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Purpose/Utility of Research

The presence of hexavalent chromium [Cr(VI)] and arsenic (As) in groundwater and soil is a global concern because these metals are classed as carcinogens and present a serious threat to human health. The remediation of Cr(VI) and As contamination in groundwater is mostly done by ex-situ methods – a costly, lengthy and often ineffective remediation approach. The focus of this research is to investigate more sustainable and effective cleanup methods for inorganic contamination in groundwater, including monitored natural attenuation and in-situ stabilization.

This work addresses one of EPA Region 2’s identified science needs – **conducting research to more fully understand natural degradation mechanisms and rates to aid in developing strategies to sustainably and cost-effectively remediate sites.**

The research is being conducted at two Superfund sites in New Jersey – the Garfield Chromium Ground Water Superfund Site, a former electroplating facility that contaminated the community’s groundwater with Cr(VI) from a tank rupture, and the Vineland Chemical Superfund Site, where a groundwater extraction and treatment remedy has attempted to treat arsenic for over 10 years at an annual cost of ~ \$3 MM per year.

At the Garfield site, spectroscopy and solid-phase extraction studies are being conducted to evaluate natural capacity of subsurface solids to reduce Cr(VI) and form insoluble Fe-Cr hydroxide precipitates. At Vineland, in-situ stabilization of arsenic via air sparging is being evaluated. Using this technique, natural reducing conditions that transport ferrous iron and arsenic in groundwater are manipulated using air sparge techniques; this favors the formation of Fe hydroxide precipitates and the sequestration of arsenic.

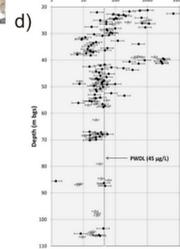
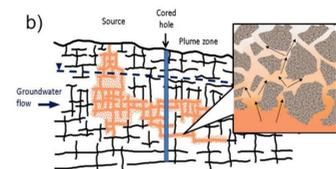
Garfield Chromium Ground Water Superfund Site

Highlights

The site is a former electroplating facility in New Jersey, U.S.A. where chromic acid was released approximately three decades ago from a ruptured storage tank to a groundwater system consisting of shallow unconsolidated sediments with underlying fractured porous sandstone and siltstone of the Passaic Formation. A plume of Cr(VI)-contaminated groundwater moving toward a major river over a distance of approximately 800m has since developed down-gradient in overburden and bedrock (see Fig. 1a).



Figure 1.
a) Map of the Garfield Superfund Site; the Cr(VI) plume migrates in a southwestern direction from the site towards the Passaic River.
b) Cored hole from the plume zone in a fractured bedrock matrix.
c) Core collection and processing at the site.
d) Porewater Cr(VI) concentrations from rock extractions (Zhao et al., 2015).



Application & Translation

Past research conducted at the Garfield Superfund site showed significant Cr(VI) contamination within the underlying bedrock aquifer. No technology currently exists to clean up the chromium within the rock matrix and restore the community’s groundwater. Our work to date demonstrates that the rock matrix has significant reduction capacity – that is, it can convert mobile Cr(VI) to the immobile and less toxic form of chromium - Cr(III). If these reactions are occurring under field conditions and are irreversible, the natural attenuation of Cr(VI) and ultimately the restoration of the groundwater resources at this site, as well as other similar contaminated sites across the country, may be achievable. The goal of the study is to investigate in more detail the processes occurring within the rock and determine if these natural processes will provide a sustainable and effective remediation approach.



Reference
Zhao, J., Al, T., Chapman, S.W., Parker, B., Mishkin, K.R., Cutt, D., and Wilkin, R.T. (2015). Determination of hexavalent chromium concentrations in matrix porewater from a contaminated aquifer in fractured sedimentary bedrock. *Chemical Geology*, v. 419, p.142-148.

Intended End users

Research to date on this project has been a collaborative effort between: US EPA Region 2, US EPA ORD, University of Guelph, University of New Brunswick, and the University of Waterloo.

Project components include:

- 1) Method development to evaluate porewater chromium concentrations
- 2) Method development to determine Cr(III) in the matrix solids, i.e., quantifying the amount of attenuated Cr
- 3) X-ray absorption spectroscopy studies of the rock matrix to detect Cr(VI) and Cr(III)
- 4) Stable Cr isotope studies of the groundwater to evaluate whether isotopic enrichment can be used as a probe of Cr attenuation

Intended End Users

- Program Offices
- Regions
- Other federal agencies
- Tribal and State regulatory agencies
- Environmental consulting community
- Industry

Lessons Learned

A method developed in this work provides a reliable procedure to analyze Cr(VI) in the porewater of bedrock samples with detection limits in the range of drinking water standards (about 50 µg/L; Zhao et al., 2015; Fig. 1b-d). Compared to the measurements of Cr(VI) in groundwater, the porewater data reveal the complex and heterogeneous nature of contamination, which results from fracture-controlled flow and diffusive mass transfer between the mobile water in fractures and the relatively immobile porewater in the rock matrix. Accumulation of Cr(VI) in the rock matrix retards growth of the plume and attenuates concentrations in fractures, but at a later stage when the plume source is removed or diminished, the mass in the matrix may provide a persistent source of Cr(VI) to the fractures via back diffusion to sustain the plume. A key issue at this site, which requires further study, is whether reduction from Cr(VI) to Cr(III) is occurring in the rock matrix, and if so, what effect it will have on the longevity of Cr(VI) releases to groundwater by back-diffusion.

Current work examines water quality at multi-level well location EPA-21BR (Fig. 1a). Chromium concentrations above 100 µg/L are present at shallow depths below about 183 ft BGS (Fig. 2). The groundwater type transitions from Ca-Cl type composition where Cr concentrations are elevated to a more evolved Na-SO₄ type at depth (Fig. 2). These samples are being analyzed for chromium isotope ratios at the University of Waterloo; we will evaluate whether there is a trend of δ⁵³Cr enrichment with decreasing Cr concentration as predicted in a geochemical model of limited Cr reduction and attenuation.

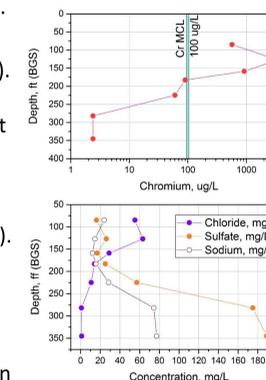


Figure 2. Water quality results from multi-level well EPA21BR.

Vineland Superfund Site

Highlights

The Vineland Chemical Company operated from 1949 to 1994 and produced arsenical herbicides and fungicides. Groundwater at the site transports arsenic in the trivalent form (arsenite) under typically iron-reducing conditions. Arsenic partitioning to iron minerals (goethite, hematite) within the aquifer is governed by several processes leading to variable partitioning coefficients and removal of arsenic.

Work to investigate alternate cleanup technologies for arsenic contamination at the Vineland Chemical Superfund site has been ongoing for several years.

Our research investigates the capability of naturally occurring mineral surfaces and enhancements using air sparging at the site to immobilize the migration of arsenic contamination. This work will help to determine more efficient and cost-effective sustainable remedies for arsenic contaminated groundwater.

Application & Translation

The in situ immobilization approach involves injection of air which leads to Fe(II) oxidation and formation of iron oxyhydroxides. These new mineral surfaces provide sites for sorption and/or co-precipitation of arsenite. The research effort has focused on the following activities (see Figure 3):

- 1) Soil and aquifer characterization to determine mineralogy using X-ray diffraction.
- 2) Soil and aquifer characterization to determine solid phase concentrations of iron and arsenic using X-ray fluorescence and digestion methods.
- 3) Sequential extractions to determine partitioning of iron and arsenic on the aquifer solids, including arsenic speciation analysis of the extracts.
- 4) Scanning electron microscopy (SEM) and X-ray analysis to study aquifer particle morphology and elemental associations with arsenic.
- 5) X-ray absorption spectroscopy studies to evaluate arsenic oxidation states and bonding environments in the solid phase.
- 6) Laboratory studies to determine arsenic adsorption isotherms.

Intended End users

Research to date on this project has been a collaborative effort between: US EPA Region 2, US EPA ORD, and the US Army Corps of Engineers.

Intended End Users

- Program Offices
- Regions
- Other federal agencies
- Tribal and State regulatory agencies
- Environmental consulting community
- Industry

Lessons Learned

Figure 3.

a) Results of mineralogy studies using X-ray diffraction. These scans show that the dominant minerals present at the site are clays (illite and kaolinite), iron oxides (goethite and hematite), and quartz. The clays and iron oxides have capacity to remove arsenic from groundwater.

b) Results of water and hydrochloric acid extractions coupled with arsenic speciation via IC-ICP-MS. Results show that the majority of the arsenic in the solid phase is As(III) and present in the acid-extractable component.

c) X-ray absorption spectroscopy data showing a characterization approach for quantifying the amount of As(III) and As(V) in the solids collected from the site.

d) Scanning Electron Microscope image of a particle from the site that contains arsenic. The arsenic is associated with iron, aluminum, and silicon.

