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Key Words:
Monitored Natural Attenuation Availability, D-Area, Arsenic, Beryllium, Nickel, Uranium, Distribution Coefficient

Retention:
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MONITORED NATURAL ATTENUATION OF INORGANIC CONTAMINANTS TREATABILITY STUDY FINAL REPORT

Waste Treatment Technology
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MAY 19, 2004

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500

SRS savannah river site ™

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AA	Atomic Absorption
AEC	Anion Exchange Capacity
APB	Acid producing bacteria
bgs	below ground surface
BRA	Baseline Risk Assessment
DAB	D-Area Ash Basin
DCP	D-Area Coal Pile
AMD	acid mine drainage
ARDRA	amplified ribosomal DNA restriction analysis
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFU	colony forming unit
cm	centimeter
cm/sec	centimeters per second
COC	constituent of concern
DCPRB	D-Area Coal Pile Runoff Basin
df	Degrees of freedom
DF	Dilution (and dispersion) Factor
DNA	deoxyribonucleic acid
DRP	D-Area Rubble Pit
EFE	ecofunctional enzymes
Eh	reduction/oxidation (redox) potential
g/L	grams per liter
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
IRB	iron reducing bacteria
K_d	linear partitioning coefficient, distribution coefficient
K_{sp}	solubility constant
M	molar (moles per liter)
mg/kg	milligrams per kilogram
mg/L	milligram per liter
mL	milliliter
MNA	monitored natural attenuation
msl	mean sea level
mV	millivolt
NA	Not analyzed
nd	Not determined
ppb	parts per billion (µg/L or µg/kg)
ppm	parts per million (mg/L or mg/kg)
RCRA	Resource Conservation and Recovery Act
SCM	surface complexation model
SRB	sulfate reducing bacteria
SRS	Savannah River Site
st dev	standard deviation

TCE	trichloroethylene
TD	total digestion
USDOE	United States Department of Energy
USEPA	United States Environmental Protection Agency
UTRA	Upper Three Runs aquifer
WPT	Waste Processing Technology
WSRC	Westinghouse Savannah River Company

1.0 EXECUTIVE SUMMARY

The identification and quantification of key natural attenuation processes for inorganic contaminants at D-Area is detailed herein. Two overarching goals of this evaluation of monitored natural attenuation (MNA) as a remediation strategy were 1) to better define the availability of inorganic contaminants as potential sources for transport to groundwater and uptake by environmental receptors and 2) to understand the site-specific mechanisms controlling attenuation of these inorganic contaminants through tandem geochemical and biological characterization. Data collected in this study provides input for more appropriate site groundwater transport models.

Significant natural attenuation is occurring at D-Area as evidenced by relatively low aqueous concentrations of constituents of concern (COCs) (Be, Ni, U, and As) at all locations characterized and the decrease in groundwater concentrations with increasing distance from the source. The observed magnitude of decrease in groundwater concentrations of COCs with distance from the D-Area Coal Pile Runoff Basin (DCPRB) could not be accounted for by the modeled physical attenuation processes of dilution/dispersion. This additional attenuation, i.e., the observed difference between the groundwater concentrations of COCs and the modeled physical attenuation, is due to biogeochemical processes occurring at the D-Area. In tandem geochemical and microbiological characterization studies designed to evaluate the mechanisms contributing to natural attenuation, pH was the single parameter found to be most predictive of contaminant attenuation. The increasing pH with distance from the source is likely responsible for increased sorption of COCs to soil surfaces within the aquifer at D-Area. Importantly, because the sediments appear to have a high buffering capacity, the acid emanating from the DCPRB has been neutralized by the soil, and these conditions have led to large K_d values at the site.

Two major types of soils are present at D-Area and were evaluated in this study: upland subsurface soils associated with a low pH/high sulfate/metals plume down-gradient of the D-Area Coal Pile Runoff Basin (DCPRB) and surface ash material discharged to the wetland from the D-Area Ash Basin (488-D). Sequential extraction studies were carried out to better define the availability of inorganic contaminant sources at D-Area.

The availability of the sorbed contaminants in the solid phase was found to depend on the contaminant geochemical conditions (e. g., pH), as well as the soil type (e.g., upland soil verses wetland ash). Typically, for cations (Be, Ni, U), the amount of the contaminant associated with the available fraction increased with the total contaminant concentration in upland soils near the DCPRB. For the more mobile contaminants such as beryllium, the soils closer to the most impacted areas (lowest pH, highest sulfate) may contribute less as a long term source of COC transport to groundwater (lower concentrations of contaminants that are less available) whereas soils down-gradient where contaminant attenuation has occurred have higher soil concentrations with a larger amount of the contaminant in the available fraction.

In contrast to the results for cationic contaminants, arsenic, which occurs predominately as an anion, was typically found associated with the less available (more crystalline) solid phases in upland soils down-gradient of the DCPRB. This tendency of arsenic to be associated with the more crystalline solid phases is likely due to favorable sorption of As to iron oxides at low pH values accounting for the high degree of attenuation of this contaminant near the DCPRB. At wetland locations, relatively high concentrations of all contaminants (Be, Ni, U, As) were measured demonstrating the potential of the wetlands to have a high attenuation capacity. Typically, less than 50 % of the total cationic contaminant concentration was associated with the more available solid phases, however, greater than 90% of the total concentration of arsenic was available which is potentially a concern because the ash material is located at the surface where it is potentially accessible for ingestion by environmental receptors.

The tendency of the sediments to sorb Be, Ni, and U followed well-established geochemical trends. Sediment sorption for U was greater than for Ni, which in turn was greater than for Be. Furthermore, over the range of pH 3 to 8, there was a significant logarithmic relationship between *in situ* K_d values (for U the pH range was 3 to 5.5) and groundwater pH. Arsenic, an anion, was sorbed strongly to wetland ash (K_d values >10,000 mL/g). This is important because it appears that the wetland is acting as an As sink. Similarly, As is also sorbed strongly to both the upland and wetland soils, albeit less strongly than the wetland ash. Based on sequential extraction procedures, it is postulated that the numerous Fe minerals in these sediments are responsible for much of the sorption capacity for the COCs. Arsenic is bound to the Fe phases (perhaps as solid solutions, i.e., poorly defined Fe precipitates) in upland soils near the DCPRB, but in the wetland ash arsenic is removed in the sequential extraction step targeting the organic matter. Because arsenic in a sample of ash taken directly from the ash basin is also associated with the organic matter extraction step, this solid phase speciation observed in the wetland ash is probably due to the As speciation in the waste as well as more favorable sorption conditions in the wetland soils.

In general, distribution of microbes at the site followed expected trends. Total activity and diversity (as measured by substrate utilization) was generally greatest in the wetlands and in zones least impacted by the plume. Conversely, upland and impacted zones of the plume generally contained fewer microbes and less diversity. Overall, the microbial community at the operable unit was relatively diverse. This is important because it suggests that several different microbial processes have the potential to interact with the COCs. These interactions can be active including biotransformation or passive including biosorption of COCs to bacteria cells or their products. The microbe, *Stenotrophomonas maltophilia*, was isolated in several upland locations. Its potential for aerobic metal biotransformation and complex formation may be an indicator of aerobic metal interactions occurring in the upland area. Bacterial isolates from a number of upland soil locations were tested for the ability to alter the groundwater pH. All six bacterial isolates were able to raise the ambient pH from 2 to 3 pH units within 24 hours. An isolated gram negative *Enterobacter* sp. was able to raise the pH of the pH 4 growth media, and it effected a 3 pH unit change within 24 hours. Enterobacter have also been demonstrated to reduce metals. While there is strong evidence for the participation of microbes at the D-Area site in the natural attenuation processes, a quantification of these microbial processes is not possible with the current data.

Ecofunctional enzyme results showed that wetland locations revealed two distinct groupings. These could be categorized as impacted, or those wetland sites nearest the source area, or nonimpacted, those locations furthest from the sources. A number of sites with ash deposition were categorized as nonimpacted while others with ash were classified as impacted based on microbiological activity. A potential indicator of MNA would be future conversion of those wetland impacted sites microbiological activity to that more like nonimpacted.

Geochemical processes can be invoked to describe attenuation at locations near the DCPRB where porewater and soil concentrations of contaminants exhibited the largest variations. A simplified conceptual hydro-geochemical model at the site is (1) the introduction of low-pH water and metals from the DCPRB; (2) soils downgradient of the source buffer the acidity (i.e., raise the pH of the groundwater); and (3) the high aqueous concentrations of dissolved ions such as As, Be, Ni, U, Fe, Mn, and Al are removed from the aqueous phase forming soil sorbed species, metal oxide/hydroxide surface coatings and precipitates. The ability of metal oxide/hydroxides in soil to possess variable surface charge accounts for sorption of both cationic and anionic contaminants. The favorable sorption of arsenic as an anion occurs at locations very near the DCPRB where the accumulation of positive charge due to the sorption of hydrogen ions (low pH) is greatest. Cations such as Be, Ni, and U compete with hydrogen ions for sorption sites and, therefore, tend to be more mobile with sorption increasing with increasing pH (decreasing hydrogen ion concentration). Although sufficient numbers of microorganisms exist at locations near the DCPRB, no clear correlation between biological parameters measured in this study (including total and viable counts as well as substrate utilization) and inorganic attenuation close to the DCPRB was observed. Because the majority of the natural attenuation was observed prior to groundwater interactions with wetland soils, the inorganic attenuation capacity of this regime could not be quantified. Given the geochemistry (elevated pH and high cation exchange capacity) and high level of microbial activity, the wetlands should provide an additional sink for COCs at the D-Area.

Because there is a large variability in transport factors (i.e., the distribution coefficients (K_d values) range over several orders of magnitude) that depends largely on the groundwater pH, a traditional single K_d approach will not be sufficient for modeling contaminant transport at the site. Finally, this work is consistent with the pH dependant transport conceptual geochemical model used in earlier modeling efforts of the operable unit (Brewer and Sochor, 2002). By reducing the uncertainty of the biogeochemical conceptual model and by providing site-specific K_d values, this study will permit future modeling efforts to: (1) use less conservative geochemical input values, and (2) more accurately account for the naturally attenuation processes occurring at the site.

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2.0 INTRODUCTION

2.1 INORGANIC MONITORED NATURAL ATTENUATION OVERVIEW

MNA has received considerable attention as an attractive alternative to more active remediation technologies. MNA 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 timeframe that is reasonable compared to that offered by other more active methods" (USEPA, 1999). Natural attenuation processes in the subsurface reduce the transport and/or environmental availability of contaminants. These natural attenuation processes include a range of physical, chemical, and biological mechanisms that reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater.

To implement MNA for remediation of inorganic contaminants in soil, a given site must first be evaluated and designated as an appropriate MNA site according to United States Environmental Protection Agency (USEPA) protocols and guidelines using site-specific data (USEPA, 1999). Data necessary for this evaluation include: historical groundwater and soil chemistry measurements, including the source term definition (quantity, chemical and physical form, and time period of contaminants released to the environment), are useful in demonstrating natural attenuation. These site-specific data should represent decreasing trends in groundwater contaminant concentrations or mass over time. Hydrogeological and geochemical data indirectly demonstrate types of active processes and rates of attenuation and are also important, as are field data, in demonstrating particular attenuation mechanisms. *In situ* mechanisms that may contribute to natural attenuation include dilution, dispersion, sorption, radioactive decay, and biodegradation as well as chemical or biological stabilization, transformation or destruction.

Because inorganic contaminants are not degraded in natural systems like many organic contaminants, the attenuation of inorganic contaminants will necessarily entail decreases in metal toxicity and mobility primarily through sorption (including adsorption and absorption) and precipitation. These mechanisms maybe abiotically or biotically mediated; for example, reduction of inorganic contaminants often reduces both metal toxicity (e.g., chromium (Cr) VI to Cr III) and mobility primarily through precipitation (e.g., UO_2 (VI) to U (IV)) and enhanced sorption.

At the Savannah River Site (SRS) D-Area, the potential for implementing MNA as a stand alone remediation is being evaluated. Alternatively, since natural attenuation options are often preferred alternatives for distal areas of contaminant plumes, MNA could be implemented at D-Area in combination with more aggressive source zone treatments (Phifer, 2001). MNA is being evaluated both for upland areas impacted by a low pH/sulfate/metals groundwater plume as well as wetland areas down-gradient impacted both by the metal-contaminated groundwater plume as well as high pH/sulfate/metals contaminated surface ash material. The success of MNA is based on physical, chemical, geological, and biological interactions associated with subsurface, near surface, and surface water conditions along D-Area wetlands and subsurface.

2.2 GOALS

This Treatability Study report is a summary of the results from studies designed to evaluate MNA for inorganic constituents of concern (COCs) at the D-Area Expanded Operable Unit (DEXOU). Tandem geochemical and microbiological investigations were carried out to identify and attempt to quantify the natural processes both abiotic and biotic controlling attenuation of the metal COCs - beryllium, nickel, uranium, and arsenic.

The goals of the work addressed in this report include:

- Evaluation of contaminant sources in D-Area in terms of COC availability for transport into ground water and for uptake by environmental receptors
    - Development of a technically defensible definition of the contaminant sources (i.e., source term definition) by operationally defining the environmentally available fraction using a sequential extraction method which approximates a range of environmental conditions under which contaminants might potentially be leached
    - Comparison of sequential extraction methods to other more traditionally used and aggressive methods [EPA 3050b (hot nitric acid) and total digestion (hydrofluoric acid)] as well as to a simplified but equivalent alternative method (single step extraction)

- Identification and quantification of key natural processes (both abiotic and biotic) contributing to and controlling inorganic contamination attenuation processes occurring in D-Area
    - Abiotic mechanisms addressed:
        - Physical processes including dilution and dispersion
        - Geochemical processes including: sorption [metals, sulfate, and hydrogen ion (soil buffering)], precipitation (COCs, Fe, Al), and the relationship of these geochemical processes to reductive and oxidative chemical processes (redox)
    - Biological mechanisms addressed: Bioreduction, biosorption, and pH buffering

- Measurement and identification of the geochemical and/or biological parameters that can be used to model the attenuation processes and the attenuation capacity of the aquifer system at D-Area for inorganic contaminants.
    - Development of more appropriate transport parameters based on site specific *in situ* sorption measurements (i.e., distribution (partition) coefficients, Kds) from matched porewater and soil pairs collected throughout D-Area at a range of locations from near-source to distal to portions of the groundwater plume.
    - Characterization of the soil geochemistry at the site to understand its relationship to sorption processes.
    - Measurement geochemical "master variables" of pH, Eh, and sulfate
    - Determination of biotic factors specific to MNA of metals.
        - Determination of the concentration of the bacterial components of the microbial community present at D-Area.
        - Characterization of specific bacterial populations present and assess their activity with respect to attenuation of inorganic contaminants

- Development of recommendations for D-Area-specific MNA protocols for future long-term monitoring.

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3.0 BACKGROUND

3.1 SITE DESCRIPTION

The D-Area Coal Plant, associated D-Area Coal Pile (DCP), and D-Area Ash Basins (DAB: 488-D and 488-4D), operating continuously since the early 1950s, are some of the oldest facilities at SRS (Figure 1). The D-Area Coal Pile Runoff Basin (DCPRB) was built in 1978 to minimize direct runoff from the DCP to Beaver Dam Creek. A large metal/sulfate/acid groundwater plume emanates from the vicinity of the DCP/DCPRB and flows from the area of highest impact (lowest pH, highest groundwater concentrations of metals) near the north western tip of the DCPRB continuing under the Ash Basins, 488-D and 488-4D, with the distal portion of the plume extending toward the wetland and Savannah River. In addition to the evaluation of natural attenuation processes associated with the large plume emanating from the vicinity of the DCP/DCPRB, surface ash contamination in the wetland originating from activities associated with operation of the DAB, 488-D and 488-4D, was also considered in this study. Additionally, the west end of the DAB (488-D and 488-4D) is a source of low pH and metal contaminants. This plume is coincident with the flow path of the plume associated with the DCP/DCPRB. Another source of low pH and metals contamination in D-Area is the D-Area Rubble Pit (DRP). Based on current modeling the DRP plume is not coincident with the plume emanating from the DCP/DCPRB. Much uncertainty is associated with the distal regions in and around the wetland area as to relative contribution from each of the respective point sources, including the DCP, DCPRB, DAB (488-4D) and D-Area wetlands. Figure 2 shows the beryllium plumes associated with each of these sources based on previous modeling efforts (Brewer and Sochor, 2002). Beryllium is one of the more mobile contaminants at D-Area. (Figure 2)

3.1.1 D-Area Coal Pile (DCP) and D-Area Coal Pile Runoff Basin (DCPRB)

The D-Area Coal Pile (DCP) and Coal Pile Runoff Basin (DCPRB) are sources of acidity, sulfate, and metals generated from sulfuric acid leachate produced by oxidation of pyrite in coal. Oxidation of pyrite occurs chemically but can also be facilitated by the catalytic coupling of bacterial oxidation of Fe^{2+} to Fe^{3+} (Equation 1) with the chemical reaction of Fe^{3+} with pyrite (FeS_2) releasing sulfate and regenerating Fe^{2+} to propagate the cycle (Equation 2) leading to high levels of acidity.

Equation 1 $$\mathbf{Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O}$$

Equation 2 $$\mathbf{FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+}$$

The acid produced leaches toxic trace metals from coal and soil and dissolves mineral surfaces leading to groundwater contamination with high levels of the major ions iron, manganese, aluminum, and sulfate.

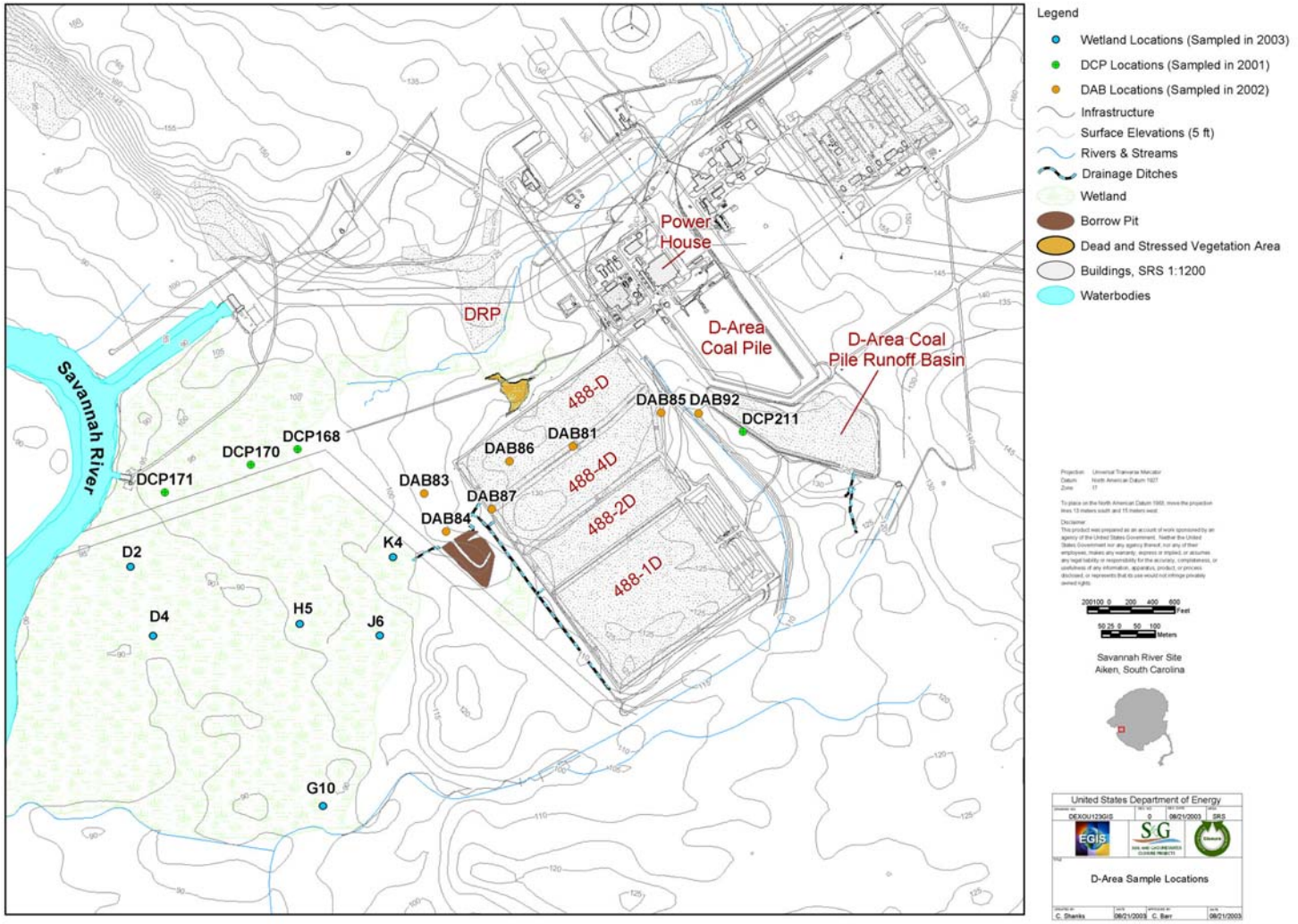

Figure 1. D-Area Map with Sampling Locations

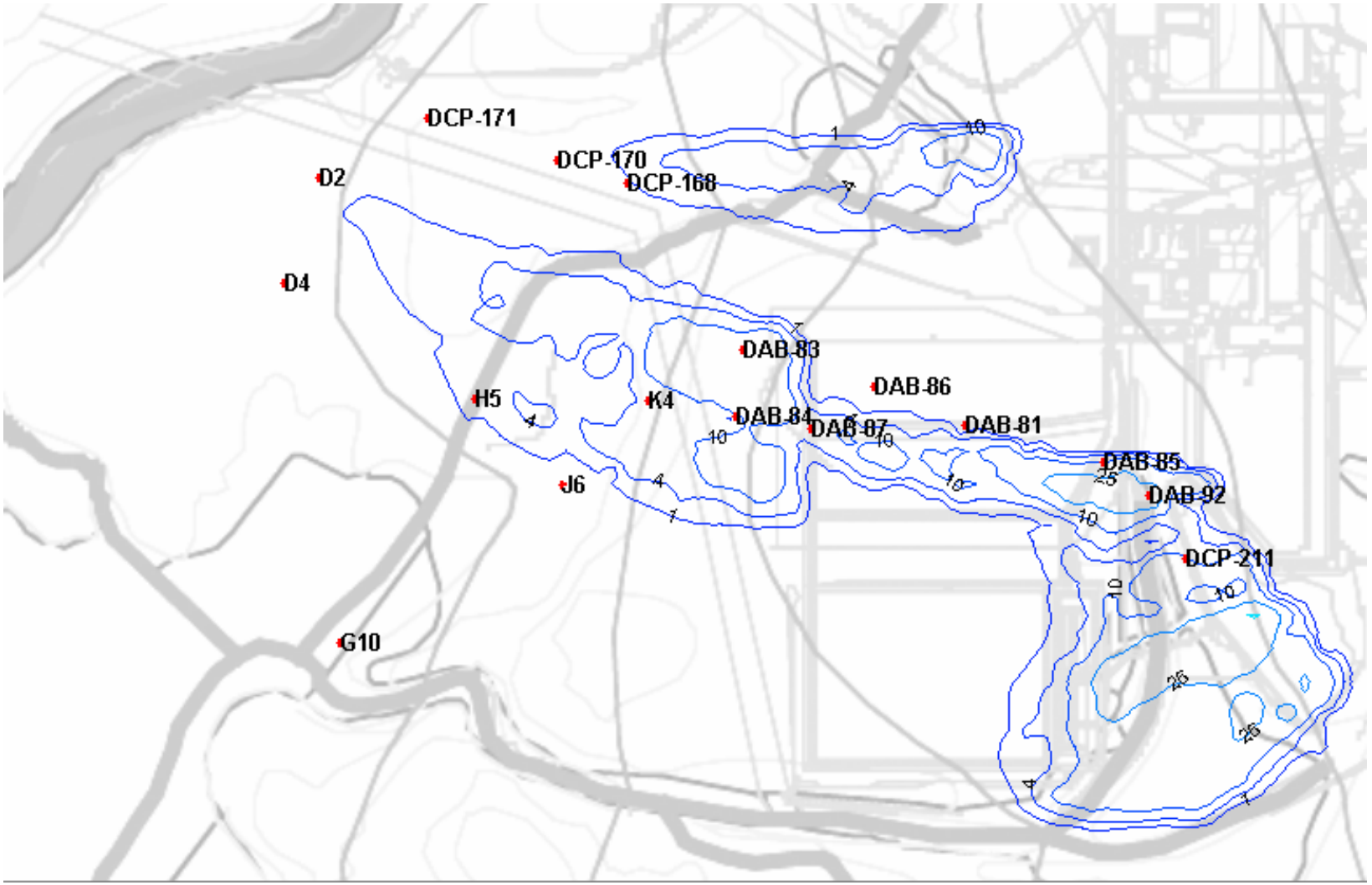

Figure 2. D-Area Site Map with groundwater contaminant plumes for beryllium from modeling (Layer 3, Brewer and Sochor, 2002).

3.1.2 D-Area Ash Basin (DAB) (488-D and 488-4D)

The 488-D Ash Basin is an unlined containment basin constructed above grade to receive ash-sluice water prior to discharge to local surface streams. After the basin was closed to ash sluice in 1976, the basin received only dry ash and coal rejects. Coal rejects were stored on the north and east edges of the basin and later were distributed throughout the surface of the basin. The western end of the 488-D is characterized by a region of low pH associated with standing water in that end of the basin. This low pH region is in contrast to the high pH perched water that characterizes the majority of the basin. Immediately beneath the DAB is a tight layer of natural clay. For this reason, transport from the DAB to the groundwater beneath the DAB is thought to be minimal. On the western end, however, the clay layer becomes thinner allowing contaminants to seep into the groundwater toward the west end and downgradient of the DAB.

3.1.3 D-Area Wetland

Historical aerial photography indicates that ash sluice was routinely discharged from the 488-D into the wetland area primarily in the 1970s prior to the closing of the basin. Figure 3 shows the aerial photography from 1956 before the ash deposition and from 1977 showing the impact to the forested wetland. (Compare the white circled area in the 1956 photo with the 1977 photo.) Figure 3 also shows the thermal delta created by discharge of Beaver Dam Creek. These disposal activities were prior to the closing of 488-D and also prior to the disposal of coal rejects in the DAB 488-D. Consequently, the ash discharged in the wetland area is not expected to contain coal rejects and should be higher than background pH rather than lower.

3.1.4 D-Area Rubble Pit (DRP)

An additional source of acidity and inorganic COCs found in D-Area is the DRP. The majority of the sampling locations characterized in this work were upgradient and far from the currently modeled plume associated with the DRP. A number of locations (DCP168, DCP 170, DCP171) evaluated in previous work (Powell et al., 2001) are distal to the plume emanating from the DCP-DCPRB. (Figure 2)

3.1.5 D-Area Hydrogeology

The Upper Three Runs Aquifer (UTRA) is the aquifer system of concern for this Treatability Study. This aquifer system has been divided into three hydrostratigraphic zones (upper UTRA, “tan clay,” and lower UTRA) based on the hydraulic geologic properties of the zones. The upper UTRA and the “tan clay” are not present in D-Area, and the water table aquifer is located in the lower UTRA. The lower UTRA is composed primarily of sands and clays deposited as Quaternary alluvium and sand, clayey sand, and calcareous sand of the Tinker/Santee Formation. The shallowest continuous unit that constitutes an aquitard below the water table aquifer is the Gordon confining unit (i.e., the “green clay”) (WSRC, 2000).

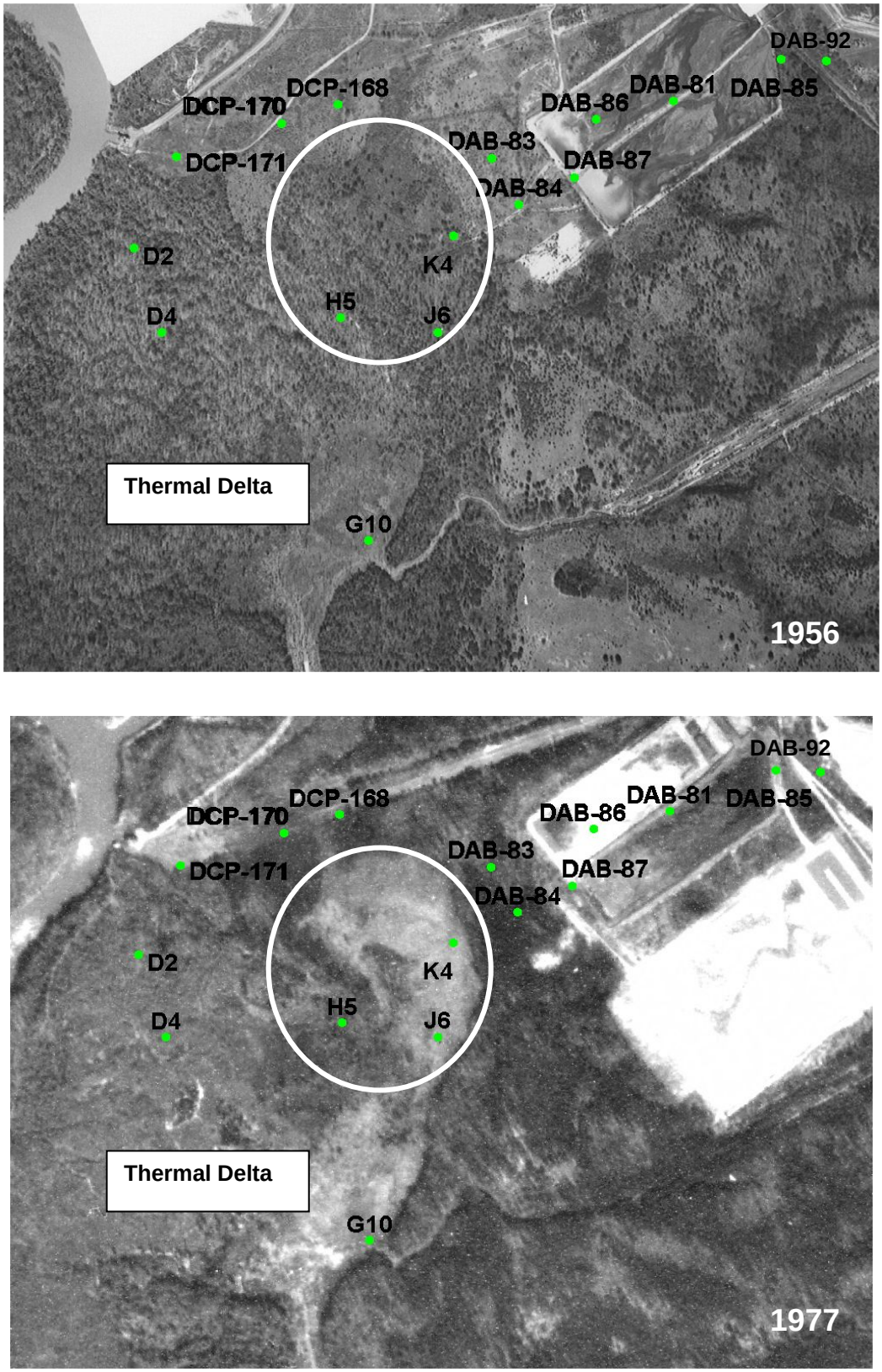

Figure 3. Aerial Photographs Showing Before (1956) and After (1977) Ash-Sluice Discharge to Wetland

Groundwater flow in the D-Area water table aquifer is predominantly east to west toward the Savannah River. Water table elevations, gathered from monitoring wells, indicate that the potentiometric surface ranges from 96.8 to 134.2 feet mean sea level (msl) at D-Area. The water table aquifer underneath D-Area ranges in thickness from approximately 40 to 60 feet. Generally, the depth of the water table below decreases until the groundwater emerges in wetlands to the west of the ash basins, east of the Savannah River. The most shallow groundwater flow is influenced by local features such as the DCPRB, the unnamed tributary to Beaver Dam Creek (i.e., the discharge ditch), the wetlands between the DCPRB and the ash basins, the ash basins, Beaver Dam Creek, and other wetland/swamp areas. The head gradient across the green clay influences deeper water table aquifer flow (Phifer et al., 1996, WSRC, 2000).

3.1.6 Low pH/Metals/Sulfate Plumes

Chemical and biological oxidation of the sulfur compounds (primarily pyrite) associated with coal produces sulfuric acid. Within the D-Area coal pile, rainwater and sulfuric acid combine to leach other trace elements from the coal, producing an acidic runoff that contains substantial metal contaminants and sulfate (low pH/metals/sulfate contamination). The predominant trace elements found in coal include aluminum, silica, sulfur, iron, calcium, zinc, magnesium, and lead (Gluskoter, 1975). Other trace elements found in coal in lesser amounts include arsenic, barium, chromium, cobalt, copper, nickel, lanthanum, manganese, thorium, uranium, and vanadium (Horton et al., 1977). Beryllium, nickel, and uranium were the three contaminants selected for previous modeling studies (Brewer and Sochor, 2002).

The runoff from the D-Area coal pile is subsequently discharged into the DCPRB where the oxidation and leaching process continues as a result of coal and coal fines within the DCPRB, and the contaminated water from the basin seeps into the water table aquifer (UTRA). The maximum extent of impact to the groundwater can be represented by sulfate, which is highly soluble and provides the highest resolution as an indicator parameter of plume migration. Groundwater sulfate concentrations exceeding 5,000 mg/L occur immediately adjacent to the coal pile and the DCPRB, and groundwater pH values of less than 3 occur in this vicinity. Sulfate concentrations are lower and pH is higher north and east of the coal pile and DCPRB (WSRC, 1991, Phifer et al., 1996, WSRC, 2000), indicating the significance of DCPRB contributions to groundwater contamination.

The groundwater beneath 488-D and the other ash basins flows westward toward the Savannah River and wetlands. The projected western boundary of the plume hydrologically extends into the wetland area near the Savannah River. This projection is based on elevated groundwater sulfate levels (greater than 100 mg/L) and depressed pH (<5) and flow predictions. The leachate plume appears to be limited to the water table aquifer (UTRA) at D-Area. Groundwater samples collected from wells below the Gordon confining unit do not show depressed pH or elevated sulfate levels. Until powerhouse operation is discontinued and the facility is decontaminated and decommissioned, the D-Area coal pile and the DCPRB are expected to continue to be a source of metals contamination to groundwater.

3.2 CONCEPTUAL MODEL OF NATURAL ATTENUATION AT D-AREA

Due to contaminated runoff from the D-Area coal pile to DCPRB, a low pH/metals/sulfate groundwater contaminant plume emanates from DCPRB. Furthermore, based on historical aerial photographs, field observations, and analytical data, it appears that a significant amount of sluiced ash overflowed from the DAB in the 1970s into the wetland area west of the DAB, providing a source of contamination in the wetland. Additionally, the west end of the 488-D DAB appears to be a source of low pH/sulfate/metals.

The D-Area site was chosen to evaluate the use of MNA to remediate inorganic constituents because it is a relatively large area with low levels of contamination. It was anticipated that environmental conditions would be favorable to this approach. For example, the groundwater plume becomes more anaerobic as it moves towards the Savannah River, and the low-pH plume would be buffered (i.e., neutralized) by the soils at the site. Both of these conditions, more reducing and increased pH, are expected to attenuate metal contaminants by sorption and precipitation processes as the plume moves towards the Savannah River.

Two distinct areas exist within the low pH and sulfate plumes. Each area is thought to have different controlling mechanisms. One area is near the DCP/DCPRB source, where the groundwater chemistry shows the highest degree of variability. In this area where the metals concentrations are highest and the pH is lowest, it is thought that the groundwater will be toxic to indigenous microbial populations and geochemical controls such as sorption will dominate attenuation processes. In the second area of the contaminant plume where the pH of the system is elevated from dilution, dispersion, and buffering from the aquifer sediments, other biotic processes (e.g., microbially mediated removal of metals by sulfate reduction and precipitation as a metal sulfide) could dominate the overall attenuation process.

3.3 METAL AVAILABILITY

In order to evaluate MNA of inorganics, more appropriate methods for determining the estimation of COCs in soil were evaluated in terms of source term and transport.

3.3.1 Estimation of the Source Term

Risk modeling typically defines the contaminant source through disposal inventories and site characterization data. Because disposal inventory records are often incomplete or absent, site characterization data must be used to estimate waste site source terms. These estimates are obtained in various ways, including analyzing contaminant concentrations in soil and groundwater samples collected from the waste site. Typically, soil concentration data are determined using partial digestions, for example USEPA Method 3050b hot nitric acid extraction. This method typically overestimates the amount of metal available to the environment under almost all environmental conditions. Source terms have also been estimated from groundwater concentrations measures at the site by calculating source terms (i.e., soil concentrations) from site-specific groundwater contaminant concentrations using a linear partitioning coefficient. These approaches are subject to large uncertainties and can lead to unrealistic estimates of risks or selection of inappropriate remediation strategies.

An estimation of the source term is needed that is based on characterized soil concentrations of COCs that does not rely on historical records and provides a technically defensible approach to estimating current COC sources *in situ*. EPA Method 3050b (hot nitric acid extraction) is an aggressive method and likely over-estimates the metal available for transport. Consequently, an eight step sequential extraction method (Miller, 1986**)** was evaluated.

Sequential extraction 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) as "the ability of a soil to maintain an aqueous concentration of [contaminants] in the soil solution"). The first six extraction steps in this operationally defined extraction sequence (described in detail in Section 4.2.2 Table 3) 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. Similarly, the harsh conditions of the EPA 3050B standard method (hot nitric acid) also 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) 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. A single-step extraction equivalent to the first six steps of the sequential extraction procedure was also evaluated.

Associated with natural attenuation of metals in groundwater by soil is the changing profile of COCs based on location in the plume and attenuation mechanism. Highest soil concentrations of mobile COCs are likely located some distance from the original source.

3.3.2 Distribution Coefficients

Once the source term has been estimated, a mathematical model that relates source concentration to groundwater concentration is developed. Typically, a linear partitioning coefficient (K_d) is used in groundwater models. K_d values are either obtained from published literature or generated from site-specific data. 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:

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

Groundwater transport models account for hydrodynamic processes such as advection and dispersion. These models are also capable of accounting for contaminant mass-reduction by processes such as radioactive decay and biodegradation. Partitioning between the groundwater and soil phases is most often represented by a single linear partitioning coefficient (K_d) that does not vary over the flow path of the model. However, previous studies (Powell et al., 2001) show that the manner in which metal contaminants at D-Area partition during groundwater transport is highly variable, but systematic with pH, along the groundwater flow path.

Distribution coefficients can be measured from matched porewater and soil samples to provide a more accurate estimation of transport. Because the value of the K_d depends not only on the porewater concentration, but also on the soil concentration, a relationship exists between the source term definition and the distribution coefficient such that overestimation of the source term leads to the development of a larger or less conservative K_d.

Once the mechanisms controlling contaminant transport have been identified, a groundwater transport model can be developed to incorporate the attenuation capacity of the system. The model should be mechanistically based and this Treatability Study is designed to identify and quantify the mechanisms controlling attenuation of the low pH and heavy metal contaminant plumes.

3.4 NATURAL ATTENUATION MECHANISMS

To implement MNA it is not enough to know that contaminant partitioning is variable and systematic with pH. Rather, to help ensure that the attenuation of COCs is persistent, a predictive model that considers the controlling attenuation mechanisms is important. In the case of D-Area, it is believed that geochemical adsorption/precipitation and microbially mediated redox processes are the main mechanisms controlling the attenuation of metal contaminants and acidity at the site.

3.4.1 Dilution and Dispersion

Dilution and dispersion are physical processes contributing to abiotic natural attenuation. SRS groundwater transport models can account for these processes. Geochemical and biological processes are responsible for attenuation not directly attributed to dilution and dispersion and must be accounted for as well in site models.

3.4.2 Geochemical mechanisms

3.4.2.1 Precipitation

Under specific conditions, the environmental availability of certain contaminants can be limited by the precipitation of solid phases. Examples of this process are numerous and include the precipitation of metals as sulfide and hydroxide solids. Thermodynamically, the following generalized reaction and mass action equation can describe this process:

Equation 3 $$aM_y + bA_z = M_aA_b\,(s)$$

where a mole of metal (M) reacts with b moles of an anion (A) to form a solid with composition M_aA_b.

The degree to which the reaction proceeds is:

Equation 4 $K_{sp} = (\{M\}_a x \{A\}_b)^{-1}$

Where K_{sp} is the solubility constant, {M} and {A} are the activities of the metal and anion in solution, each raised to their respective stoichiometric coefficients a and b. Solubility constants for many solid phases are available in the literature from laboratory studies.

The selection of controlling solid phases in field settings, however, is nontrivial, as many metastable solid phases (solids that can undergo dissolution and re-precipitation as a solid with a lower K_{sp}) are often possible. Relevant to this work is the formation of metal oxides including hydrous ferric oxide (HFO) which is the solid formed upon rapid hydrolysis of ferric iron solutions. Upon aging in aqueous solution, HFO transforms to crystalline iron oxide. Freshly precipitated HFO particles are quite small (1 to 10 nm) although with aging HFO coagulates forming porous aggregates that can be micrometer sized (Dzombak, 1990).

3.4.2.2 Soil Buffering Capacity

SRS upland soils are composed primarily of weather resistant quartz. Kaolinite (a clay mineral made of silica and aluminum) dominates the clay fraction of these soils (Looney et al., 1990). Quartz and kaolinite typically serve to provide surfaces for more reactive minerals such as iron, aluminum, and manganese oxides to coat. Metal oxides/hydroxides, kaolinite, and soil organic matter are able to possess variable surface charge and can react with hydrogen ions to buffer acidity. Organic matter is generally confined to the top twelve inches of SRS soils and would be expected to play a more important role in the buffering capacity in the wetland than in the upland subsurface.

3.4.2.3 Cation/Anion Sorption

This ability of soils to possess variable surface charge allows for favorable sorption of both cations and anions. Typically, cation sorption increases with increasing pH (decreasing hydrogen ion concentration) due to competition with hydrogen ions for sorption sites. Anion sorption exhibits the opposite trend as anions are attracted to the accumulation of positive charge at low pH. It follows that sorption of anions decreases with increasing pH (decreasing positive charge.

3.4.3 Geochemical Parameters

In order to better account for geochemical contributions to natural attenuation, a number of geochemical parameters were measured and evaluated as indicators of natural attenuation in light of site-specific metal availability data from selective extractions and site-specific distribution coefficients (K_ds). Parameters measured included pH, Eh, cation exchange capacity, extractable Fe and Al, and particle size distribution. These parameters are indicative of changes in soil properties both due to the natural heterogeneity of the soils as well as modifications due to impact from contaminant sources. Sequential extraction profiles are useful not only in considering the availability of contaminants in soil, but are also indicative of distinctive attenuation mechanisms and provide information regarding the various mineral phases present.

3.4.4 Microbiological mechanisms

The potential for success of MNA is based on a combination of several parameters, including the microbial transformation and/or sorption of contaminants in groundwater and sediments. There are two main strategies whereby metals may be detoxified or removed from groundwater and sediments as a result of bacterial activity. The first of these generally involves bacteria oxidation of metals to less toxic states. The second strategy involves reduction of metals to less mobile or bioavailable states. Some metals can even be volatilized by biological processes. For example fungi are capable of converting arsenic compounds (both organic and inorganic) into methylarsines. This process involves the aerobic conversion to arsenite, followed by stepwise methylation ending with trimethylarsines.

Bacteria (live and dead) have the ability to attenuate metals in groundwater and sediments through biosorption (Volesky, 1989). Biosorption or metal sequestration by microorganisms can occur though complexation, chelation, ion exchange, direct sorption to cell surfaces, or inorganic precipitation. Dead bacteria and fungi can act as biosorbents, which can adsorb the ionic and colloidal forms of metals. Some microbes adsorb metals selectively enough to be used for metal recovery (Odum, 2000). Humic compounds from sediments comprised of organic matter contents can also influence and/or limit contaminant bioavailability and attenuate contaminated groundwater (Fan et al., 2000) Dead microbial cells and associated structures are usually turned over rapidly in the environment (Alexander, 1994). However their sheer numbers and presence on sediment biofilms makes the biomass important in biodegradation and bioremediation of groundwater contaminants. Biosorption allows adaptation to the environment by sensitive organisms while some react and attenuate contaminants. The heavy growth of trees and other plants in the D-Area wetland in areas with several feet of deposited ash in the rhizosphere indicates an active adapting biological system.

Many bacteria that inhabit extreme (acidic) or polluted (heavy metals) possess specialized adaptive physiological features. These adaptive features have been extensively studied and include the ability to change the pH of their surrounding environment. This physiological adaptation is accomplished through the production of buffering compounds including exopolysaccharides and proteins. Bacterial capabilities to adapt to and alter extreme pH environments like this ash basin area are important to long term MNA.

3.4.5 Microbiological Parameters

Biological contributions to MNA were investigated in D-Area sediment porewater by several microbial techniques. Total bacterial densities in sediments are a measurement of overall biomass and can be used to determine site bioremediation potential. The total densities measure aerobic and anaerobic populations as well as both live and dead cells. Dead cells can also bind metals through biosorption. Aerobic culturable bacterial densities were determined since the site is mostly aerobic and these would be expected to be the dominant organisms in this system.

Anaerobic populations and specific microbial types were also measured including iron reducing bacteria (IRB), acid producing bacteria (APB), and sulfate reducing bacteria (SRB) from the upland sediments. IRB reduce Fe(III) to Fe(II) and would be active in an iron-rich reducing environment like D-Area. SRB reduce sulfate to sulfide and can directly convert some metal COCs from more mobile oxidized forms to less mobile reduced forms. APB are commonly iron-oxidizing autotrophic bacteria that use Fe^{2+} as an energy source and can contribute to groundwater acidity due to coal pile leachate.

The biological activities associated with MNA can also be measured by ecofunctional enzyme assessment. This assessment can be rapidly performed on fresh field samples through the Biolog® system. Ecofunctional enzymes (EFE) are enzymes that are being expressed or are used by or within a microbial community to enable individuals or microbial populations to survive, maintain, and grow. Alternatively, EFE may be latent enzymes ready to be expressed. Such enzymes are present in every microbial community. It is expected that in subsurface microbial communities the suite of EFE expressed is a direct reflection of the microbial populations that comprise and dominate that community and of the environmental factors impacting the ecosystem at the time of collection. Understanding ecofunctional enzyme activity in the microbial community of the ash basin area gives an understanding of the vitality and diversity of the microbial communities that are instrumental in MNA of the site.

4.0 METHODS AND SITE DESCRIPTION

4.1 SAMPLING

Soil and porewater samples analyzed herein were collected in three sets of sampling events. Upland samples (DCP 170, 171, 168, and 211) were collected previously for geochemical characterization and were not analyzed for microbiological activity. A second set of upland samples (DAB 81- 87 and 92) was collected and cores were split in the field to be used for both geochemical and microbiological characterization. DAB 86 (ash basin sample) was not analyzed for microbial activity. A third set of samples was collected from the wetland area: D-2, D-4, G-10, H-5, J-6, and K-4. Separate cores were collected for microbiological and geochemical characterization in the same sampling event from adjacent (within several inches) hand-augered cores.

4.1.1 Upland Samples

Upland soil and porewater samples from four locations (DCP 170, 171, 168, and 211; Table 1 and Figure 1) were collected in March 2001. The details of their collection and the results of sample analyses were described in a previous report (Powell et al, 2001). The analysis of samples collected in March 2001 indicated that significant attenuation of metals from the DCPRB had occurred and that the majority of the attenuation had occurred upgradient of these sample locations.

In order to implement natural attenuation as a remediation, it is necessary to identify and quantify the mechanisms responsible for natural attenuation. To this end, samples from eight additional locations (DAB 81- 87 and 92) were collected in closer proximity to the DAB than the four previous upland sample locations. Locations DAB 85 and DAB 92 were selected as locations upgradient of 488-D with DAB 92 targeting the area of lowest pH at the DEXOU slightly downgradient from the DCPRB. Subsurface samples from directly underneath the berm between 488-D and 488-4D were taken at locations DAB 81 and DAB 87. Locations DAB 83 and DAB 84 were selected as locations immediately down gradient of 488-D between 488-D and the wetland area.

Location DAB 86 was selected for collection of source material directly from the center of the ash basin (488-D) in perched water just above the clay layer immediately below the ash basin. A second location on the berm on the west side of 488-D, DAB 82, was also investigated for collection of source material. This sample rendered only fill material from the berm and was not analyzed further. Ash material from 488-D (DAB 86) was evaluated further to provide information regarding geochemical characteristics and COC composition of potential source material with very different origin, composition, and potential COC signature than the source term generated by the D-Area Coal Pile and DCPRB.

See Table 1 and Table 2 for approximate locations with respect to the DCPRB and DAB, for SRS coordinates, and for ground elevation at each location. Samples at DAB 82 (from ash basin berm) and DAB 86 (from ash basin) were collected as macrocore samples using a track rig. DAB 92 was collected as a macrocore sample using a drill rig. All other samples (DAB 81, 83, 84, 85, and 87) were collected using a rotasonic rig. Cores for samples DAB 82, 86 and 92 were 4 ft long and 1 ½ inches in diameter (as were DCP samples collected previously), while DAB 81, 83, 84, 85, and 87 were larger 4-inch diameter 10-ft long sections which were divided in order to transport the retained interval.

Table 1. Upland Sampling Locations

Location	Description	SRS Northing	SRS Easting	Ground elev. (ft)
DAB 92	Near source (DCPRB, high impact)	63907.03	19717.73	116.20
DAB 85	Up gradient of 488-D	64109.05	19447.76	130.51
DAB 81	Beneath 488-D	64335.39	18608.53	127.95
DAB 87	Beneath 488-D	64309.34	17670.53	125.02
DAB 84	Down gradient of 488-D	64389.99	17211.00	108.26
DAB 83	Down gradient of 488-D	64790.61	17252.27	107.30
DAB 86	488-D, Ash	64566.37	18058.12	127.37
DAB 82	West berm 488-D (not analyzed)	64622.50	17646.01	125.45
DCP 211	Near source (DCPRB)	63523.28	19950.48	122.75
DCP 168	Distal portion of the plume	65799.12	16552.25	97.30
DCP 170	Distal portion of the plume	65935.51	16123.21	97.06
DCP 171	Distal portion of the plume	66195.82	15337.16	97.53

Within several hours of collection, all samples were taken directly to the laboratory for further analysis. The sample of ash, DAB 86, from 488-D was analyzed in a similar manner to all other samples collected. Prior to analysis samples were stored in a refrigerator at 4 °C in clear plastic liners used to collect the samples.

4.1.2 Wetland Samples

Two samples of soil (D-2 and D-4) from a presumed unimpacted area were collected. Samples G-10, H-5, J-6, and K-4 were collected from the top 1 foot of ash deposition in the wetland area (Table 2). These samples (G-10, H-5, J-6, K-4) compacted on collection considerably more than the presumed impacted soils (D-2 and D-4) due to the ash composition.

Table 2. Wetland Sampling Locations

Location	Description	SRS Northing	SRS Easting	Ground elev. (ft)
D-2	Wetland soil, unimpacted	65824.6	14683.9	nd
D-4	Wetland soil, unimpacted	65189.1	14477.7	nd
G-10	Wetland ash, least impacted	63010.3	14808.5	nd
H-5	Wetland ash	64483.6	15631.7	nd
J-6	Wetland ash	63966.2	16162.5	nd
K-4	Wetland ash, most impacted	64485.1	16676.0	nd

nd = not determined

4.2 GEOCHEMICAL ANALYSES

Previously, "matched" porewater and soil samples (DCP168-211) were collected at adjacent but discrete depths. For the samples DAB 81-92 both porewater and soil analyses were carried out with porewater and soil separated from the same soil core sample. Porewater samples were analyzed within 6 months of collection, and soil samples were stored for up to 2 months prior to drying in air and sieving through a 2 mm sieve in preparation for further analysis.

4.2.1 Porewater Analyses

Porewater was separated from the soil of the sample core within 12 hours of the sample collection. The separation of soil and porewater 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.

Porewater redox potential and pH for each sample were measured immediately following separation from the soil. Flow-through pH and redox (E_h) electrodes with an Ag/AgCl flow-through reference electrode (Microelectronics, Inc) were used for these measurements.

Porewater analyses for DAB upland samples were carried out at the Chemical Analysis Laboratory at the University of Georgia in Athens, GA. Porewater samples were analyzed for sulfate (SO_4^{2-}) using a Braun+Luebbe Auto Analyzer II Continuous Flow System.

4.2.2 Soil Digestion Methods

Four methods were used to measure COC concentration in the soils collected. Sequential extractions (Table 3) were carried out by Clemson University or WPT in SRNL. A single-step extraction corresponding to the amorphous iron oxide step (6^{th} step) of the same sequential extraction procedure was conducted by WPT in SRNL. Total digestion (4.2.2.1) was carried out by ADS in SRNL or Clemson University. EPA Method 3050b (4.2.2.2) along with analyses of the leachate by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (suite of 30 elements) and Inductively Coupled Plasma-Atomic Mass Spectroscopy (ICP-MS) (suite of 19 elements) was performed on soil samples at the Chemical Analysis laboratory at the University of Georgia in Athens, GA.

Table 3. 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).

4.2.2.1 Total Digestion

Total digestions were carried out in the same manner as partial digestion Step 8 in the sequential extraction procedure.

4.2.2.2 EPA Method 3050b

Soil samples for the EPA Method 3050b were air dried and 1.0-2.0 g of a sieved material (10-20 mesh) were placed into a conical beaker and 10 mL of 50% nitric acid added. The beaker was covered with a watch glass and heated to 90 °C on a hot plate and refluxed for 10 minutes. This step was repeated if necessary, then evaporated to 5 mL, cooled, hydrogen peroxide added, then HCl and refluxed for 15 more minutes. The sample was allowed to settle or filtered as needed.

4.2.3 Sources of Analytical Error

4.2.3.1 Data QA

A subset (10 %) of all soil digestion calculations was recalculated from original data to validate.

4.2.3.2 Analytical Method Interferences

For the four COCs (Be, Ni, U, As) the primary analytical method utilized for both porewater and soil analyses was ICP-MS. This method can provide a suite of elements in a single analytical run, however, as with any analytical method, errors peculiar to each analyte and matrix are possible. Johnson (1995) identified several contamination and ICP-MS analytical interference issues associated with the sequential extraction procedure used herein. In particular, nickel results from the easily exchangeable step are typically poor because there is an analytical interference for all isotopes of mass 56 through 65 due to polyatomic complexes of CaO^+, $CaOH^+$, and NO_3^+ from the 0.5 M calcium nitrate solution. The acid soluble step shares these interferences from the 0.1 M calcium nitrate. High nickel blanks (relative to sample concentration) are observed in both the acid soluble and easily exchangeable sequential extraction steps. There are also matrix interferences associated with the digestion steps due to the presence of polyatomic ions of chloride and fluoride from the HCl and HF acids which affect the nickel and arsenic results. Typically a digestion matrix blank subtraction was carried out to account for this type of interference; however, matrix interferences from other elements in the soil itself are expected. Where multiple blanks were measured the error in the blank subtraction was propagated.

For arsenic, ICP-MS data was validated for all DCP soil samples by graphite furnace Atomic Absorption (AA) spectroscopy, and total digestion samples were validated by comparison with cold vapor AA.

For comparable methods, data was plotted to validate [e.g., single step extraction versus the sum of the first six steps of the sequential extraction procedure (SE sum 1-6) and also total digestion versus the sum of the eight steps (SE sum 1-8)]. This method was used to identify spurious data (typically greater than 20 % error). The most variability was found for nickel. Some variability was observed for uranium data as well for soil digestions although uranium concentrations in these samples in general were low and subject to matrix interferences as compared to the matrix blank.

Where available, sequential extraction data was used to determine the available (SE sum of steps 1-6) and total (SE sum of steps 1-8) COC concentrations in D-Area soils. Where sequential extraction data was not available, single-step extraction data was used for the available, and total digestion was used for the total COC concentration in soil.

In general, for the four trace metals Be, Ni, U, and As data from the single step extraction and SE sum 1-6 were combined to form one set of data to describe the available COC fraction in soil for all locations and total digestion and SE sum 1-8 data were combined to form a single set to describe the total COC.

4.2.4 Characterization of Soil Properties

4.2.4.1 Cation and Anion Exchange Capacity

The cation exchange capacity (CEC) was determined using an unbuffered salt extraction method by Sumner and Miller (1996), which allowed analysis of the CEC at the "field pH" of the soil. It consisted of the following steps: Saturation of the soil exchange sites with five extractions of the sample with 0.2 M ammonium chloride, followed by removal of the entrained salt with three 0.04 M ammonium chloride washes. Next, the volume of solution entrained in the soil was measured, and finally the bound ammonium ions were displaced with five extractions of the soil sample with a 0.2 M solution of potassium nitrate. The potassium nitrate extract (combined extracts diluted to a final volume of 250 mL with 0.2 M potassium nitrate) was analyzed for ammonium concentration (solution ppm) and the CEC, in centimoles of cation charge per kilogram, was calculated using the following equation:

$$CEC = (\text{weight of soil (g)} \times NH_4^+)/18 - 0.80 \times \text{volume entrained solution (mL)}$$

The anion exchange capacity (AEC) was calculated using the measured solution ppm of chloride ions in the potassium nitrate extract:

$$AEC = 0.14 \times Cl^- - 0.80 \times \text{milliliters entrained solution}$$

4.2.4.2 Particle Size Distribution by Micro-Pipette Method

Soil texture was measured with a modified method for soil mechanical analysis (Miller, 1987). Four grams of soil were shaken overnight with a dilute dispersant (1.25 % $(NaPO_3)_{13}$ in 1 M NaOH), then allowed to settle for two hours before 2.5 mL solution was slowly sampled with an adjustable pipette from a depth of 2.5 cm for determination of clay (particles < 2 μm). The sample solution was dried at 105 °C to obtain a dry mass of clay. Next, the suspension was sieved with a 270-mesh sieve to remove sand. The sand was dried and weighed as well, and silt was determined by the difference in mass of the original soil and the sum of the clay and sand fractions.

4.3 MICROBIOLOGICAL MATERIALS AND METHODS

4.3.1 Bacteria Densities

Comprehensive analysis of specific microbial populations and characterization of the metabolic activity of site microbial communities can be an effective tool to predict an environmental system's bioremediation potential. These analyses can enable monitoring the activity of specific microorganisms in reducing and/or removing harmful groundwater contaminants. In this project sediment samples were collected from fresh cores and transported to the lab for immediate microbiological processing. Five grams of sediment from each fresh core sample was weighed and mixed with 45 ml sterile Bacto FA Buffer (Difco Laboratories phosphate buffer) and vortexed for four minutes to form a 1:10 sediment slurry dilution.

4.3.2 Total Counts

Total microbial population densities in sediments were determined by a direct count method (Balkwill, 1989). The 1:10 soil slurry (Section 4.3.1) was further diluted and ten microliters of two sediment slurry dilutions (1:10,000 and 1:100,000) were placed onto wells of toxoplasmosis slides. The slides were stained with fluorescein isothiocyanate (FITC) and total bacteria were counted at 1000X magnification on a Zeiss Axioskop Epifluorescent microscope.

4.3.3 Viable Counts

The viable, culturable microbial population densities of aerobic and facultatively anaerobic, heterotrophic bacteria in sediments were determined using agar plate techniques. Viable, culturable sediment bacteria were enumerated on Nucleopore 47mm, 0.45µm polycarbonate filters, which were placed on solid agar plates. Three agar plate media types were utilized.

- Peptone-Try tone-Yeast extract-Glucose (PTYG) medium
- One percent PTYG medium (a more dilute Peptone-Try tone-Yeast extract-Glucose)
- Commercially prepared anaerobic PYG plates (Peptone-Yeast Extract-Glucose) by Anaerobe Systems of Morgan Hill, CA

One percent PTYG was used as it is a low nutrient medium simulating SRS oligotropic groundwater (Balkwill, 1989). Although the PTYG and the one percent PTYG plates contained no fungal inhibitor, i.e., cycloheximide, little fungal was detected directly from porewater. The pH of the PTYG and one percent PTYG plates was adjusted to pH 3.00, pH 4.00, and pH 5.00 for testing of the upland sediments in order to better simulate environmental conditions. The pH was adjusted to pH 7.00 for testing of the wetland samples. The initial dilution and two additional dilutions (1:1,000 and 1:100,000) of this slurry were filtered onto the Nucleopore filter and the filters were placed on the agar medium. All plates were incubated at 30 °C, and microbial colony forming units (CFU) determined at both 24 and 48 hours. Plates for anaerobic viable and culturable bacteria were incubated in Bio-Bag Environmental Chamber Type A by Becton Dickinson Microbiology Systems, Cockeysville, MD, or in BBL Anaerobic Gas Pak System Jars. Not all media types were used for all samples. Table 27 and Table 28 indicate the media types used for each sample.

4.3.4 Bacteria Identification

Select bacterial colonies from upland agar plates were picked, streaked and restreaked for purity onto Tryptic Soy Agar plates (Difco Laboratories) before being gram stained (BBL™ Gram Stain Kit) for gram reaction and cell morphology. The bacterial isolates were then streaked onto BUG (Biolog® Universal Media + 5% sheep blood), diluted into Biolog® inoculating fluid at 20% to 52% T (depending upon Gram reaction and cell type), and then inoculated into Biolog GramNegative2 or GramPositive2 plates. The Biolog® plates were read on a Biolog® plate reader after 15 to 24 hour incubation and the bacteria were identified using MicroLog 3 Software and databases.

4.3.5 Tests for Bacteria by Metabolic Function

The upland sediments were tested for iron reducing bacteria, sulfate reducing bacteria, and acid producing bacteria using MICkits™ by Bioindustrial Technologies, Inc. (BTI). Results are recorded as acid producing, iron reducing, and sulfate reducing viable bacteria per gram wet weight sediment.

4.3.6 Ecofunctional Enzyme Activity

Community-level physiological analysis using Biolog®GN2 plates can determine the substrate utilization rate of 95 carbon sources by microorganisms in the sediments. The 1:10 soil slurry (Section 4.3.1) and further dilutions of this slurry was diluted and used to inoculate duplicate Biolog® GN2 microtiter plates to determine ecofunctional enzyme activity at numerous slurry dilutions – 1/10, 1/100, 1/1000, and 1/10,000. At 24 and 48 hours incubation, the Biolog® plates were read on a Biolog® plate reader (wavelength 590nm) so that the optical density of each well in the plate could be assessed. The color intensity due to substrate utilization in the Biolog®GN2 wells was expressed and calculated as the mean of the 95-absorbance values corrected for the background control.

A trial was run to access the buffering capacity of the Biolog® GN2 microtiter plates. This trial would help in understanding if fluctuations in ecofunctional enzyme activity could be attributed to pH differences of the slurries added to them. Duplicate sets of Biolog® GN2 Microplates were inoculated with sterile filtered nano pure water that was adjusted with dilute HCl to pH 5, pH 4 and pH 3 respectively. All of the liquid in each duplicate set was tested for pH at time zero, 24 and 48 hours. Sterile tips and sterile reservoirs were changed for each pH setup.

4.3.7 Microbial Buffering Activity

Select aerobic bacteria isolates were tested from 2002 D-Area sediment samples for influence on pH. The isolates were inoculated into prepared low nutrient 1% Peptone Tryptone Yeast Extract Glucose (PTYG) broth. The cultures were then incubated on shaking platforms at room temperature. The 1% PTYG broth was selected since it is low in nutrients similar to D-Area sediment pore water. The 1% PTYG broth included 3 sets of duplicates; pH 4, pH 5 and pH 6. Based on the sulfurous D-Area coal pile conditions 6 mol H_2SO_4 was used to adjust the broth pH to 4, 1 mol H_2SO_4 was used for pH 5, and 0.1 mol was used for preparation of the pH 6 media. The cultures were then observed for growth at 24, 48, and 72 hours. Those that did not grow in the low pH media were tested for viability on pH 7 1% PTYG plates.

5.0 RESULTS

5.1 GEOCHEMICAL CHARACTERIZATION

5.1.1 Porewater Analyses

Geochemical porewater analyses are summarized in Table 4 through Table 6 (major ions), and Table 7 through Table 9 (trace metals). Sampling depth and elevation, and porewater pH, Eh and sulfate are included at each location for comparison.

5.1.1.1 D-Area Ash Basin (488-D) Porewater

Porewater from the subsurface ash sample, DAB 86, corresponds to perched water just above the tight clay residing in at the bottom of 488-D. This porewater was characterized by both oxidizing conditions (Eh = 341.3 mV) and high pH 7.50 (Table 4). Trace metals found in high concentrations included uranium (224 ppb) and arsenic (19 ppb) in levels exceeding their primary MCLs (Table 7). Major ions aluminum, iron and manganese were present in relatively low levels (Table 4). High levels of sulfate (1785 ppm), an order of magnitude greater than its secondary MCL, were also present.

5.1.1.2 pH, Redox (Eh), and Sulfate

5.1.1.2.1 Upland porewater samples

Areas of low pH, high Eh, and high sulfate serve to delineate the paths of relatively well-defined coincident plumes in the vicinity of the DCPRB (Figure 4 through Figure 10). Increasing pH, decreasing Eh, and sulfate follow the general groundwater flow path from the DCPRB beneath the 488-D toward the Savannah River with greatest impact (lowest pH, highest Eh and highest sulfate) near DAB 92 (adjacent to the DCPRB). Field measurements of pH were found to be in the range of 3.18 to 7.98 for all locations sampled (See Table 4 and Table 5).

5.1.1.2.2 Wetland porewater samples

Based on the on the assumption that the groundwater between the wetland and upland regions is connected, comparisons are made between the upland and wetland section microbiology and geochemistry. Both microbiologicals and geochemical characteristics of the groundwater change significantly between the two regions. The wetland porewater samples contained only low levels of COCs with none of the four COCs considered here over the MCL. Sulfate levels were lower by almost two orders of magnitude lower than both the ash sample (DAB 86) and the DAB upland samples such as DAB 84 28 which based on high sulfate and trace metals was likely in the center of the plume.

5.1.1.3 Major Ion and Trace Metal Analyses

Given the high concentrations of COCs measured in the 488-D ash (DAB 86) and known to exist in the DCPRB, porewater collected from all other sampling locations contained relatively low concentrations of COCs. Of the four primary trace metals analyzed (Be, Ni, U, As), beryllium had the largest number of porewater samples exceeding its MCL of 4 ppb. Uranium concentrations in porewater exceed its MCL only for the ash sample from 488-D, DAB 86. Porewater data for the elements beryllium and uranium were only available for DAB and not DCP sampling locations. Nickel exceeds the Region 9 PRG of 730 ppb at two locations near the DCPRB and at a single distal location, DCP 170-p4.

5.1.1.4 Comparison of Porewater Data to Existing Wells

Sampling locations in this study were selected, in part, based on proximity to existing well locations (Table 10). This design was to provide a reference point for comparison of data collected in this study with existing well data. In order to implement MNA, long-term monitoring will be required to validate natural attenuation. This attenuation should be demonstrated through decreasing trends in groundwater concentration of COCs over time.

Porewater data followed similar trends to existing wells for the locations listed in Table 10. For example, DAB 92 4-6 (Be = 30 ppb, Ni = 1770 ppb, U = 20 ppb, As = 0.86 ppb) collocated with well DCP 70A (Be = 26 ppb, Ni = 790 ppb, U = 14 ppb, As = no data). Typical well screens are approximately 10 ft. Given the vertical stratification of the COC concentrations in the subsurface due to the relatively narrow vertical range of plume impact (particularly in close proximity to the DCPRB), it is not surprising that the data collected in this study over approximately 1 foot intervals does not represent exactly a given adjacent well screen. Sample data from this study might be collected from a section of a given well screen with higher or lower COC concentrations than the average value measured over the heterogeneous well screen.

Table 4. Porewater Concentrations for Major Ions (Al, Fe, Mn) for DAB Locations

Sample	Sample Depth (ft b.g.s.)	Elevation (ft)	pH	E_h v SHE (mV) (± 20 mV)	Sulfate (ppm)	st dev		Aluminum (ppb)	st dev		Iron (ppb)	st dev		Manganese (ppb)	st dev
DAB92 4-6	4 to 6	112-110	3.18	568.2	**1866.23**		*	**276300**		*	**58630**		*	**11530**	
DAB92 21-23	21 to 23	95-93	4.12	511.9	202.11	1.59		4319	19	*	572	20	*	473	6
DAB85 32-33	32 to 33	99-98	5.18	340.4	**864.23**		*	390		*	9271		*	**20410**	
DAB85 45	45	86	7.25	263.8	81.05			16		*<	80		*	**225**	
DAB81 30-35	30	98	4.80	423.6	24.40			35		*<	80		*<	100	
DAB81 45	45	83	4.26	428.9	**1315.20**		*	11340		*	**153900**		*	**44930**	
DAB81 50	50	78	7.98	139.0	**422.09**			12		*	116		*<	100	
DAB87 33	33	92	3.81	422.4	**576.65**		*	16360		*	**111400**		*	**1818**	
DAB87 38	38	87	3.76	465.3	**1296.75**		*	36690		*	**262100**		*	**3798**	
DAB87 53	53	72	4.93	456.7	**1347.93**	**0.60**		441	59	*<	80		*	**2755**	**24**
DAB84 20	20	88	5.06	389.5	108.09			301		*	2076		*	339	
DAB84 28	28	80	4.56	426.7	**907.17**	**24.28**		3493	63	*	**16945**	**346**	*	**29425**	**304**
DAB84 38	38	70	5.24	403.0	47.13			15		*<	80		*<	100	
DAB83 32	32	75	6.61	291.0	**310.11**			83		*<	80			436	
DAB83 38	38	69	7.50	233.1	20.87			22		*<	80		*<	100	
DAB83 42	42	65	7.87	236.9	63.58			60		*<	80		*<	100	
DAB86 12-16	12 to 16	115-111	7.50	341.3	**1785.0**			16			965		*<	100	
MCL primary															
MCL secondary					**250**			200			300			50	
Region 9 PRG								**36000**			**11000**			**880**	
background subsurface water**					< 1										
background surface water***					37-379										

*ICP-ES
**Johnson (1995).
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Table 5. Porewater Concentrations for Major Ions (Al, Fe, Mn) for DCP Locations

Sample	Sample Depth (ft b.g.s.)	Elevation (ft)	pH	E_h v SHE (mV) (± 20 mV)	Sulfate (ppm)	st dev	Aluminum (ppb)	st dev	Iron (ppb)	st dev	Manganese (ppb)	st dev
DCP211-p1	24.5 to 26.5	98-96	4.89	481.7	^ **780**		* **3405**		* **65154**		* **2563**	
DCP211-p2	32 to 34	91-89	4.69	138.7	^ **1476**		* **67520**		* **93914**		* **11418**	
DCP168-p1	15 to 18	82-79	5.61	560.4	62.4		* **371**		* **12625**		* **775**	
DCP168-p2	28 to 31	69-66	6.31	510.7	7.56		* **<240**		* 102		* 27	
DCP168-p3	37 to 40	60-57	6.57	450.6	6.84		* **<240**		* **1192**		* **174**	
DCP170-p1	9 to 12	88-85	4.59	664.3	98.1		* **2712**		* 48		* **1034**	
DCP170-p2	17 to 20	80-77	5.83	488.8	97.5		* **<240**		* **11201**		* **541**	
DCP170-p3	30.5 to 33.5	66.5-63.5	5.68	472.4	113		* **<240**		* **1000**		* **330**	
DCP170-p4	37 to 39	60-58	5.75	458.3	69.1		* **<240**		* **8537**		* **416**	
DCP171-p1	11 to 14	86.5-83.5	5.71	497.9	^ 18.18		* **6414**		* **2128**		* **332**	
DCP171-p2	21 to 24	76.5-73.5	6.13	439	^ 85.5		* **614**		* **2527**		* **1282**	
DCP171-p3	32 to 35	65.5-62.5	6.2	399.9	^ 226.2		* **5191**		* **53389**		* **551**	
MCL primary **MCL secondary** **Region 9 PRG**					**250**		**200**		**300**		**50**	
background subsurface water** background surface water***					< 1 37-379							

^ = calculated based on sulfur concentration (ICP-ES)
*ICP-ES
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Table 6. Porewater Concentrations for Major Ions (Al, Fe, Mn) for Wetland Locations

Sample	Replicate	Soil Sample Height in Tube (in) 1 ft b.g.s.	pH	E_h v SHE (mV) (± 20 mV)	Sulfate (ppm)	Fe (ppb)	Al (ppb)	Mn (ppb)
D-2	primary	6.5	5.49	393.80	5.46	* <80	* 104.59	* <100
	duplicate	9.5						
D-4	primary	13	5.94	391.10	9.50	* **243.30**	* 180.05	* <100
	duplicate	13						
G-10	primary	5.5	6.12	370.90	72.18	* <80	* 20.68	* <100
	duplicate	6						
H-5	primary	10.5	6.02	406.70	174.47	* <80	* 24.13	* <100
	dup, trip	7.5, 7						
J-6	primary	10.5	5.13	436.40	114.78	* <80	* 251.40	* 264
	duplicate	10.5						
K-4	primary	12	4.52	470.60	101.47	* <80	* 128.82	* 128
	duplicate	11.5						
ldl						80	0.04	100
MCL primary								
MCL secondary					**250**	**200**	**300**	**50**
Region 9 PRG								
background subsurface water**					<1			
background surface water***					37-379			

*ICP-ES
**Johnson (1995).
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Table 7. Porewater Concentrations for Trace Elements (Be, Ni, U, As) for DAB Locations

Sample	Sample Depth (ft b.g.s.)	Elevation (ft)	pH	E_h v SHE (mV) (± 20 mV)	Sulfate (ppm)	st dev	Beryllium (ppb)	st dev	Nickel (ppb)	st dev	Uranium (ppb)	st dev	Arsenic (ppb)	st dev
DAB92 4-6	4 to 6	112-110	3.18	568.2	**1866.23**		**29.57**		* **1766.00**		19.712		0.86	
DAB92 21-23	21 to 23	95-93	4.12	511.9	202.11	1.59	**15.09**	**1.55**	34.12	0.74	0.578	0.084	0.13	0.08
DAB85 32-33	32 to 33	99-98	5.18	340.4	**864.23**		1.18		* 330.10		< 0.001		0.064	
DAB85 45	45	86	7.25	263.8	81.05		0.04		9.94		< 0.001		0.49	
DAB81 30-35	30	98	4.80	423.6	24.40		0.72		1.02		< 0.001		0.029	
DAB81 45	45	83	4.26	428.9	**1315.20**		**54.70**		* 687.60		0.126		0.15	
DAB81 50	50	78	7.98	139.0	**422.09**		0.08		1.31		1.945		2.05	
DAB87 33	33	92	3.81	422.4	**576.65**		**8.26**		65.67		9.675		2.47	
DAB87 38	38	87	3.76	465.3	**1296.75**		**13.63**		* 433.90		13.959		3.06	
DAB87 53	53	72	4.93	456.7	**1347.93**	**0.60**	**6.50**	**0.37**	23.84	0.25	< 0.001	0.000	0.24	0.12
DAB84 20	20	88	5.06	389.5	108.09		1.30		8.47		< 0.001		0.077	
DAB84 28	28	80	4.56	426.7	**907.17**	**24.28**	**14.90**	**2.10**	* 192.75	7.00	1.769	0.088	0.80	0.13
DAB84 38	38	70	5.24	403.0	47.13		0.52		1.69		< 0.001		0.056	
DAB83 32	32	75	6.61	291.0	**310.11**		2.60		8.36		2.008		0.018	
DAB83 38	38	69	7.50	233.1	20.87		0.07		0.65		< 0.001		1.04	
DAB83 42	42	65	7.87	236.9	63.58		0.23		1.91		0.027		5.27	
DAB86 12-16	12 to 16	115-111	7.50	341.3	**1785.0**		0.04		4.41		**224.29**		**19.74**	
MCL primary							**4**				**30**		**10**	
MCL secondary					**250**									
Region 9 PRG							73		**730**		7.3		0.045	
background subsurface**					< 1									
background surface water***					37-379									

*ICP-ES
**Johnson (1995).
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Table 8. Porewater Concentrations for Trace Elements (Be, Ni, U, As) for DCP Locations

Sample	Sample Depth (ft b.g.s.)	Elevation (ft)	pH	E_h v SHE (mV) (± 20 mV)	Sulfate (ppm)	st dev	Beryllium (ppb)	st dev	Nickel (ppb)	st dev	Uranium (ppb)	st dev	Arsenic (ppb)	st dev
DCP211-p1	24.5 to 26.5	98-96	4.89	481.7	^ **780**		nd		* 226		nd		#< 5	
DCP211-p2	32 to 34	91-89	4.69	138.7	^ **1476**		nd		* **1558**		nd		#< 5	
DCP168-p1	15 to 18	82-79	5.61	560.4	62.4		nd		*< 62		nd		#< 5	
DCP168-p2	28 to 31	69-66	6.31	510.7	7.56		nd		*< 62		nd		#< 5	
DCP168-p3	37 to 40	60-57	6.57	450.6	6.84		nd		* 438		nd		# 54	
DCP170-p1	9 to 12	88-85	4.59	664.3	98.1		nd		*< 62		nd		#< 5	
DCP170-p2	17 to 20	80-77	5.83	488.8	97.5		nd		*< 62		nd		#< 5	
DCP170-p3	30.5 to 33.5	66.5-63.5	5.68	472.4	113		nd		*< 62		nd		#< 5	
DCP170-p4	37 to 39	60-58	5.75	458.3	69.1		nd		* **749**		nd		# 48	
DCP171-p1	11 to 14	86.5-83.5	5.71	497.9	^ 18.18		nd		* 93		nd		#< 5	
DCP171-p2	21 to 24	76.5-73.5	6.13	439	^ 85.5		nd		* 66		nd		#< 5	
DCP171-p3	32 to 35	65.5-62.5	6.2	399.9	^ 226.2		nd		* 412		nd		#< 5	
MCL primary							**4**				**30**		**10**	
MCL secondary					**250**									
Region 9 PRG									**730**					
background subsurface**					< 1									
background surface water***					37-379									

nd = not determined
^ = calculated based on sulfur concentration (ICP-ES)
*ICP-ES
**Johnson (1995).
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Table 9. Porewater Concentrations for Trace Elements at Wetland Locations (ppb)

Sample	Sample Depth (ft b.g.s.)	pH	Sulfate (ppm)	Beryllium (ppb)	st dev	Nickel (ppb)	st dev	Uranium (ppb)	st dev	Arsenic (ppb)	st dev	Selenium (ppb)	st dev	Vanadium (ppb)	st dev
D-2	1	5.49	5.46	0.09		3.19		16.00		0.41		0.39		* 0.41	
D-4	1	5.94	9.50	0.54		2.90		4.51		0.48		<0.20		* 0.48	
G-10	1	6.12	72.18	0.30		4.14		1.87		6.68		2.35		* 6.68	
H-5	1	6.02	174.47	1.04		11.84		0.93		3.87		1.34		* 3.87	
J-6	1	5.13	114.78	0.59		35.88		0.59		1.29		3.55		* 1.29	
K-4	1	4.52	101.47	1.26		18.76		0.44		2.26		1.49		* 2.26	
MCL primary				**4**				**30**		**10**		**30**		**10**	
MCL secondary			**250**												
Region 9 PRG						**730**									
background subsurface**			< 1												
background surface water***			37-379												

*ICP-ES

**Johnson (1995).

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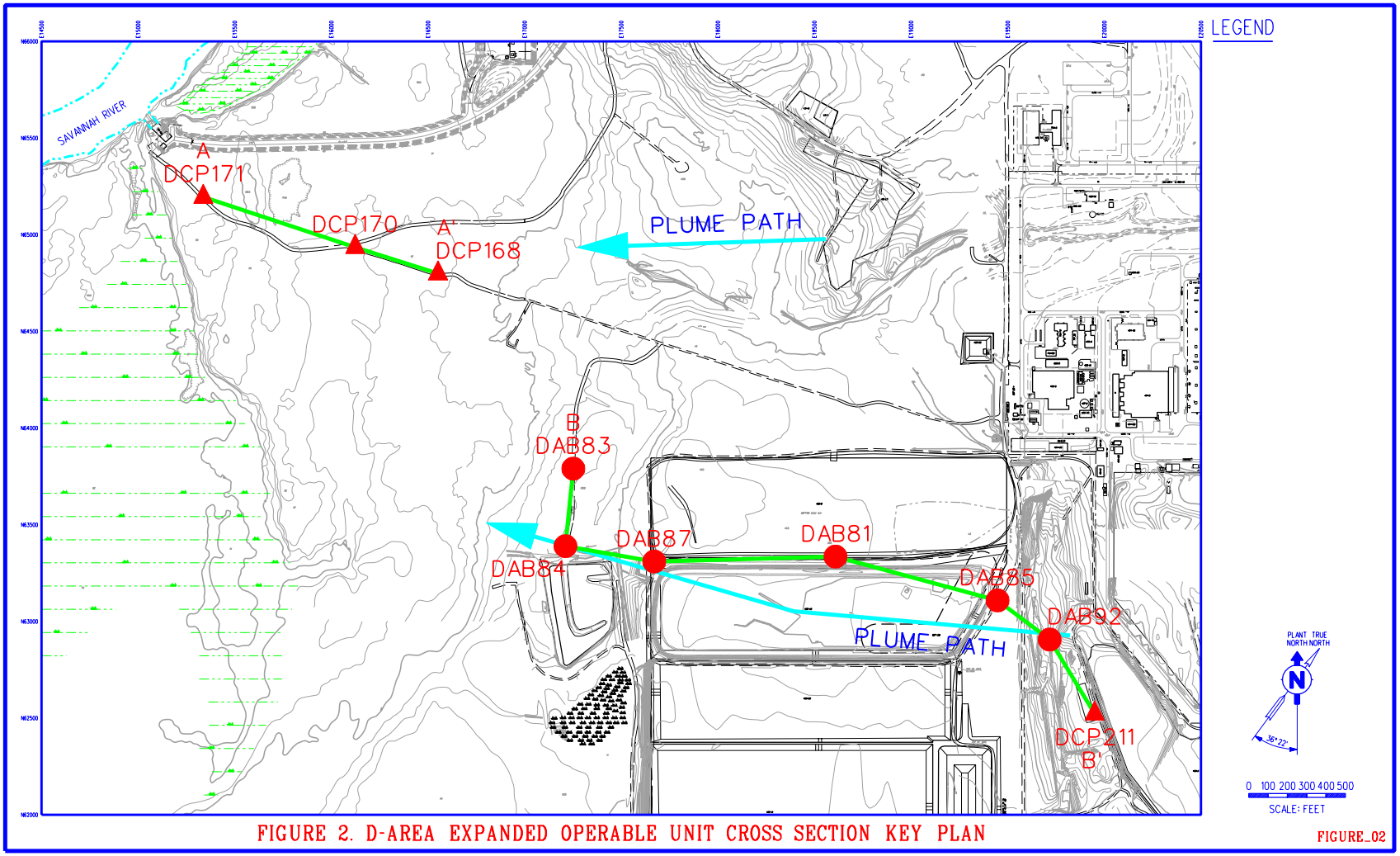


Figure 4. D-Area Expanded Operable Unit Plume Paths

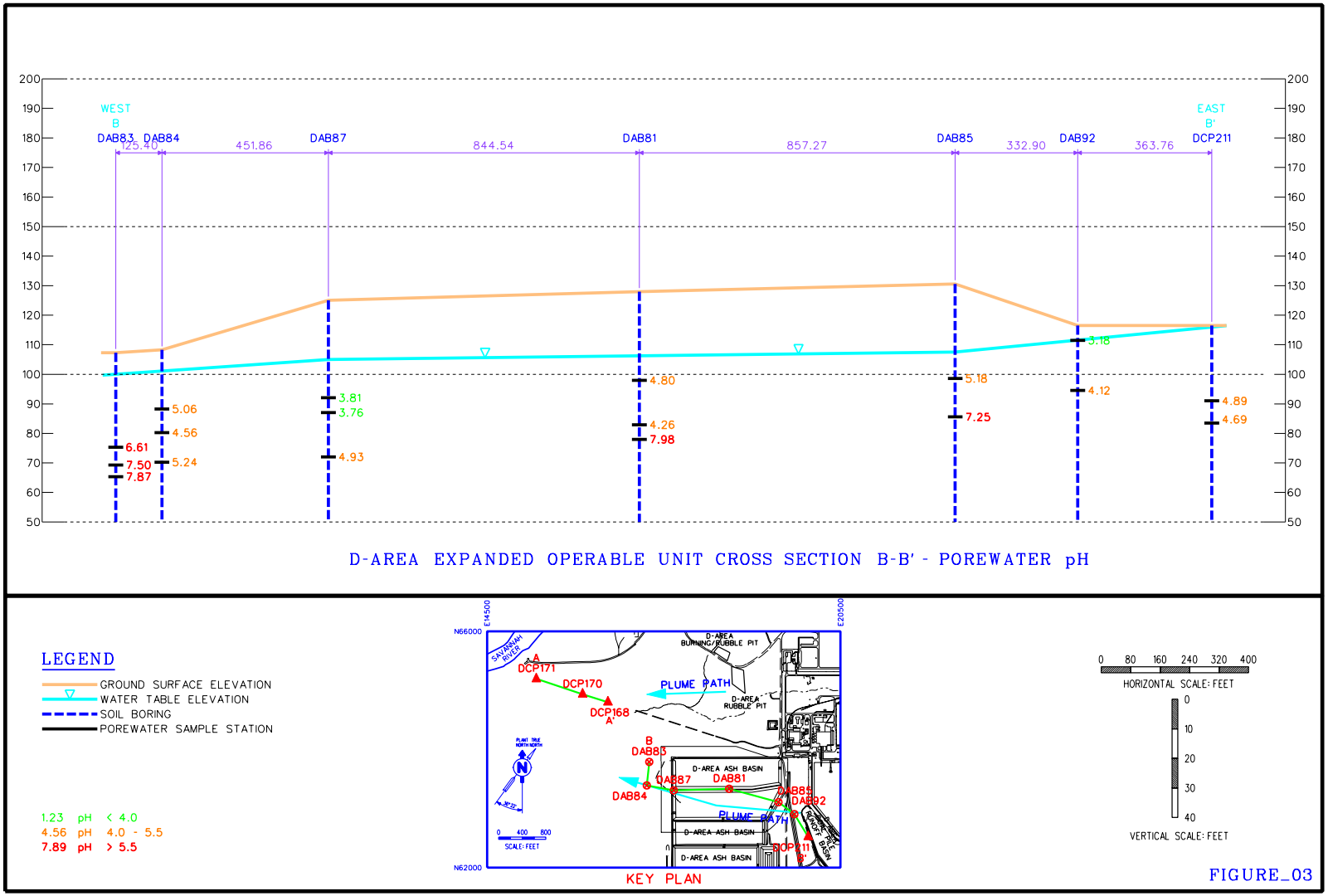


Figure 5. D-Area Expanded Operable Unit Cross Section B-B′ – Porewater pH

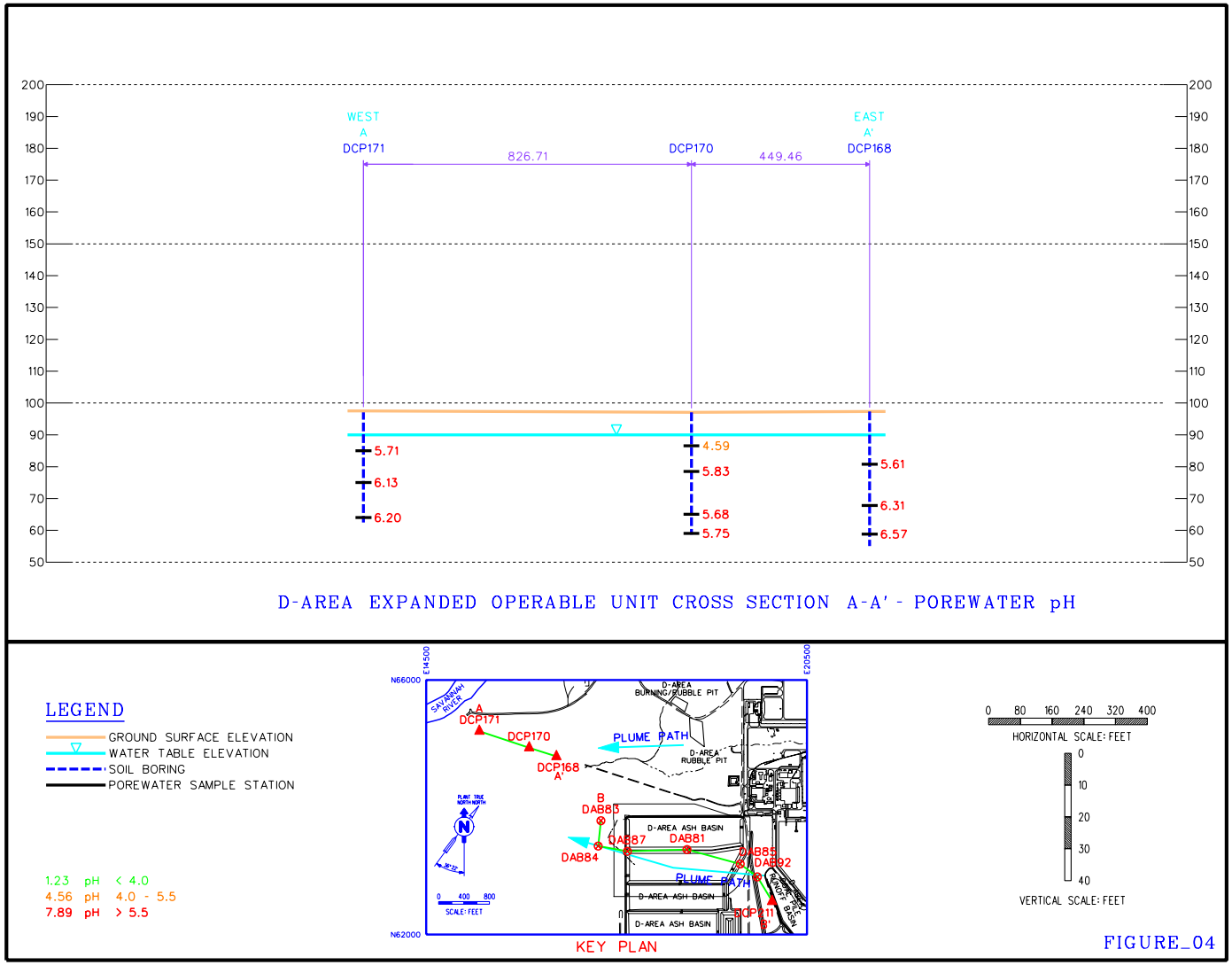


Figure 6. D-Area Expanded Operable Unit Cross Section A-A′ – Porewater pH

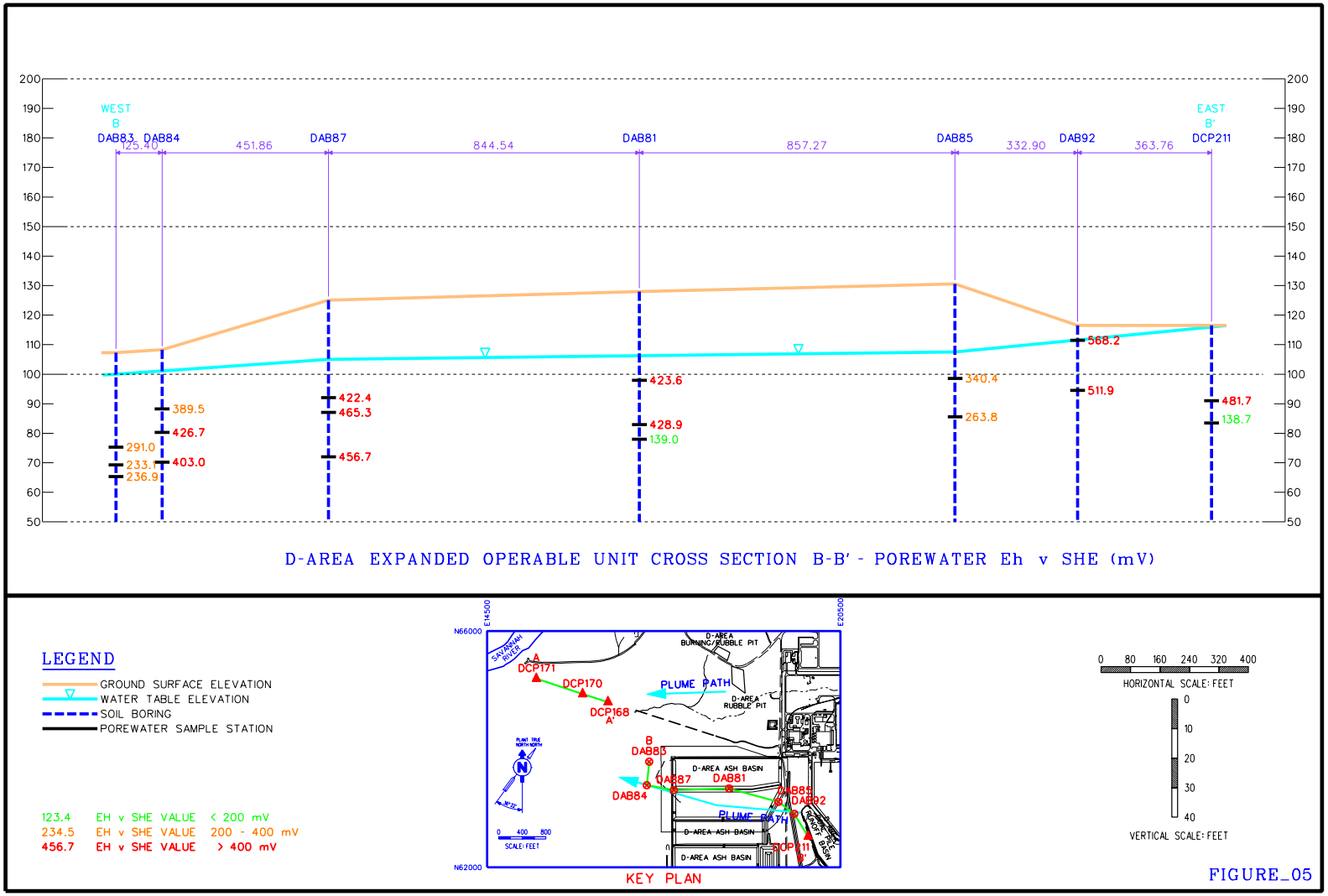


Figure 7. D-Area Expanded Operable Unit Cross Section B-B′ – Porewater E_h v SHE (mV)

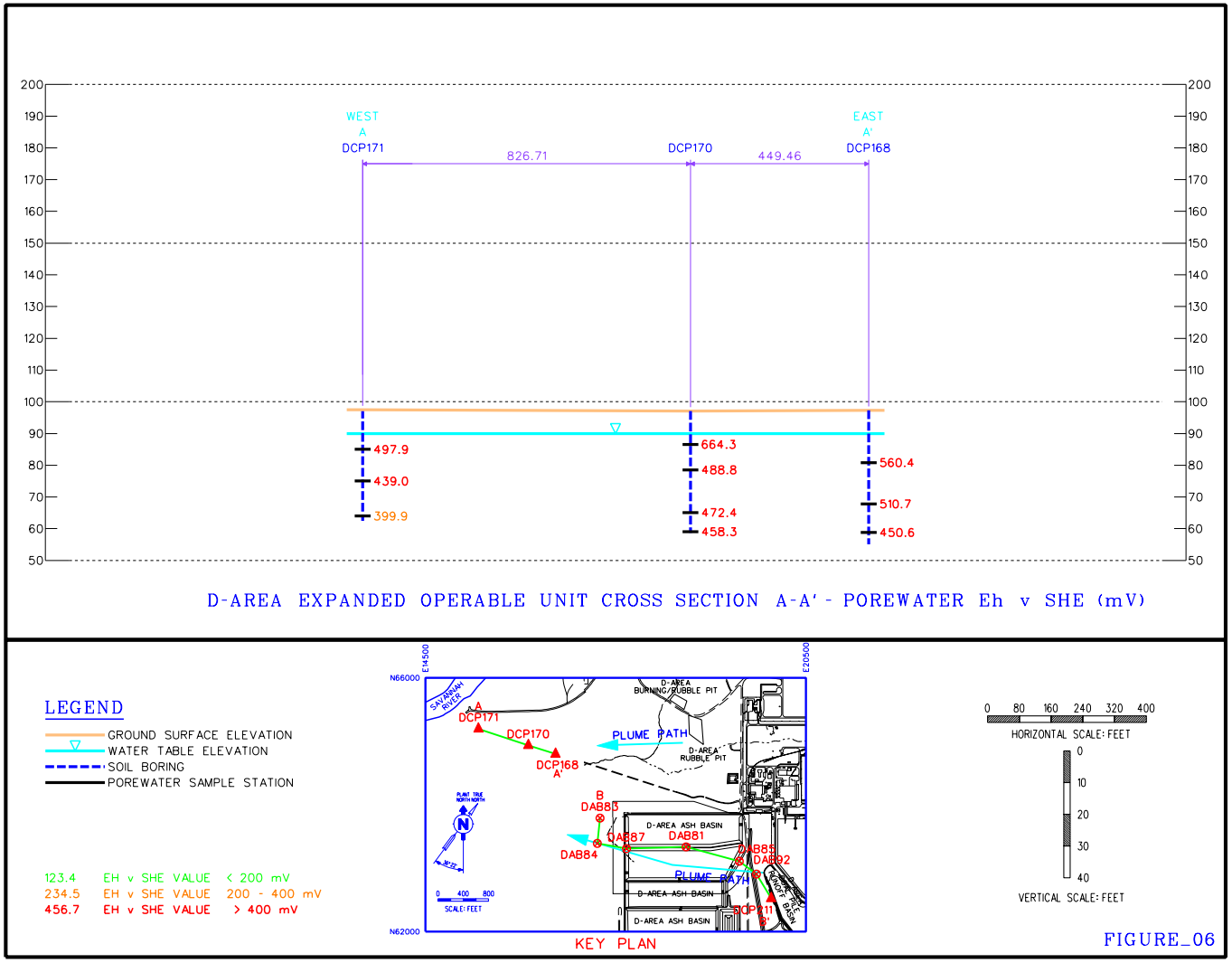


Figure 8. D-Area Expanded Operable Unit Cross Section A-A′– Porewater E_h v SHE (mV)

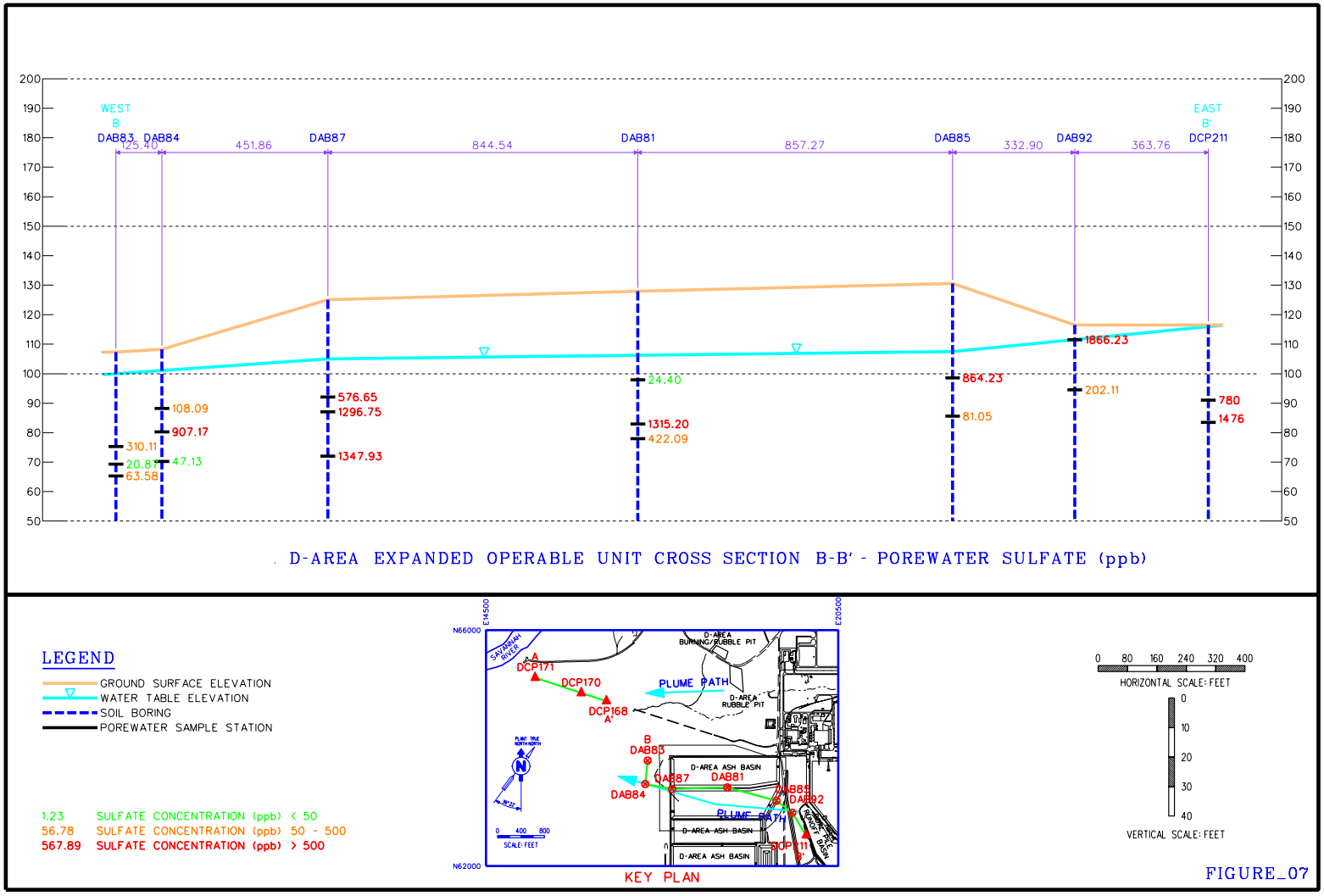


Figure 9. Area Expanded Operable Unit Cross Section B-B′ – Porewater Sulfate (ppm)

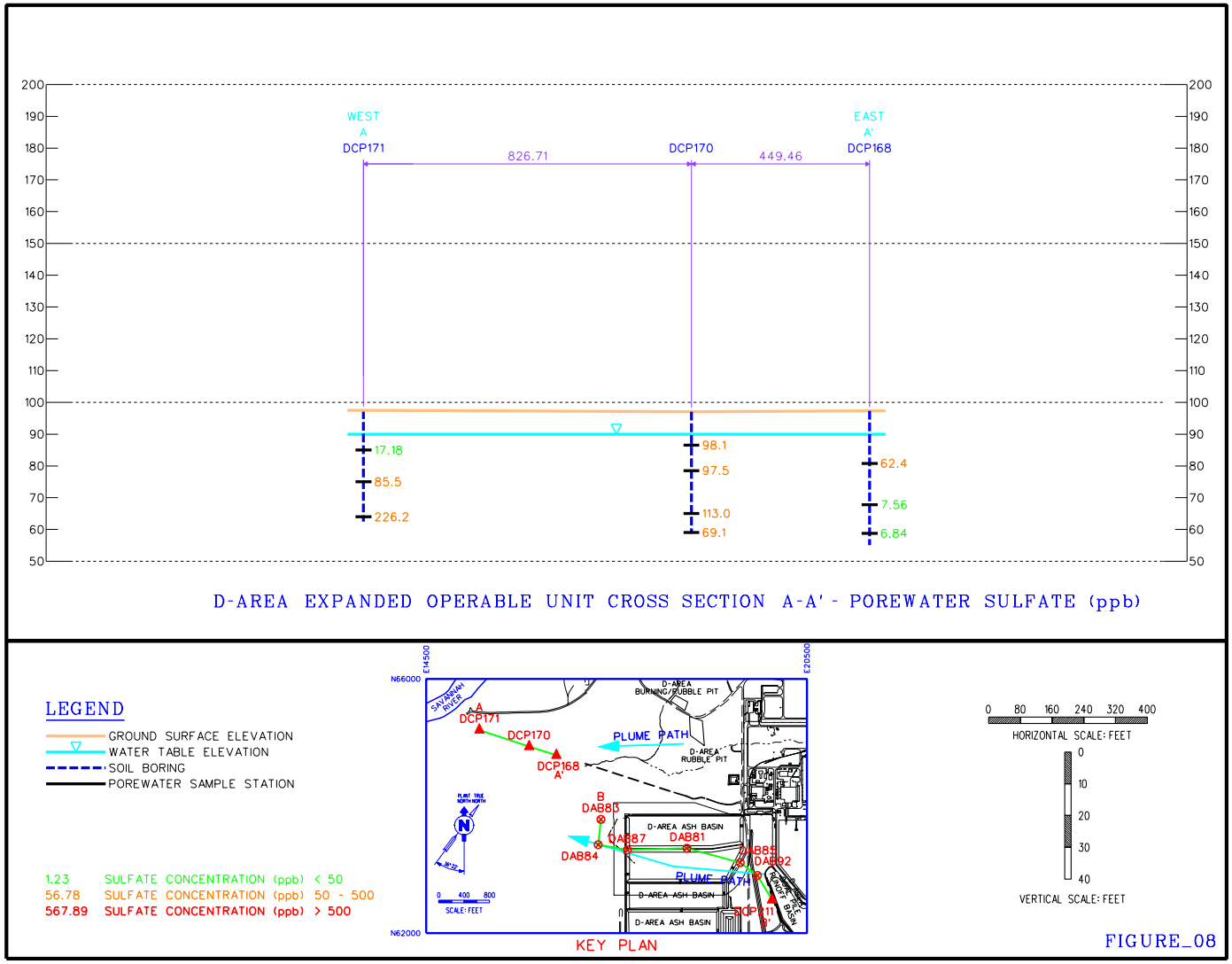


Figure 10. D-Area Expanded Operable Unit Cross Section A-A′ – Porewater Sulfate (ppm)

Table 10. Well Data for Nearby Well Locations

Sample	Sample Depth (ft b.g.s.)	Sample Elevation (ft)	Well Name	Well screen Elevation (ft)	Beryllium (ppb)	Nickel (ppb)	Uranium (ppb)	Arsenic (ppb)
DAB92 4-6	4 to 6	112-110	**DCB 70 A**	114.5-104.5	26.4	**788**	14	No data
DAB92 21-23	21 to 23	95-93	**DCB 70 B**	95.6-90.6	2.3	5.1J	0.04J	No data
DAB85 32-33	32 to 33	99-98						
DAB85 45	45	86	**DCB 38C**	90-80	**353**	128	3.3	42U
DAB81 30-35	30	98	**DCB 46C**	96-86	112J	415	0.3	42U
DAB81 45	45	83						
DAB81 50	50	78						
DAB87 33	33	92						
DAB87 38	38	87						
DAB87 53	53	72						
DAB84 20	20	88	**DCB15R**	94.5-85.2	30J	300	7	**20**
DAB84 28	28	80						
DAB84 38	38	70						
DAB83 32	32	75	**DCB 48A**	81-76	2J	26	0.03	42U
DAB83 38	38	69						
DAB83 42	42	65						
DAB86 12-16	12 to 16	115-111	**DCB 67A**	114-112				
MCL primary					**4**		**30**	**10**
MCL secondary								
Region 9 PRG						**730**		

Data with J and U designations is considered below detection.

5.1.2 Soil Properties for DAB and DCP Samples

Table 11 contains the general soil properties for the DAB and DCP samples. Cation exchange capacity (CEC), soil texture, USDA classification, and total aluminum and iron concentrations are listed. These data provide input for more sophisticated geochemical models which can be used to support future groundwater modeling efforts. Such models would provide a more robust alternative to describing the COC-sediment interaction by the single linear K_d construct. Such a model can vary COC sorption as a function of various geochemical parameters. The samples had a range of CEC values from essentially 0 meq/kg soil to 88 meq/kg soil. Some of the most contaminated sediments, e.g., DCP 211 8-12 and DCP 211 18-19 (samples collected from near the DCPRB source), had the highest CEC levels. DCP 168 20-22 also had a very large CEC considering the low clay content. This high CEC suggests that location DCP 168 is close to a source with high dissolved metals (potentially the DRP rather than the DCPRB).

Excluding DCP 211 18-19 and DCP 168 20-22 the data indicated CEC values were significantly ($p \leq 0.05$, R^2=0.77) correlated to clay content (Figure 11), but had a stronger correlation with the sum of clay and silt content (R^2=0.91) (Figure 12). The comparatively weaker correlation with clay content is likely in part the result of the surprisingly narrow range of clay concentrations: 0 to 2 wt%. With the low percentage of clay in the soils, they were all classified by their sand content and fell in the Silt Loam, Sandy Loam, Loamy Sand, and Sand categories. The data from locations DCP 168 20-22 and DCP 211 18-19 were included in the data set for comparison of CEC with clay or clay and silt content (Figure 11). However, they do not fit the observed trend. The cause of this may be attributed to the formation of precipitates since high concentrations of Fe and Al are present in porewater.

Across DCP and DAB soils there was a wide range of both total aluminum and total iron concentrations, from approximately 300 to 388,000 mg/kg and from 400 to 32,000 mg/kg, respectively. Iron is ubiquitous in SRS sediments and is involved in several different types of reactions (Denham et al. 1999). Of primary interest is that iron precipitates on sediment surfaces to form highly reactive coatings (Stumm and Morgan 1996). These coatings constitute essentially all of the exchange capacity of subsurface sediments (Kaplan 2003). Not surprisingly, the measured CEC were highly correlated to the total Fe concentration in sediments ($R^2 = 0.6247$; $p \leq 0.001$; $df = 22$). (Figure 14)

Table 12 includes both CEC and anion exchange capacity (AEC). Anion exchange capacity is similar to CEC, except it is a measure of the capacity of the sediment to exchange anions. It was anticipated that it would provide some insight into the geochemical behavior of AsO_4^- /AsO_3^- and SeO_4^{2-}/SeO_3^{2-}. An important observation that can be made from the data in Table 12 is that the same sediment can hold both anions and cations. Typically, as pH increases, the CEC increases and the AEC decreases. Not surprisingly, AEC was significantly correlated to clay content ($R^2 = 0.396$, $p \leq 0.05$, $df = 12$; Figure 14). This can be attributed to AEC being a surface area phenomenon, greater the surface area, greater the concentration of anion exchange sites.

Table 11. General Properties of Upland and Wetland Soil Samples

Sample ID	CEC (meq/kg)	Soil Texture Sand/Silt/Clay (percent)	USDA Classification	Total Al (mg/kg)**	Total Fe (mg/kg)**
DAB 92 5	34.56*	74 / 24.3 / 1.7	Loamy Sand	26887 ± 1377	7364 ± 273
DAB 92 21	2.83*	94.2 / 5.7 / 0.1	Sand	5385 ± 1095	2192 ± 454
DAB 85 32-33	5.84± 3.06	92.5 / 7.2 / 0.3	Sand	20420 ± 5722	2078 ± 597
DAB 85 45	0*	99.7 / 0.3 / 0	Sand	6453 ± 646	1060 ± 169
DAB 81 30	7.03*	88.8 / 10.8 / 0.4	Loamy Sand	36688 ± 3106	10230 ± 1208
DAB 81 45	0	96.7 / 3.2 / 0.1	Sand	13761 ± 4904	12253 ± 10399
DAB 81 50	16.42*	61.6 / 37.6 / 0.8	Sandy Loam	323 ± 73	5004 ± 500
DAB 87 33	36.10*	78.3 / 20 / 1.7	Loamy Sand	388386 ± 4840	12170 ± 901
DAB 87 38	0.76 ± 0.54	92.4 / 7.1 / 0.5	Sand	18580 ± 453	2558 ± 62
DAB 87 53	36.08*	72.7 / 25.6 / 1.7	Loamy Sand	49370 ± 3225	13573 ± 721
DAB 84 20	1.56*	98.4 / 1.5 / 0.1	Sand	8887 ± 335	437 ± 30
DAB 84 28	7.30 ± 3.31	93.1 / 6.5 / 0.4	Sand	10599 ± 161	4485 ± 50
DAB 84 38	31.01*	66.1 / 31.8 / 2	Sandy Loam	51005 ± 2846	32715 ± 1727
DAB 83 32	42.36*	77.7 / 20.3 / 2	Loamy Sand	32649 ± 5230	8341 ± 913
DAB 83 38	30.51*	66.4 / 32.1 / 1.5	Sandy Loam	37302 ±18769	15092 ± 6635
DAB 83 42	18.14 ±0.28	45.8 / 53.3 / 0.9	Silt Loam	486 ± 91	5179 ± 144
DCP 211 1-2	7.03 ± 3.31	77 / 22.5 / 0.5	Loamy Sand	15990 ± 1966	6975 ± 445
DCP 211 8-12	46.90 ± 3.58	65.3 / 3.9 / 1.8	Sandy Loam	60400 ± 13718	13050 ± 495
DCP 211 18-19	88.08 ± 7.82	76.1 / 23.1 / 0.8	Loamy Sand	20250 ± 212	4300 ± 1414
DCP 211 34-35	0.18 ± 0.34	97.9 / 2 / 0.1	Sand	1125 ± 92	3370 ± 438
DCP 168 1.5-3.5	25.19 ± 0.19	39.4 / 59.3 / 1.3	Silt Loam	43000 ± 1556	13700 ± 141
DCP 168 20-22	40.88 ± 1.69	95.6 / 4.4 / 0	Sand	15250 ± 495	20200 ± 707
DCP 168 31-33	5.64 ± 0.38	87.4 / 12.4 / 0.2	Loamy Sand	3715 ± 1252	4240 ± 127
DCP 170 1-3	14.12 ± 0.00	68.7 / 30 / 1.3	Sandy Loam	50850 ± 778	16500 ± 0
DCP 170 14-16	2.33 ± 1.58	96.1 / 3.8 / 0.1	Sand	21000 ± 1131	3560 ± 71
DCP 170 20-22	1.28 ± 0.07	95.2 / 4.7 / 0.1	Sand	31650 ± 1909	12650 ± 778
DCP 171 1-3	18.75 ± 0.03	59.7 / 39.3 / 1	Sandy Loam	36850 ± 6576	13300 ± 424
DCP 171 24-26	0.00 ± 0.36	96.2 / 3.7 / 0.1	Sand	18900 ± 2404	3495 ± 163
D-2	44.00 ± 0.68			51162 ± 14971	27724 ± 3939
D-4	60.63 ± 0.45			77305 ± 2331	38027 ± 2924
G-10	13.91 ± 8.02			68112 ± 6713	18349 ± 1211
H-5	62.17 ± 0.79			44752 ± 7415	26402 ± 2358
J-6	12.21 ± 0.12			70372 ± 8585	24731 ± 2458
K-4	0			54409 ± 6319	20435 ± 2016

* Indicates values that were not measured. These values were estimated from the data in Figure 12.
** Denotes total concentration values determined by SE method. All others determined by TD.

Table 12. Measured Cation and Anion Exchange Capacity

Sample ID	Cation Exchange Capacity (meq/kg)	Anion Exchange Capacity (meq/kg)
DAB 85 32	5.84 ± 3.06	0
DAB 81 45	0	0
DAB 87 38	0.76 ± 0.54	7.21 ± 5.10
DAB 84 28	0	0
DAB 83 42	34.38 ± 0.28	12.78 ± 0.45
DCP 211 1-2	7.03 ± 3.31	4.16 ± 5.89
DCP 211 8-12	46.90 ± 3.58	38.35 ± 13.67
DCP 211 18-19	88.08 ± 7.82	20.11 ± 3.64
DCP 211 34-35	0.24 ± 0.34	1.66 ± 2.35
DCP 168 1.5-3.5	25.19 ± 0.19	13.37 ± 2.26
DCP 168 20-22	40.88 ± 1.69	10.88 ± 4.82
DCP 168 31-33	5.64 ± 0.38	12.70 ± 1.77
DCP 170 1-3	14.12 ± 0.00	5.07 ± 0.00
DCP 170 14-16	2.33 ± 1.58	4.32 ± 0.25
DCP 170 20-22	1.28 ± 0.07	5.93 ± 6.57
DCP 171 1-3	18.75 ± 0.06	4.53 ± 1.67
DCP 171 24-26	0.26 ± 0.36	3.81 ± 5.38
D-2	44.00 ± 0.68	20.47 ± 1.64
D-4	60.63 ± 0.45	28.93 ± 3.28
G-10	13.91 ± 8.02	30.80 ± 1.86
H-5	62.17 ± 0.79	34.55 ± 0.64
J-6	12.21 ± 0.12	33.67 ± 1.27
K-4	0	40.89 ± 4.62

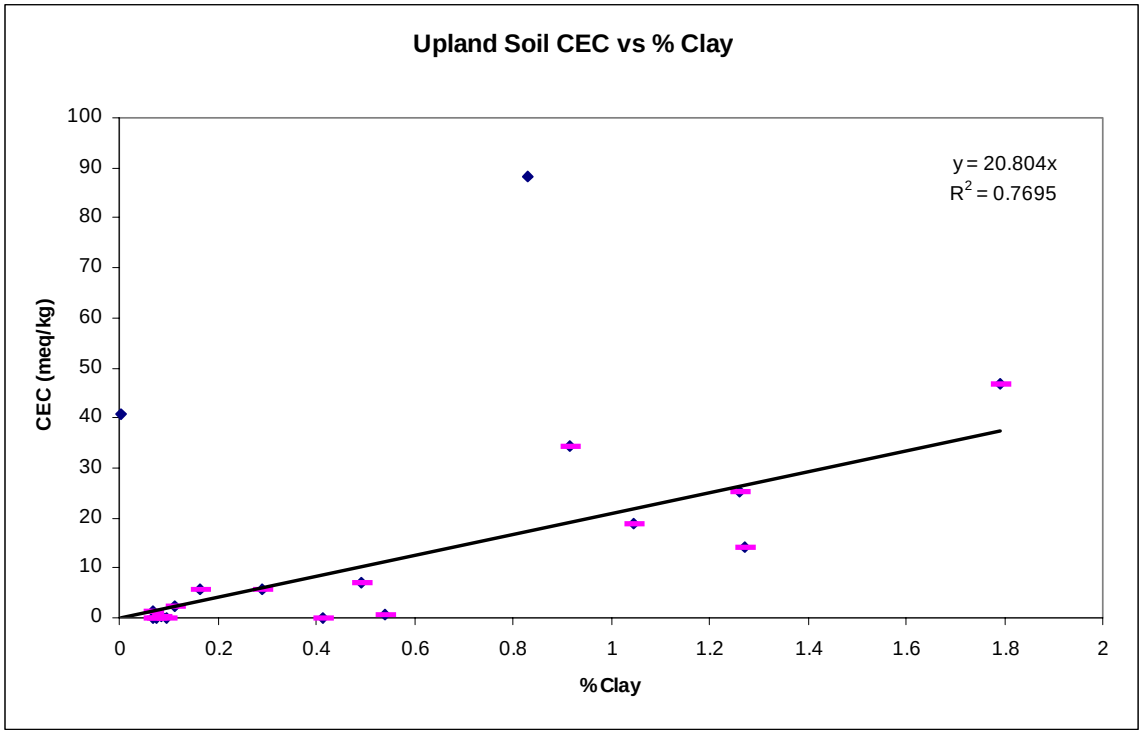


Figure 11. Correlation between measured cation exchange capacity and percent clay in upland soil samples

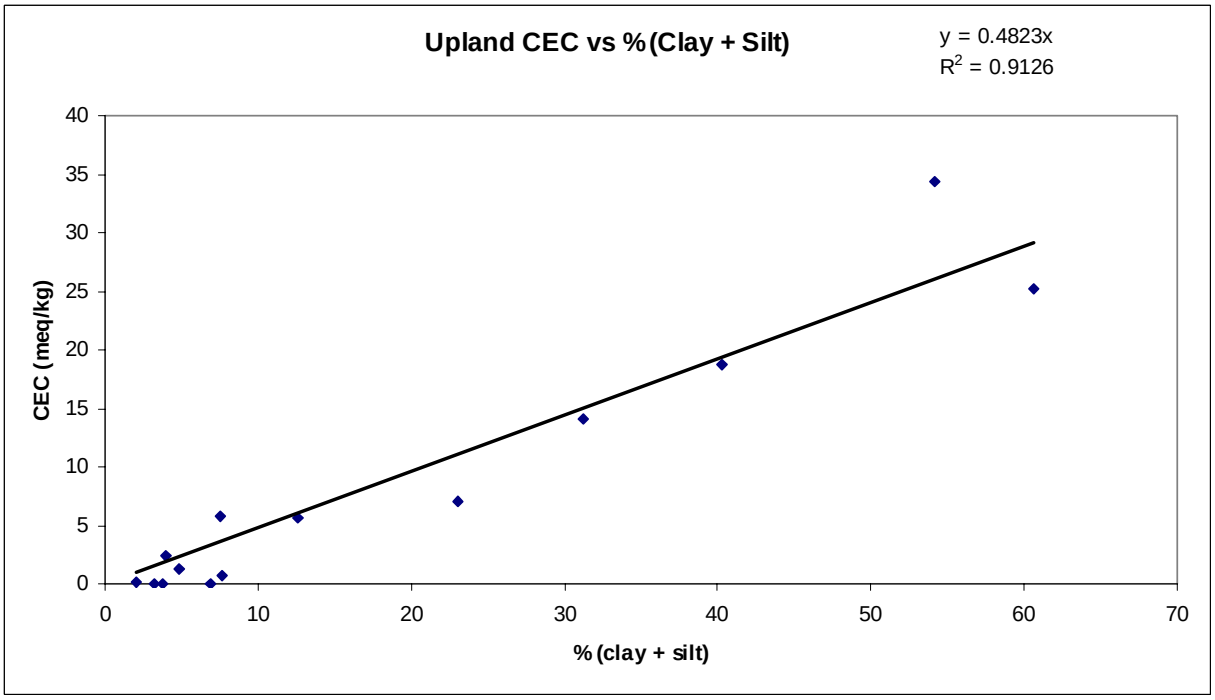
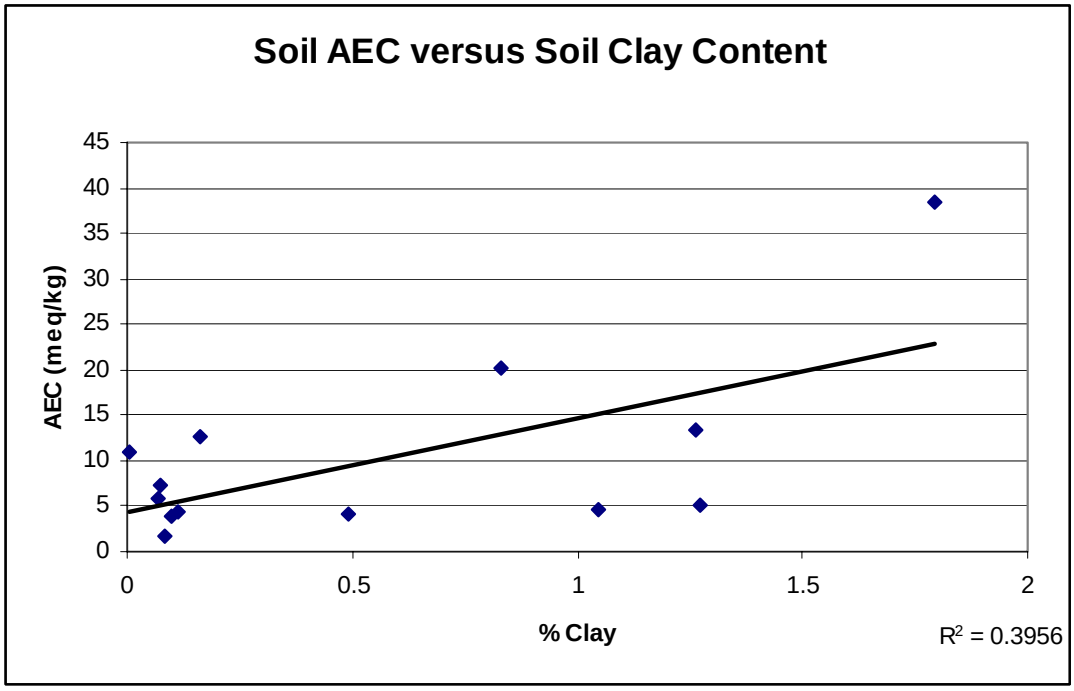


Figure 12. Correlation between measured cation exchange capacity and clay +silt in upland soil samples



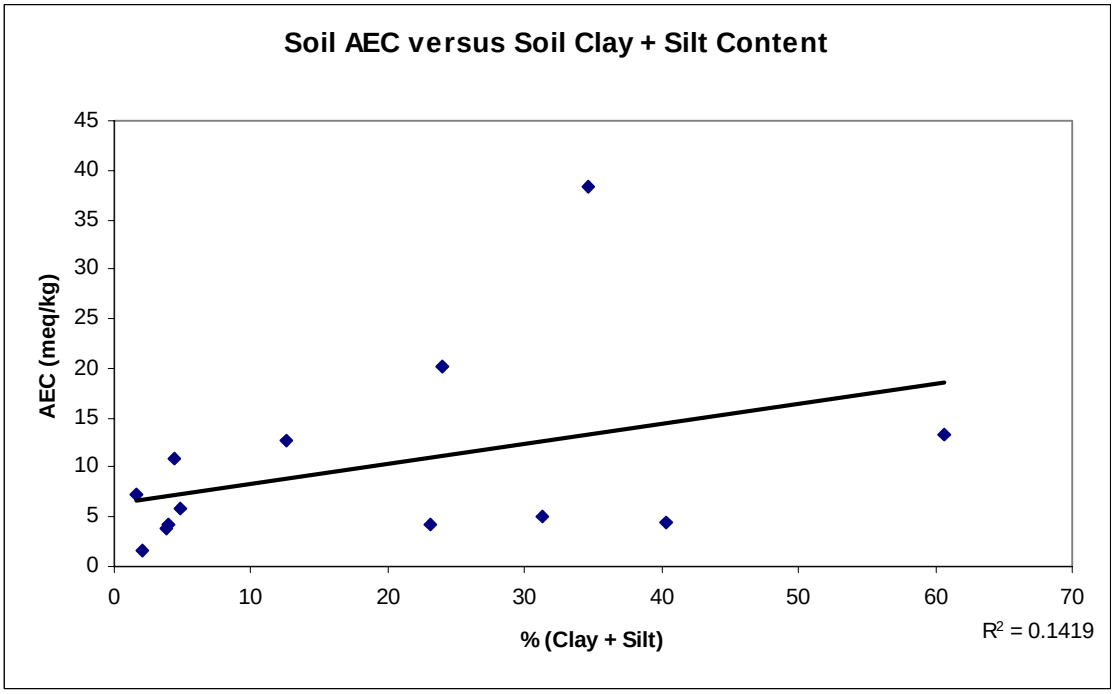


Figure 13. Soil Anion Exchange Capacity vs. Soil Clay Content and Clay + Silt

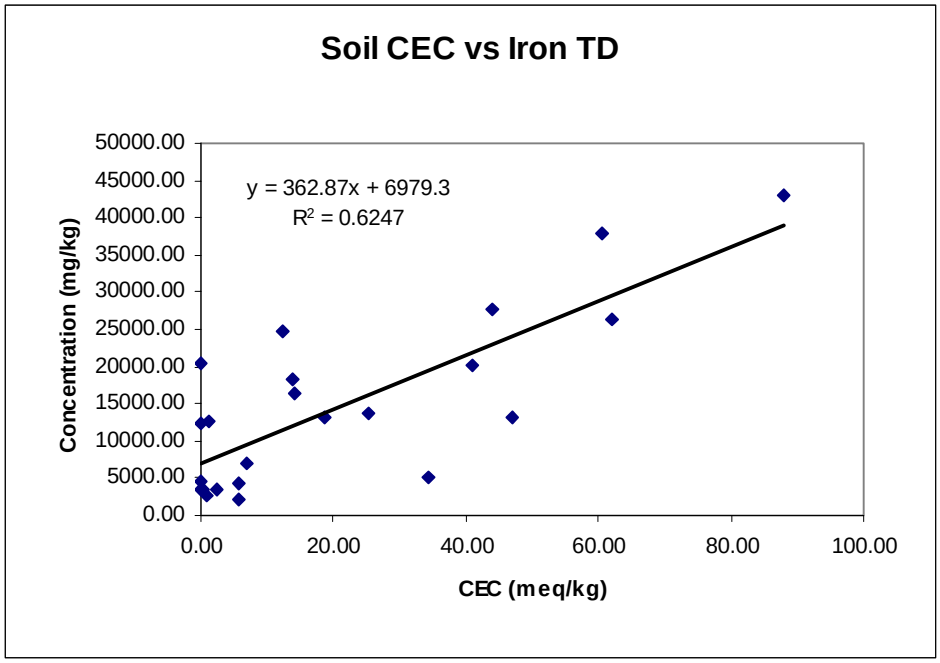


Figure 14. Correlation between measured cation exchange capacity and total iron concentration in soil samples

5.1.3 Soil Digestions

Four measures of COC concentrations are presented in Table 13 through Table 26, they are sum of sequential extraction steps 1 – 6, sum of sequential extraction steps 1 – 8, total digestion, and 3050b digestion. The sequential extraction steps are described in Table 3. The sum of steps 1 – 6 provides a measure of the concentration of COCs that are available for entering into the aqueous phase. This operational definition includes those fractions that may be expected to be desorbed from the sediment under a broad range of environmental conditions. The sum of steps 1 – 6 was used to define solid-phase concentrations for the K_d calculations presented in Section 5.2. The sum of steps 1 – 8 should provide an approximation of the total digestion concentration. The last step in the sequential extractions, Step 8, is a total digestion of the remaining sediment remaining after the previous 7 digestions. The same acids and procedure are used in Step 8 as is used in the total digestion procedure. Differences between the two values can be attributed to laboratory and analytical error associated with adding eight measurements as well as the heterogeneity between the soil samples themselves. In fact, total digestion values are commonly used as a quality assurance that the sequential extractions values are correct. Because the total digestion value is a single extraction, this approach is generally believed to be a better measure of the total COC concentrations than the Sum 1–8 value. The 3050b method uses strong acids but does not dissolve the silicates (no hydrofluoric acid). Thus, it provides a measure of all the COC, except that held in the silicate phases. The difference between the total digestions and the 3050b concentrations would be a measure of the mineral/silicate bound COC concentrations.

As shown by this discussion, the procedures are expected to yield metals concentrations in the following order: Sum 1 – 6 < 3050b < Sum 1 – 8 = Total Digestions. This ranking was generally observed for the Be, (Table 13 and Table 14), Ni (Table 15 and Table 16), U (Table 17 and Table 18), As (Table 19 and Table 20), and Se (Table 21).

Total-digestion Be concentrations at the DEXOU (Table 13 and Table 14) were all greater than the 2x average unit background value of 0.20 mg/kg Be (Table 2.3-9 in WSRC-RP-99-4067). Total-digestion Be concentrations in the 488-D (DAB 86, located within the ash basin) were the highest measured, 7.1 mg/kg. Total-digestion Be concentrations near the DCPRB (DCP211; coal pile runoff basin) were similar to values elsewhere along the sampling transect. Beryllium total concentrations in wetland soils determined by sequential extraction (sum 1-8) are higher than upland soils and similar to the concentrations found in ash material from the 488-D (DAB 86).

Total-digestion Ni concentrations at the DEXOU (Table 15) were essentially all (except at location DAB 84) greater than the 2x average unit background value of 1.81 mg/kg Ni (Table 2.3-9 in WSRC-RP-99-4067). Total-digestion Ni concentrations in the 488-D (DAB 86, within the ash basin) were the highest measured, 59.26 mg/kg Ni. Total-digestion Ni concentrations near the DCPRB (DCP 211; coal pile runoff basin) were similar to values elsewhere along the sampling transect (Table 16). Ni (sum 1-8) total concentrations in wetland soils were similar to upland soils and lower than the ash material (DAB 86).

Unit-specific background U concentrations are not available; however U concentrations of 0.5 to 1.5 mg/kg commonly exist in uncontaminated portions of the SRS (Looney et al. 1990). Based on these values, the only soils to have elevated U concentrations are from the 488-D (sample DAB 86) and DCP 168 (Table 17), located adjacent to the wetland (Figure 1). The sediments collected from near the DCPRB contained <2.12 mg/kg U in their total digestions, indicating the DCPRB is likely not an important source term for U. (Table 18)

Total digestion As concentrations at the DEXOU (Table 19) were all, except at four locations, greater than the 2x average unit background value of 0.70 mg/kg As (Table 2.3-9 in WSRC-RP-99-4067). It may be that this background concentration was measured on soils that were not representative of D-Area soils, because based on other parameters, such as pH and S concentrations, many of the sediments analyzed were not impacted or very slightly impacted by operations (discussed in more detail in Section 6.0). However, total-digestion As concentrations were elevated relative to background in the 488-D (Sample DAB 86; 37.05 mg/kg As), indicating the ash basin is likely a source term for As. Sample DCP 168 also exhibited elevated As concentrations (ranging from 3.35 to 15.86 mg/kg As). This location also had elevated Be, Ni, and U concentrations. Locations DCP 168, 170, and 171 are distal to the plume emanating from the DCPRB although they appear to be impacted by the plume from the DRP.

Total digestion As concentrations near the DCPRB (DCP 211; coal pile runoff basin) were moderately higher than the 2x average unit background value. As total concentrations in the wetland soils were measured by SE (sum of steps 1-8) and were the highest values of all locations analyzed. These high concentrations of arsenic are likely due to the high concentrations of As found in the ash material in 488-D (DAB 86). (Table 20) Despite high arsenic concentrations in the DCPRB sediment (Kaplan and Knox, 2004), the soil concentrations at locations underneath 488-D were relatively low compared to distal samples (DCP 168, DCP 170) and DAB 83 located just down gradient of 488-D. This suggests that the DCPRB is not the source for the As in these distal locations. Low solubility of As(V) likely accounts for the low mobility of As in the low pH plume from the DCPRB.

Selenium data are not available for the upland sediments, but were measured in the wetland samples (Table 21). Unit-specific background Se concentrations are not reported in the RCRA Facility Investigation/Remedial Investigation Work Plan (WSRC-RP-99-4067), however Se concentrations of <0.4 to 1.1 mg/kg commonly exist in uncontaminated portions of the SRS (Looney et al. 1990; Table 6.15). Based on these values, many of the wetland soils appear to have elevated Se concentrations.

Vanadium data are not available for the upland sediments, but was measured in the wetland samples (Table 22). Twice unit-specific background V concentrations are 5.12 mg/kg (RCRA Facility Investigation/Remedial Investigation Work Plan; WSRC-RP-99-4067). All V concentrations in the wetland sediments greatly exceeded this value. The cause for these high values is not known, given the limited amount of data.

Iron and aluminum are not COCs, yet they can provide a valuable indirect indication of how well COCs will sorb to the soils. Most of the Fe in SRS sediments is from Fe-oxyhydroxides that account for most of the sorption capacity in subsurface soils. Aluminum exists primarily in the lattice of kaolinite and other minerals and to a smaller extent as Al-oxide (gibbsite) surface coatings on minerals. A high total Al concentration in a soil may indicate the presence of gibbsite, a mineral with high cation and anion sorption capacities. Total-digestion Fe and Al concentrations varied greatly (436 to 73,632 mg/kg Fe and 323 to 51,005 mg/kg Al) and not in a systematic manner with either distance from point source or depth below ground level (Table 23 – Table 26).

Table 13. Beryllium Concentration (ppm) in Upland Soil

Soil Sample	Elevation	Pore-water	Beryllium (ppm)							
	ft	pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	0.24	0.19	1.18	0.19	1.12	0.70	0.50	0.40
DAB92 21-23	95-93	4.12	0.07	0.01	0.52	0.04	0.27	0.04	0.33	0.29
DAB85 32-33	99-98	5.18	0.25	0.05	1.49	0.27	1.52	0.14	1.04	0.12
DAB85 45	86	7.25	nd	nd	nd	nd	0.24	0	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	2.01	0.17	nd	nd
DAB81 45	83	4.26	0.33	0.08	0.98	0.30	1.17	0.35	0.85	0.24
DAB81 50	78	7.98	nd	nd	nd	nd	2.38	0.09	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	1.03	0.15	nd	nd
DAB87 38	87	3.76	0.05	0.01	0.45	0.02	0.56	0.04	0.76	0.27
DAB87 53	72	4.93	nd	nd	nd	nd	3.10	0.11	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	0.15	0.01	nd	nd
DAB84 28	80	4.56	0.08	0.01	0.64	0.11	0.43	0.04	0.50	0.12
DAB84 38	70	5.24	nd	nd	nd	nd	8.10	0.71	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	2.35	0.32	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	1.98	1.00	nd	nd
DAB83 42	65	7.87	3.48	0.07	4.23	0.14	1.29	0.27	4.30	0.03
DAB86 12-16	115-111	7.50	1.67	0.20	8.80	0.69	7.10	0.30	6.22	0.11
DCP211/2-3	121-120	vadose	0.03	0.01	0.22	0.05	0.39	0.04	0.24	0.04
DCP211/9-10	114-113	nd	0.01	0.00	0.59	0.08	0.84	0.03	0.36	0.06
DCP211/19-20	104-103	4.89	0.56	0.02	2.63	0.19	2.73	0.07	1.55	0.24
DCP211/35-36	88-87	4.69	0.26	0.03	0.84	0.03	1.98	0.14	0.51	0.05
DCP168/1.5-3.5	96-94	vadose	0.85	0.17	2.05	0.24	2.15	0.18	0.59	0.08
DCP168/20-22	77-78	5.61	4.79	0.27	5.21	0.30	3.99	1.33	2.41	0.25
DCP168/31-33	66-64	6.31	1.68	0.23	1.86	0.23	2.12	0.12	0.49	0.09
DCP170/1-3	96-94	vadose	0.06	0.04	0.31	0.15	0.46	0.17	0.29	0.09
DCP170/14-16	83-81	4.59	0.06	0.01	0.28	0.01	0.24	0.08	0.17	0.01
DCP170/20-22	77-75	5.83	0.19	0.04	0.83	0.06	0.85	0.07	0.93	0.16
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	nd	nd	1.11	0.07
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	nd	nd	0.25	0.04

nd = not determined

Table 14. Beryllium Soil Concentration (ppm) in Wetland Soil

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	0.77	0.12	1.48	0.15	nd	nd	1.44	0.28
D-4	5.94	0.69	0.04	1.83	0.27	nd	nd	1.68	0.14
G-10	6.12	1.39	0.20	7.07	0.31	nd	nd	5.24	0.63
H-5	6.02	1.40	0.15	4.55	0.59	nd	nd	3.70	0.28
J-6	5.13	1.11	0.04	6.08	0.83	nd	nd	3.95	0.20
K-4	4.52	1.41	0.05	5.27	0.69	nd	nd	3.40	0.66

nd = not determined

Table 15. Nickel Concentration (ppm) in Upland Soil

Soil Sample	Elevation	Pore-water	Nickel (soil ppm)							
	ft	pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	0.34	0.05	12.51	0.18	42.88	1.48	6.93	0.78
DAB92 21-23	95-93	4.12	1.68	1.09	nd	1.09	15.66	3.91	0.59	0.03
DAB85 32-33	99-98	5.18	26.65	5.55	38.25	6.84	42.51	3.78	6.31	0.27
DAB85 45	86	7.25	nd	nd	nd	nd	14.50	2.65	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	33.35	3.02	nd	nd
DAB81 45	83	4.26	18.31	1.59	21.00	2.75	26.79	3.09	1.74	0.04
DAB81 50	78	7.98	nd	nd	nd	nd	22.16	0.85	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	39.58	2.75	nd	nd
DAB87 38	87	3.76	31.91	7.64	40.34	8.19	2.73	0.13	3.44	0.46
DAB87 53	72	4.93	nd	nd	nd	nd	16.71	9.78	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	0.003		nd	nd
DAB84 28	80	4.56	22.81	0.43	25.75	0.50	0.47	0.66	1.44	0.04
DAB84 38	70	5.24	nd	nd	nd	nd	9.72	0.33	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	3.71	1.19	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	7.21	4.03	nd	nd
DAB83 42	65	7.87	54.10	1.78	56.49	1.79	2.08	0.33	39.02	1.09
DAB86 12-16	115-111	7.50	13.89	2.56	60.40	4.41	59.26	2.27	41.56	0.09
DCP211/2-3	121-120	vadose	4.19	2.87	14.84	5.10	nd	nd	3.78	1.00
DCP211/9-10	114-113	nd	2.52	0.37	15.85	2.58	nd	nd	3.87	0.48
DCP211/19-20	104-103	4.89	5.88	1.69	24.43	3.21	nd	nd	8.25	1.20
DCP211/35-36	88-87	4.69	7.12	1.23	13.43	1.24	9.51	0.00	0.99	0.08
DCP168/1.5-3.5	96-94	vadose	0.81	0.18	44.83	42.58	24.23	4.24	5.28	0.55
DCP168/20-22	77-78	5.61	21.51	0.74	36.14	12.59	29.78	6.18	19.12	1.91
DCP168/31-33	66-64	6.31	3.67	0.28	17.36	10.91	13.18	3.57	4.77	1.33
DCP170/1-3	96-94	vadose	0.59	0.18	26.21	10.76	13.96	0.34	4.69	1.79
DCP170/14-16	83-81	4.59	0.86	0.23	9.13	0.37	7.96	1.23	1.76	0.21
DCP170/20-22	77-75	5.83	5.68	0.37	18.34	3.41	13.87	0.68	7.50	0.12
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	nd	nd	8.99	0.21
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	nd	nd	1.87	0.35

nd = not determined

Table 16. Nickel Soil Concentration (ppm) in Wetland Soil

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	20.60	11.29	32.81	11.38	nd	nd	21.26	1.28
D-4	5.94	4.93	2.65	24.44	2.66	nd	nd	31.01	0.25
G-10	6.12	11.15	5.77	48.44	7.77	nd	nd	39.88	0.55
H-5	6.02	10.72	2.91	39.60	7.37	nd	nd	40.60	3.48
J-6	5.13	10.21	2.20	46.82	4.50	nd	nd	34.28	0.58
K-4	4.52	6.84	2.73	36.36	3.63	nd	nd	27.33	1.89

nd = not determined

Table 17. Uranium Concentration (ppm) in Upland Soil

Soil Sample	Elevation	Pore-water	Uranium							
	ft	pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	5.55	1.77	6.96	1.77	1.11	0.08	0.79	0.19
DAB92 21-23	95-93	4.12	1.20	0.58	1.23	0.59	0.29	0.09	0.15	0.08
DAB85 32-33	99-98	5.18	0.41	0.11	0.79	0.12	0.78	0.12	0.65	0.35
DAB85 45	86	7.25	nd	nd	nd	nd	0.28	0.08	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	1.28	0.04	nd	nd
DAB81 45	83	4.26	3.65	1.14	4.95	1.90	2.66	2.94	0.54	0.34
DAB81 50	78	7.98	nd	nd	nd	nd	0.74	0.07	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	2.24	0.13	nd	nd
DAB87 38	87	3.76	0.28	0.05	1.12	0.5	0.70	0.02	1.11	0.27
DAB87 53	72	4.93	nd	nd	nd	nd	1.22	0.09	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	0.21	0.01	nd	nd
DAB84 28	80	4.56	0.78	0.15	1.59	0.16	0.75	0.12	3.10	1.15
DAB84 38	70	5.24	nd	nd	nd	nd	4.55	0.04	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	3.12	0.46	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	1.52	0.89	nd	nd
DAB83 42	65	7.87	2.44	0.55	2.51	0.55	0.63	0.06	1.77	0.10
DAB86 12-16	115-111	7.50	3.14	0.79	13.25	2.82	7.27	0.17	5.12	0.01
DCP211/2-3	121-120	vadose	0.41	0.05	0.83	0.05	1.48	0.02	nd	nd
DCP211/9-10	114-113	nd	0.79	0.07	1.33	0.23	1.30	0.15	nd	nd
DCP211/19-20	104-103	4.89	1.04	0.03	2.09	0.16	2.12	0.06	nd	nd
DCP211/35-36	88-87	4.69	0.15	0.05	0.23	0.05	0.29	0.01	nd	nd
DCP168/1.5-3.5	96-94	vadose	nd	nd	nd	nd	4.03	0.35	nd	nd
DCP168/20-22	77-78	5.61	nd	nd	nd	nd	6.72	2.37	nd	nd
DCP168/31-33	66-64	6.31	1.73	0.36	3.10	0.42	2.99	0.14	nd	nd
DCP170/1-3	96-94	vadose	0.45	0.04	1.05	0.21	1.20	0.24	nd	nd
DCP170/14-16	83-81	4.59	0.11	0.01	0.44	0.08	0.51	0.09	nd	nd
DCP170/20-22	77-75	5.83	0.02	0.00	0.92	0.07	1.21	0.27	nd	nd
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	nd	nd	nd	nd
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	nd	nd	nd	nd

nd = not determined

Table 18. Uranium Soil Concentration (ppm) in Wetland Soil

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	2.45	0.47	3.71	0.58	nd	nd	2.46	0.19
D-4	5.94	1.82	0.13	3.86	0.14	nd	nd	2.97	0.04
G-10	6.12	2.80	0.48	5.93	0.58	nd	nd	4.18	0.01
H-5	6.02	2.85	0.42	4.94	0.63	nd	nd	3.22	0.00
J-6	5.13	2.24	0.08	5.29	0.39	nd	nd	3.11	0.05
K-4	4.52	2.04	0.12	3.98	0.21	nd	nd	2.96	0.05

nd = not determined

Table 19. Arsenic Concentration (ppm) in Upland Soil

Sample	Elevation	Pore-water	Arsenic							
Soil	ft	pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	0.16	0.01	2.25	0.05	1.17	0.12	1.48	0.92
DAB92 21-23	95-93	4.12	1.12	0.42	1.56	0.49	0.46	0.05	0.98	0.18
DAB85 32-33	99-98	5.18	1.91	0.49	5.61	4.80	1.84	0.17	1.79	0.21
DAB85 45	86	7.25	nd	nd	nd	nd	0.21	0.03	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	1.82	0.39	nd	nd
DAB81 45	83	4.26	0.11	0.04	0.58	0.51	1.03	0.53	0.66	0.22
DAB81 50	78	7.98	nd	nd	nd	nd	2.66	0.34	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	2.35	0.14	nd	nd
DAB87 38	87	3.76	0.05	0.01	0.72	0.03	0.84	0.40	0.59	0.12
DAB87 53	72	4.93	nd	nd	nd	nd	2.03	0.19	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	1.19	0.08	nd	nd
DAB84 28	80	4.56	0.03	0.01	0.11	0.07	0.99	0.07	1.22	0.26
DAB84 38	70	5.24	nd	nd	nd	nd	2.68	0.26	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	1.43	0.15	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	2.00	0.39	nd	nd
DAB83 42	65	7.87	1.82	0.07	3.17	0.14	2.20	0.24	14.62	1.05
DAB86 12-16	115-111	7.50	41.60	1.22	43.74	1.22	37.05	2.11	38.37	0.31
DCP211/2-3	121-120	vadose	1.22	0.20	2.78	0.21	2.01	0.04	2.14	1.21
DCP211/9-10	114-113	nd	1.32	0.05	3.29	0.23	2.56	0.14	2.89	0.32
DCP211/19-20	104-103	4.89	1.99	0.54	4.98	0.59	3.98	0.27	6.07	0.63
DCP211/35-36	88-87	4.69	2.31	0.50	2.81	0.51	1.32	0.04	1.56	0.39
DCP168/1.5-3.5	96-94	vadose	0.67	0.03	3.13	0.50	3.35	0.15	2.51	0.55
DCP168/20-22	77-78	5.61	11.39	0.20	15.87	1.71	15.86	5.10	18.03	1.45
DCP168/31-33	66-64	6.31	3.71	0.18	7.37	0.43	8.42	0.36	6.16	1.87
DCP170/1-3	96-94	vadose	0.88	0.03	3.02	0.34	1.99	0.08	5.19	0.74
DCP170/14-16	83-81	4.59	0.13	0.04	0.29	0.13	0.27	0.00	0.57	0.30
DCP170/20-22	77-75	5.83	0.34	0.03	0.75	0.09	0.79	0.05	0.99	0.43
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	nd	nd	3.33	0.05
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	nd	nd	2.33	1.08

nd = not determined

Table 20. Arsenic Soil Concentration (ppm) in Wetland Samples

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	3.62	0.33	6.36	0.73	nd	nd	3.21	0.02
D-4	5.94	3.75	0.41	7.75	0.61	nd	nd	3.00	0.88
G-10	6.12	40.42	1.88	44.24	1.89	nd	nd	24.76	1.99
H-5	6.02	75.76	13.51	77.93	13.51	nd	nd	53.97	1.81
J-6	5.13	37.66	4.38	40.81	4.42	nd	nd	28.48	1.43
K-4	4.52	75.14	5.78	78.32	5.80	nd	nd	51.01	6.41

nd = not determined

Table 21. Selenium Soil Concentration (ppm) in Wetland Samples

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	2.09	0.83	2.09	0.83	nd	nd	1.53	0.32
D-4	5.94	1.93	0.43	1.93	0.44	nd	nd	1.88	0.08
G-10	6.12	6.92	1.02	6.92	1.03	nd	nd	5.23	0.27
H-5	6.02	9.91	2.57	10.06	2.58	nd	nd	6.18	0.49
J-6	5.13	5.06	1.31	5.33	1.37	nd	nd	3.48	0.15
K-4	4.52	4.79	0.90	5.75	1.17	nd	nd	3.90	0.37

nd = not determined

Table 22. Vanadium Soil Concentration (ppm) in Wetland Samples

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	21.83	1.84	70.93	9.25	nd	nd	70.96	1.74
D-4	5.94	27.52	1.08	100.61	7.46	nd	nd	103.34	0.07
G-10	6.12	40.68	0.37	127.01	3.50	nd	nd	94.36	2.72
H-5	6.02	45.01	1.32	102.81	8.34	nd	nd	74.15	0.59
J-6	5.13	25.99	2.00	119.37	13.81	nd	nd	61.20	2.34
K-4	4.52	35.99	0.41	106.98	5.06	nd	nd	62.49	0.37

nd = not determined

Table 23. Iron Concentration (ppm) in Upland Soil

Sample Soil	Elevation	Pore-water pH	Iron Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	1334.45	53.11	nd	114.24	73632.85	272.74	5435.21	65.72
DAB92 21-23	95-93	4.12	616.70	22.18	nd	22.89	2192.09	453.96	1435.98	157.55
DAB85 32-33	99-98	5.18	794.62	108.07	2232.42	194.68	2077.70	596.62	1384.70	106.32
DAB85 45	86	7.25	nd	nd	nd	nd	1060.34	169.08	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	10230.13	1208.18	nd	nd
DAB81 45	83	4.26	312.15	120.91	11728.36	12060.72	12253.03	10399.3	1368.40	337.66
DAB81 50	78	7.98	nd	nd	nd	nd	5003.50	500.27	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	12169.85	900.77	nd	nd
DAB87 38	87	3.76	278.21	13.36	2506.72	128.77	2558.39	62.20	1904.12	224.26
DAB87 53	72	4.93	nd	nd	nd	nd	13572.85	720.75	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	436.81	29.69	nd	nd
DAB84 28	80	4.56	157.84	26.53	3721.52	443.74	4485.47	49.80	1547.11	57.31
DAB84 38	70	5.24	nd	nd	nd	nd	32714.71	1727.07	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	8341.16	912.79	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	15091.65	6634.69	nd	nd
DAB83 42	65	7.87	5055.30	402.89	12782.63	1012.69	5179.26	144.02	16143.15	725.37
DAB86 12-16	115-111	7.50	3460.22	399.21	5558.67	399.67	12169.85	900.77	23906.77	12.32
DCP211/2-3	121-120	vadose	518.65	88.63	4250.72	174.95	6975.00	445.48	4014.50	183.14
DCP211/9-10	114-113	nd	405.49	10.91	8876.36	864.37	13050.00	494.97	6472.50	144.96
DCP211/19-20	104-103	4.89	6151.74	553.62	30682.40	1517.27	43000.00	1414.21	27235.00	3358.76
DCP211/35-36	88-87	4.69	461.98	15.30	3548.04	18.19	3370.00	438.41	2984.50	253.85
DCP168/1.5-3.5	96-94	vadose	999.80	21.73	17520.63	1941.15	13700.00	141.42	7063.00	328.10
DCP168/20-22	77-78	5.61	3974.52	139.49	14500.54	2127.05	20200.00	707.11	10005.00	742.46
DCP168/31-33	66-64	6.31	1757.17	416.09	6491.02	2312.52	4240.00	127.28	4057.50	1225.42
DCP170/1-3	96-94	vadose	546.40	14.68	6533.58	1008.54	16500.00	0.00	11322.50	3899.69
DCP170/14-16	83-81	4.59	58.68	2.94	2152.45	165.5	3560.00	70.71	980.15	50.70
DCP170/20-22	77-75	5.83	1294.73	51.46	10877.17	1081.57	12650.00	777.82	7783.50	164.76
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	13300.00	424.26	12550.00	70.71
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	3495.00	162.63	3388.50	70.00

nd = not determined

Table 24. Iron Soil Concentration (ppm) in Wetland Samples

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	8296.42	321.27	27724.43	3938.85	nd	nd	28813.39	374.77
D-4	5.94	10266.99	472.19	38027.96	2924.02	nd	nd	42488.39	226.27
G-10	6.12	4199.74	45.14	18349.47	1210.72	nd	nd	14315.89	137.89
H-5	6.02	8667.03	1065.73	26402.35	2358.32	nd	nd	26553.39	233.35
J-6	5.13	3742.10	230.64	24731.63	2457.50	nd	nd	16473.39	1053.59
K-4	4.52	6609.40	1178.79	20434.66	2015.63	nd	nd	15563.39	459.62

nd = not determined

Table 25. Aluminum Concentration (ppm) in Upland Soil

Soil Sample	Elevation	Pore-water pH	Aluminum							
			Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
DAB92 4-6	112-110	3.18	320.11	38.48	nd	39.00	28603.09	1049.25	20007.41	2091.76
DAB92 21-23	95-93	4.12	185.95	10.01	nd	10.67	5384.88	1094.62	3632.70	548.10
DAB85 32-33	99-98	5.18	23.06	1.65	19041.12	219.65	20420.21	5721.73	8669.16	503.79
DAB85 45	86	7.25	nd	nd	nd	nd	6453.47	645.75	nd	nd
DAB81 30-35	98	4.80	nd	nd	nd	nd	36687.64	3106.07	nd	nd
DAB81 45	83	4.26	42.95	5.67	15271.99	9329.49	13760.95	4903.58	2175.74	245.54
DAB81 50	78	7.98	nd	nd	nd	nd	323.17	72.96	nd	nd
DAB87 33	92	3.81	nd	nd	nd	nd	38385.74	4840.10	nd	nd
DAB87 38	87	3.76	45.01	2.28	18987.54	166.03	18579.78	452.71	8755.14	1128.54
DAB87 53	72	4.93	nd	nd	nd	nd	49370.24	3225.11	nd	nd
DAB84 20	88	5.06	nd	nd	nd	nd	8886.81	334.66	nd	nd
DAB84 28	80	4.56	40.76	3.75	13301.22	6756.92	10599.10	160.59	4570.27	124.42
DAB84 38	70	5.24	nd	nd	nd	nd	51005.05	2846.27	nd	nd
DAB83 32	75	6.61	nd	nd	nd	nd	32649.23	5229.62	nd	nd
DAB83 38	69	7.50	nd	nd	nd	nd	37301.56	18768.72	nd	nd
DAB83 42	65	7.87	33.08	2.56	3186.08	832.82	486.48	90.95	6353.72	46.61
DAB86 12-16	115-111	7.50	14.26	5.38	113.08	32.25	38385.74	4840.10	28333.90	52.10
DCP211/2-3	121-120	vadose	29.16	1.90	7704.23	616.81	15990	1965.76	5635.50	1331.48
DCP211/9-10	114-113	nd	43.53	7.08	11043.28	88.93	60400	13717.87	11496.00	2381.54
DCP211/19-20	104-103	4.89	32.58	6.34	10959.44	166.55	20250	212.13	6641.00	1712.61
DCP211/35-36	88-87	4.69	320.29	8.16	972.94	8.26	1125	91.92	356.10	7.50
DCP168/1.5-3.5	96-94	vadose	1005.17	18.37	11660.69	1468.32	43000	1555.63	13360.00	1725.34
DCP168/20-22	77-78	5.61	402.86	17.54	5004.49	1231.26	15250	494.97	2212.50	348.60
DCP168/31-33	66-64	6.31	160.37	4.77	1795.35	465.44	3715	1251.58	420.10	44.41
DCP170/1-3	96-94	vadose	495.73	13.15	12168.59	830.99	50850	777.82	10769.50	2617.00
DCP170/14-16	83-81	4.59	340.00	3.48	11346.44	426.80	21000	1131.37	3207.00	173.95
DCP170/20-22	77-75	5.83	59.14	1.13	10875.96	168.37	31650	1909.19	4651.50	137.89
DCP171/1-3	96.5-94.5	vadose	nd	nd	nd	nd	36850	6576.09	15865.00	120.21
DCP171/24-26	73.5-71.5	6.13	nd	nd	nd	nd	18900	2404.16	2695.50	457.50

nd = not determined

Table 26. Aluminum Soil Concentration (ppm) in Wetland Samples

Sample	Pore-water pH	Sum 1-6	st dev	Sum 1-8	st dev	TD	st dev	3050b	st dev
D-2	5.49	45.17	1.78	51162	14971	nd	nd	46961.95	3641.60
D-4	5.94	43.68	5.10	77305	2331	nd	nd	79766.95	1385.93
G-10	6.12	30.11	1.72	68112	6713	nd	nd	36924.45	661.14
H-5	6.02	26.54	0.45	44752	7415	nd	nd	21871.95	21.21
J-6	5.13	105.60	11.54	70372	8585	nd	nd	27176.95	1258.65
K-4	4.52	131.92	8.30	54409	6319	nd	nd	23276.95	353.55

nd = not determined

5.2 MICROBIOLOGICAL CHARACTERIZATION

Table 27 presents results of the total bacterial densities, viable and culturable bacterial densities, and results from anaerobic, iron reducing bacteria (IRB), acid producing bacteria (APB), and sulfate reducing bacteria (SRB) from the upland sediments. Table 28 presents results of the total bacterial densities and viable, culturable microbial colony forming units (CFU) from the wetland sediments. Results for both Table 27 and Table 28 are reported in cells or CFU for viable, culturable bacteria per gram wet weight sediment. Biological data (total counts, viable counts, and substrate utilization) are also represented in cross-sectional form (Figure 15 through Figure 18) for a subset of upland and wetland locations to show vertical stratification. Biological data for all wetland locations is posted to map locations in Figure 19.

IRB are involved in the reduction of Fe(III) to Fe(II), and as such, would be expected to be more abundant in reducing environments. SRB are involved in reducing sulfate to sulfide; they generally require a more reducing environment than IRB. SRB may be desirable for MNA of many inorganic contaminants in the DEXOU because they may either directly convert some COCs, such as U (Lovely et al. 1991), from the more mobile oxidized form to the less mobile reduced form, or they may form sulfides that form sparingly soluble precipitates with the COC, such as Ni or UO_2^{2+} (Stumm and Morgan 1996). APB are commonly iron-oxidizing autotrophic bacteria that use Fe^{2+} as an energy source and CO_2 as a C source. They occur widely in mining regions where coal and mineral deposits contribute sulfide minerals (e.g., pyrite) to the soil and sediment. Such bacteria are typically believed to be responsible for the acidity associated with coal pile leachate.

Acid-producing bacteria (APB) were detected in only two Upland soil samples – DAB 92 21 and DAB 81 50. The presence of APB in DAB 92 21 is not surprising given the close proximity of this sample to the coal pile (DCPRB). Iron reducing bacteria (IRB) were detected in only one Upland soil sample, DAB 81 50. Sulfate reducing bacteria (SRB) were detected in only one Upland soil sample, DAB 92 21. This finding suggests that the sampling transect is largely aerobic, with limited chance for biological reduction to occur. The lack of APB, IRB, and SRB detection, with the exception of three sediment samples, typically indicate low nutrients conditions in the associated sediment and groundwater. Addition of nutrients to groundwater can stimulate the growth of these bacteria at this site (Phifer et al., 2001). Their absence may be attributed to lack of nutrients or to the redox status of the wetland.

Bacterial densities for both plate (viable) counts and total (direct) counts were generally higher in the Wetland sediments (Table 28) as compared to the Upland sediments (Table 27, Figure 16 and Figure 17). However, it is important to note that the upland sediment samples were generally collected from deeper locations (4' to 53') than the wetland samples (surface 1 ft depth). In Figure 20, all locations were sorted by direct counts with the wetland locations demonstrating the highest total numbers of organisms (right side of graph).

The wetland sediments also could be further separated into groupings based on locations and microbiological results (Table 28). Samples H-5, J-6, and K-4 (Figure 19), are located near or in an area that received sluiced coal ash (Figure 3) and to another area with a contaminated outcropping from the DCPRB plume (Figure 2). These samples had lower total direct counts and plate counts compared to wetland samples G-10, D-2, and D-4, located further from the impacted areas. G-10 is an ash sample from the ash deposition area, and D-2 and D-4 are soil samples from an area presumed to be unimpacted. Porewater from sediments at locations K-4 and J-6 had the lowest pH of the wetlands. Therefore, the lower bacterial densities could be a result of contaminant exposure as well as other environmental factors including nutrient availability.

Microbial data from sediments using Biolog® for substrate utilization demonstrated different trends for all cores tested (Table 29 and Table 30, Figure 18 and Figure 19). In Table 29 and Table 30, the difference in the number of Biolog ® positives represents the quantity of total substrates in a particular class utilized (of 95 total substrates) in sediments. Overall there appeared to be more activity in the wetland (Table 30) ash as compared to the upland soils (Table 29). Greater and wider usage of Biolog ® substrates by bacteria from the wetland sediments indicates higher species diversity. Higher diversity indicates a healthy robust microbial population with multiple functions including ability to absorb/alter contaminants. However, as mentioned previously, comparisons between these sediment samples can only be viewed as general trends because of the differences in the depth of collection.

Figure 18, Figure 19, and Figure 24 demonstrate comparative differences of Biolog® ecofunctional enzyme activity as a function of sample location. Figure 23 is sorted by sulfate concentrations and shows the percent responses to all the carbon sources. Pore water pH varies between 3 and 8 and may have slightly decreased as the sulfate concentrations increased. Clearly, there is no linear trend with percent response versus sample locations as they are arranged in either figure. The Wetland samples appear to fall in two groups. The wetland locations D-2, D-4, and G-10 all have >40% substrate activity (all carbon sources tested) while H-5, J-6, and K-4 all have <15% activity (all carbon sources tested). D-4 and G-10 had particularly active aerobic populations with ~70% substrate activity (all carbon sources tested). These locations can also be related to physical position with relation to the sites (Figure 19 and Figure 24). The wetland locations D-2, D-4, and G-10 are furthest from potential contaminant sources (including the DCP, the DCPRB (D-Area Coal Pile Runoff Basin), DAB (488-D) (Figure 3), and the wetland outcropping located north and east of sample H5 (Figure 2). Therefore the increase microbial activity associated with these latter sites is likely due to natural conditions and lack of contamination. Conversely, locations H-5, J-6, and K-4 are all nascent to the contaminant source areas. The Biolog ® results indicate that even though H-5, J-6, and K-4 are in the wetland area and sediment samples were taken at the same depths (1 ft) as locations D-2, D-4 and G-10, the microbial activity is significantly different.

Discriminant Analysis of the Biolog® testing of the soil slurry indicated that the Biolog structures of H-5 and K-4, (i.e., the way microbial communities in sample H-5 and K-4 utilized various carbon substrates) were more similar to microbial communities in Upland soils than wetland soils (Figure 25). By way of example, the red lines in Figure 25 identify the region where the microbial community has a 75% chance of having the typical Upland type of Biolog® test results. The cause for this result may be attributed to a number of spatial attributes, including the proximity of these sample locations to: 1) the sluiced coal ash, 2) a potential contaminant groundwater outcropping, and 3) to the Upland area. Another possibility is that this outcome is the result of simple natural heterogeneity. This latter explanation is less likely because this discussion is already based on statistics, which by definition accounts for variability. The implications of this finding may be that the microbial community of H-5 and K-4 are impacted by operations in a manner similar to Upland microbial communities. As such, the ability of the transformed microbial community to contribute to attenuation contaminant transport will take on more of the character of the Upland communities than of the Wetland communities. It may also indicate that the microbial communities may be expected to change as the plume moves through a site, not an altogether surprising conclusion. Additional notes on the Discriminant Analysis are presented in Appendix D.

Ecofunctional enzyme activity also varied as a function of physical and chemical parameters (Figure 26). As was stated previously, the wetland samples were all taken at shallow depths while the upland samples varied in depth (Figure 26). When comparing chemical parameters including As, Be, Ni, SO_4, and U, porewater concentrations, two or three of the wetlands samples would often demonstrate distinctive differences (Figure 26). Since these porewater contaminant concentrations are below the toxicity concentration for most microbes, the diversity between samples should be associated with removal, not with toxicity to the microorganisms. Examination of the analytical and microbiological data indicates that both contaminant concentrations and location were correlated with microbial activity. D-2 and D-4, the two wetland sites closest to the Savannah River and furthest from the source zone, had very low porewater sulfate concentrations (< 10ppm) (Table 6) and had high ecofunctional enzyme activity. G-10 also had low sulfate porewater concentration in comparison to other wetland sample locations (Table 6) and had very high (69%, all carbon sources tested) aerobic ecofunctional enzyme activity. Conversely, H-5, J-6, and K-4 had high porewater sulfate concentrations (>100ppm) (Table 6) and low (< 15%, all carbon sources tested) aerobic ecofunctional enzyme activity (Figure 25).

Figure 26 demonstrates the relationship between EFE (all carbon sources tested by Biolog) and As, Be, Ni, S, and U. While all metal concentrations were lower than toxicity levels, there were relationships observed between microbial activity and contaminant concentrations. Wetlands were higher in As porewater concentrations than most upland samples, especially G-10, H-5, and K-4. Of the higher As wetland grouping only G-10 showed high EFE activity. Nonimpacted wetland locations D-4 and D-2 also showed high EFE activity. For Ni and Be, the uplands generally tested higher than wetland sediments and there was little relation to EFE activity. U was similar to As in that wetland locations were higher that correlated to increased EFE activity.

The results of the pH buffering capacity test are given in Table 31. The Biolog® GN Microplates, as used in the ecofunctional enzyme study, have a strong and immediate buffering capacity to the liquids added to them. Any initial differences in the pH range of 4 to 5 of the added soil slurries would be buffered to near neutral when added to the Biolog® GN Microplates. As such, this strong buffering capacity is an experimental artifact in that it tests the microbes at a pH other than their natural pH. Although these culture conditions may compromise the data, it still remains that the tests provide a useful index that may not be possible if the pH was permitted to fluctuate.

In a subsequent series of experiments the ability of isolated D-Area bacteria (Table 32) to adjust pH was successfully tested. See Table 33 through Table 35 for further information.

Table 27. Upland Soils Bacterial Counts

(Results expressed as a percentage of positive responses for carbon substrates tested by type of substrate as well as for all carbon sources.)

	DAB-92 4' - 6'	DAB-92 21'	DAB-92 23'	DAB-81 30'	DAB-81 45'	DAB-81 50'	DAB-87 33'	DAB-87 38'	DAB-87 53'	DAB-84 20'	DAB-84 28'	DAB-84 38'	DAB-83 32'	DAB-83 38'	DAB-83 42'
Sampling Date	6/12/02	6/12/02	6/12/02	7/25/02	7/25/02	7/25/02	7/29/02	7/29/02	7/29/02	7/30/02	7/30/02	7/30/02	7/23/02	7/23/02	7/23/02
Total Direct Counts (# cells/g wet wt)	2.11E+08	7.77E+08	6.88E+08	8.68E+05	2.78E+06	2.21E+07	5.60E+07	8.89E+08	9.38E+07	1.10E+07	2.59E+08	1.20E+08	6.24E+06	2.18E+07	2.27E+08
IRB* / (# cells/g wet wt)	< 10	< 10	< 10	< 10	< 10	1.00E+01 to 1.00E+02	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
APB* / (# cells/g wet wt)	< 10	1.00E+01 to 1.00E+02	< 10	< 10	< 10	1.00E+04 to 1.00E+05	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
SRB* / (# cells/g wet wt)	< 10	1.00E+01 to 1.00E+02	>10E+06	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
PTYG (CFU/g) pH 7.0 incubated aerobically	1.10E+04	2.50E+04	<25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PTYG (CFU/g) pH 5.0 incubated aerobically	4.00E+04	>3.00E+06	1.10E+05	5.00E+04	5.00E+05	6.00E+04	<25	1.48E+06	2.40E+05	ND	3.90E+06	>3.00E+06	9.00E+04	3.00E+04	6.00E+04
PTYG (CFU/g) pH 4.0 incubated aerobically	<25	5.00E+04	2.00E+03	5.00E+04	>3.00E+05	>3.00E+06	<25	6.50E+05	1.76E+06	ND	2.00E+06	2.00E+06	1.70E+05	6.10E+05	1.11E+06
PTYG (CFU/g) pH 3.0 incubated aerobically	2.40E+04	1.00E+03	3.00E+04	2.00E+04	1.10E+05	1.10E+05	<25	<25	1.56E+06	ND	>3.00E+06	7.40E+05	7.20E+04	1.20E+04	1.00E+03
1% PTYG (CFU/g) pH 7.0 incubated aerobically	7.90E+04	<25	<25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1% PTYG (CFU/g) pH 5.0 incubated aerobically	6.00E+04	1.50E+05	3.00E+04	<25	<25	3.00E+05	<25	>3.00E+06	<25	ND	ND	<25	1.50E+05	1.12E+06	1.26E+06
1% PTYG (CFU/g) pH 4.0 incubated aerobically	7.00E+04	4.00E+04	5.00E+04	<25	1.00E+04	>3.00E+05	<25	<25	<25	ND	2.60E+06	<25	2.00E+05	5.00E+04	<25
1% PTYG (CFU/g) pH 3.0 incubated aerobically	<25	5.00E+03	1.00E+02	<25	N.D.	1.10E+05	<25	<25	<25	ND	5.60E+05	>3.00E+05	<25	<25	7.00E+03
Anaerobic PYG (CFU/g) incubated anaerobically	<25	<25	<25	<25	<25	<25	<25	<25	<25	ND	<25	<25	<25	<25	<25
PTYG pH 7.0 (CFU/g) incubated anaerobically	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1% PTYG pH 7.0 (CFU/g) incubated anaerobically	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

CFU/g = Colony Forming Unit per gram wet weight soil
IRB = Iron Reducing Bacteria
APB = Acid Producing Bacteria
SRB = Sulfate Reducing Bacteria
ND = not determined

Table 28. Wetland Soils Bacterial Counts

Wetland Soils Bacterial Counts	G-10 1 ft	D-2 1ft	D-4 1ft	H-5 1ft	J-6 1ft	K-4 1ft
Sampling Date	6/25/03	6/26/03	6/26/03	7/22/03	7/22/03	7/22/03
Total Direct Counts (# cells/g wet wt)	2.02E+11	2.72E+10	7.18E+10	1.77E+09	2.07E+10	3.51E+09
IRB* / (# cells/g wet wt)	ND	ND	ND	ND	ND	ND
APB* / (# cells/g wet wt)	ND	ND	ND	ND	ND	ND
SRB* / (# cells/g wet wt)	ND	ND	ND	ND	ND	ND
PTYG (CFU/g) pH 7.0 incubated aerobically	1.26E+05	2.68E+07	1.34E+07	1.89E+07	1.38E+07	1.05E+07
PTYG (CFU/g) pH 5.0 incubated aerobically	ND	ND	ND	ND	ND	ND
PTYG (CFU/g) pH 4.0 incubated aerobically	ND	ND	ND	ND	ND	ND
PTYG (CFU/g) pH 3.0 incubated aerobically	ND	ND	ND	ND	ND	ND
1% PTYG (CFU/g) pH 7.0 incubated aerobically	2.91E+04	1.45E+07	1.69E+07	1.27E+07	6.29E+04	1.18E+05
1% PTYG (CFU/g) pH 5.0 incubated aerobically	ND	ND	ND	ND	ND	ND
1% PTYG (CFU/g) pH 4.0 incubated aerobically	ND	ND	ND	ND	ND	ND
1% PTYG (CFU/g) pH 3.0 incubated aerobically	ND	ND	ND	ND	ND	ND
Anaerobic PYG (CFU/g) incubated anaerobically	ND	ND	ND	9.27E+06	1.33E+07	1.31E+07
PTYG pH 7.0 (CFU/g) incubated anaerobically	1.25E+04	1.22E+07	1.28E+07	1.12E+07	9.62E+03	1.37E+04
1% PTYG pH 7.0 (CFU/g) incubated anaerobically	< 25	3.92E+06	5.72E+06	< 25	6.99E+03	7.30E+03

CFU/g = Colony Forming Unit per gram wet weight soil IRB = Iron Reducing Bacteria
APB = Acid Producing Bacteria SRB = Sulfate Reducing Bacteria ND = not determined

Table 29. Biolog® Testing of Upland Soil Slurry

Sample	Dilution Tested		all carbon sources tested (95 total)	polymers (5 total)	carbohydrates (28 total)	esters (2 total)	carboxylic acids (24 total)	amides (3 total)	amino acids (20 total)	aromatic chemicals (4 total)	amines (3 total)	alcohols (2 total)	phosphorylated chemicals (3 total)
DAB 92 4 – 6 ft	1/1000	% positive	16	0	14	0	25	67	10	25	0	0	0
DAB 92 21 ft	1/1000	% positive	6	0	4	0	8	0	5	0	0	50	0
DAB 92 23 ft	1/1000	% positive	3	0	7	0	4	0	0	0	0	0	0
DAB 81 30 ft	1/100	% positive	46	40	54	50	54	67	40	0	33	50	0
DAB 81 45 ft	1/100	% positive	2	40	0	0	0	0	0	0	0	0	0
DAB 81 50 ft	1/100	% positive	42	40	7	100	58	33	70	25	67	50	0
DAB 87 33 ft	1/100	% positive	7	0	7	0	13	33	5	0	0	0	0
DAB 87 38 ft	1/100	% positive	0	0	0	0	0	0	0	0	0	0	0
DAB 87 53 ft	1/100	% positive	0	0	0	0	0	0	0	0	0	0	0
DAB 84 20 ft	1/1000	% positive	2	40	0	0	0	0	0	0	0	0	0
DAB 84 28 ft	1/1000	% positive	29	20	39	0	42	0	30	0	0	0	0
DAB 84 38 ft	1/1000	% positive	4	0	7	50	4	0	0	0	0	0	0
DAB 83 32 ft	1/100	% positive	0	0	0	0	0	0	0	0	0	0	0
DAB 83 38 ft	1/100	% positive	0	0	0	0	0	0	0	0	0	0	0
DAB 83 42 ft	1/100	% positive	42	0	46	100	42	0	50	0	0	100	100

Table 30. Biolog® Testing of Wetland Soil Slurry

	Dilution Tested		all carbon sources tested (95 total)	polymers (5 total)	carbohydrates (28 total)	esters (2 total)	carboxylic acids (24 total)	amides (3 total)	amino acids (20 total)	aromatic chemicals (4 total)	amines (3 total)	alcohols (2 total)	phosphorylated chemicals (3 total)
G-10, 1 ft	1/100	% positive	69	40	71	50	63	33	80	75	67	100	100
D-2, 1 ft	1/100	% positive	41	0	39	50	46	0	60	50	33	0	33
D-4, 1 ft	1/100	% positive	72	100	86	50	54	0	70	100	67	50	100
H-5, 1ft	1/100	% positive	4	0	7	0	4	0	0	0	0	0	0
J-6, 1 ft	1/100	% positive	14	20	25	0	8	0	5	25	0	0	0
K-4, 1 ft	1/100	% positive	0	0	0	0	0	0	0	0	0	0	0

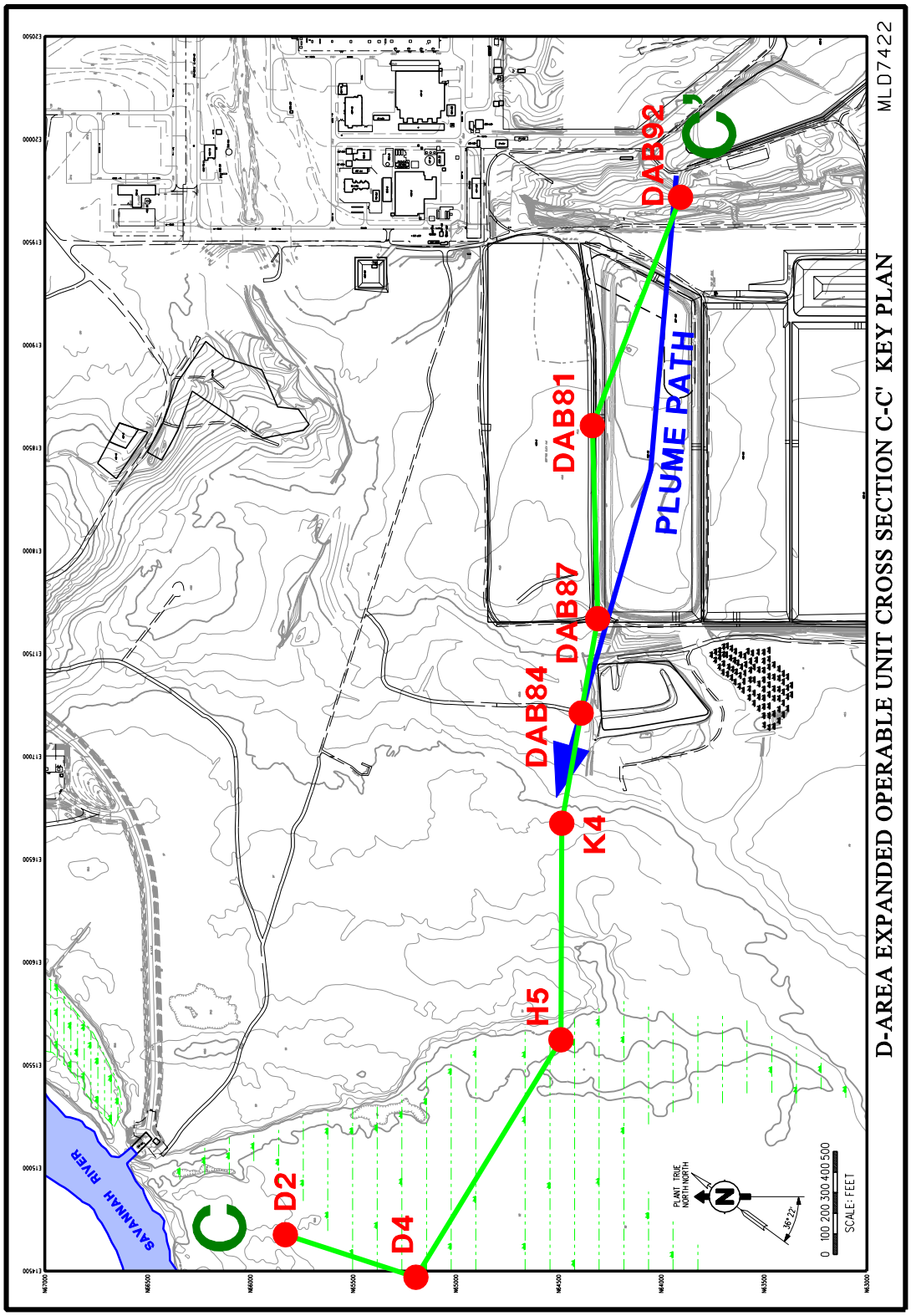


Figure 15. D-Area Expanded Operable Unit Key Plan−Cross Section C-C′−Biological data

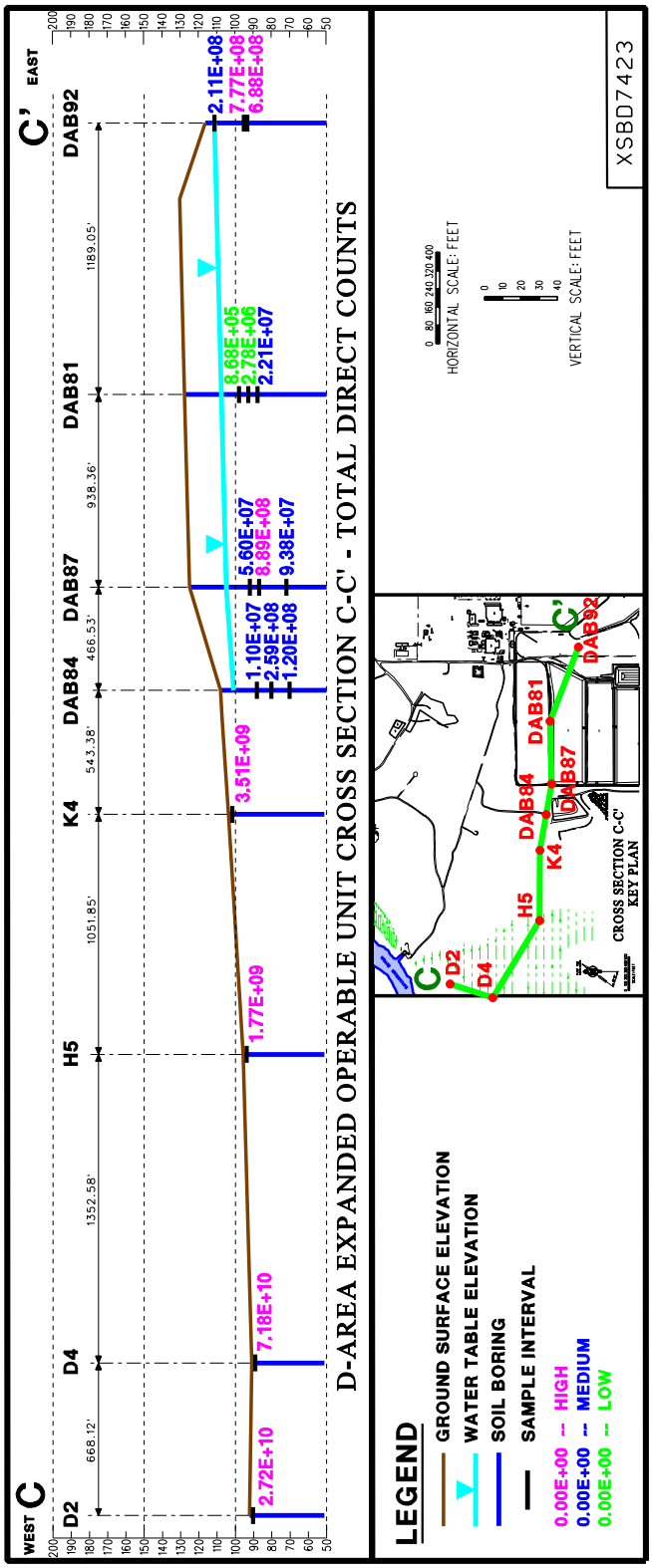


Figure 16. D-Area Expanded Operable Unit Cross Section C-C′−Total Direct Counts

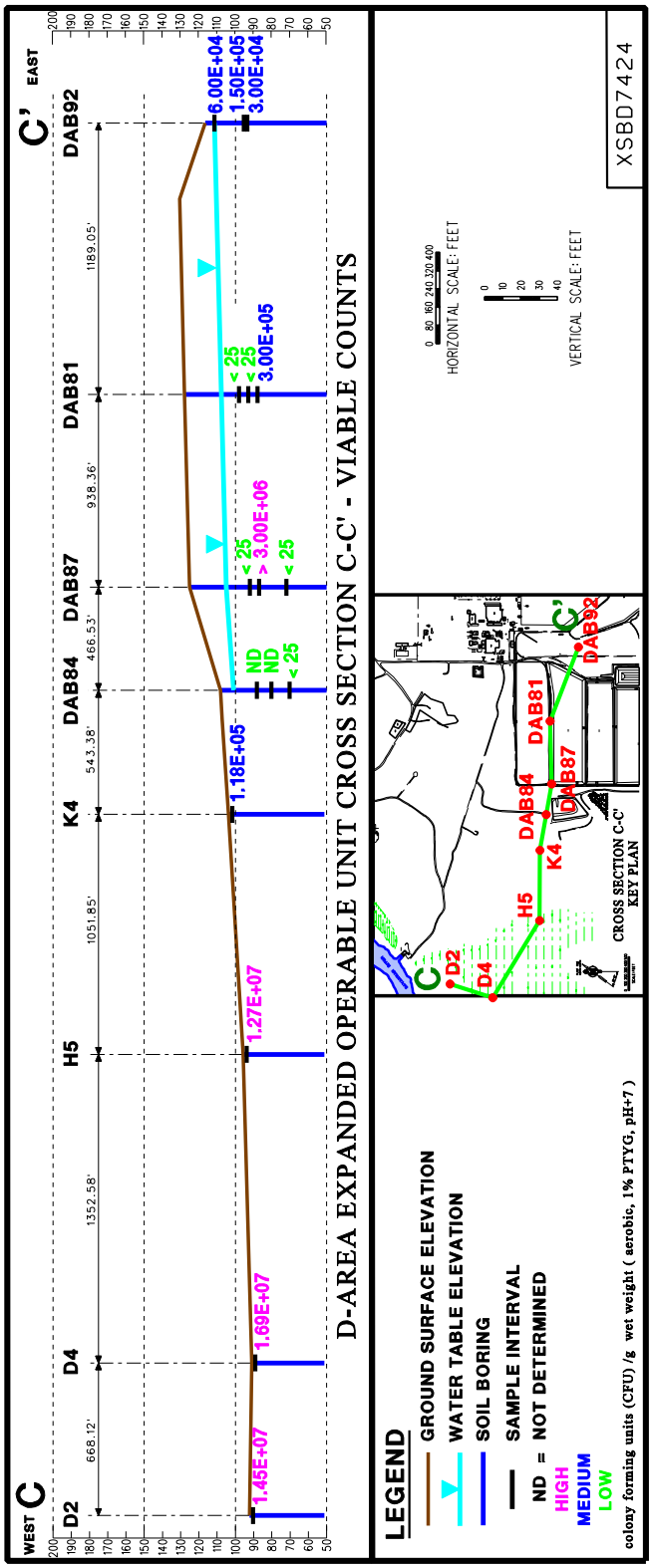


Figure 17. D-Area Expanded Operable Unit Cross Section C-C′−Viable Counts

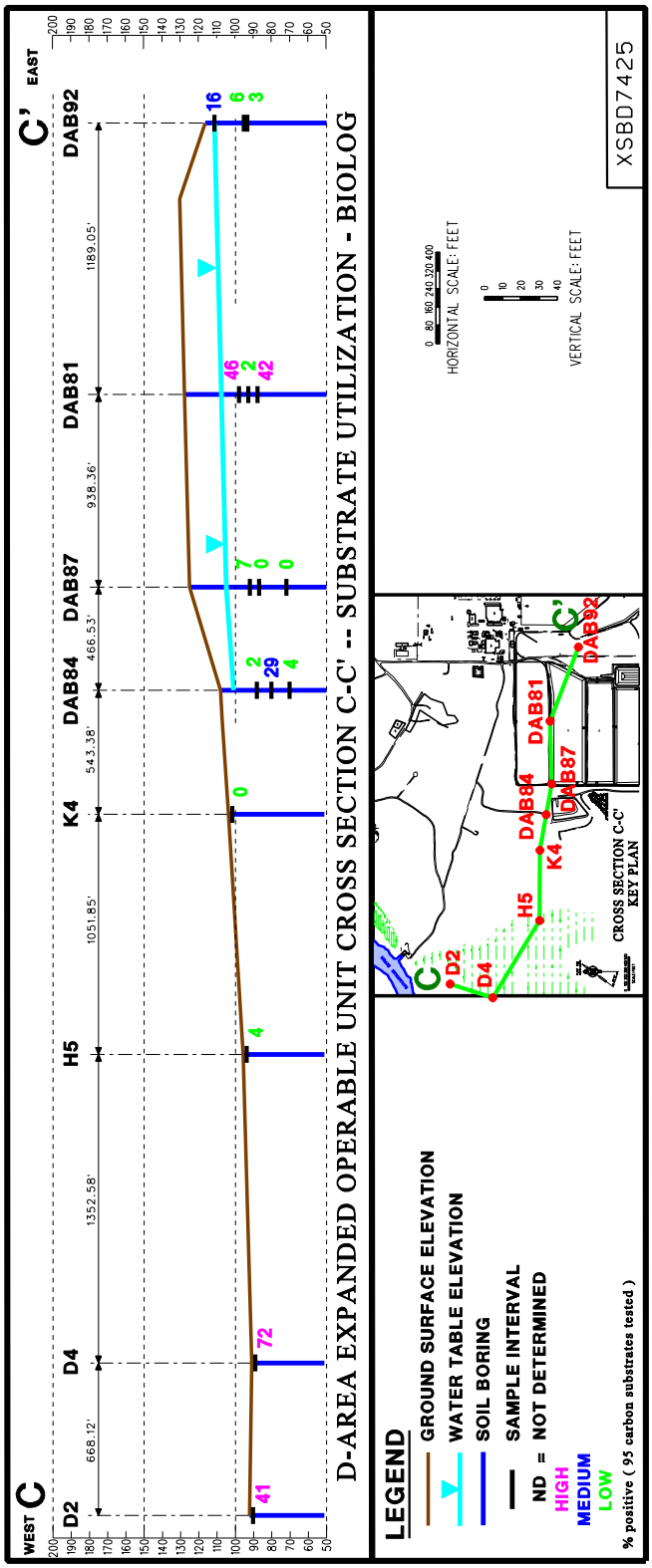


Figure 18. D-Area Expanded Operable Unit Cross Section C-C′−Substrate Utilization by Biolog®

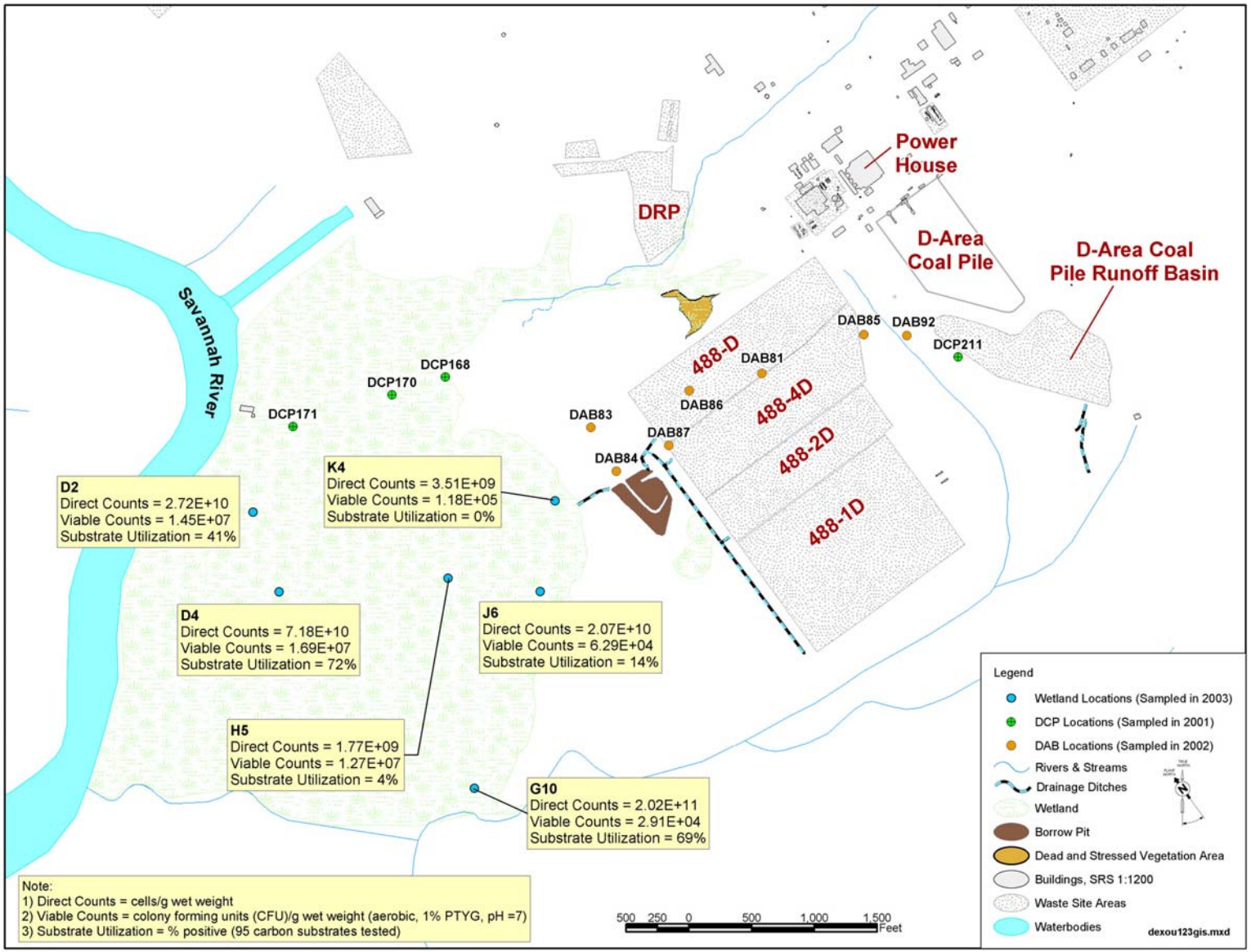


Figure 19. Microbiological Data for Wetland Locations

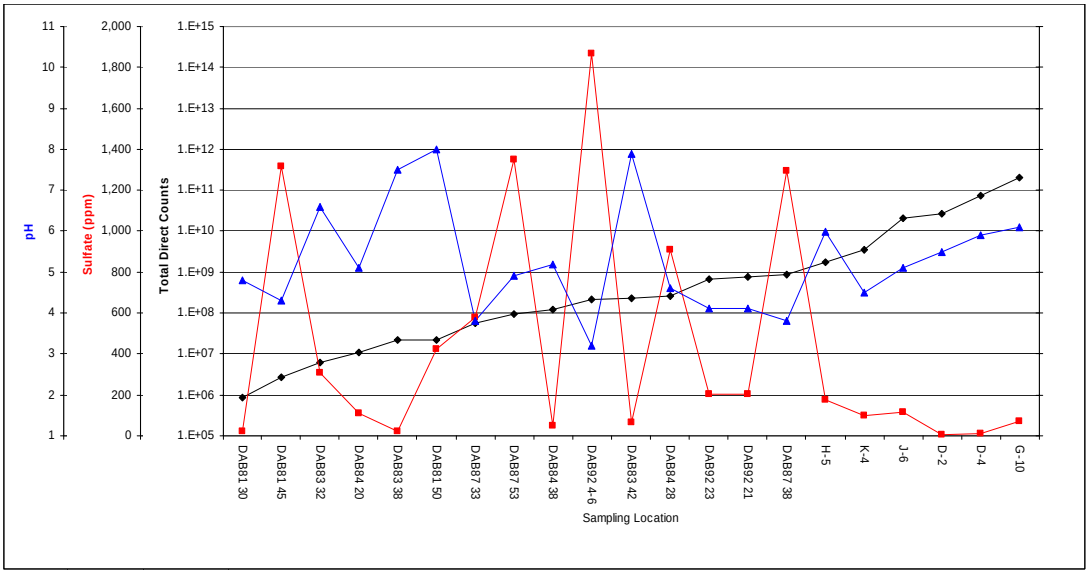


Figure 20. Plot of pH, Sulfate, and Direct Counts Ordered by Direct Counts

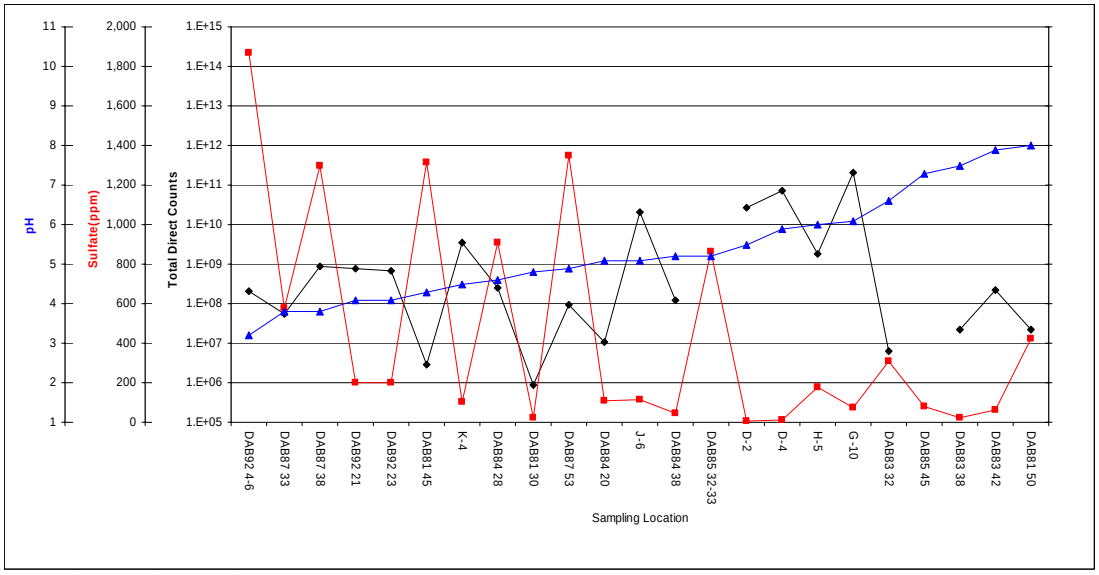


Figure 21. Plot of pH, Sulfate, and Direct Counts Ordered by pH

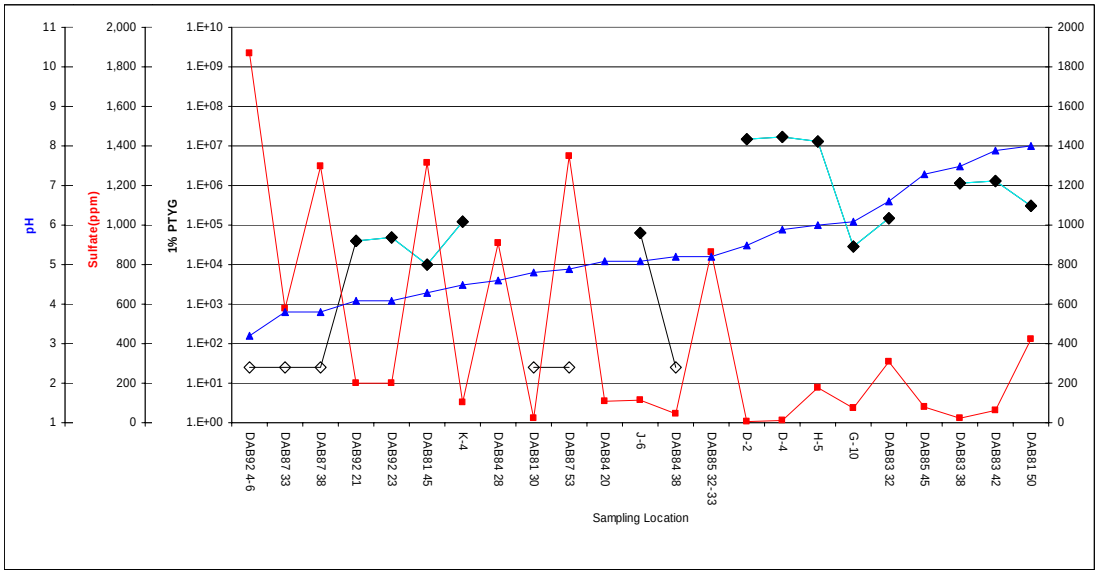


Figure 22. Plot of pH, Sulfate, and 1% PTYG (pH 5.0) Ordered by pH [less-than detect 1%PTYG (values=25) are plotted without coloring in the diamond]

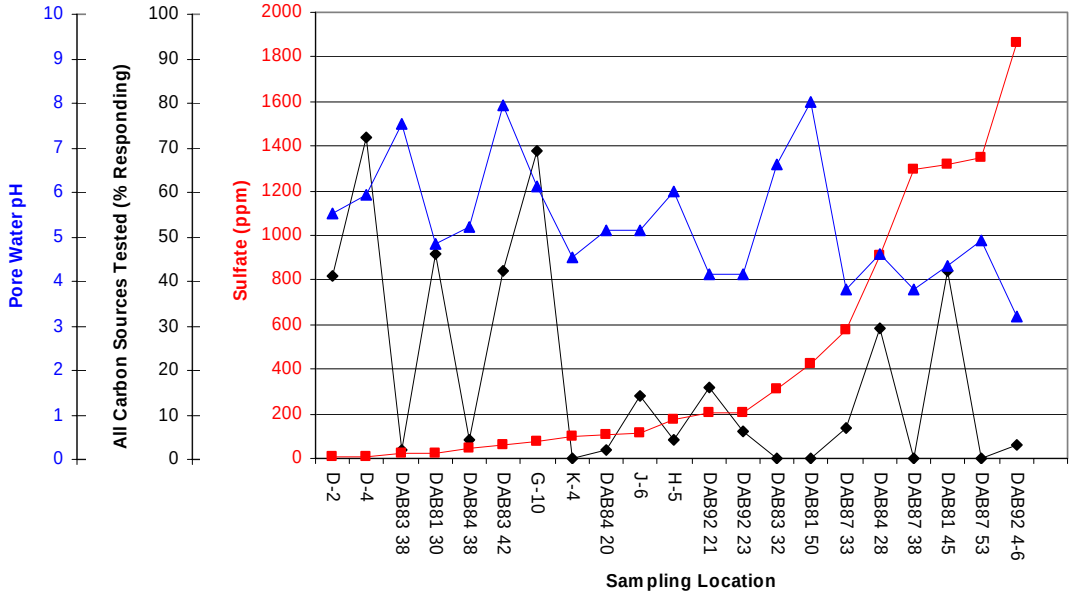


Figure 23. pH, Sulfate (ppm), and Percent Response for All Carbon Sources (Ordered by Sulfate)

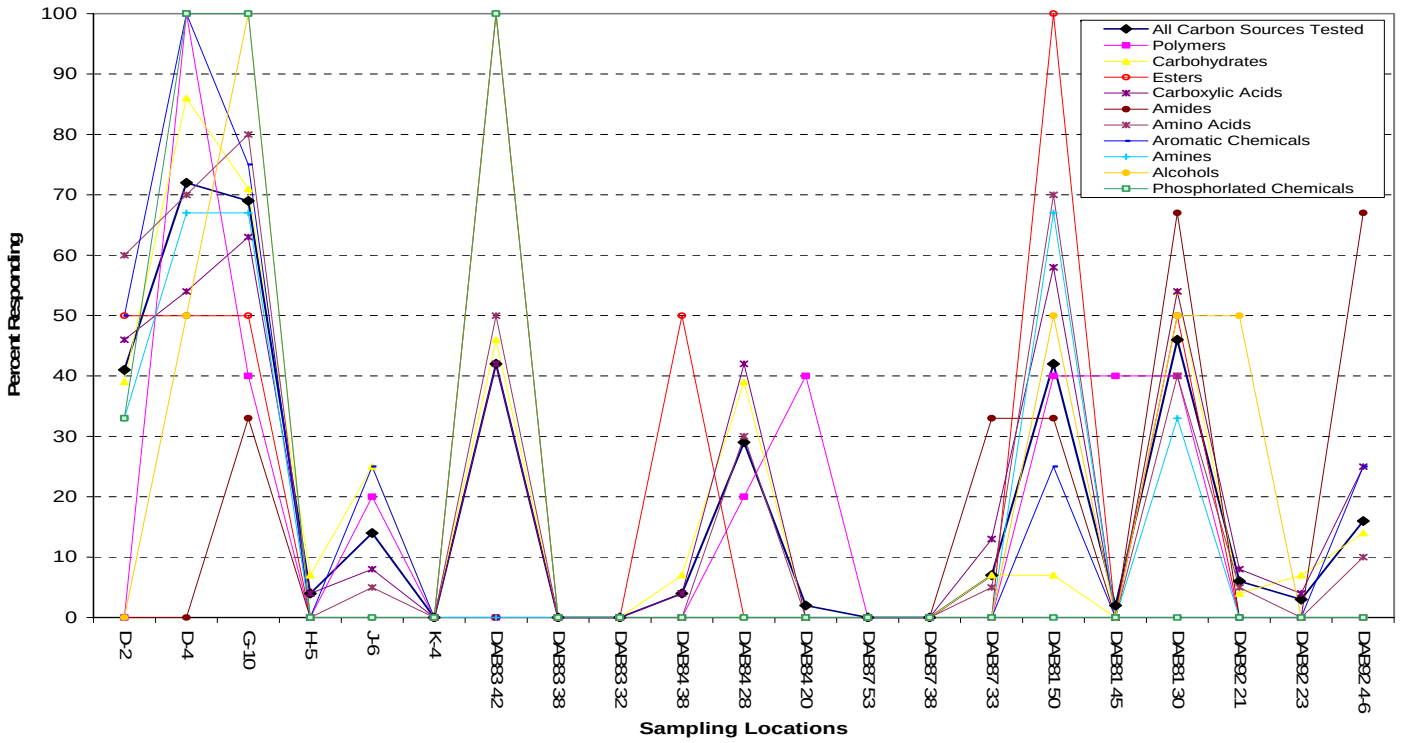


Figure 24. Overlay Plot of Percent of Total for all Biolog® Sources by Sample Location

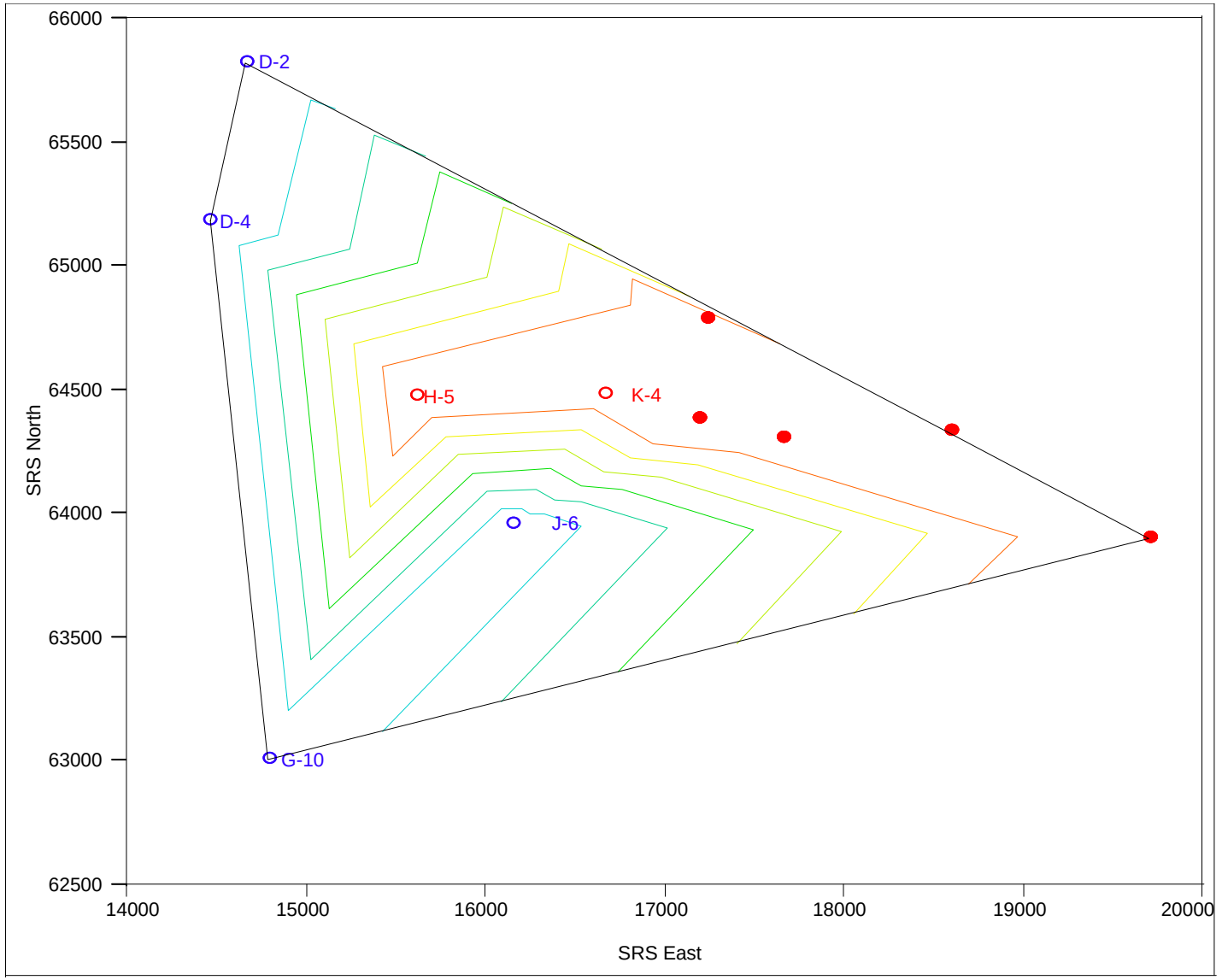
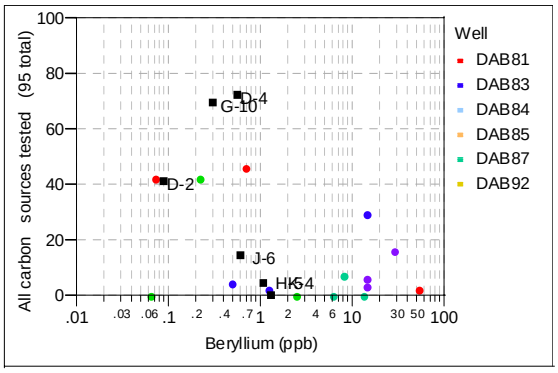
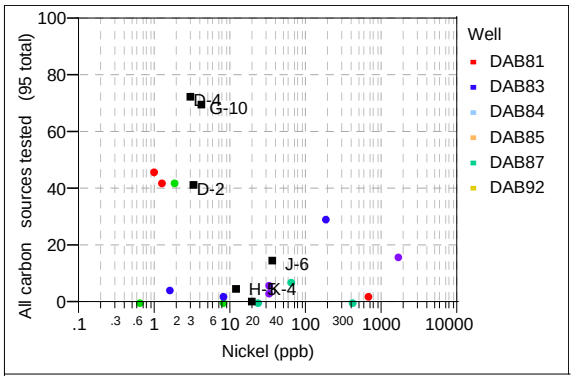


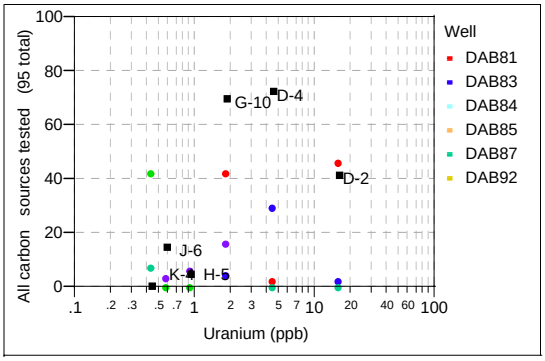
Figure 25. Posterior Probability that the Microbial Structure as Defined by the Biolog® Assays Belongs to the "Upland Region" Class (Based on a Training Set of the Original 15 DAB and 6 Wetland Sampling Locations)



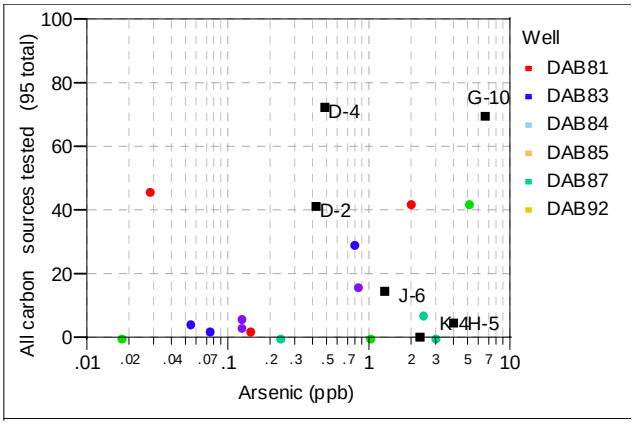
Plot of All carbon sources tested (95 total) by Beryllium



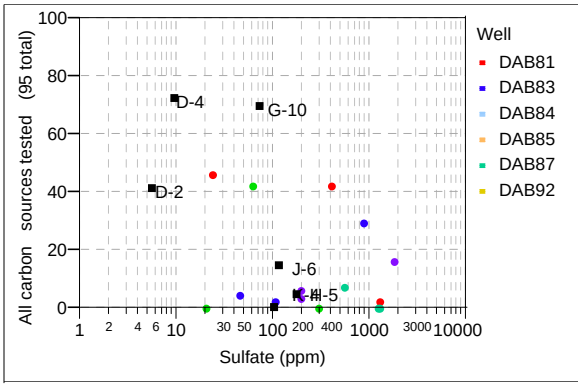
Plot of All carbon sources tested (95 total) by Nickel



Plot of All carbon sources tested (95 total) by Uranium



Plot of All carbon sources tested (95 total) by Arsenic



Plot of All carbon sources tested (95 total) by Sulfate

Figure 26. Comparison of Substrate Utilization Data from Biolog® with Porewater Concentrations of COCs (Be, Ni, U, As) and Sulfate

Table 31. Buffering Capacity of Biolog® GN Microplates

pH of added water	pH of added water at Time 0	pH of added water at Time 24 hours	pH of added water at Time 48 hours
5.00	6.91	6.94	6.99
4.00	6.93	7.00	6.95
3.00	6.91	6.91	6.96

The gross morphology of most of the colonies growing on the agar plates looked similar. These similar colony types were noted particularly on plates from DAB 83 and DAB 84. In an effort to determine the identity of this predominant colony type, bacterial colonies were picked from DAB 83 and DAB 84 agar plated samples. These colonies were restreaked numerous times for bacterial isolation, and the isolates were gram-stained and processed with Biolog® for identification. Of the 27 isolates that were tested, 70% of all isolates were identified as *Stenotrophomonas maltophilia* (Table 32). 19% of all isolates were identified as *Bacillus* species, and 11% of all isolates were identified as *Enterobacter* species. *Stenotrophomonas maltophilia* was the predominant colony type seen on these agar plates. The *Bacillus* species and *Enterobacter* species were bacteria that were growing in close conjunction to *Stenotrophomonas maltophilia* colonies.

Table 32. Identification of Bacteria in Samples DAB 83 and DAB 84

Origin	number of isolates	Identification
DAB 83 32	7	*Stenotrophomonas maltophilia*
DAB 83 32	4	*Bacillus* species
DAB 83 38	4	*Stenotrophomonas maltophilia*
DAB 83 38	1	*Enterobacter* species
DAB 83 38	1	*Bacillus* species
DAB 83 42	5	*Stenotrophomonas maltophilia*
DAB 83 42	1	*Enterobacter* species
DAB 84 38	3	*Stenotrophomonas maltophilia*
DAB 84 38	1	*Enterobacter* species

5.3 MICROBIOLOGICAL FUNCTION

Six D-Area bacteria isolates from four 2002 D-Area sediment samples were tested for their impact on pH. Four of these isolates have been identified to be *Stenotrophomonas maltophilia,* one isolate is a gram-positive rod, *Bacillus*, and one was an *Enterobacter* species that is gram negative. The isolates and their sediment origins are as follows:

- DAB 83 32 *Stenotrophomonas maltophilia* labeled # 4[a]
- DAB 83 38 *Stenotrophomonas maltophilia* labeled #11[a]
- DAB 83 42 *Stenotrophomonas maltophilia* labeled # 6
- DAB 84 38 *Stenotrophomonas maltophilia* labeled # 20
- DAB 83 32 *Bacillus sp.* labeled # 1B
- DAB 83 42 *Enterobacter sp.* labeled # 13B

Within 24 hours, all 6 D-Area bacterial isolates had raised the pH of the growth media between 2 and 3 pH units that was in the range of pH 5 and pH 6 at time zero, see Table 33 and Table 34. Only one of the D-Area bacterial isolates, the gram negative *Enterobacter sp*. was able to raise the pH of the pH 4 growth media, and it effected a 3 pH unit change within 24 hours, see Table 35. Table 35 shows very little change in pH over 72 hours for the *Stenotrophomonas maltophilia* and *Bacillus sp*

Table 33. Growth of D-Area Isolates at pH 6

Isolate	Time 0	24 hours	48 hours	72 hours
	pH	pH	pH	pH
4A	6.10	8.03	7.35	8.04
11A	6.10	7.31	8.08	8.10
6	6.10	8.07	8.14	8.18
20	6.10	8.05	8.21	8.05
1B	6.10	7.93	8.04	8.01
13B	6.10	7.77	7.83	7.70

Table 34. Growth of D-Area Isolates at pH 5

Isolate	Time 0	24 hours	48 hours	72 hours
	pH	pH	pH	pH
4A	4.90	7.91	7.86	8.00
11A	4.90	8.08	8.25	8.17
6	4.90	8.10	8.10	8.16
20	4.90	8.09	8.00	7.95
1B	4.90	8.13	7.98	7.96
13B	4.90	7.31	7.70	7.60

Table 35. Growth of D-Area Bacteria at pH 4

Isolate	Time 0	24 hours	48 hours	72 hours
	pH	pH	pH	pH
4A	4.12	4.24	4.48	4.50
11A	4.12	4.40	4.40	4.41
6	4.12	4.25	4.29	4.28
20	4.12	4.41	4.43	4.41
1B	4.12	4.24	4.16	3.80
13B	4.12	7.31	7.44	6.76

All 6 bacterial isolates were plated onto 50% Tryptic Soy Agar from the pH 4 1%PTYG media after 72 hours. All 6 isolates were recovered from the pH 4 media demonstrating viability and recovering their colony forming unit capabilities. These results show that all the bacteria isolated from the D-Area sediment were tolerant of pH 4.

6.0 DISCUSSION

6.1 DILUTION AND ATTENUATION

Attenuation of some COCs is evidenced by decreasing porewater concentrations of COCs in soil samples collected near the DCPRB (closest to the right side of figure) and wetland area (left side of figure) (Figure 27). For example, Be and Ni concentrations tend to be somewhat greater closer to Well DAB92 (near the DCPRB) than the wetland, sample. Conversely, As concentrations vary greatly and not in a trend with the order of the wells in Figure 27. The lowest sulfate concentrations were found in wetland sites D-2 and D-4 (Figure 28). These sites are furthest from the source area. The metal concentrations at these sites were generally lower than upland and wetland sites closer to the source (Figure 27). Vertical stratification of porewater COC concentrations is evident at location DAB 81 where porewater concentrations of COCs (Be, Ni, U) and major ions (Al, Fe, Mn) vary ~3 orders of magniture between DAB 81 30 (or DAB 81 50) and DAB 81 45.

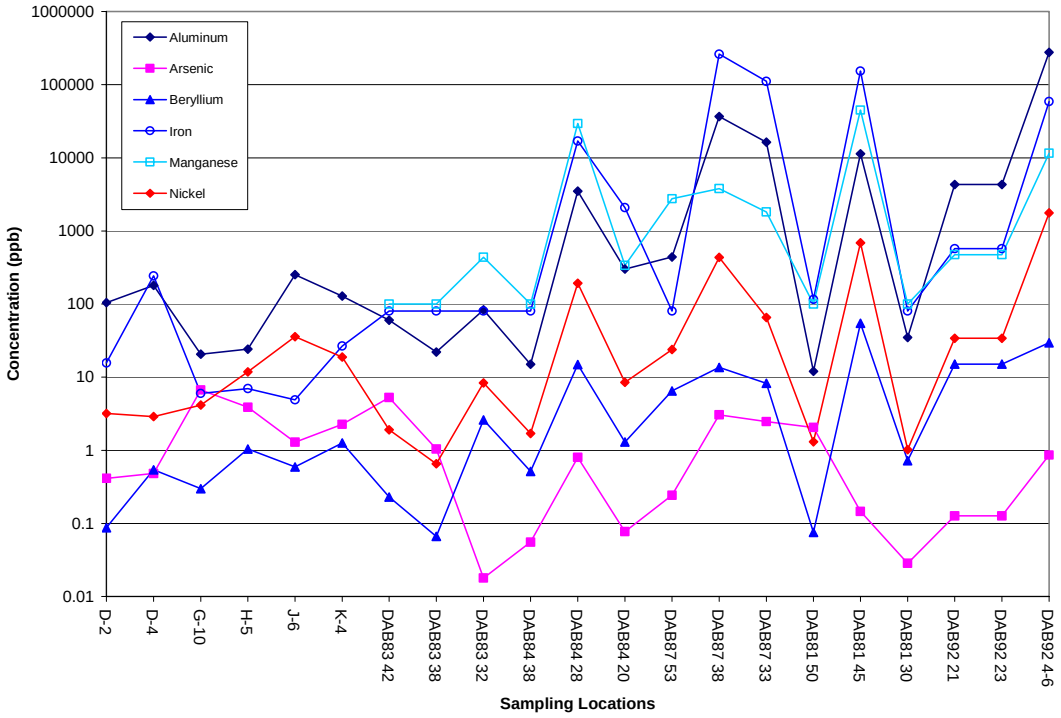


Figure 27. Porewater concentrations of COCs in D-Area (most impacted by DCPRB (right) to wetlands (left))

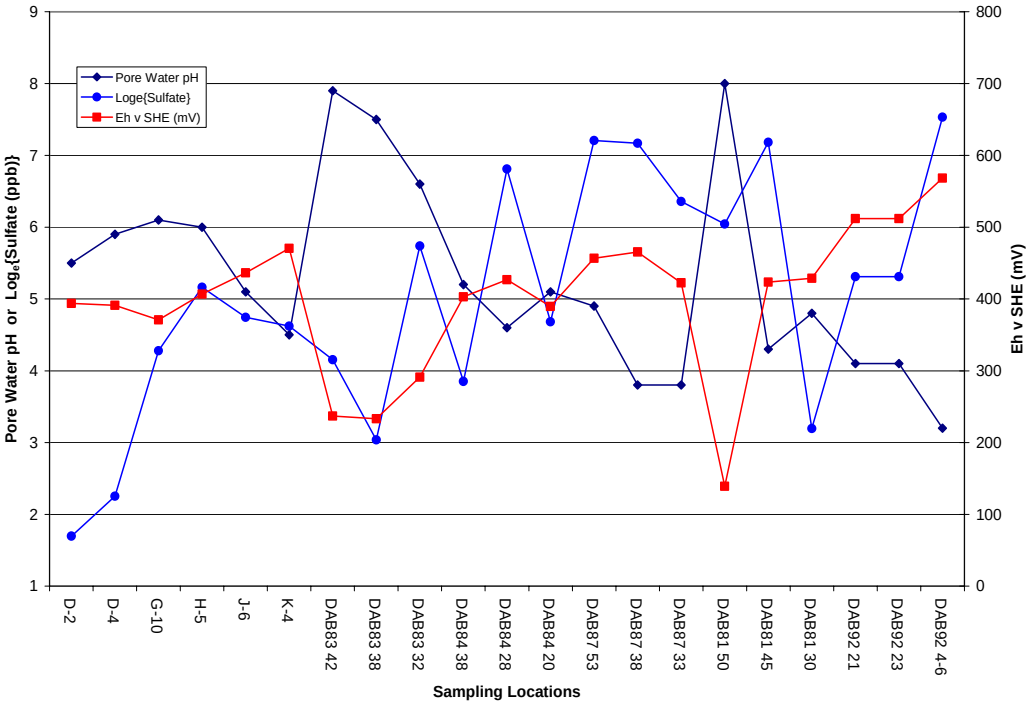


Figure 28. Porewater pH, Sulfate, and Eh values for DAB Upland and Wetland Locations

In order to compare the relative contribution of dilution to other factors contributing to attenuation of COCs in D-Area groundwater (e.g., sorption and microbiological effects), data generated using the D-Area groundwater transport model methodology reported previously (Brewer and Sochor, 2002) was compared with porewater COC concentration data collected in the field. In order to predict relative concentrations based on physical attenuation mechanisms, dilution, and dispersion only, the transport model was run without sorption input with a 100 ppb source line near DAB 92 4-6. The plume shown in Figure 29 and Figure 30 was generated based on only the source loaded near the DCPRB. Figure 2 shows the beryllium plume for multiple sources in D-Area. Likely, there is additional contaminant influx near the end of the DAB (location 87) which is not accounted for based solely on source loading near the DCPRB (DAB 92). It should be noted that this comparison is only based on relative concentration and not actual concentrations used in and predicted by the model. A significant amount of uncertainty is associated with the mass loading and area over which it is loaded. Additionally, the original calibration of the model was not based on porewater data included in this report.

The extent of dilution and dispersion was estimated using the dilution faction (DF):

Equation 5

$$DF = \frac{C_0}{C_i}$$

where C_0 is the source term concentration (100 ppb) and C_i is the concentration at location *i*. Therefore, the lower the concentration at location *i*, the greater the dilution factor. The "no sorption" model in layers 3 and 4 (Figure 29 and Figure 30) predicts a dilution (and dispersion) factor (DF) range of 2 to 28 in the vicinity of the upland samples (Table 36).

A second construct referred to as the dilution attenuation factors (DAFs) were calculated according to Equation 6.

Equation 6

$$DAF = \frac{C_{DAB92}}{C_i}$$

where C_{DAB92} is the porewater solute concentration measured in sample DAB 92 4-6 and C_i is the concentration at location *i*. Comparison of DF (modeled) and DAF (field values) provides an estimate of the relative contribution of dilution/dispersion versus all other contributions (i.e., sorption, microbial) to natural attenuation at the site. No numerical transport modeling was conducted to calculate *DAF;* instead the porewater data in Table 36 was used. Dilution attenuation factors ranged from 2 to 40 for sulfate and 0.5 to 700 for beryllium (Table 36). DAF values for nickel and uranium are on average even greater than those for beryllium. DAF values observed for arsenic are lower than the cations beryllium, nickel, and uranium although arsenic concentrations at DAB 92 4-6 are quite low in both porewater as well as soil. Likely, the majority of arsenic in the low pH source area is attenuated before reaching DAB 92 4-6. This observation is consistent with the low solubility of As(V) at low pH and also favorable sorption of As(V) to Fe-oxyhydroxide at a pH 4. Furthermore, Kaplan and Knox (2004) measured quite high concentrations of arsenic in sediments from the DCPRB (234.6 ppm) indicating that As is as readily sorbed prior to reaching the locations evaluated in this study.

Based on this comparison of field data to modeled dilution, a significant amount of attenuation of the COCs in D-Area can likely be attributed to attenuation by factors other than dilution and dispersion. These geochemical and microbiological processes contributing to this attenuation are addressed in Sections 6.2-6.4.

Table 36. Dilution Attenuation Factors from Field Data near DCPRB and DAB

Sample Soil	Model Layer	Porewater pH	C_o/C model	DAF Sulfate	DAF Be	DAF Ni	DAF U	DAF As
DAB92 4-6	1	3.18		1.0	1.0	1.0	1.0	1.0
DAB92 21-23	3	4.12	11	9.2	2.0	51.8	34.1	6.8
DAB85 32-33	3	5.18	3	2.2	25.1	5.3	>39424.0	13.5
DAB85 45	3,4	7.25	6	23.0	710.5	177.6	>39424.0	1.8
DAB81 45	3,4	4.26	4, 5	1.4	0.5	2.6	157.0	5.9
DAB81 50	4	7.98	5	4.4	391.9	1350.3	10.1	0.4
DAB87 33	3	3.81	18	3.2	3.6	26.9	2.0	0.3
DAB87 38	3,4	3.76	18, 21	1.4	2.2	4.1	1.4	0.3
DAB87 53	4	4.93	21	1.4	4.6	74.1	>19712.0	3.6
DAB84 20	3	5.06	23	17.3	22.8	208.5	>39424.0	11.2
DAB84 28	3,4	4.56	23, 28	2.1	2.0	9.2	11.1	1.1
DAB84 38	4	5.24	28	39.6	57.3	1043.2	>39424.0	15.5
DAB83 32	4	6.61	13	6.0	11.4	211.2	9.8	48.2
DAB83 38	4	7.50	13	89.4	446.8	2701.2	>39424.0	0.8
DAB83 42	4	7.87	13	29.4	129.0	925.1	738.8	0.2

6.2 SOURCE AVAILABILITY

6.2.1 pH, Redox, and Sulfate

In general, pH increased with distance from the source as well as with depth. This broad generalization holds true except for two sampling locations directly beneath (DAB 81 and 87) and one location just downgradient (DAB 84) of 488-D. At all three of these locations porewater from the shallowest sampling depth was slightly higher in pH than the sampling depth below. Lower sulfate concentrations at these depths as compared to the locations directly below them suggest that these more shallow sampling depths are higher in elevation than the most impacted region of the low pH/high sulfate plume. Another explanation for this observation could be neutralization of the low pH plume by infiltration from the high pH perched water within the 488-D (DAB 86 pH =7.50). Due to the tight clay layer directly below the 488-D, vertical flow from the ash basin is expected to be minimal, although near the west end of the DAB low pH leachate from coal spoils in the basin is potentially breaching the clay layer. In addition to the ash basin material sample DAB 86, three soil sampling locations near 488-D had sampling depths with pH > 7. The pH values at these locations are considerably higher than any pH measured for distal samples DCP 168-171 despite the closer proximity to the DCPRB, a source of low pH. They are, however, from greater depth below ground surface than samples from the distal region. These distal samples may be impacted by the plume emanating from the DRP (Figure 2).

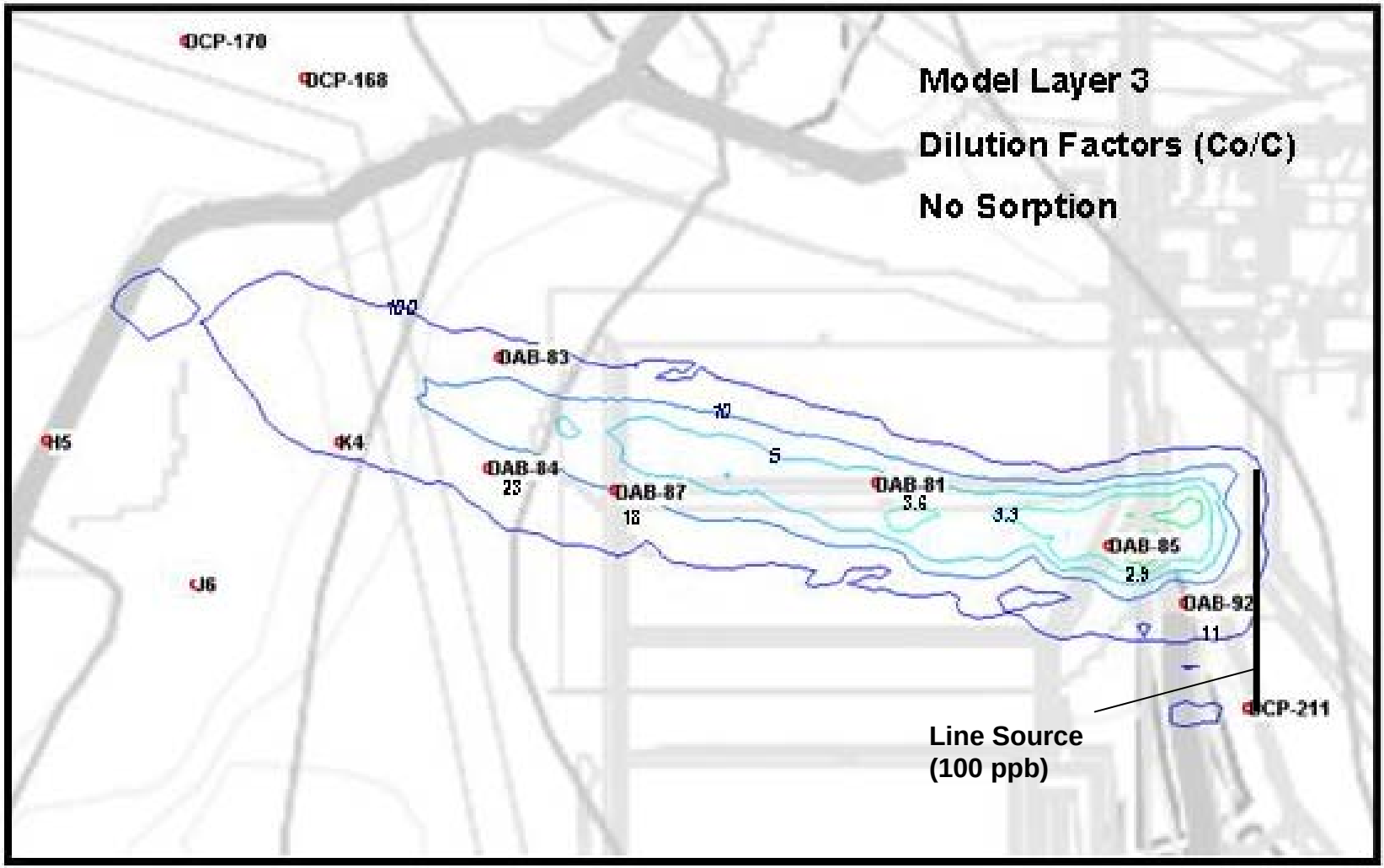


Figure 29. D-Area Coal Pile Runoff Basin plume under 488-D and 488-4D (Layer 3). No sorption model with 100 ppb line source loaded in the vicinity of DAB 92 4-6.

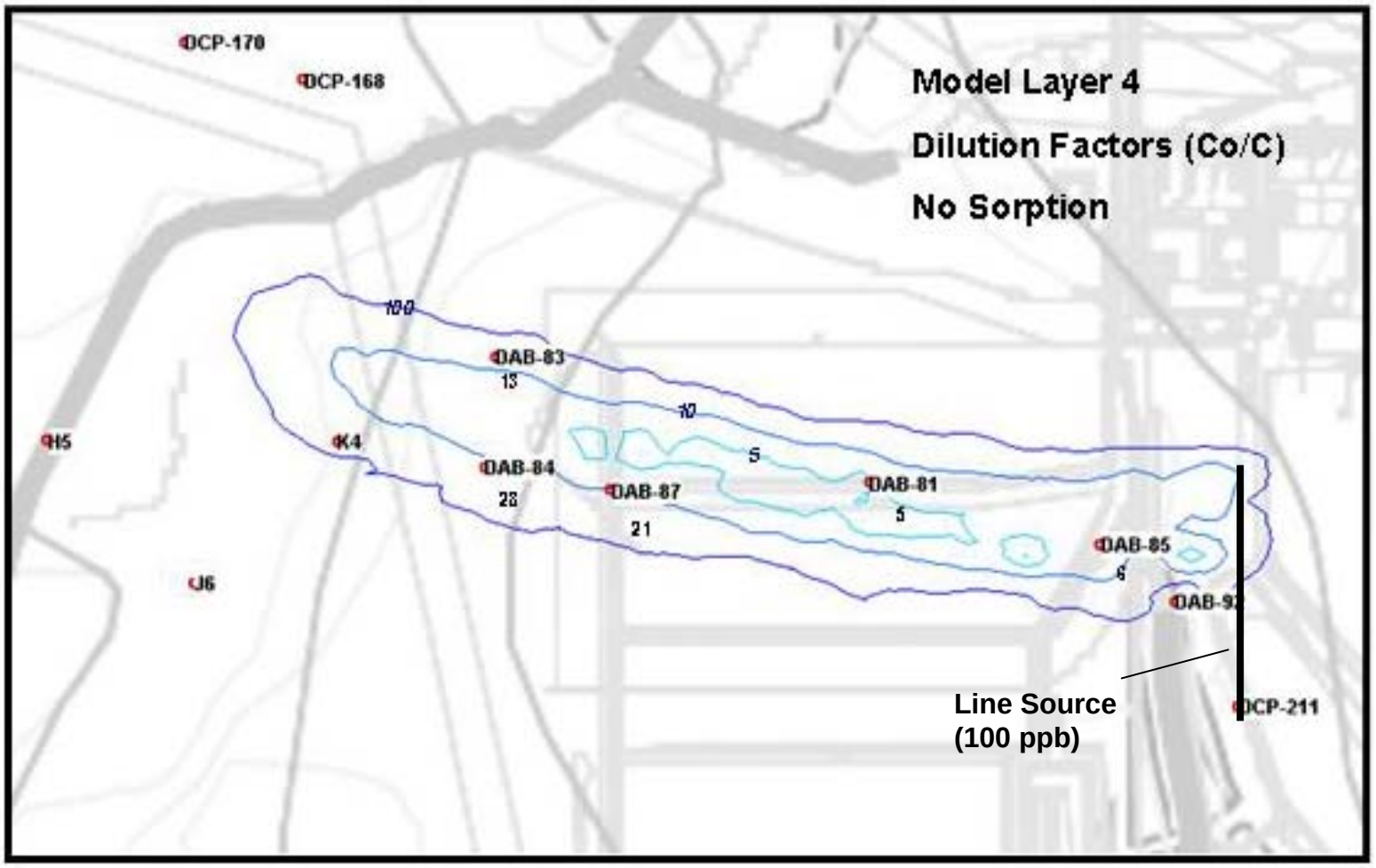


Figure 30. D-Area Coal Pile Runoff Basin plume under 488-D and 488-4D (Layer 4). No sorption model with 100 ppb line source loaded in the vicinity of DAB 92 4-6.

It was a significant finding that all 6 of D-Area sediment bacterial isolates tested were able to change the pH of their media up to 3 units (Table 33 through Table 35). The *Enterobacter* species tested was found to thrive at pH 4 and adjust it's media to pH 7. *Enterobacter* sp have also been proven to reduce metal contamination (Rege et al., 1997). Bacteria adjust the media in their surrounding environment to survive and proliferate as one of their physiological adaptations. In this study a low nutrient media was used to emulate D-Area porewater. By raising *in situ* groundwater pH they could in turn indirectly reduce associated metal speciation and availability. It was also of interest that all the bacteria tested, even those did not grow at pH 4, were still alive and recovered quickly in other media. This demonstrates that these bacteria are acid tolerant, although it suggests that geochemical mechanisms likely dominate in the regions where pH is lower than 5.

Conversely to pH, Eh decreased with increasing distance from the source and increasing depth. Notable exceptions to this generalization were DAB 81, 84 and 87, the same locations and depths that did not follow the general pH trends. Redox measurements for all locations were in the range of 664.3 to 138.7 mV. This range is consistent with a highly oxidized soil environment. These redox potentials are all higher than those necessary for Fe(III) reduction (<100 mV) or sulfate reduction (<-100 mV). Although the overall sediment redox is quite oxidizing, this high overall Eh does not rule out that microbial meditated anaerobic reduction processes could be occurring in microenvironments in the subsurface. The presence of sulfate reducing bacteria in DAB 92 indicates pockets of anaerobic activity. Another consideration is bacterial aerobic biotransformation of metals in this environment. The predominance of *Stenotrophomonas maltophilia* in some of the upland sediment bacterial isolations is evidence of potential MNA activity in this site although *Stenotrophomonas maltophilia* was only identified at locations downgradient of the DAB and not at location DAB 92 near the DCPRB.

Eh is correlated with pH for all porewater samples (Figure 32). As Eh decreases, pH increases. In a previous report (Powell et al 2001), it was noted that the turbidity of porewater sample DCP 211-p2 (pH= 4.69, Eh =138.7 mV v SHE) was likely causing spurious redox measurements for this sample.

As pH increased and Eh decreased, sulfate concentrations decreased (Figure 28 and Figure 32. Wetland samples of surface ash (K-4, H-5, J-6, G-10) contained lower concentrations of sulfate (~100 ppm) similar to distal samples (DCP 168, 170, 171) (~100 ppm) rather than to the porewater of the samples of ash (DAB 86) taken from inside 488-D (~1785 ppm). These high concentrations of sulfate in the ash from 488-D are similar to concentrations near DCPRB (DAB 92 4-6, 1866 ppm; DAB 211-p2, 1476 ppm). Interpretation of sulfate, pH, and Eh data at upland locations is complicated by the apparent influx of low pH leachate from the west end of the DAB (Figure 2) which is reflected on lower pH at DAB 87 33 and DAB 87 38 than at upgradient location DAB 81.

For this reason, trends with distance from the DCPRB are complicated due to overlapping plumes. Regardless, despite the potential influx of additional contaminants from the DAB (both directly and indirectly), by the time the DCPRB plume reaches the wetland pH is only slightly elevated at wetland locations K-4 and H-5. Relative to background wetland soils (D-2, D-4), sulfate at wetland locations has been attenuated by an order of magnitude, and redox conditions (Eh = 370 - 470 mV) at the surface of the wetland are more reducing than the shallow locations near the DCPRB (DAB 92 4-6, Eh = 568.2 mV).

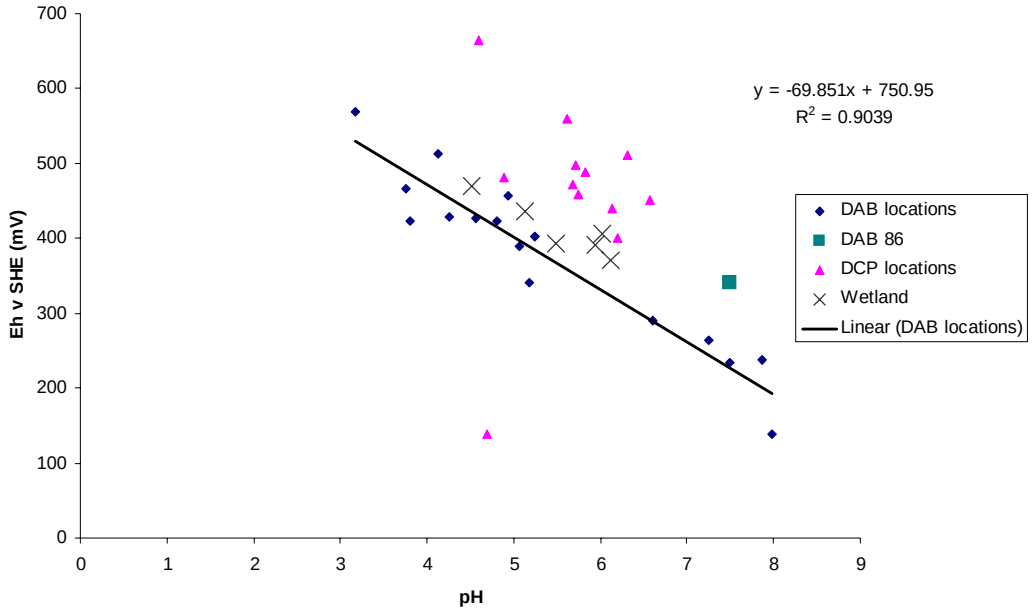


Figure 31. Plot of Redox Potential (E_h) versus pH for All Porewater Samples

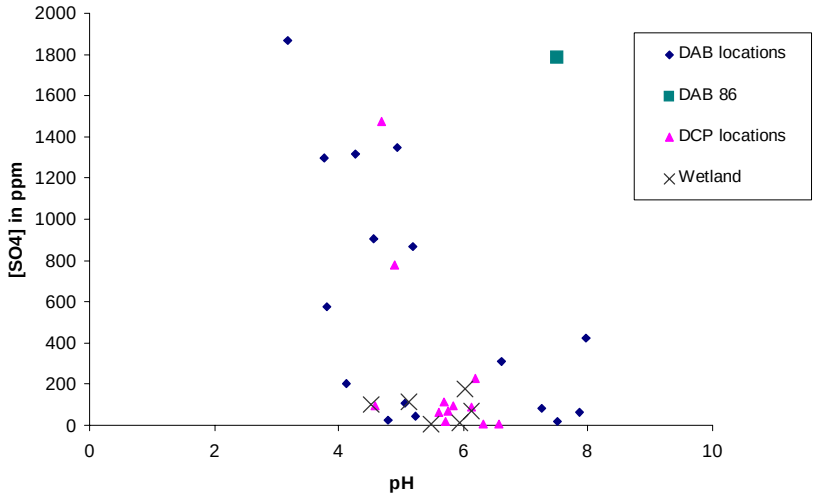


Figure 32. pH versus Sulfate Concentration in Porewater for All Locations

6.2.2 Major Ions in porewater

Low pH leachate from the DCP/DCPRB promotes the protonative dissolution of aluminum, iron, and manganese oxides/hydroxides found in soil. Consequently, very high concentrations of dissolved aluminum, iron, and manganese are observed in locations near the DCPRB (DAB 92 and DCP 211) and at locations such as DAB 87 33 and DAB 87 38 with low pH and high sulfate concentrations (other indicators of plume impact). As mentioned previously, kaolinite, an aluminum-containing mineral, dominates the clay fraction of SRS soils. The dissolution of kaolinite was modeled using a geochemical model, MINTEQA2. Figure 33 shows the curve for the modeled kaolinite data along with the observed porewater concentrations of aluminum for all locations sampled. Decreasing porewater concentrations of aluminum, iron and manganese with increasing pH is an important indicator of natural attenuation because the formation of metal oxide/hydroxide coatings and precipitates is expected to contribute to natural attenuation by increasing the ability of the soils to sorb trace metals by increasing the cation/anion exchange capacities of the soils. Similarly, iron and manganese concentrations decrease with increasing pH (Figure 34 and Figure 35, respectively). Trace metals such as the COCs considered herein may sorb to freshly precipitated surfaces and/or form coprecipitates with metal oxides, particularly iron oxides/hydroxides.

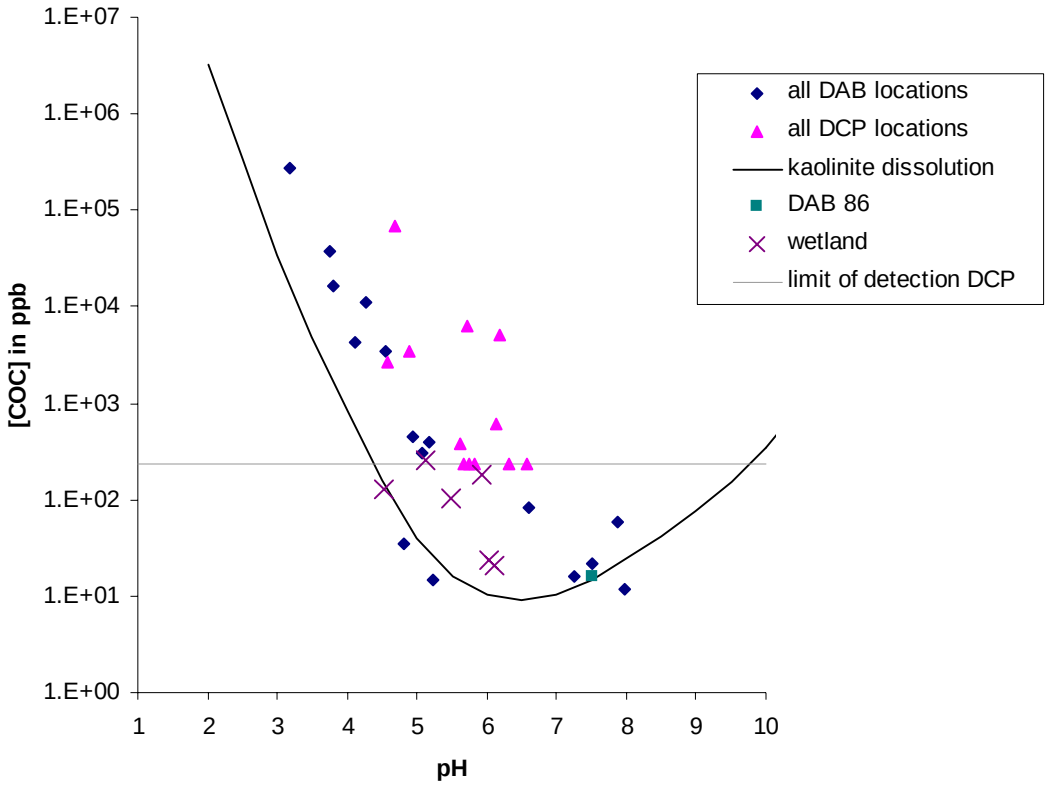


Figure 33. Aluminum Concentration in Porewater as a Function of pH (log scale)

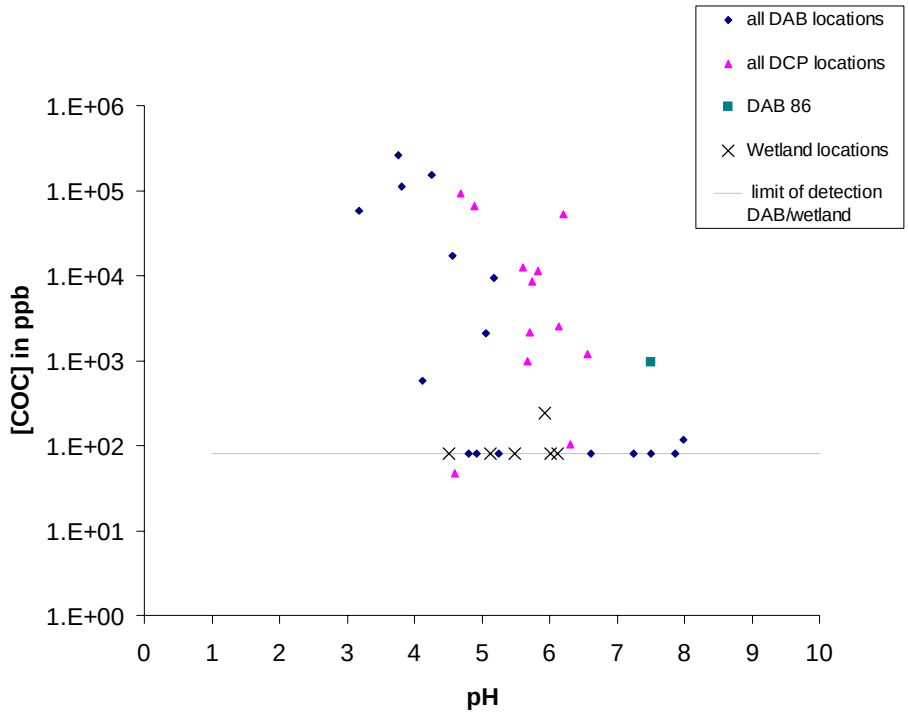


Figure 34. Iron Concentration in Porewater as a Function of pH (log scale)

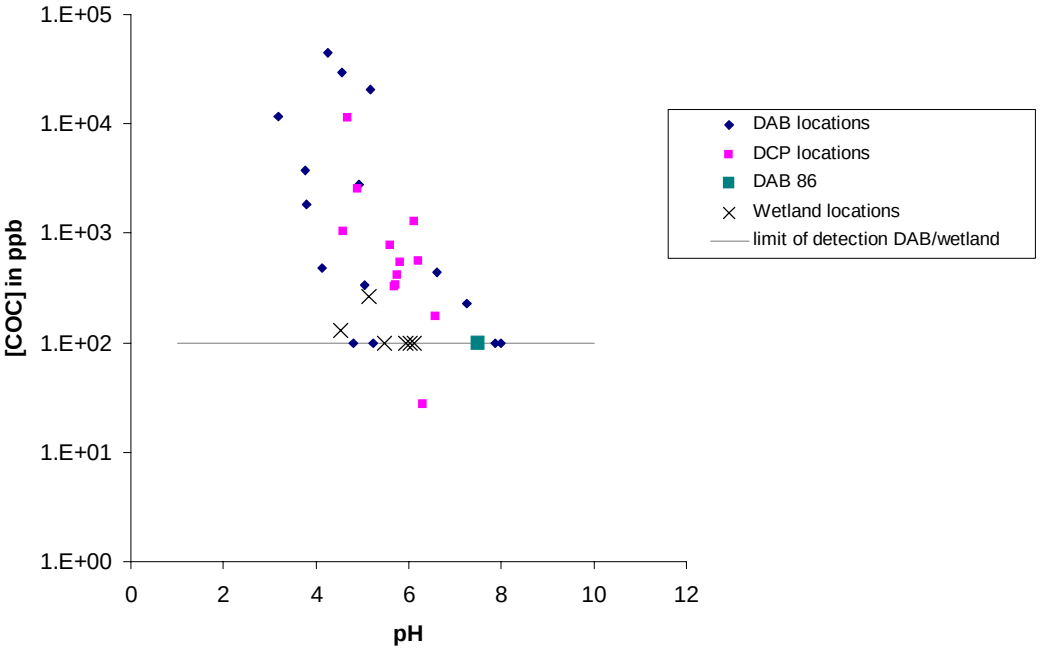


Figure 35. Manganese Concentration in Porewater as a Function of pH (log scale)

6.2.3 Trace Metals in porewater

The chemical speciation of the trace metal COCs (Be, Ni, U, As) analyzed in this study provides insight into the geochemical mechanisms controlling porewater COC concentrations measured in field samples. It is important to note that trace metals were in relatively low concentrations at most locations analyzed in this study. Beryllium and nickel exist as divalent cations under environmental conditions and would be expected to compete with hydrogen ions for sorption sites on metal oxide/hydroxide surfaces in soils. Consequently, porewater beryllium and nickel concentrations are significantly correlated with pH [Be: R^2 = 0.696, $p < 0.001$, df =22; including porewater data from upland DAB locations, wetland, and ash from 488-D (DAB 86)][Ni: R^2 = 0.3048, $p < 0.001$, df =30; including upland DAB locations, upland DCP locations (excluding data below detection), wetland, and ash from 488-D (DAB 86)](where R^2 = correlation coefficient, p = uncertainty, df = degrees of freedom). Figure 38 and Figure 39 are plots of beryllium and nickel porewater concentration as a function of porewater pH for upland and wetland locations. Logarithmic correlation for the DAB sampling locations only is shown on the plots. Despite the differences in composition of the solid phases between upland soil and wetland ash including higher solid phase COC concentrations for most wetland locations as compared to upland, pH is an excellent predictor of COC concentrations in porewater for both Be and Ni. This relationship is likely due to competition between hydrogen ions and cationic COCs for sorption sights.

In contrast to the divalent cations Be and Ni, uranium can exist as cationic (UO_2^{2+}, UO_2^{+}, UO_2OH^{+}), neutral (UO_2CO_3), and/or anionic [$UO_2(CO_3)_2^{2-}$] species under the range of environmental conditions at D-Area (pH = 3 to 8; Eh = 570 mV to 140 mV)(Figure 36). At pH values less than 5.5, uranium behaves as a cation, and similarly to Be and Ni, U porewater concentrations are significantly correlated with pH (Figure 40). Above pH 5.5 (Figure 36), both neutral and anionic species are possible.

Arsenic exists as anionic species arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) in environmental waters (Figure 37). Arsenite [As(III)] is by far the more soluble of the two species although in oxic waters arsenate [As(V)] is the predominant form. Arsenic is found in low concentrations at locations in this study except for the sample of ash from the 488-D (DAB 86). The high pH of this sample likely accounts for the solubility of As due to desorption of anions. Likely, most of the arsenic in the coal pile leachate is sorbed as arsenate (AsV) near the DCPRB. Arsenate has a low solubility and tends to be found associated with iron. Sorption of As to HFO is favored at pH 4, and As can also coprecipitate with iron oxides/hydroxide. Arsenic transported downgradient of the DCPRB to the locations analyzed in this study exhibits solubility behavior with pH that is consistent with arsenite (AsIII) sorption to HFO which has a broad sorption maximum around pH 7 (Figure 41).

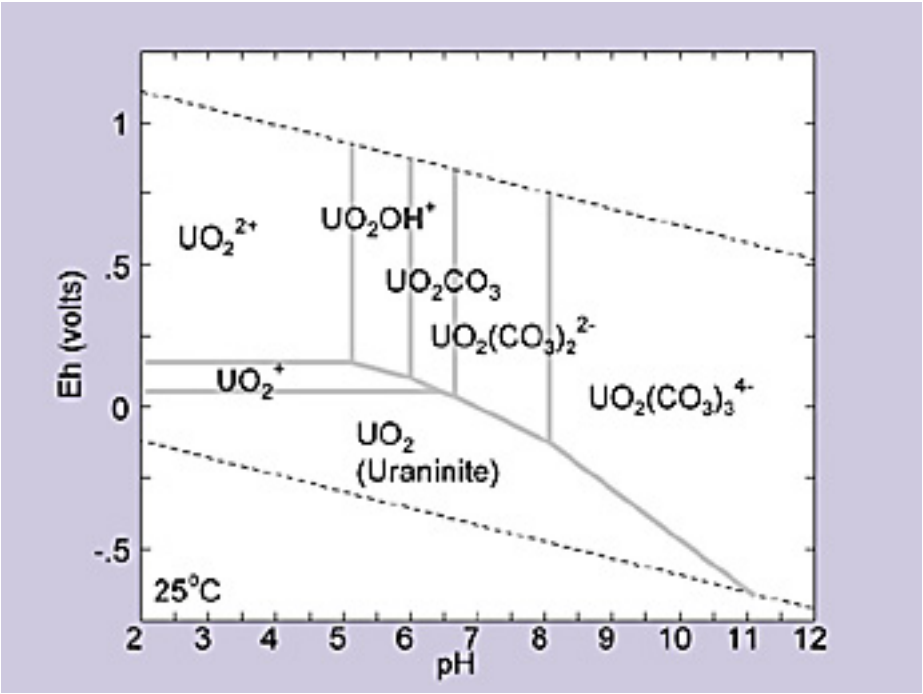


Figure 36. Eh-pH Diagram for Uranium

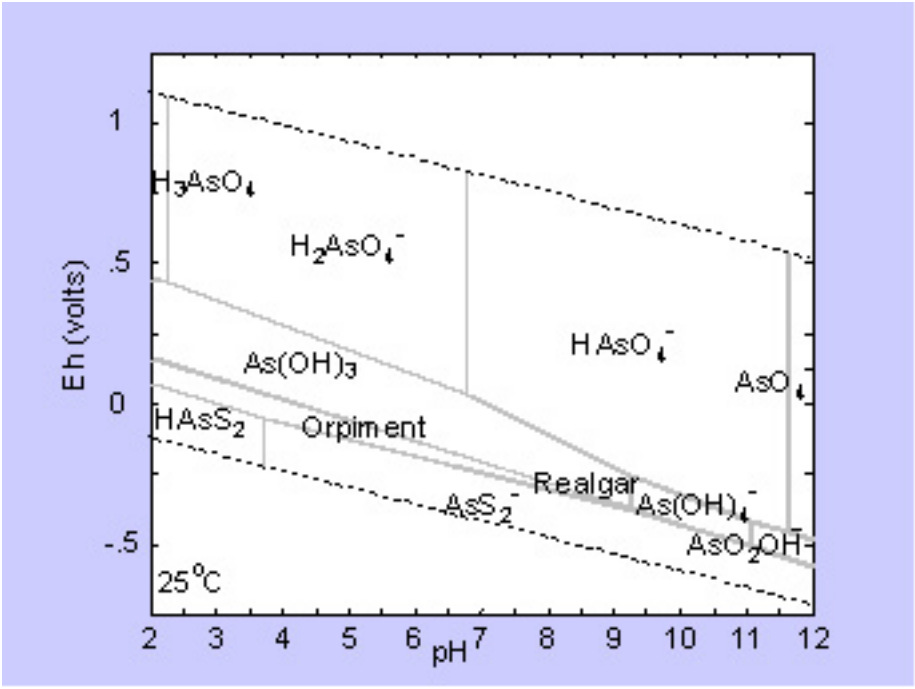


Figure 37. Eh-pH Diagram for Arsenic

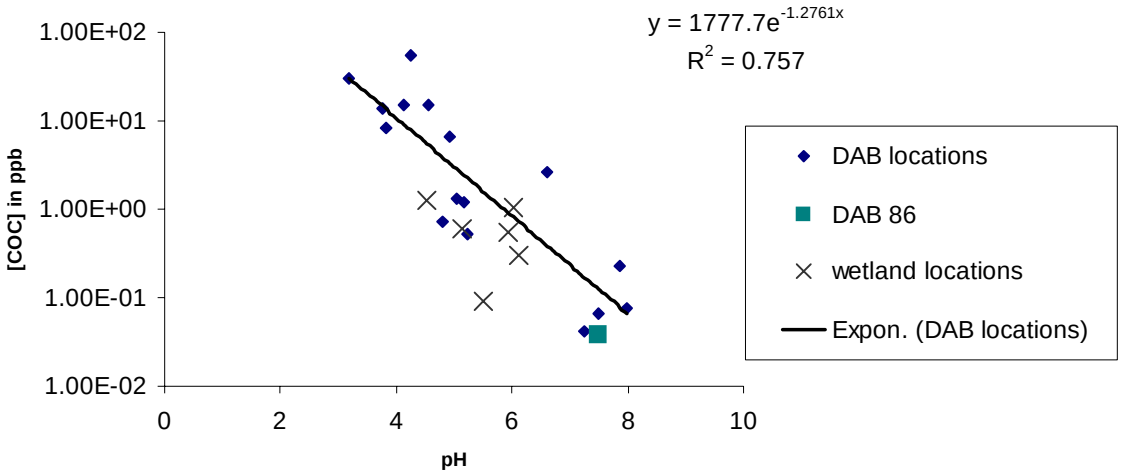


Figure 38. Beryllium Concentration in Porewater as a Function of pH (log scale)

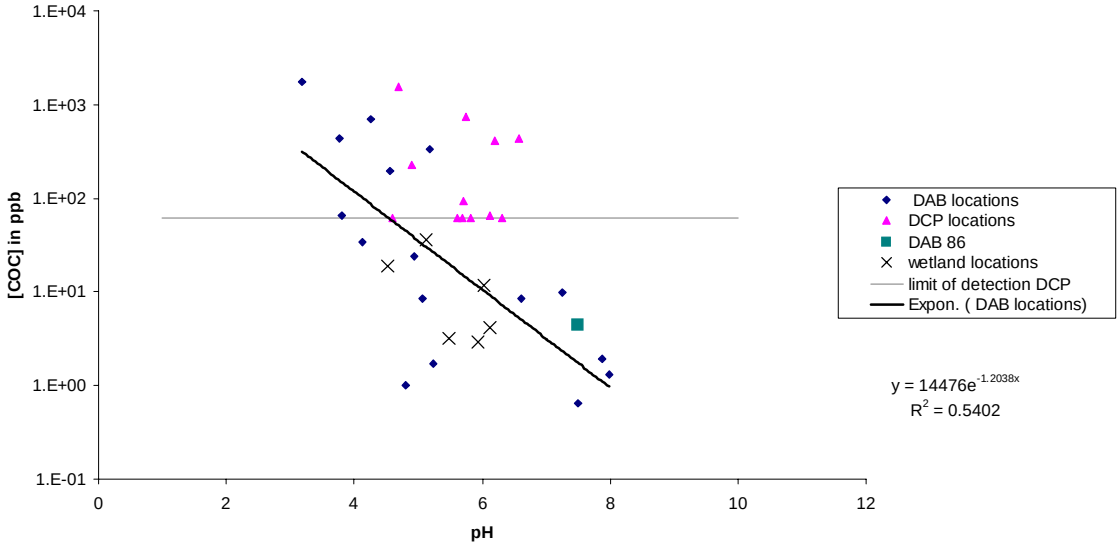


Figure 39. Nickel Concentration in Porewater as a Function of pH (log scale)

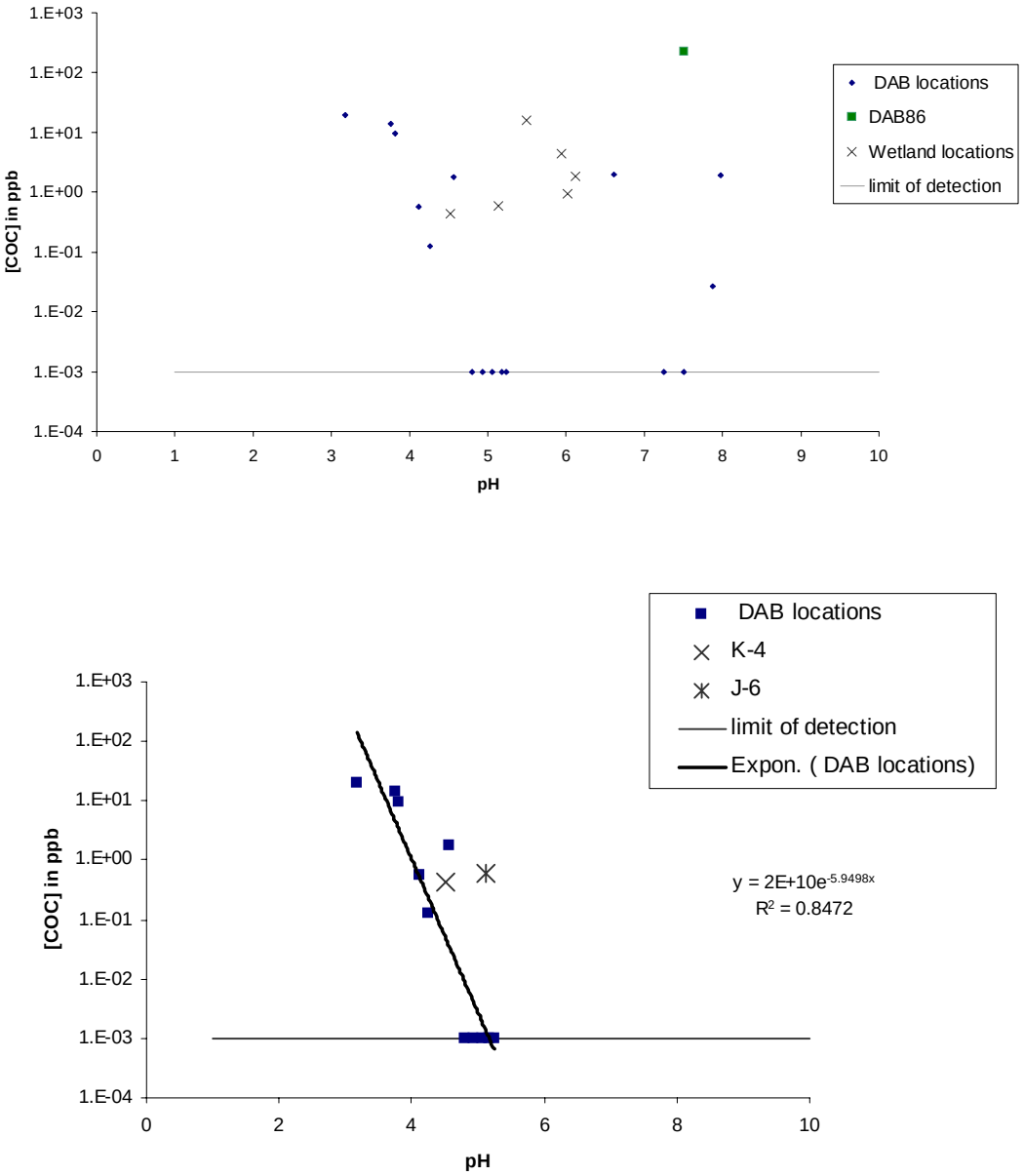


Figure 40. Uranium Concentration in Porewater as a Function of pH (log scale) (Data DCP locations not available) (Top - all measured data; Bottom - only data below pH 5.5)

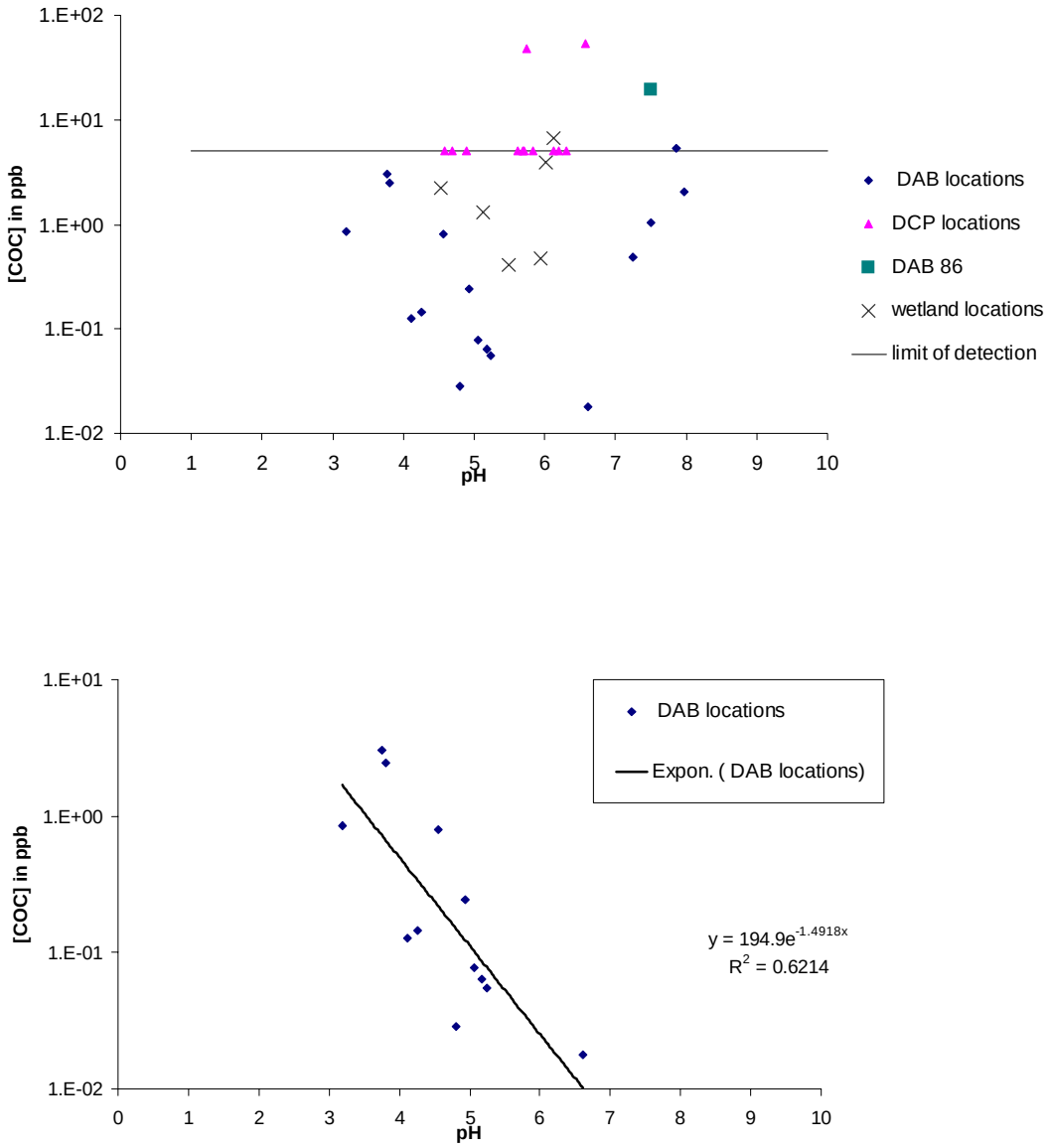


Figure 41. Arsenic Concentration in Porewater as a Function of pH (log scale) (Top - all measured data; Bottom - only DAB data below pH 7)

6.2.4 Available Fraction

The sediment metal fraction available to the mobile aqueous phase was estimated using the sequential extraction data (Equation 7):

Equation 7 $$\%\ Available = \left(\frac{C_{F1} + C_{F2} + C_{F3} + C_{F4} + C_{F5} + C_{F6}}{C_{F1} + C_{F2} + C_{F3} + C_{F4} + C_{F5} + C_{F6} + C_{F7} + C_{F8}} \right) \times 100$$

where C represents constituent concentration and subscripts, F1, F2, F3, F4, F5, F6, F7, and F8 represent sequential extraction fractions 1 through 8. Where sequential extraction data was not available, the % Available was calculated based on a single step extraction equivalent to the sum of the first 6 sequential extraction fractions and total digestion data equivalent to the sum of all 8 sequential extraction steps. Trace metal availability values are presented in Table 37.

6.2.4.1 Beryllium and Nickel

Closer to the DCPRB, where soil concentrations of these COCs were highest, the available fraction of Be and Ni tended to increase. This observation is consistent with natural attenuation. The soils most impacted by the low pH plume would be expected to have lower metal concentrations as leaching of any available metals if favored. As natural attenuation occurs, metals removed from the ground water to the soil would tend to be associated with the most available fractions.

Samples from the wetland have concentrations of metals as high as or higher than those closer to the DCPRB although the availability is closer to that of the DAB ash sample (DAB 86, 19 %) rather than upland soil.

6.2.4.2 Uranium

Soil concentrations of uranium at DAB 92 4-6 (the most impacted area nearest the DCPRB) are the highest of any in the plume associated with the DCPRB, which indicates that even close to the source area uranium is likely sorbed by the soil. Samples close to the source tend to have a higher percentage of available uranium.

The ash sample (DAB 86) had higher concentrations of uranium with lower availability (24 %) and the wetland samples had approximately 50 % availability of uranium.

6.2.4.3 Arsenic

Arsenic concentrations in soil at locations associated with the DCPRB plume tend to be low and also less available. Because porewater concentrations of arsenic are low at these locations, likely much of the arsenic is attenuated prior to reaching the sampling area in the plume associated with the DCPRB. Precipitation/sorption of As V with/to iron oxides/hydroxides could account for both the attenuation of As near the DCPRB as well as its tendency to be associated with the crystalline mineral phases.

Table 37. Summary of Trace Metal Availability (% available = available/total x 100 %)

Sample	Porewater	Be		Ni		U		As	
Soil	pH	Total ppm	% available	Total ppm	% available	Total ppm	% available	Total ppm	% available
DAB92 4-6	3.18	1.18	20	12.51	3	6.96	80	2.25	7
DAB92 21-23	4.12	0.52	13	15.66	11	1.23	98	1.56	72
DAB85 32-33	5.18	1.49	17	38.25	70	0.79	52	5.61	34
DAB85 45	7.25	0.24	46*			0.28	25*	0.21	42
DAB81 30-35	4.80	2.01	28*			1.27	134*	1.82	17
DAB81 45**	4.26	0.98	34	21.00	87	4.95	74	0.58	19
DAB81 50	7.98	2.38	295*			0.74	171*	2.66	31
DAB87 33	3.81	1.03	14*			2.24	42*	2.35	14
DAB87 38	3.76	0.45	11	40.34	79	1.12	25	0.72	7
DAB87 53	4.93	3.10	29*			1.22	32*	2.03	4
DAB84 20	5.06	0.15	13*			0.21	25*	1.19	1
DAB84 28	4.56	0.64	12	25.75	89	1.59	49	0.11	28
DAB84 38	5.24	8.10	32*			4.55	57*	2.68	14
DAB83 32	6.61	2.35	103*			3.12	127*	1.43	6
DAB83 38	7.50	1.98	71*			1.52	108*	2.00	20
DAB83 42	7.87	4.23	82	56.49	96	2.51	97	3.17	57
DAB86 12-16	7.50	8.80	19	60.40	23	13.25	24	43.74	95
DCP211/2-3	vadose	0.22	14	14.84	28	0.83	49	2.78	44
DCP211/9-10	nd	0.59	2	15.85	16	1.33	59	3.29	40
DCP211/19-20	4.89	2.63	21	24.43	24	2.09	50	4.98	40
DCP211/35-36	4.69	0.84	31	13.43	53	0.23	66	2.81	82
DCP168/1.5-3.5	vadose	2.05	42	44.83	2	4.03	nd	3.13	21
DCP168/20-22	5.61	5.21	92	36.14	60	6.72	nd	15.87	72
DCP168/31-33	6.31	1.68	100	17.36	21	3.10	56	7.37	50
DCP170/1-3	vadose	0.31	19	26.21	2	1.05	43	3.02	29
DCP170/14-16	4.59	0.28	21	9.13	9	0.44	25	0.29	45
DCP170/20-22	5.83	0.83	23	18.34	31	0.92	2	0.75	45
D-2	5.49	1.48	52	32.81	63	3.71	66	6.36	57
D-4	5.94	1.83	38	24.44	20	3.86	47	7.75	48
G-10	6.12	7.07	20	48.44	23	5.93	47	44.24	91
H-5	6.02	4.55	31	39.60	27	4.94	58	77.93	97
J-6	5.13	6.08	18	46.82	22	5.29	42	40.81	92
K-4	4.52	5.27	27	36.36	19	3.98	51	78.32	96

* indicates % available calculated based on single-step extraction and total digestion results

Wetland samples contained higher concentrations of arsenic with high availability >90 %. The concentration of arsenic in the wetland samples exposed to ash sluice and the ash sample (DAB 86) have comparable concentrations of arsenic (> 40 ppm) with similar high availability. Arsenic in these wetland samples is associated with the organic fraction. It is not clear if this shift from upland (more crystalline) to wetland (more available) is due to a shift in mechanism or rather simply due to the nature of the ash material itself since arsenic is also associated with the organic fraction in the ash sample from 488-D (DAB 86). Evaluation of the soils immediately below the ash deposit would provide relevant information regarding attenuation of As in the wetland.

6.3 TRANSPORT FACTORS

6.3.1 K_d Values

In situ K_d values based on the available fraction, K_{davail}, were calculated for matched sets of soil and porewaters, using Equation 8:

Equation 8

$$K_{d\,avail} = \frac{C_{F1} + C_{F2} + C_{F3} + C_{F4} + C_{F5} + C_{F6}}{C_{porewater}}$$

where C represents COC concentration and subscripts F1 through F6 represent sequential extraction step fraction 1 through fraction 6. $C_{porewater}$ represents the porewater COC concentrations. The sum of the first six sequential extraction steps is assumed in these calculations to be representative of the likely desorbable or available fraction. From the point-of-view of modeling groundwater risk, it is more conservative (providing lower K_d values) if lower soil COC concentrations are assumed. Thus, it is much more conservative with respect to modeling risk for the groundwater pathway to assume the sum of Fractions 1 – 6 accounts for the sorbed fraction, and not the total digestible concentration.

The K_{davail} values of each of the sediments is presented in Table 38 Each COC has a wide range of K_{davail} values: Be K_d values ranged from 4 to 93,000 mL/g, Ni K_d values ranged from 0.19 to 6,500 mL/g, U K_d values ranged from 20 to 3,400,000 mL/g, and As K_d values ranged from 16 to 5,200 mL/g. The overall median K_{davail} value for:

- Be was 1114 mL/g, Ni was 105 mL/g, U was 3100, and As was 742 mL/g.
- For the Upland sediments (the DAB and DCP samples), the median K_{davail} value for: Be was 212 mL/g, Ni was 67 mL/g, U was 29,000, and As was 395 mL/g.
- For the Wetland sediments (D – K samples), the median K_{davail} value for: Be was 1900 mL/g, Ni was 1700 mL/g, U is 3100, and As is 20,000 mL/g.

Median K_d values in the Wetland were greater than in the Upland sediments for Be, Ni, and As: U K_d values were greater in the Upland sediments. The greater Be, Ni and As K_d values in the Wetland sediments can likely be attributed to the generally greater cation exchange capacity (due to greater organic carbon contents) in the Wetland than the Upland sediments. The cause for the greater U K_d values in the Upland sediments is not known.

Simple correlation coefficients were calculated separately with the Upland and the Wetland sediment data presented in Table 38 (Table 39). For the Upland sediments, pH was significantly correlated to Be and Ni K_d values (Figure 42 and Figure 43). Both these COC exist as cations in SRS groundwater, and therefore the positive correlation with pH is expected. In the Wetland sediments, As had a significant inverse correlation with pH. Again, this is expected because As is an anion and its tendency to sorb to surfaces increases under acidic conditions.

In the Wetland samples the correlation between Be and Ni was highly significant. The fact that U K_d values were generally negatively (inversely) correlated Be and Ni K_d values, but positively (directly) correlated to As K_d values suggests that the U existed primarily as an anion. Additional indirect evidence supporting the contention that U existed primarily as an anion is that it was significantly correlated to sulfate concentrations in the Upland and Wetland sediments.

For many of the DCP locations, the actual K_d should be larger that the calculated value due to the porewater concentration falling below the limit of detection.

pH was significantly correlated ($p \leq 0.01$; $df = 22$) to Be (Figure 42) and Ni (Figure 43) Ni K_{davail}. With increasing pH there is a corresponding increase in beryllium and nickel K_{davail}. This can be attributed in part to the increased cation exchange capacity and increased Fe-oxyhydroxide concentrations in the sediment expected with increased pH.

Likewise for uranium at upland locations with pH less than 6, pH is correlated with K_{davail} ($R^2 = 0.7$; $p \leq 0.01$; $df = 22$) (Figure 44). At these lower pH levels, aqueous U exists primarily as cationic species (UO_2^{2+}, UO_2OH^+) and as such they would tend to sorb more as the cation exchange capacity of the sediment increases with pH. As mentioned earlier, the increased cation exchange capacity can be attributed to changing surface charge of soil minerals and also to the increased formation of Fe-oxyhydroxides. For the wetland samples and for the upland DAB samples with pH levels greater than 6, pH is not well correlated with K_{davail}, although these values are quite high (>650 mL/g) regardless. The sample taken from the 488-D (DAB 86; ash basin) had the lowest U K_{davail}. This is likely attributable to the relatively high pH of this sample, pH 7.50, at which essentially all dissolved U likely exists as neutral or anionic species, such as $UO_2CO_3^0(aq)$, $UO_2(OH)_2^0(aq)$, $(UO_2)_2CO_3(OH)_3^-$, and $UO_2(CO_3)_2^{2-}$ (Krupka et al., 1999) (Figure 36). Neutral and anionic species are not expected to sorb strongly to sediments (Sposito, 1989).

Table 38. Summary of K_{davail} Based on Equation 1; Sum of Sequential Extraction Steps 1 – 6 and Porewater COC Concentrations

Sample Soil	Porewater pH	Porewater Sulfate (mg/L)	Be Kd_{avail} (mL/g)	Ni Kd_{avail} (mL/g)	U K_{davail} (mL/g)	As K_{davail} (mL/g)
DAB92 4-6	3.18	1866.2	8	0.19	282	186
DAB92 21-23	4.12	202.1	5	49	2.1E+03	8.8E+03
DAB85 32-33	5.18	864.2	212	81	8.2E+05	3.0E+04
DAB85 45	7.25	81.1	2.6E+03*		1.4E+05*	179*
DAB81 30-35	4.80	24.4	786*		3.4E+06*	1.1E+04*
DAB81 45	4.26	1315.2	6	27	2.9E+04	754
DAB81 50	7.98	422.1	9.3E+04*		655*	395*
DAB87 33	3.81	576.7	17*		97*	131*
DAB87 38	3.76	1296.7	4	74	20	16
DAB87 53	4.93	1347.9	137*		3.9E+05*	306*
DAB84 20	5.06	108.1	15*		1.1E+05*	151*
DAB84 28	4.56	907.2	5	118	441	38
DAB84 38	5.24	47.1	5.0E+03*		5.2E+06*	6.9E+03*
DAB83 32	6.61	310.1	928*		2.0E+03*	5.2E+03*
DAB83 38	7.50	20.9	2.1E+04*		3.3E+06*	389*
DAB83 42	7.87	63.6	1.5E+04	2.8E+04	9.1E+04	345
DAB86 12-16	7.50	1785.0	4.6E+04	3.1E+03	14	2.1E+03
DCP211/19-20	4.89	780.0		26		>398
DCP211/35-36	4.69	1476.0		5		>462
DCP168/20-22	5.61	62.4		>347		2.3E+03
DCP168/31-33	6.31	7.6		>59		742
DCP170/14-16	4.59	98.1		>14		26
DCP170/20-22	5.83	97.5		>92		68
D-2	5.49	5.5	8.6E+03	6.5E+03	153	8.8E+03
D-4	5.94	9.5	1.3E+03	1.7E+03	403	7.8E+03
G-10	6.12	72.2	4.6E+03	2.7E+03	1.5E+03	6.1E+03
H-5	6.02	174.5	1.3E+03	906	3.1E+03	2.0E+04
J-6	5.13	114.8	1.9E+03	284	3.8E+03	2.9E+04
K-4	4.52	101.5	1.1E+03	364	4.6E+03	3.3E+04

* indicate K_d values based on a single step extraction.

Table 39. Correlation Coefficients for K_{davail}, pH, and Sulfate Values Presented in Table 38

Upland data only					
	pH	**Sulfate**	**Be K_d**	**Ni K_d**	**U K_d**
Sulfate	-0.374				
Be K_d	0.648**	0.007			
Ni K_d	0.636**	-0.256	0.287		
U K_d	0.066	-0.442*	-0.076	-0.056	
As K_d	-0.083	-0.060	-0.179	-0.110	0.243

* Significant correlation at $p < 0.05$ for 22 degrees of freedom (df) is 0.423
** Significant correlation is significant at $p < 0.01$ for 22 degrees of freedom (df) is 0.537.

Wetland data only					
	pH	**Sulfate**	**Be K_d**	**Ni K_d**	**U K_d**
Sulfate	-0.098				
Be K_d	0.166	-0.566			
Ni K_d	0.261	-0.677	0.960**		
U K_d	-0.643	0.795*	-0.634	-0.777*	
As K_d	-0.810*	0.631	-0.558	-0.672	0.941**

* Significant correlation at $p < 0.05$ for 5 degrees of freedom is 0.755.
** Significant correlation at $p < 0.05$ for 5 degrees of freedom is 0.875.

Arsenic exhibited a broad range of K_d values (16 to 3 E+04 mL/g; Figure 45). Maximum K_d values observed were in the pH range between 4 and 6. This observation is consistent with the sorption of As (III) to metal oxides/hydroxides. A sorption maximum around 7 for As III on hydrous ferric oxide has been reported, whereas As V has a sorption maximum around pH 4. As pH increased above 6, lower K_d were observed likely due to desorption of arsenic, an anion, with increasing pH. The highest K_d values were associated with the wetland samples. The measurement of high K_d values for wetland samples is consistent both with similar K_{davail} values for the ash sample (DAB 86) and also with expectations that the wetlands should favor attenuation of arsenic due to increased biomass and less oxidizing conditions. Arsenic is strongly bound by soil organic matter (Cullen and Reimer, 1989). The lowest K_ds values were associated with the lowest pH locations in the vicinity of the DCPRB plume.

In summary, Be Ni, and U K_d values followed well established trends with pH. Because pH is an easy and routine parameter measured at the SRS, it will provide an excellent ancillary parameter for predicting the K_d values for these COCs. In the case of Be and Ni, pH across the entire range evaluated, pH 3 to 8, was an excellent predictor of K_d values. For U, pH was a good predictor of K_d values between pH 3 and 5. These observations are readily interpreted in light of geochemical sorption mechanisms based on expected metal speciation.

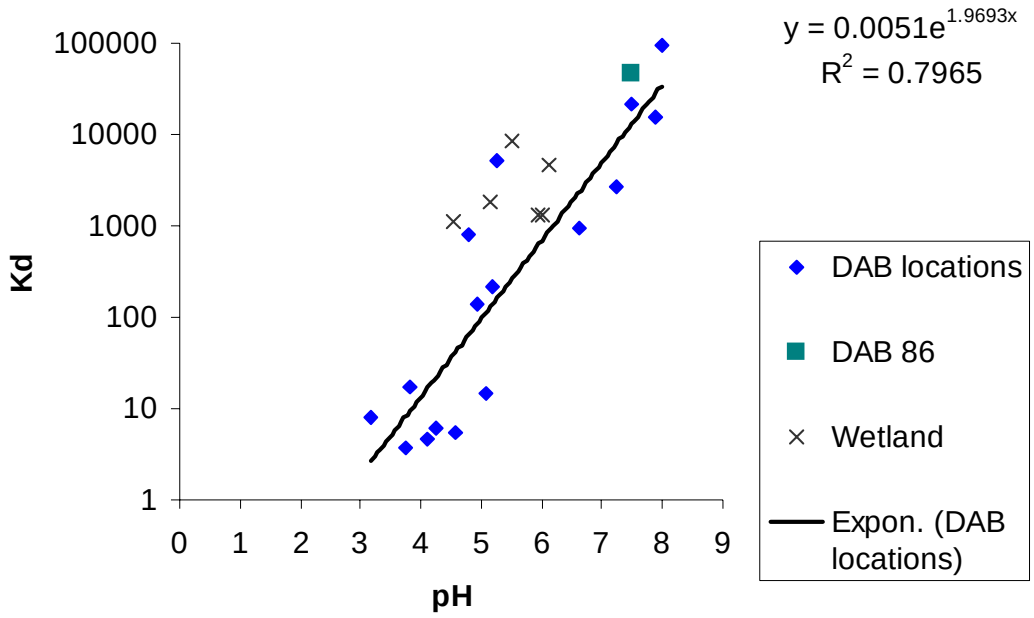


Figure 42. Beryllium Distribution Coefficients (mL/g; Based on Available Beryllium Sediment Concentrations) versus pH (log scale)

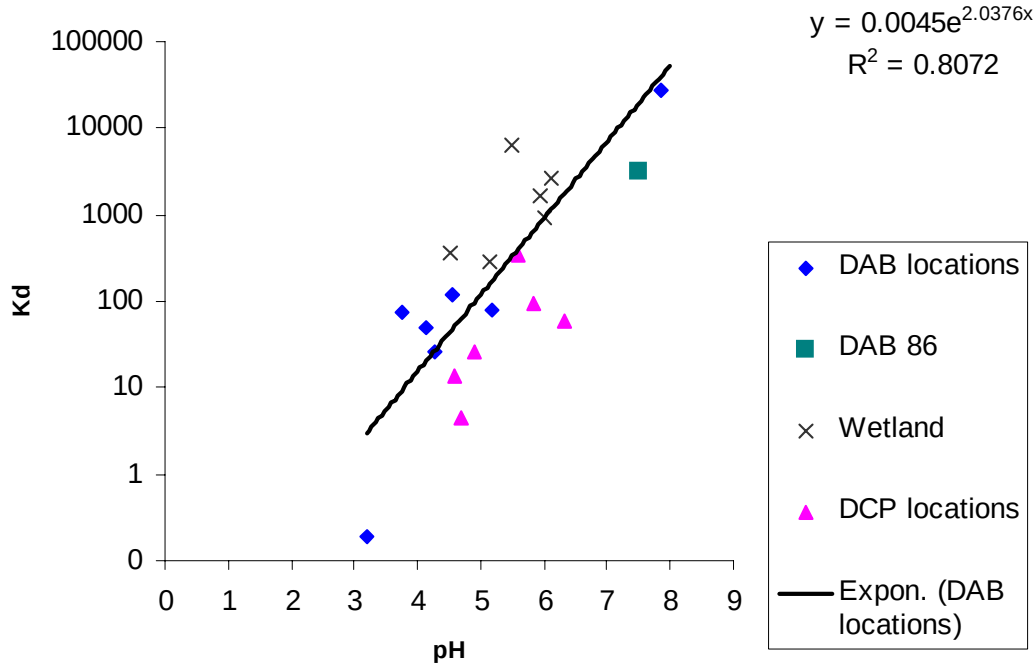


Figure 43. Nickel Distribution Coefficients (mL/g; Based on Available Nickel Sediment Concentrations) versus pH (log scale)

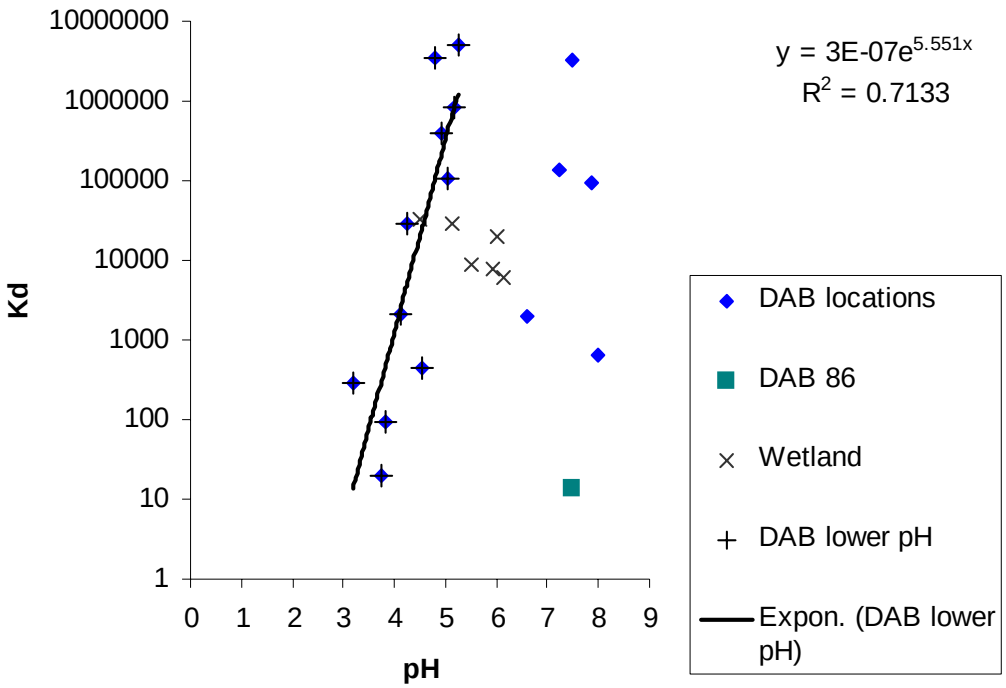


Figure 44. Uranium Distribution Coefficients (mL/g; Based on Available Uranium Sediment Concentrations) versus pH (log scale)

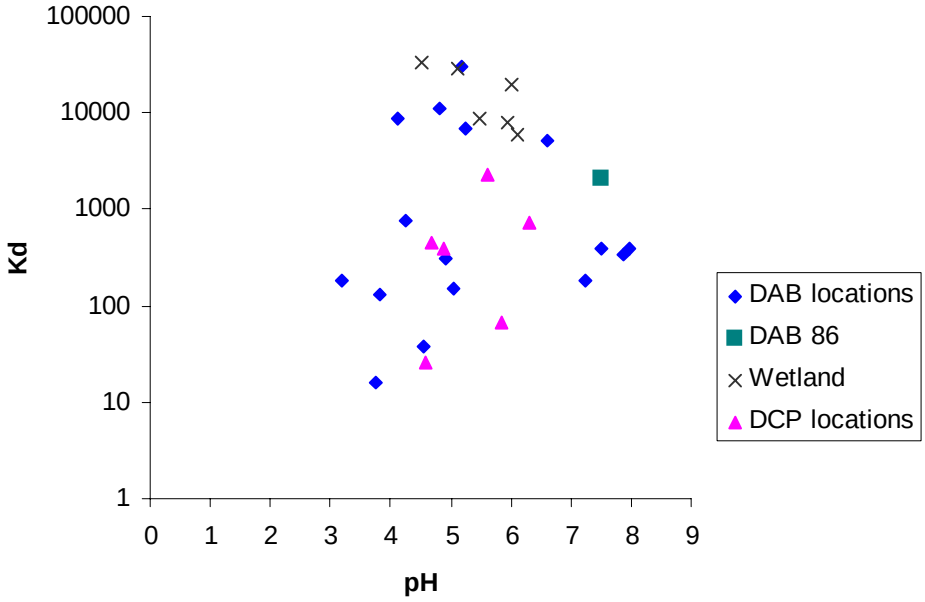


Figure 45. Arsenic Distribution Coefficients (mL/g; Based on Available Arsenic Sediment Concentrations) versus pH for all locations (log scale)

6.4 MICROBIOLOGY

Two sections of the contaminant plume were evaluated for biological and geochemical activity related to MNA. One section was under the ash basin, and sediment samples were taken at twelve different sites and depths down to 42 feet (estimated to be in the contaminant plume emanating from the DCPRB). The second section was in the D-Area wetland where shallow sediment cores were taken in four locations that were thought to be part of the DCPRB plume outcrop area, an area north of location H5 (Figure 2). Two additional wetland sites were on the distal fringe of the wetland and were thought to be unimpacted by either the ash discharged from the DAB or the DCPRB plume. Evaluation of the wetland area soil microbiology is complicated by the fact that an undetermined amount of ash was surficially deposited on this site due to past disposal practices. Much of the ash is still present in some wetland locations yielding ash layers of up to 1 m in depth below a shallow soil covering. Therefore some sections of the wetland are presumed to be impacted both by outcrop of the contaminant plume as well as ash deposited at the surface. The impact of these two contaminant sources was demonstrated through the use of discriminant analysis by region analysis of Biolog® data (Section 5.2). This data indicated that the two sample locations nearest the ash and contaminant plume outcropping area, K-4 and H-5, had bacteria structures more similar to those in impacted upland soils than wetland soils. Comparisons of the two sections, although difficult, were made in this report based on the assumed groundwater connectivity based on site hydrology characterization.

6.4.1 Microbial densities

Microbial densities (both total and viable) varied greatly with depth and site (Table 27 and Table 28, Figure 16 and Figure 17). In some sediments, no or very few viable aerobic cultures (plate counts) were detected (DAB 87 38) and yet the total counts were similar to other sites (Table 27). This lack of CFUs could be due to several reasons, including the fact that some bacteria require more specialized media, longer incubation times, or other culture conditions.

Since the media used was specific for aerobic culturable bacteria, few fungal colonies were seen on the culture media. D-Area fungi relative to metal removal could be examined in future studies. Several weeks after the initial sampling and plating, cultures from DAB 92 were replated to see if *Stenotrophomonas maltophilia* colonies were present in those sediment samples. Again, *S. maltophilia* is involved in a number of reactions that enhance contaminant sorption to sediments, including metal reduction (Se), production of insoluble metal precipitates, raising sediment pH, and desulfurization (discussed in detail in Section 6.4.3). The DAB 92 plates contained primarily fungal colonies and little *S. maltophilia* was culturable. The reason for these finding could be that fungal spores were present in the porewater but initially repressed in the media. Fungal populations likely are present in these sediments and could be contributing to MNA of the contaminants. This would take specific culture techniques to quantify the fungal relative densities and activity.

Limited numbers of sulfate reducing bacteria were detected in the Upland samples. Since many sulfate reducing populations are sensitive to oxygen exposure, it is possible that some were not detected because of extensive oxygen exposure during the sampling process. Sulfate reducers can play an important role in the MNA of sites contaminated with metals. An ongoing project (Phifer et al. 2003) in 488-D (the D-Area Ash Basin) shows the rise in sulfate reducers corresponding to the precipitation of metal sulfides in groundwater. These results were the result of biostimulation in the subsurface. The sulfate reducing bacteria use sulfate as an electron acceptor resulting in the production of sulfide and the subsequent in situ precipitation of metal sulfides.

Few acid-producing bacteria were found in the uplands in this study (Table 27). This is most likely due to nutrient limitations as these organisms prefer robust fermentative conditions. These results are promising for MNA in that it is preferred that the pH at the site go up rather than down for purposes of metal removal.

6.4.2 Ecofunctional Enzymes

Limited Biolog® substrate utilization was demonstrated in DAB 84 20 feet (located downgradient of 488-D, Figure 1) while none was seen in DAB 87 38 feet (located beneath the 488-D). These could be due to strictly anaerobic or viable but non-culturable bacteria at these sites. It may be possible to attribute community-level metabolic diversity to a population that becomes active only under controlled conditions; whereas under field conditions the same population may be stressed and/or inactive.

The Biolog® substrate utilization patterns measured aerobic ecofunctional enzyme activity in D-Area porewater demonstrating that the subsurface communities contained a diverse microbial population. Although significant differences in substrate utilization were measured in sediments tested, only some of the substrate types were significantly different in all of the sites. This suggests that these measured differences may reflect the normal variability inherent from sample to sample, rather than a definite spatial pattern in metabolic potential. For example, the carbon substrate utilization profiles detected a significant difference in metabolic activities with depth in upland sediments (Figure 18). Wetland sediments were taken at all locations at only one depth and showed significant spatial differences (Figure 19).

The principal component analysis of Biolog® data did separate microbial communities based on location within the contaminant plume. Differences between depths of sediment samples make comparisons of uplands vs. wetlands difficult. This indicates that either the range of contaminant concentrations (ppb-low ppm) chosen for this study was too narrow to influence metabolic activity, or that the variability inherent in natural communities over such a heterogeneous physical area is so great that activity towards 95 substrates could not be used to successfully separate the communities. In addition, the usefulness of Biolog® information in microbial ecological studies is further limited by the potential of populations to thrive within a substrate containing well under controlled laboratory conditions.

If there is an advantage of Biolog® over direct cell enumeration to characterize microbial ecology at the community level, it is the capability of Biolog® to describe the potential rate of metabolic function and activity towards a wide range of substrates (Bochner and Savageau 1977, Garland and Mills 1991, Gordon et al. 1993, Guckert et al., 1996) With the proper controls, this database can potentially describe the activity and function of entire microbial communities, as opposed to merely indicating a 'snap shot' of total cell densities or of a specific cell type. Future MNA studies using the Biolog® community-level analysis should try to measure the percentage of the community that is responsible for a majority of specific activity, as well as addressing the ecological relevance of the substrates to the environment being examined.

6.4.3 Identification of Cultured Isolates

Stenotrophomonas maltophilia, the predominant bacterial type isolated from DAB 83 and DAB 84, is a commonly found aerobic environmental gram-negative bacillus. *Stenotrophomonas maltophilia* has been isolated from aquatic environments, from soils, and from vegetation (Bollet et al., 1995) and is becoming increasingly prevalent in infections in immuno compromised patients, particularly those with cystic fibrosis (Denton et al. 2000). *Stenotrophomonas maltophilia*, isolated from uranium mining wastes, has been proven capable of forming uranium complexes by binding processes (Merroun et al., 2002). In addition, *Stenotrophomonas maltophilia*, isolated from a seleniferous agricultural evaporation pond sediment in California was capable of reducing selenium oxyanions (selenate and selenite) to elemental selenium at oxygen levels less than 0.1 mg/L and is being investigated for bioremediation purposes to treat seleniferous wastewater (Dungan et al., 2003). There has been evidence of the presence of *Stenotrophomonas maltophilia* in petroleum contaminated soils containing dibenzothiophene (DBT) and in sulfurous oil contaminated sediments. Gene amplification studies of the genes that encode enzymes involved the desulphurization of these compounds has associated *Stenotrophomonas maltophilia* with this process (Duarte et al., 2001). *Stenotrophomonas maltophilia*'s potential ability for metal reduction, insoluble metal complex formation, and desulfurization, along with its predominance in these SRS sediment samples, may be significant factors in the monitored natural attenuation of this SRS site. In this study, this bacterium was only identified and found to be predominant in DAB 83 and 84. Isolated bacteria including *Stenotrophomonas maltophilia* and *Enterobacter* have the ability to raise pH as demonstrated here and can reduce metal availability that can enhance MNA of metals.

Future work would examine specific metal and sulfur biotransformation at this site in relation to *Stenotrophomonas maltophilia* and *Enterobacter* sp. In addition, molecular techniques could be applied to determine the distribution and activity of these organisms at the site.

7.0 SUMMARY AND CONCLUSIONS

Low aqueous concentrations of metals and large distribution coefficients (K_d values) are strong indicators that natural attenuation is occurring to a significant degree at D-Area. For the plume emanating from the vicinity of the D-Area Coal Pile (DCP) and D-Area Coal Pile Runoff Basin (DCPRB) significant attenuation of all metal COCs evaluated is occurring in groundwater relative to modeled dilution effects. This conclusion was further supported in a separate task to this project in which it was shown that DCPRB sediment had an extraordinarily high capacity to sorb several contaminants (Kaplan and Knox, 2004). The magnitude and relative contributions to this attenuation from geochemical and biological effects were evaluated in terms of pH, redox, sulfate, porewater COC concentrations, and % metal in soil available for transport, *in situ* transport factors, and biological indicators.

Large distribution coefficients demonstrate the high attenuation capacity of the D-Area soil for the four COCs in this study (Be, Ni, U, As). Distribution coefficients for each of the COCs followed well-established geochemical trends for pH dependent sorption mechanisms. A number of operationally defined methods were evaluated to better define the fraction of COCs likely available for transport in a range of D-Area soils in order to develop a more appropriate definition of the sources of COCs in these soils as well as to better define the distribution coefficients or *in situ* K_d values used to model the transport of these sources.

MNA at D-Area can be interpreted and quantified based on geochemical mechanisms. The large buffering capacity of the upland soils in D-Area for the acid emanating from the DCPRB accounts for attenuation of acidity. This buffering capacity is attributed to the metal oxides/hydroxides present in D-Area soils. Attenuation of acidity leads to precipitation of dissolved metal oxides/hydroxides (Al, Fe, Mn) that further increases the sorption capacity (as evidenced by high cation exchange capacities) of these soils for trace metal COCs. This effect is quantified in terms of the pH dependence of the distribution coefficients (K_d).

The microbiological community evaluation revealed the presence of microorganisms at all tested locations including low pH, high sulfate plume regimes as well as in the wetland area (both nonimpacted sites as well as sites impacted by ash sluice). Aerobic functional and structural diversity of microbial communities were identified from most D-Area sediment cores. Microbial diversity and concentration increased with distance from the D-Area Coal Pile and D-Area Coal Pile Runoff Basin.

Both aerobic (*Stenotrophomonas maltophilia*) and anaerobic sulfate reducing bacteria (SRBs) microbial species capable of desulfurization and metal reduction were found at the site indicating potential contribution of microbial community to natural attenuation. The isolation and predominance of *Stenotrophomonas maltophilia* from upland locations and its potential for aerobic metal biotransformation and complex formation may be strong indicators of aerobic metal interactions occurring in the upland areas. Sulfate reducers were at low concentration in the uplands soils.

Microbial evidence also indicates natural contaminant attenuation potential in the wetland/upland interface, but could not be quantified from these studies. This is evidenced by decreasing aqueous sulfate concentrations and increased bacterial counts as the plume moves further into the wetlands. Distinct differences in bacterial counts and structure were measured between the upland and wetland locations. The greater bacterial counts in the wetlands may contribute to natural attenuation through biosorption. Comparison of wetland to upland samples showed a commonality between substrate utilization for the wetland samples closest to the discharge area and upland samples. Those wetland locations most impacted by the contaminants, K-4, J-6, and H-5, had low EFE as compared to those sites further from the source, D-4, D-2, and G-10 (Figure 23).

Because geochemical and microbiological effects on the attenuation of inorganics are necessarily related through numerous relationships such as redox, it is difficult to isolate the individual contribution of each in the natural environment. Based on the lower abundance of organisms in the areas of highest impact (low pH, high sulfate), it is likely that geochemical effects such as sorption and precipitation dominate here. pH was found to be the most significant predictor of attenuation as evidenced by porewater concentrations, % availability of COC in soil, and distribution coefficients. As the COC plume approaches higher pH regimes in the wetland areas the microbial community is more active and likely contributes to a higher degree in the attenuation of COCs.

8.0 RECOMMENDATIONS

Based on the findings in this report, the following recommendations are made.

1. It is recommended that MNA be invoked at the DEXOU. There is a preponderance of evidence documented in this report supporting this approach, including porewater COC concentration trends, soil sorption data, and soil microbial characterization data.

2. To account for many of the natural attenuating processes occurring at the site, it is recommended that future risk/groundwater modeling use the pH-dependent K_d values reported here. This is consistent with conceptual hydrogeochemical model of pH-dependent transport factors documented in Brewer and Sechor (2002). These pH-dependent K_d values should be the site-specific values generated in this study based on COC desorption, the rate-limiting reaction, as compared to (ad)sorption. Furthermore, these values are technically defensible and they greatly reduce the uncertainty associated with literature-derived or theoretically-derived K_d values. Additionally, pH is recommended as a "master variable" for determining K_d values at the site because: 1) it was highly correlated to several groundwater secondary parameters that influence COC sorption in this system (e.g., Eh, sulfate, and cation exchange capacity) and, therefore, these K_d values to some degree account for variations in these secondary parameters, 2) it is easy to measure, and 3) there is a large amount of historical pH data available for the site. More sophisticated sorption models were evaluated. However, the current state-of-the-art does not permit for a quantitative model for metals attenuation by microbial processes. Therefore, the implementation of a more sophisticated model for either biotic or geochemical processes is not warranted at this time.

3. It is recommended that additional natural attenuation of COC be accounted for in future modeling by including only the "available fraction" of COC in the source term. By doing so, the mass of COC available for entering into the mobile aqueous phase may be decreased by as much as 90%. The "<u>non</u>available fraction" is that fraction of the total COC pool that is strongly bound by the source material.

4. If MNA were to be implemented, a monitoring network based on existing wells and sampling strategy will need to be developed. It is recommended that this sampling strategy include: pH, Eh, organic carbon content, chemical and biological oxygen demand, aqueous COC concentrations on a relatively frequent basis and, on a less frequent basis available soil concentrations and microbial densities and activities.

5. Although there is a high degree of certainty for the effectiveness of MNA of inorganics at the D-Area, the following are data gaps that should be considered:

    a. Work is currently being conducted on more active source remediation techniques (Phifer et al., 2003). If this approach, or an alternative approach, is implemented, then the effects of the source remediation on the attenuation processes at the site will need to be evaluated.

    b. Although the majority of the attenuation of metals is currently going on in the upland areas of the waste site, the wetlands at the D-Area are a large, yet unaccounted for, attenuation capacity. The hydrologic flow through this system, however, is not well known and could be beneficial to the MNA approach, if additional attenuation capacity is necessary. This should include an evaluation of the flow fields in the wetlands under high- and low-water level conditions.

    c. Characterization of wetland soils below the ash deposition in the wetland would provide additional validation of geochemical assumptions in previous modeling (pH and sorption of COCs).

    d. The work completed in this study is represents a "snapshot" in time. The temporal effects (e.g., seasonal changes) should be examined.

    e. Transport of arsenic has not been modeled. Given that arsenic exists as anionic species and demonstrates a departure in sorption behavior from previously modeled cations (Be, Ni, U). The reversibility of sorption of arsenic near/in the DCPRB should be evaluated as geochemical conditions are expected to change with source control.

6. Microcosm studies with D-Area groundwater could be used for estimations of metal attenuation rates. Experiments with D-Area microbial biomass could be designed to assess metal biosorption in the subsurface. Follow-up microbiological testing of ground water wells and wetlands can be used to validate long term MNA biological potential as well as seasonality of activity. Future work should be designed to characterize the behavior of these metals as related to redox, cationic vs. anionic sp., sediments vs. groundwater, alkaline vs. acidic conditions, and oxidative vs. reducing conditions.

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APPENDIX A.
SEQUENTIAL EXTRACTION PROCEDURE

I. PURPOSE

This procedure provides a method of identifying the trace metals and contaminates sorbed on to specific soil phases of a sample. Through selective chemistry, 8 different soil phases are identified and removed utilizing a sequential extraction procedure as outlined by Miller (1986). Samples extracted from this procedure can be analyzed by ICP-MS.

II. REQUIRED EQUIPMENT/REAGENTS

A. Equipment

1. 50-ml Oak Ridge centrifuge tubes
2. #10 (2-mm) soil sieve
3. 0.45-µm cellulose acetate or cellulose nitrate syringe filters
4. 0.45-µm PTFE syringe filters
   a. or #42 Whatman filter paper and plastic filtering funnels
5. 30-ml syringes
6. 1-liter volumetric flasks
7. 1-liter reagent bottles
8. 125-ml glass reagent bottle
9. 50-ml plastic volumetric flasks
10. 30-ml sample bottles
11. 60-ml sample bottles
12. Hot acid digestion bombs with PTFE inserts
13. Disposable transfer pipettes
14. Test tube racks for 50-ml Oak Ridge tubes
15. Aluminum foil
16. Aluminum drying dishes
17. High-speed centrifuge
18. 25-ml graduated cylinders
19. 50-ml graduated cylinders

B. Equipment

1. Ultra-pure 72% nitric acid [HNO_3]
2. Ultra-pure 48% hydrofluoric acid [HF]
3. Ultra-pure 36% hydrochloric acid [HCl]
4. Hydroxylamine-hydrochloride [$NH_2OH•HCl$]
5. Ammonium oxalate [$(NH_4)_2C_2O_4•H_2O$]
6. Calcium nitrate [$Ca(NO_3)_2•4H_2O$]
7. 99.5% Glacial acetic acid [CH_3COOH]
8. Sodium pyrophosphate [$NaP_2O_7•10H_2O$]
9. Oxalic acid [C2H2O4] or oxalic acid dihydrate [$C2H2O4•2H_2O$]
10. Citric acid monohydrate [$C_6H_8O_7•H_2O$ or $HOC(CH_2CO_2H_2)_2CO_2H•H_2O$]
11. Sodium citrate dihydrate [$NaC_6H_5O_7•2H_2O$]
12. Sodium hydrosulfite or hyposulfite dithionite [$Na_2S_2O_4•H_2O$]
13. Distilled, deionized (DDI) water

III. PROCEDURE

A. Preparation of Reagents

1. Exchangeable Reagent
   a. Add 118 g of calcium nitrate to a 1-liter volumetric flask.
   b. Fill the flask about half full with DDI water and swirl to dissolve calcium nitrate
   c. Dilute to the mark with DDI water.
2. Acid Soluble Reagent
   a. Add 23.6 g of calcium nitrate and 25.4 ml of glacial acetic acid into a 1-liter volumetric flask
   b. Dilute up to the mark with DDI water to make a 0.44 M acetic acid 0.1 M calcium nitrate solution.
3. Manganese Oxide Occluded Reagent
   a. Add 0.694 g of hydroxylamine-hydrochloride and 6.3 ml of 72% nitric acid into a 1-liter volumetric flask.
   b. Dilute up to the mark with DDI water to obtain a 0.01 M hydroxylamine-hydrochloride/0.1 M nitric acid solution.
4. Organically Bound Reagent
   a. Add 44.6 g of sodium pyrophosphate into a 1-liter volumetric flask.
   b. Dilute to the mark with DDI water to make a 0.1 M solution.
5. Amorphous Iron Oxide Reagent:
   a. 24.9 g of ammonium oxalate and 9.00 g of oxalic acid (or 12.6 g of oxalic acid dihydrate) into a 1-liter volumetric flask
   b. Dilute to the mark with DDI water to make a 0.175 M ammonium oxate/0.l M oxalic acid solution.

6. Crystalline Fe Oxide Reagent:
   a. Add 44.1 g of sodium citrate dihydrate and 10.51 g of citric acid hydrate to a 1-liter volumetric flask.
   b. Dilute to the mark with DDI water to make a 0.15 M sodium citrate/ 0.05 M citric acid solution.
7. Aqua Regia
   a. In a fume hood add 20 ml of 72% nitric acid and 60 ml of 36% hydrochloric acid in a 125-ml labeled storage bottle.
   b. Leave the bottle uncovered overnight to allow gas from reaction to escape.
   c. Store in an approved acid storage area.
8. Calcium Nitrate Wash Solution
   a. Add 3 g of calcium nitrate to a 1-liter volumetric flask.
   b. Dilute to the mark with DDI water to make a 0.0127 M so1ution.

B. Sample Preparation

1. Sieve the air-dried soil sample through a 2-mm sieve.
2. Record the weight of clean, dry, 50-ml Oak Ridge centrifuge tubes. 4 tubes are required for each sample (three repetitions and one blank).
3. Add approximately 0.750 g of the air-dried, sieved soil into each pre-weighed centrifuge tube (except the blank).

C. Soluble Fraction

1. Add 30-ml of DDI water to each tube
2. Record the weight of the tube and added water. Calculate and record the actual volume of water added.
3. Shake for 16 hours on a wrist-action shaker at approximately 90 cycles per minute.
4. Centrifuge at 10,000 RPM for 30 minutes.

NOTE: During this entire procedure, use a transfer pipette to carefully remove the supernate from the tubes and transfer it to the syringe barrel or discard it.

5. Filter supernate from each tube through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
6. Acidify the supernate with 150 µl of 72% nitric acid and save for analysis.
7. Weigh and record the weight of each tube and extract. Record the actual volume of extract removed from each tube.
8. Add 20 ml of DDI water to each tube.
9. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
10. Centrifuge for 30 minutes at l0,000 rpm.
11. Discard the supernate.

D. Easily Exchangeable Fraction

1. Record the weight of tube and residue.
2. Add 30 ml of exchangeable reagent to each tube.
3. Record the weight of the tube and added reagent. Calculate and record the actual volume of reagent added.
4. Shake for 16 hours on a wrist-action shaker at approximately 90 cycles per minute.
5. Centrifuge for 30 minutes at 10,000 rpm**.**
6. Filter supernate from each tube through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
7. Acidify supernate with 150 µl of 72% nitric acid and save for analysis.
8. Record the weight of tube and residue. Calculate the actual amount of supernate extracted.
9. Add 20 ml of calcium nitrate wash solution to each tube.
10. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
11. Centrifuge for 30 minutes at 10,000 rpm.
12. Discard the supernate.

E. Acid Soluble Fraction

1. Record the weight of tube and residue.
2. Add 30 ml of the acid soluble reagent to each tube.
3. Record the weight tube and residue. Calculate the amount of reagent added.
4. Shake for 8 hours on a wrist-action shaker at approximately 90 cycles per minute.
5. Centrifuge for 30 minutes at 10,000 rpm**.**
6. Filter supernate from each tube through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
7. Acidify supernate with 150 µl of 72% nitric acid and save for analysis.
8. Record the weight of tube and residue. Calculate the actual amount of supernate extracted.
9. Add 20 ml of calcium nitrate wash solution to each tube.
10. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
11. Centrifuge for 30 minutes at l0,000 rpm.
12. Discard the supernate.

F. Manganese Oxide

1. Record the weight of tube and residue.
2. Add 30 ml of the acid soluble reagent to each tube.
3. Record the weight tube and residue. Calculate the amount of reagent added.
4. Shake for 30 minutes on a wrist-action shaker at approximately 90 cycles per minute.
5. Centrifuge for 30 min. at 10,000 rpm.
6. Filter the supernate through a 0.45-µm cellulose acetate filter and into a 30-ml sample bottle.
7. Acidify supernate with 150 µl of 72% nitric acid and save for analysis.
8. Record the weight of tube and residue. Calculate the actual amount supernate extracted.
9. Add 20 ml of calcium nitrate wash solution to each tube.
10. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
11. Centrifuge for 3to minutes at 10,000 rpm.
12. Discard the supernate.

G. Organically Bound Fraction

1. Record the weight of tube and residue.
2. Add 30 ml of the organically bound reagent to each tube.
3. Record the weight tube and reagent. Calculate and record the actual volume of reagent added.
4. Shake for 24 hours on a wrist-action shaker at approximately 90 cycles per minute.
5. Centrifuge for 30 min. at 10,000 rpm.
6. Filter the supernate through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
7. Acidify the supernate with 150 µl of 72% nitric acid and save for analysis.
8. Record the weight of each tube and residue. Calculate the actual amount of supernate extracted.
9. Add 20 ml of calcium nitrate wash solution to each tube.
10. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
11. Centrifuge for 30 minutes at l0,000 rpm.
12. Discard the supernate.

H. Noncystalline Aluminosilcates and Hydrous Oxides

NOTE: Steps 2 through 10 must be completed in such a manner to prevent ultra-violet light from influencing the sample. Steps 2, 3, and 7, and when loading or unloading tubes from the centrifuge should be performed under red light if possible. The presence of ultra-violet light causes the removal of the crystalline as well as the non-crystalline phases.

1. Record the weight of tube and residue.
2. Label and record the weight of a 15 cm by 15 cm sheet of aluminum foil for each tube.
3. Add 30 ml of amorphous iron oxide reagent to each tube and immediately wrap the tube in aluminum foil.
4. Record the weight of each tube, reagent and foil. Calculate and record the actual volume of reagent used.
5. Shake for 4 hours on a wrist-action shaker at approximately 90 cycles per minute.
6. Centrifuge the tubes for 30 minutes at 10,000 rpm.
7. Filter the supernate through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
8. Record the weight of the each tube, residue and foil. Calculate the actual volume of supernate extracted.
9. Add 20 ml of calcium nitrate wash solution to each tube.
10. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
11. Discard the foil and centrifuge each tube for 30 minutes at 10,000 rpm.
12. Discard the supernate.

I. Crystalline Iron Oxides and Aluminum Oxides

1. Record the weight of tubes and residue.
2. Add 30 ml of crystalline oxide reagent to each tube.
3. Add 0.75 g of sodium hydrosulfite to each tube.
4. Record the weight of each tube and reagent. Calculate and record the actual volume of reagent added.
5. Shake for 0.5 hours in a water bath at 50°C at approximately 90 cycles per minute.
6. Centrifuge for 30 minutes at l0,000 rpm.
7. Filter the supernate through a 0.45-µm cellulose-acetate filter and into a 30-ml sample bottle.
8. Acidify the supernate with 150 µl of 72% nitric acid and save for analysis.
9. Record the weight of tube and residue. Calculate the actual volume supernate extracted.
10. Add 20 nil of calcium nitrate wash solution to each tube.
11. Vortex each tube for 5 to 10 seconds to loosen soil from the tube.
12. Centrifuge for 30 minutes at 10,000 rpm.
13. Discard the supernate.

J. Total and Partial Digestions of Samples

1. Label and weigh an aluminum drying dish for each tube.
2. Spray ≈5 ml of DDI water into each tube and vortex the tube long enough to break up the pellet at the bottom.
3. With the aid of a DDI water rinse, transfer the tube's contents to a drying dish.
4. Dry the soil residue at l05°C in an oven until a constant weight is reached.
5. Place approximately 200 mg of oven-dried soil residue from each tube into an acid digestion bomb insert.
6. Add approximately 200 mg of original soil which has been air-dried and passed through a #10 sieve into an acid digestion bomb insert.

DANGER: Steps 7, 11, 12, and 13 must be performed inside a fume hood.

7. Add to each 1 ml of aqua regia and 10 ml of 48% HF to each vessel.
8. Place the bomb inserts into the digestion bomb shells and tighten until just hand tight.
9. Place bombs into a 105°C oven for 3 hours.
10. Remove the bombs from the oven and allow to cool for at least 15 minutes.
11. Filter the extract from the bomb inserts flasks through either PTFE syringe filters into a plastic 50-ml volumetric flask.
12. Dilute to 50 ml with DDI water.
13. Transfer to a 60-ml sample bottle for storage and transfer.

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APPENDIX B.
SEQUENTIAL EXTRACTION DATA

Table B- 1. Abbreviations for sequential extraction steps

Abbreviation	Sequential Extraction Step
DDI	Water Soluble
CN	Easily Exchangeable
AA	Acid Soluble
HH	Easily Reducible
HP	Organic Bound
AO	Amorphous Oxide Bound
SD	Crystalline Oxide Bound
PD	Residual

Table B- 2. Wetland beryllium in soil (ppm)

Beryllium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.00	0.04	0.34	0.06	0.29	0.04	0.02	0.69
stdev	0.00	0.00	0.10	0.00	0.07	0.01	0.00	0.09
D4 1	0.00	0.05	0.25	0.06	0.30	0.03	0.03	1.11
stdev	0.00	0.02	0.03	0.00	0.02	0.01	0.03	0.27
G10 2	0.00	0.05	0.60	0.22	0.47	0.05	0.00	5.68
stdev	0.00	0.05	0.18	0.00	0.08	0.00	0.00	0.23
H5 1	0.00	0.03	0.69	0.24	0.39	0.04	0.00	3.15
stdev	0.00	0.01	0.12	0.01	0.08	0.00	0.00	0.57
J6 2	0.00	0.03	0.43	0.22	0.40	0.03	0.00	4.97
stdev	0.00	0.00	0.02	0.00	0.04	0.01	0.00	0.83
K4 2	0.00	0.08	0.51	0.23	0.56	0.02	0.01	3.86
stdev	0.00	0.04	0.01	0.02	0.02	0.00	0.00	0.69

Table B- 3. Wetland aluminum in soil (ppm)

Aluminum ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	4.00	34.96	5.74	0.35	0.00	0.13	15.12	51102.09
stdev	0.83	0.42	1.50	0.01	0.02	0.18	3.75	14971.23
D4 1	1.62	35.71	5.74	0.50	0.00	0.10	12.64	77248.24
stdev	0.97	5.00	0.38	0.10	0.02	0.01	0.67	2331.23
G10 2	1.23	26.58	1.07	0.00	0.34	0.88	75.47	68006.83
stdev	0.80	0.50	1.25	0.00	0.49	0.52	3.44	6713.22
H5 1	1.92	20.75	2.45	0.02	0.39	1.00	46.00	44679.49
stdev	0.01	0.42	0.07	0.03	0.02	0.13	3.35	7415.49
J6 2	1.21	97.21	4.83	0.00	0.96	1.39	55.51	70211.12
stdev	1.20	2.19	2.73	0.00	0.43	0.07	12.19	8584.49
K4 2	1.60	123.09	5.70	0.13	0.00	1.41	57.14	54220.23
stdev	0.26	9.96	1.40	0.18	0.02	0.35	11.32	6318.70

Table B- 4. Wetland nickel in soil (ppm)

Nickel ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.01	0.63	17.41	0.36	2.01	0.18	0.51	11.70
stdev	0.00	0.19	11.28	0.04	0.52	0.03	0.08	1.42
D4 1	0.00	0.51	1.86	0.44	1.89	0.23	0.76	18.74
stdev	0.00	0.27	2.64	0.02	0.10	0.05	0.09	0.21
G10 2	0.07	1.44	3.88	0.85	4.49	0.43	0.71	36.57
stdev	0.00	0.30	5.48	0.00	1.78	0.03	0.01	5.19
H5 1	0.02	2.06	2.75	0.93	3.19	1.77	0.99	27.88
stdev	0.00	0.26	2.82	0.03	0.70	0.12	0.12	6.77
J6 2	0.10	1.56	4.28	0.69	2.97	0.62	0.94	35.67
stdev	0.00	0.17	2.13	0.02	0.56	0.11	0.34	3.90
K4 2	0.06	0.00	1.86	0.30	3.68	0.94	1.08	28.44
stdev	0.02	0.17	2.63	0.04	0.36	0.61	0.16	2.38

Table B- 5. Wetland arsenic in soil (ppm)

Arsenic ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.01	0.23	0.58	0.08	0.69	2.03	1.90	0.84
stdev	0.00	0.05	0.16	0.02	0.17	0.23	0.56	0.32
D4 1	0.01	0.22	0.25	0.08	0.48	2.71	2.79	1.21
stdev	0.00	0.06	0.05	0.00	0.01	0.40	0.37	0.26
G10 2	0.07	0.13	2.51	2.98	23.21	11.51	2.30	1.51
stdev	0.01	0.01	0.75	0.01	1.73	0.10	0.08	0.15
H5 1	0.16	0.06	5.26	7.08	48.77	14.44	1.05	1.12
stdev	0.02	0.04	0.10	0.24	13.48	0.80	0.05	0.18
J6 2	0.02	0.06	2.30	3.07	28.32	3.88	0.84	2.31
stdev	0.01	0.09	0.17	0.72	4.24	0.79	0.06	0.62
K4 2	0.02	0.35	0.96	1.62	51.68	20.51	1.85	1.34
stdev	0.01	0.11	0.07	0.02	5.25	2.41	0.48	0.07

Table B- 6. Wetland selenium in soil (ppm)

Selenium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.00	0.23	1.16	0.21	0.14	0.34	0.00	0.00
stdev	0.01	0.33	0.73	0.02	0.20	0.03	0.07	0.00
D4 1	0.00	0.46	0.90	0.15	0.00	0.42	0.00	0.00
stdev	0.00	0.34	0.25	0.01	0.03	0.10	0.07	0.00
G10 2	0.03	0.44	0.08	0.27	5.75	0.35	0.00	0.00
stdev	0.04	0.15	0.11	0.01	1.00	0.08	0.07	0.00
H5 1	0.09	0.36	0.55	0.49	8.21	0.21	0.15	0.00
stdev	0.01	0.02	0.29	0.01	2.55	0.07	0.22	0.00
J6 2	0.01	0.55	0.51	0.32	3.63	0.03	0.27	0.00
stdev	0.02	0.13	0.68	0.13	1.11	0.01	0.39	0.00
K4 2	0.02	0.41	0.17	0.29	3.45	0.45	0.96	0.00
stdev	0.02	0.51	0.24	0.08	0.70	0.04	0.74	0.00

Table B- 7. Wetland uranium in soil (ppm)

Uranium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.44	0.00	0.92	0.40	0.58	0.11	0.08	1.18
stdev	0.37	0.00	0.18	0.03	0.22	0.02	0.00	0.34
D4 1	0.05	0.00	0.39	0.53	0.68	0.16	0.13	1.92
stdev	0.02	0.00	0.12	0.02	0.03	0.03	0.03	0.04
G10 2	0.02	0.00	0.25	0.89	1.35	0.30	0.05	3.08
stdev	0.00	0.00	0.03	0.04	0.48	0.00	0.02	0.32
H5 1	0.00	0.00	0.11	0.72	1.73	0.28	0.06	2.03
stdev	0.00	0.00	0.04	0.01	0.42	0.03	0.01	0.47
J6 2	0.00	0.00	0.09	0.55	1.42	0.19	0.04	3.01
stdev	0.00	0.00	0.01	0.06	0.05	0.03	0.00	0.38
K4 2	0.00	0.00	0.14	0.68	1.04	0.18	0.02	1.92
stdev	0.00	0.00	0.00	0.04	0.12	0.02	0.00	0.16

Table B- 8. Wetland iron in soil (ppm)

Iron ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	5.45	0.04	24.16	473.70	3998.59	3794.47	8664.89	10763.12
stdev	1.99	0.00	1.84	10.67	76.26	311.89	1180.09	3744.15
D4 1	1.54	0.04	47.87	626.25	3762.71	5828.59	13769.93	13991.04
stdev	0.72	0.00	0.46	25.17	170.68	439.54	1865.29	2201.74
G10 2	0.90	0.04	147.25	624.80	2596.34	830.41	808.93	13340.80
stdev	0.26	0.01	5.47	7.82	8.74	43.25	124.21	1203.49
H5 1	2.50	0.06	40.97	662.36	3597.65	4363.48	699.65	17035.68
stdev	1.41	0.03	0.48	5.32	148.21	1055.36	32.09	2103.53
J6 2	0.05	0.48	64.63	451.21	2125.83	1099.91	531.53	20458.00
stdev	0.05	0.08	1.22	11.99	211.30	91.66	38.64	2446.35
K4 2	0.21	0.51	100.46	526.18	3683.34	2298.70	593.34	13231.93
stdev	0.00	0.13	0.28	6.84	34.24	1178.27	47.93	1634.30

Table B- 9. Wetland vanadium in soil (ppm)

Vanadium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
D2 1	0.99	0.96	0.04	1.51	12.64	5.69	19.58	29.51
stdev	1.33	0.91	0.05	0.03	0.49	0.73	2.84	8.61
D4 1	0.04	0.10	0.19	1.96	13.09	12.14	31.61	41.49
stdev	0.00	0.09	0.09	0.12	0.97	0.45	4.40	5.93
G10 2	0.41	0.04	2.34	9.77	27.86	0.25	2.28	84.04
stdev	0.02	0.01	0.04	0.10	0.18	0.31	0.43	3.46
H5 1	0.52	0.11	1.42	10.83	31.85	0.26	0.92	56.88
stdev	0.08	0.10	0.16	0.22	1.25	0.32	0.09	8.24
J6 2	0.08	0.03	1.11	4.99	19.74	0.04	0.74	92.63
stdev	0.04	0.01	0.27	0.15	1.97	0.05	0.02	13.66
K4 2	0.02	0.04	0.69	4.28	27.12	3.84	1.09	69.90
stdev	0.02	0.01	0.04	0.07	0.33	0.24	0.11	5.04

Table B- 10. Upland beryllium in soil (ppm)

Beryllium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	0.00	0.59	0.18	0.03	0.02	0.02	0.01	1.19
stdev	0.00	0.12	0.12	0.00	0.00	0.01	0.01	0.18
168 / 20	2.24	2.07	0.36	0.04	0.06	0.01	0.00	0.42
stdev	0.13	0.24	0.02	0.00	0.00	0.00	0.00	0.13
168 / 31	1.05	0.58	0.03	0.00	0.02	0.00	0.00	0.18
stdev	0.02	0.22	0.04	0.00	0.00	0.00	0.00	0.09
170 / 1	0.00	0.04	0.01	0.00	0.00	0.01	0.00	0.25
stdev	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.15
170 / 14	0.01	0.02	0.00	0.00	0.02	0.01	0.00	0.22
stdev	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
170 / 20	0.16	0.00	0.01	0.01	0.00	0.02	0.00	0.64
stdev	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.05
211/ 2	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.19
stdev	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.05
211/ 9	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.57
stdev	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.08
211/ 19	0.01	0.17	0.10	0.03	0.16	0.09	0.67	1.40
stdev	0.00	0.01	0.00	0.00	0.01	0.02	0.07	0.18
211/ 35	0.06	0.09	0.03	0.01	0.06	0.00	0.58	0.00
stdev	0.00	0.03	0.01	0.01	0.00	0.00	0.02	na
92 / 5	0.02	0.16	0.00	0.04	0.02	0.01	0.00	0.94
st dev	0.01	0.18	0.00	0.04	0.02	0.00	0.00	na
92 / 21	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.45
st dev	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.03
85 / 32	0.00	0.02	0.06	0.03	0.11	0.04	0.01	1.23
st dev	0.00	0.01	0.01	0.00	0.05	0.01	0.01	0.27
81 / 45	0.02	0.04	0.08	0.02	0.10	0.07	0.09	0.56
st dev	0.01	0.01	0.05	0.01	0.05	0.04	0.04	0.28
87 / 38	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.39
st dev	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02
84 / 28	0.00	0.02	0.02	0.01	0.02	0.01	0.03	0.53
st dev	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.11
83 / 42	0.00	0.00	0.81	2.51	0.13	0.02	0.30	0.46
st dev	0.00	0.00	0.03	0.06	0.01	0.00	0.09	0.08
86 / 12	0.00	0.14	0.85	0.24	0.29	0.16	0.12	7.01
st dev	0.00	0.19	0.03	0.00	0.05	0.00	0.01	0.66

Table B- 11. Upland aluminum in soil (ppm)

Aluminum ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	0.00	365.77	228.42	27.24	76.20	307.56	211.68	10443.83
stdev	0.00	17.32	0.22	0.40	4.96	3.58	1.11	1468.21
168 / 20	27.35	275.65	56.43	7.55	10.75	25.13	19.21	4582.42
stdev	2.60	8.08	0.08	0.01	15.20	2.09	2.11	1231.14
168 / 31	2.59	116.37	30.45	2.65	3.35	4.96	4.58	1630.39
stdev	0.21	2.78	1.30	0.76	3.53	0.56	0.05	456.42
170 / 1	1.81	272.57	135.28	6.34	60.73	18.99	304.88	11367.99
stdev	0.00	8.17	1.32	0.42	10.17	0.92	0.85	830.88
170 / 14	5.14	95.15	150.25	12.55	52.90	24.02	18.51	10987.93
stdev	0.39	0.96	1.86	0.58	2.54	0.89	1.29	426.78
170 / 20	1.72	0.50	6.62	0.71	10.41	39.19	15.27	10801.55
stdev	0.30	0.35	0.19	0.31	0.97	0.05	1.83	168.36
211/ 2	0.00	21.38	0.00	1.10	6.69	0.00	13.72	7661.35
stdev	0.00	1.88	0.00	0.05	0.30	0.00	4.15	616.79
211/ 9	0.22	36.83	0.00	1.36	5.12	0.00	8.32	10991.43
stdev	0.00	7.02	0.00	0.20	0.85	0.00	0.20	88.65
211/ 19	0.56	25.63	0.00	1.11	5.28	0.00	4.22	10922.64
stdev	0.12	6.09	0.00	0.01	1.76	0.00	2.97	166.40
211/ 35	4.12	255.01	0.00	2.44	58.71	0.00	112.53	540.13
stdev	0.22	1.85	0.00	0.38	7.94	0.00	1.25	na
92 / 5	1.40	135.90	26.06	17.08	16.81	122.86	136.68	nd
st dev	0.64	17.39	6.47	2.63	3.13	33.46	6.34	nd
92 / 21	0.97	3.93	58.28	18.01	59.48	45.27	13.82	nd
st dev	0.12	2.44	7.01	2.86	1.46	5.91	3.68	nd
85 / 32	0.01	4.07	7.98	7.77	2.28	0.95	20.92	18997.15
st dev	0.01	0.13	1.57	0.40	0.13	0.27	0.16	219.65
81 / 45	0.17	5.71	17.74	6.62	8.76	3.95	55.90	15173.14
st dev	0.11	0.83	0.58	1.51	4.12	3.43	21.75	9329.46
87 / 38	1.01	15.56	16.12	8.23	2.83	1.27	43.53	18899.00
st dev	0.73	1.84	0.65	0.89	0.06	0.31	0.40	166.01
84 / 28	0.00	4.03	19.43	7.39	6.23	3.69	22.45	13238.01
st dev	0.00	0.43	3.21	0.56	1.28	1.26	2.71	6756.92
83 / 42	0.06	0.08	19.88	0.00	7.59	5.47	58.31	3094.68
st dev	0.05	0.01	1.62	0.05	1.90	0.65	9.93	832.75
86 / 12	5.44	8.80	0.02	0.00	0.00	0.00	98.82	nd
st dev	1.03	5.28	0.05	0.05	0.00	0.00	31.80	nd

Table B- 12. Upland nickel in soil (ppm)

Nickel ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	0.00	0.56	0.05	0.02	0.09	0.08	0.92	43.11
stdev	0.00	0.14	0.08	0.01	0.07	0.00	0.10	42.58
168 / 20	15.43	4.16	0.09	0.05	1.46	0.31	1.01	13.62
stdev	0.62	0.40	0.08	0.01	0.05	0.02	0.28	12.57
168 / 31	1.69	0.75	0.43	0.09	0.69	0.03	0.70	12.99
stdev	0.03	0.26	0.07	0.02	0.09	0.00	0.09	10.91
170 / 1	0.04	0.28	0.09	0.02	0.14	0.01	1.01	24.62
stdev	0.06	0.02	0.12	0.03	0.11	0.01	0.20	10.76
170 / 14	0.00	0.55	0.02	0.00	0.20	0.09	0.81	7.46
stdev	0.00	0.12	0.03	0.00	0.19	0.03	0.27	0.08
170 / 20	2.72	0.00	2.33	0.00	0.55	0.09	0.58	12.08
stdev	0.20	0.00	0.15	0.00	0.26	0.02	0.02	3.40
211/ 2	0.01	0.15	3.27	0.10	0.61	0.04	0.10	10.54
stdev	0.02	0.21	2.85	0.06	0.22	0.00	0.10	4.22
211/ 9	0.01	0.00	1.80	0.09	0.58	0.03	0.00	13.34
stdev	0.00	0.00	0.37	0.00	0.01	0.01	0.00	2.55
211/ 19	0.13	1.17	3.46	0.16	0.90	0.06	0.58	17.97
stdev	0.01	1.04	1.33	0.03	0.13	0.00	0.06	2.73
211/ 35	0.38	0.15	6.17	0.07	0.35	0.01	0.58	5.72
stdev	0.00	0.22	1.21	0.01	0.04	0.00	0.17	na
92 / 5	0.25	0.00	0.00	0.07	0.00	0.01	0.25	11.92
st dev	0.04	0.00	0.00	0.01	0.00	0.01	0.18	na
92 / 21	0.06	0.18	0.72	0.72	0.00	0.00	0.11	nd
st dev	0.03	0.25	1.01	0.32	0.00	0.00	0.04	nd
85 / 32	0.02	24.98	1.43	0.04	0.14	0.03	0.05	11.55
st dev	0.01	5.48	0.88	0.01	0.06	0.01	0.07	3.99
81 / 45	0.03	17.58	0.65	0.01	0.03	0.01	0.92	1.76
st dev	0.00	1.29	0.92	0.00	0.01	0.02	0.20	2.23
87 / 38	0.03	23.16	8.63	0.03	0.04	0.01	0.02	8.40
st dev	0.02	7.06	2.92	0.01	0.01	0.02	0.03	2.95
84 / 28	0.01	21.68	1.07	0.01	0.04	0.01	0.06	2.87
st dev	0.01	0.14	0.40	0.00	0.04	0.00	0.04	0.25
83 / 42	0.10	17.49	32.07	1.97	1.95	0.53	0.81	1.57
st dev	0.04	1.20	1.27	0.25	0.17	0.10	0.08	0.17
86 / 12	0.05	1.50	8.24	1.91	1.32	0.87	1.59	44.92
st dev	0.00	2.02	1.55	0.04	0.22	0.05	0.02	3.60

Table B- 13. Upland arsenic in soil (ppm)

Arsenic ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	0.01	0.01	0.07	0.02	0.30	0.24	0.39	2.07
stdev	0.00	0.00	0.03	0.00	0.00	0.01	0.16	0.47
168 / 20	0.38	0.09	0.48	4.00	5.54	0.89	1.26	3.23
stdev	0.03	0.04	0.02	0.04	0.19	0.01	0.98	1.39
168 / 31	0.11	0.02	0.48	1.24	1.67	0.20	0.63	3.02
stdev	0.01	0.00	0.09	0.14	0.06	0.01	0.31	0.25
170 / 1	0.00	0.00	0.01	0.01	0.42	0.44	1.86	0.27
stdev	0.00	0.00	0.01	0.00	0.03	0.02	0.23	0.25
170 / 14	0.00	0.00	0.03	0.04	0.05	0.01	0.05	0.12
stdev	0.00	0.00	0.02	0.00	0.04	0.00	0.00	0.13
170 / 20	0.01	0.00	0.02	0.02	0.21	0.09	0.05	0.36
stdev	0.00	0.00	0.00	0.00	0.03	0.00	0.03	0.08
211/ 2	0.00	0.72	0.03	0.01	0.07	0.38	0.40	1.16
stdev	0.00	0.20	0.02	0.01	0.02	0.05	0.01	0.03
211/ 9	0.00	0.86	0.03	0.01	0.05	0.38	0.94	1.03
stdev	0.00	0.05	0.01	0.00	0.01	0.01	0.05	0.22
211/ 19	0.00	1.31	0.05	0.02	0.09	0.51	1.27	1.72
stdev	0.00	0.53	0.01	0.00	0.01	0.09	0.15	0.20
211/ 35	0.00	2.22	0.06	0.01	0.01	0.01	0.38	0.11
stdev	0.00	0.50	0.03	0.01	0.00	0.00	0.10	na
92 / 5	0.02	0.00	0.00	0.00	0.00	0.14	0.59	1.49
st dev	0.01	0.00	0.00	0.00	0.00	0.00	0.05	0.00
92 / 21	0.01	0.00	1.07	0.02	0.02	0.00	0.08	0.36
st dev	0.00	0.00	0.42	0.00	0.01	0.00	0.12	0.20
85 / 32	0.00	0.00	0.00	0.01	0.09	1.81	0.33	3.37
st dev	0.00	0.01	0.00	0.00	0.03	0.49	0.05	4.77
81 / 45	0.00	0.00	0.00	0.00	0.01	0.10	0.11	0.35
st dev	0.00	0.01	0.00	0.00	0.00	0.04	0.10	0.50
87 / 38	0.00	0.00	0.00	0.00	0.01	0.03	0.05	0.61
st dev	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01
84 / 28	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.05
st dev	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.07
83 / 42	0.00	0.00	0.00	0.37	0.22	1.23	0.69	0.66
st dev	0.00	0.01	0.00	0.03	0.02	0.05	0.09	0.08
86 / 12	1.68	1.33	11.56	17.43	1.55	8.04	0.58	1.56
st dev	0.12	1.20	0.06	0.19	0.02	0.07	0.09	0.03

Table B- 14. Upland uranium in soil (ppm)

Uranium ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	nd	0.03	0.24	nd	nd	0.09	0.05	2.32
stdev	nd	0.01	0.04	nd	nd	0.01	0.03	0.10
168 / 20	nd	0.31	1.21	nd	nd	0.41	0.15	2.82
stdev	nd	0.01	0.05	nd	nd	0.02	0.00	0.74
168 / 31	1.08	0.08	0.28	0.07	0.13	0.09	0.08	1.30
stdev	0.33	0.03	0.03	0.01	0.11	0.01	0.03	0.23
170 / 1	0.00	0.01	0.18	0.03	0.15	0.07	0.06	0.54
stdev	0.00	0.01	0.03	0.01	0.02	0.00	0.01	0.20
170 / 14	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.33
stdev	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.08
170 / 20	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.89
stdev	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.07
211/ 2	0.00	0.04	0.04	0.03	0.29	0.01	0.00	0.42
stdev	0.00	0.01	0.01	0.00	0.05	0.00	0.00	0.00
211/ 9	0.00	0.07	0.00	0.04	0.65	0.03	0.03	0.51
stdev	0.00	0.02	0.00	0.00	0.07	0.00	0.00	0.22
211/ 19	0.00	0.04	0.01	0.09	0.58	0.31	0.34	0.72
stdev	0.00	0.00	0.00	0.02	0.02	0.02	0.07	0.14
211/ 35	0.00	0.03	0.00	0.01	0.12	0.00	0.00	0.07
stdev	0.00	0.01	0.00	0.01	0.04	0.00	0.00	na
92 / 5	2.13	0.01	3.29	0.01	0.10	0.01	0.00	1.41
st dev	1.34	0.01	1.15	0.00	0.02	0.00	0.00	0.00
92 / 21	0.39	0.00	0.74	0.00	0.05	0.01	0.01	0.01
st dev	0.21	0.00	0.54	0.00	0.02	0.00	0.02	0.00
85 / 32	0.00	0.32	0.00	0.00	0.04	0.05	0.00	0.38
st dev	0.00	0.10	0.01	0.01	0.05	0.02	0.00	0.02
81 / 45	0.00	3.61	0.00	0.00	0.00	0.05	0.00	1.29
st dev	0.00	1.14	0.01	0.01	0.00	0.00	0.00	1.52
87 / 38	0.00	0.14	0.00	0.00	0.09	0.05	0.00	0.84
st dev	0.00	0.05	0.01	0.01	0.01	0.00	0.00	0.49
84 / 28	0.00	0.68	0.00	0.00	0.07	0.03	0.00	0.81
st dev	0.00	0.14	0.01	0.01	0.04	0.01	0.00	0.05
83 / 42	0.00	1.42	0.08	0.90	0.03	0.01	0.00	0.07
st dev	0.00	0.54	0.03	0.11	0.01	0.00	0.00	0.02
86 / 12	0.07	0.16	0.47	0.91	0.55	0.98	5.94	4.17
st dev	0.02	0.06	0.10	0.14	0.13	0.75	2.71	0.18

Table B- 15. Upland iron in soil (ppm)

Iron ppm	DDI	CN	AA	HH	HP	AO	SD	PD
168 / 1.5	0.61	28.85	348.84	46.45	144.25	430.80	1612.26	14908.57
stdev	0.75	0.03	1.40	0.33	6.54	20.66	11.03	1940.99
168 / 20	1297.42	527.64	372.86	146.39	1363.02	267.19	376.41	10149.62
stdev	29.61	21.25	3.83	1.32	130.35	33.49	180.99	2114.74
168 / 31	290.62	269.58	186.56	30.20	893.16	87.05	265.93	4917.91
stdev	408.38	17.76	9.13	1.82	77.03	4.66	170.92	2268.35
170 / 1	2.93	2.64	15.45	25.52	46.17	453.70	2896.75	3090.42
stdev	0.19	0.92	1.04	2.59	14.25	1.96	26.19	1008.09
170 / 14	4.21	1.60	2.54	36.20	10.96	3.18	121.80	1971.96
stdev	2.91	0.13	0.06	0.28	0.09	0.26	0.77	165.47
170 / 20	424.30	52.60	136.91	4.26	587.75	88.92	237.61	9344.83
stdev	45.58	1.93	10.49	0.40	20.77	5.00	119.05	1073.76
211/ 2	0.02	1.28	16.90	24.37	75.51	400.57	1912.85	1819.22
stdev	0.03	1.03	3.42	0.31	1.01	88.55	66.53	135.37
211/ 9	0.04	3.09	7.95	8.09	47.94	338.38	5310.57	3160.31
stdev	0.00	1.23	0.47	0.10	0.75	10.80	37.21	863.50
211/ 19	10.07	71.42	56.93	170.80	552.19	5290.34	12941.90	11588.75
stdev	0.50	1.61	1.37	9.19	29.84	552.74	1004.44	993.32
211/ 35	44.23	13.49	36.78	66.98	87.51	212.99	2805.41	280.70
stdev	0.91	0.28	0.49	4.14	1.71	14.59	9.84	na
92 / 5	386.97	9.08	53.74	25.67	205.57	653.42	2533.96	nd
st dev	50.47	2.10	0.37	4.98	2.80	15.39	101.15	nd
92 / 21	271.98	10.26	17.16	16.99	161.59	138.73	93.91	nd
st dev	2.78	14.45	4.58	1.34	2.38	15.71	5.69	nd
85 / 32	0.04	0.04	28.90	17.57	124.36	623.71	130.34	1307.46
st dev	0.00	0.01	6.02	0.21	8.55	107.56	21.22	160.54
81 / 45	0.19	0.04	21.08	14.21	67.47	209.17	604.75	10811.46
st dev	0.12	0.01	6.06	7.26	20.64	118.76	257.75	12057.36
87 / 38	0.75	0.04	20.58	9.90	59.10	187.84	602.02	1626.48
st dev	0.15	0.01	0.66	0.40	0.57	13.32	88.38	92.70
84 / 28	0.04	0.04	12.15	13.98	60.25	71.37	291.23	3272.46
st dev	0.00	0.01	4.93	4.76	17.53	18.70	70.16	437.36
83 / 42	0.20	0.04	5.97	1158.84	2855.64	1034.61	3018.38	4708.95
st dev	0.14	0.01	0.97	60.11	360.58	169.37	360.42	856.34
86 / 12	0.04	269.56	455.16	582.32	390.79	1762.35	2098.45	nd
st dev	0.00	381.16	7.42	13.91	39.93	110.64	19.14	nd

APPENDIX C.
AMORPHOUS OXIDE SINGLE STEP EXTRACTION RESULTS (ppm)

AO SS ppm	Beryllium	Aluminum	Nickel	Arsenic	Uranium	Iron
92/5	0.068	4.949	0.749	0.130	0.126	513.370
92/21	0.177	2.686	0.339	0.013	0.116	707.078
85/32	0.295	3.771	0.382	1.518	0.433	219.226
85/45	0.109	13.476	0.514	0.088	0.070	485.368
81/30	0.565	3.225	0.567	0.311	1.702	262.031
81/45	0.481	4.359	0.274	0.116	0.139	7697.497
81/50	7.015	1.101	2.282	0.811	1.274	327.920
87/33	0.144	4.075	0.267	0.323	0.934	249.183
87/38	0.064	4.826	0.183	0.049	0.512	208.165
87/53	0.889	6.549	0.177	0.074	0.394	3.905
84/20	0.019	10.409	0.170	0.012	0.053	19.667
84/28	0.064	7.266	0.169	0.030	0.237	68.129
84/38	2.602	3.302	0.578	0.381	2.598	1400.714
83/32	2.415	2.783	0.507	0.092	3.970	685.128
83/38	1.418	3.400	2.167	0.404	1.645	449.420
83/42	3.775	3.641	4.830	0.851	2.074	2028.944
86	1.814	0.986	4.829	36.767	3.907	0

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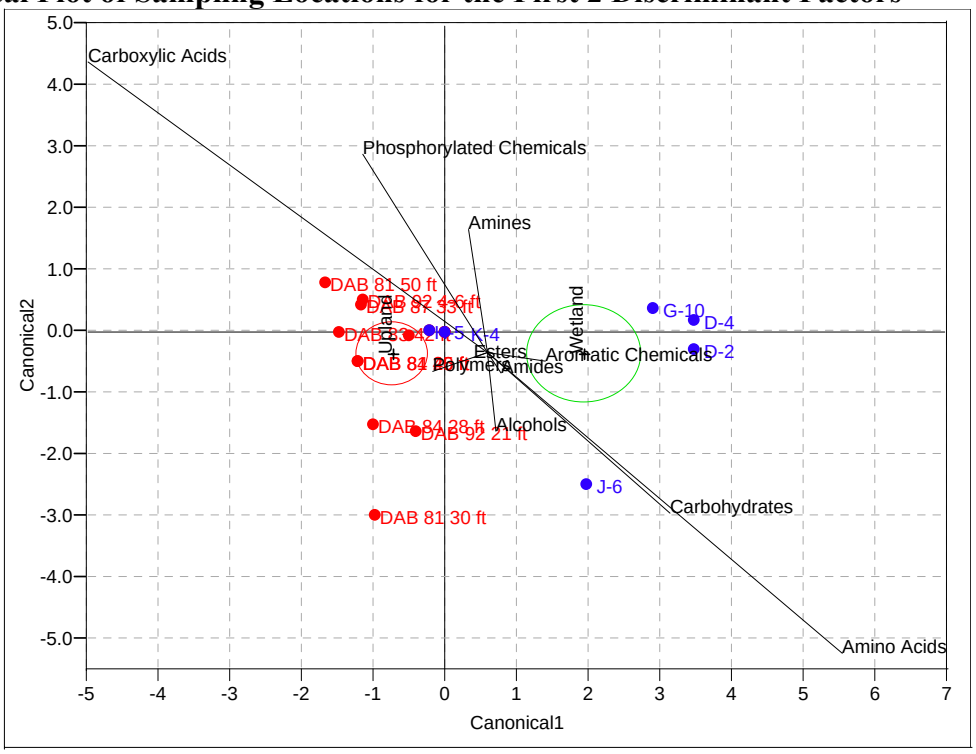
APPENDIX D.
NOTES ON DISCRIMINANT ANALYSIS BY REGION ON THE BASIS OF BIOLOG® TESTING OF SOIL SLURRIES

Part 1 of 3, Discriminant Analysis by Region

Carbon Source Means by Region

Area	Upland	Wetland	All
Number of Sampling Locations	15	6	21
% for Carbon Source			
Polymers	12	27	16
Carbohydrates	12	38	20
Esters	20	25	21
Carboxylic Acids	17	29	20
Amides	13	6	11
Amino Acids	14	36	20
Aromatic Chemicals	3	42	14
Amines	7	28	13
Alcohols	17	25	19
Phosphorylated Chemicals	7	39	16

Canonical Plot of Sampling Locations for the First 2 Discriminant Factors



Discriminant Scores

Number Misclassified	2
Percent Misclassified	9.524
-2LogLikelihood	5.12

Eigenvectors	Coefficient Scores
Polymers	-0.0303
Carbohydrates	0.1072
Esters	-0.0060
Carboxylic Acids	-0.2368
Amides	0.0086
Amino Acids	0.1797
Aromatic Chemicals	0.0363
Amines	-0.0118
Alcohols	0.0035
Phosphorylated Chemicals	-0.0519

This discriminant analysis between upland & wetland groups assumes that the wetland & upland wells were correctly classified. However, the results indicate that 2 wetland wells appear to be consistent with upland the biolog structure. Since there are 2 populations, upland & wetland, there is only one linear discriminant function used to separate the populations. The coefficient scores for this discrimant function are given in the table just above. A good discrimant function should have an interpretation that makes sense to the scientist. This function weights carbohydrates, carbolic acids, & amino acids most heavily. This is pictured in the canonical plot on the left. These canonical plots are created to depict the 2 most important discrimant functions, one on the horizontal axis & two on the vertical axis. Since only 1 discrimant function is used here, the distances along the x-axis are meaningful; the distances on the y-axis are not.

Sample ID and Depth of Sample	Actual	SRS East	SRS North	Dist(Actual)	Prob(Actual)	Plot Log(Prob)	Predicted
DAB 92 4-6 ft	Upland	19717.73	63907.03	66.12819	0.9908		Upland
DAB 92 21 ft	Upland	19717.73	63907.03	63.66330	0.9363		Upland
DAB 92 23 ft	Upland	19717.73	63907.03	53.27497	0.8970		Upland
DAB 81 30 ft	Upland	18608.53	64335.39	67.18845	0.9854		Upland
DAB 81 45 ft	Upland	18608.53	64335.39	56.77335	0.9924		Upland
DAB 81 50 ft	Upland	18608.53	64335.39	66.89187	0.9976		Upland
DAB 83 32 ft	Upland	17252.27	64790.61	52.34673	0.8372		Upland
DAB 83 38 ft	Upland	17252.27	64790.61	52.34673	0.8372		Upland
DAB 83 42 ft	Upland	17252.27	64790.61	67.37177	0.9962		Upland
DAB 84 20 ft	Upland	17211	64389.99	56.77335	0.9924		Upland
DAB 84 28 ft	Upland	17211	64389.99	66.33681	0.9861		Upland
DAB 84 38 ft	Upland	17211	64389.99	61.83614	0.9511		Upland
DAB 87 33 ft	Upland	17670.53	64309.34	53.76716	0.9910		Upland
DAB 87 38 ft	Upland	17670.53	64309.34	52.34673	0.8372		Upland
DAB 87 53 ft	Upland	17670.53	64309.34	52.34673	0.8372		Upland
G-10	Wetland	14808.48	63010.24	60.42786	0.9980		Wetland
D-2	Wetland	14683.87	65824.63	63.09266	0.9995		Wetland
D-4	Wetland	14477.71	65189.11	63.42609	0.9996		Wetland
H-5	Wetland	15631.71	64483.6	57.60270	0.1030		Upland
J-6	Wetland	16162.52	63966.16	59.14601	0.9750		Wetland
K-4	Wetland	16676	64485.06	55.62161	0.1628		Upland

'*' indicates misclassified

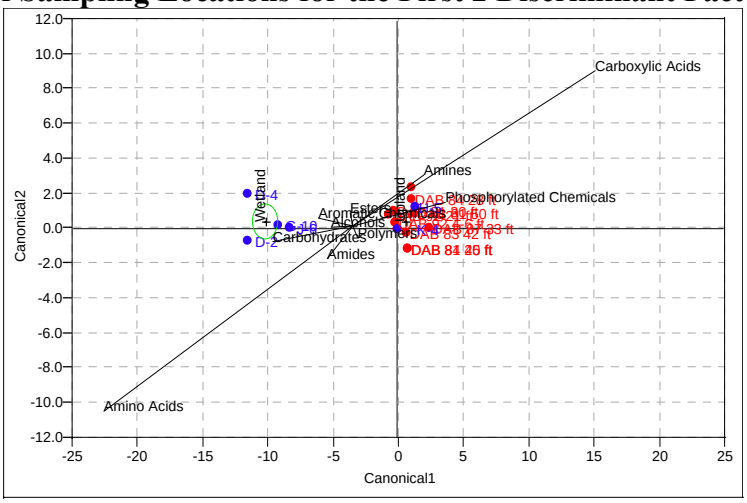
Counts: Actual Rows by Predicted Columns	Upland	Wetland
Upland	15	0
Wetland	2	4

Part 2 of 3, Discriminant Analysis by Region, Excluding Sampling Locations H-5 and K-4 from the Training Set

Carbon Source Means by Region

Area	Upland	Wetland	All
Number of Sampling Locations	15	4	19
% for Carbon Source			
Polymers	12	40	18
Carbohydrates	12	55	21
Esters	20	38	24
Carboxylic Acids	17	43	22
Amides	13	8	12
Amino Acids	14	54	22
Aromatic Chemicals	3	63	16
Amines	7	42	14
Alcohols	17	38	21
Phosphorylated Chemicals	7	58	18

Canonical Plot of Sampling Locations for the First 2 Discriminant Factors



Discriminant Scores

Number Missclassified	0
Percent Misclassified	0
-2LogLikelihood	0

Eigenvectors	Coefficient Scores
Polymers	0.0175
Carbohydrates	-0.2994
Esters	-0.0046
Carboxylic Acids	0.8432
Amides	-0.0808
Amino Acids	-0.7675
Aromatic Chemicals	-0.1632
Amines	0.2540
Alcohols	-0.0481
Phosphorylated Chemicals	0.2259

This discriminant analysis takes the 2 wetland groups that were classified as upland areas & removes them from the basis data set that creates the discrimant function. The discriminant function coefficients are given in the table above. Note that the carbolic acis & amino acids are still predominant. The weighting of the carbohydrates has fallen (relative two these other two predictors) nearly down to the level of mines & phosphorylated chemicals. The canonical plot on the left show this. Remember that only the horizontal component is interpretable. Predictions are made for the 2 wetland wells (H-5 & K-4) that are not in the basis set used to create the discriminant function. Both still classify as upland wells

Sample ID and Depth of Sample	Actual	SRS East	SRS North	Dist(Actual)	Prob(Actual)	Plot Log(Prob)	Predicted
DAB 92 4-6 ft	Upland	19717.73	63907.03	64.02570	1.0000		Upland
DAB 92 21 ft	Upland	19717.73	63907.03	62.34307	1.0000		Upland
DAB 92 23 ft	Upland	19717.73	63907.03	52.57484	1.0000		Upland
DAB 81 30 ft	Upland	18608.53	64335.39	64.93167	1.0000		Upland
DAB 81 45 ft	Upland	18608.53	64335.39	54.96029	1.0000		Upland
DAB 81 50 ft	Upland	18608.53	64335.39	64.13137	1.0000		Upland
DAB 83 32 ft	Upland	17252.27	64790.61	51.01007	1.0000		Upland
DAB 83 38 ft	Upland	17252.27	64790.61	51.01007	1.0000		Upland
DAB 83 42 ft	Upland	17252.27	64790.61	64.33398	1.0000		Upland
DAB 84 20 ft	Upland	17211	64389.99	54.96029	1.0000		Upland
DAB 84 28 ft	Upland	17211	64389.99	63.83888	1.0000		Upland
DAB 84 38 ft	Upland	17211	64389.99	59.85359	1.0000		Upland
DAB 87 33 ft	Upland	17670.53	64309.34	55.37184	1.0000		Upland
DAB 87 38 ft	Upland	17670.53	64309.34	51.01007	1.0000		Upland
DAB 87 53 ft	Upland	17670.53	64309.34	51.01007	1.0000		Upland
G-10	Wetland	14808.48	63010.24	58.48613	1.0000		Wetland
D-2	Wetland	14683.87	65824.63	60.00650	1.0000		Wetland
D-4	Wetland	14477.71	65189.11	60.33676	1.0000		Wetland
H-5	Wetland	15631.71	64483.6	.	.		Upland
J-6	Wetland	16162.52	63966.16	59.59683	1.0000		Wetland
K-4	Wetland	16676	64485.06	.	.		Upland

'*' indicates misclassified

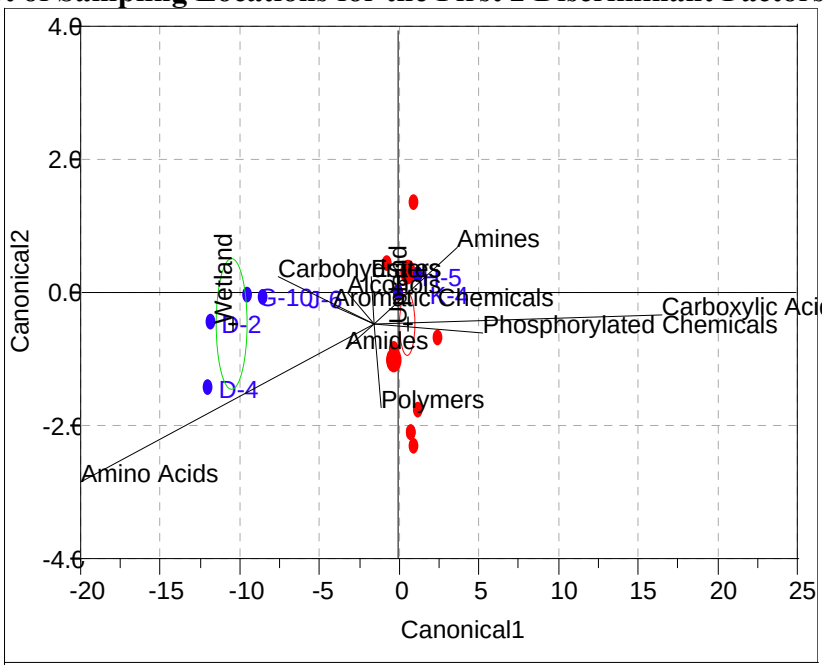
Counts: Actual Rows by Predicted Columns	Upland	Wetland
Upland	15	0
Wetland	0	4

Part 3 of 3, Discriminant Analysis by Region, Reassigning Sampling Locations H-5 and K-4 to the Wetlands Region

Carbon Source Means by Region

Area	Upland	Wetland	All
Number of Sampling Locations	17	4	21
% for Carbon Source			
Polymers	10.59	40.00	16.19
Carbohydrates	11.29	55.25	19.67
Esters	17.65	37.50	21.43
Carboxylic Acids	14.94	42.75	20.24
Amides	11.76	8.25	11.10
Amino Acids	12.35	53.75	20.24
Aromatic Chemicals	2.94	62.50	14.29
Amines	5.88	41.75	12.71
Alcohols	14.71	37.50	19.05
Phosphorylated Chemicals	5.88	58.25	15.86

Canonical Plot of Sampling Locations for the First 2 Discriminant Factors



Discriminant Scores

Number Missclassified	0
Percent Misclassified	0
-2LogLikelihood	0

Eigenvectors	Coefficient Scores
Polymers	0.0198038
Carbohydrates	-0.306494
Esters	-0.005201
Carboxylic Acids	0.8490139
Amides	-0.079055
Amino Acids	-0.770392
Aromatic Chemicals	-0.169592
Amines	0.2553354
Alcohols	-0.049207
Phosphorylated Chemicals	0.2302248

As a check, the 2 wetland wells (H-5 & K-4) were reassigned as upland wells and a new discriminant function was created. The coefficient scores above show that carbolic acids & amino acids are the most heavily weighted Biolog constituents. Carbohydrates, amines, & aromatic chemicals are secondary

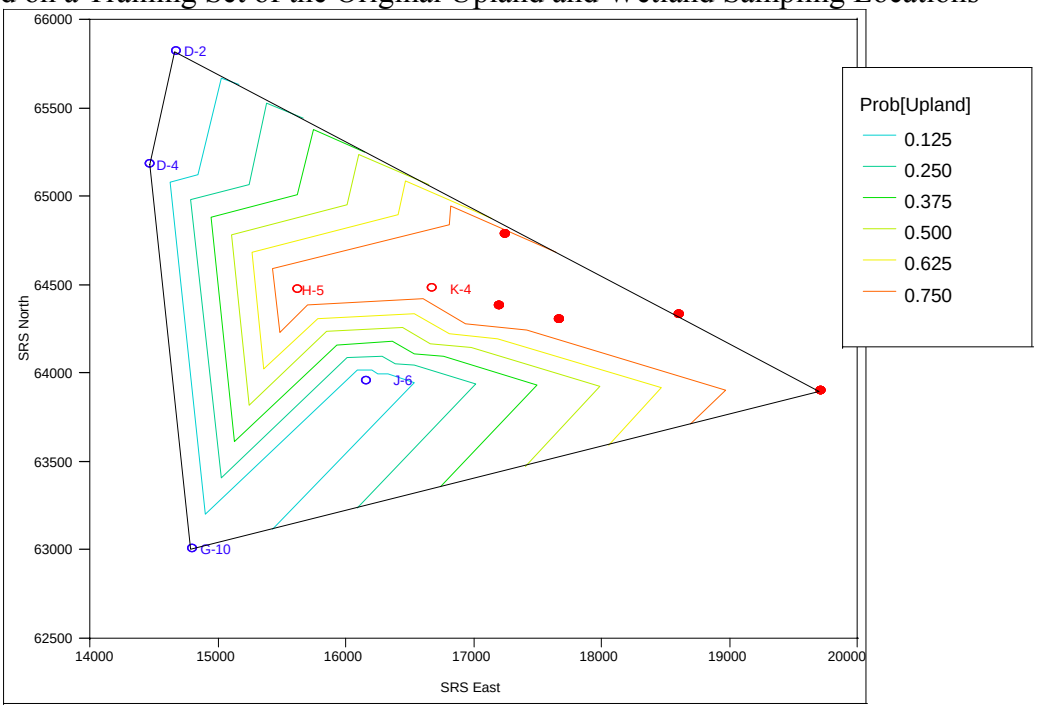
Sample ID and Depth of Sample	Actual	SRS East	SRS North	Dist(Actual)	Prob(Actual)	Plot Log(Prob)	Predicted
DAB 92 4-6 ft	Upland	19717.73	63907.03	64.99638	1.0000		Upland
DAB 92 21 ft	Upland	19717.73	63907.03	63.10531	1.0000		Upland
DAB 92 23 ft	Upland	19717.73	63907.03	51.05847	1.0000		Upland
DAB 81 30 ft	Upland	18608.53	64335.39	66.04712	1.0000		Upland
DAB 81 45 ft	Upland	18608.53	64335.39	54.83253	1.0000		Upland
DAB 81 50 ft	Upland	18608.53	64335.39	65.15841	1.0000		Upland
DAB 83 32 ft	Upland	17252.27	64790.61	49.87498	1.0000		Upland
DAB 83 38 ft	Upland	17252.27	64790.61	49.87498	1.0000		Upland
DAB 83 42 ft	Upland	17252.27	64790.61	65.35979	1.0000		Upland
DAB 84 20 ft	Upland	17211	64389.99	54.83253	1.0000		Upland
DAB 84 28 ft	Upland	17211	64389.99	64.46536	1.0000		Upland
DAB 84 38 ft	Upland	17211	64389.99	59.69228	1.0000		Upland
DAB 87 33 ft	Upland	17670.53	64309.34	54.89232	1.0000		Upland
DAB 87 38 ft	Upland	17670.53	64309.34	49.87498	1.0000		Upland
DAB 87 53 ft	Upland	17670.53	64309.34	49.87498	1.0000		Upland
G-10	Wetland	14808.48	63010.24	58.61693	1.0000		Wetland
D-2	Wetland	14683.87	65824.63	60.14682	1.0000		Wetland
D-4	Wetland	14477.71	65189.11	60.80149	1.0000		Wetland
H-5	Upland	15631.71	64483.6	51.05847	1.0000		Upland
J-6	Wetland	16162.52	63966.16	59.86155	1.0000		Wetland
K-4	Upland	16676	64485.06	49.87498	1.0000		Upland

'*' indicates misclassified

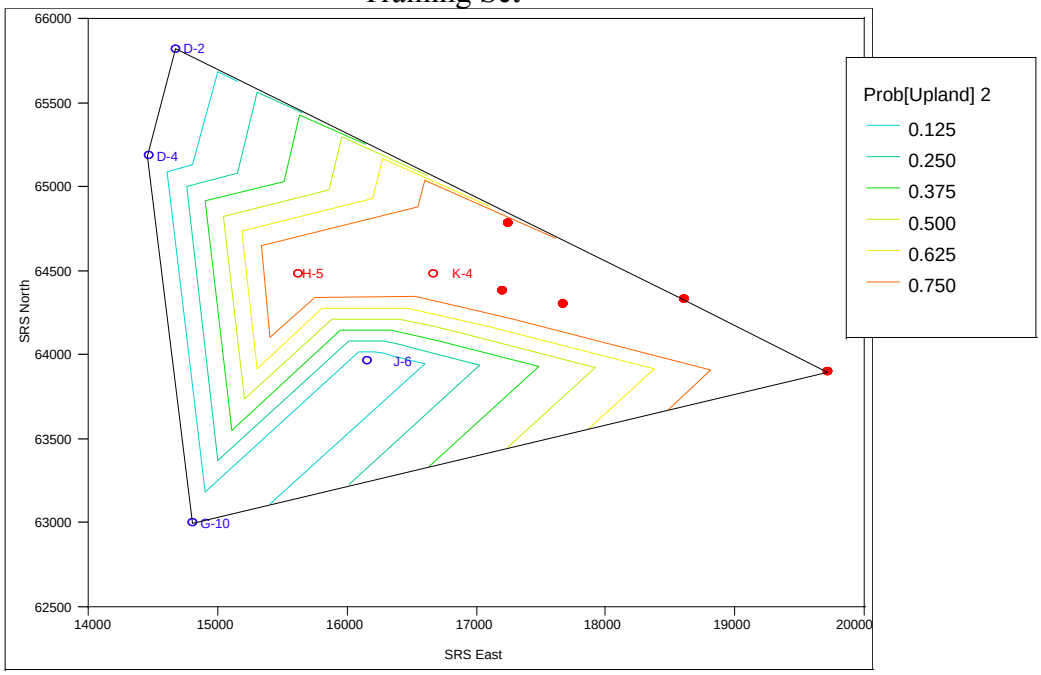
Counts: Actual Rows by Predicted Columns	Upland	Wetland
Upland	17	0
Wetland	0	4

Contour Plots of the Posterior Probability that the Sampling Location is in the Upland Region

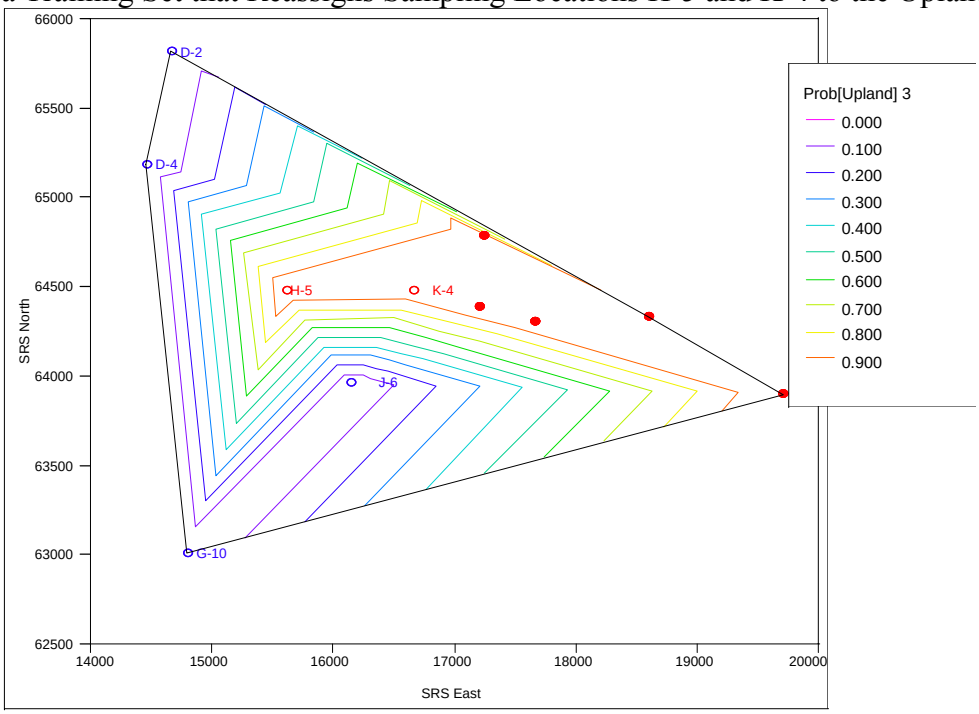
(a) Based on a Training Set of the Original Upland and Wetland Sampling Locations



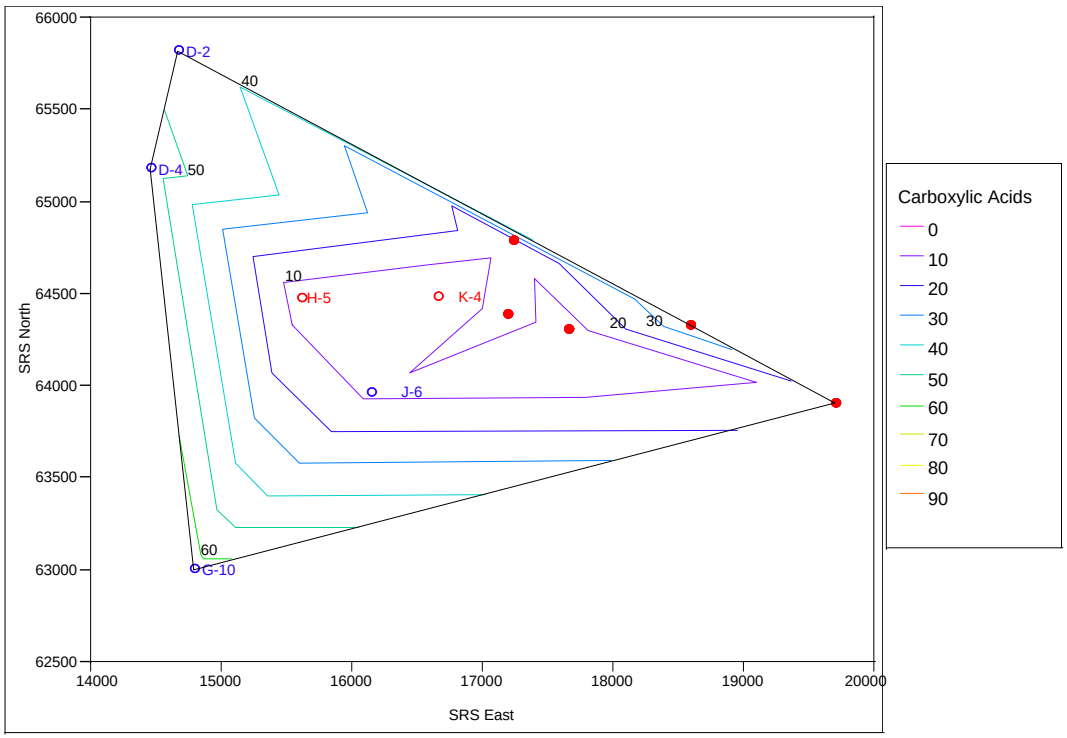
(b) Based on a Training Set that Excludes Sampling Locations H-5 and K-4 from the Training Set

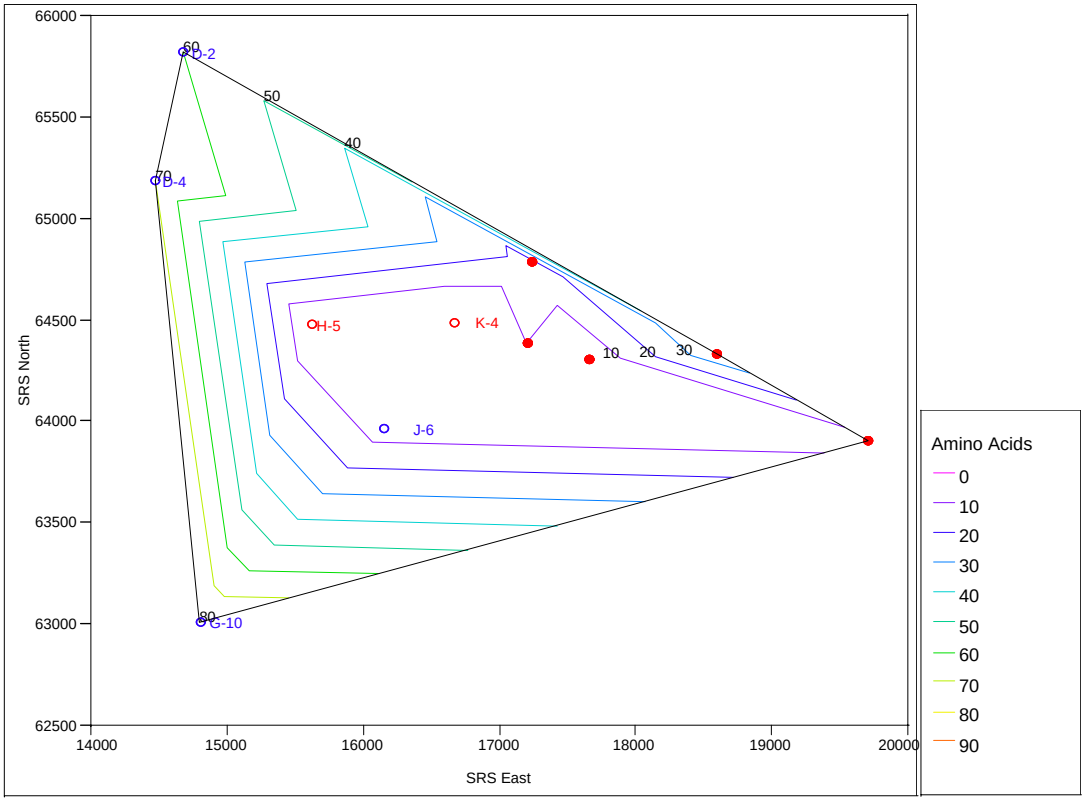


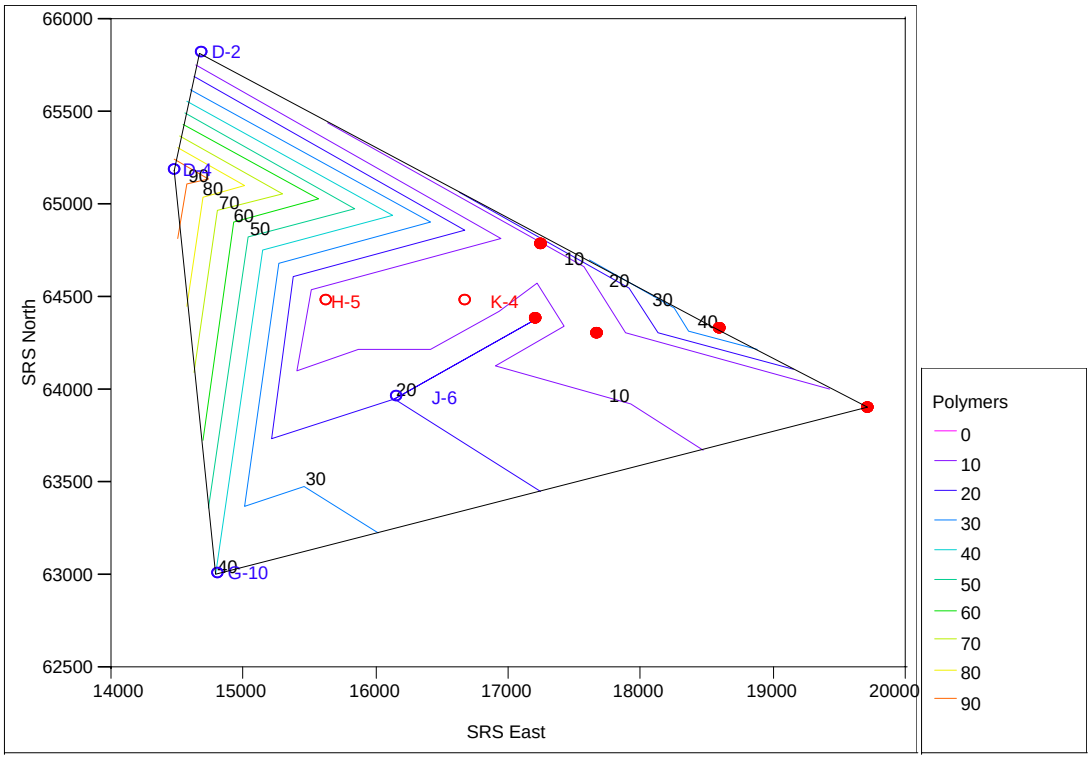
(c) Based on a Training Set that Reassigns Sampling Locations H-5 and K-4 to the Uplands



Contour Plots of % from Carbon Sources



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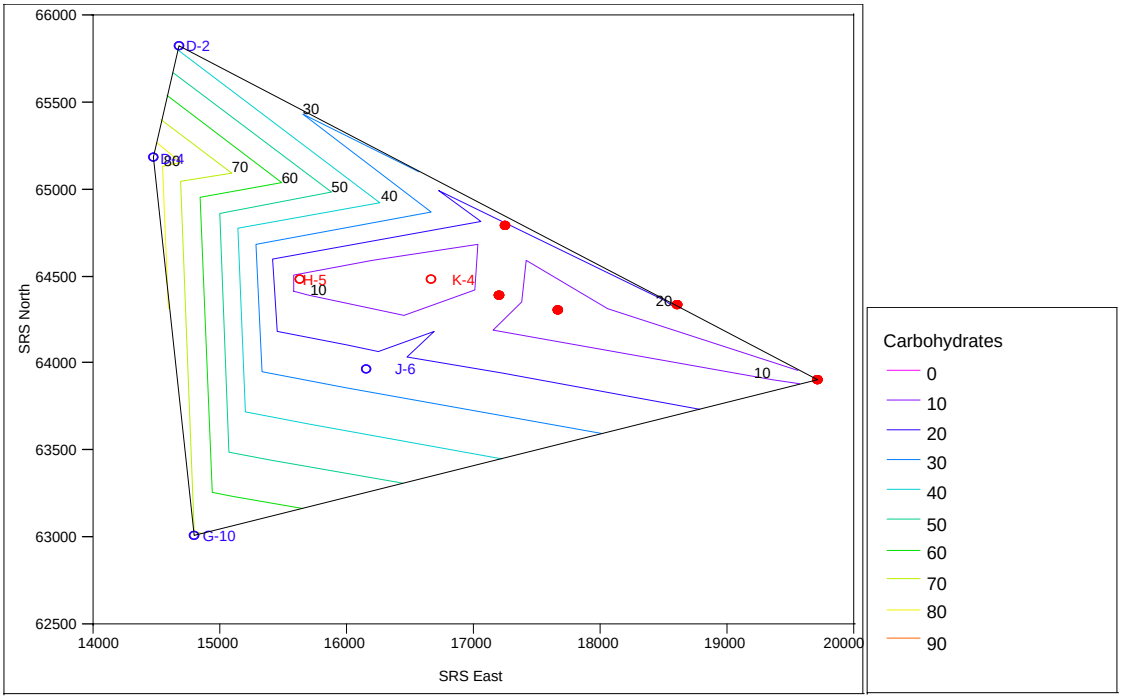
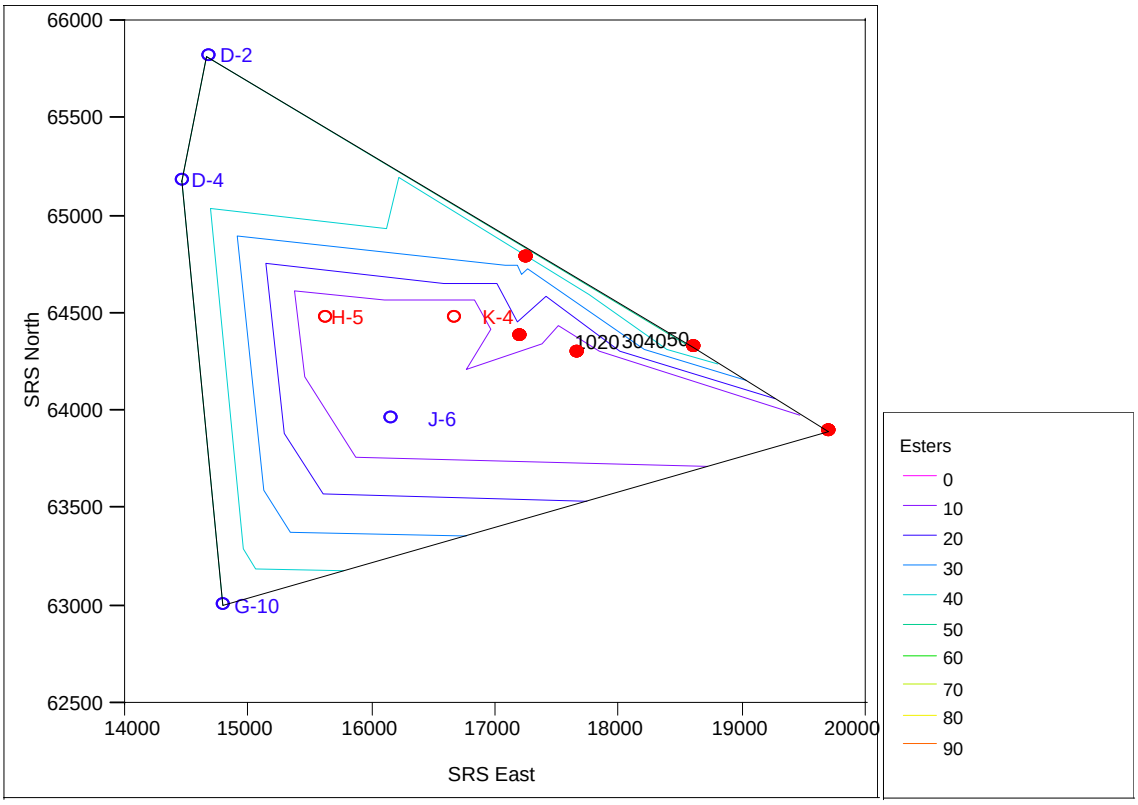
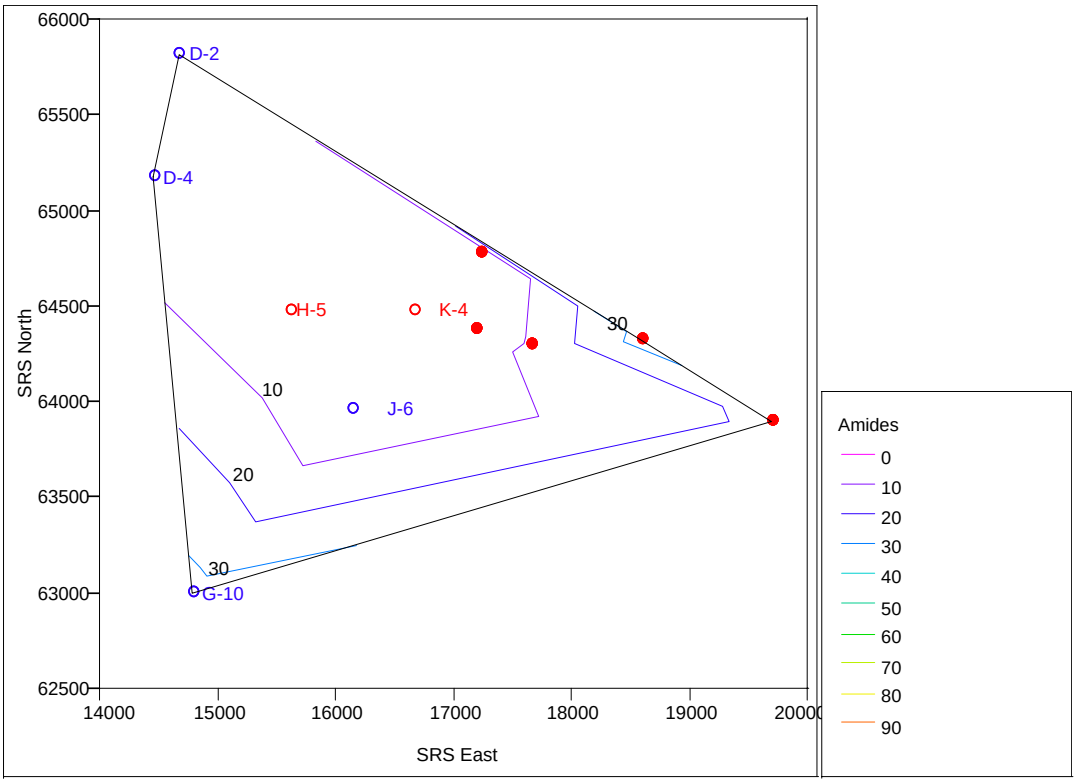
Contour Plots of % from Carbon Sources







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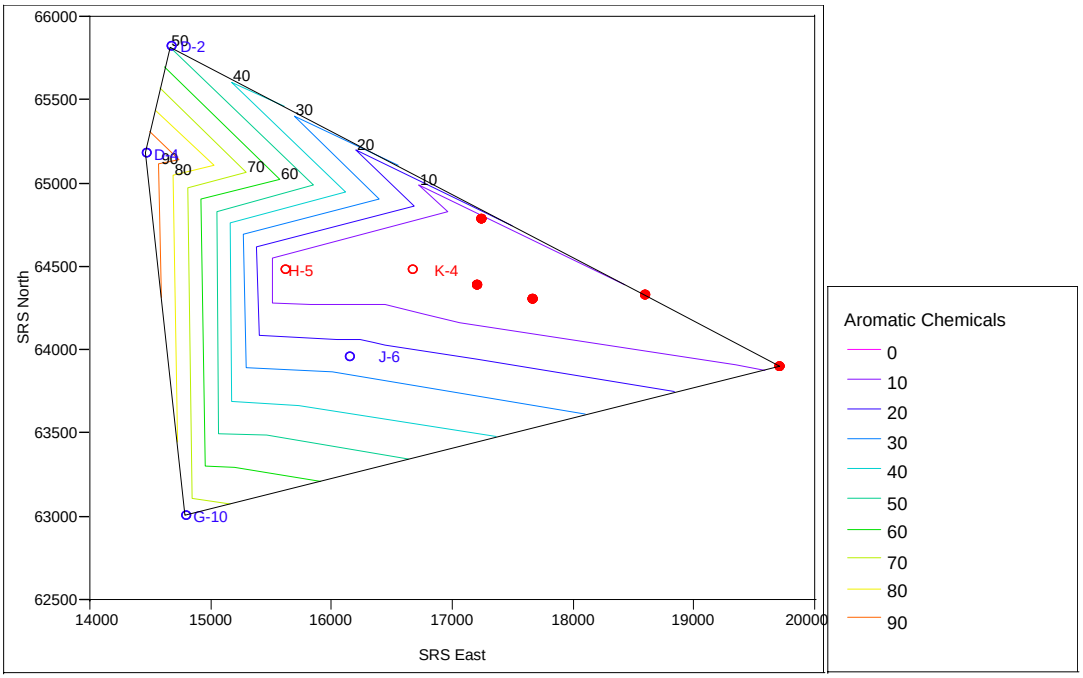

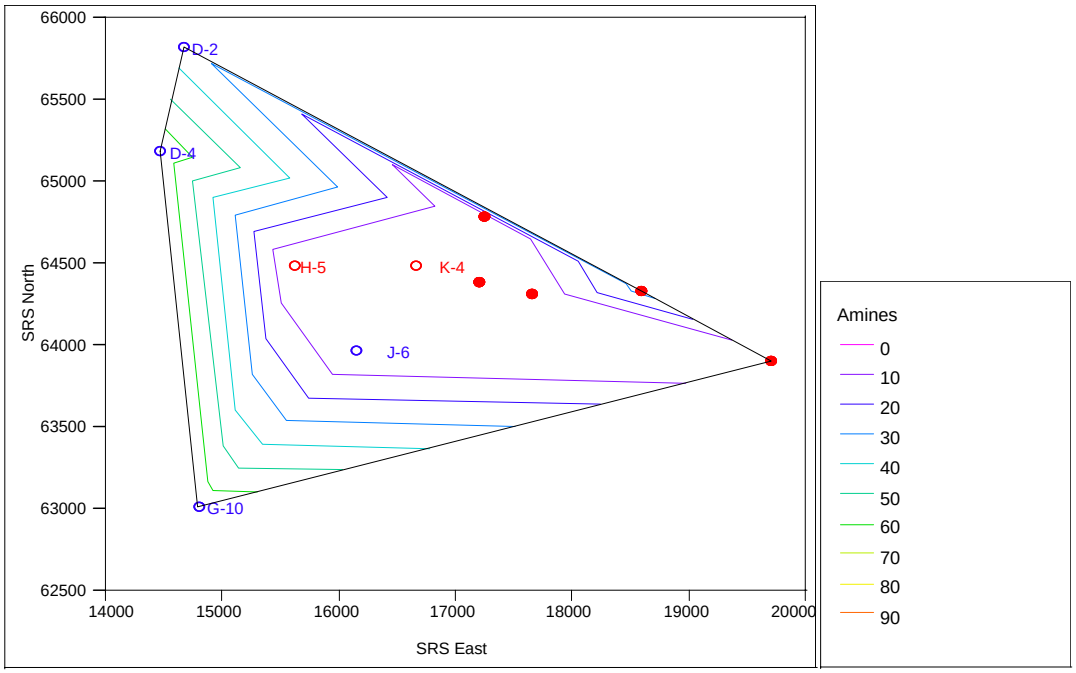

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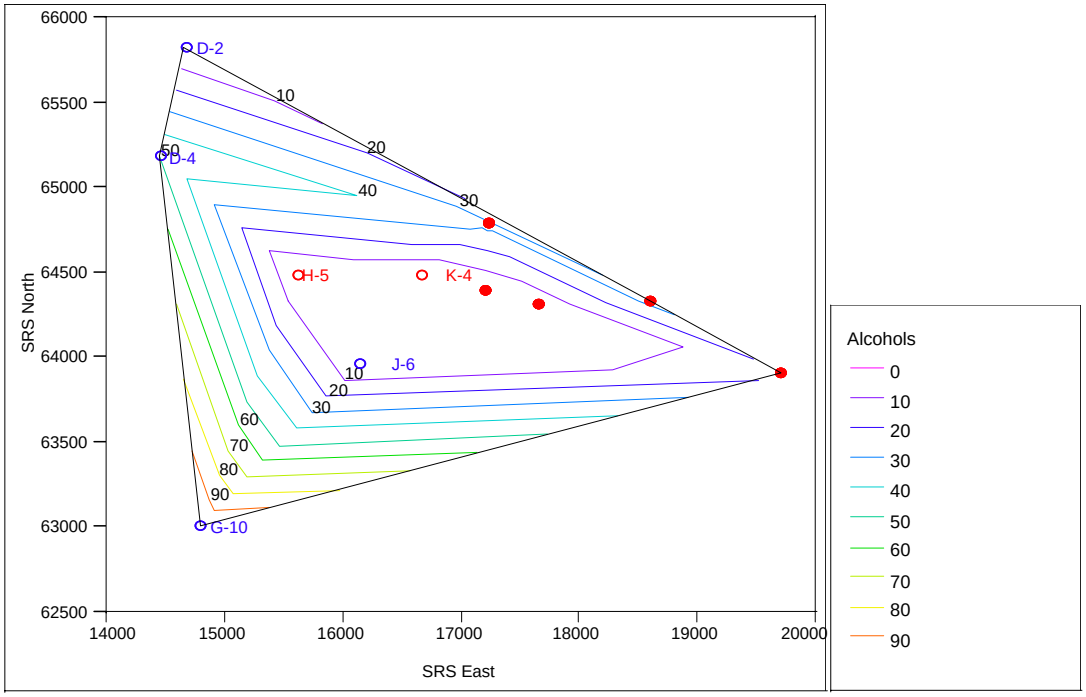

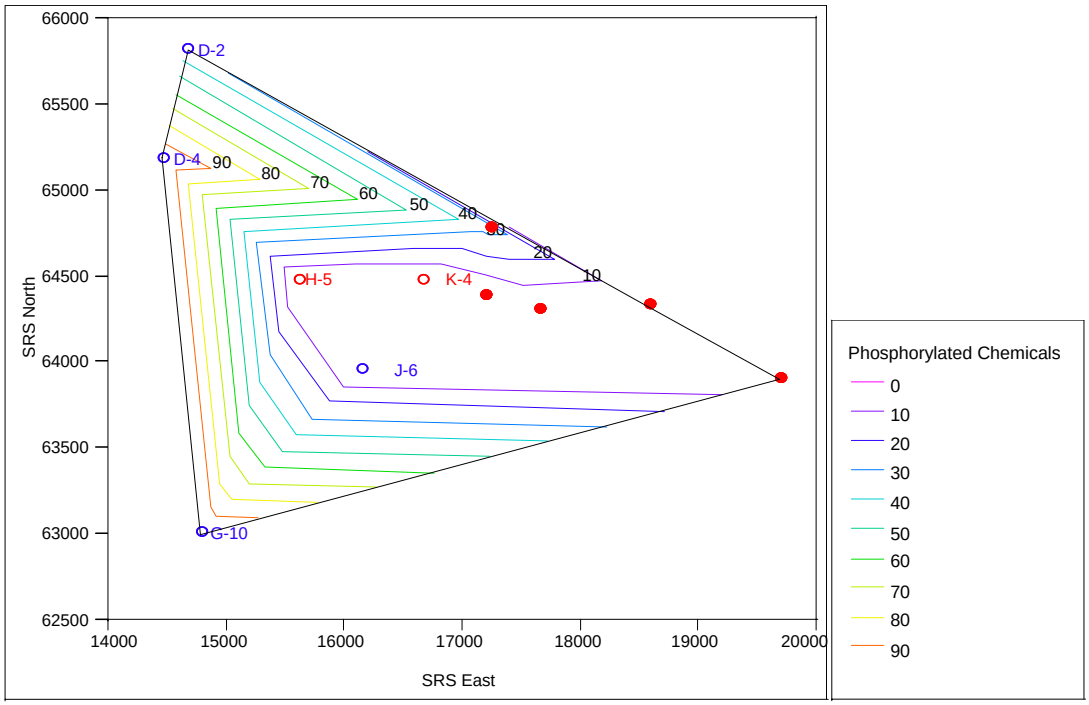
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APPENDIX E.
D-AREA TREATABILITY STUDY WORK PLAN CROSSWALK

Treatability Study Work Plan Objective	DEXOU MNA Report Section	Comment
1 ***Overall Objectives***		
a Provide a technically defensible definition of the contaminant sources (heavy metal and acidity) present at D-Area by the following: - Collecting samples in the upland and wetland areas impacted by coal plant operations to evaluate the quantity of metal contaminants, redox potential, and acidity - Characterizing the availability of inorganic COCs using operationally defined sequential extraction techniques	2.2, 3.3.1 4.1 4.2 5.1 6.2	The tendency of the sediments in the operable unit to sorb Be, Ni, and U followed well established geochemical trends. Sediment sorption for U was greater than for Ni, which in turn was greater than for Be. Four methods were used to measure COC concentrations in soils including; an 8-step sequential extraction (SE) procedure, a single step extraction corresponding to the amorphous iron oxide step (6^{th} SE step), EPA method 3050b, and total digestion. In general, data from the single step extraction and SE steps 1-6 were comparable, as was total digestion and SE steps 1-8. The EPA method is aggressive and may overestimate the metal fraction available for transport.

Treatability Study Work Plan Objective	DEXOU MNA Report Section	Comment
b Provide data that can be used to model the attenuation capacity of the aquifer system at D-Area for metal contaminants and acidity. This part of the study will be designed to collect data to quantify the relative contributions of geochemical and microbial processes (as well as the interactions between these two processes) in the attenuation observed at D-Area. The overall objective of this portion of the Treatability Study is to determine the predominant mechanisms, both abiotic and biotic, controlling the attenuation of inorganic COCs at D-Area.	2.2 3.3.2 3.4 5.1 6.0	Significant MNA is occurring at the study site. This was directly observed by significant decreases in the COC (Be, Ni, U, and As) concentrations as a function of distance from the respective point sources in the operable unit. Sediments were found to have a large tendency to sorb all four COCs, i.e., they had large distribution coefficients, Kd values. COC sorption was strongly pH dependent. Importantly, because the sediments appear to have a high buffering capacity for the acid emanating from the D-Area Coal Pile Runoff Basin, much of the site has quite high Kd values. Increasing microbial densities evident in the wetlands can be correlated to greater biomass and diversity. The more biomass present in a system the higher metal sorption and biotransfor-mation that occurs. Attenuation of pH and sulfate was also demonstrated in the wetlands. In the wetlands there are two potential sources of contaminants, from surface deposition as well as emerging plumes from the coal piles.
2 ***Geochemical Processes***		
a Identify the controlling geochemical attenuation mechanisms in the distal portion of the plume.	2.2 6.0	A large capacity for geochemical attenuation exists near source areas for As, U, Ni, and Be. With the exception of Be all COCs are below MCLs before reaching the wetland. More biological activity in the wetlands may indicate a departure from geochemical dominated behavior. Elucidating geochemical attenuation mechanisms in the wetlands is complicated by ash dumped into the wetlands which represents another source distinct from the groundwater plume. However, the wetlands exhibit a high capacity for attenuation as evidenced by high Kds for the COCs.

Treatability Study Work Plan Objective	DEXOU MNA Report Section	Comment
b Collect data (e.g., groundwater pH, E_h, metals concentrations) to develop an understanding of the changes in geochemical attenuation along the groundwater flow path.	4.2 5.1 6.2.1 6.2.2 6.2.3	Geochemical parameters follow expected trends for attenuation, i.,e., increasing pH, decreasing Eh and decreasing pore water concentrations of COCs with increasing distance from the source and depth.
c From field data, develop site-specific transport factors (sorption coefficients) along the groundwater flow path.	6.3	The tendency of the sediments in the operable unit to sorb Be, Ni, and U followed well established geochemical trends. Sediment sorption for U was greater than for Ni, which in turn was greater than for Be. Furthermore, over the range of pH 3 to 8, there was a significant logarithmic trend with *in situ* Kd values (for U the pH range was 3 to 5.5). Arsenic, an anion, sorbed exceptionally strongly to wetland sediments (Kd values >10,000 mL/g). This is important because the wetland sediments may act as an As-sorbing zone. Arsenic also sorbed strongly to aquifer sediments, albeit less strongly than the wetland sediment. Based on selective extraction procedures, it is postulated that the numerous Fe minerals in these sediments are responsible for much of the sorption capacity for the COCs. Arsenic may be bound to the sediment's natural organic matter and Fe phases (perhaps as solid solutions, i.e., poorly defined Fe precipitates).
d Characterize the soil geochemistry (e.g., sorption capacity and mineralogy) at the site and the manner in which these properties relate to sorption processes for COCs.	5.1.2	Soil mineralogy and its relation to sorption processes was characterized by the measurement of COCs associated with each phase defined by a sequential extraction procedure as described in 3c above. Characterization of soil texture, cation and anion exchange capacity, and extractable Al, Fe was also performed.

	Treatability Study Work Plan Objective	DEXOU MNA Report Section	Comment
e	Evaluate the metal availability of the source contamination for its transport from upland and wetland sediments into groundwater or surface water systems.	3.3 5.1.3 6.2 6.3	Section 6.2 is a discussion of COC concentrations and their availability. Section 6.3 summarizes Kds for COCs based on available metal fraction in soil. Figures 42-45 plot COC Kds vs pH based on the available fraction.
f	In conjunction with the microbial processes portion of this Treatability Study, develop an understanding of the manner in which geochemical conditions affect microbial communities and the manner in which microbial processes impact the site geochemistry with respect to site-specific transport factors.	5.2 5.3 6.4	The contaminants at this site are not at concentrations particularly toxic to bacteria. In fact bacteria were found at all locations in relatively high numbers. Just as the BIOLOG plates were found to buffer pH, biomass and associated proteins and carbohydrate production buffer groundwater.
3	***Microbial Processes***		
a	Determine whether direct monitoring of highly selected microbiological parameters can serve as a surrogate for defining the capacity of natural attenuation.	4.3 5.2 5.3 6.4	Ecofunctional enzyme activity and limited microbial isolations did show correlation of select microbial activity with location in the plume.
b	Evaluate the contribution of naturally occurring microorganisms to the attenuation of metals concentrations and the low-pH groundwater at D-Area groundwater and surface water plumes.	4.3 5.2 5.3 6.4	Indirect evidence indicates density shifts and different microbial populations along contaminant gradients.
c	Determine the concentration of the bacterial components of the community present in D-Area groundwater plume and determine if the bacterial communities are associated with the porewater, sediments, or wetland habitats.	4.3 5.2	Microbial concentrations were determined in only sediment porewater for this project.

	Treatability Study Work Plan Objective	DEXOU MNA Report Section	Comment
d	Characterize bacterial populations present and assess their activity with respect to D-Area plume.	4.3 5.2 5.3 6.4	Microbial activity was closely linked to location and geochemistry. Heterogeneity of microbial and geochemistry in subsurface sediments in upland as compared to wetland was evident. Greater diversity with distance from source.
e	Investigate the correlation between presence, density and activity of identified bacteria and natural attenuation of D-Area plume using selected immunoprobes.		No microbes isolated that probes were available for.
f	Determine the activity of selected naturally occurring microorganisms to reduce heavy metal concentrations, reduce sulfate concentrations, and increase pH values using selected sequential extraction techniques.		Specific reduction tests not done with extractions do to extra labor involved.
g	Evaluate the effects of naturally occurring microorganisms on the sequestration or removal of metal contaminants (thus the naturally occurring K_ds) following modification of the mineral phases in the soil by sequential extraction.		Specific metal removal tests not done with extractions do to extra labor involved.

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