



## Interparticle migration of metal cations in stream sediments as a factor in toxics transport

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### Abstract

Sorption of metal cations by stream sediments is an important process affecting the movement of released contaminants in the environment. The ability of cations to desorb from one sediment particle and subsequently sorb to another can greatly affect metal transport rates but rates for this process have not been reported. The objective of this study was to determine the rate at which sorbed metals can migrate from contaminated sediment particles to uncontaminated sediment particles as a function of the concentration of the contaminating solution and the duration of the contact with the contaminating solution. Samples of small sediment particles were exposed to solutions containing cobalt, after which they were rinsed and combined with larger uncontaminated sediment particles in the presence of stream water. Initial concentrations of the contaminating solution ranged from 1 ng/l to 1000 mg/l and exposures to the contaminating solution ranged from 6 h to 14 days. The rate of the migration increased with increasing concentrations in the contaminating solution and with decreasing times of exposure to the contaminating solution. Under the conditions of these experiments, the time required for the migration to reach equilibrium was on the order of months or longer. In separate experiments, the kinetics of adsorption and desorption of cobalt were measured as a function of concentration of the contaminating solution. The time required to reach adsorption equilibrium increased with increasing concentration in the contaminating solution. Times to sorption equilibrium were on the order of months. Desorption was much slower than adsorption and, together with intraparticle diffusion, probably controls the rate of migration from contaminated to uncontaminated sediment. The results of this study show that interparticle migration of metal cations can proceed at significant rates that are strongly influenced by the length of time that the metal has been in contact with the sediment. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The transport of charged toxic substances in an aqueous environment while sorbed on sediments is a well-recognized phenomenon. Attempts have been made to develop mathematical models to describe, and perhaps predict, such toxics transport (e.g. Dzombak and Ali [1]). Many processes affect the transport of toxic substances. Our intent here was to describe one such process that has drawn little or no attention in the literature, i.e. the transfer of toxic substances from contaminated sediment particles to uncontaminated sediment particles during temporary bed storage. Such a process has the potential to significantly alter the rate of downstream transport of toxics when the migration is from one particle size to another. Because the shear stress, required to initiate sediment movement, generally increases with increasing sediment particle size, a migration of toxics from highly mobile clays to much less mobile gravels, for example, can be expected to significantly decrease the rate of toxics transport. In this report, an effort has been made to document the interparticle transfer of one class of toxics, specifically some of the strongly adsorbed metal cations.

The external surface area per unit mass of small sediment particles such as clays is much greater than that for larger sediment particles, leading many to conclude that sorption capacity decreases with increasing particle size. However, previous studies have shown that large aggregates of fine particles can have considerable amounts of accessible internal surface area and significant sorption capacities for metal ions [2–5]. As a result of mechanical weathering and erosion of well-lithified fine-grained rocks, the sediments in transport can consist of aggregates of clays and/or silts up to boulders in size. Reactive surfaces can be expected to exist throughout these larger sediment aggregates. Wood et al. [6] have reported that even granitic fragments can have minute fractures lined with reactive clays resulting from chemical weathering. These internal surfaces can be just as reactive as those on the exterior, but diffusion is required before the reaction can occur, decreasing sorption rate but not sorption capacity. In a study of the mineralogy of clays, silts, and sands from 21 streams throughout the United States, the proportions of sand-sized fragments (0.061–1 mm) in stream beds composed of multiple particles ranged from 7 to 78% [2]. Sand-sized particles consisting of silts and clay ranged from <1 to 38%. Cation exchange capacity (CEC) for the sands ranged from 0.2 to 17 meq/100 g in single samples. The median CEC for the sands was in the range of 1–2 meq/100 g.

As pointed out by Jobson and Carey [7], toxic substances are frequently associated with silt and clay-sized particles, and these fine particles go through a sequence of transport and storage cycles as they move downstream. During storage, these fines can and do infiltrate bed sediments that are considerably coarser. Depending upon the climate and weather, the contaminated fines can be buried in the bed for times ranging from minutes to years until the next higher velocity period occurs. During storage when sediments are in close proximity, substances sorbed on particles can desorb, move through the interstitial fluid, and be re-adsorbed on other particles. As a matter of experimental convenience and to emphasize the effect on transport, we have studied movement of metal ions from smaller aggregates onto larger aggregates under oxidizing conditions only.

In order to understand how metal ions might be transferred from one particle to another, one needs to consider some of the processes that cause metal ions to be taken up from or released to oxidized solution. There appears to be a range in the binding energies with which

ions are held on fine-grained sediments [3,8,9]. A range of binding energies is consistent with studies that find that adsorbed cobalt forms surface complexes whose structure depends on the amount of cobalt adsorbed [10–12]. If the concentration of metal ions in the solution is very low, only the highest energy sites on the sediments will be filled. As more of the solutes become available, the solutes will be sorbed at sites with lower binding energy. However, there will be an equilibrium between sorbed and dissolved metal ions, sometimes described by a distribution coefficient,  $K_d$  (ml/g), defined as the ratio of the concentration of metal sorbed to the sediment (mg/g) to the concentration of metal in the solution at equilibrium (mg/ml). When the concentration of a dissolved metal in solution is very low,  $K_d$  can be very high, e.g. on the order of  $10^4$  ml/g or greater. Kennedy et al. [3] showed that for lead,  $K_d$  decreased from 32 000 to 2700 ml/g as the lead concentration in solution increased from 0.5 to 190  $\mu\text{g/l}$  at  $\text{pH} = 8.3$ . This means that if a particle bearing high sorbed concentrations of metals is washed into a stream and deposits next to an uncontaminated particle, at least two things can happen. While the contaminated particle will release metal ions easily into the solution from its low-energy sites, the clean particle will take up the metal ions strongly on its higher-energy sites. An equilibrium is ultimately established in which the sorbed concentrations on both particles are simultaneously in equilibrium with the solution. There has now been a transfer of metal ions from the contaminated particle to the clean particle. If the sizes of the particles differ, the rate of downstream transport of the adsorbed metal will have been changed, speeding downstream transport if transfer was from larger to smaller particles and slowing transport if transfer was from smaller to larger particles.

The rate at which the particle-to-particle transfer occurs will depend on the rate of release from the source particle as well as the rate of transport to and uptake by the host particle. Convection and diffusion in the interstitial water are factors as well as diffusion into and out of the porous aggregates. Davis and Kent [13] found that the adsorption step itself is rapid but that the apparent rate of sorption is limited by the rate of diffusional transport to sorption sites. Malcolm and Kennedy [14] found that about 90% exchange of barium for potassium occurred on clay in less than 10 s, so actual adsorption can occur rapidly on very small particles whose reactive surface is readily accessible. However, because some of the trace metals have very high distribution coefficients, it is likely that the mechanism of adsorption may differ from that of the alkalis and the alkaline earth. Nevertheless, there is some evidence [15] that zinc and cadmium rapidly equilibrate between pore water and associated solids.

## 2. Methods

The sediments samples used in these studies were collected from the streambed of Little Lost Man Creek, Humboldt County, CA. The sediments in this stream were predominantly (>95%) cobble of fine-grained aggregates ranging upto 25 cm in diameter. The sediments were wet sieved with stream water at the time of collection to eliminate all materials coarser than 10 mm or finer than 0.1 mm. The retained sediments were dried and returned to the laboratory where two size classes were isolated by dry sieving: the small sediment with diameters in the range 1.00–1.16 mm and the large sediment with diameters in the range 3.35–4.00 mm. The resulting small and large sediments were washed with distilled water to remove any fines that had accumulated, and were then dried and stored.

Table 1  
Composition of synthetic stream water

Component	Concentration (mM)
NaHCO <sub>3</sub>	0.29
HCl	0.17
CaCO <sub>3</sub>	0.14
MgCO <sub>3</sub>	0.08
H <sub>2</sub> SO <sub>4</sub>	0.03
KHCO <sub>3</sub>	0.02

All water used in these experiments was synthetic stream water having approximately the same composition of major cations and anions and the same pH as Little Lost Man Creek [16]. Composition of the synthetic stream water is given in Table 1. It was prepared by adding reagent-grade chemicals to double distilled water and adjusting to the final pH of 7.6 using a small addition of 1N NaOH.

All the experiments were conducted in 500 ml polyethylene beakers sealed with paraffin film that were agitated on a rotary shaker. The Little Lost Man Creek sediments are lightly metamorphosed siltstones and mudstones that will mechanically disaggregate if vigorously shaken. Because the formation of a separate set of fine particles could significantly affect the migration process, it was important to avoid this disaggregation. However, to avoid the possibility that slow diffusion in a stagnant liquid would limit migration rate, some agitation was necessary. We found that agitating at 100 rpm on the shaker resulted in gentle motion of the liquid with little or no motion of the sediment in the bottom of the beaker, completely avoiding disaggregation.

In order to design the migration, adsorption, and desorption kinetics studies, it was necessary to determine the equilibrium sorption characteristics of each metal on both the large and small sediments as a function of the total concentration of the metal in the solution contacting the sediment. Based on preliminary experiments, distribution coefficients were measured by contacting 2 g of dry sediment with 200 ml of a synthetic stream-water solution containing known concentrations of radiolabelled cobalt (<sup>58</sup>Co(NO<sub>3</sub>)<sub>2</sub>) and stable (non-radiolabelled) cobalt (CoCl<sub>2</sub>). After an 1-month contact time, the sediment was separated from the liquid by decanting, washed quickly with distilled water, and placed in a 20 ml counting tube. All counting was done with an EG&G Ortec germanium detector (all trademarks are used for identification only and do not constitute endorsement by the US government) and the results were analyzed using software by Micrad Inc. The sediment and a 10 ml sample of the liquid were counted to determine the concentrations of sorbed cobalt on the sediment and in the liquid, from which the distribution coefficient was determined. It was assumed that radioactivity in the pore fluid within the particle was negligible. Because the volume of the intraparticle pore fluid was probably less than 10% of the particle volume and because the concentration in the pore fluid was orders of magnitude less than the concentration sorbed on the particle, this assumption was justified. The same approach that was used to determine distribution coefficients for cobalt was used for strontium and rubidium using <sup>89</sup>SrCl<sub>2</sub> and <sup>86</sup>RbCl as the radioactive tracers and SrCl<sub>2</sub> and RbCl as the stable species.

Cation-exchange capacity (CEC) was measured by saturating 4 g samples with barium acetate for 2 days at 25°C, pH = 7.0 and then displacing with calcium chloride for 2 days. Calcium uptake was determined by measuring the loss of calcium from the displacing solution using atomic absorption spectroscopy. The long saturation and displacement times allowed diffusion into both sizes to the extent permeability permitted. Sediment samples were sent to the Division of Agricultural and Natural Resources Analytical Laboratory at the University of California, Davis for analysis of organic matter, iron, and manganese. Organic matter was 0.32 and 0.68%, iron was 3.35 and 3.89%, and manganese was 679 and 543 mg/kg for the small and large sediment, respectively. These values are consistent with average compositions for shales reported by Brownlow [17].

The migration experiments employed uncontaminated (metal-free) and contaminated (metal-loaded) sediments. A contaminating process, referred to below as an exposure process, was used to prepare the metal-loaded sediments. The exposure solution was prepared by adding radiolabelled stock solution and stock solutions of stable (non-radiolabelled) metal to synthetic stream water. Radiolabelled  $^{115m}\text{Cd}$ ,  $^{58}\text{Co}$ ,  $^{89}\text{Sr}$ , and  $^{86}\text{Rb}$  were obtained from Amersham Corp. The cobalt was carrier-free (specific activity > 5 mCi/ $\mu\text{g}$ ) and we estimated it could have contributed a maximum of 1 ng/l of total cobalt to the solutions to which the tracer was added. The radiolabelled cadmium had a specific activity 0.1–1.0 mCi/mg, and we estimated it could have contributed a maximum of 0.05 mg/l of total cadmium to the solutions to which it was added. Radioactive stock solutions of each metal were made by diluting the material as received. Enough radiolabelled stock solution was added to the synthetic water to give approximately 100 000 total counts per minute. Stable stock solutions were prepared by dissolving the nitrate salt of the metal in distilled water. Final concentrations of stable metal in the prepared solutions were usually 0, 1, 10, 100, and 1000 mg/l. Note that where the metal concentration is reported as 0 mg/l, this indicates that the only metal present came from the radiolabelled stock solution.

The exposure process consisted of exposing a known quantity of dried sediment (usually 15 g of small sediment) to the solution containing the metal in a sealed, agitated 500 ml beaker. Because the duration of the exposure process was of interest in these studies, various exposure periods were used, ranging from 6 h to 14 days. At the conclusion of the exposure process, the liquid was decanted from the sediments. The sediments were quickly washed three times with small volumes of distilled water to remove any residual metal-laden exposure solution and then counted to determine the initial metal levels.

For the migration experiments, 15 g of radioactive, freshly exposed small sediment was combined with 15 g of unexposed large sediment and covered with 200 ml of synthetic stream water in a sealed, agitated 500 ml beaker. Periodically, the beakers were removed from the shaker and the small and large sediments were separated by wet sieving on a 2 mm stainless steel screen. The large sediment caught on the sieve was placed in a 20 ml counting tube. The liquid was decanted from the small sediment and retained. The small sediment was then placed in a 20 ml counting tube. The separated sediments were immediately counted. Liquid samples were not counted during the migration experiments because the counts from the liquid were only slightly above background, and reliable measurements could not be obtained. After counting, the sediments and the retained liquid were recombined in the original beaker, covered, and returned to the shaker.

For decay-correction purposes, a 10 ml sample of the original exposure solution was retained in a sealed 20 ml counting tube. This “standard” was always counted along with samples. Counts for each sample were decay corrected using the counts of the standard.

Long-term sorption kinetics experiments were conducted in much the same manner as the exposure process used for the migration experiments, although less sediment was used in order to assure that the rate would not be limited by the availability of metal in the solution phase. A 2 g weighed sample of sediment was placed in a sealed, agitated beaker with 200 ml of exposure solution that was amended with stable metal to attain various initial concentrations of the stable metal. The sediment was periodically separated from the liquid, placed in a counting tube, and counted. After counting, the sediment and liquid were recombined in the original beaker and returned to the shaker.

Long-term desorption experiments were conducted using unamended synthetic stream water and sediments from the 3-month-long sorption kinetics experiments. At the end of the adsorption experiments, the 2 g sediment samples were removed from their containers, washed rapidly three times with distilled water to remove any interstitial fluid from the previous experiment, and returned to their original plastic beakers, which had been washed and refilled with 200 ml of synthetic stream water. These sediments were periodically separated and counted. A solution of 10 ml aliquots of the aqueous phase were found to have no detectable radiolabelled cobalt and were not counted after a few initial attempts.

During the migration experiments with sediment that had been subjected to 6 h exposure, replicates were run to determine the reproducibility. Comparing the adsorbed concentrations at the end of the exposure process, replicates were found to differ from one another by as much as 21% with an average deviation from the mean of 5.3%. Deviations were larger at lower concentrations.

Although, radioactive counting statistics would suggest an accuracy (3 S.D.) of about  $\pm 1\%$  for most of our counts except those near the end of the cobalt experiment, our data suggested a counting accuracy of only about  $\pm 5\%$ . We believe the additional errors were the result of variable counting geometry attributable to the variable packing of the sediments in the counting tubes. Combining the effects of counting and reproducibility errors, we estimated that our errors in concentrations and fractions of original contaminant having migrated to be  $\sim \pm 8\%$ . Because errors in liquid concentrations were large due to the small differences between actual and background counts, values of  $K_d$  were less reliable. We estimated that the errors in  $K_d$  were  $\sim \pm 25\%$ .

### 3. Results and discussion

#### 3.1. Distribution coefficients

For all metals, the distribution coefficient,  $K_d$ , was found to decrease with increasing concentration of the metal in solution (Fig. 1). This is consistent with the behavior reported by Kennedy et al. [3] and Fu and Allen [9]. It is also consistent with the finding of Benjamin and Leckie [8] that the strength of binding of a given metal to a surface may vary by an order of magnitude or more from one site to another. They attributed the decrease in  $K_d$  at higher solution concentrations to the fact that the strongest binding sites are filled at low

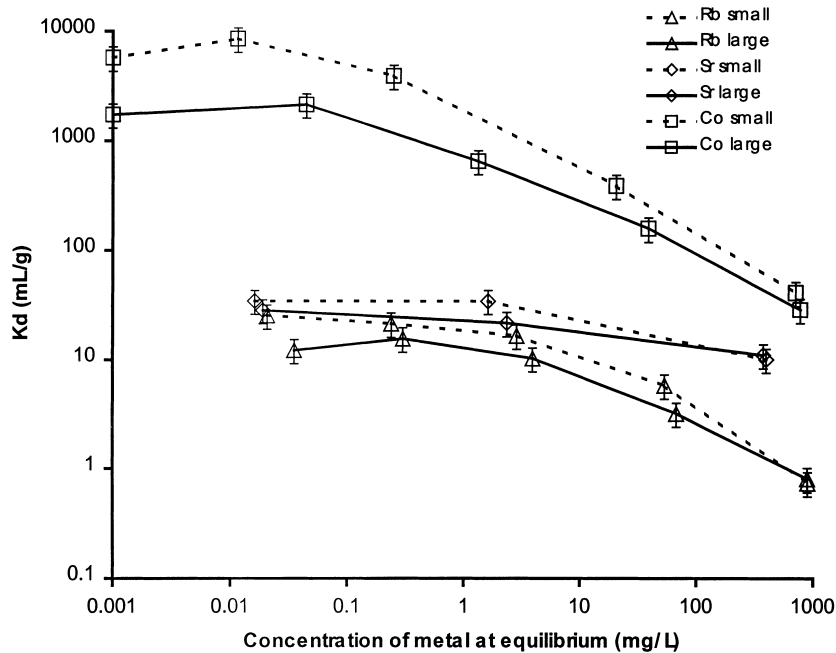


Fig. 1. Distribution coefficients for two sediment sizes as a function of concentration of metal in a background of synthetic stream water at pH = 7.6.

solution concentrations. The purpose for determining the variation of  $K_d$  with the solution concentration of rubidium and strontium was to determine whether the tendency for such variation was present with the alkalis and alkaline earth as well as with the trace metals. The experiments to measure this variation with cadmium were accidentally destroyed.

Values of  $K_d$  for the small sediment were typically 2–3 times greater than those for large sediment for all metals studied. The CEC's were  $11.0 \pm 0.5$  and  $3.0 \pm 0.5$  meq/100 g for the small and large sediment, respectively. However, organic matter and iron, factors associated with adsorption of trace metals on sediments, were greater in the larger sediment than in the small. Organic matter was 0.32 and 0.68%, iron was 3.35 and 3.89% in the small and large sediment, respectively. Manganese was slightly greater in the small sediment than in the large sediment, 679 compared to 543 mg/kg. The variation of both  $K_d$  and CEC with particle size is consistent with the variation of mineralogy with particle size previously reported by Jackman and Ng [4]. They reported that sediments from Little Lost Man Creek showed slight variations in mineralogy for particles ranging in size from 0.25 mm to nearly 1 cm in diameter. The quartz (very low sorption capacity) content tended to increase somewhat and the illite/mica (moderate sorption capacity) content tended to decrease somewhat with increasing particle diameter. Petrographic examination of thin sections of both particle sizes showed a slight increase in the number of larger quartz grains in the larger sediment, but also showed definite evidence of silica deposition in veinlets and on pre-existing quartz grains in the larger sediment. This silica deposition is presumed to be due to mild metamorphism that has affected the rocks in the area. Both sizes were composed almost entirely of cemented

aggregates of silt and clay-sized grains. It is probable that during weathering, the rock fragments which were least cemented broke down to the smallest particles, and larger particles resulted from more thorough cementation. Hence, lower porosity and permeability would be expected in the larger particles, which would yield lower  $K_d$ 's and CEC's for the coarse particles than for the finer ones.

### 3.2. Particle-to-particle migration

A series of preliminary migration experiments (results not shown) were conducted using very short-lived  $^{203}\text{Pb}$  and  $^{107}\text{Cd}$  as the radiolabelled species. Because of the very short half-lives of these radioisotopes (52.1 and 6.5 h, respectively), experiments were limited to 24–48 h. It was found that during such short time intervals, only a small percentage of the metal initially present on small sediments would migrate to the large sediment. There was a rapid migration of approximately 5% of the metal initially present on small sediments, occurring during the first hour, followed by a period in which a small amount of migration occurred at a very low rate. These experiments revealed the need for longer-lived isotopes to study the slower migration process.

Next, a longer-term cadmium-migration experiment was performed using  $^{115\text{m}}\text{Cd}$  with a half-life of 44.6 days as the radiolabelled tracer (Fig. 2). No stable cadmium was added for these experiments, and the  $^{115\text{m}}\text{Cd}$  in the liquid was below detection limits throughout the experiment. Migration was rapid at the outset with about 6% of the cadmium migrating from small sediment to large sediment during the first 24 h. Thereafter, migration proceeded at a much slower pace, resulting in an additional 15% of the cadmium migrating in the next 77 days.

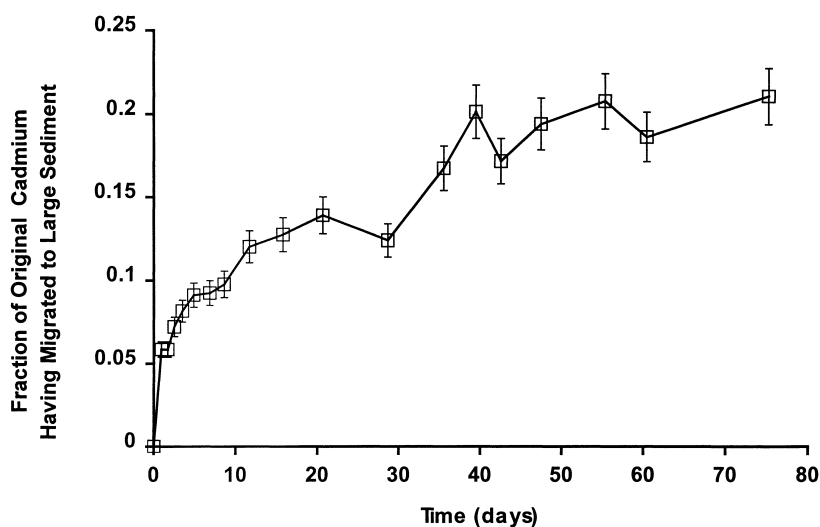


Fig. 2. Migration of  $^{115\text{m}}\text{Cd}$  from 15 g of small sediment to 15 g of large sediment in 200 ml of synthetic stream water.



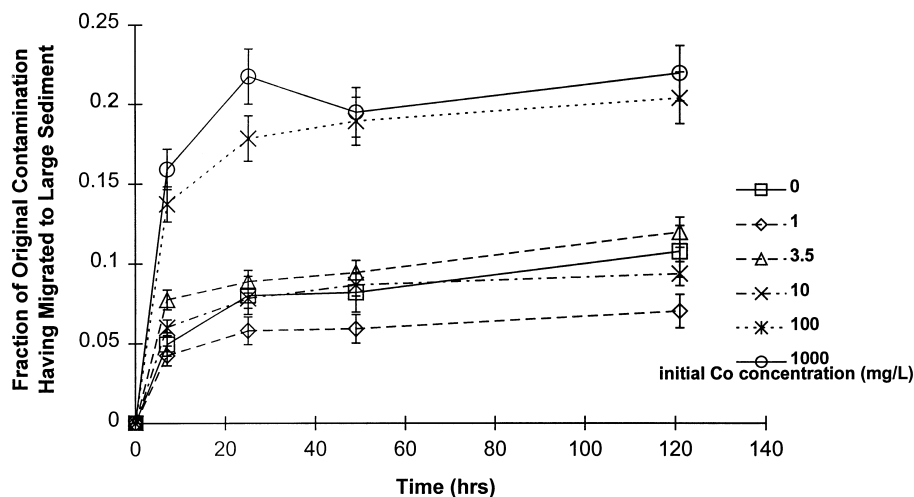


Fig. 3. Effect of concentration of exposure solution on the migration of cobalt from small particles to large particles with 6 h exposure time (2 g sediment in 200 ml solution).

A more extensive set of migration experiments was performed using various concentrations of stable cobalt and  $^{58}\text{Co}$  with a half-life of 70.8 days as the radiolabelled tracer. Migration from small to large sediment was studied as a function of both the initial cobalt concentration in the exposure solution (Fig. 3) and the duration of the exposure process (Fig. 4). Both of these factors influenced the total loading of cobalt onto the small sediment during the exposure process.

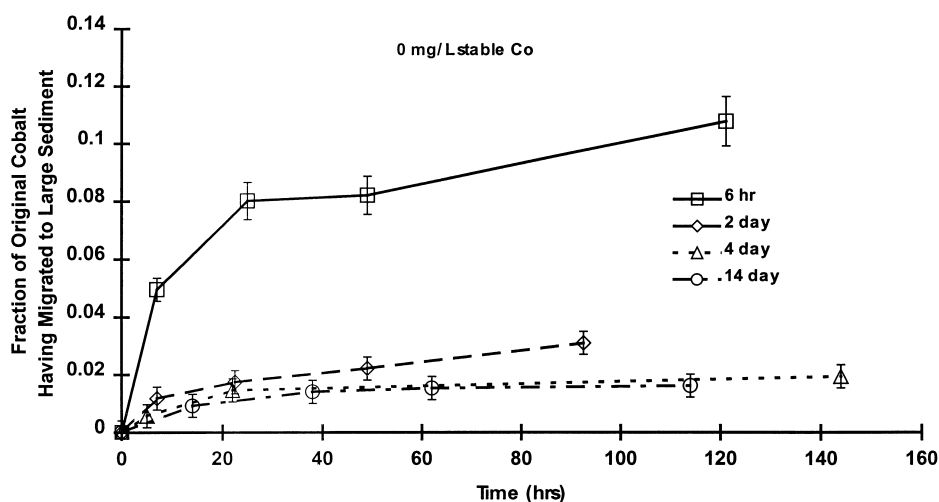


Fig. 4. Effect of exposure time on migration of cobalt from small particles to large particles at 0 mg/l stable Co (2 g of each sediment in 200 ml solution).

Fig. 3 shows the effect of initial stable cobalt concentrations in the exposure solution (ranging from 0 to 1000 mg/l) on the migration of cobalt from exposed small sediment to unexposed large sediment over a 5-day period. At cobalt concentrations less than 10 mg/l, stable cobalt concentration in the exposure solution had little effect on migration and the differences observed appear to be attributable to experimental error. The results are similar to those in the cadmium migration experiments. A rapid migration occurred during the first few hours, followed by a period during which migration was much slower. At cobalt concentrations of 100 and 1000 mg/l a much larger fraction of the original cobalt, approximately 20%, migrated from small to large sediment during the first 48 h. The concentrations of cobalt on the small sediment at the start of the experiment were 0.066, 0.64, 5.6, and 45 mg/g, respectively, for the 1, 10, 100, and 1000 mg/l exposure treatments. We speculate that, at high cobalt concentrations, most of the cobalt occupied sites with low binding affinity and, therefore, more easily migrated from the small sediment to the large sediment. At low cobalt concentrations, most of the cobalt occupied high-affinity sites from which it would desorb more slowly. This is consistent with our finding that  $K_d$ 's for cobalt decrease significantly, particularly at concentrations greater than 10 mg/l (see Fig. 1) and with the multiple-site adsorption reported by Benjamin and Leckie [8]. Note that the range and absolute values for binding affinities ( $K_d$ ) for strontium and rubidium are much less than for cobalt, suggesting that the sediments used here possessed many sites with a relatively high affinity for cobalt.

The exposure time greatly affected interparticle cobalt migration rates in the absence of stable cobalt (Fig. 4). About four times as much migration occurred in the first 48 h for a 6 h exposure time when compared with the 2-, 4-, or 14-day exposure times. There was little difference in migration rates for the 2-, 4-, and 14-day exposure times. Clearly 6 h was not enough time for cobalt at low concentrations to diffuse into the small sediment particles and sorb to all the high-affinity sites. These results are consistent with those of Ainsworth et al. [18] who studied the effect of the length of adsorption on adsorption–desorption hysteresis of cobalt, cadmium, and lead on hydrous iron oxide. They found little hysteresis for short times, but an increase in hysteresis with increasing duration of the contact of the hydrous iron oxide with a soluble metal.

At the higher concentrations of stable cobalt in the exposure solution (100 and 1000 mg/l) greater rates of migration were observed for all durations of the exposure process. Further, the large difference between 6 h exposure and longer periods of exposure at 0 mg/l was significantly reduced though not entirely eliminated (results not shown).

### 3.3. Long-term sorption kinetics

The time dependence of sorption on both small and large sediments was measured over a range of cobalt concentrations. Fig. 5a shows the results for small sediment over a period of 16 days. The initial sorption rate was high and decreases rapidly after the first day. After 4 days, uptake was essentially complete for samples exposed to initial cobalt concentrations of 0, 1, and 10 mg/l. Because both the 100 and 1000 mg/l samples appeared to be continuing to sorb cobalt after 15 days, the samples were retained and analyzed again at 105 days. It was found that both the 100 and 1000 mg/l samples had continued to sorb, with the 100 mg/l sample having sorbed over 90% of the cobalt originally present in the solution. Although,

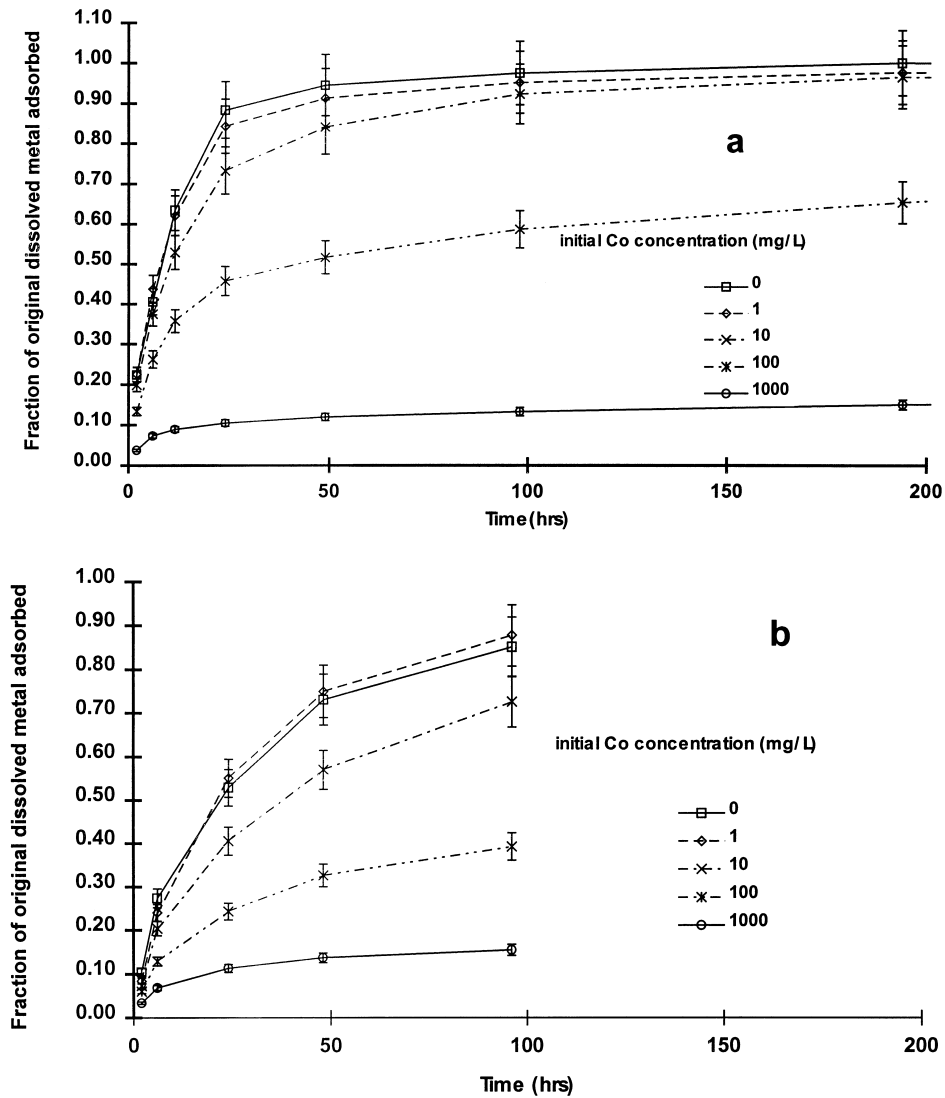


Fig. 5. Sorption of  $^{58}\text{Co}$  onto (a) small sediment, and (b) large sediment with time in the presence of various concentrations of stable metal.

the 1000 mg/l sample had continued to sorb, about 80% of the original cobalt remained in solution, suggesting that the sediment was near its maximum capacity for cobalt sorption.

The sorption results for the large sediment are shown in Fig. 5b. These samples were closely monitored for 4 days and then analyzed again at 105 days. Here, the 10, 100, and 1000 mg/l samples appeared to sorb more slowly during the first 4 days. However, at 105 days, more than 95% of the original cobalt had been sorbed from all samples except the

1000 mg/l sample where about 80% remained in solution. There is some concern regarding the solubility of cobalt at the 1000 mg/l levels. MINTEQ calculations [19] show a very small supersaturation of  $\text{CoCO}_3$  at the highest concentration (1000 mg/l). Thus, it is possible that our 1000 mg/l data could have been affected by the formation of a small amount of precipitate, although 80% of the cobalt was still in the 1000 mg/l solution at 105 days.

Our results suggest that at higher initial concentrations of cobalt, sorption occurred in a two-stage process. The first stage is relatively rapid, reaching completion in several hours. The second stage is much slower. Nearly all of the cobalt in solution was adsorbed during the first 4 days from the solutions that initially contained 0, 1, and 10 mg/l of stable cobalt. However, even after 105 days, about 80% of the 1000 mg/l of cobalt in the initial solution remained. It would appear that the occupancy of the easily accessible adsorption sites was nearly in equilibrium after about 4 days. The additional sorption that occurred in the next several months must have resulted from a process other than adsorption to exterior surface sites on the aggregates.

These results do not permit us to determine the rate-controlling step for either stage of the two-stage process. However, Jackman and Ng [4] showed that the rate of exchange of calcium and strontium ions on Little Lost Man Creek sediments is controlled by diffusion in the aggregates for particles the size of our large sediment and jointly controlled by diffusion in the aggregates and external film diffusion for particles the size of our small sediment. These processes required several hours to reach equilibrium. The duration of first stage for the results reported here is similar to the duration of cation-exchange on sediments from the same site, suggesting the possibility that diffusional processes are rate-limiting for the first stage.

These sorption results are consistent with two-stage sorption kinetics that have been reported by other investigators working with other materials. Davis et al. [20] proposed a two-step model to describe observed kinetics of cadmium sorption on calcite with a fast step, which consisted of adsorption with slow diffusion into hydrated calcite, and a slow step involving formation of a solid solution of cadmium in calcite. Fuller et al. [21] found that sorption of arsenate on hydrous ferric oxides proceeded in two steps with a fast uptake on the exterior of the aggregate and a slow uptake limited by the rate of intraparticle diffusion. Barrow et al. [22] studied adsorption kinetics of nickel, zinc, and cadmium on goethite and concluded that the observed two-stage kinetics corresponded to a fast initial adsorption followed by a slow diffusion of the metal ions into the goethite. Middleburg and Comans [23] studied sorption of cadmium on hydroxyapatite. They found that adsorption from solutions with concentrations less than the solubility of cadmium carbonate displayed an initial rapid uptake followed by a slow process that had not reached equilibrium after 28 days. They suggested that the slow phase is consistent with the enrichment of cadmium in phosphorite deposits. Considering the complex mineralogy of the aggregates used here, it is certainly possible that a slow solid phase diffusion process was responsible for the slow uptake during the second stage.

Another adsorption kinetics study was performed using the same protocol used for the long-term adsorption experiments except that all experiments received identical amounts of carrier-free radiolabelled cobalt stock solutions having varying concentrations of calcium (0, 0.67, 6.7, 67, and 670 mg/l of calcium). The objective of these experiments was to determine whether high concentrations of a competing cation would affect the rate of cobalt sorption. These experiments (results not presented) showed that calcium had no significant effect on

the rate of sorption of cobalt under these conditions. Most of the cobalt must have been adsorbed on high affinity sites and, therefore, the  $K_d$  values for cobalt must have been high and nearly independent of calcium concentration.

### 3.4. Long-term desorption

The long-term desorption measurements were conducted as described in Section 2 and monitored over a period of 6 months. During this time, no detectable desorption occurred from any sample, regardless of the concentration of stable cobalt to which it had been exposed during the adsorption kinetics experiment. There are two possible explanations for this: either the undetectably small concentrations of cobalt in the aqueous solution were high enough that the sediments and solutions were in equilibrium, or, because the cobalt was so strongly bound, the desorption process was so slow as to be imperceptible.

Another experiment, conducted in parallel with the desorption experiment described above, shed additional light on this issue. The 2 g sample of small sediment that had been used as the control in the 105 day calcium sorption kinetics study (0 mg/l Ca) was desorbed over the 6-month period with the desorbing solution being replaced with fresh synthetic stream water every time the sediment was separated and counted, a total of seven replacements during the period. As was the case with the other desorption experiments, no significant desorption of cobalt was observed. We, therefore, concluded that nearly all of the cobalt that was bound to the sediment after the 105 day sorption period was so tightly bound that it could not be readily desorbed.

From the above results, it is clear that the sediments used here possessed sorption sites with a great affinity for cobalt. If very high concentrations of calcium had no effect on the sorption of cobalt from dilute solution, one would expect that water with the ionic strength and cation distribution of our synthetic stream water would be ineffective in desorbing such strongly bound cobalt. Although, adsorption occurred in two steps, the first of which was relatively rapid, the desorption step for the strongly bound cobalt appears to be a very slow process that could limit the rate of interparticle migration. There are many reports of such strong binding of metals to sediments, the bound metals being referred to as fixed or non-labile. Cerling and Spalding [24] and Cerling and Turner [25] reported that, at low cobalt concentrations, nearly all of the sorbed cobalt was associated with hydrous manganese oxide in the sediment and that cobalt was released only when the manganese oxide was removed by dissolution or abrasion. Brusseau and Zachara [26] studied transport of cobalt in columns packed with sands. Pang and Close [27] have recently reported very similar results for cadmium transport in columns packed with alluvial gravels. They found that the transport was influenced by nonequilibrium sorption. This would suggest that transport/fate models employing the local equilibrium assumption would be inappropriate to describe cobalt transport on our sediments.

## 4. Conclusions

Fine-grained aggregates in stream sediments can be expected to adsorb significant amounts of soluble metal cations from adjacent sediments with which they are not in chemical equilib-

rium. When the sediments from which the cations are migrating can be transported relatively rapidly by the stream, because of a smaller size or lower density, the migration of cations to larger or denser sediment particles will cause a decrease in the rate of transport of the affected cations. The particle-to-particle migration process should be considered in attempts to predict the rate of transport of metal cations in streams. If the cations involved are toxic and their release will require subsequent remediation, the size of the area requiring remediation will be strongly influenced by the rate of the particle-to-particle migration process.

The length of exposure and the concentration of the exposing solution influence the ease with which the contaminant can migrate from an exposed particle to an unexposed particle. The shorter the exposure time, the greater the rate and extent of redistribution to unexposed sediment, and the higher the concentration of contaminant to which the particle has been exposed, the faster the migration.

The rate of migration between particles proceeds very slowly and full equilibrium of the particle-to-particle migration process may require months for particles in the sand and small gravel size range. Migration rates are slower for the strongly bound cobalt than for the less tightly bound cadmium. Therefore, a long period of co-deposition of contaminated and non-contaminated particles on the streambed between storms is conducive to the migration process.

The concentration of cobalt in the interstitial solutions during migration experiments was extremely low. Nevertheless, migration from one particle size to another was great enough to have a significant impact on contaminant transport.

The tendency for the distribution coefficient to decrease with increasing solute concentration suggests that a large clean particle will be a very effective sink for contaminants migrating from a smaller contaminated particle. This migration will be more rapid if all adsorption sites do not have a uniform affinity for the cation.

These studies show that cobalt adsorption was almost unaffected by the presence of calcium, even at concentrations as high as 670 mg/l. This demonstrated that cobalt can occupy sites that are not significantly affected by moderate concentrations of calcium. Further study is needed to determine the extent of interparticle transport of metals, which are less strongly bound than cobalt.

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