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From sequential extraction to transport modeling, monitored natural attenuation as a remediation approach for inorganic contaminants

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To quantify metal natural attenuation processes in terms of environmental 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 in South Carolina. Despite significant heterogeneity resulting both from natural and anthropogenic factors, sequential extraction results demonstrate that pH is a controlling factor in the prediction of the distribution of metal contaminants within the solid phases in soils at the site as well as the contaminant partitioning between the soil and the soil solution. Results for beryllium, the most mobile metal evaluated, exhibit increasing attenuation along the plume flow path which corresponds to an increasing plume pH. These laboratory- and field-scale studies provide mechanistic information regarding partitioning of metals to soils at the site (one of the major attenuation mechanisms for the metals at the

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field site). Subsequently, these data have been used in the definition of the contaminant source terms and contaminant transport factors in risk modeling for the site.

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, therefore, 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." Many natural processes in the soil act to mitigate transport and availability of contaminants and include a range of physical, chemical, and biological processes that reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water without the aid of human intervention. Implementation of MNA as a remediation strategy requires a mechanistic understanding of the natural attenuation processes occurring at the subject waste site. For inorganic contaminants, natural attenuation typically involves a decrease in metal concentration, toxicity and/or mobility. These natural processes that lead to natural attenuation include: dilution, dispersion, sorption (including adsorption, absorption, and precipitation), and redox transformations.

To implement monitored natural attenuation for remediation of inorganic contaminants in soil, the site must first be evaluated and designated as an appropriate MNA site according to EPA protocols and guidelines using site-specific data. To lay the groundwork for establishing and validating MNA at the DEXOU, matched porewater/soil samples were collected along the plume flow path at the site. Soils were subjected to sequential extractions to provide site-specific metals availability data designed to elucidate the sorption processes contributing to natural attenuation of inorganic contaminants. Sequential extraction (2) (3) is a desorption technique that has been useful for characterizing metal association with soils as well as characteristics of reactive soil sorption surfaces. When considering the metal availability and transport of the contaminant, the porewater chemistry and the solid-phase metal speciation are important in defining the environmental availability of the contaminant (where environmental availability is defined by Amonette et al (4) as “the ability of a soil to maintain an aqueous concentration of [contaminants] in the soil solution”). Therefore, the sequential extraction methodology needs to be matched to site conditions for maximum utility.

Sequential extraction and major ion chemistry data will ultimately be used as input for risk-based models used in the remedial decision making process. The degree to which the risk-based models embody and accurately describe the major environmental processes that influence contaminant attenuation, therefore, has a direct affect on the appropriateness, cost effectiveness, and overall success of the site remediation.

Conceptual model

Contaminated runoff from the D-Area Coal Pile to the D-Area Coal Pile Runoff Basin has resulted in a low pH/metals/sulfate groundwater contaminant plume that emanates from the D-Area Coal Pile Runoff Basin. It was anticipated that environmental conditions at D Area would be favorable to the attenuation of metal contaminants (See Figure 1 for site features and groundwater flow direction). The groundwater plume becomes more anaerobic as it moves towards the Savannah River (i.e., from pyrite oxidation conditions near the Coal Pile Runoff Basin to sulfate reducing conditions in the wetland) and pH rises due to acid-buffering from the site soils. Both of these conditions, more reducing E_h and increased pH, are expected to attenuate metal contaminants by sorption and precipitation processes as the plume moves towards the Savannah River.

In addition to the primary source emanating from the vicinity of the D-Area Coal Pile Runoff Basin, a number of additional sources of metals contamination exist in D Area. A significant amount of sluiced ash overflowed from the D-Area Ash Basin in the 1970s into the wetland area west of the Ash Basin, leaving metals contaminated ash in the wetland. Additionally, from the west end of the Ash Basin as well as the D-Area Rubble Pit there appears to be sources of low pH/sulfate/metals. The vertical stratification of the plume emanating from the vicinity of the Coal Pile Runoff Basin as well as multiple sources areas serve to confound interpretation of metal attenuation data strictly based on distance along the groundwater flow path from the primary source near the Coal Pile Runoff Basin. Nevertheless, the readily measurable parameter pH is thought to be a good predictor of metal attenuation at the site.

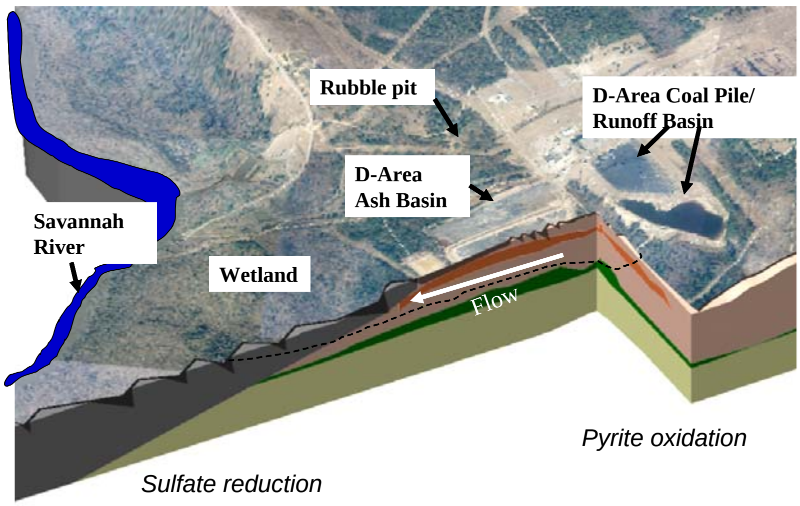

Figure 1 D-Area Features

Materials and Methods

Sampling

Soil cores were collected at multiple locations along the approximate flow path of the plume and also in the wetland area. Soil cores were collected at multiple subsurface depths for a given location with the exception of the wetland locations (D-2, D-4, G-10, H-5, J-6, K-4) which were collected from the top 1 foot of ash deposition in the wetland area and DAB 86 which was collected from the bottom of the ash basin in perched water just above the clay layer below the ash basin. Soils were stored in sealed containers at 4 °C.

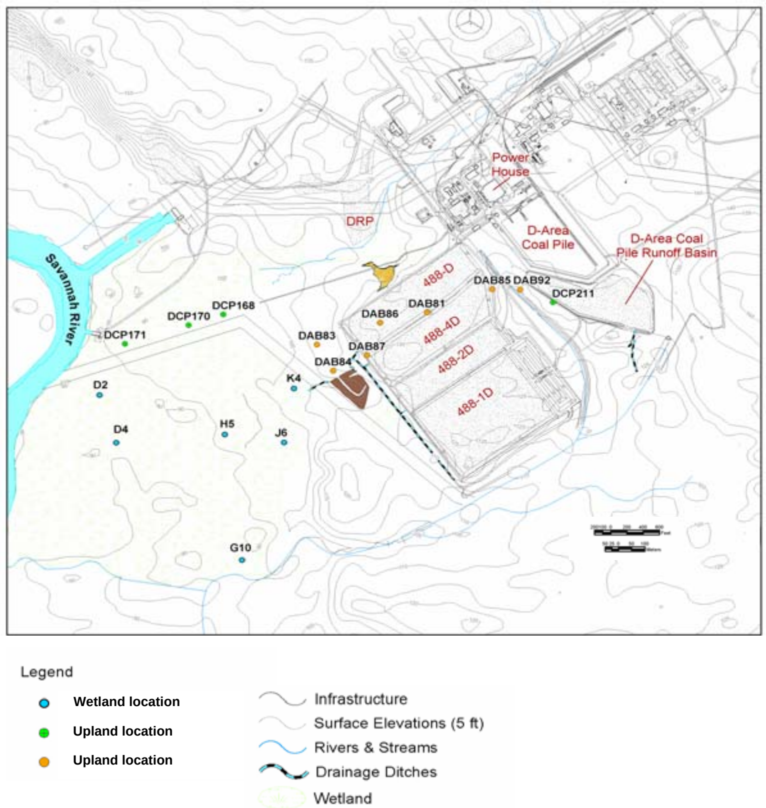

Figure 2. D-Area Map with Sampling Locations

Pore water analyses

Pore water was separated from a portion of the soil core within 12 hours of 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. E_h 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), and for sulfate (SO_4^{2-}) using a Bran+Luebbe Auto Analyzer II Continuous Flow System.

Soil extraction/digestion methods

An eight step sequential extraction procedure (Table I) was carried out on subsurface soils collected along with two other partial digestion methods: EPA method 3050b (hot nitric acid and hydrochloric acid) and a single step extraction (corresponding to the amorphous iron oxide step (6th step) of the sequential extraction procedure (Table I)). Leachates were analyzed by ICP-AES and ICP-MS.

Results and Discussion

Methods Comparison

Only a fraction of the total metal concentration in a given soil is expected to be available for partitioning to the aqueous phase. Findley (5) has demonstrated that the bulk of naturally occurring trace metals in soil are only accessible under harsher extraction conditions (sequential extraction steps 7 and 8, Table I) that are not likely to represent conditions present in the environment. The available metals concentration in soil is important when considering both the source term as well as the partition coefficient derived from contaminated soil samples. By considering only the available metal concentration rather than the total metal concentration in soil a large fraction of the naturally occurring trace metals pool is eliminated from consideration in fate and transport modeling of the site.

In this study, the sum of the metal mass in the first six sequential extraction steps ($\sum_{i=1}^{6} C_i$ where C_i is the metal concentration in soil for the ith extraction and i = 1 through 6, Table I) has been operationally defined as the available metal concentration in soil. As a second method of defining the available metal concentration in soil, a single step extraction equivalent to step 6 of the sequential extraction procedure was found to yield equivalent concentrations compared to summing the first six sequential extraction steps in a series of split

Table I Summary of Sequential Extraction Steps

Availabilty	*Fraction*	*Reagent*	*Description*	*Extraction Conditions*	*Targeted Phase*
↑	**1**	Distilled deionized water		Tumble for 16 hours at rt	easily soluble salts and ions
	2	0.5 M calcium nitrateor $MgCl_2$	neutral salt	Tumble for 16 hours at rt	Easily exchangeable ions on soil surfaces
	3	0.44 M acetic acid & 0.1 M calcium nitrate	weak acid with neutral salt	Tumble for 8 hours at rt	carbonate minerals, acid exchangeable metals on the soil surfaces
	4	0.01 M hydroxylamine-hydrochloride & 0.1 M nitric acid	weak reducing agent	Tumble for 0.5 hours at rt	Manganese oxides
	5	0.1 M sodium pyrophosphate (SP) or hydrogen peroxide (HP)	oxidizing agent	Tumble 24 hours at rt/SP or 85 °C for 5 hours /HP	Organic matter
	6	0.175 M ammonium oxalate & 0.1 M oxalic acid	buffered mild reducing agent	Tumble 4 hours in darkness at rt	Amorphous iron oxides
	7	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	48% hydrofluoric acid & aqua regia	Strong corrosive	Microwave digestion	all remaining solids

rt = room temperature
based on Miller (2) and Tessier (3)

samples. This single step extraction and $\sum_{i=1}^{6} C_i$ are used interchangeably herein as the available metal concentration. The available metals concentration in soil can also be defined by EPA 3050B extraction method (hot nitric acid). Data for all digestions are not presented in entirety herein but have been reported previously (6). Figure 3 presents a selection of representative data for the study site. Sequential extraction data for beryllium concentration in soil [stacked data: steps 7-8 (top); steps 1-6 (bottom)] is presented to the left of the EPA 3050B data for each location included. Upland locations both near the source (low pH) and further downgradient (higher pH) as well as wetland data are presented. A background (unimpacted) wetland sample and a sample of ash from the ash basin were also included for comparison with the wetland sample. For the majority of the samples analyzed in this study, the EPA 3050B method over predicts the available concentration of contaminant in soil relative to the sequential extraction method ($\sum_{i=1}^{6} C_i$) and the single step method (step 6).

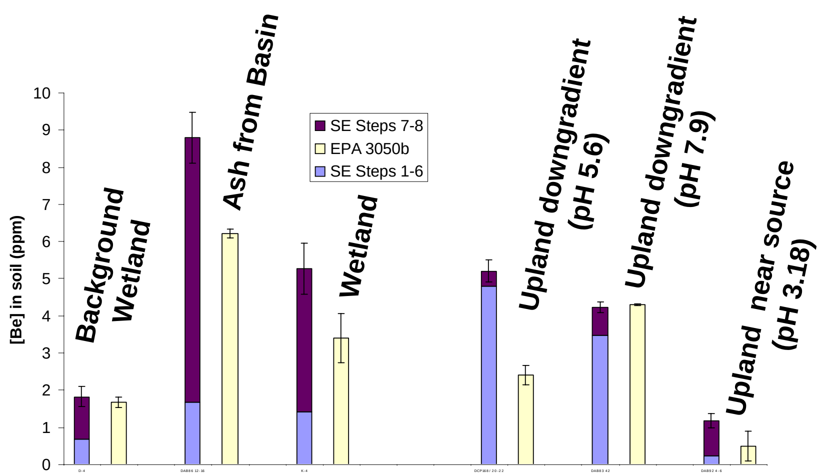

Figure 3 Beryllium concentration in soil for selected locations as determined by sequential extraction and EPA 3050B methods.

For upland soils, metal concentrations (both available and total) are correlated with porewater pH [e. g., lower concentrations in soils with lower pH (nearer the source area)] (Figure 3). This observation is consistent with transport of beryllium from low-pH soils to higher-pH soils where beryllium is attenuated by increased sorption. The wetland is characterized by high total beryllium concentration in soil although a larger fraction of this total concentration in soil is defined as unavailable. Because the wetland was contaminated with ash material, it is difficult to determine whether the higher concentrations are due to a natural shift in attenuation mechanism from upland to wetland soils or from physical transport of beryllium containing ash into the wetlands. More likely, the observed results are due to the physical transport of ash material from the basin which is also characterized by high concentrations of beryllium the unavailable fractions.

Beryllium Availability in Soil

The percentage of the total beryllium concentration in soil potentially available to the mobile aqueous phase was estimated using sequential extraction data:

$$\%\ Available = \left(\frac{\sum_{i=1}^{6} C_i}{\sum_{i=1}^{8} C_i} \right) \times 100$$

where Ci is the metal concentration in soil for the ith extraction and i = 1 through 6, or i= 1 through 8 respectively (Table I).

Sequential extraction availability profiles are useful not only in considering availability in terms of the source term definition (i. e., what percentage of the metal pool is available), but also as indicative of distinctive attenuation mechanisms. For beryllium, typically, lower total metal concentrations in soil were found in areas most impacted (lowest pH). These soils also exhibited lower percentages of the total beryllium in the available fraction suggesting that the more available beryllium had been preferentially leached by the low-pH plume. Higher soil concentrations with a higher percentage of beryllium in the available fraction were found to correlate with attenuation of acidity (higher pH). The percentage of available metal in soil was highly correlated to pH (the regression is significant at 1 % level of probability $p<0.01$; 18 degrees of freedom) (Figure 4). At higher pH the variable surface charge becomes increasingly negative resulting in a corresponding increase in sorption of cationic beryllium. Alternatively or in addition to the increasingly negative charge at higher pH values, formation of Fe-(oxy)hydroxides at higher pH values are also expected to increase the sorption of cations in this system.

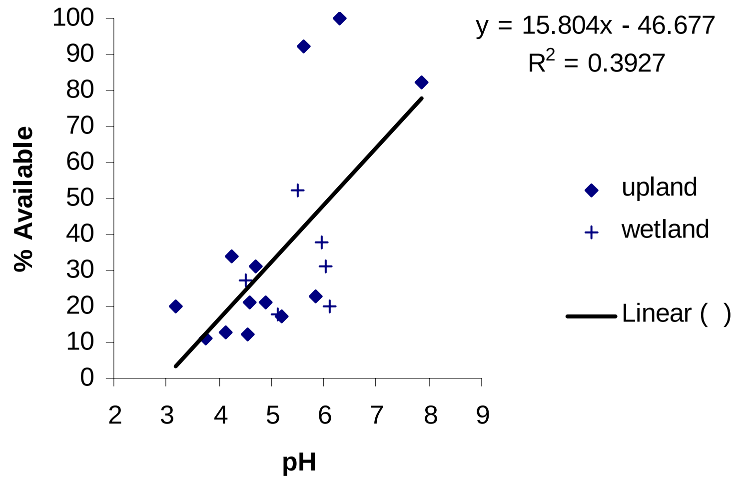

Figure 4 Percentage of the available beryllium concentration in soil as a function of pH.

Distribution Coefficient

Typically, a linear partitioning coefficient (K_d) is used in groundwater models. K_d values are most often obtained from published literature, generated in lab-scale batch sorption experiments, or generated from contaminated soils in desorption experiments. Variations of three to four orders of magnitude are not uncommon for K_d values from the literature or even from the same waste site where there are large geochemical gradients.

The distribution coefficient (K_d) is defined as follows:

$$K_d\ (\text{mL/g}) = \frac{\text{Available Contaminant concentration in soil (mg/kg)}}{\text{Contaminant conc. in the solution contacting the soil (mg/L)}}$$

Because only the available metal concentration would be expected to partition to the aqueous phase, K_d values were calculated based on the available concentration of beryllium in soil. The log of K_d is significantly correlated to pH (Figure 5). K_d values are quite large indicating the high attenuation capacity of the D Area soil for beryllium. At the D-Area site K_d values vary over four orders of magnitude, clearly a single linear K_d approach would not be appropriate for modeling beryllium transport. Alternatively, a model based on Kd as a function of pH is being evaluated for this site (7).

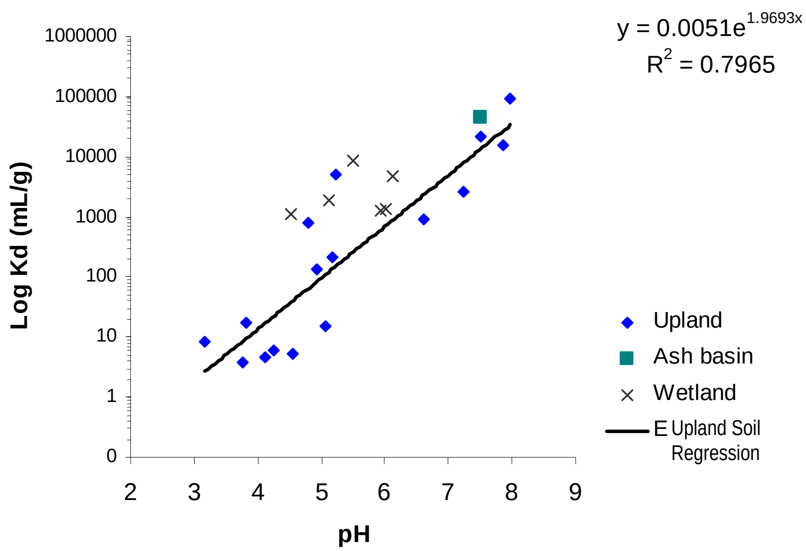

Figure 5 Log K_d as a function of pH

Conclusions

Beryllium attenuation in soil was significant at the characterized field site impacted by coal plant operations. Despite natural and anthropogenic heterogeneities at the site and the inherent difficulties associated with the interpretation of field data, the attenuation of beryllium was highly correlated with the readily measurable parameter pH. Higher soil concentrations of beryllium with a higher percentage of the metal in the available fraction corresponded to soils with higher pH indicating beryllium attenuation. Sequential extraction data was used to define the percentage of the beryllium concentration in soil that was available as well as the partitioning coefficients associated with this available fraction. Both of these site specific parameters are correlated with pH and provide input for groundwater modeling efforts at the site.

Acknowledgements

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