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Colloid Mobilization in the Field Using Citrate to Remediate Chromium

by Carol R. Johnson[1,2], Lucas A. Hellerich[3,4], Nikolaos P. Nikolaidis[3], and Philip M. Gschwend[1]

Abstract

We investigated the feasibility of cleaning aquifer sediments, long contaminated with chromium (Cr) from a metal plating facility, by detaching colloid-sized sorbents from the immobile aquifer solids and then pumping those colloids to the surface for treatment. In laboratory experiments using aquifer solids from the site, several solutions (water at various pHs, phosphate, oxalate, ascorbate, citrate) were examined for their ability to disperse colloids and Cr. Based on these tests, a 5 mM citrate solution at pH 7 was selected. Subsequently, such a citrate solution was used in the field in two single-well injection-withdrawal experiments. Large quantities of colloids were released immediately after injection. The colloidal particles mobilized by citrate in the field had more than 20 times higher Cr concentrations than did the average aquifer sediments, implying success in mobilizing Cr-associated phases. Further, laboratory and field tests showed that anion exchange of citrate for chromate caused some additional release of Cr from these aquifer solids.

Introduction

Pump-and-treat systems do not efficiently remediate subsurface sites where the pollutants are overwhelmingly associated with the aquifer solids (Fetter 1999). The rate of pollutant removal from the aquifer may depend on the low equilibrium tendency to partition into the dissolved phase or on slow diffusion from less permeable zones. Thus, subsurface solids can serve as long-lived pollutant reservoirs, slowly releasing contaminants into the ground water and thus maintaining unacceptable concentrations.

In sand and gravel aquifers, the primary pollutant sorbents are not the sand and gravel framework grains, but rather the clays, organic matter, and metal oxides (e.g., Fe or Al) that coat the larger grains (Holmén and Gschwend 1997). These materials have properties (e.g., high surface areas, reactive surface moieties, hydrophobic microenvironments) that cause them to dominate as the subsurface sorbent phases for pollutants. If these sorbent materials could be detached from framework grains and dispersed into particles small enough to travel with the ground water, they and their associated pollutants could be pumped from the aquifer. We refer to this process of detachment and dispersing aquifer sorbents into suspended solids as "colloid mobilization." Colloid mobilization could accelerate aquifer remediation by eliminating the slow pollutant release step. Colloid, in this case, refers to a particle small enough that it can be pumped from the aquifer under the remediation conditions. The exact size of colloidal particles would vary with site-specific aquifer and pumping conditions, but would likely be on the order of 10 μm or less in diameter (Elimelech et al. 1995; Degueldre et al. 2000). The goal of our research was to explore the feasibility of using colloid mobilization to remediate pollutants that are slowly released from aquifer solids.

To test the utility of colloid mobilization as an aquifer remediation method, we applied the technique to remediation of a chromium-contaminated aquifer underlying National Chromium Company Inc. in Putnam, Connecticut. In aquifers, chromium can exist in two oxidation states, Cr(VI) and Cr(III), and is distributed among a variety of phases. Hexavalent chromium occurs in the ground water at National Chromium as $HCrO_4^-$ which is highly soluble, but it also adsorbs to mineral oxide and clay surfaces forming a surface complex (Rai 1989; Richard 1991; Nikolaidis et al. 1994). Hexavalent chromium can be reduced to Cr(III) by sulfide, ferrous iron, or natural organic matter (Rai 1989; Richard 1991; Palmer and Wittbrodt 1991). Slow Cr(III) oxidation kinetics, except in the presence of manganese oxide surfaces, allows Cr(III) minerals to persist in aerobic environments (Bartlett and James 1979; Richard 1991; Palmer and Wittbrodt 1991). The Cr(III) cation can form complexes with dissolved and solid-phase organic matter and with other organic and inorganic ligands. In natural waters, Cr(III) exists primarily as the hydroxide complex that precipitates to form $Cr(OH)_3$ solid. If Fe(III) is present, however, dissolved $Cr(OH)_3$ forms an amorphous $(Cr, Fe)(OH)_3$ solid solution that has an even lower chromium solubility than the pure $Cr(OH)_3$ mineral (Palmer 1991).

Asikainen and Nikolaidis (1994) used selective extractions to quantify the distribution of chromium in the aquifer underlying National Chromium. Based on their data, the chromium exists approximately 1% as dissolved chromate, 20% as ion exchangeable with phosphate, 10% bound to organic matter, and 40% incorporated into amorphous iron and manganese oxides. The remaining 30% of

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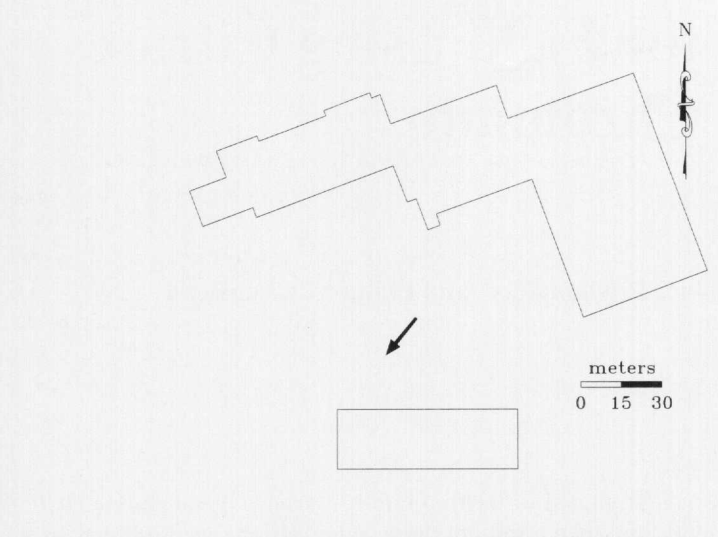

Figure 1. Locations of wells and soil cores at National Chromium Company Inc., Putnam, Connecticut.

the total chromium can be removed only by extreme methods (i.e., refluxing with nitric acid and peroxide). Hence, the chromium-contaminated aquifer underlying National Chromium is a suitable site for exploring the utility of colloid mobilization as a remediation technique because: (1) 99% of the chromium in a unit volume of aquifer is associated with the solid phase; and (2) about 70% of the chromium is associated with solid phases (i.e., the organic matter, aluminosilicates, and Fe/Mn oxides phases adding to about 2% of the total solids), which might be susceptible to detachment and dispersion into colloidal particles.

Previous investigators have demonstrated the efficacy of controlled colloidal detachment in a variety of laboratory and field settings. Ryan and Gschwend (1994) used aquifer sands from beach deposits of the New Jersey Pine Barrens and showed colloid releases could be achieved after flushing with ascorbic acid. Seaman et al. (1995), Swartz and Gschwend (1998), and Seaman and Bertsch (2000) also showed that colloids could be detached in laboratory columns filled with Southeastern Coastal Plain aquifer sediments. Also, Swartz and Gschwend (1999) demonstrated colloid releases from such aquifer solids could be accomplished in the field by injecting appropriate solutions designed to reverse colloid surface charges.

To enhance chromium removal from the aquifer underlying National Chromium, we targeted the secondary mineral oxide phases and associated organic matter for detachment and dispersing. Since we had not previously worked with the mixture of aquifer solids found at this site, we tested various aqueous solutions in the laboratory for their ability to release colloids from our site's aquifer solids. Citrate solutions were found to be the most effective solutions in mobilizing chromium-containing colloids from aquifer sediments. The laboratory tests also showed these solutions were useful for stripping the aquifer solids of the ion exchangeable load of chromate, but this contributes only about 20% of the total. Subsequently, two injection-withdrawal experiments were conducted in the field to investigate the ability of a citrate solution to mobilize Cr-containing colloids from in situ aquifer solids.

Field Site

National Chromium Company Inc., a Cr-plating company founded in 1939, is located in northeastern Connecticut on the border of Putnam and Woodstock Townships. Past manufacturing and waste disposal practices at the plant led to contamination of the underlying aquifer with Cr at levels ranging from 2 to 46 mmole Cr /kg sediment and up to 2 mM Cr in the ground water (Nikolaidis et al. 1994).

The aquifer at National Chromium is formed from both glacial and flood plain deposits. It consists of moderately to poorly sorted, fine sand and silt with interbedded gravel and small stones. At the location of our experiments, the unconsolidated aquifer extends to a depth of 9 to 14 m with the water level lying approximately 3 m below ground. The underlying bedrock consists of granitic gneiss (Nikolaidis et al. 1994). The Cr-plating plant lies approximately 12 m upgradient from the study site atop a terrace (Figure 1). Downgradient from the study site lies a marshy area that ends at the Little River about 150 m from the plant.

Materials and Methods

Aquifer Properties

We collected sediment cores and installed several wells in the course of this study (Figure 1). Core materials were used to determine aquifer properties, mineralogy, and contaminant levels. Two-foot sediment cores were collected using either hollow-stem auger or pneumatic hammer drilling methods. Generally less than 0.3 m (one foot) of sediment material was recovered in each plastic 0.6 m (2-foot) core sleeve. Core subsections removed for analysis and used in batch experiments varied in length from 7 to 30 cm. Sediment properties at well ML1A were measured in 1992 when that well was installed. For newly collected solids, we measured aquifer porosity and bulk density by weighing wet and dried samples. Sediment size fractions (< 2 mm and < 63 μm in diameter) were digested by refluxing with nitric acid and hydrogen peroxide (U.S. EPA 1997). Digests were analyzed for Cr and Fe by graphite furnace atomic absorption (AA) spectroscopy (4100ZL Zeeman Atomic Absorption Spectrometer, Perkin Elmer, Norwalk, Connecticut). X-ray diffraction spectra were obtained using sediments less than 2 μm in diameter. Organic carbon measurements were made using a 2400 CHN Elemental Analyzer (Perkin Elmer, Norwalk, Connecticut).

The amounts of anion-exchangeable chromate and sulfate adsorbed on aquifer sediments adjacent to the screened interval of well P11 were estimated by exchange with phosphate. To measure phosphate-exchangeable chromate, sediments passing through a 2 mm sieve were extracted twice with 0.1 M phosphate, pH 7.0, each time for 24 hours at room temperature. A soil:solution ratio of 1:20 was used. The soil slurries were centrifuged at 1150*g* for 25 minutes. The supernatant was removed and acidified with nitric acid. The phosphate extracts were analyzed for Cr by AA. The amount of exchangeable sulfate on aquifer solids was determined by measuring the quantity of sulfate released during a phosphate sorption experiment. One gram P11 (diameter < 2 mm) was mixed with 30 mL of 6 mM sodium phosphate, pH 4. The slurry was incubated for five hours at room temperature, centrifuged at 1150*g* for 30 minutes, and then the supernatant was removed. The remaining sediment was washed once with 20 mL water (pH 4) and three times with 10 mL of a 1:1 isopropanol:water (pH 4) solution. The solids were extracted a final time with 30 mL water (pH 11) for 20 minutes. The phosphate and alkaline extracts were analyzed for sulfate by ion chromatography (Model 16 Ion Chromatograph, Dionex Corp., Sunnyvale, California). Exchangeable sulfate was defined as the sum of the sulfate measured in the phosphate and alkaline extracts.

Table 1
Dispersant Solutions Tested and Mechanisms of Action

Solution (pH Range)	Expand Double Layers	Reverse Surface Charge on Iron Oxides	Weaken Iron Oxide Bonds by Complexing Fe(III)	Weaken Iron Oxide Bonds by Reducing Fe(III)	Hydrolyze Metal Bonds	Displace Chromate Adsorbed on Iron Oxides
Phosphate (4.5–8.3)		X				X
Oxalate (4.5–6.1)		X	X			X
Citrate (2.1–8.3)		X	X			X
Ascorbate (3.7–6.1)				X		
Water (4.3–12.3)	X	X (high pH)			X (high pH)	X (high pH)

Batch Test Methodology for Dispersant Selection

In the laboratory, we used portions of sediment from highly contaminated horizons to test the ability of various dispersant solutions to detach and disperse aquifer colloids. Since previous investigations had determined that the aquifer was oxic (Nikolaidis et al. 1994), we did not isolate the cores from oxygen. The solutions tested for their ability to mobilize colloids (Table 1) were selected because they could disrupt one or more of the mechanisms by which colloids are held attached to aquifer solids, including electrostatic attractions, cross-bonding, cementitious phases (including the oxide itself), and van der Waals forces (Swartz and Gschwend 1998). Four aquifer samples (core P1 at 4.4 m, core P2 at 4.5 m, core P2 at 5.3 m, and core P3 at 3.7 m) were exposed to dispersant solutions to determine which solution was most effective in mobilizing aquifer colloids. All chemicals were used as the acid or sodium salt. Dispersant concentrations ranged from 0.5 to 10 mM. Ascorbate was tested only in combination with oxalate or citrate. When necessary, pH was adjusted with hydrochloric acid or sodium hydroxide solutions.

Our procedure involved mixing 0.5 to 1 g dry sediment with 10 mL of dispersant solution in 15 mL polypropylene centrifuge tubes and inverting five times. The sediment and dispersant slurries were incubated at room temperature for 15 to 90 minutes with the tubes occasionally inverted to mix their contents. Slurries with rapidly changing pH values were allowed to react overnight to allow pH levels to stabilize. If the dispersant solution contained an organic acid, the centrifuge tubes were protected from light to prevent photoreduction of Fe(III) (Abrahamson et al. 1994). At the end of the incubation period, the tubes were inverted several times and the sediments then allowed to settle for 15 minutes. During this period, particles nominally larger than about 10 µm in diameter, calculated using Stokes law and assuming solid density of 2.6 g/mL, would have settled below the top several milliliters of the solution. Solution was then carefully withdrawn from the top, and the turbidity of the test solution determined using either light scattering (Hach turbidimeter) or optical density at 500 nm (Beckman DU spectrophotometer). The turbidity of the aliquot reflected the mass of particles suspended in the solution. Subsamples of the aliquot were also analyzed for total and, after centrifugation, for dissolved Cr and Fe. To separate particulate metals from dissolved metals, aliquots were centrifuged at 23,000g for 30 minutes. The supernatant from the centrifuged samples was analyzed for dissolved Cr and Fe. All samples for metal analysis were digested in 1% hydrofluoric acid at room temperature until clear (two to three days). The digests were diluted with 5% nitric acid and analyzed by AA.

Well Construction

Two injection-withdrawal experiments were performed in the field at National Chromium. The wells used, ML1A and P11, differ in history and construction (Figure 2). Well ML1A is the deepest well in a well nest installed in 1992 (Nikolaidis et al. 1994). This well consists of a 1.90 cm outer diameter (O.D.) polyvinyl chloride (PVC) pipe attached to a 15.2 cm screen centered at about 5.5 m below ground with 0.0254 cm wide slots. Aquifer material was allowed to collapse around the screen after well installation in a 10.2 cm diameter bore hole. For this study, the well was retrofitted by placing a 1.59 cm O.D., cold-tempered PVC (CPVC) pipe inside the well. In the bottom 30 cm of the pipe, holes were drilled to act as a diffuser. The bottom of the diffuser is plugged with a silicone rubber stopper. A second silicone rubber stopper, cored and covered with Teflon tape, slipped over the outside of the CPVC pipe to a position 30 cm from the bottom of the well and formed a seal between the CPVC pipe and the inner wall of the well casing. This seal isolated the well screen from the rest of the well. A 0.32 cm inner diameter (I.D.) Teflon tube ran inside the CPVC pipe from the surface and connected to the top of the diffuser. Total volume of the apparatus from well screen to sampling bottle at the surface was 95 mL.

The second well, P11, was installed on September 25, 1998, and was designed specifically to perform injection-withdrawal experiments. The well consisted of a hollow PVC rod (3.3 cm O.D.) with a 0.79 cm I.D. Teflon tube running down through the length of the rod from the ground surface. At 3.5 m below surface, the Teflon tubing connected to a 14.6 cm long diffuser (1.9 cm O.D.) with holes drilled in it. A Teflon septum sealed the bottom of the diffuser. A 15 cm slotted PVC screen (3.3 cm O.D. and 0.0254 cm slot width) fit over the diffuser section and threads to the PVC rod above. Solid PVC rod extends below the well screen about 0.9 m. The well was installed in a 5.1 cm hole drilled by a Geoprobe pneumatic hammer

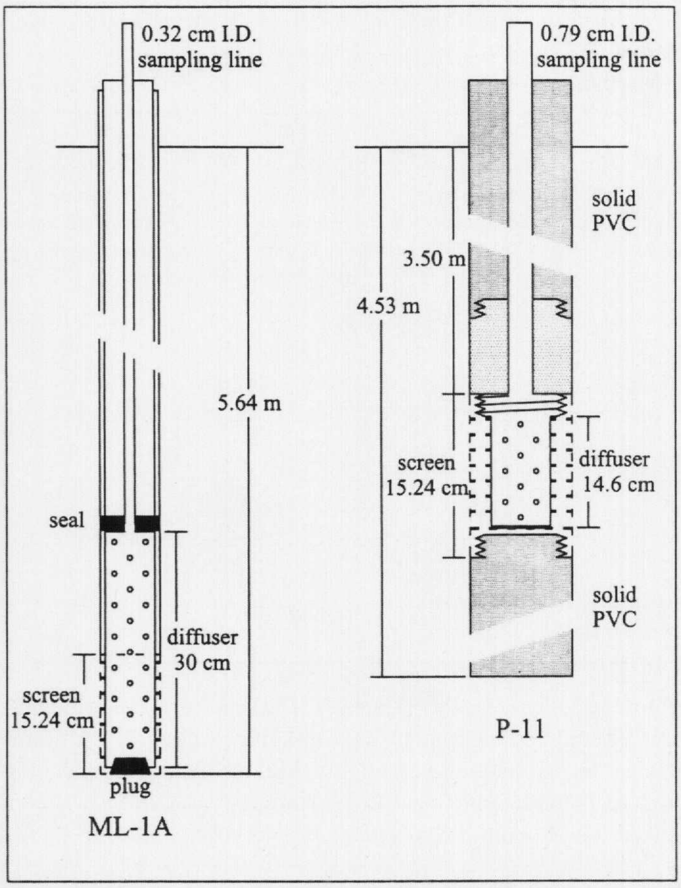

Figure 2. Well construction used for injection-withdrawal testing. Well ML1A was retrofit as shown, while well P11 was constructed especially for the field injections with minimal dead volume.

(Geoprobe® Systems, Salina, Kansas). Aquifer sediments were allowed to collapse around the well after installation. Borehole collapse for at least 30 cm above the well screen was confirmed by inserting a rod in the annulus next to the well. Total volume of the apparatus from well screen to sampling bottle at the surface was 185 mL. To remove particulate material mobilized by well installation, P11 was pumped about a day at 85 to 150 mL/min the week before the field experiment. Additional details on construction and installation of wells ML1A and P11 are described by Hellerich (1999).

Injection-Withdrawal Experiments

In the first experiment, performed at well ML1A, two injection-withdrawals were completed using, first, a control solution on August 25, 1998, and then a dispersant citrate solution on August 28, 1998. In the second experiment, performed at well P11, an injection-withdrawal was done using a control solution on October 12, 1998, using the citrate solution on October 13, and using the control solution again on October 14, 1998. In experiments at both wells, the dispersant solution consisted of 0.093 mM citric acid, 4.9 mM citric acid trisodium salt (5 mM total citrate), and 1.2 mM sodium bromide dissolved in deionized water to yield a solution with pH 7.1. The control solution used in both wells consisted of ground water collected from the well to which 1.2 mM sodium bromide was added to act as a tracer. On the evening preceding each injection, the well was pumped at 100 mL/min until the ground water's turbidity remained constant. The pumping rate was then lowered to 22 to 55 mL/min and the well pumped overnight. The following morning, the pumping rate was returned to 100 mL/min, and the well pumped until constant ground water turbidity was regained (less than an hour). Once constant turbidity was regained, either the control or the dispersant solution was injected into the aquifer at 100 mL/min. The volume of solution injected was always between 11.4 and 12.0 L. Immediately after the solution was injected, the pump direction was reversed and water was withdrawn from the well at 100 mL/min. From 29.2 to 38.5 L of ground water were removed from the aquifer during the withdrawal portion of the tests.

Water Analysis

Using an apparatus similar to that described by Swartz and Gschwend (1999), water was pumped from the aquifer and sampled before the peristaltic pump to prevent loss or alteration of colloids on the pump tubing. Ground water turbidity and pH were measured on site using a Ratio X/R turbidimeter (Hach Co., Loveland, Colorado) and a pH probe with temperature compensation. Samples for anion analysis were filtered on-site through 0.2 μm syringe filters (Ion Chromatography Acrodisk, Pall Gelman Sciences, Ann Arbor, Michigan). Samples for citrate analysis were acidified with phosphoric acid to $pH < 2$ to inhibit microbial degradation. Samples for citrate analysis from well P11, but not from well ML1A, were filtered before acidification through 0.2 μm syringe filters. Tests using samples from the dispersant selection experiments indicated that acidification of the unfiltered citrate samples did not alter citrate concentrations in the liquid phase. Samples for total Cr analysis were acidified with nitric acid. The most turbid water samples were digested by refluxing with concentrated nitric acid before Cr analysis by AA. Bromide, sulfate, nitrate, chloride, fluoride, phosphate, and chromate were measured by ion chromatography (IC-40 System Ion Chromatograph, Dionex Corp., Sunnyvale, California). Citrate was measured by HPLC using a Luna C18(2) analytical column (15 cm × 4.60 mm I.D., Phenomenex, Torrance, California) with ultraviolet detection at 215 nm. The mobile phase was 0.05 M phosphate, pH 2.3. Electrical conductivity was measured in the lab using a conductivity meter (VWR brand Bench/portable, West Chester, Pennsylvania). Ground water total organic carbon was measured using a TOC 5000, Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan).

Ground water samples from the well P11 citrate injection-withdrawal test were filtered through 30 nm polycarbonate filters (Osmonics, Minnetonka, Minnesota) to collect particles mobilized from the aquifer. The water samples were stored in glass amber vials at 4°C for four weeks before filtering. It is possible that storage in the citrate injection solution caused iron oxide particles to dissolve or additional adsorbed chromate to exchange with citrate from particle surfaces. Thus, particle masses and particulate chromium concentrations presented here may underestimate those collected on the day of the experiment. Filters and particles were digested by refluxing in concentrated nitric acid. Cr levels in the particles were measured by AA. To determine the relationship between the masses of particles mobilized and ground water turbidity, water samples were filtered through tared 30 nm polycarbonate filters. The filters were dried and then weighed using a Cahn 25 automatic electrobalance (Cahn/Ventron, Cerritos, California.)

Results and Discussion

Aquifer Properties

The site's sediments contain a wide range of particle sizes (cobbles, pebbles, and gravel to fine sand and silt). Consistent with the region's geological nature, X-ray diffraction analysis revealed the

Table 2
Aquifer Characteristics

Ground Water Characteristics[a]	ML1A (5.6 m)	P11 (3.5 m)
Water level (m below ground)	2.04	1.85
pH	4.5	3.7
Total organic carbon (mg/L)	n.m.[c]	1
Turbidity (NTU)	0.06	0.17
Electrical conductivity (μS/cm)	153	226
Total chromium (mM)	0.30	1.0
Sulfate	0.15	0.26
Bromide (mM)	< 0.01	0.02
Chloride (mM)	0.47	0.50
Nitrate (mM)	0.09	0.09
Sediment Characteristics	**ML1A (5.8 m)[b]**	**P11 (3.5 m)**
Porosity	0.37	0.32
Bulk density (g/cm^3)	1.65	1.89
Percent organic carbon	< l.o.q.[d]	< l.o.q.[d]
Chromium (mmole/kg)	5.29	11.3
Iron (mmole/kg)	408	200

[a] Concentrations of bromide in the ground water at well ML1A 5.6 and of fluoride and phosphate in ground water at both wells were below detection limits. (0.05 mM fluoride, 0.01 mM bromide and phosphate).
[b] Nikolaidis et al. 1992
[c] Not measured.
[d] Limit of quantitation, 1% organic carbon.

predominance of quartz, feldspar, and mica in aquifer sediments. Chlorite and/or vermiculite may also be present. No crystalline iron oxides were observed in the < 2 μm fraction or in the borate mobilized colloids we examined using X-ray diffraction, implying that the iron oxides present in the aquifer were amorphous and likely of secondary origin. A diffraction peak that may have indicated the presence of gibbsite was observed in the X-ray analysis of one sediment from P2 at 5.1 m depth, but this was not seen in the other samples. Otherwise, no significant qualitative difference was observed among the diffractograms obtained from the various sediments or from the particles mobilized by a pH 9.2 borate buffer. The fraction of organic carbon was less than 1% in sediments from well P11, well ML1A, and in the sediments used in laboratory tests to select a dispersant.

Aquifer sediments had variable Cr concentrations and particle size distributions. Cr concentrations varied from 1.6 to 11 mmole/kg, with the more poorly sorted sediments generally having higher Cr concentrations. The injection-withdrawal experiments were deliberately sited in strata with relatively high Cr concentrations (Table 2).

Dispersant Selection

The fraction of Cr mobilized as particle-bound varied among the sediments and dispersant solution combinations tested (Figure 3). In some cases, only about 2% of the Cr was released (e.g., water at pH 5.5 to 5.7), while in others more than 30% was mobilized (e.g., ascorbate/citrate). We generally observed the greatest percent Cr released when organic acids were used. The pH dependence of the release was determined for sediments exposed to citrate solutions (Figure 4). Over the range of pH values tested (pH 3 to 8.3), the amount of dissolved Cr released appeared pH independent while the amount of particle-associated Cr released increased somewhat at higher pH values. We also observed greater releases of particulate iron at higher pH values (data not shown). Citrate solutions that mobilized colloidal chromium also mobilized more total iron than did citrate solutions that did not mobilize colloidal chromium (Table 3). These results are consistent with our hypothesis that achieving surface charge reversal of iron oxides enabled greater Cr mobilization at this site.

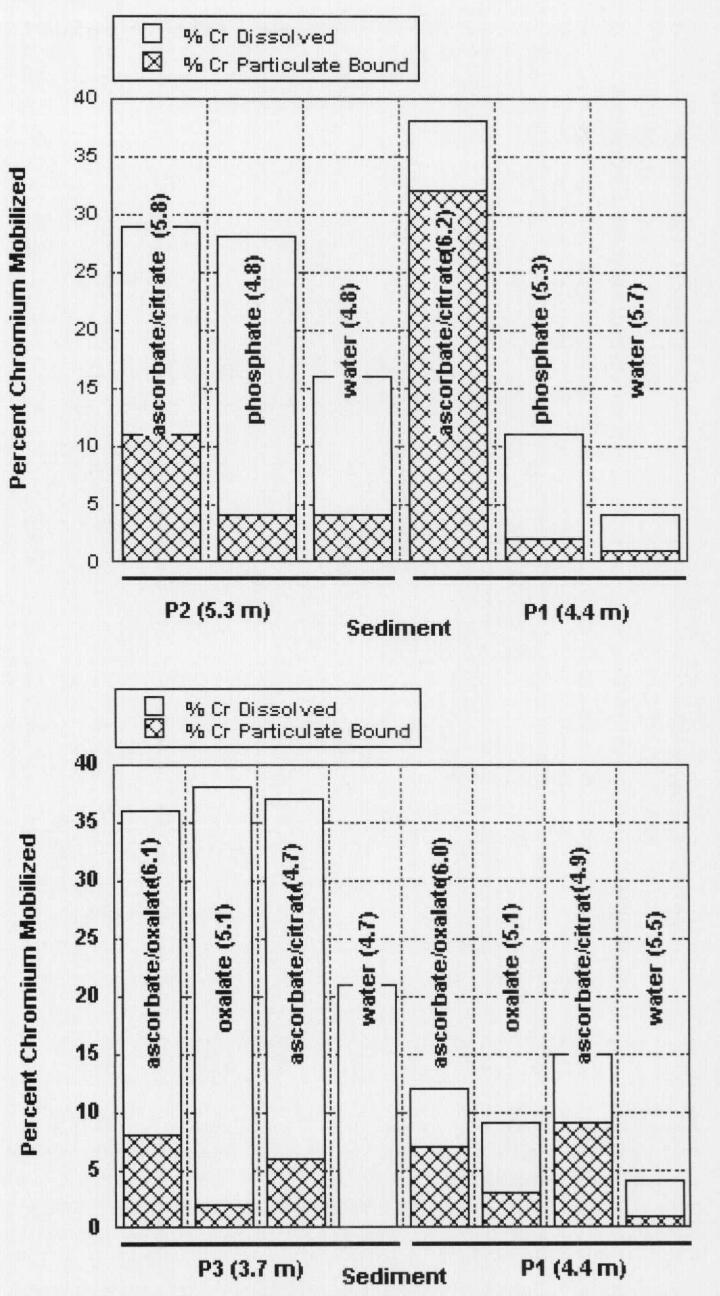

Figure 3. Effectiveness of various dispersant solutions to mobilize dissolved and particle-bound Cr from aquifer sediments. Slurry pH after incubation listed in parentheses. Upper panel: dispersant concentrations and initial pH values were: ascorbate:citrate 0.5:0.5 mM, pH 5.4; phosphate 10 mM, pH 4.5; water pH 5.7. Lower panel: dispersant concentrations and initial pH values were: ascorbate:oxalate 1:2 mM, pH 4.5; oxalate 3 mM, pH 4.5; ascorbate:citrate 1:2 mM, pH 4.5; water pH 4.5.

Surface charge reversal appeared to be a necessary and sufficient condition for colloid mobilization in aquifer sediments at National Chromium. Of all the dispersant solutions tested, low ionic strength solutions (water) at pH values less than 8.5 produced the least turbidity in sediment slurries. Surface-charge altering dispersants, citrate (pH > 6), phosphate (pH > 6.8), and alkaline water (pH > 8.5), all created substantial turbidity in slurries with sediment. Preliminary experiments indicated that oxalate, which also

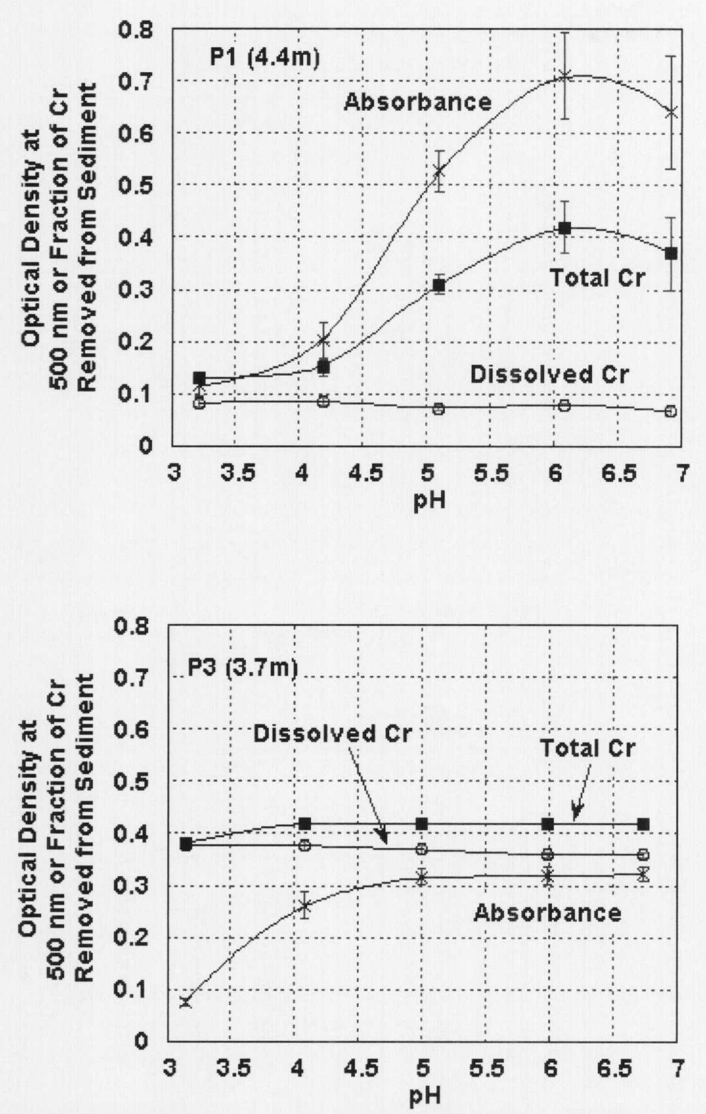

Figure 4. Dependence of colloid and Cr mobilization on pH in sediment slurries with 2 mM citrate. Optical density at 500 nm is proportional to turbidity.

alters iron oxide surface charge, could mobilize colloids at pH values greater than 6. However, extensive tests were not performed using this compound, since oxalate's toxicity does not make it a good candidate for field injections. For citrate, phosphate, and water, maximum turbidity occurred above a threshold pH (e.g., Figure 4 for citrate solutions). Addition of ascorbic acid to citrate solutions did not measurably increase colloid mobilization. These data suggest that surface charge reversal is the necessary condition for colloid mobilization at this site. Although citrate, oxalate, and alkaline water can disrupt oxides by breaking covalent bonds, phosphate can alter only oxide surface charge, suggesting that surface charge reversal by itself could mobilize colloids at our site.

The data for this particular glacial outwash site are consistent with the Pine Barrens setting studied by Ryan and Gschwend (1994) where electrostatic forces were chiefly responsible for stabilizing oxides and clays in those aquifer sediments. Seaman et al. (1995) also observed that surface charge reversal controlled colloid dispersion in an iron oxide-dominated system; although, in their experiments, colloid mobilization occurred when sediment surfaces became more positive rather than more negative as in our work. In contrast, Swartz and Gschwend (1998) found that a South Carolina beach deposit required addition of ascorbate to phosphate solutions (pH 5.2) to achieve substantial colloid release, implying that dissolution of iron oxyhydroxide bonding phases was critical. Our observations also differ from the case reported by Khilar and Fogler (1984) where reduction in ionic strength alone was enough to cause dispersion of clays in a Berea Sandstone. Clearly, variations in aquifer geology from site to site lead to differential requirements for mobilizing those sites' colloids.

Table 3
Chromium and Iron Mobilized from P1 (4.4 m) by Dispersant Solutions

Dispersant (pH of slurry)	Total Cr (%)	Dissolved Cr (%)	Total Iron (%)
10 mM phosphate (5.2)	11	8	1
1 mM ascorbate (5.8)	4	2	1
1 mM citrate (7.1)	40	6	7
0.5 mM citrate + 0.5 mM ascorbate (6.5)	36	5	6

Citrate (pH > 6) was selected as the optimum dispersant for the National Chromium site to mobilize colloids from aquifer sediments. Citrate mobilized colloids at as low or lower pH than the other dispersants tested. The effectiveness of dispersants acting only at high pH values would be quickly negated in the aquifer from ground water (pH 3.7 to 4.4) mixing with the injection solution and lowering its pH. Citrate has a high buffering capacity at pH 6.4 that helps maintain the solution's pH and thus its effectiveness in mobilizing colloids. Citrate is biodegradable and nontoxic. Citrate was able to mobilize not only colloids but also adsorbed Cr from all sediments tested. In the laboratory, almost 40% of the Cr in sediments P1 (from 4.4 m) and P3 (from 3.7 m) was mobilized by 2 mM citrate at pH 6 (Figure 4).

Anion Exchange

Depending on the dispersant used, between 14% and 94% of the Cr mobilized in batch experiments was dissolved (i.e., nonsettling at 23,000*g* for 30 minutes. For example, samples P2 (5.3 m) and P3 (3.7 m) released 20% to 30% of their initially immobile Cr as dissolved Cr in solutions containing oxalate, phosphate, citrate, ascorbate/oxalate, and ascorbate/citrate (Figure 3). Water at pH 4.5 to 5 also mobilized 10% to 20% of these sediments' Cr as dissolved Cr. The amount of chromium that could be released as dissolved chromium also varied among sediment samples. For example, from sediment P1 (4.4 m), no dispersant solution released more than 10% of the sediment's Cr as dissolved Cr (Figure 3).

We believe that anion exchange of adsorbed chromate for citrate was responsible for the release of initially sediment-bound Cr as dissolved Cr in our tests. Hexavalent Cr (chromate), citrate, phosphate, and oxalate all form surface complexes with iron and aluminum oxides (Mesuere and Fish 1992; Geelhoed et al. 1998). Iron oxides adsorb chromate more strongly than aluminum oxides (Ainsworth et al. 1989), and previous work implicates the importance of iron oxides to Cr at this site (Asikainen and Nikolaidis 1994). Consequently, here we focused on iron oxide interactions. The relative stability of anion surface complexes can be estimated from the relative stability of their aqueous iron complexes (Sigg and Stumm 1981). Based on their aqueous complex stabilities, both phosphate and citrate should form more stable surface complexes with iron oxides than does chromate. Thus, both phosphate and citrate could thus displace chromate through anion exchange reactions. Chromate, which is highly soluble, would remain in solution after

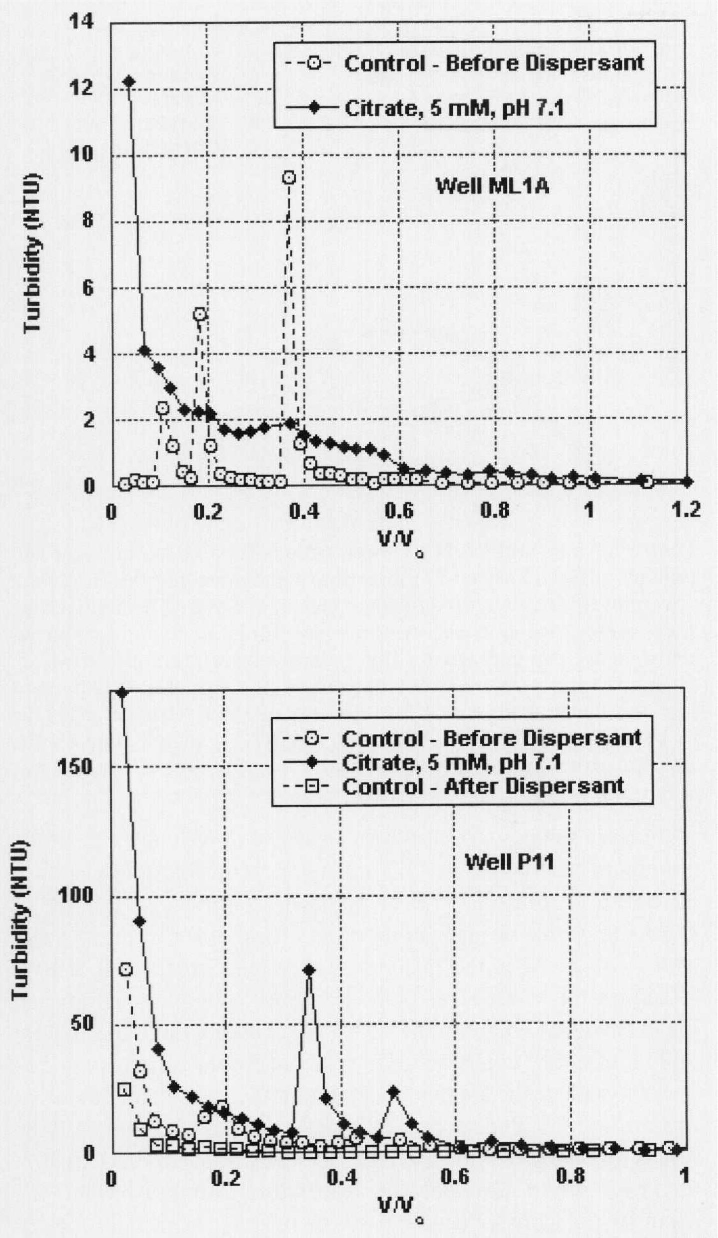

Figure 5. Turbidity versus ground water volume withdrawn for injection-withdrawal experiments. Ground water volume normalized by volume of control or dispersant solution injected into aquifer.

leaving the solid surface. The differing fractions of Cr released as dissolved and particle-associated Cr by the various aquifer solid samples reflects heterogeneity of Cr speciation in the aquifer.

Injection-Withdrawal Experiments

In field experiments at both wells, injection of the dispersant created more turbidity than injection of bromide spiked ground water (Figure 5). Turbidity levels in the ground water remained more than background until more than 1.2 times (well ML1A) and 1.6 times (well P11) the injection volumes had been withdrawn. Turbidity levels at well P11 exceeded those observed at well ML1A for both control and dispersant injections. We believe that difference in ground water turbidity observed between the two wells was largely the result of differences in aquifer solid characteristics such as particle size distribution and chemical composition. It is also possible that our relatively recent installation of well P11 contributed to the difference (only three weeks passed between installation and use.) Sediments that had been recently disturbed might be more easily mobilized by the injection-withdrawal experiment. Nonetheless, it was clear that we succeeded in mobilizing colloids in the field at both sites.

Although turbidity levels remained above background until over one injection volume had been withdrawn, they dropped to less than a quarter of their initial value after only about 0.1 injection volumes had been removed. Rapidly falling pH levels and dispersant concentrations undoubtedly account for this declining turbidity (Figure 6). Citrate recoveries were only 50% for both experiments. These data indicate that injectate-aquifer solids interactions strongly influence the ground water composition. Such interactions diminish the injectate's capacity to reverse iron oxide surface charge and cause the associated colloid-bound Cr releases. Clearly, colloid mobilization solutions need to be designed to account for dispersant losses onto aquifer surfaces if sustained colloid releases are to be accomplished.

The particles collected during the dispersant injection were enriched in Cr compared to bulk aquifer sediments. Particles filtered from water at well P11 during the dispersant injection-withdrawal test contained 270 ± 20 mmole Cr/kg and 1,100 ± 100 mmole Fe/kg. These mobilized particles were enriched in Cr and Fe compared to aquifer sediments less than 2 mm in diameter (11.3 ± 0.3 mmole Cr/kg and 198 ± 9 mmole Fe/kg) or even sediments less than 63 μm in diameter (72.5 ± 0.5 mmole Cr/kg and 610 ± 20 mmole Fe/kg). Turbidities and masses of filterable particles in three ground water samples collected from P11 during the dispersant injection-withdrawal test were: 179 NTU, 144 mg/L; 41 NTU, 34 mg/L; and 24 NTU, 21 mg/L. The average ratio of particle concentration to turbidity was 0.84 ± 0.04 mg/L NTU. Based on the average ratio of particulate concentration to turbidity and the average concentration of chromium per kg filterable particles, the samples removed from well P11 at the beginning of the withdrawal experiment with turbidities of 179, 90, and 41 NTU contained particle-associated Cr at 40, 21 and 9.6 μmole/L.

Citrate also displaced adsorbed chromate and sulfate from aquifer solids. More than 99% of the Cr removed from the aquifer during our relatively short field tests was dissolved chromate. Both chromate and sulfate concentrations in the ground water rose to greater than ambient levels during the dispersant injection-withdrawal experiments (Figure 7). Chromate and sulfate concentrations remained at ground water levels during control injections (data not shown). The concentrations of phosphate-exchangeable chromate and sulfate in P11 sediments were 1.6 mmole chromate and 0.72 mmole/kg sulfate sediments. Thus, the reservoir of phosphate-exchangeable sulfate was more than 10 times higher than the dissolved sulfate load in this part of the aquifer, while the reservoir of exchangeable chromate was about six times higher than the dissolved Cr mass. More than enough exchangeable chromate and sulfate were available to account for the elevated ground water concentrations of these ions observed during the dispersant solution withdrawal. Based on the stability of the aqueous complexes formed with iron by citrate, sulfate, and chromate, citrate should form a stronger surface complex with iron oxides than either sulfate or chromate and could displace them from iron oxide surfaces (Martell and Smith 1982; Dzombak and Morel 1990). In a similar way, Swartz and Gschwend (1999) observed release of silicate and sulfate anions when they injected phosphate into a sandy aquifer; they proposed that phosphate anions exchanged with sulfate and silicate anions adsorbed to aquifer surfaces.

Nitrate and chloride concentrations did not rise above their ambient ground water levels during any of the injection-with-

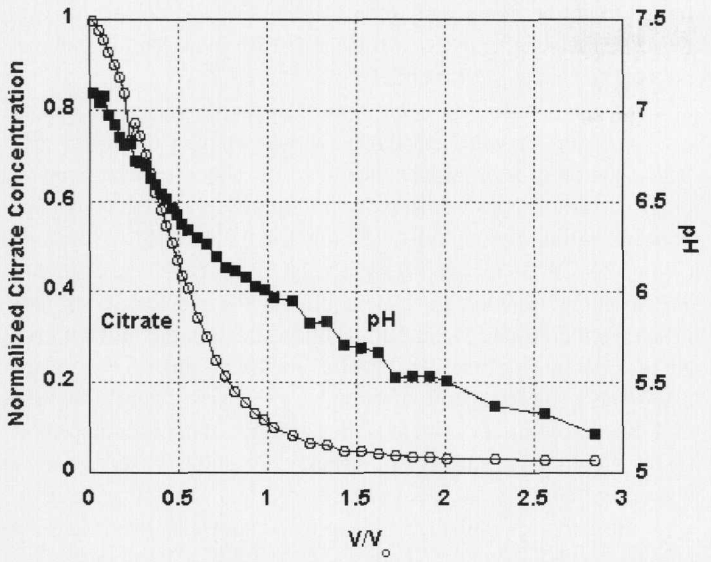

Figure 6. Citrate concentration and pH versus ground water volume withdrawn for well P11 dispersant injection-withdrawal test. Citrate concentrations are normalized by the dispersant's citrate concentration. Ground water volume is normalized by the volume of dispersant injected. Normalized citrate profiles for dispersant injection-withdrawal tests at wells P11 and ML1A were nearly identical, so only data for the experiment at well P11 are shown.

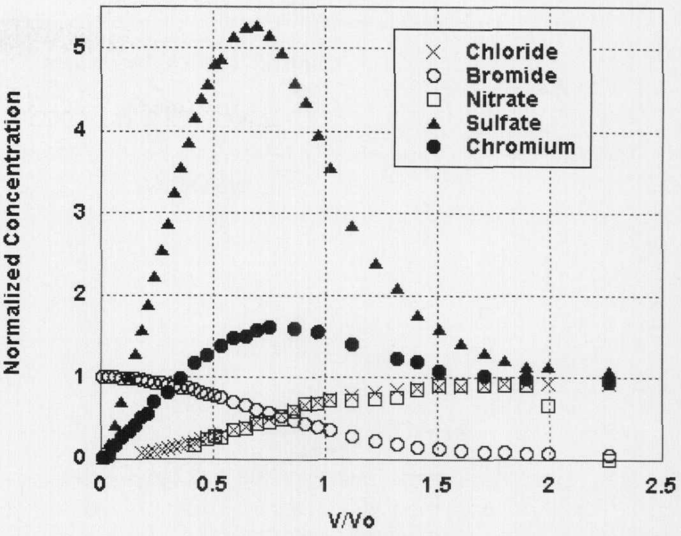

Figure 7. Anion and total Cr concentrations versus ground water volume withdrawn for well P11 injection-withdrawal test. Sulfate, total chromium, nitrate, and chloride concentrations are normalized by their ground water concentrations (see Table 2). Bromide concentrations are normalized by the bromide injectate concentration. Ground water volume is normalized by the volume of dispersant injected. Anion and total Cr profiles were qualitatively similar for the dispersant experiments at wells P11 and ML1A, so only data for the test performed at well P11 are shown.

drawal tests (Figure 7). Nitrate and chloride form outer sphere complexes with positively charged aquifer surfaces. Outer sphere complexes are less stable than the inner sphere complexes formed by chromate and sulfate (Stumm 1992; Dzombak and Morel 1990). The presence of so much sulfate and chromate in the ground water at this site implies that chloride and nitrate would not have been associated with those aquifer surfaces and, therefore, could not have been released from the solids by exchange with citrate.

Feasibility of Colloid Mobilization as a Remediation Method

To estimate the amount of Cr released from the aquifer by the injected dispersant solution, one must account for the Cr from the ambient ground water that mixed into the injected solution. We used the concentration of bromide in the withdrawn dispersant solution to make this calculation. We assumed the amount of ground water that mixed into the dispersant solution before it was withdrawn was inversely proportional to the decrease in bromide concentration in the dispersant solution. Bromide is an appropriate conservative tracer for the dispersant solution because it was not detected in ambient ground water and because 96% of the bromide injected with the dispersant solution was recovered at P11. After correcting for ground water mixing, it was determined that 20% of the exchangeable chromate in the aquifer volume affected by the injected solution was recovered from the aquifer during our single injection-withdrawal experiment at well P11. Approximately 24 mmoles of citrate were lost to the aquifer, while 14 mmoles each of chromate and sulfate were gained after correcting for ground water dilution. A similar result was seen for the experiment at well ML1A, although we cannot specify the mass balances so precisely due to the poor bromide recovery (74%) for that test (Hellerich et al. submitted).

Based on the results obtained from the injection-withdrawal experiment at P11, we estimated the number of pore volumes of 5 mM citrate solution that would be needed to remove the 20% of the chromium adsorbed in an ion exchanging form. To displace surface adsorbed chromium with citrate, we assumed 14 mmole of chromium would be released for every 56 mmole of citrate injected, as was observed in the injection-withdrawal experiment at P11. Assuming this result extrapolates to greater volumes, to remove all ion exchangeable chromium from 1 m^3 aquifer would thus require 2400 L of 5 mM citrate solution or about 8 pore volumes.

To estimate the amount of citrate solution needed to remove Cr in association with detached colloidal particles, we again used the results from the experiment at P11. Here we assume as much as 50% of the Cr might ultimately be susceptible to mobilization (i.e., about 10 mol Cr/m^3 of aquifer based on selective extractions is associated with organic and secondary oxides after Asikainen and Nikolaidis 1994). Since the colloids we mobilized contained 270 mmole Cr/kg, assuming we could sustain turbidity of 25 NTU (0.84 ± 0.04 mg/L NTU), then about 600 pore volumes of 5 mM citrate would be needed to remove all this fraction of chromium from the aquifer in association with colloidal particles.

Conclusions

We found that injection of mM citrate solution at circumneutral pH at a chromium-contaminated field site enabled recovery of both ion exchangeable and colloid-bound chromium upon subsequent pumping. This result suggests that controlled colloid mobilization may be a viable remedial approach for removing highly sorptive pollutants from aquifers.

Obviously, further work is needed to determine if colloids can continue to be mobilized in sufficient quantities and for sufficient durations to efficiently remove sorbed pollutants from aquifers. Our field results do not indicate how far colloids could have traveled to reach a withdrawal well. The particles captured at our withdrawal well may have originated from sediments immediately adjacent to that well, while particles mobilized farther from the well redeposited on aquifer sediments. Work is still needed to determine whether colloid release levels can be sustained and over what distances mobilized colloids can travel.

Remediation schemes that include the injection of complexing agents must be carefully planned to avoid creating more problems than they solve. Citrate's biodegradability and low toxicity recommended the chemical for our experiments. However, these same properties ensure extended use of citrate would promote microbial growth. Growing microorganisms would not only reduce citrate concentrations but also would deplete oxygen in the aquifer. Whether or not anaerobic conditions would stabilize or mobilize aquifer pollutants would depend on specific site conditions. Microbial growth can also cause aquifer and well screen clogging, further degrading remediation efforts that involve injection and withdrawal wells. In addition, agents that alter surface charge will remain bound to aquifer sediment surfaces after treatment finishes. This adsorbed chemical will be released over time into the ground water. The impact of low concentrations of the remediating agent on downstream wells and on water bodies accepting ground water discharge must be considered.

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