt concentrations. Consequently, the observed release must be due to shear stress and physical impact. A simple logistic function was found to fit the experimental data well. This function was then used to model mechanical release over time. Logistic functions are used to model resource-limited exponential growth. After an initial phase during which the amount of released particles increases exponentially, particle release rates decrease and the amount of released particles begins to level off, never exceeding a certain limiting value  $L$ . Here, the limiting value is the maximum potential number of particles that could be detached from the matrix Eq. (1). The calculated mechanical release, based on the model, was subtracted from overall particle release in the experiments described above, delivering values for release due only to variations in ionic strength of the solution. Results obtained with this method were then compared to the second set of batch experiments as described below. It should be noted that shear becomes more influential as the strength of particle attachment decreases, meaning that particle release due to shear forces is probably underestimated at lower salinities. However, these two effects appear to be impossible to separate.

**2.2.1.2. Method 2.** The second set of experiments was carried out using essentially the same set-up. Salt concentration was decreased stepwise, resulting

in the following concentrations: 1.19, 0.28, 0.10, 0.034, 0.02, 0.012, 0.002 mol/l for the Sand and 1.6, 1.2, 0.7, 0.3, 0.22, 0.15, 0.11, 0.10, 0.05, 0.02, 0.012, 0.002, 0.001 mol/l (values combined from several series) for the HS. However, instead of subtracting mechanically derived particle release afterwards, this phenomenon was minimized during the shaking process. This was achieved by fitting a circular metal mesh (stainless steel, 0.25-mm openings, 30-mm diameter) into the polypropylene container so that the sediment would stay in place and no longer move with the solution during the shaking process. As a result, physical impact and much of the shear forces acting on the sediment grains were considerably reduced and could be assumed negligible. This means that all detached particles are the result of chemical release only (neglecting some potential detachment due to abrasion between sediment grains). Each series was run in four repetitions. An additional sample with constant salinity ( $\sim 1$  mol/l) was used as a control to confirm the negligibility of mechanical release.

Although both methods are simple and straightforward, we thought it worthwhile to separate chemical from physical detachment, compare their magnitude, and verify that physical detachment can be easily eliminated in batch experiments.

### 2.2.2. Column experiments

The column experiments were carried out with both Sand and HS. Stepwise decreasing concentrations of NaNO<sub>3</sub> solution (from 5 to 0.001 M) were applied from a sequence of pre-prepared containers to a vertical sediment column of 5-cm length and 3.5-cm diameter. Prior to the experiments, the sediment was first saturated with CO<sub>2</sub> to prevent air bubbles from being trapped in the pores. Next, water (low salinity:  $<0.05$  mol/l NaNO<sub>3</sub>) was applied from the outlet below the column until the column was saturated. Then solutions were applied at the top end of the column for each concentration for three pore volumes. Pore volumes were determined from the amount of water needed to saturate the column. Throughout the experiment, flow rates were kept at 1.3–1.4 ml/min, corresponding to an effective velocity of 0.30–0.35 cm/min. Samples were collected with a fraction collector (Gilson<sup>®</sup>, Model MFK Fractionator). Particle concentration (measured by light absorption) and EC

of the outflow were measured as described in Section 2.2.1.

As hydrodynamic forces, and thus hydrodynamic release, was minimal/minimized in all three types of experiments, consistency in the resulting CSC values was expected.

### 3. Results and discussion

#### 3.1. Sediment properties

The HS is mineralogically heterogeneous, while the Sand is essentially pure quartz (99%) with low traces of metals, and uniform shape and particle size. The  $d_{60}/d_{10}$  value (uniformity coefficient) of the HS is 3.03, compared to 1.20 for the Sand (Schroth et al., 1996), illustrating the significant contrast between the physical properties of the heterogeneous and homogeneous sediments (Table 2).

The mineralogy of the HS is dominated by anorthitic plagioclase and ferromagnesian minerals common to basalt (augite and hornblende). Quartz is a relatively minor component of the HS, reflecting the absence of this mineral in basalt. Clay minerals are only a trace component and include mica (biotite and muscovite). In general, the clay content is < 10% and probably represents undispersed mud fragments or cemented soil clasts.

The detached particles of the HS (taken from effluent samples) consist of a mixture of clay and nonclay minerals. The clay mineral assemblage includes smectite (montmorillonite), mica (most likely muscovite and biotite), chlorite, and kaolinite. Mica appears to dominate the clay assemblage of both the <20- and <5- $\mu\text{m}$  fractions, but smectite is generally enriched in the finer sediment concentrate. Clay minerals make up about 40–50% of the detached particles, although clays are more abundant in the <5  $\mu\text{m}$  fraction (60–70%). The non-clay fraction includes quartz, Ca-rich plagioclase, augite, horn-

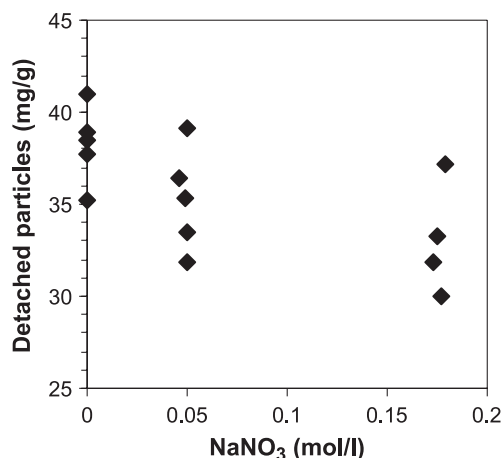


Fig. 1. Illustration of the natural variability in the amount of fine particles released from Hanford sediment (unwashed, <2 mm fraction). Each salt concentration was applied to five samples of 2.5 g of Hanford sediment and put on the shaker for 4 h (mechanical release was not subtracted). Variations of  $\sim \pm 10$  mg/g were found between samples.

blende, traces of K-feldspar, and iron oxides. Quartz abundance exceeds that of plagioclase and may represent glacial silt derived from the upper Columbia River basin during episodic glacial outburst floods. About 30% of the fine fraction detached from the Sand was clay (mainly biotite mica, with some kaolinite and a little feldspar) and about 70% was fine quartz particles.

Mineralogical heterogeneity of the HS, coupled with the small sample size, resulted in significant variations in total particle release from different sediment samples under similar conditions (Fig. 1). Standard deviations of up to 10% (compared to <0.1% for the Sand) were found between samples. The size of the released particles ranged from 0.4 to 2  $\mu\text{m}$  ( $\sim 70\%$  of the particles) for the Sand and >2  $\mu\text{m}$  ( $\sim 80\%$ ) for the HS (from sequential filtration of column outflow).

Electrophoretic mobility of suspensions of the released fine particles from both sediments (obtained

Table 2  
Selected chemical analyses and physical properties of the sediments employed

Sediment	K (ppm)	Ca (meq/100 g)	Mg (meq/100 g)	Na (meq/100 g)	Mn (ppm)	Fe (ppm)	$d_{60}/d_{10}$	$d_{50}$ (mm)
Sand	39	<0.1	<0.1	<0.1	0.1	2.5	1.20	0.36
Hanford sediment	121	4.9	1.4	0.63	0.4	4.6	3.03	0.67

from column experiments) ranged from  $-2.5$  to  $-3.5 \mu\text{m S}^{-1}/(\text{V cm}^{-1})$  for the Sand, and from  $-2.9$  to  $-3.5 \mu\text{m S}^{-1}/(\text{V cm}^{-1})$  for the HS. The pH values of the effluent samples during these measurements ranged from 6.6 to 7.2, while salinity was low (below the CSC), with concentrations between 0 and 0.05 mol/l  $\text{NaNO}_3$ .

### 3.2. Batch experiments

#### 3.2.1. Release due to hydrodynamic shear forces

Agitating a sediment sample continuously for several hours while measuring particle concentration at intervals demonstrates the effect of shear stress and mechanical impact on particle release. Particle detachment in milligrams (released particles)/gram (sediment) from the Sand was 0.5 mg/g as compared to 30 mg/g from the HS (Fig. 2). The slight decrease in the amount of particles (from 9.4 to 8.8 mg) at the end of the shaking process suggests the occurrence of re-deposition processes in the Sand.

#### 3.2.2. Method 1: modeling and subtracting mechanical particle detachment

To factor out particle release due to shear stress from overall particle release, a relationship between mechanical release (release due to shaking) and agitation time was determined. This was achieved by

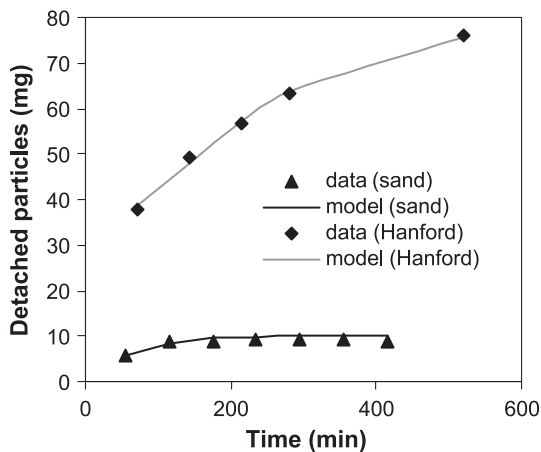


Fig. 2. Particle release due to shear stress as a function of shaking time (at 0.82 mol/l  $\text{NaNO}_3$  for the Hanford sediment and 1.17 mol/l  $\text{NaNO}_3$  for the Sand). A logistic function was fitted to the data (model).

fitting an empirical logistic function (Eq. (1)) to the particle release data at high salinity, where chemical release mechanisms do not come into play (Fig. 2).

$$N(t) = \frac{N_{\max}}{1 + \left[ \frac{N_{\max}}{N_0} - 1 \right] e^{-kt}} \quad (1)$$

where  $k$  (1/min) is the release rate,  $t$  (min) is time on the shaker, and  $N_0$  and  $N_{\max}$  are the initial and maximum amounts of particles that are released/available, respectively. This function was chosen as it includes an availability-dependent term limiting further release as the number of released particles approaches maximum availability. The model fits with  $R^2$  of 0.923 for the Sand and 0.998 for the HS ( $N_{\max} = 10$ ,  $N_0 = 3$ ,  $k = 0.021$  for the Sand and  $N_{\max} = 79.29$ ,  $N_0 = 28.78$ ,  $k = 0.007$  for the HS).

The mechanical release value was subtracted from overall release (while decreasing salinity stepwise) to obtain particle release as a function of CSC alone. For the Sand, the resultant CSC was 0.015–0.032 mol/l  $\text{NaNO}_3$ , with the amount of chemical release being significantly greater than that of mechanical release around the CSC. For the HS, the mechanical release was of the same order of magnitude as the calculated chemical release. This resulted in high potential for error (including negative values and inexplicable trends) when subtracting the mechanical from the overall particle release and diminished the ability to determine CSC accurately with this procedure (Fig. 3).

#### 3.2.3. Method 2: reducing mechanical particle detachment

By using a mesh to hold the sediment in place at the bottom of the container, the mechanical release was minimized to the point that it could be assumed negligible. Using this method, the release curves for the HS showed a much clearer signal attributable to the CSC (Fig. 4B). The pattern of particle release from the HS showed a small, but consistent release rate prior to the main peak (Fig. 4B). The relatively large amount of fine particles detached above the CSC is likely to be due to the heterogeneous mineralogy of the released particles, which include clay minerals as well as a non-clay fraction. Different fractions of the attached fine particles with different mineralogy, and

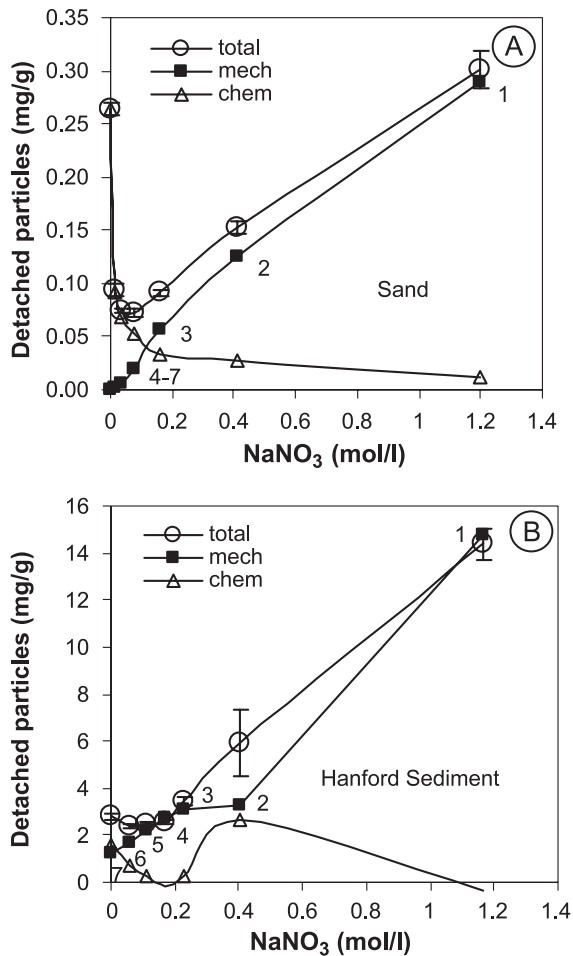


Fig. 3. Batch experiment, method 1. Total, mechanical and chemical (=total – mechanical) release of particles from (A) sand; (B) Hanford sediment. Note that mechanical release depends not on salinity but on the corresponding shaking time (in hours) given next to each data point. Error bars signify  $\pm$  one standard deviation within the set of five samples. Further explanation is given in Section 3.2.2.

thus different chemical properties, would be expected to be released at different CSCs, causing superposition of several peaks of particle detachment. Furthermore, characterization of the detached fine particles at each salt concentration step would be needed to improve the understanding of this behavior. A possible explanation could also be particle release induced by sudden swelling of montmorillonite, as suggested for Stevens sandstone by Mohan and Fogler (1997). Swelling is likely to happen at higher salinities than

release, due to the increasing repulsion forces between fine particles and the grain surfaces. Montmorillonite is present in the HS, suggesting that this process might also influence the release behavior in our study.

### 3.3. Column experiments

Column experiments were carried out for both sediments in order to compare the CSCs to the results obtained with the batch experiments (Fig. 5). A

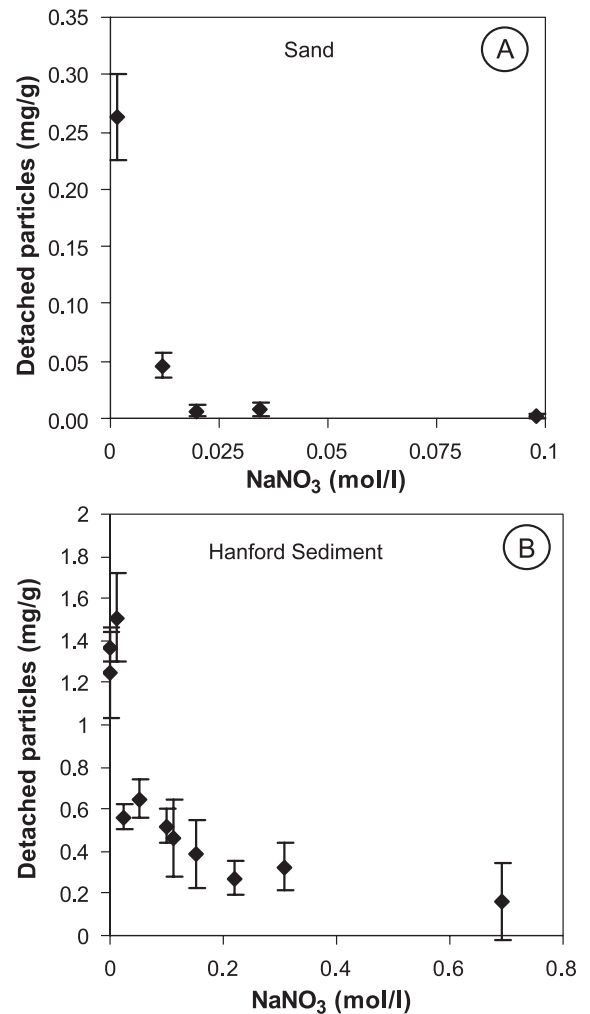


Fig. 4. Batch experiment, method 2 (no mechanical release). Particle release from three to six replications with (A) Sand and (B) Hanford sediment (average values  $\pm$  one standard deviation). Note that minor release of particles was observed above the critical salt concentration (CSC) for the Hanford sediment.

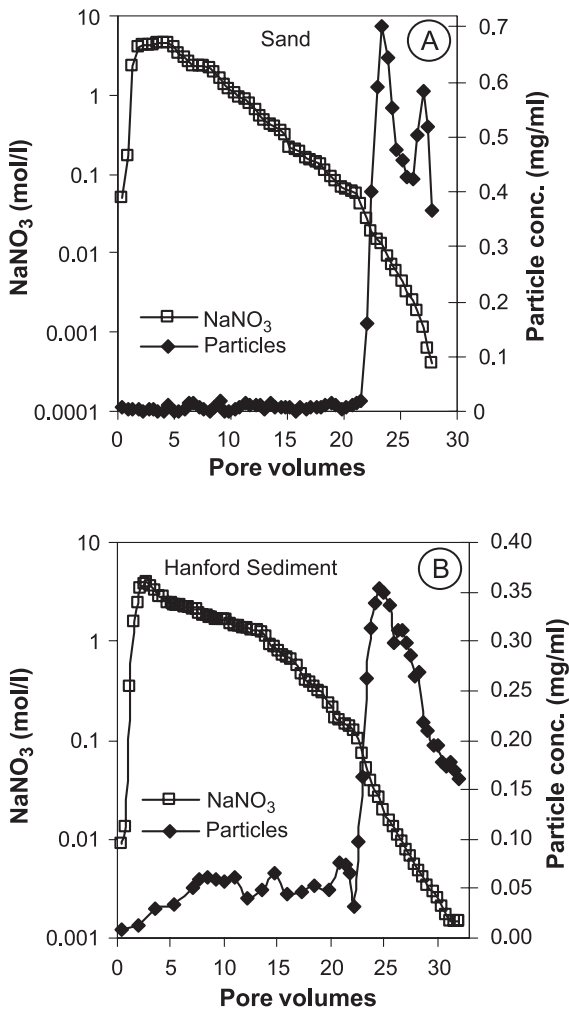


Fig. 5. Column experiment with (A) Sand and (B) Hanford sediment. Stepwise decreasing salt concentration and resulting particle release. Again, note that minor release of particles was observed above the critical salt concentration (CSC) for the Hanford sediment.

sudden release of fine particles was clearly seen as the salt solution reached the CSC. As in the batch experiments, significant amounts of particles also detached from the HS at higher salt concentrations. This phenomenon was observed only in the HS, in both batch and column experiments (Figs. 4 and 5). It should be noted that detachment of fine particles from the HS at salt concentrations above the CSC could be of special importance at the Hanford Site, where colloid-facilitated transport of radionuclides is of major concern.

Previous studies carried out with the HS have shown that mobile colloids significantly facilitate the transport of radionuclides (e.g., Flury et al., 2002).

### 3.4. Comparison of CSCs

The three methods used in this study provided similar CSC values for the HS. The CSC values for the Sand were within close range, with the values determined in the column experiment being slightly higher. However, some of this apparent discrepancy could be due to the fact that the column experiment was run without replicates. In the first batch method, the CSC ranged from 0.015 to 0.032 mol/l NaNO<sub>3</sub> for Sand and from 0.11 to 0.17 mol/l NaNO<sub>3</sub> for HS. In the second batch method where shear stress was minimized, the CSC ranged from 0.015 to 0.02 mol/l NaNO<sub>3</sub> for Sand and from 0.10 to 0.11 mol/l NaNO<sub>3</sub> for HS (Fig. 4). The column experiments resulted in CSCs of 0.028–0.042 mol/l NaNO<sub>3</sub> for Sand and about 0.10–0.13 mol/l NaNO<sub>3</sub> for HS. All values are summarized in Table 3. Note that the values for the batch experiments are averages of three to six repetitions, while the column experiments were run without duplication. The slightly higher CSC for the HS determined with the first method of batch experiments might be due to the anticipated underestimation of the influence of shear forces at lower salinities.

CSCs are given in ranges, with the limits of these ranges being the concentrations that were applied; thus, release would indicate a CSC falling between these values. This critical range was determined by calculating the slopes of the release functions. The criterion for beginning particle detachment was an increase in slope ( $P_{C2} - P_{C1} / C_1 - C_2$ , where  $P_{C1}$  and  $P_{C2}$  are the detached particle concentrations at salt concentration  $C_1$  and  $C_2$ , respectively) to a value of 2 or more. When more than one set of batch experiments was run, the resulting ranges were overlain

Table 3  
Critical salt concentrations obtained with the three different methods

Experiment	Sand (mol/l)	Hanford sediment (mol/l)
Batch	0.015–0.032	0.11–0.17
Batch (with mesh)	0.015–0.020	0.10–0.11
Column	0.028–0.042	0.10–0.13

and the minimum lower and maximum upper boundaries were determined. For the column experiments, the CSCs were determined by the first sharp increase of particle concentration at the beginning of the peak.

CSCs of Sand and HS differed by about one order of magnitude. This is not unexpected due to the considerable differences in surface chemistry of the matrix and the particles, as well as in the availability of particles on the surfaces. The CSC values found for the HS exceeded most values reported in the literature for ideal systems (Table 1). However, for natural soils, CSC values of the same order of magnitude have been reported by Quirk and Schofield (1955) and Groli-mund et al. (1998). The latter authors noted that a quantitative analysis based on the DLVO theory is not considered meaningful for highly heterogeneous natural porous media and in situ borne fine particles. The CSC reported by Mohan and Fogler (1997) for Stevens sandstone is also high (0.25 M NaCl). In this case, it is attributed to the presence of montmorillonite, which causes particle release due to sudden expansion. As montmorillonite is a component of the HS, this phenomenon could also provide a possible explanation for the high CSC value observed here. The particle detachment over a range of salt concentrations above the CSC, as seen with HS, would require further investigation to be conclusively explained; however, it is most probably the result of the mineralogically heterogeneous nature of both the sediments and the attached particles.

#### 4. Summary and conclusions

CSCs for Sand and HS were determined with both batch and column experiments. The batch method described here rendered satisfying results and can indeed be used to determine CSCs in natural sediments.

The total fine particles released from the HS amounted to 3–4 mg/g, compared to about 0.3 mg/g for Sand. The large amount of released particles holds potential importance for either change in sediment permeability by pore clogging due to the accumulation of fine particles, or migration of contaminants with high affinity to the solid phase by rapid transport of colloids through the pores. At the

Hanford Site, naturally borne particles can be detached from the sediment matrix when salinity falls below the CSC due to dilution of the contaminant plume. However, the exact amount of released particles under field conditions is difficult to estimate from the experiments conducted in this study because (a) the sediment has been washed and sieved prior to the experiment, resulting in a reduced amount of potentially mobile particles, while (b) the fact that the sediments are disturbed and disoriented might cause an increase in particle release (e.g., Bunn et al., 2002). The high CSC value and particle detachment observed even at salinities significantly above the CSC are especially important in places where radionuclides might migrate with the detached particles. In particular, the fact that a considerable amount of particles detach above the CSC can lead to unexpected early mobilization of contaminants. This needs to be taken into account when assessing the risk of colloid-facilitated contaminant transport in places such as the Hanford Site. The complex interactions between final salinity, hydrodynamic forces, availability, and mineralogy of particles on the matrix surfaces all have an impact on particle release and are often difficult to distinguish. The method described here could facilitate a more detailed study of these influences and their relative importance for particle release from sediments as a result of changing salinity.

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