WSRC-MS-2004-00337

From Sequential Extraction to Transport Modeling, Monitored Natural Attenuation as a Remediation Approach for Inorganic Contaminants

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00J04115.p65

ABSTRACT

FROM SEQUENTIAL EXTRACTION TO TRANSPORT MODELING, MONITORED NATURAL ATTENUATION AS A REMEDIATION APPROACH FOR INORGANIC CONTAMINANTS

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Implementation of monitored natural attenuation (MNA) as a remediation method requires a mechanistic understanding of the natural attenuation processes occurring at a given site. For inorganic contaminants, natural attenuation typically involves a decrease in metal toxicity and/or mobility. These natural processes include dilution, dispersion, sorption (including adsorption, absorption, and precipitation), and redox processes. In order to better quantify these processes in terms of metal availability, sequential extraction experiments were carried out on subsurface soil samples impacted by a low pH, high sulfate, metals (Be, Ni, U, As) plume associated with the long-term operation of a coal plant at the Savannah River Site. These laboratory scale studies provide mechanistic information regarding the solid phases in the soils associated with natural attenuation of the contaminant metals. This data provides input to be evaluated in the definition of the contaminant source term as well as transport of contaminants for site transport models.

Introduction

A large groundwater contaminant plume at the D-Area Expanded Operable Unit (DEXOU) at the Savannah River Site is characterized by high levels of acidity (low pH), metals, and sulfate. This plume is the result of the weathering of coal, coal ash and coal spoils (materials that did not meet the specifications for combustion). The large plume and relatively low contaminant concentrations make monitored natural attenuation (MNA) an attractive remediation strategy for inorganic contaminants at this site.

MNA (as defined by the US EPA-OSWER Directive 9200.4-17P, April 1999)[1] is the "reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." Natural processes in the soil act to mitigate transport and availability of contaminants. These natural attenuation processes include a range of physical, chemical, and biological processes that

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reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water without the aid of human intervention.

In order to implement monitored natural attenuation as a means of remediation of inorganic contaminants in soil, a given site must first be evaluated and designated as an appropriate MNA site according to EPA protocols and guidelines using site-specific data. In order to lay the groundwork for establishing and validating MNA at the DEXOU, laboratory sequential extraction studies were carried out on subsurface samples collected from the waste site to provide site-specific data used to elucidate the processes contributing to natural attenuation of inorganic contaminants. Sequential extraction[2] is a desorption technique that has been useful for identifying both leachate and solid-phase chemistry. When considering the source term and transport of the contaminant, the leachate chemistry and the solid-phase form are important in defining the environmental availability of the contaminant (where environmental availability is defined by Amonette et al (1994)[3] as "the ability of a soil to maintain and aqueous concentration of [contaminants] in the soil solution").

Sequential extraction data, along with other site-specific data, will, ultimately, be used as input for risk-based models which are often used as a primary determinant in the decision making process for remediating contaminated sites. The degree to which the risk-based models embody and accurately describe the major environmental processes that influence contaminant availability has a direct affect on the appropriateness, cost effectiveness, and overall success of the site remediation.

Materials and Methods

Pore water analyses

Pore water was separated a portion of the soil from the sample core within 12 hours of the sample collection. The separation of soil and pore water was carried out using 50 mL centrifuge filter tubes each fitted with a 20 mL capacity filter insert with either a 0.45 µm polypropylene membrane or 10 µm polypropylene mesh. Typically, six tubes were filled to the insert capacity with soil and centrifuged at 7000 rpm for 10 minutes (0.45 µm filter) or at 1000 rpm for 10 minutes (10 µm filter). The insert was removed and the soil reserved for further analysis. Pore water redox potential and pH for each sample were measured immediately following separation from the soil. Flow through pH and redox (E_h) electrodes with a Ag/AgCl flow through reference electrode (Microelectronics, Inc) were used for these measurements. Pore water samples were analyzed for major ions by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (suite of 30 elements), trace metals by Inductively Coupled Plasma-Atomic Mass Spectroscopy (ICP-MS) (suite of 19 elements), and for sulfate (SO_4^{2-}) using a Braun+Luebbe Auto Analyzer II Continuous Flow System.

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Table 1 Description of sequential extraction procedure steps

Fraction	Reagent	Description	Extraction Conditions	Targeted Phase
1 DDI	Distilled deionized water		Tumble for 16 hours at room temperature	easily soluble salts and ions already present in the soil solution
2 CN or MC	0.5 M calcium nitrate or $MgCl_2$	neutral salt	Tumble for 16 hours at room temperature	Easily exchangeable ions on soil surfaces
3 AA	0.44 M acetic acid & 0.1 M calcium nitrate	weak acid w/ neutral salt	Tumble for 8 hours at room temperature	carbonate minerals, acid exchangeable metals on the soil surfaces
4 HH	0.01 M hydroxylamine-hydrochloride & 0.1 M nitric acid	weak reducing agent	Tumble for 0.5 hours at room temperature	Manganese oxides
5 SP or HP	0.1 M sodium pyrophosphate (SP) or hydrogen peroxide (HP)	oxidizing agent	Tumble 24 hours at room temperature/SP or 85 °C for 5 hours/HP	Organic matter
6 AO	0.175 M ammonium oxalate & 0.1 M oxalic acid	buffered mild reducing agent	Tumble 4 hours in darkness at room temperature	Amorphous iron oxides
7 SD	0.15 M sodium citrate, 0.05 M citric acid, & 25 g/L sodium dithionite	buffered strong reducing agent	Shake for 0.5 hours in water bath at 50°C	Crystalline iron oxides
8 PD	48% hydrofluoric acid & aqua regia	Strong corrosive	Microwave digestion	all remaining solids
Total Digestion TD	48% hydrofluoric acid & aqua regia	Strong corrosive	Microwave digestion	Total digestion of untreated soil

Note: Adapted from Miller et al. (1986).[2]

Soil digestion methods

An eight step sequential extraction procedure (Table 1) was carried out on subsurface soils collected along with three other digestion methods including EPA method 3050b (hot nitric acid and hydrochloric acid), total digestion (hydrofluoric acid/aqua regia), and a single step extraction (corresponding to the amorphous iron oxide step (6th step) of the sequential extraction procedure). Leachates from all digestion methods were analyzed by ICP-AES and ICP-MS.

Results and Discussion

The first six extraction steps in this operationally defined extraction sequence (Miller 1986; Table 1)[2] represent an approximation of the total of all the metals that would possibly be available if the soil were perturbed under a range of environmental conditions. The last two steps of the extraction procedure target crystalline mineral phases. Inorganic contaminants associated with these crystalline phases would likely not be readily available for transport. By comparison, the harsh conditions of the EPA 3050B standard method (hot nitric acid) do not represent conditions likely to be encountered in the environment. By considering only the environmentally available fraction, (approximated by summing the first six steps of the sequential extraction method) a large fraction of the naturally occurring trace metals is eliminated from consideration in this measure of metal availability. Findley (1998)[4] has demonstrated that the bulk of trace metals in soil are only accessible under harsher extraction conditions (sequential extraction steps 7 and 8) that are not likely to represent conditions present in the environment.

For the four contaminants, beryllium, nickel, uranium, and arsenic, analyzed in this study, differences in the availability profiles are useful not only in considering each contaminant and its availability in terms of the source term definition, but also as indicative of distinctive attenuation mechanisms. In subsurface samples from locations nearest the source area, arsenic and uranium are sorbed most strongly and beryllium least strongly as evidenced by pore water and soil concentrations. For beryllium, typically, lower total metal concentrations in soil were found in areas most impacted (lowest pH, highest sulfate) and a lower percentage of the total beryllium was found in the available fraction. Higher soil concentrations with a higher percentage of beryllium in the available fraction were found to correlate with attenuation of acidity (higher pH) and attenuation of sulfate (decreasing sulfate concentration). Similar trends were observed for nickel with lower availability and concentrations of nickel in soil samples near the source with the percentage of available metal increasing rapidly with distance from the source. For uranium, however, locations closest to the source area have both higher total soil concentration and higher availability of uranium than a number of down gradient locations indicating favorable sorption even at low pH. Arsenic concentrations in all soils analyzed was relatively low with low availability of arsenic. As an anion, favorable sorption of arsenic at low pH is expected and arsenic was likely sorbed to a significant degree upgradient of the samples analyzed.

Because of the heterogeneous nature of sorption surfaces, as a result of both the natural heterogeneity and alteration by the contaminant plume, on soils at this site and the highly variable geochemical conditions, a more complex sorption/precipitation model than the traditional single linear contaminant partitioning model (i.e., the K_d approach) is being developed to account for these natural attenuation mechanisms.

References

1. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, April 1999,"Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites". OSWER Directive 9200.4-17P.

2. Miller, W., D. Martens, L. Zelazny, 1986, "Effect of Sequence in Extraction of Trace Metals from Soils," Journal of the Soil Science Society of America 50:598-601.

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