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HEAVY METAL PARTITIONING IN SOILS OF VARIABLE TEXTURE AND REDOX POTENTIAL: AN EVALUATION OF SEQUENTIAL CHEMICAL EXTRACTIONS

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Robert J. Ellis

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HEAVY METAL PARTITIONING IN SOILS OF VARIABLE TEXTURE AND REDOX POTENTIAL: AN EVALUATION OF SEQUENTIAL CHEMICAL EXTRACTIONS

By

Robert J. Ellis

A THESIS

Submitted to

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for the degree of

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Department of Geological Sciences

1999

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ABSTRACT

HEAVY METAL PARTITIONING IN SOILS OF VARIABLE TEXTURE AND REDOX POTENTIAL: AN EVALUATION OF SEQUENTIAL CHEMICAL EXTRACTIONS

By

Robert J. Ellis

The fates of metals (e.g. Fe, Cu, and Zn) have been studied in soils at a former tannery site. Soil at the site varied in degree of water saturation, oxidation-reduction state, organic matter content, and metals concentrations. These conditions afforded the opportunity to study how biogeochemical soil conditions affect the formation, alteration, and sequestering ability of environmentally reactive metal binding phases. Sequential chemical extractions (SCEs) and porewater chemistry were used to determine metal partitioning within soil, and between solid and fluid phases, respectively. Information gained from SCEs, developed for oxic systems, was evaluated for anoxic systems.

In oxic soils, the easily reducible (ER - reactive Fe oxides), moderately reducible (MR - Fe oxides), and basic oxidizable (OX1 - organic matter) were the most important sequestering phases of metals. In anoxic soils these three phases were also important, but the mineralogical substrates comprising the ER and MR phases were unclear. Detailed analyses of meta-stable, water saturated, anoxic soils including: porewater redox potential determination; geochemical modeling; SCEs; acid volatile sulfide extractions; magnetic mineral fractionation; and x-ray diffraction, were preformed to determine mineralogical substrates comprising the ER and MR phases. SCEs performed on pure minerals, identified in anoxic soils, demonstrated that the SCE method used could not selectively distinguish between substrates that were found to comprise the ER and MR phases.

For my mother,

Janet M. Friske,

who has struggled for many years to support our family,

and has shown me, by example,

the value of hard work, dedication and perseverance

-- R.J.E

ACKNOWLEDGEMENTS

My development as a geologist has been guided by several teachers and fellow students. Foremost among them, my advisor, David T. Long, who has been very influential at several critical stages of my academic career. Others include: my thesis committee members, Michael Velbel, Sharidan Haack, and Duncan Sibley, who provided helpful reviews of early drafts of this thesis; and my good friends, Jon Kolak and Gary Icopini, fellow graduate students, who provided technical guidance and encouragement that helped me accomplish the goals of this research. Several others assisted with laboratory work and sample analyses during this research. Among them were Jennifer McGuire, Nathan Mellot, Sarah Hayes, Raullie Casteel, Page Vassar, Jeff Vought, Michael Klug, Michael Roberts, Jane Matty, Paul Laconto, and Susan Sipple. I thank them all.

This research was funded by a grant from a corporate sponsor who wishes to remain anonymous.

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I. INTRODUCTION

Concern over possible human health risk and ecological effects of heavy metal contaminated of soil due to improper disposal of industrial waste has prompted studies to gain insight into the fate of heavy metals in soil environments (e.g. Jenne, 1977; Tessier et al., 1979; Luoma and Bryan, 1981; Harrison et al., 1981; Hickey and Kittrick, 1984; Gibson and Farmer, 1986; Shannon and White, 1991; Yong et al., 1993; and Fielder et al., 1994). The fate of heavy metals is difficult to access because soils and sediments contain complex mixtures of sequestering phases. The exchangeable, carbonate, amorphous oxide, crystalline oxide, organic matter, and sulfide phases are considered important sinks for heavy metals due to their ubiquitous nature and environmental reactivity. However, their reactivity also makes these phases susceptible to alteration (e.g. dissolution) during natural biogeochemical processes (Jenne, 1977; Tessier et al., 1979; Nirel and Thompson, 1987). Since the reactive phases have different affinities for heavy metals and some are more susceptible to alterations than others, knowledge of the relative partitioning of metals among the reactive phases of soil is necessary to predict their potential mobility and bioavailability. Therefore, the purpose of this study is to investigate how variable and dynamic biogeochemical soil conditions affect the formation, alteration, and sequestering ability of environmentally reactive metal binding

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phases. This study will also evaluate the effect different phases in soils have on analytical methods used to determine metal partitioning.

The traditional method for investigating metal partitioning in soils and sediments has been the use of sequential chemical extractions. In this procedure, chemical reagents are applied to solid samples in sequence to remove metals from target phases of a soil or sediment sample. The selectivity of each extraction for a targeted mineral or organic phase is based on the chemical environment created by the various reagents. Consequently, the phases are only "operationally defined" by the reagents chosen. The relative partitioning of metals among targeted phases (e.g., carbonates, poorly crystalline Fe-oxides, crystalline-Fe oxides, organic matter and sulfides) is calculated from the concentrations of metals measured in the extraction leachate fluids.

Criticism of this approach has focused on the possible non-specific nature of the extractions and possible re-adsorption of metals during the procedure (e.g. Robinson 1984; Tipping et al., 1985; Nirel et al., 1985; Nirel and Thompson, 1987; Rapin et al., 1986; Gruebel et al.,1988; Rauret et al., 1989). Examples of potential non-specific extraction criticisms are the partial dissolution or destruction of phases not being targeted during a particular extraction. Evidence has suggested that some of these arguments have merit, but several researchers have shown the application of sequential chemical extractions to oxic sediments can be useful for determining metal partitioning and gaining insight into biogeochemical cycling of metals, as long as the limitations are recognized and interpretations are made accordingly (Tessier et al., 1979; Gephart, 1982; Chao, 1984; Belzile et al., 1989; and Fielder et al., 1994).

The most common extraction procedure, developed by Tessier et al. (1979) and modified by others including Tessier et al. (1982) and Belize et al. (1989), has been

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shown to give reproducible and fairly accurate information about metal partitioning in soil and sediment samples collected from oxic environments. This extraction procedure has also been routinely applied to soil and sediment samples collected from anoxic environments. However, extension of sequential chemical extractions to anoxic soils and sediments has proven to be a bit more tenuous due to problems with selectivity of the reagents for phases present in anoxic systems (Tessier et al., 1979; Rapin et al., 1983; and Martin et al., 1987). Two of the extractions within the procedure were designed to reductively dissolve iron (Fe) and manganese (Mn) oxides. Partitioning results from previous studies indicate that these two extractions often yield the highest percentage of metals in soils and sediments from both oxic and anoxic systems. Since Fe- and Mn-oxides are unlikely to form or persist under anoxic conditions, questions arise as to what minerals are being dissolved during these two extractions and what information is gained from using sequential extractions on soil or sediment samples from anoxic environments. Answering these questions is essential to accurate interpretation of metal partitioning results because the interpretations depend on the ability to identify the substrates comprising each operationally defined phase.

To evaluate the substrates comprising the operationally defined phases and information gained from use of sequential chemical extractions on soil samples from anoxic environments, investigation of metal partitioning behavior in well constrained anoxic systems that have been rigorously characterized is necessary. Knowledge of metal partitioning in similar materials existing under oxic conditions is also needed as a benchmark. The site chosen for this study is unique in that it contains similar soil textures that originated from the same parent material currently existing under a wide

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range of environmental conditions, thus allowing comparison between similar materials existing under different oxidation-reduction (redox) conditions.

Investigation of the soils, to characterize the variability in metal partitioning among the soil types and textures encountered at the site, began with initial soil sampling events in September and October 1996. Soil samples collected during this initial effort were subjected to sequential chemical extractions and leachate fluids were analyzed to determine partitioning of iron (Fe), copper (Cu), and zinc (Zn) among sequestering phases.

Several more sampling events in the late summer and fall of 1997 were conducted to collect soil porewater samples from a wetland area at the site. The purpose of this work was to determine the redox chemistry and the disequilibrium state of the porewater in direct contact with solid soil phases. Evaluation of the pore water data provided insight into the geochemical and microbiological processes controlling the redox state in water saturated wetland soil environments. In addition, analysis of the porewater chemistry data by geochemical modeling helped predict mineral phases that were likely to be stable and actively forming in the anoxic water saturated soils at the site.

Results from the pore water analysis and the geochemical modeling prompted more detailed solid phase analyses in an attempt to verify the presence of predicted mineral phases. These analyses included acid volatile sulfide determination, magnetic separation, and x-ray diffraction on samples collected in November 1997. Once mineral phases were identified, either by direct and/or indirect lines of evidence, pure forms of selected minerals were subjected to the same sequential extraction procedure to give some indication as to how they respond to the chemical reactants in the sequential extraction procedure. Information gained from the combination of analyses aided the

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interpretation of metal partitioning in soil samples from the site and illustrated some of the limitations of using sequential chemical extractions on samples collected from anoxic systems. Results of this study emphasize the importance of fully characterizing the redox chemistry and mineralogy of soil environments when making interpretations of metal partitioning based on sequential chemical extraction results.

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II. BACKGROUND INFORMATION

2.1 Site Description

The following sections describe the study site location, site history, land surface characteristics, and general soil characteristics at the study site. The name and description of the site location purposefully lack detail at the request of the anonymous corporate sponsor that owns the property.

2.1.1 - Study Site Location:

The study site is located along a major water way in northern Michigan. The site layout including, property fence lines, study area boundary within the site property, shoreline, roads, and locations of former buildings is presented in Figure 1. Field investigations in support of this research were conducted both within and outside the study area at the site. Field activities outside the study area were conducted to obtain background samples and increase diversity of sample populations.

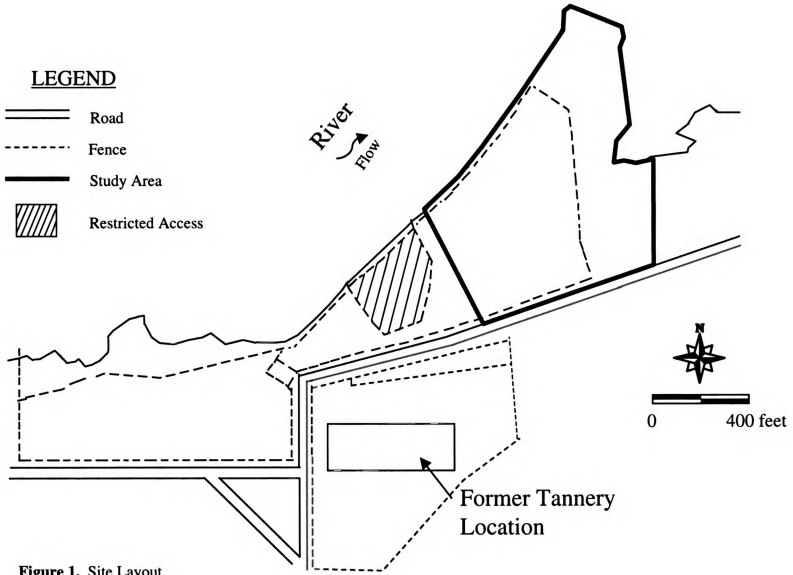

Figure 1. Site Layout.

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2.1.2 - Site History

Historically, the property was the location of a leather tannery operated from the late 1890's until approximately 1958. Typical tanning processes included, placing animal hides in large metal vats containing strongly acidic solutions (e.g. hydrochloric acid [HCl]) that cleaned and conditioned the hides, followed by the addition of a dichromate salt (e.g. sodium dichromate [$Na_2Cr_2O_7^+$]), and finally the addition of a strongly basic solution (e.g. sodium dithionate [$Na_2S_2O_3$], sodium hydroxide [NaOH], or sugar) to reduce the $Na_2Cr_2O_7^+$, to chromic salts (e.g. chromium sulfate [$Cr_2(SO_4)_3$] or chromium hydroxide [$Cr(OH)_3$]) (T.C.Thorstensen, 1958). The precipitation of chromic salts on the surface of the hides helped cross-link the collagen fibers to form a stable, durable leather product (E.B.Thorstensen, 1958). This chrome tanning technique was inherently inefficient and resulted in the production of large volumes of liquid waste, which contained chromic salts and dissolved organic-chromium complexes released from the animal hide. The acidic chromium (Cr) solutions could have solublized metals from the surfaces of the large metal vats in which the tanning occurred and/or any piping used to transport the acidic and/or basic solution into and out of the vats. The liquid waste may have contained Fe, Zn, Cu and other metals if the vats used to soak the hides were made of galvanized metal and if the pipes used to transport the tannery solutions to the vats in the tannery buildings were made of Cu.

A low-lying area along the river was used as a disposal area for liquid and solid tannery waste. Liquid waste was also discharged directly from the tannery buildings via drainage pipes to three locations in the low-lying area.

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Previous investigations at this site have concluded that disposal of waste generated from leather tanning operations resulted in significant heavy metal contamination, especially Cr, of the near surface soils to a maximum depth of approximately six feet below land surface (ft bls). As a result, site assessments and field investigations by previous investigators at the site have focused on determining the extent and magnitude of metals impacted soils at the site. However, sequential chemical extractions have not been used to investigate partitioning of metals in soils at the site. Therefore, results from this study will enhance information about the total metal concentrations of Fe, Cu and Zn by identifying phases that are important in sequestering each metal. Understanding what phases of the soil are sequestering metals will aid in the long-term prediction of heavy metal behavior at the site.

2.1.3 – Site Specific Hydrogeology and Landsurface Topography:

A 15-foot high ridge, extending east to west across the middle of the site, separates areas of higher elevation (upland area) to the south and lower elevation (low-lying area) to the north. Due to its proximity to the river, the low-lying area has land surface elevations at or below the groundwater table. This, along with the engineered embankment along the shoreline, has resulted in an extensive wetland containing poorly drained, water-saturated soil. In some areas of slightly higher elevation the soil is only occasionally water-saturated.

Stone rip-rap was installed along the shoreline of the site property in the early 1990's to eliminate erosion and transport of heavy metals impacted soil from the site by the river flowing adjacent to the site. The rip-rap has altered the natural hydrology at site by restricting the natural flow of surface water from the low lying area to the river. The

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causing saturated conditions. Wooded and grassy wetland areas make up the bulk of the low-lying portion of the site. Four small ponds, some with stagnant water and some with running water supported by natural springs are present within the wetland.

The area south of the ridge, and away from the river, contains woodlands and open grassy meadows with well-drained soils. The distinction between grassy and woodland areas is made because of the difference in soil development that occurs in the two different areas. Less water is available for soil leaching in unshaded areas and there is limited production of mobile organic acids during decomposition of organic matter in these soils. These conditions may yield slower rates of weathering and reduce the loss of weathering products through the soil (Schlesinger, 1991). These drier soils may have more developed accumulation of oxide coatings on mineral grains at depth than in soils of woodland origin.

2.1.4 - Soil Characteristics:

Soil types and textures at the site are spatially heterogeneous, ranging from oxic quartz sand to anoxic organic rich peat. Detailed description of the soil textures is given in Section 4.1. To avoid confusion with the sediments of the river adjacent to the site, the term soil is being used here and throughout the text to describe the near surface unconsolidated geologic and detrital organic material in both upland areas and low-lying wetland areas of the site.

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2.2 Environmental Chemistry of Metals and Substrates

2.2.1 - Soil Constituents and Distribution of Metals in Soils:

Soil is a complex system of competing phases. As a result, metals can exist in one or more phase, as described by Shuman (1991):

1.) dissolved in an aqueous soil solution,
2.) occupying exchanges sites on inorganic soil constituents,
3.) specifically adsorbed on inorganic soil constituents,
4.) associated with insoluble soil organic matter,
5.) precipitated as pure or mixed solids,
6.) present in the structure of secondary, and/or
7.) present in the structure of primary minerals.

The aqueous fraction and those solid phases that are in disequilibrium with it are of primary importance when considering metal partitioning because they are the most environmentally reactive. In fact, it is these environmentally reactive phases that are target by sequential chemical extractions. The particle surfaces on reactive soil phases also play an important role in the cycling of metals. Thus, understanding processes that occur at the particle level will help explain how and why solid phases of soil sequester metal ions from soil solutions. The next three sections will briefly describe the physical nature of the particle surfaces, the different forms metals ions take in an aqueous solution, and finally, the physiochemical attraction between particle surfaces and metal ions. Section 2.2.5 will discuss general geochemical properties of Fe, Cu, and Zn and potential co-precipitating substrates in soil environments.

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2.2.2 - Surface Functional Groups and Surface Charge:

Weathering reactions in soils produce a complex mixture of oxide and/or silicate precipitates on surfaces of soil grains (Sposito, 1984; Coston et al., 1995). The surfaces of mineral grains and weathering products are further altered by the accumulation of organic matter and/or poorly crystalline hydroxides (Jenne, 1977; Davis, 1982; Coston et al., 1995). Because of the density of functional groups present at their surfaces, Fe- and Mn- oxides and organic matter are thought to be the most important sequestering phases for many heavy metals in the environment. Therefore, an understanding of the origin and occurrence of reactive surfaces on soil particles is important. There are many processes that occur at the particle-pore fluid interface which affect the mobility of metals; discussion of all of them is beyond the scope of this study and only a few will be discussed.

Solid phases that comprise a soil and sequester metals have a variety of reactive surface functional groups to which metals are attracted to varying degrees. Surface functional groups are molecular entities that are part of a solid but located at the particle-fluid interface and are reactive toward ions and molecules present in the surrounding fluid. Each surface functional group contributes to the net surface charge of the solid, depending on the origin of the functional group and the pH of the surrounding fluid.

Surface charge can be created by isomorphous substitution of lower charged cations for higher charged cations in tetrahedral (Al^{3+} for Si^{4+}) and/or octahedral (Mg^{2+}or Fe^{2+} for Al^{3+}) layers of (2:1) aluminosilicate clays. Charge derived in this manner is termed permanent charge and is always net negative (Sposito, 1989; McLean and Bledsoe, 1992). Inorganic -OH groups also provide pH dependant surface and edge

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charge in some clays (e.g. kaolinite, smectite, and illite) and metal oxides, hydroxides and oxyhydroxides (e.g. ferrihydrite, goethite, hematite, lepidocrocite, magnetite, and gibbsite). Organic matter contains biochemicals and humic substances, which provide net negatively charged sites (acid functional groups, such as carboxylic, phenolics, alchoholic, hydroxide (OH^-), and amino groups) for metal sorption (Kerndorf and Schnitzer, 1980; Sposito, 1989; and McLean and Bledsoe, 1992). Sulfide minerals (iron monosulfide [FeS] and pyrite [Fe_2S]) have also been found to have sites with high surface energy (e.g. regions of excess strain associated with crystal defects, dislocations, microfractures, etc) where surface reactions can take place. Metals in solution can replace atoms at etch pits, fracture lines and grain edges by oxidization-reduction reactions. Also, these high surface energy sites function as nucleation sites for metals in solution (Jean and Bancroft, 1986; Hyland and Bancroft, 1990).

2.2.3 - Metal Ions in Solution:

Metals exist in aqueous solutions as uncomplexed metals ions (*free ions*), in soluble complexes with soluble inorganic or organic ligands, or associated with mobile colloidal material (McLean and Bledsoe, 1992). Free ions can be hydrated by one or more spheres of water and the affinity of a cation for water increases as the charge of the ion increases and the radius of the ion decreases. This affinity for water molecules affects the type of bond an ion creates with reactive surfaces. Some metal ions form soluble complexes with inorganic anions, such as chloride (Cl^-), sulfate (SO_4^{2+}), OH^-, and carbonate (CO_3^-), or organic molecules, such as aliphatics, aromatics, amino acids and soluble fulvic acids. Metal ions can also be associated with mobile colloidal material such as Fe-oxide, clay, or organic particles by the same mechanisms as for larger,

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immobile particle surfaces (McLean and Bledsoe, 1992), which are described in the next section.

2.2.4 - Adsorption, Complexation and Co-precipitation:

The principal mechanisms of adsorption, a general term for reaction between surface functional groups and ions or molecules in an aqueous solution, are inner-sphere complexation, outer-sphere complexation, and association with a diffuse ion swarm (Sposito, 1989). Adsorption-desorption reactions affect the partitioning of metals between the solid and liquid phase in soils, and hence the mobility of metals at the study site. An inner sphere complex is an association between a surface and an ion with no water molecules between the surface and the ion. An outer sphere complex is an association between a surface and an ion with one or more hydration spheres in between. Diffuse ion swarm adsorption is an association between an ion and a surface that is purely an electrostatic attraction. Several layers of water separate the ion from the surface and the adsorption is not with any particular functional group.

Inner sphere complexes have ionic and/or covalent character to their binding. Metals adsorbed in this manner, termed specific adsorption, are relatively immobile. With increasing concentration, adsorbing metals saturate the available specific sites and the non-specific or exchange sites are filled. Non-specific adsorption results in a higher potential for exchange by other common cations (e.g. potassium [K^+], magnesium [Mg^{2+}], and calcium [Ca^{2+}]), and hence greater potential for mobility. Soils at the site with elevated concentrations of metals may exhibit this increased potential for mobility, which should be evident from the partitioning results of the sequential chemical extractions.

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Surface precipitation is an association between an ion and a surface functional group that results in polymerization and precipitation of a three dimensional mineral structure (Sposito, 1989 and McLean and Bledsoe, 1992). For this to occur, only the fluid immediately surrounding the surface needs to be at or beyond saturation with respect to the mineral that is precipitating, so measurement of bulk solution chemistry may not reflect interfacial conditions. Also, formation of co-precipitates can lower the solubility of metals as predicted by the thermodynamic equilibrium with pure minerals or amorphous precipitates (McBride, 1994).

2.2.5 - Geochemistry of Iron, Copper, Zinc and Sulfur and Carbonate:

This section will give a general description of the geochemical behavior of Fe, Cu, and Zn and common substrates that these metals are likely to react with, given the porewater chemistry at the study site. These generalizations are based on the surface chemistry of particles and attraction between ions and reactive surfaces discussed in the previous three sections.

The ubiquitous nature, large surface areas, and surface chemical reactivity of Fe solid phases such as (Fe (II,III) oxyhydroxides, FeS_2, FeS, siderite ($FeCO_3$) and Fe-silicates, facilitate adsorption of various solutes. These properties result in the interdependency of the Fe cycle with that of many other elements, especially heavy metals, sulfur and carbonate. The solid state and surface chemistry of some Fe phases allow the inorganic catalysis of redox reactions (Stumm, 1992). The high redox potential of Fe(III), and the rapidity of the inter-conversion of Fe(III) to Fe(II) also promote the utilization of Fe (III) by microorganisms in their metabolic activities (Myers and Nealson, 1991).

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Reduced Fe phases are produced directly and indirectly by reactions coupled to the oxidation of organic matter (OM) by microorganisms (Lovley, 1991). The reduction of Fe oxides can lead to considerable redistribution of heavy metals in soils when they become water saturated (McBride, 1994). It was therefore considered important to identify the form of iron in various soil types at the study site, especially soil environments where these transformations have occurred or are presently occurring.

Copper is a chalcophile, which usually occurs in soils and aqueous solutions as a +2 cation, but reduction to Cu^{+} and Cu^{0} is possible under reducing conditions, especially if sulfide ions are present. In reducing environments, most organic material in soils adsorb Cu^{2+} strongly thus restricting its mobility dramatically. Organically adsorbed copper is bound more strongly than any other divalent metal (McBride, 1994). Cu also has a high affinity for soluble organic ligands and at high pH the formation of these complexes may also increase its mobility (McLean and Bledsoe, 1992).

Zinc is readily adsorbed onto clay minerals, carbonates, sulfides, and hydrous oxides. As with most trace metals, Zn adsorption increases with increasing pH, and formation of complexes with inorganic and organic ligands also tends to increase mobility. Zinc hydrolyzes at pH 7.7 and the resulting species generally sorb strongly to soil particle surfaces. Under oxidizing conditions, Zn^{2+} is highly soluble and thus very mobile. As conditions change from oxidizing to reducing, such as during a soil flooding event, release of Zn from reduction of Fe oxides may increase its mobility, but this mobility is ultimately controlled by the extreme insolubility of wurtzite (ZnS) (McBride, 1994 and McLean and Bledsoe, 1992).

Sulfide (S^{2-}) is generated by sulfate reduction as microbes utilize SO_4^{2-} as a terminal electron acceptor during OM oxidation (Bertolin et al., 1995). Under reducing

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conditions, iron oxides and oxyhydroxides are reduced and the ferrous iron ions generated react with the S^{2-} to produce a variety of sulfide minerals including FeS, greigite (Fe_3S_4), and eventually FeS_2 (Morse and Cornwell, 1987; Casas and Crecelius, 1994,). Sulfide may also react with many other metal heavy metal cations (e.g. Cu^{2+} and Zn^{2+}) to form insoluble monosulfides. Due to the relative insolubility of these metal monosulfides, pore water concentrations of the transition row metal ions are low in anoxic systems where sulfide is present (Allen et al., 1993).

The major factors controlling how much metal monosulfide (e.g. FeS, CuS, and FeS_2) can form are the amounts of organic matter, reactive Fe minerals present and the availability of dissolved sulfide (Berner, 1984). Figure 2 is a diagrammatic representation of the overall process of FeS, metal monosulfide, and Fe_2S formation. Sulfate and Fe (III) reducing microorganisms play key roles in the interaction between the various forms of sulfur and Fe.

Microorganisms also drive the carbon cycle. Heterotrophic microorganisms convert organic carbon bound up in complex organic matter to inorganic forms of carbon (carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-)). Carbonic acid is produced during the complete oxidation of organic carbon by microorganisms to CO_2 and H_2O and resulting reactions that follow (Berner and Berner, 1996):

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O$$

$$CO_2 + H_2 \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Note: Me^{2+}

Figure 2. D
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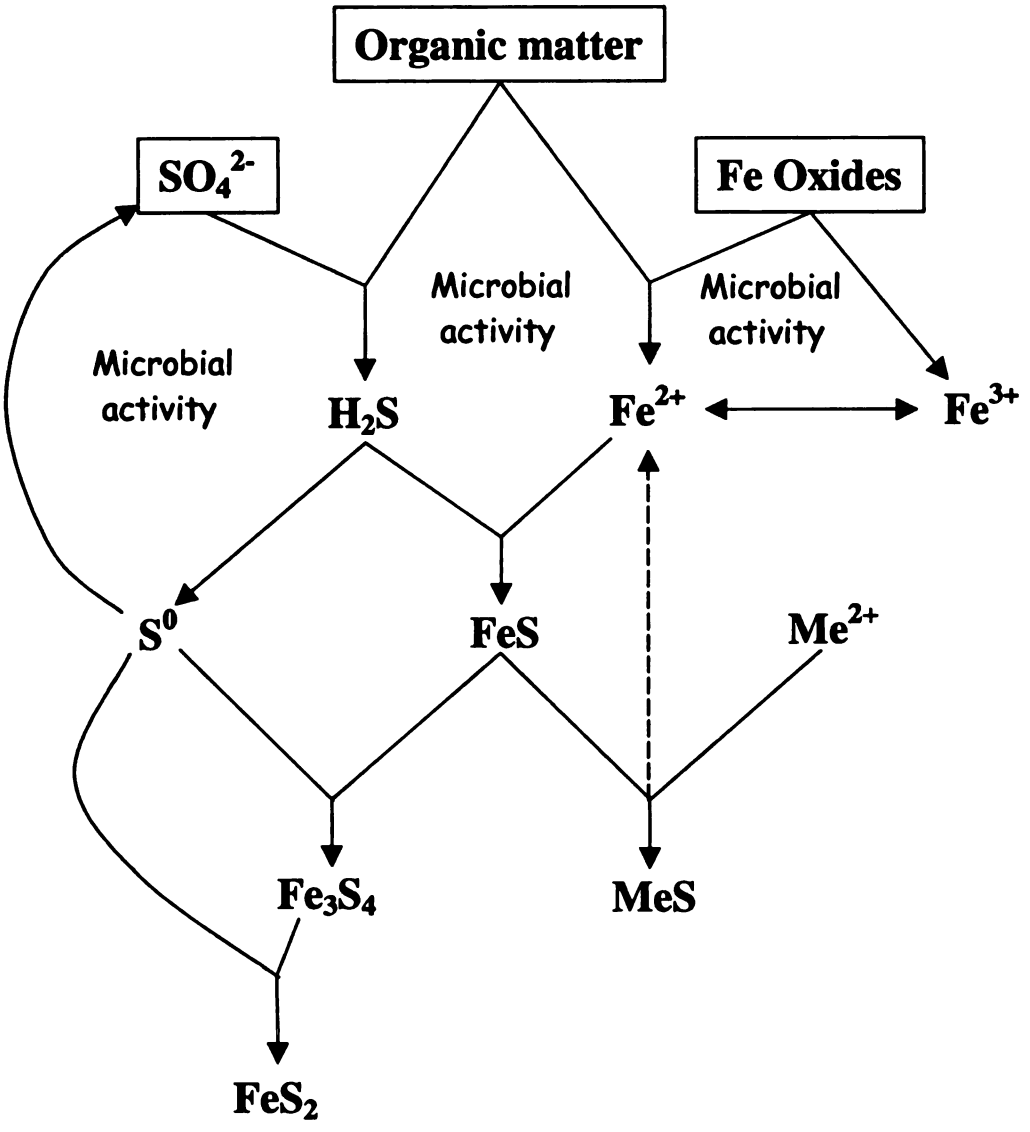

Note: Me^{2+} represents any metal cation that forms a more soluble sulfide than FeS.

Figure 2. Diagrammatic representation of the overall process of FeS, metal monosulfide, and pyrite formation (modified after Berner,1984).

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The carbonic acid produced can then react with and dissolve silicate, carbonate and oxide minerals during chemical weathering or the H^+ can be displaced by ions in solution yielding carbonate precipitates (e.g. calcite ($CaCO_3$) and $FeCO_3$).

2.3 - Metal Cycling in Response to Changes in Redox Conditions

The solid phases and surface chemical properties that developed under one set of redox conditions are unlikely to be preserved once a change in redox potential occurs. Thus, considerable redistribution of metals can occur as the solution chemistry changes and solid phases re-precipitate under the new conditions (McBride, 1994).

When soil becomes saturated with water, a sequence of microbiologically catalyzed redox reactions occur that exert control over the solution pH, redox, and concentration of important geochemical elements such as oxygen, nitrogen, iron, sulfur, and carbon (Stone, 1987). Initially, metal species exist in solution and on surfaces (e.g. minerals or organic matter coatings) primarily as oxides, hydroxides, or oxyhydroxides until microbial activity depletes the aqueous system of oxygen (O_2) and a shift to anoxic conditions occurs. Anaerobic microorganisms then begin to utilize alternative terminal electron acceptors in their metabolism. In soils and sediments, the sequence of dominant terminal electron accepting processes (TEAPs) can be observed spatially in horizontal or vertical layers. The dominance of one TEAP over others is based on the competitive advantage groups of organisms have over others resulting from utilization of available metabolic substrates and terminal electron acceptors that maximize energy yield (Atlas and Bartha, 1993). Although one TEAP may dominate at a particular time and location, more than one TEAP can occur simultaneously. The result of the succession of TEAPs is

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Due to direct and indirect microbial reduction of Fe oxides under water saturated anoxic conditions, Fe and absorbed metals become mobilized, then re-precipitate as mineral phases stable in the new redox environment (carbonates and metal sulfides). When the soil becomes unsaturated, or oxic again, reduced phases can be re-oxidized forming oxides, hydroxides, and oxyhydroxides. The potential for incorporating metals into oxides during redox/saturation cycles is increased because freshly precipitated oxides have more reactive surfaces and are more effective absorbents for metals (McBride, 1994). These processes, driven by microorganisms, are most likely occurring in the upland soils and cyclically water saturated wetland soils at the site and the effects on metal partitioning in different soil types should be observable in the results of the sequential chemical extractions.

III. METHODS

3.1 - Sample Grid Development, Surveying, and Site Locations

A grid of equally spaced sampling locations was developed in a manner that would give the best spatial coverage, reduce bias in the sample population and best characterize the variability in soil conditions at the site. First, a grid of points was generated graphically. Then, the grid was overlain on an existing site map so that one of the grid points corresponded to a pre-existing land survey marker.

Sample locations were located by measuring linear and angular distances with surveying equipment and a 200 foot steel tape starting from the existing land survey marker and continuing to successive sampling locations. Once located, each sampling location was marked with a labeled wooden staked. The locations of the 80 sampling locations that resulted are shown in Figure 3. One area of the site near the shoreline, which received the highest loading of tannery waste, had restricted access. As a result no field activities were conducted in this area.

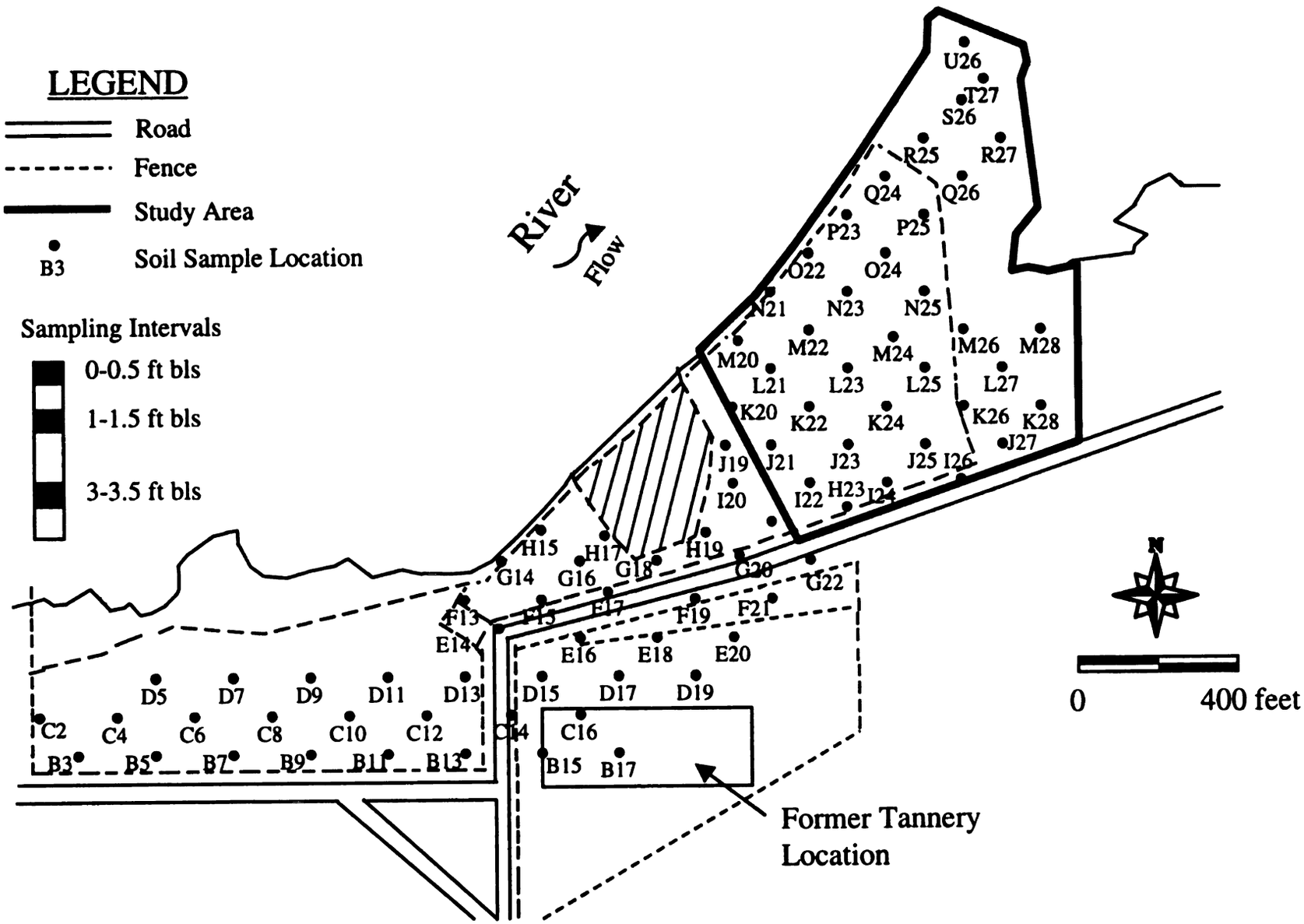

Figure 3. Locations of soil samples collected in September and October, 1996.

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3.2 - Soil Sample Collection

Undisturbed soil cores collected for sequential chemical extractions and other solid phase analyses were obtained using an AMS™ two-inch diameter spilt-spoon stainless steel coring device with 6-inch plastic liner tubes. The coring device was advanced into the ground with an AMS™ weighted hand slide hammer. Extension bars were attached to the slide hammer to take cores at depth.

At each sampling location an attempt was made to retrieve cores from three intervals (0-0.5 ft bls, 1-1.5 ft bls, and 3-3.5 ft bls) corresponding to observed soil horizons at each of the 80 sampling locations. At several sample locations, however, discontinuous layers of solid waste (e.g. cans, scrap metal), wood boards, and coarse gravel prevented the retrieval of cores at depth. The split-spoon coring device was disassembled then cleaned with plastic brushes, rinsed with distilled water and dried with paper towels between each coring to prevent cross contamination between samples. Cores were sealed with end caps, which were secured with electrical tape, then stored frozen (-20° F) within one to six hours.

Each of the soil samples were described in the field upon retrieval, then later given one of seven descriptive soil texture classifications based on field descriptions and organic carbon results. Field descriptions of cores and organic matter content results are shown in Appendices 1A and 1B.

3.3 - Clean Procedures

Water used for preparing solutions, mixing reagents, and washing glassware was distilled deionized water (DDW) manufactured using house deionized water and further distilling it in a Corning™ water still (model AG-22). All glassware was rinsed three

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times with DDW, acid-washed in 10 % HCl for 24 hours then rinsed again three times with DDW, and then soaked in DDW for 24 hours. After the DDW water soak, items were placed in lined polyethylene containers and dried completely in a class 100 hood. Once dry, glassware was capped and placed in lined drawers until needed. Capped sample bottles, filtration components, and other reusable parts were sealed in acid washed plastic bags and then placed in lined drawers. Nucleopore polycarbonate membrane filters (0.4 micrometer (μm)) used for filtering extraction leachate from samples were cleaned by a 24 hour dilute HNO_3 soak, then rinsed three to five times with DDW, and finally soaked in DDW for 24 hours. Filters were stored soaking in DDW in acid-washed polyethylene containers until use. Acid-washed plastic forceps were used to handle the filters during loading of Millipore Swinex filter holders.

3.4 - Sequential Chemical Extractions

The sequential chemical extraction procedure used to determine metal partioning in this study was similar to that developed by Tessier et al. (1979), with modifications by Belzile et al. (1989). An outline of the procedure is presented in Table 1. The extraction procedure used is described in detail in Appendix 2A. An additional extraction (OX1), which utilized a five to seven per cent solution of sodium hypochlirite (NaOCl) acidified to pH = 9.5 with hydrochloric acid (HCl), was included to help distinguish between metals associated with soil organic matter and those associated with sulfides. In their work on peat samples and pure minerals Papp et al. (1991) showed that sodium hypochlorite (NaOCl) (pH = 9.5) is more selective in releasing metals bound to organic matter than the hydrogen peroxide (H_2O_2, pH = 2 with nitric acid (HNO_3)) solution typically used in the Tessier et al. (1979) method. They also demonstrated that NaOCl

Table 1. Summary of Sequential Chemical Extraction Procedure
(modified after Tessier et al. (1979)).

Target Substrate	Operationally Defined Extraction Phase	Extraction Solution*	Extraction Conditions
Exchange Sites	Exchangeable (EX)	1.0M $MgCl_2$, pH 7 10 milliliters (mL)	20°C, 1 hour
Carbonates	Weakly Acid Soluble (WAS)	1.0M NaOAc, pH 5 10 mL	20° C, 5 hours
Reactive Fe-Oxides and Mn- Oxides	Easily Reducible (ER)	0.1M NH_2OHHCl in 0.1M HNO_3 25 mL	25° C, 5 hours
Crystalline Fe-Oxides	Moderately Reducible (MR)	0.04M NH_2OHHCL v/v 25%HOAc 20 mL	96° C, 6 hours
Organic Matter	Basic Oxidizable (OX1)	NaOCl, pH 9.5 3 times, 6 mL	96° C, 15 min.
		then 3.2M NH_4OAc 5 mL	25° C, 1 hour
Pyrite	Acid Oxidizable (OX2)	0.02M HNO_3 3 mL 30% H_2O_2, pH2 8mL	85° C, 5 hours
		3.2M NH_4OAc 5mL then add DDW to make 25mL	25° C, 1 hour

* volumes optimized for 1.0g samples

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did not significantly dissolve selected oxides and sulfides. This was an attractive addition to the Tessier method primarily because much of this site is comprised of organic rich, water saturated, anoxic soils. Metal partitioning results are presented and discussed in section 4.2

3.5 - Procedures for Metals Analysis

Metal concentrations in sequential chemical extraction leachate fluid samples were determined using a Perkin Elmer 5100pc atomic absorption spectrophotometer (AAS). Fe and Zn in leachate samples were analyzed by flame-AAS. Cu in leachate samples was analyzed by graphite furnace-AAS with Zeeman background correction.

Calibration standards for leachate sample analyses were prepared using DDW and the extraction chemicals to form the background matrix and certified 1000 milligrams per liter (mg/L) stock solutions (J.T. Baker Analyzed). Care was taken when making standards and necessary dilutions of leachate samples to maintain similar matrices between samples and standards. All chemicals and reagents used were analytical grade or better.

Analytical precision, in terms of the relative standard deviation of response for three concentration determinations, was set at less than 15 % for all AAS. Analytical accuracy was assessed by comparison to National Institute of Standards and Testing (NIST) standard reference materials (SRM). Standard calibration curves were compared to SRM 1643c or 1643d (Trace Elements in Water) values, which were required to be

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within 15 % of certified values. Metals concentration in the leachate fluids were converted to solid phase concentrations and reported on a dry weight basis.

3.6 - Organic Matter Content Determination

Organic matter content of soils was determined, on sub-splits of homogenized soil taken prior to the sequential chemical extractions, by a loss on ignition method. The method was modified after a procedure developed by researchers from the Department of Soil Science at the University of Wisconsin, Madison, WI (Shulte et al., 1991). Samples were submitted to the Plant and Soil Testing Lab at Michigan State University for analysis. Results of the organic matter determinations are presented and discussed in Section 4.1.

3.7 - Porewater Sampling

Porewater was obtained using two different types of samplers, both based on the principal of in-situ dialysis membrane equilibration. The "Peeper" samplers (Hesslein, 1976; Carignan, 1984; Carignan and Nriagu, 1985; Carignan, et al. 1985) consist of a 2 ft long block of acrylic with twenty-eight individual sample compartments. A schematic drawing of a pepper is shown in Figure 4. To prepare a peeper for deployment, sample compartments were filled with deoxygenated, distilled-deionized water (DDDW), then a sheet of acid washed dialysis membrane (0.2μm pore diameter Biodyne B™ nylon membrane, Pall Corp.) was carefully placed over the sample compartments followed by thin acrylic faceplate. The faceplate was secured to the sampler with nylon screws. Care was taken to avoid trapping air bubbles under the nylon membrane.

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The "barrel" samplers were modified from dialysis membrane multilevel sampler apparatus designed by U.S. Filter/Johnson Screens Corp. Each barrel consists of a hollow polyethylene tube (one-inch in diameter, three-inches in length) with screw-on 0.2 μm nylon filters at both ends. A schematic drawing of a pepper is shown in Figure 5. To complete the assembly, three barrels were strapped together with plastic cable ties.

Once assembled, both types of samplers were submerged in a cylinder filled with DDDW and deoxygenated by bubbling with N_2 or Ar gas for a minimum of three days before transport to the site and deployment. At each site, the samplers were taken from the cylinder and inserted into water-saturated soils within two minutes to avoid introducing oxygen to the compartments. Samplers were left in place for period of two to three weeks (Hesslein, 1976; Carignan, 1984; Carignan et al., 1985; and Tessier et al., 1985). During this time, dissolved ions and molecules (<2μm) in the porewater came into equilibrium with the DDDW inside the sampler. Porewater analytical results are presented and discussed in Section 4.4

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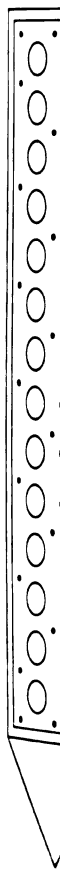

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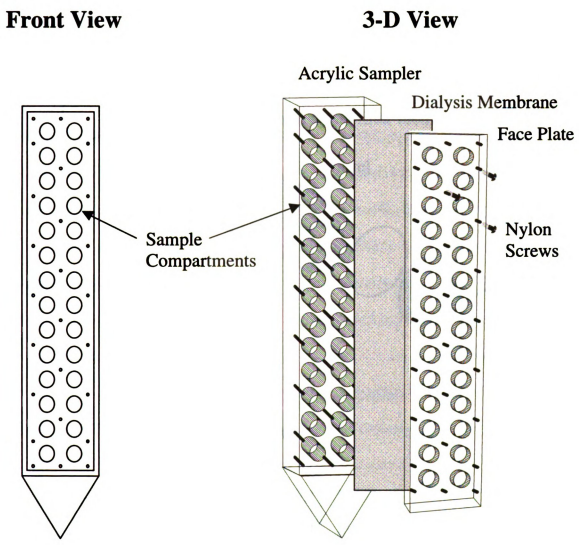

Figure 4. Schematic diagram of a "Peeper" pore water sampler.

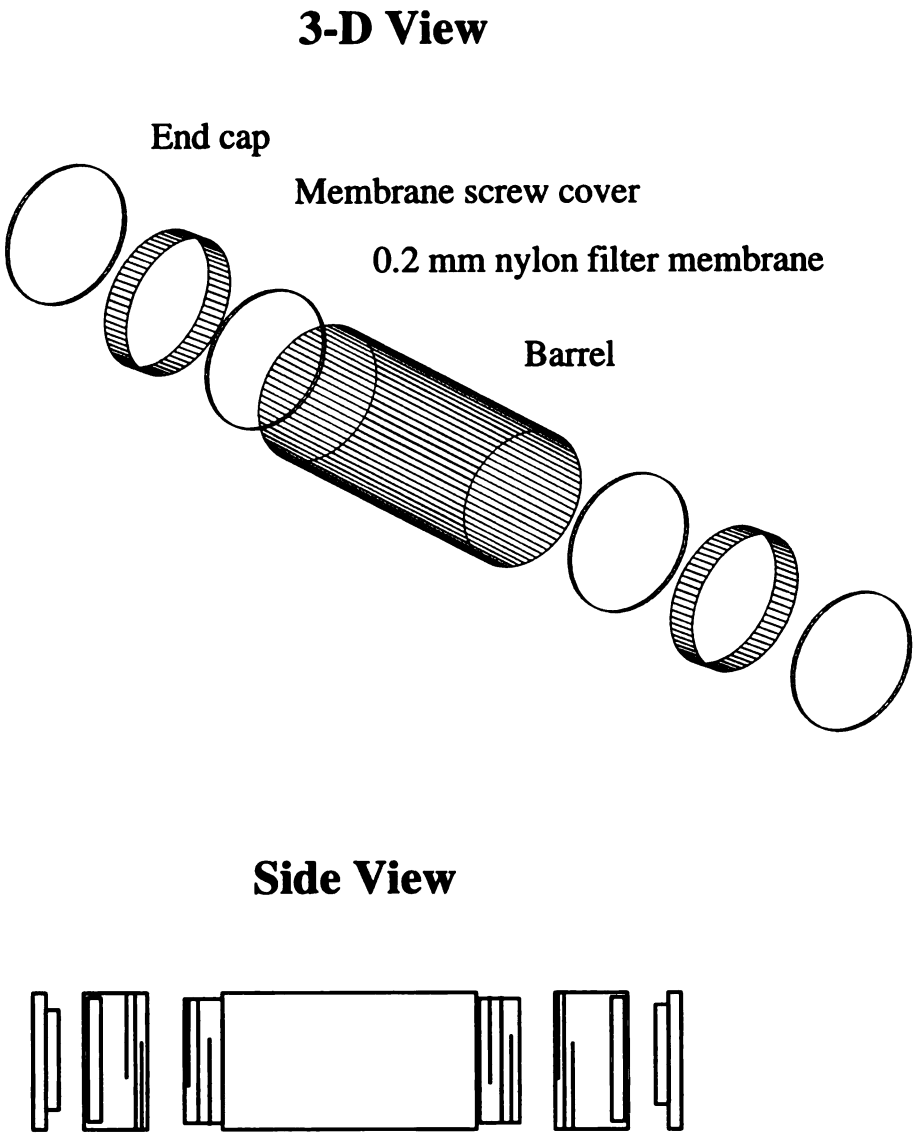

Figure 5. Schematic diagrams of a "barrel" porewater sampler.

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3.8 - Porewater Field Measurements

A complete geochemical analysis was performed on the equilibrated fluids within the pore water samplers. To obtain enough fluid, groups of four to six peeper ports were sampled as if they were the one compartment and the group of three barrels that were strapped together were sampled as a single compartment. Geochemical parameters measured in the field included: temperature, pH, redox (Eh) potential, alkalinity, S^{2-}, Fe^{2+}, and Cr^{6+}. Aliquots were collected for cations (majors and transition row trace metals), anions (Cl^-, bromide [Br^-], nitrate [NO_3^-], nitrite [NO_2^-], SO_4^{2-}, and ammonia [NH_4]), methane (CH_4), and dissolved organic carbon (DOC). Detailed methodology for sampling and analyzing each parameter is given in Appendix 2B. Results of the porewater field measurements are presented and discussed in Section 4.4.

3.9 - Measuring Redox Potential

Redox potential is a measure of the ability of a solution to donate electrons to or accept electrons from a chemical species. This potential can be measured directly as Eh (mV) by introducing an electrode into a solution. However, investigators have discovered that these measurements are problematic because electrodes respond to few of the geochemically important redox couples and low temperature aqueous environments rarely reach redox equilibrium. The redox potentials observed in natural waters are usually mixed potentials, which are impossible to relate to a single dominant redox couple (Lindberg and Runnels, 1984). An alternative approach is to measure specific redox couples such as Fe^{2+}/Fe^{3+}, $NH_4^+/NO_3^-/NO_2^-$, and S^{2-}/SO_4^{2-}. Interpretations of redox conditions in this study were based on electrode measured Eh values for general assessment of redox potential, while more refined statements about redox state are based

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3.10 - Geochemical Modeling

Geochemical modeling of pore water chemistry data was performed using PHREEQC (Parkhurst 1995) with the MINTEQ database to predict the presence and stability of minerals in the water saturated anoxic soils. PHREEQC is a computer program that was designed to use known water chemistry data to perform thermodynamic calculations which predict the level of mineral disequilibrium, charge balance, metal complexing, Eh from measured redox couples, possible aqueous redox species, and the potential for minerals to precipitate or dissolve. Parkhurst (1995) gives background information on the development of this model and the algebraic equations used within it. The MINTEQ database was selected over the more traditional WATEQ database because MINTEQ has a more robust assemblage of thermodynamic reactions for minerals composed of Fe, Cu and Zn. Results of the geochemical modeling are presented and discussed in Section 4.6.

3.11 - Acid Volatile Sulfide Analysis

Acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) determinations were preformed by methods described by Allen et al. (1993) and Lasorsa and Casas (1996). The procedure is only summarized here but explained in depth in Appendix 2C. Briefly, AVS in a sample is converted to hydrogen sulfide (H_2S) by addition of 1M hydrochloric acid at room temperature. The sulfide evolved is trapped in a 0.5 M NaOH solution and reacted with mixed diamine reagent (MDR) to create

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methylene blue, which is then measured colorimetrically. The acid solution used to dissolve AVS and evolve hydrogen sulfide (H_2S) is filtered and the simultaneously extracted metals (SEM) in the fluid measured by flame or furnace AAS. It has been noted that Fe_2S and organic-sulfur compounds are not soluble in 1N HCl (25° C) and therefore it is generally assumed that only amorphous iron sulfide and other metal sulfides (with the exception of CuS) are being attacked (DiToro et al., 1990; Allen et al., 1993; and Lasorsa and Casas, 1996). The AVS/SEM reaction apparatus used is shown in Figure 6. Results of the AVS/SEM analyses are presented and discussed in Section 4.7.

3.12 - Magnetic Fraction Separations

The magnetic mineral fraction was separated from sub-splits of homogenized soil saved from the AVS/SEM analysis. Three to five grams of wet soil were mixed with DDW in an Erlenmeyer flask to create a slurry. A magnetic stir bar was added and the slurry was magnetically stirred for 10 minutes, with occasional gentle shaking of the flask. A magnetic rod was then used to remove the stir bar from the flask. Gentle drips of DDW were used to remove any nonmagnetic material from the stir bar. The recovered magnetic minerals were then leached with concentrated HNO_3 at 96° C for several hours. The leachate was filtered through acid washed 0.4 μm Nucleopore filters into acid washed Nalgene polypropylene bottles. The leachate samples were analyzed for metals by FAAS as described in Section 3.5.

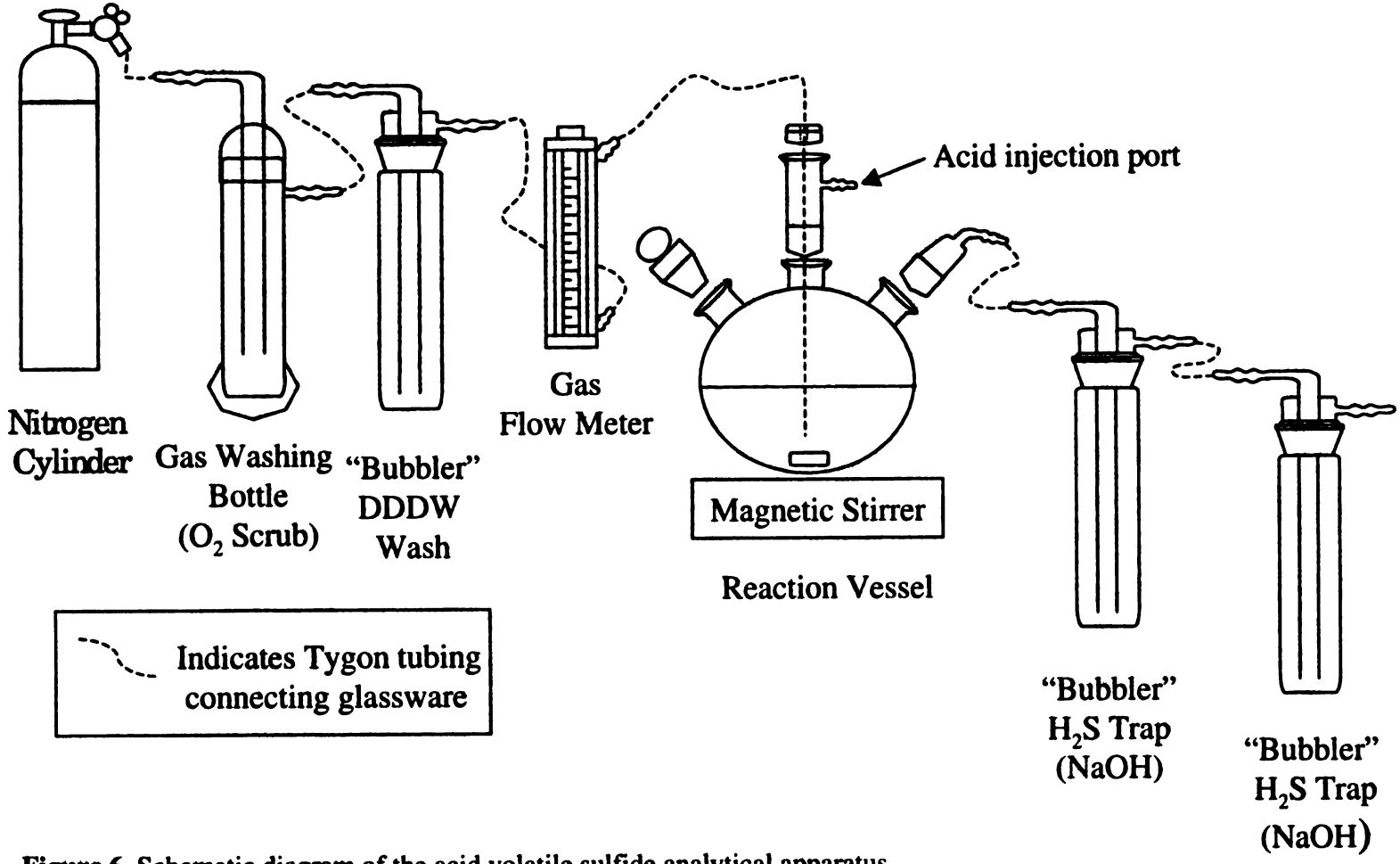

Figure 6. Schematic diagram of the acid volatile sulfide analytical apparatus.

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3.13 - X-ray Diffraction

X-ray diffraction of oriented samples were analyzed to determine the mineralogy of the clay and fine silt size fractions (<20μm). An estimation of the amount of clay in samples was used to calculate the amount of sample that will be required to yield about 0.5 gram (g) of clay (Soil Survey Staff 1975). Clay, silt, and sand size particles were separated by a cylinder sedimentation method and settling times were calculated using Stoke's Law. Samples having greater than five per cent organic matter were subjected to successive extractions with NaOCl (pH 9.5) to remove organic matter prior to grain size separation.

Mounts were made according to one of two methods outlined by Moore and Reynolds (1989). Particle suspensions were decanted into a Millipore filtration system and the particles were collected by vacuum suction of the suspension through a 0.4 μm Millipore filter. Magnesium chloride ($MgCl_2$) and potasium chloride (KCl) saturation was achieved on separate sample splits by adding one molar (M) solutions to the filtration system at the end of the suspension filtration. Then the filter cake was rinsed with DDW to remove most of the Cl^-. Before all of the DDW rinse water passed through the filter the vacuum was removed and the system was brought back to atmospheric pressure. The remaining DDW was decanted and the moist filter cake was carefully placed upside down on a microscope slide. After three to five minutes, the filter was peeled off leaving the oriented clay and/or silt size particles on the slide. Results of the XRD analyses are presented and discussed in Section 4.9.

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3.14 - Pure Mineral Extractions

Pure powdered minerals (FeS, CuS, ZnS, PbS from Aldrich Chemical Co. and $CaCO_3$, Fe_3O_4, FeS_2 from Wards Geology Catalogue) were subjected to sequential chemical extractions. Sequential extraction of some of these minerals (CuS, ZnS, PbS Fe_3O_4) using the Tessier (1979) method have not previously been conducted so the results presented in Section 4.3 are the first of their kind. The procedure for the pure mineral sequential extractions followed exactly that for samples described in Section 3.4. The pure minerals were handled and extracted under a nitrogen (N_2) or argon (Ar) atmosphere to avoid oxidation of the monosulfides. All extractions were preformed in triplicate. Results of the pure mineral extractions are presented in Section 4.8.

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IV. RESULTS AND DISCUSSION

4.1 Soil Texture Descriptions

Soil textures were described in the field during soil boring and collection of soil samples during the initial site characterization. Two distinct soil types were observed at the site including a histosol in the low lying wetland area, characterized by organic rich peat, and a spodosol in the upland area with well developed O, A, and B and C horizons.

Solid waste generated from leather tannery processes and industrial and domestic trash (fill), was laterally discontinuous and ranged from zero to at least six ft bls within the upland and wetland areas of the site. The fill was comprised of scrap leather, animal hair, scrap wood, bricks, concrete, scrap metal, glass, cans, etc. In areas that were intensely impacted with tannery waste (near soil borings G14, E16 and E18) contained green colored soils to depths of at least three ft bls.

The peaty soil in the wetland area was comprised of dark brown to black, decaying organic matter varying amounts of fine to medium grained quartz sand (20-50 %) and silt (10-30%) with trace mafic mineral grains. There was a sharp contact, which ranged from one to four ft bls throughout the wetland area, between the peaty soil interval and silty sand glacial/fluvial sediments below. The lower interval consisted of tan to dark gray, fine to coarse grained, quartz sand (60-90%) and silt (10-40%) with minor clays and mafic mineral grains. The water table was observed to fluctuate from several inches above land surface to not more than six inches below land surface (bls) soil in the

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wetland area generally resulting in generally saturated conditions most of the year. Soil redox conditions in the wetland area were determined by analysis of the porewater at several locations. Results of the porewater analysis are presented and discussed in Section 4.4.

Soil in the upland area had developed soil horizons beginning with an O horizon, which extended from land surface to about three inches bls and contained mainly decomposing organic material. The A soil horizon extended from approximately three inches to one ft bls and was comprised of well-sorted, fine to coarse, rounded to sub-angular, quartz sand (70-90%), silt and clays (10-30%), and organic matter ranging from (1-5%). The B soil horizon extended from one to three ft bls throughout the upland area. This horizon contained rusty-orange, well-sorted, fine to coarse, quartz sand (60-90%), and silt (10-40 %) with discontinuous lenses of clayey silt. The rusty-orange color was interpreted to indicate the presence of Fe-oxides on the quartz grain surfaces. Organic carbon content in this interval ranged from 0.5 to 3 % in areas that were not impacted by tannery waste. Grain size within the B soil horizon generally coarsened with depth in the C horizon. The C soil horizon was generally encountered at three ft bls and was composed of tan, medium to coarse grained quartz sand (60-100%) and silt (0-40%) with discontinuous lenses of fine gravel. The organic carbon content in this horizon range from 0.2 to 1.1% in areas that were not impacted with tannery waste. Soils containing tannery waste generally contained greater than 20 percent organic matter, most of which appeared to originate from the tannery waste (e.g. scraps of leather and unrecognizable material), as opposed to detrital of plant material. In general, soils were moist throughout the first three and a half ft bls, but no groundwater was encountered during soil borings in the upland area of the site. Soil redox conditions were not directly measured, but these

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well drained soils had rusty orange staining on quartz grains, which was interpreted too indicate the presence of Fe-oxides and oxic conditions.

Soil samples collected represent a full spectrum of soil textures as well as geochemical and microbiological conditions found in near surface soils at the site. Table 2 summarizes these texture descriptions. General location at the site, number of samples collected, and average organic matter content for each soil type are also given in Table 2. Field descriptions of individual cores and organic matter content results are presented in Appendix 1A. Soil texture and organic matter content and ecological interpretation maps illustrating spatial variability throughout the site are shown in Figures 7-9, respectively.

Redox conditions in unsaturated soils from the upland area of the site were not directly measured. However, due to the observed unsaturated conditions of these well-drained soils, it is assumed that $O_{2\,(g)}$ is commonly present in the soil at depth, except possibly during heavy rain or spring thaw flooding events. The intense rusty orange color Fe-oxides on sand grains as deep as three feet below land surface supports this position. Redox conditions in water saturated soils in the wetland area were measured and in general suggest anoxia occurs within one inch of the soil-air or soil-water interface in the wetland. These results are discussed in Section 4.4.

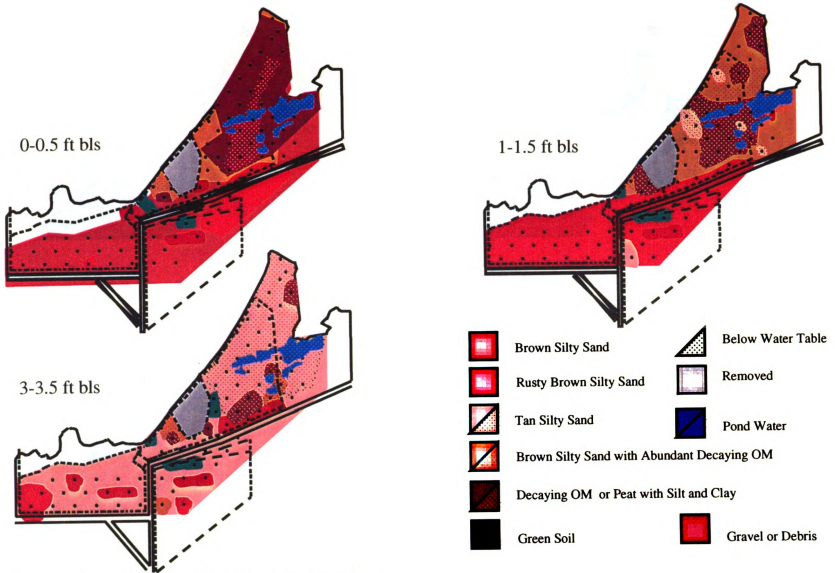

Figure 7. Maps of soil textures for three depth intervals.

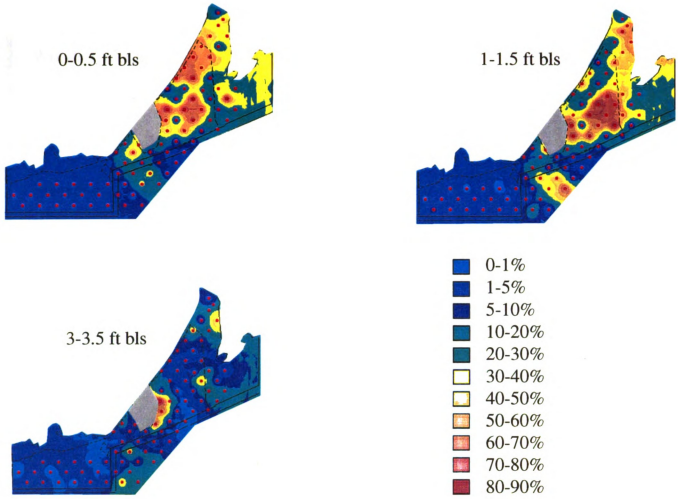

Figure 8. Organic matter content (weight %) for three depth intervals.

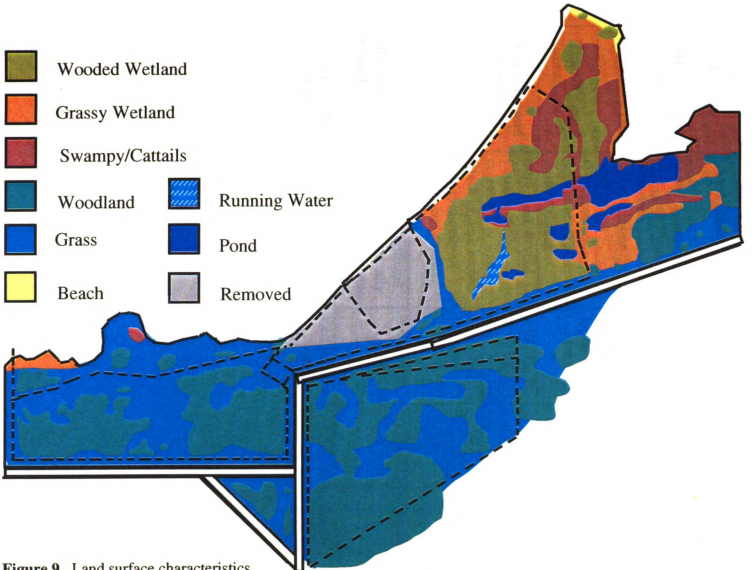

Figure 9. Land surface characteristics.

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Table 2. Soil texture descriptions and classifications with general location of each, number of samples, and average organic matter (OM) content for each texture.

Soil Texture	Soil Horizon And Description	General Location	Number of Samples	Average OM Content
Brown silty sand	O and A horizon soils, rich in humus	Upland area (topsoil)	31	3.9%
Rusty silty sand	B-horizon soils with rusty stains on quartz sand grains	Upland area (1-1.5')	47	2.8%
Tan silty sand (unsaturated)	C horizon soils, devoid of visible oxide staining	Upland area (3-3.5')	25	1.94%
Tan silty sand (saturated)	Silty sand, devoid of oxide stains, permanently water	Wetland area below peat (3-3.5')	21	6.0%
OM>50%	Black or dark brown peat cyclically or permanently water saturated	Wetland area	47	58.1%
Silty sand with abundant OM	Soil with significant OM that is cyclically or permanently water saturated	Wetland area	35	21.4%
Gravel/Debris (fill)	Tannery waste or construction scrap	Old tannery area	15	29.6%

4.2 - Metal Partitioning

Results of the sequential chemical extractions performed on the 240 soil samples collected for the initial site characterization are discussed in this section. Metal partitioning among target phases was evaluated for each metal after metal concentrations detected in the leachate fluids from each extraction were converted to solid phase concentrations. Solid phase concentrations are reported on a dry weight basis.

4.2.1 - General Metal Partitioning Results:

In general, the relative partitioning of Cu, Fe, and Zn among dominant sequestering phases (operationally defined) is similar between the oxic soils of the upland area and the anoxic, water saturated soils in the wetland area of the study site. However, variations in the relative importance of the dominant phases and the partitioning among less dominant phases were identified among the different soil textures, The three most dominant sequestering phases for Cu are the OX1, MR, and ER, as shown in the summary of metal partitioning in Table 3. The most dominant phases sequestering Fe and Zn also include the ER and MR phases, but the third most dominant phase varies between the WAS and OX1 among different soil types.

4.2.2 - Detailed Metal Partitioning Results:

Metal partitioning trends are presented using two types of graphical diagrams. Pie diagrams are used to show average partitioning results among all of the extraction phases. Ternary diagrams are used to show individual data points plotted in ternary space with the three most dominant sequestering phases at the vertices. One advantage of presenting partitioning data in ternary space is that it allowed clearer visualization and recognition of

Table 3. Summary of relative partitioning of Fe, Cu, and Zn, as determined by sequential chemical extractions among, target phases of the soil.

Soil Texture	Fe	Cu	Zn
Brown silty sand	MR>>ER>WAS> OX1, EX and OX2=0	OX1=ER>MR> OX2>WAS	MR>ER>EX> WAS>OX1>OX2
Rusty silty sand	MR>>ER>WAS EX, OX1, OX2 = 0	MR ≅ ER> OX1>OX2>WAS	MR>ER>WAS> OX1>EX>OX2
Tan silty sand (unsaturated)	MR>>ER>WAS, EX, OX1, and OX2 = 0	MR>ER>OX1> OX2>WAS	MR>WAS>ER> OX1>EX, and OX2=O
Gravel/Debris	MR>ER>OX2>WAS >OX1, EX=0	OX1>ER>MR =OX2>WAS	ER>MR>OX1> WAS>EX>OX2
Tan silty sand (saturated)	MR>>ER>WAS >EX, OX1 and OX2 = 0	OX1>ER>MR> OX2>WAS	MR>ER>WAS> OX1=EX>OX2
OM>50%	MR>ER>OX1>EX >WAS=OX2	OX1>>ER>MR> OX2>WAS	ER>MR>WAS> OX1>EX>OX2
Silty sand with abundant OM	MR>ER>WAS>OX1 >EX>OX2	OX1>ER>MR> OX2>WAS	ER>MR>OX1> WAS>EX>OX2

EX	Exchangeable	MR>ER	indicates one phase more dominant than another
WAS	Weakly Acid Soluble		
ER	Easily Reducible	OX2=0	indicates metal was not detected in leachate fluid for this phase
MR	Moderately Reducible		
OX1	Basic Oxidizable (OM)	OM	organic matter
OX2	Acid Oxidizable		

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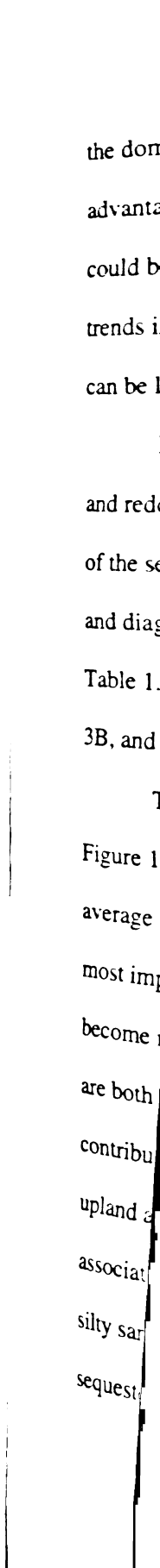

the dominance, or lack of dominance, of one sequestering phase over the others. Another advantage is that individual sample rather than average values for sample populations could be viewed graphically. A third advantage of using ternary plots is that spatial trends in partitioning could be discerned because individual samples or groups of samples can be labeled within the plots.

It was thought that trends in metal partitioning might be related to the soil texture and redox conditions. Consequently, metal partitioning is presented graphically in terms of the seven soil textures described in Table 2. The abbreviations (e.g. ER) in the tables and diagrams refer to the target phases of the sequential chemical extractions given in Table 1. Tables of partitioning results for Fe, Cu and Zn are given in Appendices 3A, 3B, and 3C, respectively.

The relative partitioning of Fe among all soil types is similar as can be seen in Figure 10a and 10b. The MR phase (Fe-oxides) dominates the sequestering, up to an average of 92 % for unsaturated tan silty sand. The ER phase is consistently the second most important sequestering phase for all soil types. Phases other than the ER and MR become more important in silty sand with abundant OM and soils with OM>50%, which are both generally anoxic, as well as gravel/debris soils. The EX and OX2 phases contribute to Fe partitioning only in the wetland area soils, but almost not at all in the upland area soils. The increased Fe in the EX may reflect Fe in pore water, as well as Fe associated with clays and exchange sites. The importance of the OX1 and OX2 for the silty sand with abundant OM and soils with OM>50% could indicate increased sequestering ability of OM at high soil OM concentrations and/or a difference in the

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form(s) that inorganically bound Fe exists in these anoxic soils vs. oxic soils. The latter will be discussed further in Sections 4.10 and 4.11.

Figure 11 is a trilinear diagram of Fe partitioning results plotted in ER-MR-OX1 space. Most of the data points fall on or along the ER-MR axis. The only soil types that show significant deviation from this pattern are the silty sand with abundant OM and soils with OM>50% in which some samples trend away from the center of the ER-MR axis toward the OX1 vertex.

The pattern of relative partitioning for Cu, presented in Figures 12a and 12b, shows more complex distributions than that of Fe. The OX1 and ER are the dominant sequestering phases of Cu in all soil types except for rusty silty sand and unsaturated tan silty sand. The MR is the dominant sequestering phase of Cu in these soil types. The importance of the OX1 phase in sequestering Cu increases as the OM content of the soil increases.

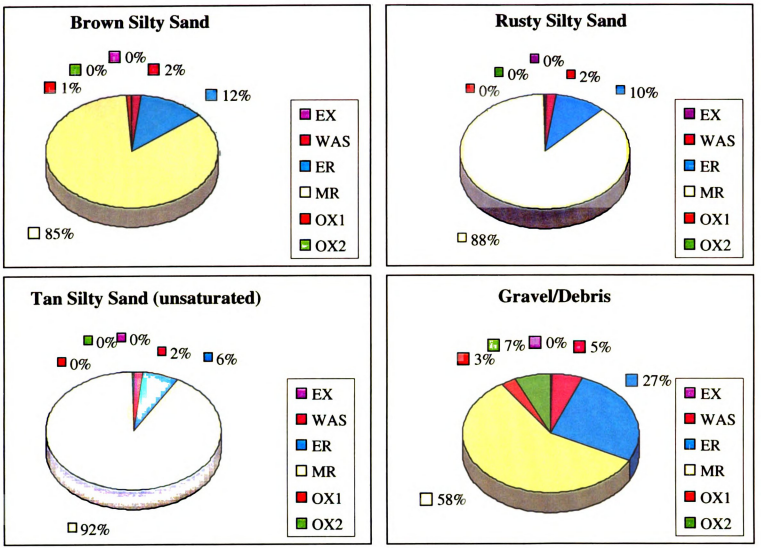
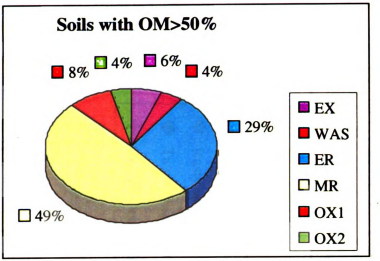
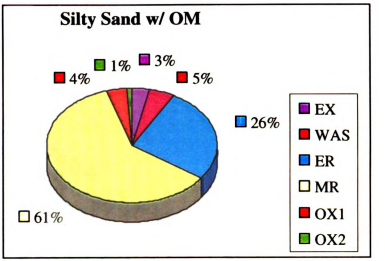


Figure 10a. Pie diagrams showing Fe partitioning in oxic soils.





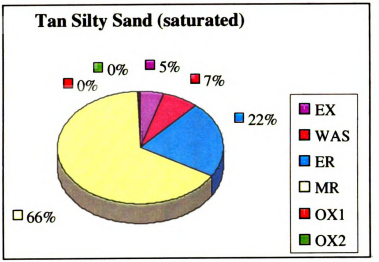


Figure 10b. Pie diagrams showing Fe partitioning in anoxic soils.

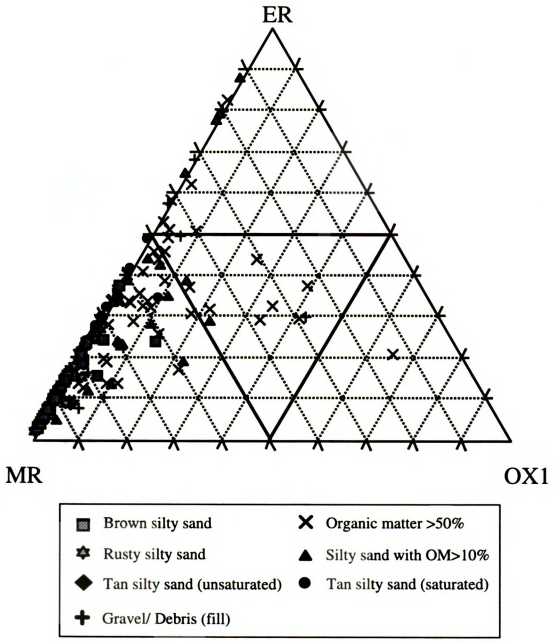
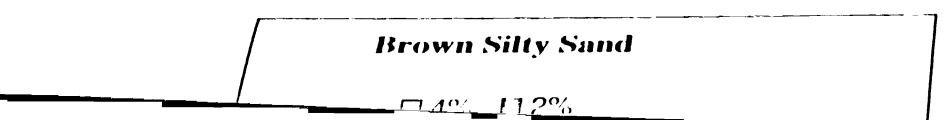
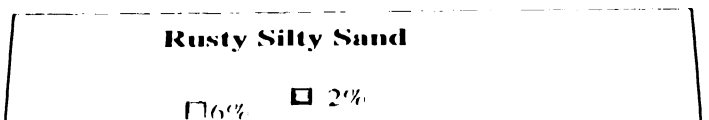


Figure 11. Trilinear plot of Fe partitioning data in ER-MR-OX1 space.


Brown Silty Sand


Rusty Silty Sand
6%
2%

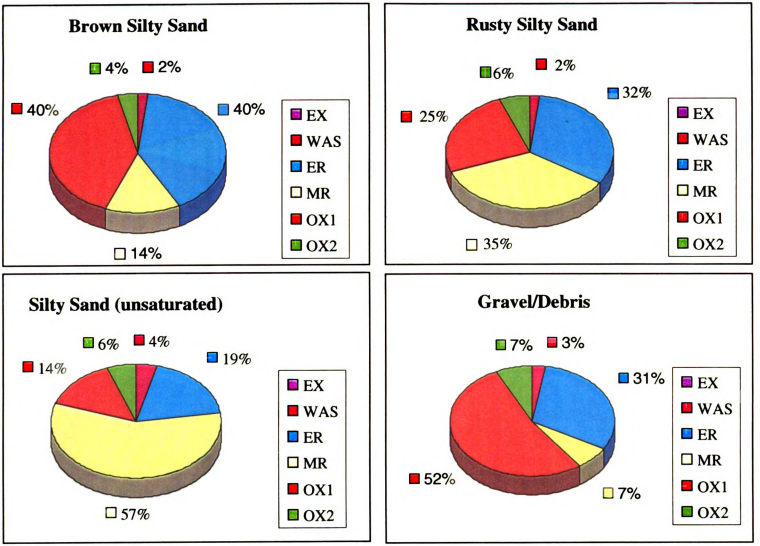
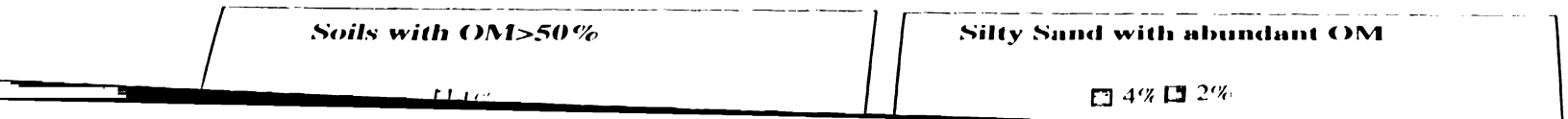
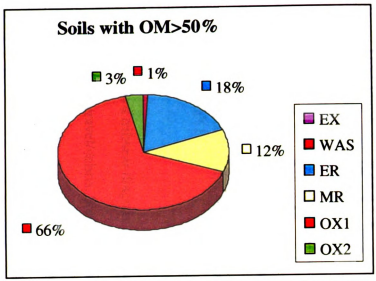
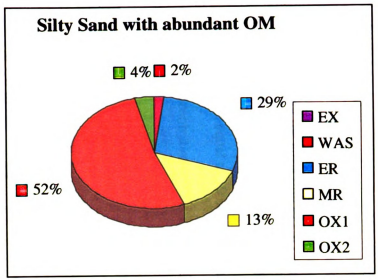


Figure 12a. Pie diagrams showing Cu partitioning in oxic soils.


Soils with OM>50%
Silty Sand with abundant OM
4%
2%





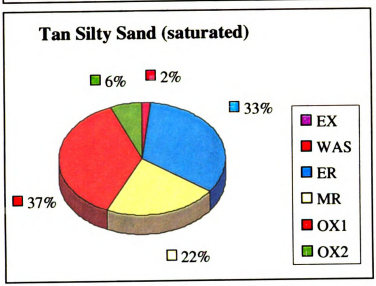


Figure 12b. Pie diagrams showing Cu partitioning in anoxic soils.

The OX1 accounts for up to 66 % of the Cu in soils with greater the 50 percent OM. Interestingly, even when the OM content is low (e.g. brown silty sand, rusty silty sand, and tan silty sand-unsaturated) the importance of the OX1 phase remains significant, demonstrating the attraction of Cu by organic matter. The relationship between organic matter and Cu in the OX1 is shown in Figure 13. The WAS and OX2 combined account for less than or equal to 10 % of the Cu partitioning in all soils, with no distinguishable trends. Concentrations of Cu in the EX fraction were below detection for all samples analyzed.

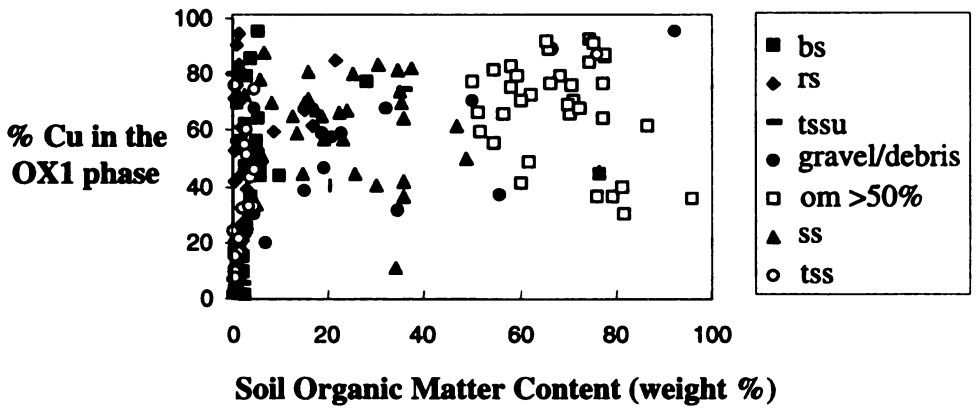


Figure 13. Relationships between soil organic matter content and percent of Cu in the OX1 Cu.

Figure 14 is a trilinear diagram of Cu partitioning results plotted in ER-MR-OX1 space. Most of the gravel/debris, brown silty sand, silty sand with OM and soil with OM >50% data points plot along the ER-OX1 axis. Rusty silty sand points plot along both the ER-OX1 and ER-MR axes, but not along the MR-OX1 axis. The association between Cu and the MR phase in rusty silty sand indicates the sequestering ability of crystalline Fe-oxides when organic matter content is low and oxide surface coatings are prevalent.

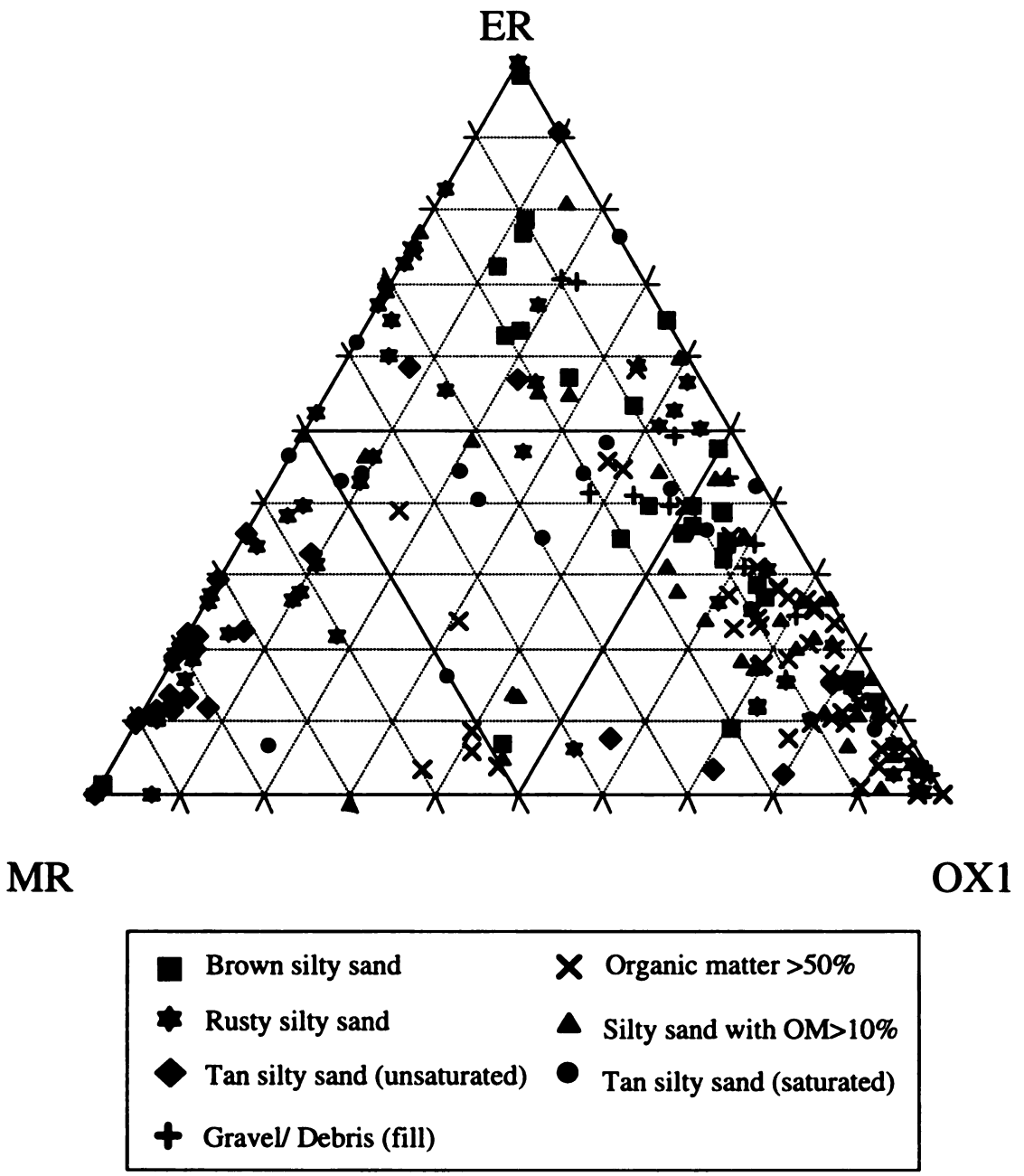


Figure 14. Trilinear plot of Cu partitioning data in ER-MR-OX1 space.

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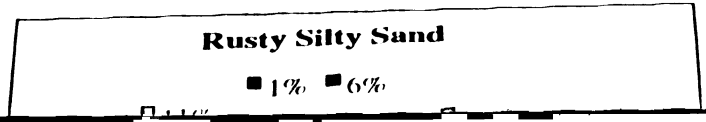
The relative partitioning of Zn among the six target phases is similar for all soil types in that the ER and MR phases are consistently the dominant sequestering phases (Figure15a and 15b). The MR phase is most important in sequestering Zn in brown silty sand, rusty silty sand, and tan silty sand (unsaturated) and tan silty sand (saturated). The ER is the most important phase in the gravel/debris, soils with OM>50% and silty sand with abundant organic matter. The EX and WAS phases are slightly more important in sequestering Zn in the unsaturated oxic soils than in the anoxic saturated soils indicating that Zn in the oxic soils may potentially be more reactive and mobile under unsaturated oxic conditions. The sequestering ability of the OX1 phase, which generally accounts for 10 to 15 % of the total Zn, is similar among the different soil types, with the exception of tan silty sand (saturated) in which the OX1 accounts for only three per cent of the total. The OX2 phase is relatively unimportant in the sequestering of Zn accounting for two per cent, or less, of the extractable Zn in all soil types.

Figure 16 shows a trilinear diagram of Zn partitioning in ER-MR-OX1 space. Most of the data points plot along or near the ER- MR axis. This diagram illustrates the importance of the ER and MR in sequestering Zn. Several silty sand with OM, OM>50% and brown silty sand points trend away from the ER-MR axis toward the OX1 vertex indicating a relationship between organic matter content and Zn associated with the OX1 for some samples.


Brown Silty Sand


Rusty Silty Sand
1%
6%

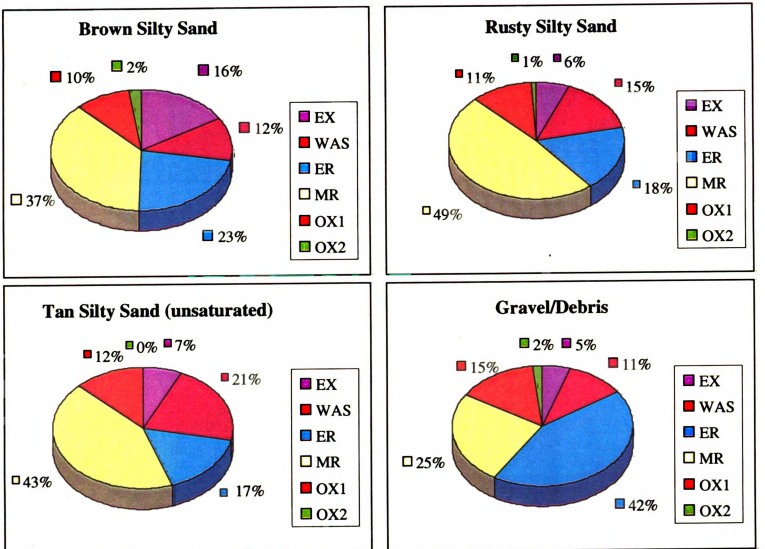
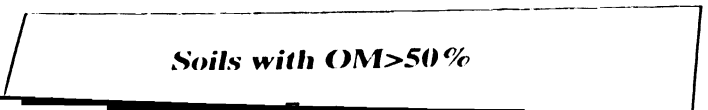
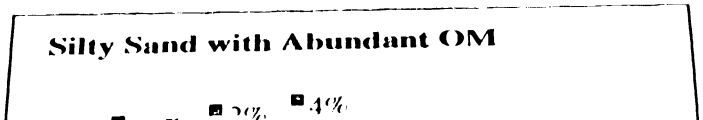
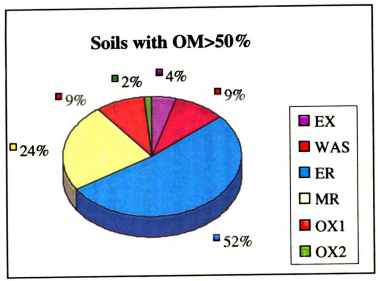
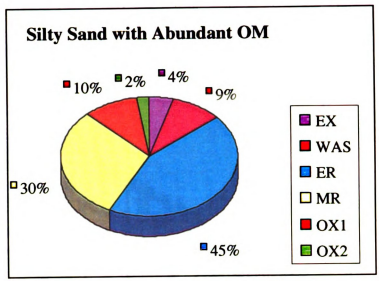


Figure 15a. Pie diagrams showing Zn partitioning in oxic soils.


Soils with OM>50%


Silty Sand with Abundant OM
2%
4%





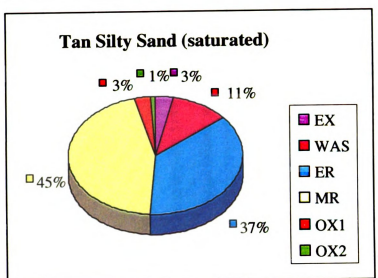


Figure 15b. Pie diagrams showing Zn partitioning in anoxic soils.

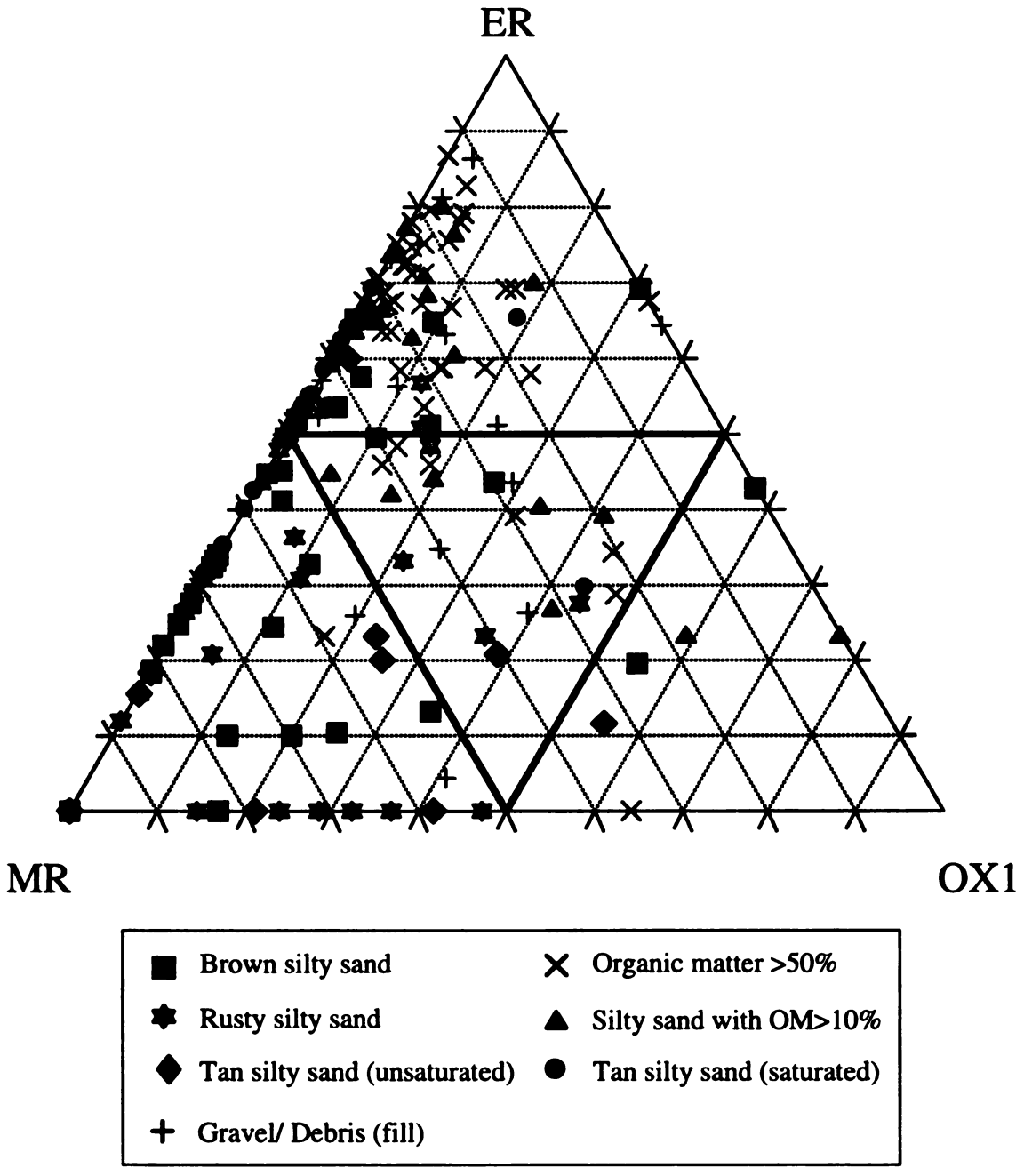


Figure 16. Trilinear plot of Zn partitioning data in ER-MR-OX1 space.

4.2.3 - Comparison of partitioning from this study to other studies:

The dominant sequestering phases for Cu, Fe, and Zn at this study site are similar to those found for soil and sediments from both oxic and anoxic environments at other sites. A summary of partitioning results from selected studies that used the sequential chemical extraction scheme modified after the Tessier et al. (1979) procedure is presented in Table 4. Although sample collection, pretreatment, and some extraction procedures varied slightly among each of these studies, general comparisons can be made. It is clear from this and other studies that the ER, MR and organic matter phases are generally the most dominant in sequestering metals in both oxic and anoxic environments. But because of differences between mineral phases stable in oxic and anoxic soil environments, it is not clear what these results mean. For example, in oxic environments, for which the extractions were designed, the ER and MR phases are generally considered to be comprised of poorly crystalline Fe-oxides (and Mn-oxides) and crystalline Fe-oxides, respectively. However, the lack of oxygen in anoxic pore waters and the capability of anaerobic microorganisms to directly, or indirectly, dissolve oxides would imply that Fe-oxides (especially reactive poorly crystalline forms) are not likely to form and/or persist for long periods. Furthermore, the production of reduced elemental species (e.g. S^{2-}) make alternative substrates energetically favorable and available to precipitate out of solution with dissolved metals in the pore water.

4.2.4 - Identifying Phases Not Targeted By Sequential Chemical Extractions:

The operational definitions for phases targeted in these extractions do not include reduced forms, other than pyrite. Other solids commonly found in anoxic environments

Table 4. Summary of partitioning results from selected studies that used similar selective chemical extraction schemes modified after Tessier et al., 1979.

Study	Environmental Setting	General Partitioning Results
Lion et al., 1982	Estuarine particulate matter	Fe - MR>OX>WAS>EX Cu - OX>WAS>MR>EX
Rapin et al., 1983	Oxic and anoxic Marine sediments	Fe- MR>OX>WAS>EX Zn - MR>WAS>OX>EX Cu - OX>WAS>MR>EX
Hickey and Kittrick, 1984	Contaminated soils	Cu - OX>MR>WAS>EX Zn - MR>WAS>EX>OX
Tessier et al., 1985	Oxic and anoxic sediments From three small lakes	Fe - MR>OX>ER>WAS>EX Cu - ER>OX>MR>WAS>EX Cu - OX>MR>ER>WAS>EX Cu - OX>MR>ER>WAS>EX Zn - OX>MR>EX>ER>WAS Zn - MR>WAS>OX>ER>EX Zn - MR>OX>ER>WAS>EX
Gibson and Farmer, 1986	Contaminated soils	Cu – OX>MR>WAS>EX>ER Zn - OX>MR>ER>WAS>EX
McKee, 1990	Oxic and anoxic sediments from Lake Superior	Fe – MR>>OX>>ER>EX>WAS Cu – OX>>MR>>WAS≈ER>EX Zn – MR>>WAS≈OX>ER>EX

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include minerals such as $FeCO_3$, magnetite (Fe_3O_4) marcasite (FeS), covellite (CuS), or sphalerite (ZnS).

At this point in the study two questions needed to be addressed. First, how does the presence of reduced solid phases influence the results of sequential chemical extractions, and second, how do these substrates that form under reducing conditions influence metal partitioning and metal cycling at the study site? In order to investigate these questions several methods of analyses were pursued during a second phase of field sampling events and laboratory analyses. The first was to subject pure minerals that form in reduced environments to the same sequential extraction procedure used for soil samples. The results of these extractions were used to determine the potential for the selected minerals to be dissolved by each chemical extractant within the procedure. The second step was to analyze the pore water geochemistry and identify terminal electron accepting processes (TEAPs) occurring in the wetland area of the site. This information was used to identify the presence of substrates that control metal cycling and characterize the thermodynamic equilibrium state with respect to reduced mineral phases.

4.3 - Pure Mineral Extractions

Knowledge of how individual mineral phases are effected by the chemical reactants that make up sequential chemical extraction procedures has traditionally been interpreted from a variety of studies that have looked at how a particular mineral or small set of minerals respond to treatment by a single extractant. The results of these studies have been interpreted and extrapolated to predict how minerals respond to a sequence of chemical additions. The type of extractant, reaction conditions (e.g., temperature,

duration, etc.) and sequence of the extractions has been designed in part by identifying which set of chemical conditions effect or do not effect a particular mineral phase. For example, early work by Arrhenius and Korkish (1959), Chester and Hughes (1967), Choa (1972), Choa and Theobald (1976), Chao and Zhou (1983), and Gruebel et al. (1988), demonstrated that hydroxylamine hydrochloride mixed with dilute HNO_3 and hydroxylamine hydrochloride mixed acetic acid can be used to dissolve amorphous and crystalline Fe oxides (ER and MR extractions, respectively) with relatively good effectiveness and selectivity. Nirel et al. (1986) applied the sequential extraction method designed by Tessier et al. (1979) to individual substrates including montmorillonite, $CaCO_3$, Fe oxides, Mn oxides, humic acids and quartz that had been spiked with various trace metals. Their work showed that, $CaCO_3$ was completely dissolved after the sodium hydroxide NaOAc extraction (pH=5). Heron et al. (1994) used several reagents to determine the most effective and selective extractant for various Fe-bearing minerals and found that $FeCO_3$ was not significantly effected by the NaOAc (pH=5) extraction, but could be dissolved with more acidic and higher temperature extractions. More recently, Papp et el. (1991) showed that both NaOCl (pH=9) and H_2O_2 (pH=2) do not significantly effect goethite (FeOOH). The effect of the extractions on selected carbonate and silicate minerals (quartz, calcite, feldspar amphibole, mica, and chlorite; kaolinite, vermiculite and hydroxy interlayer vermiculite) identified in a soil sample was also addressed in this study and the results are discussed in Section 4.9.2.

Prior to this study, pure forms of metal monosulfides, other than FeS, had not been subjected to sequential chemical extractions. While FeS has been found to be dissolved during the MR extraction (Tessier et al., 1979), other metal monosulfides have apparently been thought to be oxidized during a peroxide (H_2O_2) (pH=2) extraction (the

OX2 extraction designed to dissolve Fe_2S). Other minerals that have not been well characterized in terms of their response to sequential chemical extractions include $FeCO_3$ and magnetic minerals such as magnetite.

In an effort to characterize how these minerals may affect the results of sequential chemical extractions on soil samples collected from reduced environments, extractions were performed on pure forms of selected minerals. The sequential extraction of pure minerals may or may not reflect what occurs during the sequential extraction of an actual soil sample containing mixtures of these minerals. The presence of multiple mineral phases and organic matter in a soil sample probably has some affects on the capacity of the chemical extractants to dissolve individual minerals. However, this approach has been used to give indication of the effectiveness and selectivity of an extraction for minerals that form in oxic environments (e.g., Fe-oxides).

Results of pure mineral extractions from this study, summarized in Table 5 and presented in full in Appendix 3F-1, indicate that sequential extractions exhibit varying degrees of selectivity for dissolution of these pure minerals. This means that some minerals were dissolved almost exclusively during one extraction while others were partially dissolved during two or more extractions in the procedure. Extractions were performed on sub-splits of varying masses of powdered or granulated minerals with little effect on the results, even though the largest sub-splits were not completely dissolved during the extractions. Relatively large masses of mineral samples were used to assure that mineral grains were still present during the extractions at the end of the sequential chemical extraction procedure so that the partitioning trends were not biased by complete dissolution of the minerals during extractions early in the procedure.

Table 5: Summary of results from sequential chemical extractions of pure minerals. Results are given as average per cent of metal recovered from each extraction with respect to the sum total metal recovered. Values in bold indicate the extraction that yielded the highest percentage of metal from that particular mineral.

Mineral	EX %	WAS %	ER %	MR %	OX1 %	OX2 %
Siderite	n.d.	0.4	7.8	**83.8**	2.0	6.0
Magnetite	n.d.	0.5	2.3	**91.0**	4.1	2.1
Pyrite	0.1	0.2	0.7	2.7	11.9	**83.3**
FeS	1.1	5.6	11.3	**62.9**	16.4	2.8
CuS	n.d.	n.d.	0.1	0.1	**87.9**	12.0
ZnS	n.d.	n.d.	21.6	5.7	**72.5**	n.d.

Extraction results indicate a slightly progressive attack of FeS with 70.9% of the total Fe recovered in the first four steps of the extraction from FeS. The MR extraction released the highest percentage of Fe (62.9%) from FeS. The progressive release of Fe from FeS prior to the MR extraction could be an artifact of impurities in the FeS or sample handling not necessarily a lack of selectivity of the method. The partitioning pattern (or selectivity) was independent of the amount used in the extractions over the range of 79 μmol to 238 μmol FeS.

The MR extraction, which was designed to dissolve Fe oxides, exhibited fairly selective dissolution of $FeCO_3$ and magnetite, yielding 83.8 % and 91.0 % of the total extracted Fe, respectively. This finding suggests that soil samples containing trace metals adsorbed to the surface $FeCO_3$ and/or magnetite could yield similar partitioning results to soil samples containing trace metals adsorbed to Fe(III)-oxides and/or Fe(III)-oxyhydroxides. Therefore, misinterpretations of trace metal partitioning results could

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occur if Fe(III)-oxides are not present in soil sample, yet trace metals are found to be associated with the MR phase.

Sequential chemical extraction of Fe_2S also resulted in selective dissolution with 83.3% of the total Fe recovered being released during the OX2 extraction. The partial dissolution from Fe_2S during the OX1 extraction was not expected based on work of Papp et al. (1991), who found NaOCl (extraction chemical in OX1, this study) not to significantly dissolve Fe_2S. Differences in the Fe_2S used in the two studies may explain these data. An alternative explanation for the difference may be related to the choice of chemicals used to dissolve any recently precipitated Fe-oxides. Papp et al. (1991) used an HCl (pH 2) acid wash after NaOCl treatments, while NH_4OAc (pH 2 with HNO_3) was used in this study. The choice of NH_4OAc over HCl was based on knowledge of the conditions under which Fe_2S dissolves (e.g. oxidizing, low pH). To avoid these conditions and specifically target the recently precipitated Fe-oxides the addition of NH_4OAc (pH=2), after organic matter extraction with NaOCl, was used to create a low pH reducing wash solution. Another alternative is that the four extractions prior to the OX1 (e.g. EX, WAS, ER, and MR) changed the surface properties of the Fe_2S which resulted in release of Fe from surface coatings that may not have the mineral structure of Fe_2S. This would not have been observed by Papp et al. (1991) because their work did not include any extractions prior to their NaOCl treatment. Whatever the case, Fe released from Fe_2S during an OX1 extraction of a real soil sample will be relatively minor and dependent on the amount of Fe_2S and organic matter in the sample. Presence of fresh organic matter would likely reduce the capacity of the NaOCl to affect any Fe_2S because the organic matter would be preferentially oxidized. For samples with little or no Fe_2S, this would not be an issue.

Extraction results show selective dissolution of CuS with 87.9% of the total Cu recovered being associated with the OX1 extraction. The release of 12 % of the Cu during the OX2 could be due to saturation of the OX1 fluids with respect to CuS or conversion of the CuS to other forms during the first couple of extractions in the procedure. The OX1 extraction also yielded the most Zn (72.5%) from ZnS. However, the selectivity of the OX1 for Zn was lower due to significant release of Zn (21.6%) during the ER extraction. This could be due to impure or mixed forms of ZnS in the purchased stock powder or due to partial oxidation of the ZnS to another more reactive form during the EX and WAS extractions.

4.4 - Porewater Chemistry

4.4.1 - Porewater Results:

Geochemical parameters measured during porewater sampling events include temperature, pH, redox potential (Eh), alkalinity, NH_3, NO_3^-, S^{2-}, SO_4^{2-}, CH_4, Fe^{2+}, Cr^{+6}, Br^-, Cl^-, and total cations (Ca, K, Na, Mg, Fe, Cd, Co, Cr, Mn, Pb, and Zn). Data from four different pore water sampling events are presented in Appendix 3E and locations for pore water sampling are shown in Figure 17. Many locations (I22, K28, L27, M22, M24, M28, P23, Q26, S26 and U26) were sampled only once to get a snap shot of the pore water geochemistry of the wetland soils (Ellis et al., 1997 and Icopini et al., 1997). Other locations were sampled once in support of this initial characterization and later resampled.

The final pore water sampling event occurred in November 1997. During this sampling event porewater field measurements and pore water samples were collected from peepers within approximately 20 minutes of collecting soil samples for solid phase

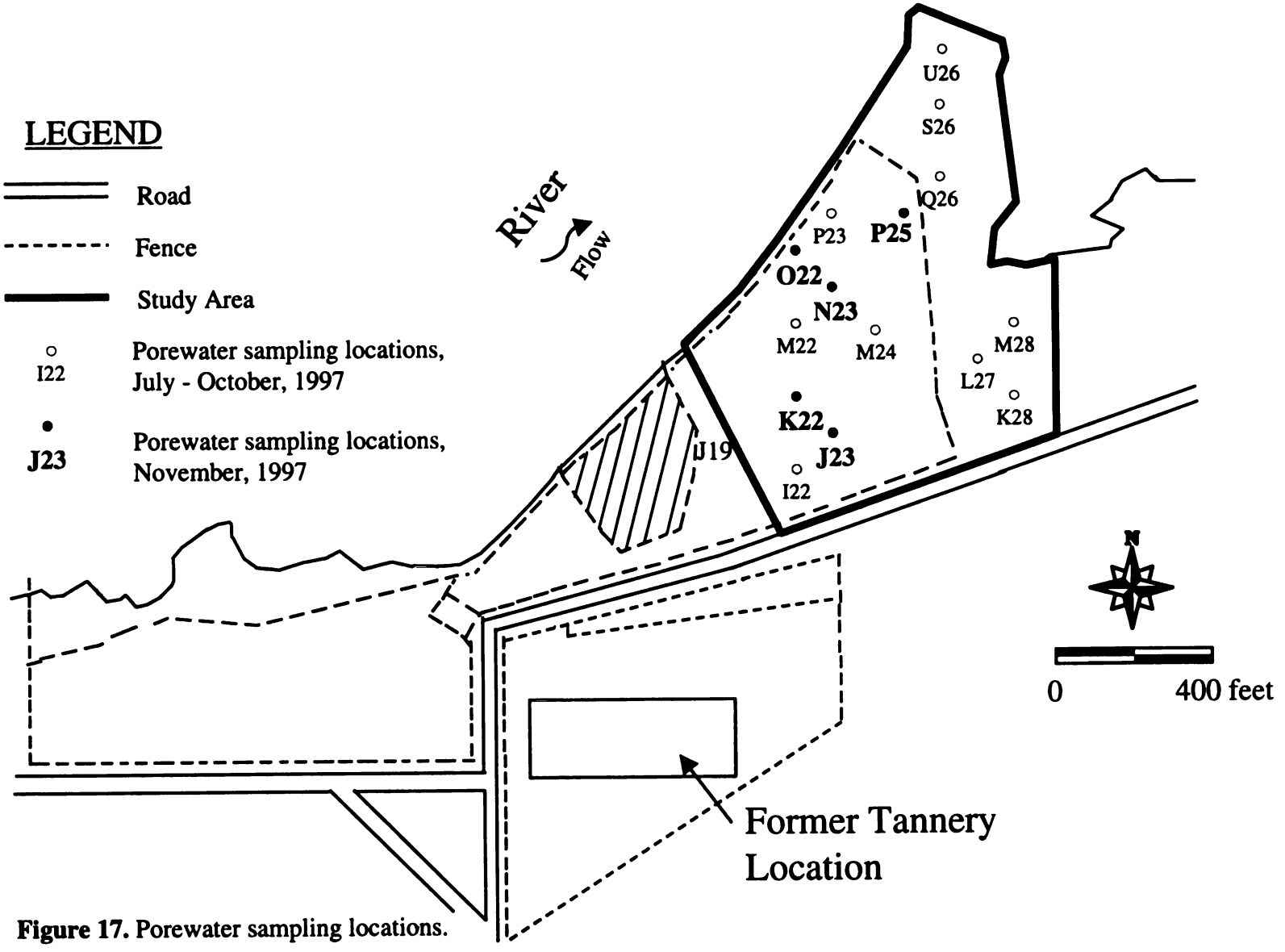

Figure 17. Porewater sampling locations.

analyses. The peeper interval sampled for pore water corresponded to the depth interval from which the soil samples were taken. The objective was to obtain geochemical data for porewaters in direct contact with solid phase samples collected at locations selected for another round of sequential extractions as well as more detailed analyses (J19, J23, K22, N23, O22 and P25). These detailed analyses, discussed in the following sections, were designed to further investigate how substrates that form in reducing environments influence the results of sequential chemical extractions and metal cycling at the site. Consequently, emphasis is placed on interpreting data from that porewater sampling event. A summary of pore water data from the November 1997 sampling is shown in Table 6.

The soil textures at sites chosen for this detailed work range in physical character from an organic rich A horizon soil containing tannery waste (J19) to peat comprised of decaying organic matter with varying amounts of silt and clay (J23, K22, N23 and P25) to gray silty sand (O22). All of these sites were sampled for both porewater and solid material from two inches to eight inches bls except for O22 at which the sampling interval was three to three and a half feet bls. The two to eight inch interval was selected to avoid oxidized soil and porewater existing in the top two inches of the wetland sediments, as indicated in previous porewater sampling events. The land surface at J19 was a bit higher in elevation than the other sites and unsaturated so porewater sampling was not conducted.

Measurement and analysis of porewater chemistry was used to gain insight into the conditions under which minerals were precipitating or dissolving, as well as, microbial processes that may be influencing the local environment. However, due to the

Table 6. Summary of selected pore water chemistry data for sites selected for detailed solid phase analysis (November 1997).

Parameter	J19	J23	K22	N23	O22	P25
pH	--	6.80	6.75	6.43	7.19	6.57
Eh (mV)	--	-82	58	-17	47	-42
Alk. (mg/L)	--	156.7	141.4	141.4	428.1	122.3
CH_4(mg/L)	--	0.07	1.98	1.75	8.48	1.17
S^{2-} (mg/L)	--	0.66	n.d.	n.d.	0.17	n.d.
SO_4^{2-}(mg/L)	--	12.94	5.23	0.66	5.72	n.d.
NH_3 (mg/L)	--	0.61	0.61	0.22	12.99	1.09
Fe_{total} (mg/L)	--	0.32	1.98	13.66	1.56	7.44
Fe^{2+} (mg/L)	--	0.21	1.59	12.43	1.49	7.09
Fe^{3+} (mg/L)	--	n.d.	0.39	1.23	n.d.	0.35
Fe^{3+}/Fe^{2+}	--	0	0.24	0.1	0	0.05
Mn (µg/L)	--	73.48	392.61	517.20	404.66	350.16
Ni (µg/L)	--	2.11	1.60	1.88	1.72	2.27
Zn (µg/L)	--	10.82	14.05	83.51	2.34	17.87
Cu (µg/L)	--	5.35	3.44	4.44	9.16	1.99
Cd (µg/L)	--	3.91	1.26	1.19	1.10	1.17
Pb (µg/L)	--	0.64	n.d.	0.32	0.73	1.46
Inferred TEAP	O_2 Respiration	SO_4^{2-} Reduction	Fe(III) Reduction	Fe(III) Reduction	SO_4^{2-} Reduction/ Methanogenesis	Fe(III) Reduction

design of the peeper samplers and volume of fluid required to conduct field measurements and pore water sampling, three pairs of ports were sampled for different geochemical parameters over a six inch interval. It is possible that this approach may have resulted in sampling different redox zones if the zones changed rapidly with depth.

Pore water pH values were generally very slightly acidic with values for J23, K22, N23 and P25 ranging from 6.43 to 6.80. Only one site (O22) had a slightly basic pH of 7.19. This range of values is similar to those measured previously for these sites (Icopini et al., 1997, and Ellis et al., 1997). Alkalinity, as bicarbonate (HCO_3^-), values were similar among all sites, ranging from 122.3 - 156.7 mg/L, except O22, which had a

concentration of 428.1 mg/L, more than three times that of the other sites. The solid phase material in contact with porewater at each of the sites may contribute to the differences observed in the pH and alkalinity. The solid phase material at O22 had by far the lowest organic matter content of all the sites and this site has the highest pH and alkalinity. The significantly alkalinity in the porewater sample from O22 is unique among the sites investigated and may reflect a different solid phase geochemistry and/or different microbial community. The greater amount of decaying organic matter present at the other sites likely results in lower pH values because greater amounts of organic acids were being released to the surrounding porewater.

4.4.2 - Porewater Redox Conditions and Terminal Electron Accepting Processes

Pore water redox conditions and concentrations of microbial metabolic end products were used to infer the dominant terminal electron accepting processes occurring in the saturated soil environment. However, it was recognized that the presence of a particular TEAP end product might not necessarily indicate that a TEAP was occurring at the time of sampling, rather that it had occurred and the end products had not been consumed, precipitated, or transported away. Electrode measurements of the soil pore fluid redox potential were used only as a general indication of redox conditions, because electrode measurements have been found to not accurately predict predominant TEAPs (Lindberg and Runnels, 1984 and Lovley and Goodwin, 1988).

Electrode-measurements of redox potential (Eh) were slightly higher during the November, 1997 sampling than they had been for previous sampling events, but still generally indicate anoxic conditions. Electrode-measured redox potential values in pore waters of saturated soils for all sampling events ranged from +50 to –188 mV. These

values generally fall in the range that has been reported for Fe- reduction and sulfate reduction in flooded soils (Yoshida, 1975; Watanabe and Furusaka, 1980; Lovley and Goodwin, 1988). The ambient air and pore water temperatures during the November, 1997 sampling (2-5°C) may have affected the performance of the electrode. These near freezing conditions probably also affected the microbial activity and rates of TEAPs, thus resulting in lowered production of metabolites. This was reflected in the concentrations of CH_4 and S^{2-}, which were lower for this sampling than previously measured for most locations. Minor amounts of S^{2-} were detected in pore waters at K22, N23 and P25 during previous events but not this sampling event.

Concentrations of Fe^{3+} in pore water at K22, N23, and P25 were relatively minor compared to the concentration of Fe^{2+}. Fe^{3+} was not directly measured, but rather calculated by the difference between Fe_{total} and Fe^{2+}. The detection limit of both the Fe^{2+} and the Fe_{total} methods was about 0.1 mg/L so calculated Fe^{3+} concentrations below this value were considered non-detect. The Fe^{3+}/Fe^{2+} ratios indicate that Fe^{2+} was the dominant aqueous species of Fe in pore water at all of the locations. The presence of Fe^{3+} in otherwise anoxic pore waters may reflect active dissolution of Fe(III) oxides or mixed valence minerals such as magnetite $Fe(III)[Fe(II)Fe(III)]O_4$. Dissolved Fe^{2+} concentrations were elevated at K22, N23, and P25 and Eh values in were the range reported for Fe reduction.

The location with the highest measured redox potential during the November 1997 sampling event was K22 (Eh = +58). This site did not have any detectable S^{2-}, but did have a fair amount dissolved SO_4^{2-} (5.23 mg/L). Concentrations of CH_4, NH_3, Fe_{total}, and Fe^{2+} were low (1.98, 0.61, 1.98, 1.59 mg/L, respectively) as were concentrations of

most trace metals. This pore water chemistry suggests that the dominant TEAP process occurring at the time of sampling was likely Fe reduction.

The Eh value measured in porewater from N23 was –17. Pore water concentrations of CH_4, SO_4^{2-}, NH_3, were all relatively low (1.75, 0.66, and 0.22, respectively), and S^{2-} was not detected. Concentrations of Fe_{Total}, Fe^{2+}, Fe^{3+}, Mn and Zn were the highest of all the sites during the last sampling (13.66, 12.43, 1.23, 0.517 and 0.083 mg/L respectively). However, concentrations of the other trace metals were relatively low. This pore water chemistry suggests that the dominant TEAP process occurring at the time of sampling was likely iron reduction.

Pore water at P25 had a measured Eh value of –42. Low concentrations of CH_4, and NH_3 (1.17 and 1.09 mg/L) were detected in this sample. Neither S^{2-},nor SO_4^{2-}, were detected in pore water in this sample. Relatively high concentrations of Fe_{Total} and Fe^{2+} (7.44 and 7.09mg/L) were detected, but trace metal concentrations were low. This pore water chemistry suggests that the dominant TEAP process occurring at the time of sampling was likely iron reduction.

The lowest dissolved Fe_{total} concentrations occur in samples with the lowest Eh values and the highest measured S^{2-} concentrations (J23 and O22), possibly indicating that sulfate reduction was the dominant TEAP occurring at the time of sampling.

During the November 1997 sampling of pore water, J23 had the lowest Eh (-82) of all the locations sampled. This location also had the highest dissolved S^{2-} (0.66 mg/L) and SO_4^{2-} (12.94 mg/L) concentrations. Pore water concentrations of CH_4, NH_3, Fe_{total}, and Fe^{2+} at J23 were the lowest of all the sites (0.07, 0.61, 0.32 and 0.21 mg/L, respectively) and Fe^{3+} was not detected. Trace metal concentrations were also low. The presence of S^{2-} and the relatively low concentrations of Fe and trace metals suggests that

sulfate reduction was the dominant TEAP occurring at the time of sampling. This porewater chemistry also suggests that the precipitation of metal monosulfides may have occurred.

The apparent Fe-reducing conditions may have caused reduced Fe bearing minerals, including FeS, Fe_3O_4, or $FeCO_3$, to become supersaturated with respect to pore water chemistry, resulting in precipitation of one or more of these minerals. Precipitation of the $FeCO_3$ may be most likely at O22, which has the highest alkalinity and pH measured at the site, 428.1 mg/L (as HCO_3^-) and 7.19, respectively. $FeCO_3$ can compete with magnetite formation for Fe(II) in environments with high bicarbonate concentrations and elevated pH by the following reaction:

$$Fe^{2+} + HCO_3^- \leftrightarrow FeCO_3 + H^+$$

Since Fe(III) reduction occurs in anoxic environments prior to SO_4^{2-} reduction the formation of Fe_3O_4 and $FeCO_3$ could occur prior to S^{2-} accumulation and subsequent precipitation of Fe^{2+} as FeS, thus explaining the presence of three different reduced Fe-bearing minerals (Lovley, 1991).

The interpretation of the dominant TEAP at O22 is complicated by presence of a significant amounts of S^{2-}, CH_4, and NH_3^+ in pore water (0.17mg/L, 8.48 mg/L and 12.99 mg/L, respectively). Several scenarios could explain the simultaneous presence of three TEAP end products in porewater. The presence of significant concentrations of CH_4, S^{2-}, and NH_3 at site O22 may indicate that three different TEAPs had occurred, or that more than one was occurring concurrently. Ammonia may have been produced via dissimilatory nitrate reduction concurrent with the other TEAPs or may have occurred

prior to sampling and the accumulated end-product had not been utilized or transported away. The S^{2-} in the pore water could result from previous and, or concurrent sulfate reduction or from the oxidation of S^0 to SO_4^{2-} and subsequent reduction to S^{2-}. The presence of CH_4 may indicate concurrent methanogenesis, or diffusion of CH_4 from deeper layers of the water-saturated soil. Interestingly, this location had an electrode measured Eh value of +47, which was higher than expected given its pore water chemistry and may have been the result of electrode malfunction at low temperatures.

In summary, analyses of pore water from the sites sampled in November 1997 are similar to those of previous sampling events and indicate that iron and sulfate reduction are the dominant TEAPs occurring in the wetland area of the site. These microbial processes influence the cycling of metals at the site by changing the redox potential and the substrates available for precipitation and/or adsorption.

4.5 - Selected Site Sequential Chemical Extraction Results

With the redox conditions of the porewater sampling locations characterized, sequential extractions were performed on soil samples collected from these locations selected for detailed analysis (J19, J23, K22, N23, O22, and P25). The objective for collecting more soil samples from the wetland area further investigation was to identify differences in partitioning among sites from differing environments and correlate, if possible, these findings to measured physical, chemical and microbiological parameters (e.g. soil type, porewater chemistry, TEAP). Most of the sites selected for this detailed work were from the wetland area because metal partitioning in soils from the oxic upland area is thought to be relatively straightforward in comparison to the water saturated anoxic soils area. Again, the ER and MR phases are known to comprise Fe-oxides and

the OX1 is likely comprised of organic matter in oxic soils, but these phases are still in question for anoxic soils.

Partitioning results for the six sites selected for detailed analysis are shown in Tables 7-9. As discussed in the previous section, pore water in direct contact with the solid phase indicates that anoxic (reducing) conditions exist at each of the sites except J19, which is unsaturated. The dominant sequestering phases for Fe, Cu, and Zn in these individual samples are similar to those identified in the initial partitioning investigation. The ER and MR are the dominant sequestering phases for Fe and Zn and the OX1 is the dominant sequestering phase of Cu followed by the ER and MR.

There is a distinct difference in the partitioning of Fe, Cu, and Zn among the six samples analyzed in this portion of the study. The most striking difference in partitioning is between the unsaturated sample (J19) and the water-saturated anoxic samples. Fe is predominantly associated with the MR and ER fractions for all six samples, but samples from K22, N23 and P25 had significant Fe associated with the EX phase, 23.8, 27.8, and 28.3%, respectively. O22 had a significant proportion of its total Fe associated with the WAS and OX2 phases, 17.0 and 16.5%, respectively. In contrast, the unsaturated oxic location, J19, did not exhibit much variation in Fe partitioning with the EX, WAS, OX1and OX2 combined accounting for only seven per cent of the total Fe. Cu was predominantly associated with the OX1 phase for all samples, except J19 in which the ER and MR were most important. J23, K22, N23, O22, and P25 all had greater than 86% of the Cu associated with the OX1 phase, while at J19 the ER, MR, and OX1 accounted for 47.8%, 25.7 and 24.9% of the total Cu, respectively. Zn is primarily associated with the MR, and OX1 phases for J19, the ER and MR for J23 and K22, the ER, MR, and

Table 7. Organic matter content (%), total Fe micromoles per gram (μmol/g) and partitioning for selected sites.

SampleID	OM %	ΣFe (μmol/g)	EX %	WAS %	ER %	MR %	OX1 %	OX2 %
J19	31.4	96.3	0.2	2.7	**15.0**	**78.7**	2.3	1.2
J23	35.9	68.4	1.8	3.4	**36.5**	**41.4**	3.6	**13.3**
K22	36.8	115.0	**23.8**	3.4	**31.6**	**30.9**	5.3	5.0
N23	10.3	118.3	**27.8**	8.8	**25.0**	**28.0**	2.7	7.7
O22avg	5.5	77.8	0.2	**17.0**	**21.3**	**34.3**	9.7	**16.5**
P25	36.3	113.2	**28.3**	7.0	**24.5**	**34.3**	2.0	3.8

Table 8. Organic matter content (%), total Cu (μmol/g) and partitioning for selected sites.

Sample ID	OM %	ΣCu (umol/g)	EX %	WAS %	ER %	MR %	OX1 %	OX2 %
J19	31.4	3.25	n.d.	1.0	**47.8**	**25.7**	**24.9**	0.6
J23	35.9	2.25	n.d.	n.d.	6.1	1.9	**90.0**	2.0
K22	36.8	1.25	n.d.	n.d.	10.2	2.8	**86.5**	0.4
N23	10.3	1.03	n.d.	n.d.	3.1	4.5	**91.5**	0.9
O22avg	5.5	0.39	n.d.	n.d.	n.d.	2.8	**94.1**	3.1
P25	36.3	1.13	n.d.	n.d.	10.5	2.7	**86.6**	0.2

Table 9. Organic matter content (%), total Zn (μmol/g) and partitioning for selected sites.

Sample ID	OM %	ΣZn (μmol/g)	EX %	WAS %	ER %	MR %	OX1 %	OX2 %
J19	31.4	1.09	3.0	9.2	9.2	**42.1**	**25.5**	11.1
J23	35.9	3.40	0.7	10.1	**36.9**	**38.3**	11.6	2.5
K22	36.8	8.12	3.0	13.1	**57.7**	**19.5**	5.7	0.9
N23	10.3	4.82	1.2	6.7	**52.1**	**21.6**	**17.2**	1.1
O22avg	5.5	5.41	0.1	4.1	12.9	12.9	**69.2**	0.8
P25	36.3	1.93	n.d.	**17.2**	**35.8**	**30.5**	**16.5**	n.d.

OX1for N23 and P25. The sample from O22 is the only one of this group to have only the OX1 dominate the partitioning of Zn.

The pattern of Cu partitioning among this group of samples was consistent with what would be expected based on the traditional interpretations of sequential extraction results. Cu was strongly associated with OX1 phase of the soil for those samples with high organic matter content and little apparent probability of Fe oxides present (J23, K22, N23, and P25). The one sample that was unsaturated and likely contained some Fe-oxides (J19) showed a much different pattern of partitioning in that the ER and MR phases became relatively more important in sequestering Cu.

The pattern of Zn partitioning in this group of samples was a little less consistent with what was expected given the soil type and conditions. There was more variability in the pattern among the water saturated wetland samples suggesting that partitioning may be controlled by factors that were more sample specific than for the partitioning of Cu. Before more detailed interpretations concerning Zn partitioning can be made some discussion about the form(s) of Fe that make up the ER and MR phases would be necessary. The concentration of Fe found in the ER and MR fractions was somewhat surprising considering that no Fe-oxides were thought to be present in the wetland soils. To investigate this further and also explain the differences in partitioning found among these wetland area samples, the pore water chemistry associated with the solid phase samples was considered a first.

Solid phase Fe partitioning appears to be related to the degree of water saturation, $Fe^{3+}$and S^{2-} porewater concentrations and Fe^{3+}/Fe^{2+} porewater ratio. The ER and MR accounted for greater than 90% of the total Fe for the sample from J19, which was unsaturated. This pattern is similar to that expected for soil having Fe-oxides as the

dominant form of solid phase Fe. In contrast, the water saturated samples exhibit a pattern of Fe partitioning in which other phases were relatively important in sequestering Fe.

The two samples with detectable dissolved S^{2-} concentrations and non detectable Fe^{3+}, J23 and O22, exhibit similar partitioning in that the OX2 fraction accounts for a relatively significant portion of the solid phase Fe. In contrast, sequential extraction results for the other samples (K22, N23, and P25) indicate that the EX, ER, and MR phases were about equally important in Fe partitioning, each accounting for 25-30% of the total extracted Fe. This difference in the Fe partitioning among samples from the six sites seemed curious and deserving of further investigation.

4.6 - Geochemical Modeling Results

To continue to investigate the partitioning patterns observed for the water saturated samples geochemical modeling was performed to identify or predict the presence of solid phases that may affect the results of the sequential chemical extractions. Perhaps a phase or phases other than Fe-oxides were present in the samples that could yield a sequential extraction partitioning pattern similar to that of Fe-oxides (eg. ER and MR most important phases), resulting in a misinterpretation of the phases which make up the ER and MR phases.

4.6.1 - Mineral Saturation Indices

Pore water analytical data for samples collected during the November 1997 porewater sampling event were used for geochemical modeling. All geochemical

parameters shown in Appendix 3E (Table 3E-4) were used to create input files for geochemical modeling with PHREEQC (Parkhurst, 1995), with the exception of CH_4.

Selected mineral saturation indices determined by PHREEQC modeling of the pore water data are shown in Table 10. Saturation indices (SI) were determined during the modeling by dividing the log of the calculated ion activity product (IAP) of aqueous species needed to form a mineral by the log of the calculated solubility product (K_{sp}) for that mineral. Mineral saturation indices indicated whether a mineral phase was thermodynamically under-saturated (SI<0), saturated (SI=0), or supersaturated (SI>0) with respect to the fluid chemistry at the time of sampling. From this information, interpretations were made concerning what minerals were likely to precipitate or dissolve in this system.

In the manner that PHREEQC was used in this study, it did not account for the microbially mediated process that drive many of the precipitation/dissolution reactions involving redox sensitive elements. Also, the MINTEQ database, in the form used for this modeling, did not accept input for CH_4. Consequently, the Eh value calculated by the model and used to determine aqueous speciation and mineral saturation indices does not reflect the HCO_3^-/ CH_4(aq) redox couple. Therefore, the results of the modeling may not be accurate for those locations where methanogenesis controlled or contributes to the redox conditions. Also, calculation of mineral disequilibrium was not possible in cases where a parameter necessary for the formation of that mineral had an aqueous concentration of zero. For instance, FeS disequilibrium could not be calculated when the porewater concentration of S^{2-} was zero.

Table 10. Saturation indices (SI = log IAP/K_{sp}) of selected minerals calculated by PHREEQC with the Minteq database for pore waters at sites J23, K22, N23, P25, and O22.

		Saturation Indices				
Mineral Phase	**Formula**	**J23**	**K22**	**N23**	**P25**	**O22**
Aragonite	$CaCO_3$	-1.29	-1.37	-1.8	-1.83	0.02
Calcite	$CaCO_3$	-1.13	-1.2	-1.63	-1.66	0.18
Chalocite	Cu_2S	11.52	--	--	--	11.57
Chalcopyrite	$CuFeS_2$	17.04	--	--	--	18.76
Covellite	CuS	8.05	--	--	--	9.26
Cuprousferrite	$CuFeO_2$	1.63	15.25	--	--	--
$Fe_3(OH)_8$	$Fe_3(OH)_8$	-12.25	3.01	3.66	2.89	--
Ferrihydrite	$Fe(OH)_3$	-5.01	2.31	--	2.1	--
FeS(ppt)	FeS(ppt)	-0.01	--	--	--	--
Galena	PbS	4.64	--	--	--	5.34
Geothite	FeOOH	-1.48	5.85	6	5.58	--
Greigite	Fe_3S_4	4.46	--	--	--	--
Hematite	Fe_2O_3	1.94	16.59	16.9	16.06	--
Lepidocrocite	FeOOH	-1.49	5.83	6.03	5.62	--
Mackinawite	FeS	0.73	--	--	--	1.34
Maghemite	Fe_2O_3	--	8.02	8.41	7.6	--
Magnesite	$MgCO_3$	-2.17	-2.22	--	--	-1.82
Magnetite	Fe_3O_4	1.25	16.51	--	16.21	--
Millerite	NiS	1.56	--	--	--	--
Pyrite	Fe_2S	13.67	--	--	--	16.57
Siderite	FeCO3	1.56	-0.59	--	-0.55	-0.03
Sphalerite	ZnS	2.53	--	--	--	2.59
Sulfur	S	0.3	--	--	--	2.72
Wurtzite	ZnS	0.4	--	--	--	0.5
ZnS(a)	ZnS(a)	-0.31	--	--	--	-0.21

-- indicates a saturation index for that mineral was not calculated by the model.

4.6.2 - Predictions of mineral precipitation and dissolution:

Mineral saturation indices for pore water at J23 and O22 indicate that soil pore fluids are supersaturated with respect to many metal sulfides, which were likely to be precipitating out of solution. This was expected given the concentration of S^{2-} and insolubility of metal sulfides. Pore fluids have negative saturation indices for ferric Fe-bearing minerals such as goethite and ferrihydrite, indicating that they were undersaturated with respect to these minerals. If goethite and ferrihydrite were present as minerals in the solid phase, the modeling predicts that they were dissolving. Pore fluids were supersaturated with respect to the mixed Fe(II)/Fe(III) oxide at J23, but not at O22. Pore water at J23 had both Fe^{2+} and Fe^{3+}, but O22 did not have detectable Fe^{3+} so the calculation of magnetite disequilibrium was not possible at O22. Pore fluid was supersaturated with respect to $FeCO_3$ at J23 and very close to saturation with respect to $FeCO_3$ at O22.

Results of the geochemical modeling for K22, N23, and P25 indicate that the fluids were supersaturated with respect to Fe(III) oxides. The lack of S^{2-} in porewater at these locations makes the precipitation of metal sulfides unlikely, as predicted by the model. However, the model cannot predict whether precipitation of sulfides had occurred prior to sampling. Pore fluid was very close to saturation with respect to $FeCO_3$ at K22 and P25. Pore fluids were supersaturated with respect to magnetite at K22 and P25.

The modeling suggests that there may have been forms of Fe-bearing minerals present in the samples that are not included in the operational definitions of the sequential chemical extractions. It also suggests that Fe(III)-oxides may have been present in some

of the wetland samples that were thought to be reducing beyond the point were oxides would persist. The next three sections describe efforts to positively identify phases of Fe that make up the total mass of extractable Fe in the soils. Identifying these phases will help interpret the results of the sequential chemical extractions and indicate which phases in an anoxic soil make up the ER and MR fractions.

Initially it was assumed that no Fe oxides were present in the wetland soils and that the extractable Fe was composed of phases containing only reduced forms of Fe. As each phase was independently identified and measured (when possible) the contribution of that phase to the total mass of Fe was evaluated.

4.7 - Acid Volatile Sulfide and Simultaneously Extracted Metals Results

The detection of sulfide in porewater at some locations in the wetland area and results of the geochemical modeling prompted investigation into the presence of metal sulfides in the anoxic soils. It was thought that if a significant mass of sulfide was present in the soil that a significant amount of Fe could be bound to it.

Sulfide minerals are generally classified as either acid volatile sulfides (AVS), which includes amorphous iron monosulfide and monosulfides of other metals (e.g. cadmium, lead, mercury, nickel, silver, zinc), or more crystalline forms such as Fe_2S (Morse and Cornwell, 1987 and Lasorsa and Casas, 1996).

A summary of the AVS extraction results for six soil samples is presented in Tables 11a and 11b. Calculations for these data are shown in Appendix 3-D. The soil sample from J19 had no detectable AVS and P25 had an AVS concentration just above detection. Site J19 was not expected to have any detectable AVS given that this location is generally unsaturated and probably has O_2 in soil gas within the pore spaces. Given these conditions, it is unlikely that microbially mediated sulfate reduction occurred at rates significant enough to yield detectable soil AVS. The lack of AVS and dissolved SO_4^{2-} and S^{2-} at P25 suggests that either the soil at this site is sulfur limited or the sulfur is bound up in an unreactive phase such as Fe_2S. Soil samples from J23, K22, N23, and

Table 11a. Concentrations of AVS measured simultaneously extracted metals (SEM) for J19, J23, K22, N23, O22, and P25 in µmol/g dry weight soil.

Sample ID	[AVS] (µmol/g)	Σ [SEM]$_{TM}$ (Cd, Ni, Pb, Zn) (µmol/g)	[AVS] - Σ [SEM]$_{TM}$ (µmol/g)	[SEM]$_{Fe}$ (µmol/g)
J19 AVS	n.d.	33.41	-33.40	66.96
J23 AVS	10.58	7.30	3.28	33.15
K22 AVS	6.69	8.53	-1.84	110.43
N23 AVS	11.61	4.26	7.35	76.10
O22 AVS	11.87	2.34	9.53	24.95
P25 AVS	n.d	1.87	-1.78	101.70

Table 11b. Calculations of FeS, and Fe Other$_{(min)}$ and Fe Other$_{(max)}$ and concentration of total extractable Fe as determined by the sum of the sequential chemical extractions (SCEs) for comparison.

Sample ID	[AVS] - Σ [SEM]$_{TM}$ = FeS (µmol/g)	[SEM]$_{Fe}$ – ([AVS] –[SEM]$_{TM}$) = Fe Other $_{(max)}$ (µmol/g)	[SEM]$_{Fe}$- [AVS] =Fe Other $_{(min)}$ (µmol/g)	ΣFe from SCEs (µmol/g)
J19 AVS	0	66.96	66.96	96.3
J23 AVS	3.28	29.87	22.57	68.4
K22 AVS	0	110.43	103.74	115.0
N23 AVS	7.35	68.75	64.49	118.3
O22 AVS	9.53	15.42	13.08	77.78
P25 AVS	0	101.70	101.70	113.2

O22 had significant concentrations of AVS. This is in good agreement with the redox measurements and dissolved Fe^{2+} and S^{2-} concentrations from J23 and O22. However, the pore water chemistry did not suggest, and the geochemical modeling did not predict, the presence of sulfides at K22 and N23. As mentioned in Section 4.4.2, minor amounts of S^{2-} were detected at these sites during sampling events prior to the November 1997 porewater/solid phase sampling event. It is probable that the AVS formed and accumulated some time prior to a shift in redox caused by a change in the dominant TEAP.

It is difficult to determine the exact concentration of each metal monosulfide present in a particular sample because of the complex nature of sulfide geochemistry and the potential for metals to be released by the AVS/SEM extraction from phases other than monosulfides. It is known that preferential binding of trace metals by S^{2-} occurs when a system is at equilibrium, because the S^{2-} ion successfully out-competes all commonly present dissolved or particulate ligands to form insoluble metal sulfides (DiToro et al. 1992). Also, more soluble metal sulfides, such as FeS, can be converted to more insoluble sulfides (e.g. PbS and CuS) by direct displacement reactions:

$$FeS + Me^{2+} \rightarrow MeS + Fe^{2+},$$

where Me^{2+} is any cation which forms a more insoluble metal sulfide (see Table 12). Because Fe forms one of the most soluble sulfides, this approach seemed an appropriate way to estimate the concentration of FeS in soil samples.

Table 12. Solubility product constants of selected sulfides at 25°C (from Faure, 1991).

Mineral		(pK_{sp})	Mineral		(pK_{sp})
MnS	(green)	13.5	α-ZnS	Sphalerite	24.7
FeS	α-triolite	16.2	CdS	Greenockite	27.0
PbS	galena	17.5	CuS	Covellite	36.1
α-NiS		19.4	FeS_2	Marcasite	41.8
β-ZnS	wurtzite	22.5	FeS_2	Pyrite	42.5
γ-NiS		26.6	Fe_2S_3	Greigite	88.0

With this in mind, the sum of the simultaneously extracted metal (SEM) concentrations of the trace metals (TM) (Σ $[SEM]_{TM(Cd, Ni, Pb, Zn)}$), was subtracted from the AVS concentrations, on a molar basis ([AVS] - Σ $[SEM]_{TM}$). The difference yielded the amount of sulfide that would theoretically be available to form FeS. It should be noted that CuS is not considered an AVS because it has been shown to not dissolve in 1N HCl at 25°C (Allen et al., 1993). Consequently, the concentration of Cu measured in the AVS/SEM leachate was not included in the $[SEM]_{TM}$.

Three of the six samples analyzed (J19, K22, and P25) had no AVS remaining after accounting for the more insoluble metal sulfides (see Table 11a). The typical calculations performed with AVS/SEM data end here, but some AVS was still unaccounted for and the amount of Fe released during the AVS/SEM analysis appeared to be significant and worthy of further investigation. Continuing on, the amount of

[SEM_{Fe}] and the remaining AVS were used to calculate the amount of FeS that could be present in the soils. Next, the amount of $[SEM]_{Fe}$ that could not be attributed to FeS, was calculated as $Fe\text{-}Other_{(max)}$. This value is one end-member estimate for Fe that was likely not associated with sulfide but may originate from other easily dissolved Fe-bearing minerals that comprise the ER and MR phases, and assumes that all $[SEM]_{TM}$ originate from monosulfides. The $Fe\text{-}Other_{(max)}$ end-member assumes that all of the trace metals extracted as SEM originated from metal monosulfides. The final calculation represents the other theoretical end-member, $Fe\text{-}Other_{(min)}$, in which the SEM trace metals are assumed to be not associated with monosulfides. For $Fe\text{-}Other_{(min)}$, all of the AVS was subtracted from the SEM Fe. Both theoretical end-member calculations yielded similar values for Fe-other.

The AVS/SEM results indicate the presence of metal monosulfides in samples from the wetland area of the site. Calculations with the AVS and SEM_{Fe} suggest that FeS is likely present in the wetland soils but the mass of FeS is small in comparison to the total mass of extractable Fe determined by summation of sequential extraction data. This means that another phase (or phases) must account for the majority of the Fe in the wetland soil.

4.8 Magnetic Mineral Separations

To continue the search for phases that might contribute Fe to the ER and MR phases, magnetic separations were performed on soil samples from J19, J23, K22, N23, O22, and P25. The separations yielded detectable amounts of one or more fine-grained magnetic minerals. The data generated is likely an underestimation of the magnetic

fraction present in the soil because due to the rather crude method used very fine-grained minerals may not have been effectively separated and collected.

Visual inspection under low magnification revealed they had irregular, flake, and needle shapes grains, ranging in diameter or length from barely visible to approximately three millimeters (mm). This apparent structural and size difference may indicate the presence of different magnetic minerals and/or different genesis of the same mineral. The exact mineralogy of this magnetic fraction was not investigated, but the most likely candidates given the conditions of the soil were magnetite ($Fe(III)[Fe(II)Fe(III)]O_4$) and biogenically produced magnetic Fe-sulfides including greigite, (Fe_3S_4), or pyrrhotite (Fe_7S_8) (Bazylinski et. al, 1991). Presence of magnetic minerals in soils could be the result of exogenic weathering, transport, and subsequent deposition; authigenic inorganic processes (Maher 1991); magnetotactic dissimilatory Fe(II) reduction (Lovley, 1991); or biogenically derived by magnotactic bacteria (Bzylinski et al., 1991).

Fe, Cu and Zn concentrations in leachate samples from extraction of the magnetically separated fraction are shown in Table 13. It was assumed that most of this fraction would consist of Fe-bearing magnetic minerals. Cu and Zn were analyzed in an attempt to determine the importance of adsorption onto magnetic minerals. Fe was the only metal present in detectable concentrations in the leachate samples.

Site K22 had both the largest observable magnetic fraction and the highest detected concentration of Fe in leachate fluid (12.07 μmol/g dry soil used for the separation). This is in good agreement with the interpretation of the dominant TEAP occurring at this location and presence of both Fe^{2+} and Fe^{3+} in the pore water. The concentrations of Fe in leachate fluids for samples from the other five locations was significantly lower indicating less magnetite in the soil at those locations.

Table 13. Concentrations of Fe, Cu and Zn in leachate samples from extraction of the magnetically separated fraction of selected soils, reported in μmol/g dry soil used for the magnetic separation. Total extractable Fe as determined by sequential chemical extractions is shown for comparison.

Sample ID	Fe (μmol/g)	Cu (μmol/g)	Zn (μmol/g)	ΣFe from SCEs (μmol/g)
J19	0.64	n.d.	n.d.	96.3
J23	2.53	n.d.	n.d.	68.4
K22	12.07	n.d.	n.d.	115.0
N23	1.66	n.d.	n.d.	118.3
O22	0.63	n.d.	n.d.	77.78
P25	0.06	n.d.	n.d.	113.2

n.d. indicates constituent was not detected

Similar to the AVS/SEM work, the mass of Fe associated with the magnetic fraction is small in comparison to the total amount of extractable Fe as determined by summing the sequential chemical extractions. This indicated that some other phase must account for the Fe in the ER and MR leachates. Other Fe bearing minerals that would likely form or exist under reducing conditions are $FeCO_3$, chlorite, and Fe bearing amphiboles, pyroxenes and feldspars. The only available technique to identify the presence of these minerals was x-ray diffraction.

4.9 - X-ray Diffraction Results

4.9.1 – XRD results for samples from anoxic soils:

Several soil samples were analyzed by X-ray diffraction (XRD) in an attempt to identify the presence of carbonates (e.g. $FeCO_3$), Fe-oxides, layered silicate minerals (e.g., chlorite), chain silicates (e.g., amphibole, pyroxenes) and framework silicates (e.g., feldspar). Detailed x-ray diffractogram peak identifications and mineral identifications for these samples are given in Appendix 3G and are only briefly summarized below.

X-ray diffraction of samples from J19, J23, K22, N23 and O22 did not show evidence for the presence of chlorite, amphibole, pyroxene, feldspar or Fe-oxides. Low concentrations, poor crystal structures, and/or sample pretreatment could have resulted in non-detection by XRD methods. If $FeCO_3$ or crystalline Fe-oxides were present in the samples it would likely be only minor amounts. However, poorly crystalline Fe-oxides cannot be ruled out because their amorphous character causes them to be unidentifiable by XRD.

4.9.2 - Effect of ER and MR extractions on carbonate and silicates

One sample outside the wetland area, D11 1-1.5, was subjected to selected extractions within the sequential chemical extraction procedure used in this study in an attempt to determine the effect of these extractions on carbonate and silicate minerals. Sample D11 1-1.5 was selected for analysis because it was very low in organic matter content (0.3 % of dry soil weight) and had a moderate clay size fraction. This reduced

the number of variables and avoided the need for pre-treatment prior to XRD analysis that could alter the samples and allowed several sub-splits for analysis.

Minerals identified in the <10μm fraction of sample D11 1-1.5 prior to chemical extractions include: quartz, calcite, feldspar (possibly both plagioclase and microcline), amphibole, mica (muscovite and/or illite), and chlorite; and there was suggestive evidence for kaolinite, vermiculite and hydroxy interlayer vermiculite. Of all the minerals identified initially, only calcite was not present after the WAS extraction. This demonstrates the specificity of NaOAc (pH 5) for dissolution of carbonate minerals. No significant decrease or loss of peaks was observed after the ER or MR extractions for this sample, suggesting that the silicate and clay minerals (including chlorite) identified in the untreated sample were not significantly dissolved by these extractions.

4.10 - Summary of the Search for Fe-Bearing Minerals Present in Anoxic Soils

The relatively small mass of Fe attributable to the AVS and magnetically separated fractions in samples from the wetland area, along with the non-detection of Fe bearing carbonates and silicates was somewhat perplexing given the anoxic soil conditions and the significance of the ER and MR fractions in Fe partitioning. A summary of Fe concentrations from the ER and MR phases and identified minerals for the samples from the wetland area is given in Table 14. The ER and MR phases account for 50 to 80% of the extracted Fe for samples from the wetland area. The ER and MR phases account for about 94% of the extracted Fe for the sample from J19, the only unsaturated sample. Subtracting the masses of Fe attributable to FeS and magnetite yields the mass of Fe that was unaccounted for by these reduced forms of Fe that were presumably precipitated under anoxic conditions.

Table 14. Summary of Fe concentrations in selected samples including the sum total from sequential chemical extractions (ΣSCE); the percent of total Fe extracted by ER + MR, the concentration of Fe extracted by ER+ MR fractions; Fe attributed to FeS; Fe attributed by magnetite; and Fe from unidentified phases extracted by ER and MR.

Sample	Σ SCE (Fe_{total})	ER+MR	ER+MR	Fe_{FeS}	$Fe_{Mag.}$	$Fe_{Unidentified}$	$Fe_{Unidentified}$
ID	(μmol/g)	(%)	(μmol/g)	(μmol/g)	(μmol/g)	(μmol/g)	% of Fe_{total}
J19	96.3	93.7	90.2	0.0	0.6	89.6	93.0
J23	68.4	77.9	53.3	3.3	2.5	47.5	69.4
K22	115.0	62.	71.9	0.0	12.1	59.8	52.0
N23	118.3	53.0	62.7	7.4	1.7	53.6	45.4
O22	113.2	55.6	62.9	9.5	0.6	52.8	46.6
P25	77.8	58.8	45.7	0.0	0.1	45.6	58.7

Since the most likely reactive reduced phases have been identified and found to be insufficient to account for the mass of Fe released from these anoxic samples, other possible substrates and environmentally reactive phases must be considered and include the following:

- pH sensitive Fe-organic matter-complexes/coatings,
- Fe-oxides that persist under anoxic conditions,
- less common Fe phases such as Fe phosphate (e.g. $FePO_4 \cdot 2H_2O$).

The first two possibilities would be consistent with the results of the sequential chemical extraction results. This would mean that Fe released during the ER extraction could originate from pH sensitive organic matter coatings, while the Fe released during the MR phase could originate from continued release from the organic coating or relic Fe-oxides.

Agitation of the samples during the first couple of extractions could have resulted in removal of some of the organic coatings on soil grains. Preservation of Fe oxides under anoxic conditions may have been facilitated by organic matter coatings which inhibited microbial reduction of the Fe-oxides. The final alternative phase suggested would have depended on the amount of available substrate (e.g. PO_4) present in the anoxic soil environment. This less common substrate was not identified in the course of this research and it is not known whether or not it would have contributed Fe to the ER or MR phases.

4.11 - Composition of Phases Identified by Sequential Chemical Extractions: Interpreting Results of Sequential Chemical Extractions

The samples chosen and methods employed in this study allow an evaluation of the composition of phases that are targeted during sequential chemical extractions. Potential for phases that form under one set of environmental conditions (e.g. oxidizing or reducing) to persist after conditions have changed has been recognized and underscores the importance of complementary analysis of both porewater and solid phase mineralogy when applying sequential chemical extractions to anoxic or cyclically oxic/anoxic soils or sediments. Porewater geochemistry at the study site suggested anoxic conditions exist throughout the wetland area soils. Consequently, Fe-oxides were originally thought to be absent in the wetland area of the site, where these anoxic porewater conditions were shown to exist. However, because Fe reduction was one of the dominant TEAPs, would there not need to be Fe-oxides present to support this apparent metabolically favored process? If Fe-oxides were present in anoxic soils (and sediments) and other phases have been created in response to the changes in redox

conditions (e.g. $[Fe(III)_2Fe(II)]O_4$ and FeS), the question that followed was how does this affect interpretations of sequential chemical extraction results? Also, if trace metals are found in leachates of the ER and MR extractions, were they associated with Fe-oxides currently undergoing microbial reductive dissolution or did they originate from phases that formed under the anoxic conditions (e.g. metal-monosulfides) that dissolve in response to the low pH of the ER and MR extractions?

Identifying where the trace metals originate has important implications if results of sequential chemical extractions are to be used to predict trace metal behavior at this site or any other site. If the trace metals were associated with the oxide surfaces existing under anoxic conditions, then continued reducing conditions would presumably result in the continued release of trace metals to the surrounding porewater. The concentration of metals in porewater (and hence bioavailability and toxicity) would then be dependent on the microbial production of substrates, such as S^{2-}, to precipitate the metals out of solution. On the other hand, if the trace metals were associated with reduced phases, then the trace metals would likely not be released to the surrounding porewater or soil solution until a shift back to oxidizing conditions was experienced.

It is possible that some soils are too complex for sequential chemical extractions to be used to accurately predict the behavior of trace metals in the environment. With these concerns in mind, a discussion of the composition of phases that can be present in wetland soils follows.

Data from this study show that in water saturated, anoxic soils, Fe in the EX phase increases as the pore water concentration of Fe increases. This is true especially when the molar concentrations of dissolved metals exceed the molar concentration of available sulfide, which ordinarily controls the solubility of metals in anoxic systems.

However, it was found that the actual contribution of Fe from pore water to the EX phase is insignificant. This can be seen by calculating the volume of pore fluid in a mass of soil used for extractions (assuming a fluid density of one gram/milliliter), then dividing by the concentration of metal measured in pore water in the field. These calculations are shown in Table 15. The amount of Fe that the pore water contributes to the EX is one to two orders of magnitude less than the amount of Fe derived from solid phase exchange sites.

Table 15. Calculations of the amount of Fe in fluid portion of samples extracted by sequential extractions along with values of Fe in EX phase.

Sample ID	Soil wet weight (g)	Percent fluid in wet soil (% water)	Vol. of fluid in wet soil (mL)	Fe conc. in pore water (µmol/L)	Fe in fluid of ~1g sample (µmol/g wet soil)	Fe conc. in EX (µmol/g wet soil)
J19	1.1	0.65	0.72	--	--	0.052
J23	1.16	0.88	1.02	5.73	0.005	0.142
O22avg	1.03	0.49	0.51	27.93	0.014	0.043
K22	1.07	0.86	0.92	35.45	0.032	3.855
P25	1.1	0.85	0.93	133.21	0.124	4.834
N23	1.04	0.80	0.83	244.58	0.202	6.708

X-ray diffraction results from this study agree with those of Tessier et al. (1979) who reported low concentrations of Si, S, Al and OM in the $MgCl_2$ solution after the EX extraction indicating no significant destruction of silicates, sulfides or organic matter. Results of the pure mineral extractions in this study show very little or no dissolution of FeS, $FeCO_3$, magnetite, Fe_2S, CuS and ZnS, which supports the observations of Tessier et al. (1979). Thermodynamic calculations and observations by Tessier et al. (1979)

suggest that Fe and Mn oxides should not be significantly solubilized by this pH 7 extraction fluid. It is likely that metals released during the EX extraction probably originate from some form of outer-sphere complexes or exchange sites on clays.

The chemical reagent used in the WAS extraction, NaOAc (pH 5), has been successfully used for dissolution of $CaCO_3$ and $MgCO_3$ in many applications, most notably in pretreatment of samples for XRD analysis (Jackson, 1969; Kunze and Dixon 1986). X-ray diffraction results from this study support the effectiveness of this extraction. Analysis of the diffraction peaks indicates the presence of calcite in soil samples prior to treatment with NaOAc (pH 5) and disappearance of the calcite peaks after treatment.

The WAS extraction appears to be relatively selective for dissolution of calcite. However, an undesirable effect of this extraction, rarely discussed by current researchers, is the effect this extraction may have on metals adsorbed to Fe- and Mn- oxides. Tessier et al. (1982) suggest that metals released during a NaOAc (pH=5) extraction are mainly adsorbed rather than carbonate bound. Potential phases affected are pH dependant Fe-oxide edge sites and organic matter functional groups. Metals may be released during this extraction due to the slight acidity (pH 5) of the extraction fluid resulting in competition between metal ions and H^+ at pH dependent adsorption sites. Dissolution of the Fe-oxide edge sites is also pH dependent and has been shown to begin below ~ pH 6 (Essen and El Bassam, 1981 and McLean and Bledsoe, 1992). As a result, metals released during the WAS extraction could be derived from specifically adsorption surface sites on Fe-oxides and organic matter, in addition to those associated with calcite and dolomite. Studies of adsorption of metals onto humic materials have generated adsorption curves as a function of pH that indicate differences in the affinity of humic

materials for heavy metals. Fe and Cu appear to reach maximum sorption to humic materials around pH 5, while Zn does not even begin to plateau at pH 6 (Kerndorf and Schnitzer 1980). This suggests that the NaOAc (pH 5) extraction may affect metals associated with humic substances as well. The appreciable amounts of Fe released during the extractions on samples in this study likely originate from Fe-oxides rather than carbonate bound Fe.

Data from the pure mineral extractions in this study show that $FeCO_3$ should not be included as a phase in the WAS as had been previously speculated, but not tested, by Tessier et al. (1979). Dissolution of $FeCO_3$ by NaOAc (pH 5) was not observed in this study. This finding is in agreement with results from Heron et al. (1994) who also found NaOAc (pH 5) to not significantly dissolve $FeCO_3$. This extraction also does not appear to significantly affect CuS, FeS, FeS_2, ZnS, or Fe_3O_4.

Low temperature leaching with acidified hydroxylamine hydrochloride (ER extraction) has been reported to cause specific and effective dissolution of Mn-oxides (Chao, 1972) and amorphous Fe oxides without significant dissolution of crystalline Fe-oxides in oxic soils and sediments and pure mineral substrates (Chao and Zhou, 1983 and Gruebel et al. 1988). Results from the pure mineral extractions in this study show this extraction caused partial dissolution of FeS, ZnS, $FeCO_3$ and magnetite. Consequently, use of this extraction on anoxic soils and sediments containing these minerals could cause misinterpretation of the partitioning of Fe, Zn and any other metal adsorbed to the mineral surfaces.

The MR extraction hydroxylamine hydrochloride in acetic acid at high temperature has been shown to completely dissolve crystalline Fe oxides with little or no destruction of silicate and clay minerals (Tessier et al. 1979). X-ray diffraction results

from this study show no decrease in peaks representing feldspar, amphibole, mica, kaolinite, vermiculite and chlorite after this extraction. Tessier et al. (1979) also reported similar results for mica and chlorite but noted a slight decrease in XRD peaks for smectite. The MR extraction exhibited fairly selective dissolution of $FeCO_3$ and Fe_3O_4 and continued partial dissolution of FeS according to results in this study. Up to 40 µmol of $FeCO_3$ could be dissolved by this extraction (See Appendix 3F-1). It is apparent that different Fe bearing minerals formed in both oxic and anoxic environments could potentially comprise the MR phase, thus complicating the interpretation of metal partitioning. This might be especially true for studies of soils and sediments from locations with variable or cyclic redox conditions.

In the study by Papp et al. (1991), comparing the selectivity and effectiveness of NaOCl (pH 9.5) and three other common reagents used in partial extraction procedures, peat samples with up to 40% C_{org} were extracted with no reported difficulties. Papp et al (1991) found extraction with NaOCl was the most selective for releasing metals from organic matter and not sulfides. However, they noted that the alkaline conditions may promote precipitation of some metals from samples with low OM content.

The dissolution of CuS and ZnS primarily in the OX1 (NaOCl pH 9.5) in this study demonstrates that this extraction is not as selective toward organic matter as Papp et al. (1991) had shown. Their study based the selectivity of NaOCl (pH 9.5) for organic matter in part on extraction of silica mixtures with FeOOH, Fe_2S, $CuFeS_2$, and FeS but their study did not include other sulfides such as CuS and ZnS. The release of CuS and ZnS during the NaOCl extraction in this study indicates a possible overestimation of the importance of organic matter in sequestering Cu and Zn in anoxic systems. Data from this study do agree well with the Papp et al. (1991) results in terms of limited dissolution

of FeS_2 by NaOCl (pH 9.5). However, the surface chemistry of Fe_2S may not be preserved after this extraction due to formation of a protective surface coating, possibly Fe-oxide or $FeCl_3$, observed visually during the pure mineral extractions.

The largest percentage of Fe released from Fe_2S during pure mineral extractions was in the OX2 (H_2O_2, pH 2), which indicates relative selectivity of this extraction for FeS_2 by the sequential chemical extraction scheme used for this study. It was determined that this extraction could dissolve up to approximately 15 µmol of Fe_2S (see Appendix 3F-1). Continued oxidation of refractory organic matter probably occurs during this extraction. This may or may not result in significant release in metals depending on the ability of this refractory material to adsorb metals. Of more concern is the potential decrease in the ability of this extraction to effectively dissolve FeS_2 caused by the decreased oxidizing capacity of the H_2O_2.

4.12 Fate on Fe, Cu, and Zn in Soil at the Site

Despite the problems associated with the specificity of the sequential chemical extraction method, their use along with the additional biogeochemical analyses have given valuable insight into the sequestering substrates and natural processes that control the mobility of Fe, Cu and Zn in soils at the site. In general, organic matter and reactive Fe-bearing mineral surfaces play a very important role in limiting the mobility of metals. Organic matter has a strong affinity for Cu among all soil textures and in all soil environments at the study site. Reactive Fe-oxide surfaces have a strong influence on the mobility of Fe and Zn in the upland forested and grassy soils. Anaerobic metabolism of organic carbon in reducing soil environments causes dissolution of Fe-oxides, releasing adsorbed metals, and produces alternative substrates, such as sulfide, to precipitate with

metals that are released to pore water when the soils become saturated and redox conditions favor dissolution of substrates that sequestered metals under oxic conditions.

Low concentrations of Cu and Zn in porewater at the sampling locations in the wetland area indicate that these metals are immobilized, probably due to adsorption by reactive sequestering phases and/or co-precipitation with substrates such as sulfide. Porewater concentrations of Fe ranged from almost non-detect to more than ten milligrams per liter indicating that adsorption and/or precipitation of reduced Fe bearing minerals does not equal the reductive dissolution of reactive Fe bearing minerals in dis-equilibrium with the pore fluids. The porewater data suggests that the production of sulfide by microbial sulfate reduction, is not sufficient to equal the flux of Fe to the porewater.

V. CONCLUSIONS

5.1 Principle Findings

During the initial site characterization, approximately 200 soil samples from three depths at 80 sampling boring locations were collected and described. The study site was found to be diverse with respect to soil types and textures. Two soil types with several soil textural differences exit across the site resulting from topographic variability and soil horizon development.

Results of the sequential chemical extractions performed the 200 samples indicated that Fe, Cu and Zn were predominantly sequestered by the ER, MR and OX1 operationally defined phases regardless of soil redox conditions, which is similar results reported in other studies. However, variations in patterns of metal partitioning among operationally defined phases, were observed among the different soil textures across the site. The variability in metal partitioning was correlated to the presence of soil porewater, the amount of organic carbon, and soil redox conditions, which are driven by microbial metabolic terminal electron accepting processes. Specifically, Fe was found to be associated mostly with the MR fraction for all soil textures and types, but the relative importance of the other fractions (ER, WAS, OX1, EX and OX2) increased in samples from areas that had reducing conditions. Copper was found to be associated predominantly with the OX1 phase in samples with significant amounts of organic matter, but the ER and MR phases were important sequestering phases in samples with lower amounts of organic carbon. Zinc was found to be associated primarily with the

MR followed by ER phases with the importance of the ER increasing over the MR in samples taken from reducing conditions or with higher organic matter content.

After the initial characterization of metal partitioning in soil samples from across the study site, a smaller set of sampling locations were analyzed in more detail to identify minerals that comprise the ER and MR phases in samples from anoxic soils to help interpret the sequential chemical extraction results. Porewater sampling and analyses indicated the presence of reduced aqueous species and TEAP indicators of anoxic conditions in the water-saturated wetland area of the site. Evidence for Fe-reduction, sulfate reduction, and methanogenesis was found at several sites within inches below land surface. Geochemical modeling of the porewater chemistry indicated that conditions were favorable for reduced mineralogical species to be present in the solid phase. Acid volatile sulfide/simultaneously extracted metal, magnetic separation and X-ray diffraction analytical methods performed on solid phase samples confirmed the presence of these reduced species. Metal mono-sulfides and a magnetic mineral, possibly magnetite, were identified and attempt was made to quantify the amounts of Fe mono-sulfide and magnetite and then compare those values to amounts of Fe partitioned among ER and MR phases of the soil as determined by sequential chemical extractions. Calculations revealed that the masses of the identified Fe bearing minerals could not account for all of the Fe released from soil samples during the ER and MR extractions. This was interpreted to mean that other forms, possibly oxidized forms, of Fe bearing minerals or phases must have been present in the soils from the wetland area of the study site. Potential alternative environmentally reactive phases include pH sensitive Fe- bearing organic matter-complexes/coatings, Fe-oxides that persist under anoxic conditions, and/or Fe-phosphate.

Some of the reduced mineral phases (e.g., $FeCO_3$, Fe_3O_4, and metal mono-sulfides), that were predicted and/or identified by pore water and solid phase biogeochemical analyses are not generally included in the operational definitions for phases targeted by sequential chemical extractions. In order to predict which operationally defined phases these reduced minerals would likely be associated with in a soil sample, pure mineral samples were subjected to the same sequential extracted procedure used for soil samples. Siderite, magnetite, and FeS were found to be dissolved most significantly by the MR extraction. CuS and ZnS were dissolved/oxidized most significantly by the OX1 extraction and Fe_2S was most significantly dissolved/oxidized by the OX2 extraction. The EX, WAS and ER extractions appeared to be ineffective in degrading the integrity of these mineral structures, with the exception of ZnS which was slightly affected by the ER extraction.

5.2 Evaluating the Use of Sequential Chemical Extractions in Anoxic Environments

Potential problems with the use of sequential chemical extractions on samples collected from anoxic soils have been identified during the course of this research. The ability of Fe(III)oxides, Fe oxyhydroxides, Fe(II)oxide minerals, Fe (II)carbonate, and Fe (II) sulfides to exist simultaneously in meta-stable anoxic (or cyclically oxic-anoxic) environments complicates interpretations of the results of sequential chemical extractions, because the operational definitions for phases targeted in these extractions do not include minerals such as $FeCO_3$, FeS, and Fe_3O_4, which are common in anoxic environments. In addition, metal monosulfides (e.g. FeS, CuS, and ZnS) do not exhibit the same partitioning behavior so they cannot be operationally defined together as a group as has been done traditionally. It is clear that hydroxylamine hydrochloride

extractable Fe in oxic soils and sediments (ER and MR) likely originates mainly from Fe-oxides. Hydroxylamine hydrochloride extractable Fe in anoxic soils and sediments does not exclusively indicate the presence of reactive Fe-oxides, because dissolution of pure FeS, $FeCO_3$, and Fe_3O_4 has been shown to occur.

It has been demonstrated that the sequential chemical extraction procedure used in this study cannot selectively distinguish between these different Fe-bearing minerals and that they all likely comprise the most important operationally defined phase (MR) for sequestering some metals. If the underlying goal for the use of information derived by sequential chemical extractions is to gain insight into cycling and potential mobility of metals, distinction between metals associated with an Fe(III) oxides, Fe(II)-mineral or a sulfide is essential. Just as these mineral phases form under different conditions, they dissolve and/or are transformed differently in response to environmental changes caused by chemical and biological activity. Consequently, metals associated with each mineral will be released under different conditions and at different rates, thus complicating prediction of metal mobility.

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APPENDIX 1

Solid Phase Sample Descriptions

Table 1A-1:
Sample Location and Soil Core Descriptions

[illegible] ID	Description of sample location	Interval (feet)	Description of soil
B3	Hardwood forest with undergrowth	0.0-0.5	Dark brown silty sand, with roots, grades to rusty medium brown silty sand
		0.5-1.0	Dark brown silty sand, with roots, grades to rusty medium brown silty sand
		1.0-1.5	Rusty medium brown silty sand grades to dark brown silty sand
		1.5-3.0	Rusty medium brown silty sand
		3.0-3.5	Rusty medium brown silty sand
B5	Opening in a forest with undergrowth	0.0-0.5	Dark brown silty sand, with roots and wood chips
		0.5-1.0	Rusty orangish brown silty sand
		1.0-1.5	Rusty organish brown silty sand
		1.5-3.0	Rusty medium brown silty sand grades to rusty tan silty sand
		3.0-3.5	Light tan silty sand
B7	Mixed hardwood and evergreen forest	0.0-0.5	Dark brown/black silty sand, grades to light brown silty sand
		0.5-1.0	Light brown silty sand grades to rusty brownish orange near bottom
		1.0-1.5	Rusty brownish orange silty sand
		1.5-3.0	Rusty brownish silty sand grades to tan silty sand
		3.0-3.5	Tan silty sand then sharp contact with brown silt three inches from top of core
B9	Grassy covered man made berm	0.0-0.5	Dark rusty brown silty sand
		0.5-1.0	Dark rust brown then dark brown silty sand
		1.0-1.5	Rusty dark brown to rusty light brown
		1.5-3.0	Rusty light brown to tan
		3.0-3.5	Tan silty sand
B11	Site is in brush in a wooded area	0.0-0.5	Dark brown silty sand
		0.5-1.0	Dark brown to dark rusty brown silty sand
		1.0-1.5	Rusty light brown silty sand
		1.5-3.0	Rusty light brown silty sand grades to rusty to tan silty sand
		3.0-3.5	Tan silty sand
B13	Site is in a wooded area	0.0-0.5	Black to dark brown silty sand
		0.5-1.0	Dark brown silty sand with dark rusty brown silty sand near one foot
		1.0-1.5	Dark rusty brown silty sand
		1.5-3.0	Dark rusty brown grading to tan silty sand
		3.0-3.5	Light tan silty sand
B15	Opening at edge of hardwood forest	0.0-0.5	Dark brown silty sand, high OM

Table 1A-1 (con't.):

B15		0.5-1.0	Dark brown silty sand with melted looking ore - angular reddish brown
		1.0-1.5	Dark brown material, sharp contact with creamy clumpy sand
		1.5-3.0	Creamy tan grades to light brown silt w/lots of hair to dark brown with hair
		3.0-3.5	Dark brown hair with some sand and silt
B17	Wooded area	0.0-0.5	Dark brown/black silty sands with lots of organic material
		0.5-1.0	Dark brown grades into a rusty tan sandy silt
		1.0-1.5	Rusty tan silty sand
		1.5-3.0	Rusty tan silty sand
		3.0-3.5	Rusty tan to dark rusty brown silty clay
C2	Small opening in a hard wood forest	0.0-0.5	Dark brown silty sand, roots present
		0.5-1.0	Brown silty sand, with roots
		1.0-1.5	Medium rusty brown silty sand
		1.5-3.0	Medium rusty brown silty sand grades to medium rusty brown sand
		3.0-3.5	Light brown silty sand
C4	Hardwood forest with sparse vegitation rusty scrap metal and trash near site	0.0-0.5	Dark brown silty sand, roots and wood chips
		0.5-1.0	Dark brown silty sand grades to rusty tan silty sand roots present
		1.0-1.5	Slightly rusty medium tan silty sand, roots and wood chips present
		1.5-3.0	Medium tan, slightly rusty silty sand, grades to light rusty tan sand with silt
		3.0-3.5	Top rusty brown silty sand, tan rusty coarse sand, then rusty tan silty sand
C6	Hardwood forest with light underbrush	0.0-0.5	Black-dark brown silty sand in upper two inches grades to light brown silty sand
		0.5-1.0	Light brown silty sand grading to rusty brown silty sand
		1.0-1.5	Dark rusty brown silty sand
		1.5-3.0	Rusty tan silty sand grades to light tan silt with fine sand
		3.0-3.5	Light tan silty sand
C8	Edge of forested area	0.0-0.5	Black silty sand, with roots
		0.5-1.0	Dark brown silty sand grades to rusty brown silty sand, with roots
		1.0-1.5	Dark rusty brown silty sand grades to rusty brown silty sand
		1.5-3.0	Rusty brown silty sand grades to light tan silty sand
		3.0-3.5	Light tan silt with fine sand
C10	Brush on the edge of a wooded area	0.0-0.5	Dark brown silty sand
		0.5-1.0	Dark brown sand grading to dark rusty brown
		1.0-1.5	Dark rusty brown silty sand and free roots
		1.5-3.0	Dark rusty brown grading to rusty brown and the rusty tan

Table 1A-1 (con't.):

C10		3.0-3.5	Rusty brown
C12	Site is in the trees	0.0-0.5	Black silty sand with many roots
		0.5-1.0	Dark rusty brown silty sand
		1.0-1.5	Rusty brown silty sand
		1.5-3.0	Rusty brown silty sand grading to tan silty sand, increasing clay with depth
		3.0-3.5	Dark tan silty sand with clay
C14	Grassy open area	0.0-0.5	Organic rich, dark brown, silty sand
		0.5-1.0	Organic rich, dark brown, silty sand grading to tan silty sand
		1.0-1.5	Tan, silty sand
		1.5-3.0	Tan, silty sand
		3.0-3.5	Tan, silty sand-disturbances occurred regarding core
C16	Opening in a sparse hardwood forest	0.0-0.5	Dark brown silty sand with roots
		0.5-1.0	No sample taken
		1.0-1.5	No sample taken
		1.5-3.0	No sample taken
		3.0-3.5	No sample taken
D3	Fairly open grassy area, near a pine tree	0.0-0.5	Dark brown silty sand
		0.5-1.0	Light brown silty sand grades to bright rusty brown silty sand
		1.0-1.5	Rusty brown silty sand
		1.5-3.0	Rusty brown silty sand grades to light tan silty sand, stones
		3.0-3.5	Light tan silty sand
D7		0.0-0.5	Dark brown silty sand
		0.5-1.0	Dark brown silty sand grades to rusty tan silty sand
		1.0-1.5	Reddish brown silty sand
		1.5-3.0	Reddish tan silty sand
		3.0-3.5	Reddish tan silty sand
D11	Brush on the edge of a small clearing	0.0-0.5	Top four inches dark brown silty sand, bottom two inches tan silty sand
		0.5-1.0	Rusty tan silty sand
		1.0-1.5	Rusty tan silty sand grades to rusty silty sand with clay
		1.5-3.0	Rusty light tan silty sand grades to light tan silty sand with clay
		3.0-3.5	Dark tan to light brown silty sand and clay - sample is wet and muddy
D13	Wooded area	0.0-0.5	Roots, worm, black to dark brown silty sand

Table 1A-1 (con't.):

D13		0.5-1.0	Dark brown grading into rusty brown
		1.0-1.5	Rusty brown silty sand
		1.5-3.0	Rusty tan silty sand
		3.0-3.5	Medium tan silty sand
D15	Opening in hardwood forest	0.0-0.5	Dark brown silty sand
		0.5-1.0	Brown silty sand grades to rusty tan silty sand and gravel
		1.0-1.5	Rusty tan silty sand
		1.5-3.0	Rusty tan grades into light tan silty sand
		3.0-3.5	Light tan silty sand
D17	Opening in hardwood forest	0.5-1.0	Dark brown coarse sand w/pebbles, roots present, peat material
		1.0-1.5	Peaty materials with pebbles
		1.5-3.0	Peaty materials with silty clay and pebbles
		3.0-3.5	Peaty materials w/ silty clay and pebbles grades to dark tan silt and clay
D19	Wooded area	0.0-0.5	Dark brown coarse sand grades to coarse sand and gravel, roots throughout
		0.5-1.0	Dark brown gravel
		1.0-1.5	Dark brown gravel
		1.5-3.0	Reddish black gravel grades to clumps of clay then beck to gravel
		3.0-3.5	Top three inches -red-black gravel grades to red-brown gravel/coarse sand and clay
E16	Edge of hardwood forest moderate Underbrush	0.0-0.5	Dark rich organic coarse sand
		0.5-1.0	Dark rich organic coarse sand
		1.0-1.5	Dark rich organic coarse sand
		1.5-3.0	Green soil with hides and hair, boards were between two and three feet
		3.0-3.5	No sample taken
E18	Wooded area	0.0-0.5	Brown, OM rich coarse sand/pebbles, last two inches, dark grey/green silty clay
		0.5-1.0	Dark gray green silty clay mixed with brown silty clay, pieces of hide
		1.0-1.5	Dark gray green silty clay mixed with brown silty clay, pieces of hide
		1.5-2.5	Dark gray green silty clay mixed with brown silty clay, pieces of hide
		2.5-	Hit a wooden plank, unable to go farther
E20	Wooded are at the edge of a cement pad	0.0-0.5	Dark brown to rusty brown coarse sand
		0.5-1.0	Dark brown coarse sand
		1.0-1.5	Rusty brown coarse sand and pebbles
		1.5-3.0	Coarse gravel
		3.0-3.5	No Sample Taken

Table 1A-1 (con't.):

F13	Edge of wooded area	0.0-0.5	Top five inches, dark brown silty sand with OM; bottom, rusty tan silty sand
		0.5-1.0	Light rusty tan silty sand
		1.0-1.5	Light rusty tan silty sand grading into light rusty tan sandy silt
		1.5-3.0	Light rusty tan sandy silt grades into light tan sand
		3.0-3.5	Fine light tan sand
F15	Grassy open area w/shrubs	0.0-0.5	Dark brown silty sand with clumps of green clay
		0.5-1.0	Dark brown silt
		1.0-1.5	Dark brown silty sand
		1.5-3.0	Rusty tan silty sand
		3.0-3.5	Rusty tan sand, wet sample
F19	Wooded area at top of a ridge	0.0-0.5	Dark brown sand with abundant organic material including roots
		0.5-1.0	Dark rusty brown sand with lots of roots
		1.0-1.5	Rusty brown silty sand
		1.5-3.0	Rusty brown silty sand to light tan silty sand
		3.0-3.5	Light tan silty sand
F21	Small gully at the top of a hill	0.0-0.5	Hair at land surface, dark brown silty sand grades to rusty brown w/root and hair
		0.5-1.0	Rust tan silty sand
		1.0-1.5	Rust tan silty sand
		1.5-3.0	Rust tan silty sand
		3.0-3.5	Rust tan silty sand
G14	Grassy swamp on edge of forest scrap wood and metal nearby	0.0-0.5	Dark brown silty sand grading into greenish gray silty sand
		0.5-1.0	Greenish gray silt sand
		1.0-1.5	Greenish gray silt sand
		1.5-3.0	Greenish gray silt sand to black silty sand with greenish tinge, lots of hair
		3.0-3.5	Black silty sand with a greenish tinge
G16	In cattails with some surface water	0.0-0.5	Roots, smells like H2S, very moist, mostly OM with clay and silt
		0.5-1.0	Roots, smells like H2S, very moist, mostly OM with clay and silt
		1.0-1.5	Roots, smells like H2S, very moist, mostly OM with clay and silt
		1.5-3.0	Roots, smells like H2S, very moist, mostly OM with clay and silt
		3.0-3.5	Roots, smells like H2S, very moist, mostly OM with clay and silt
G18	Along fence in tall shrubs	0.0-0.5	Black silty sand

Table 1A-1 (con't.):

G18		0.5-1.0	Dark brown silty sand grades to rusty tan silty sand
		1.0-1.5	Rusty tan silty sand
		1.5-3.0	Tan silty sand grades to silty sand with clay
		3.0-3.5	Tan silty sand
G20	Grassy open area next to fence	0.0-0.5	Brown silty fine sand
		0.5-1.0	Rusty tan silty fine sand
		1.0-1.5	Rusty tan silty sand
		1.5-3.0	Tan silty sand
		3.0-3.5	Tan silty sand, wet
H15	Swampy grassy area	0.0-0.5	Black/dark brown silt with lots of OM
		0.5-1.0	Dark silt grades into light tan sand with pebbles - water in the hole
		1.0-1.5	Light tan silty sand - wet
		1.5-3.0	Light tan silty sand saturates grades to dark brown silty sand - wet
		3.0-3.5	Black, saturated silty sand, H2S odor
H17	Swampy grassy area	0.0-0.5	Dark brown silt and OM, very moist
		0.5-1.0	Same as above
		1.0-1.5	Saturated OM and silty clay, dark brown
		1.5-3.0	Same as above
		3.0-3.5	Saturated OM and silty clay, dark brown
H19	Grassy open area under a large tree	0.0-0.5	Black silty sand with clumps of white gravely material
		0.5-1.0	Black silt with gravel - melted rock/ore
		1.0-1.5	Black silt with clumps of white irregular angular material
		1.5-3.0	Black silt
		3.0-3.5	Reddish black silt with hair and industrial waste
H21	Open field with waist high brush	0.0-0.5	Dark brown silty sand grades to tan sand
		0.5-1.0	Dark brown sandy silt
		1.0-1.5	Brown silty fine sand
		1.5-3.0	Brown fine sand grades to dark tan silty sand grades to rusty tan to tan sand
		3.0-3.5	Reddish tan silty sand
H23	Grassy, brushy open area	0.0-0.5	Very dark brown organic rich sand to rusty tan silty sand
		0.5-1.0	Rusty tan silty sand
		1.0-1.5	Rusty tan silty sand

Table 1A-1 (con't.):

H23		1.5-3.0	Rusty tan silty sand
		3.0-3.5	Rusty tan silty sand
I20	Hardwood forest	0.0-0.5	Dark, brown organic rich silty sand with hides near bottom
		0.5-1.0	Dark brown organic rich silty sand with tan and green gray hides
		1.0-1.5	Dark brown OM rich silty sand with green hides with glass fragments and pebbles
		1.5-3.0	Dark brown OM rich silty sand with green hides to dark green/black coarse sand
		3.0-3.5	Reddish black gravelly sand with gray green areas and brick
I22	Swampy area with running water 3 in.	0.0-0.5	Very dark brown silt with lots of roots and OM
		0.5-1.0	Very dark brown silt with lots of roots and OM
		1.0-1.5	Very dark brown silt with lots of roots and OM
		1.5-3.0	Very dark brown silt with lots of roots and OM, tan silty sand in bottom half foot
		3.0-3.5	Dark brown wood and rusty tan silty sand
I24	Dead hard wood forest	0.0-0.5	Dark brown silt to rusty tan silty sand
		0.5-1.0	Rusty tan silty sand
		1.0-1.5	Rusty tan silty sand
		1.5-3.0	Rusty tan silty sand
		3.0-3.5	Rusty tan silty sand
I26	Grassy open area next to fence	0.0-0.5	Black/very dark brown silty sand with OM
		0.5-1.0	Black/very dark brown silty sand with OM
		1.0-1.5	Black/very dark brown silty sand with OM and coarse sand
		1.5-3.0	Black/very dark brown gravely material
		3.0-3.5	No sample taken
J19	Edge of road in a wooded/grassy area scrap metal at surface	0.0-0.5	Dark brown organic rich silty sand
		0.5-1.0	Dark brown organic rich silty sand
		1.0-1.5	Dark brown organic rich silty sand
		1.5-3.0	Dark brown organic rich silty sand at top, tannery wastes, hides and hair at two feet
		3.0-3.5	Reddish dark brown silty sand and tannery waste
J21	Grassy, semi- open birch tree Forrest	0.0-0.5	Very dark brown organic rich silty sand with rusty tan silty sand
		0.5-1.0	Rusty tan silty sand to brown silty sand
		1.0-1.5	Brown silty sand to very dark brown organic material with wood chips
		1.5-3.0	Brown silty sand
		3.0-3.5	Wood

Table 1A-1 (con't.):

J23	Cattail, grass swamp, standing water	0.0-0.5	Very dark brown to red brown organic rich silt with lots of roots
		0.5-1.0	Very dark brown, organic rich silt
		1.0-1.5	Very dark brown, organic rich silt
		1.5-3.0	Very dark brown, organic rich silt, wood at two and a half feet, tan silty sand bottom
		3.0-3.5	Dark brown organic rich material with tan silty sand
J25	Wooded area with lots of urban trash	0.0-0.5	Black organic rich silty sand, large and small roots
		0.5-1.0	Reddish dark brown rich silty clay
		1.0-1.5	Reddish dark brown decaying tree matter with some silt
		1.5-3.0	Reddish brown decaying tree matter with some silt
		3.0-3.5	No sample taken
J27	Grassy open area trash pile of cans and bottles nearby	0.0-0.5	Organic rich very dark brown silty sand, water in the hole
		0.5-1.0	Organic rich very dark brown silty sand grades to gray tan silty sand
		1.0-1.5	Grey tan silty sand
		1.5-3.0	Rock or cement
		3.0-3.5	No sample taken
K20	Low area with grass, cattails and trees	0.0-0.5	Very dark brown silt with lots of roots and OM, wet
		0.5-1.0	Wood
		1.0-1.5	Wood
		1.5-3.0	Reddish black decaying OM
		3.0-3.5	Dark gray silty sand
K22	Low area with cattails and small trees	0.0-0.5	Very dark brown/black organic rich silt with roots, wet
		0.5-1.0	Very dark brown/black organic rich silt with roots, wet
		1.0-1.5	Mostly wood chips
		1.5-3.0	Wood and very dark brown organic rich silt
		3.0-3.5	Brown silty sand
K24	Boggy, grassy area with small trees	0.0-0.5	Silty, dark brown organic rich sediment and roots present, wet
		0.5-1.0	Silty, dark brown OM rich sediment and roots present, wet, with chips of wood
		1.0-1.5	Silty, dark brown OM rich sediment and roots present, wet, with decaying wood
		1.5-3.0	Silty, dark brown organic rich sediment, 2'- wood, bellow tan silty sand
		3.0-3.5	Tan silty sand
K26	Grassy open area, with water at surface	0.0-0.5	Organic rich, very dark brown, coarse sand with roots
		0.5-1.0	Organic rich, very dark brown, coarse sand with roots
		1.0-1.5	Organic rich, very dark brown, coarse sand with roots

Table 1A-1 (con't.):

K26		1.5-3.0	Organic rich, very dark brown, coarse sand with roots
		3.0-3.5	Organic rich, very dark brown, coarse sand with roots
K28	Wooded area	0.0-0.5	Organic rich very dark brown silty sand. Water in the hole
		0.5-1.0	Organic rich very dark brown silty sand.
		1.0-1.5	Organic rich very dark brown silty sand. hit wood, new hole one foot away
		1.5-3.0	Wood, trash, telephone receiver
		3.0-3.5	No sample taken
L21	Grassy area with small trees	0.0-0.5	Dark brown silty sand grades, bottom one inch, tan silty sand
		0.5-1.0	Tan silty sand
		1.0-1.5	Tan silty sand to gray sand
		1.5-3.0	Wood, very dark brown coarse sand and pebbles
		3.0-3.5	Wood, very dark brown coarse sand to gray brown silty sand
L23	Small tree, cattails and grass in a swamp	0.0-0.5	Black to very dark brown organic rich sediment with clay and silt, wet
		0.5-1.0	Black to very dark brown organic rich sediment with clay and silt, wet
		1.0-1.5	Black to very dark brown organic rich sediment with clay and silt, wet
		1.5-3.0	Black to very dark brown organic rich sediment at two feet, tan coarse sand
		3.0-3.5	Tan coarse sand
L25	Wooded area	0.0-0.5	Dark brown silty sand
		0.5-1.0	Tan silty sand with localized rusty clumps
		1.0-1.5	Tan silty sand grades to decaying wood
		1.5-3.0	Dark brown decaying tree matter
		3.0-3.5	Wood chips and light brown silt
L27	Pond with three inches of water	0.0-0.5	Organic rich, very dark brown, coarse sand with roots
		0.5-1.0	Organic rich, very dark brown, silty sand
		1.0-1.5	Organic rich, very dark brown silty sand in half the core-then disturbances occurred
		1.5-3.0	Tan, silty sand
		3.0-3.5	Tan silty sand-disturbances occurred retreiving core
M20	Grassy open area	0.0-0.5	Dark, brown organic rich silty sand, bottom two inches, rusty tan silty sand
		0.5-1.0	Rusty tan silty sand
		1.0-1.5	Tan silty sand, wood at bottom two inches
		1.5-3.0	Wood
		3.0-3.5	No sample taken
M24	A beaver pond shoreline	0.0-0.5	Dark brown silt and decaying OM

Table 1A-1 (con't.):

M24		0.5-1.0	Dark brown silt and decaying OM and large red brick
		1.0-1.5	Dark brown silt and decaying OM with chips of red brick
		1.5-3.0	Tan coarse sand
		3.0-3.5	Tan coarse sand
M26	Wooded, swampy area, grass	0.0-0.5	Organic rich, dark brown sand with roots and water in the hole
		0.5-1.0	Organic rich, dark brown sand with roots and water in the hole
		1.0-1.5	Organic rich, dark brown sand with roots and water in the hole
		1.5-3.0	No sample taken-hit wood
		3.0-3.5	No sample taken-hit wood
M28	Shoreline of a pond, water at surface with bricks, rocks, debris	0.0-0.5	Organic rich very dark brown silt.
		0.5-1.0	Organic rich dark brown silt.
		1.0-1.5	Dark gray coarse sand with cobbles couldn't get through, moved to new location
		1.5-3.0	Tan silty sand -- sample taken
		3.0-3.5	No sample taken
N21	Grassy, semi-wooded area	0.0-0.5	Very dark brown silt with lots of roots and other OM
		0.5-1.0	Very dark brown silt with lots of roots and other OM with wood chips
		1.0-1.5	Very dark brown silt with lots of roots and other OM with wood chips
		1.5-3.0	Wood
		3.0-3.5	No sample taken
N23	Grassy open area with standing water	0.0-0.5	Dark brown OM with some silt
		0.5-1.0	Dark brown OM with some silt
		1.0-1.5	Dark brown OM with some silt grades to grey-brown silty sand
		1.5-3.0	Grey silty sand grades to coarse sand, back to gray silty sand with wood and hair
		3.0-3.5	Grey silty sand, Obtained core by pushing tube into auger.
N25	Wooded area 25 ft N of a beaver pond	0.0-0.5	Dark brown organic rich silty sand at top dark grades to gray silty sand at bottom
		0.5-1.0	Dark gray silty sand grades to pebbly, coarse, dark gray sand
		1.0-1.5	Dark gray coarse sand with wood, water in the hole
		1.5-3.0	Wood then dark gray silty with some fine sand
		3.0-3.5	Some wood at the top, mostly dark gray silty sand
O22	Grassy open area	0.0-0.5	Dark brown organic rich silty sand with hair
		0.5-1.0	Dark brown organic rich silty sand with hair
		1.0-1.5	Dark brown silty sand with lesser OM and hair
		1.5-3.0	Dark brown silty sand grades to dark gray silty sand, water in the hole at two feet
		3.0-3.5	Dark gray silty sand

Table 1A-1 (con't.):

O24	Wooded area	0.0-0.5	Very dark brown, OM silty with roots, water in the hole
		0.5-1.0	Very dark brown, OM silty with roots, water in the hole
		1.0-1.5	Very dark brown, OM silty with roots, water in the hole
		1.5-3.0	Very dark brown, OM rich silty, hair, grades to gray silty sand, water in the hole
		3.0-3.5	Gray silty sand
P23	Grassy open area	0.0-0.5	Dark brown organic rich silty sand with hair and roots
		0.5-1.0	Dark brown organic rich silty sand with hair and leather grades to tan silty sand
		1.0-1.5	Tan silty sand with chunks of grayish green hair, water in the hole
		1.5-3.0	Tan silty sand with hair grades to dark hair rich silt then to dark gray silty sand
		3.0-3.5	Dark gray silty sand with hair
P25	Swamp, with grass and standing	0.0-0.5	Very dark brown decaying OM, with some silt
		0.5-1.0	Very dark brown decaying OM, with some silt and hair
		1.0-1.5	Very dark brown decaying OM, with some silt and hair
		1.5-3.0	Very dark brown decaying OM, with some silt and hair grades to gray/brown sand
		3.0-3.5	Gray/brownish sand
Q24	Grassy open area	0.0-0.5	Dark Brown organic rich silty sand
		0.5-1.0	Dark Brown organic rich silty sand grades to tan silty sand at bottom
		1.0-1.5	Brown silty sand with a lot of hair and other OM
		1.5-3.0	Brown silty sand with hair and OM, hit wood, sample taken two and a half feet
		3.0-3.5	
Q26	Low lying wooded area	0.0-0.5	Black mud, rich detrital clay
		0.5-1.0	Wood boards
		1.0-1.5	No sample taken
		1.5-3.0	Wood boards
		3.0-3.5	No sample taken
R25	Grassy/weedy open area	0.0-0.5	Very dark brown organic rich clay
		0.5-1.0	Very dark brown organic rich clay, wet and hair present
		1.0-1.5	Very dark brown organic rich clay, wet, brown sand at bottom of the core
		1.5-3.0	Dark brown sand
		3.0-3.5	Dark brown sand
R27	Cattail swamp with surface water	0.0-0.5	Very dark brown with cattail roots and silt
		0.5-1.0	Very dark brown with cattail roots and silt
		1.0-1.5	Very dark brown with cattail roots and silt
		1.5-3.0	Very dark brown with cattail roots and silt, hit a board, then sand then clay

Table 1A-1 (con't.):

		3.0-3.5	Wood sand and clay
S26	Grassy open area	0.0-0.5	Very dark brown silt with lots of organic material
		0.5-1.0	Very dark brown silt with lots of organic material with bricks
		1.0-1.5	Very dark brown silt with lots of organic material, with boards
		1.5-3.0	Wood boards
		3.0-3.5	No sample taken
T27	Near shore in a brushy area	0.0-0.5	Very dark brown silt, organic rich with roots and hair
		0.5-1.0	Mostly roots and hair with some silt and clay and green hide chunks
		1.0-1.5	Mostly roots and hair with some silt and clay and green hide chunks
		1.5-3.0	Wood
		3.0-3.5	No sample taken
U26	On the beach with grass and shrubs	0.0-0.5	Brown sand
		0.5-1.0	Brown sand to dark brown sand with hides, hair, and OM, wet
		1.0-1.5	Dark brown sand with a lot of OM, hair, and roots
		1.5-3.0	Dark brown sand grading into greenish black sand, increasing clay with depth
		3.0-3.5	Dark brown sand with OM

Table 1B-1:
Organic Matter Content

Sample ID	%OM	Sample ID	%OM	Sample ID	%OM
B3a0-0.5	2.2	B31-1.5	5.2	B33-3.5	1.0
B50-0.5	0.8	B51-1.5	0.7	B53-3.5	1.1
B70-0.5	0.6	B71-1.5	0.6	B73-3.5	0.3
B9a0-0.5	2.4	B91-1.5	2.8	B93-3.5	0.3
B110-0.5	NA	B111-1.5	0.8	B113-3.5	0.9
B130-0.5	2.3	B13a1-1.5	1.8	B133-3.5	0.5
B150-0.5	5.3	B151-1.5	15.2	B153-3.5	35.8
B170-0.5	5.5	B171-1.5	0.6	B173-3.5	21.5
C20-0.5	2.3	C21-1.5	0.3	C23-3.5	0.3
C40-0.5	2.3	C41-1.5	1.1	C43-3.5	0.6
C60-0.5	0.4	C61-1.5	1.0	C63-3.5	0.1
C80-0.5	4.2	C81-1.5	0.7	C83-3.5	0.9
C100-0.5	2.1	C101-1.5	1.3	C103-3.5	2.0
C120-0.5	2.9	C121-1.5	0.4	C123-3.5	0.2
C140-0.5	5.2	C141-1.5	0.3	C143-3.5	0.4
C160-0.5	1.8	C161-1.5	NA	C163-3.5	NA
D50-0.5	1.8	D51-1.5	1.1	D53-3.5	0.7
D70-0.5	4.2	D71-1.5	0.4	D73-3.5	0.7
D90-0.5	3.7	D91-1.5	0.7	D9a3-3.5	0.6
D110-0.5	0.7	D111-1.5	0.3	D113-3.5	0.2
D130-0.5	3.7	D131-1.5	0.5	D133-3.5	0.6
D150-0.5	2.1	D151-1.5	1.8	D153-3.5	0.8
D170-0.5	32.1	D171-1.5	30.6	D173-3.5	4.3
D190-0.5	19.2	D191-1.5	71.0	D193-3.5	18.8
E140-0.5	1.9	E141-1.5	3.5	E143-3.5	0.4
E160-0.5	28.2	E161-1.5	49.8	E163-3.5	35.8
E180-0.5	34.5	E181-1.5	55.7	E183-3.5	NA
E200-0.5	2.2	E201-1.5	1.8	E203-3.5	NA
F130-0.5	1.8	F131-1.5	0.9	F133-3.5	0.3
F150-0.5	20.7	F151-1.5	20.4	F153-3.5	0.3
F170-0.5	5.5	F171-1.5	0.6	F17a3-3.5	0.2
F190-0.5	5.4	F191-1.5	1.4	F193-3.5	0.5
F210-0.5	0.7	F211-1.5	0.6	F213-3.5	0.8
G140-0.5	7	G141-1.5	4.5	G143-3.5	0.6
G160-0.5	65.8	G161-1.5	8	G163-3.5	6.4
G180-0.5	4.9	G181-1.5	0.6	G183-3.5	0.3
G200-0.5	2.8	G201-1.5	0.8	G203-3.5	0.3
G220-0.5	1.9	G221-1.5	2.3	G223-3.5	0.4
H150-0.5	14.8	H151-1.5	5.9	H153-3.5	15.8
H170-0.5	34.2	H171-1.5	56.7	H173-3.5	5.8
H190-0.5	22.9	H191-1.5	23.1	H193-3.5	70.2

Table 1B-1 (con't.):

Sample ID	%OM	Sample ID	%OM	Sample ID	%OM
H210-0.5	0.2	H211-1.5	8.5	H213-3.5	0.4
H23a0-0.5	2	H231-1.5	0.5	H233-3.5	0.2
I200-0.5	48.9	I201-1.5	79.4	I203-3.5	66.6
I220-0.5	65.3	I221-1.5	74.5	I223-3.5	0.4
I240-0.5	3	I241-1.5	0.3	I243-3.5	0.3
I260-0.5	16.7	I26a1-1.5	5.1	I263-3.5	NA
J19a0-0.5	65.3	J191-1.5	76.3	J193-3.5	92.1
J210-0.5	2.6	J211-1.5	1.2	J213-3.5	NA
J230-0.5	74.4	J231-1.5	70.7	J233-3.5	0.4
J250-0.5	23.8	J251-1.5	96	J253-3.5	2.3
J270-0.5	9.6	J271-1.5	0.5	J273-3.5	NA
K200-0.5	81.3	K201-1.5	NA	K203-3.5	3
K220-0.5	76.5	K221-1.5	81.7	K223-3.5	0.2
K240-0.5	72.2	K241-1.5	77.7	K243-3.5	1.1
K260-0.5	4.7	K261-1.5	60.3	K263-3.5	30.1
K280-0.5	25.8	K281-1.5	35.8	K28-3.5	NA
L210-0.5	2.1	L211-1.5	2.9	L213-3.5	NA
L230-0.5	77.3	L231-1.5	86.6	L233-3.5	1.2
L250-0.5	2.1	L251-1.5	76.1	L25a3-3.5	49.5
L270-0.5	77.5	L271-1.5	12.8	L273-3.5	0.3
M200-0.5	2.7	M201-1.5	22.2	M203-3.5	NA
M220-0.5	12.5	M221-1.5	13.5	M223-3.5	2.1
M240-0.5	25.0	M241-1.5	75.0	M243-3.5	0.2
M260-0.5	35.3	M261-1.5	50.0	M263-3.5	NA
M280-0.5	19.3	M281-1.5	15.2	M283-3.5	0.6
N210-0.5	68.4	N211-1.5	58.0	N213-3.5	NA
N230-0.5	77.3	N231-1.5	2.2	N233-3.5	4.6
N250-0.5	3.4	N251-1.5	34.9	N253-3.5	3.7
O220-0.5	69.9	O22a1-1.5	38.1	O223-3.5	4.5
O240-0.5	54.3	O241-1.5	18.8	O243-3.5	3.2
P230-0.5	61.9	P231-1.5	2.1	P23a3-3.5	8.4
P250-0.5	62.1	P251-1.5	58.2	P253-3.5	4.4
Q240-0.5	54.4	Q24a1-1.5	25.0	Q243-3.5	34.4
Q260-0.5	15.7	Q261-1.5	NA	Q263-3.5	NA
R250-0.5	51.5	R251-1.5	17.4	R253-3.5	2.7
R270-0.5	37.2	R271-1.5	59.4	R273-3.5	51.2
S260-0.5	35.8	S261-1.5	66.1	S263-3.5	NA
T270-0.5	46.7	T271-1.5	60.3	T273-3.5	NA
U260-0.5	1.0	U261-1.5	5.6	U263-3.5	3.1

NA – indicates that no sample was taken for that interval

Table 1C-1.

Samples Sorted by Soil Texture Classifications

Brown silty sand	Rusty silty sand	Tan Silty sand (unsat.)	OM>50%	Silty sand W/OM	Tan silty sand (sat.)	Gravel/ Debris (fill)
B30-0.5	B33-3.5	B53-3.5	D191-1.5	B153-3.5	J233-3.5	D170-0.5
B31-1.5	B51-1.5	B73-3.5	G160-0.5	D171-1.5	J253-3.5	D173-3.5
B50-0.5	B71-1.5	B93-3.5	G161-1.5	G163-3.5	J271-1.5	D190-0.5
B70-0.5	B91-1.5	B113-3.5	H171-1.5	H150-0.5	K203-3.5	D193-3.5
B90-0.5	B111-1.5	B133-3.5	H193-3.5	H151-1.5	K223-3.5	E161-1.5
B110-0.5	B131-1.5	C63-3.5	I201-1.5	H153-3.5	K243-3.5	E163-3.5
B130-0.5	B151-1.5	C83-3.5	I220-0.5	H170-0.5	L211-1.5	E180-0.5
B150-0.5	B171-1.5	C103-3.5	I221-1.5	H173-3.5	L233-3.5	E181-1.5
B170-0.5	B173-3.5	C123-3.5	I223-3.5	H191-1.5	L273-3.5	F150-0.5
C20-0.5	C21-1.5	C143-3.5	J230-0.5	I200-0.5	M223-3.5	G140-0.5
C40-0.5	C23-3.5	D53-3.5	J231-1.5	J190-0.5	M243-3.5	G141-1.5
C60-0.5	C41-1.5	D113-3.5	J250-0.5	J191-1.5	M283-3.5	G143-3.5
C80-0.5	C43-3.5	D133-3.5	J251-1.5	J210-0.5	N233-3.5	H190-0.5
C100-0.5	C61-1.5	D153-3.5	K200-0.5	J211-1.5	N253-3.5	I203-3.5
C120-0.5	C81-1.5	E143-3.5	K220-0.5	K260-0.5	O223-3.5	J193-3.5
C140-0.5	C101-1.5	F133-3.5	K221-1.5	K263-3.5	O243-3.5	M281-1.5
C160-0.5	C121-1.5	F153-3.5	K240-0.5	K280-0.5	P233-3.5	
D50-0.5	C141-1.5	F173-3.5	K241-1.5	K281-1.5	P253-3.5	
D70-0.5	D51-1.5	F193-3.5	K261-1.5	L210-0.5	R253-3.5	
D90-0.5	D71-1.5	F213-3.5	L230-0.5	L271-1.5	U263-3.5	
D110-0.5	D73-3.5	G183-3.5	L231-1.5	M200-0.5		
D130-0.5	D91-1.5	G203-3.5	L250-0.5	M201-1.5		
D150-0.5	D93-3.5	G223-3.5	L253-3.5	M221-1.5		
E140-0.5	D111-1.5	H233-3.5	L270-0.5	M221-1.5		
E160-0.5	D131-1.5		M220-0.5	M260-0.5		
F130-0.5	D151-1.5		M240-0.5	M280-0.5		
F170-0.5	E141-1.5		M241-1.5	N231-1.5		
F190-0.5	E200-0.5		M261-1.5	N251-1.5		
G180-0.5	E201-1.5		N210-0.5	O221-1.5		
G200-0.5	F131-1.5		N211-1.5	O241-1.5		
H210-0.5	F151-1.5		N230-0.5	P231-1.5		
J270-0.5	F171-1.5		N250-0.5	Q241-1.5		
	F191-1.5		O220-0.5	Q243-3.5		
	F210-0.5		O240-0.5	R251-1.5		
	F211-1.5		P230-0.5	U260-0.5		
	G181-1.5		P250-0.5	U261-1.5		
	G201-1.5		P251-1.5			
	G220-0.5		Q240-0.5			

Table 1C-1 (con't.)

Brown silty sand	Rusty silty sand	Tan Silty sand (unsat.)	OM>50%	Silty sand W/OM	Tan silty sand (sat.)	Gravel/ Debris (fill)
	G221-1.5		Q260-0.5			
	H211-1.5		R250-0.5			
	H213-3.5		R270-0.5			
	H230-0.5		R271-1.5			
	H233-3.5		R273-3.5			
	I240-0.5		S260-0.5			
	I241-1.5		S261-1.5			
	I243-3.5		T270-0.5			
	I260-0.5		T271-1.5			
	I261-1.5					

APPENDIX 2

Supplemental Description of Methods

APPENDIX 2A:

Sequential Chemical Extraction Procedure

Sample preparation:

Due to the high number of samples taken for the initial investigation, three groups of eight cores were processed each week for a period of ten weeks. On subsequent sampling events for more detailed work, fewer cores were taken allowing less of a delay before extractions were performed. In all cases, soil cores were frozen (-20°C) until just before chemical extractions were to begin.

After the cores were thawed, they were placed in a glove bag, which was then evacuated and purged twice with N_2 (g) or Ar (g) to ensure an inert atmosphere. A Teflon stirrer was used to transfer about 50 grams of soil from the bottom of each core into acid washed 120mL plastic vials for homogenization. Visible debris, wood, and roots were excluded in the transfer. After homogenization, five grams (± 0.5g) of wet soil were weighed out on an acid washed watch glass for wet weight/ dry weight determination. A separate one gram (± 0.2 g) aliquot was placed into an acid washed 30 ml centrifuge tube for sequential chemical extractions (SCE). The remaining homogenized soil was saved for organic carbon (C_{org}) determination by loss on combustion. Once the weighing was completed in the glove bag the watch glasses were placed in a convection oven for 24 hours at 50°C to completely dry the soils.

Method for Sequential Chemical Extractions of Metals:

Each sequential chemical extraction step began with addition of a chemical reagent under an inert atmosphere, followed by agitation of the tightly secured centrifuge tubes to completely mix the soil/chemical mixture. Each chemical addition reacts with the soil to strip off the bound metals from targeted solid phases. After each prescribed

reaction time the leachate was separated from the soil by centrifugation at 15,000 rpm for 20 minutes. Leachate fluids were siphoned off or decanted into acid washed 30 ml syringes, then filtered through 0.4μm acid washed Nucleopore membrane filters into acid washed Nalgene™ polypropylene bottles and acidified to pH< 2 to prevent adsorption to the container walls and precipitation of metals from solution. Samples were stored in a dark 4°C refrigerator until analysis.

Methods for Sequential Chemical Extractions of Metals (modified from Matty,1992):

From each homogenous sample remove two aliquots.

Aliquot 1: place on tared watch glass; dry in oven at 50°C for 24 hours; reweigh and record percent water; perform HNO_3 microwave digestion.

Aliquot 2: place in tared centrifuge tube; perform sequential chemical extractions under N_2 using the following procedures:

I. Exchangeable Fraction

1. Place 1.0 g wet sediment into acid-washed tared centrifuge tube.
2. To each sample, SRM, and blank, add 10 mL 1.0M $MgCl_2$ (pH 7); with wrist action shaker agitate continuously for 1 hour at 20°C.
3. Centrifuge for 20 minutes at 15,000 rpm.
4. Remove leachate with a syringe and filter through 0.4µm Nuclepore filter into an acid-washed 8 or 30 mL bottle. Acidify to pH<2 with optima HNO_3.
5. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 revolutions per minute (rpm); remove supernatant and discard.

II. Weak-Acid Soluble Fraction

1. To sediment from (I) add 10 mL of 1.0M NaOAc (pH 5 with HOAc) and agitate with shaker for 5 hours at 20°C.
4. Centrifuge for 20 minutes at 15,000 rpm.
5. Remove leachate with a syringe and filter through 0.4µm Nuclepore filter into an acid-washed 8 or 30 mL bottle. Acidify to pH<2 with optima HNO_3.
6. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 rpm; remove supernatant and discard.

III. Easily Reducible Fraction

1. To sediment from (II) add 25 mL of 0.1M $NH_2OH{\cdot}HCl$ in 0.01N HNO_3 and agitate in shaker for 0.5 hours at 20°C.
2. Centrifuge for 20 minutes at 15,000 rpm.
3. Remove leachate with a syringe and filter through 0.4µm Nuclepore filter into an acid-washed 30 mL bottle.
4. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 rpm; remove supernatant and discard.

IV. Moderately Reducible Fraction

1. To sediment from (III) add 20 mL of 0.04M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc. Place sample in a water bath at 96°C for 6 hours; agitate every 30 minutes.
2. Centrifuge for 20 minutes at 15,000 rpm.

3. Remove leachate with a syringe and filter through 0.4μm Nuclepore filter into an acid-washed 30 mL bottle.
4. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 rpm; remove supernatant and discard.

V. Oxidizable Fraction I (not done under N_2)

1. To sediment from (IV) add 6 mL of NaOCl (pH 9.5 with HCl just prior to use). Place sample in a water bath at 96°C for 15 minutes.
2. Centrifuge for 20 minutes at 15,000 rpm.
3. Remove leachate with a syringe and filter through 0.4μm Nuclepore filter into an acid-washed 30 mL bottle.
4. Repeat steps 1 through 3 two more times (except for the third step of the third addition), using the vortex mixer to resuspend the sample after each addition of NaOCl.
5. Add 5 mL of 3.2M NH_4OAc (pH 2 with HNO_3) to the solution-sample mixture of the last NaOCl addition. Agitate with shaker for 1 hour at 20°C.
6. Centrifuge for 20 minutes at 15,000 rpm.
7. Remove leachate with a syringe and filter through 0.4μm Nuclepore filter into an acid-washed 30 mL bottle.
8. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 rpm; remove supernatant and discard.

VI. Oxidizable Fraction II (not done under N_2)

1. To sediment from (V) add 3 mL of 0.02N HNO_3 and 8 mL of 30% H_2O_2 (pH 2 with HNO_3) in 500 μL aliquots; agitate every 30 minutes for 5 hours in a water bath heated to 85°C; leave caps unscrewed.
2. Place samples in Wrist Action Shaker to cool.
3. Add 5 mL of 3.2M NH_4OAc(pH 2 with HNO_3). Agitate with shaker for 1 hour at 20°C.
4. Centrifuge for 20 minutes at 15,000 rpm.
5. Remove leachate with a syringe, empty the syringe into an acid-washed 25 mL volumetric flask and dilute up to 25 mL with DDW. Filter the diluted solution through a 0.4μm Nuclepore filter. Transfer solution to an acid washed 30 mL bottle.
6. Rinse sediment with 10 mL DDW in vortex mixer; centrifuge for 20 minutes at 15,000 rpm; remove supernatant and discard.

APPENDIX 2B:

Porewater Sampling and Analytical Methods

Pore Water Sampling

Geochemical parameters measured in the field included: temperature, pH, alkalinity, S^{2-}, Fe^{2+}, and Cr^{6+}. Sampler fluid preserved for laboratory analyses included separate aliquots for cations (majors and trace metals), anions (Cl^-, Br^-, NO_3^-,NO_2^-, SO_4^{2}), NH_4, CH_4, and dissolved organic carbon (DOC).

Filtration of fluid in the samplers was unnecessary because the 0.2 μm membranes used during the dialysis equilibration excluded particles from the sampler during the equilibration period.

Peeper samplers were sampled immediately upon removal from sediments at each sample location. To ensure enough fluid for analysis, four to six peeper compartments were sampled as a unit representative of an interval rather than a discrete level below the land surface. The barrel samplers were capped with air tight end caps to prevent changes in redox sensitive parameters, then returned to a central processing location for sampling. Similarly, the group of three barrels was treated as a unit.

The most redox sensitive parameters were sampled and, or, analyzed first. Aliquots for dissolved gasses CH_4, NH_4, and S^{2-}, and iron speciation were taken first, followed by aliquots for cations, anions, pH, alkalinity, dissolved organic carbon (DOC). Usually the complete sampling of a peeper was achieved within 10 minutes by a team of three to four personnel.

Analytical measurements

Temperature was measured in-situ with a digital thermometer or a conventional mercury thermometer.

An aliquot of fluid from the samplers was taken for pH measurement with a glass electrode calibrated with standard pH 4 and pH 7 buffers. The same aliquot was also titrated to below pH 4.5 with a standardized H_2SO_4 solution to determine alkalinity as HCO_3^-. Eh was measured using a silver-silver chloride single junction electrode. Redox state measurements using electrodes have often been viewed with suspicion due to the potential for disequilibrium between the redox couples in the fluid of interest (Lindberg and Runnels, 1984). Therefore, in addition to the electrode measured Eh, the concentrations of several aqueous redox couples were measured including, ferrous (Fe^{2+})-ferric (Fe^{3+}) iron, sulfide (S^{2-})-sulfate (SO_4^{2-}), and the nitrate (NO_3^-)-nitrite(NO_2^-)-ammonia(NH_4^+) triad, as well as dissolved methane(CH_4).

Ferrous iron was analyzed by the phenanthroline method (Chin 1994). The method begins by pipetting 2.5 ml of sample fluid into a spectrophotometer cuvette pre-acidified with 100 µl of Optima HCl. Then, 1 ml of phenanthroline solution, 0.5 ml of ammonium acetate, and 1 ml of DDW was added. After two to five minutes, the absorbance were measured with a Spectronic Spec 20D+ at 625 nm and compared to a three point calibration curve created in the lab by plotting concentration versus absorbance

Sulfide was analyzed by one of two methylene-blue colorimetric methods. In one procedure, 7.3 ml of sample was transferred to two Milton Roy™ 1 cm path length spectrophotometer cells. To one cell, 0.5 ml amino sulfuric acid reagent (N,N dimethyl-

p-phenylenediamine oxalate in diluted H_2SO_4) and to the other (the method blank) 0.5 ml H_2SO_4 1+1 with DDW was added. To both cells 0.15 ml $FeCl_3$ solution was added. The cells were inverted once to mix the solutions. Color developed in the first cell, if sulfide was present, by creation of methylene blue. After 3-5 minutes 1.6 ml of $(NH_4)_2H\ PO_4$ was added to both cells to reduce potential interference of excess $FeCl_3$. After 5-10 minutes the method blank cell was used to zero the instrument and then the absorbance of the sample cell was measured. Absorbances were measured with a Spectronic Spec 20D+ at 625 nm and compared to an 8 point calibration curve created in the lab by plotting concentration obtained from a titrimetric iodine procedure versus absorbance obtained from the methylene blue procedure (Cline 1979, AWWA et al., 1986).

The second procedure utilized Chemetrics Vacu-Vials™ which are self filling ampoules containing appropriate mixtures of reagents. The difference in the two analytical methods was found to be less than 10%.

Fluid samples for methane analysis were taken by simultaneously piercing the nylon membrane of a sampler and the butyl rubber septum of a scintillation vial with a double-ended needle. This method allowed the sample to be taken without the fluid coming in contact with air. A syringe and single ended needle were used to evacuate air from the scintillation vial allowing fluid to be drawn into the vial by partial vacuum.

Aliquots for NH_4 determination were stored in 10ml polypropylene Nalgene bottles and frozen on dry ice in the field. In the lab, samples were thawed and analyzed by ion selective electrode after conversion of NH_4 to NH_3^+ with a buffer solution and an ionic strength adjuster.

Aliquots for cations were pipetted into pre-acidified acid washed Nalgene™ polyethane bottles and stored at (4°C). Cation samples were acidified (pH<2) with Optima™ HNO_3. Anion samples were analyzed by ion chromatography.

Heavy metals (Cu, Mn, Pb, Zn) and major cations (Mg, Na, K) in pore water samples were analyzed on a VG-Elemental Plasma Quad 1 inductively coupled plasma-mass spectrometry (ICP-MS). Ca and Fe were determined by flame atomic absorption (FAA) spectrophotometry (Perkin-Elmer model 5100) because of interference caused by similarities in mass between ^{40}Ca and the ^{40}Ar carrier gas used in ICP-MS.

Appendix 2C:

Method for Determination of Acid Volatile Sulfide and Simultaneously Extracted Metals

Acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) determinations were preformed as described by Allen et al. (1993) and Lasorsa and Casas (1996). A schematic diagram of the AVS/SEM analytical apparatus is shown in Figure 6.

Apparatus description:

Nitrogen gas was used to purge the apparatus of oxygen prior to beginning the extractions and to act as a carrier gas for the H_2S generated during the reaction. A vanadous chloride solution was used to scrub the N_2 free of oxygen prior to entering the reaction vessel. Vanadous chloride solution was prepared by adding 4g of ammonium metavanadate boiled with 50 ml concentrated hydrochloric acid to a 500 ml volumetric flask and diluting to the mark. Amalgamated zinc, prepared by placing 15g of zinc metal in 10-20 ml distilled deionized water (DDW) before adding three drops (0.15ml) of concentrated hydrochloric acid and then adding a small amount of elemental mercury to complete the amalgamation, was added to the vanadous chloride solution (Di Toro et al. 1990). All glassware was connected with minimum lengths of Tygon tubing.

Method Development and Calibration:

The nitrogen flow rates and reaction times were varied during initial method development to determine the most efficient conditions for S^{2-} recovery. Many trial runs were performed with $NaS_2 \cdot 9H_2O$ solutions of varying concentrations to determine

trapping efficiency of the apparatus and overall performance of the method prior to sample analysis.

Low range (0-5 μmol S^{2-}/100ml) and normal range (0-25 μmol S^{2-}/100ml) calibration curves were made relating absorbance to concentration (Figure A2C1). Calibration standards, each made from a 0.05 M (50μmol S^{2-}/1ml) $NaS_2 \cdot 9H_2O$ stock solution, were made in triplicate by adding known amounts of S^{2-} to 100ml flasks filled with 80ml of 0.5 M NaOH trapping solution, adding 10 ml of mixed diamine solution (MDR), and diluting to the mark with DDDW. The MDR was prepared by mixing two solutions. For the first, 2.25g of N,N dimethyl-p-phenylenediamine oxalate was added to 660ml H_2SO_4 + 340 ml DDDW after the acid cooled. The second solution was made by adding 5.4g $FeCl_3 \cdot 9H_2O$ to 100 ml HCl, then diluting to 200 ml with DDDW (Allen et al. 1993). After 30 minutes, but not more than 2 hours, standards were diluted by a factor of 10 with 1 M H_2SO_4 in a Milton Roy spectronic cell. After another 30 minutes absorbance was measured at 670nm in a Spectronic 20D+ spectrophotometer. The average of three measurements was used to define points in the calibration curves. All standards and samples were analyzed within 3 hours.

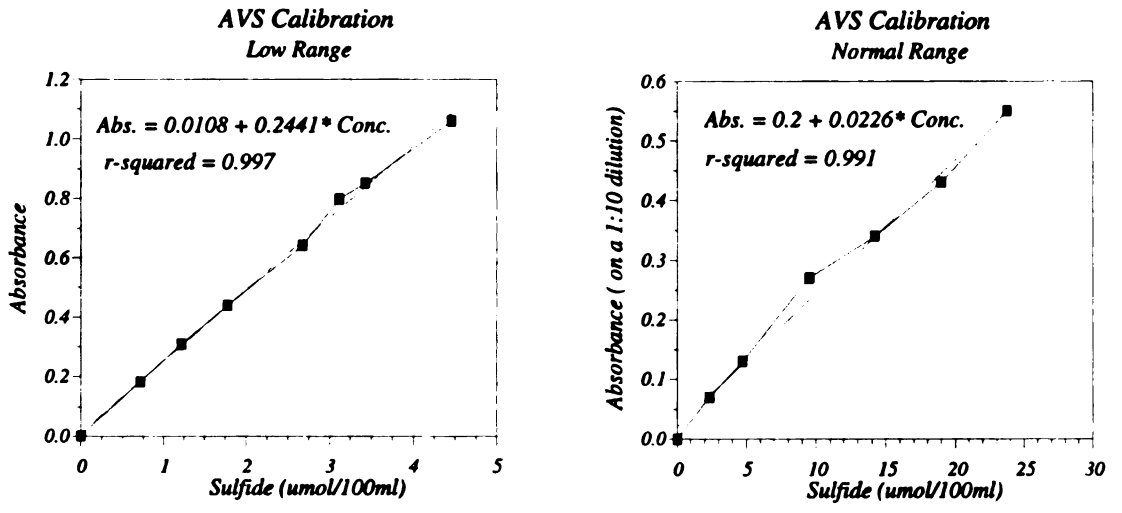

Figure A2C1. Low and normal range calibration curves for AVS method.

Sample AVS/SEM Analysis:

Undisturbed soil cores for AVS/SEM analyses were retrieved as described previously in section 3.2. Samples were frozen (-20 °C) within one hour of collection and stored for no more than three weeks. Samples were thawed, homogenized, sub-split, and weighed in a glove bag under a N_2 atmosphere.

To begin the procedure one hundred ml of DDDW and a magnetic stirring bar were added to a 250ml round ball flask in which the AVS liberation reaction would occur. Each bubbler trap was filled with 80 ml of 0.5 M NaOH. The apparatus was purged with N_2 for 10 minutes at a flow rate if 100 cm^3/min.

Three to five gram sub-splits of sediment were delivered to the reaction chamber on a piece of Parafilm™. The remaining homogenized soil was saved for sequential chemical extractions and other detailed work described below.

The reaction apparatus was purged for 10 minutes at a flow rate of 45 cm^3/min. Then 20 ml of deoxygenated 6N hydrochloric acid was injected into the reaction chamber

from a syringe attached to the tubing above the reaction vessel. This yielded a final concentration of 1N hydrochloric, causing the conversion of AVS to H_2S. Nitrogen was bubbled through the sample-acid mixture at a flow rate of 45 cm^3/min while the mixture was magnetically stirred for 35-40 minutes.

After the prescribed reaction time had elapsed, 10 ml of MDR was added to each NaOH bubblers to create methylene blue by reaction with the trapped S^{2-}. The solution was transferred to a 100 ml volumetric flask and diluted to the mark with DDDW. After 30 minutes an aliquot of this solution was either measured directly with a Spectronic™ Spec 20D+ at 670nm or diluted by a factor of ten with 1M H_2SO_4 and then measured after another 30 minutes. Methylene blue is produced by reaction between S^{2-} and the MDR. The leachate fluid in the reaction vessel containing the SEM was decanted and filtered through a 0.4µm acid washed Nuclepore™ filter into acid washed 30 ml Nalgene™ bottles.

APPENDIX 3

Supplemental Data Tables

Table 3A-1:
Sequential Chemical Extraction Data for Iron
sol'n indicates concentration detected in leachate solution, mg/L
sed indicates concentration in sediment, mg/kg (dry weight basis)
nd indicates not detected, -- indicates not measured

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
B3a0-0.5	0.42	4.3	5.52	55.9	8.36	211.6	88.00	1781.9	n.d.	n.d.	n.d.	n.d.	2053.7
B3b0-0.5	0.38	4.2	5.56	61.3	7.16	197.4	77.90	1718.0	n.d.	n.d.	n.d.	n.d.	1980.9
B3c0-0.5	0.38	3.6	5.96	57.2	6.92	166.1	82.30	1580.3	n.d.	n.d.	n.d.	n.d.	1807.3
B31-1.5	n.d.	n.d.	2.04	21.6	7.28	193.0	23.70	502.6	4.68	114.1	n.d.	n.d.	831.4
B33-3.5	n.d.	n.d.	2.48	25.2	4.32	109.6	69.60	1412.7	n.d.	n.d.	n.d.	n.d.	1547.5
B50-0.5	n.d.	n.d.	0.44	4.3	3.08	75.7	44.90	882.9	n.d.	n.d.	n.d.	n.d.	962.9
B51-1.5	n.d.	n.d.	1.40	15.2	2.52	68.3	59.50	1289.4	n.d.	n.d.	n.d.	n.d.	1372.8
B53-3.5	n.d.	n.d.	2.04	24.1	2.00	59.1	112.20	2652.5	n.d.	n.d.	n.d.	n.d.	2735.7
B70-0.5	n.d.	n.d.	1.40	13.4	2.80	67.0	11.50	220.0	n.d.	n.d.	n.d.	n.d.	300.4
B71-1.5	n.d.	n.d.	2.00	19.8	4.72	117.0	52.20	1035.3	n.d.	n.d.	n.d.	n.d.	1172.2
B73-3.5	n.d.	n.d.	2.04	22.3	2.04	55.8	14.00	306.5	n.d.	n.d.	n.d.	n.d.	384.6
B9a0-0.5	n.d.	n.d.	0.80	8.4	5.44	143.3	232.40	4898.4	n.d.	n.d.	n.d.	n.d.	5050.2
B9b0-0.5	n.d.	n.d.	0.84	9.3	5.32	147.0	230.70	5098.7	n.d.	n.d.	n.d.	n.d.	5254.9
B9c0-0.5	n.d.	n.d.	0.84	8.8	5.44	142.1	239.50	5006.4	n.d.	n.d.	n.d.	n.d.	5157.4
B91-1.5	n.d.	n.d.	2.76	29.6	2.48	66.5	165.10	3543.6	n.d.	n.d.	n.d.	n.d.	3639.7
B93-3.5	n.d.	n.d.	1.28	13.7	1.20	32.0	28.70	613.2	n.d.	n.d.	n.d.	n.d.	658.9
B110-0.5	n.d.	n.d.	1.64	20.1	7.56	231.7	--	--	n.d.	n.d.	n.d.	n.d.	--
B111-1.5	n.d.	n.d.	3.04	33.6	3.48	96.2	63.60	1406.7	n.d.	n.d.	n.d.	n.d.	1536.5
B113-3.5	n.d.	n.d.	2.32	26.5	1.44	41.1	61.70	1409.0	n.d.	n.d.	n.d.	n.d.	1476.6
B130-0.5	n.d.	n.d.	3.28	35.1	10.76	288.2	200.40	4293.7	1.30	32.0	0.75	20.1	4669.2
B13a1-1.5	0.12	1.3	7.04	73.5	11.44	298.6	97.10	2027.7	n.d.	n.d.	n.d.	n.d.	2401.1

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
B13b1-1.5	0.12	1.3	6.60	74.1	10.64	298.7	92.00	2066.2	n.d.	n.d.	n.d.	n.d.	2440.4
B13c1-1.5	0.18	2.1	6.56	75.8	10.72	309.7	102.40	2366.8	n.d.	n.d.	n.d.	n.d.	2754.4
B133-3.5	n.d.	n.d.	2.96	30.9	2.96	77.3	54.50	1138.2	n.d.	n.d.	n.d.	n.d.	1246.4
B150-0.5	n.d.	n.d.	1.36	14.7	14.00	378.7	72.50	1568.8	0.92	22.9	0.12	3.2	1988.3
B151-1.5	0.94	10.5	5.28	58.8	19.12	531.9	129.40	2880.1	4.12	105.5	0.59	16.4	3603.1
B153-3.5	n.d.	n.d.	1.08	17.0	57.24	2258.1	733.00	23132.8	29.84	1083.0	n.d.	n.d.	26490.9
B170-0.5	n.d.	n.d.	1.80	19.2	20.00	532.6	133.80	2850.3	1.18	28.9	2.02	53.8	3484.8
B171-1.5	n.d.	n.d.	4.84	48.9	9.68	244.5	107.90	2180.2	n.d.	n.d.	n.d.	n.d.	2473.6
B173-3.5	1.52	31.9	42.52	891.6	42.52	2228.9	234.10	9817.1	4.96	239.2	0.56	29.4	13238.0
C20-0.5	n.d.	n.d.	0.92	9.8	5.08	134.8	143.30	3042.6	n.d.	n.d.	n.d.	n.d.	3187.2
C21-1.5	n.d.	n.d.	1.00	9.6	1.80	43.1	32.20	617.4	n.d.	n.d.	n.d.	n.d.	670.2
C23-3.5	n.d.	n.d.	1.00	10.1	1.36	34.4	51.10	1033.3	n.d.	n.d.	n.d.	n.d.	1077.7
C40-0.5	n.d.	n.d.	1.20	13.0	4.32	117.2	134.30	2916.0	n.d.	n.d.	n.d.	n.d.	3046.2
C41-1.5	n.d.	n.d.	2.64	27.3	4.32	111.7	92.40	1912.0	n.d.	n.d.	n.d.	n.d.	2051.0
C43-3.5	n.d.	n.d.	4.00	38.4	4.96	119.2	118.20	2271.6	n.d.	n.d.	n.d.	n.d.	2429.2
C60-0.5	n.d.	n.d.	1.24	12.1	1.32	32.2	12.70	247.8	n.d.	n.d.	n.d.	n.d.	292.0
C61-1.5	n.d.	n.d.	2.12	20.5	6.08	147.2	98.30	1904.1	n.d.	n.d.	n.d.	n.d.	2071.9
C63-3.5	n.d.	n.d.	1.32	12.8	1.08	26.1	22.30	431.4	n.d.	n.d.	n.d.	n.d.	470.3
C80-0.5	0.14	1.5	4.00	43.6	12.16	331.1	56.30	1226.3	n.d.	n.d.	n.d.	n.d.	1602.4
C81-1.5	0.68	8.0	2.28	26.8	2.08	61.0	35.70	837.7	n.d.	n.d.	n.d.	n.d.	933.5
C83-3.5	n.d.	n.d.	2.48	25.6	2.56	66.0	29.60	610.9	n.d.	n.d.	n.d.	n.d.	702.6
C100-0.5	n.d.	n.d.	1.16	13.2	3.84	109.6	83.50	1906.2	n.d.	n.d.	n.d.	n.d.	2029.0
C101-1.5	n.d.	n.d.	3.48	34.4	4.20	103.7	106.20	2097.1	n.d.	n.d.	n.d.	n.d.	2235.1
C103-3.5	n.d.	n.d.	4.04	43.3	6.64	177.9	139.80	2996.9	n.d.	n.d.	n.d.	n.d.	3218.2
C120-0.5	n.d.	n.d.	1.92	21.3	5.40	150.0	113.80	2528.2	n.d.	n.d.	n.d.	n.d.	2699.5

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
C121-1.5	n.d.	n.d.	2.84	27.9	3.36	82.4	61.00	1197.4	n.d.	n.d.	n.d.	n.d.	1307.7
C123-3.5	n.d.	n.d.	1.04	12.2	1.68	49.1	39.50	923.1	n.d.	n.d.	n.d.	n.d.	984.3
C140-0.5	n.d.	n.d.	1.28	15.1	19.60	578.4	105.40	2488.3	1.34	36.4	0.24	7.1	3125.2
C141-1.5	n.d.	n.d.	3.16	33.2	3.76	98.7	47.80	1004.2	n.d.	n.d.	n.d.	n.d.	1136.2
C143-3.5	n.d.	n.d.	1.64	18.6	5.12	145.1	134.60	3051.8	n.d.	n.d.	n.d.	n.d.	3215.5
C160-0.5	n.d.	n.d.	1.32	15.5	10.52	309.7	90.80	2138.6	n.d.	n.d.	0.35	10.3	2474.2
D50-0.5	n.d.	n.d.	0.60	5.8	3.44	83.7	84.40	1643.6	n.d.	n.d.	n.d.	n.d.	1733.1
D51-1.5	n.d.	n.d.	2.28	24.4	3.24	86.8	68.20	1461.7	n.d.	n.d.	n.d.	n.d.	1572.9
D53-3.5	n.d.	n.d.	2.00	22.9	2.20	62.9	100.80	2306.2	n.d.	n.d.	n.d.	n.d.	2392.0
D70-0.5	n.d.	n.d.	12.88	144.4	19.96	559.2	42.20	945.9	n.d.	n.d.	n.d.	n.d.	1649.5
D71-1.5	n.d.	n.d.	2.80	27.2	3.36	81.5	26.50	514.0	n.d.	n.d.	n.d.	n.d.	622.6
D73-3.5	n.d.	n.d.	2.48	29.3	4.44	131.0	27.30	644.2	n.d.	n.d.	n.d.	n.d.	804.4
D90-0.5	n.d.	n.d.	1.12	11.5	4.72	121.5	71.50	1471.9	n.d.	n.d.	n.d.	n.d.	1604.8
D91-1.5	n.d.	n.d.	0.92	10.2	1.28	35.5	16.20	359.0	n.d.	n.d.	n.d.	n.d.	404.6
D9a3-3.5	n.d.	n.d.	1.24	13.8	2.56	71.3	25.10	559.4	n.d.	n.d.	n.d.	n.d.	644.5
D9b3-3.5	n.d.	n.d.	1.48	16.6	3.32	93.1	29.00	650.6	n.d.	n.d.	n.d.	n.d.	760.3
D9c3-3.5	n.d.	n.d.	1.32	15.5	2.76	80.8	26.80	627.7	n.d.	n.d.	n.d.	n.d.	724.0
D110-0.5	n.d.	n.d.	0.60	5.7	4.00	94.5	82.50	1558.6	n.d.	n.d.	n.d.	n.d.	1658.7
D111-1.5	0.60	6.2	0.42	4.4	1.20	31.1	52.00	1078.0	n.d.	n.d.	n.d.	n.d.	1119.7
D113-3.5	1.48	14.7	0.72	7.2	0.40	10.0	21.00	418.1	n.d.	n.d.	n.d.	n.d.	450.0
D130-0.5	0.24	2.5	8.44	88.9	14.00	368.8	162.60	3426.7	n.d.	n.d.	n.d.	n.d.	3886.9
D131-1.5	0.14	1.3	4.60	44.0	3.32	79.4	42.40	811.2	n.d.	n.d.	n.d.	n.d.	935.9
D133-3.5	n.d.	n.d.	2.56	28.6	3.48	97.3	69.20	1547.2	n.d.	n.d.	n.d.	n.d.	1673.0
D150-0.5	n.d.	n.d.	1.68	18.4	13.88	380.1	100.10	2193.1	n.d.	n.d.	n.d.	n.d.	2591.6
D151-1.5	n.d.	n.d.	4.32	43.1	12.80	319.0	259.60	5176.3	n.d.	n.d.	n.d.	n.d.	5538.4

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
D153-3.5	n.d.	n.d.	5.68	58.7	8.68	224.1	81.40	1681.5	n.d.	n.d.	n.d.	n.d.	1964.3
D170-0.5	0.10	1.6	4.76	74.0	26.64	1034.9	257.50	8002.7	27.72	990.7	3.08	119.7	10223.6
D171-1.5	0.22	3.2	1.40	20.5	23.56	862.2	90.90	2661.1	29.86	1005.3	0.93	34.0	4586.3
D173-3.5	0.18	2.1	8.68	103.2	40.84	1213.8	104.70	2489.5	n.d.	n.d.	n.d.	n.d.	3808.7
D190-0.5	n.d.	n.d.	2.72	33.5	22.16	682.2	255.40	6290.2	7.98	226.0	4.08	125.6	7357.5
D191-1.5	0.58	11.0	7.44	141.0	22.96	1088.2	101.40	3844.7	32.50	1417.1	1.66	78.7	6580.7
D193-3.5	n.d.	n.d.	47.00	559.4	108.24	3220.5	34.30	816.4	n.d.	n.d.	1.59	47.3	4643.6
E140-0.5	n.d.	n.d.	1.00	10.5	9.84	258.5	66.80	1404.0	n.d.	n.d.	n.d.	n.d.	1673.0
E141-1.5	n.d.	n.d.	6.48	73.6	23.48	666.7	340.00	7723.4	n.d.	n.d.	n.d.	n.d.	8463.7
E143-3.5	n.d.	n.d.	2.00	21.7	12.00	326.1	176.40	3834.6	n.d.	n.d.	n.d.	n.d.	4182.4
E160-0.5	n.d.	n.d.	0.96	14.5	6.72	253.2	42.60	1284.0	2.98	103.3	1.47	55.4	1710.3
E161-1.5	n.d.	n.d.	0.80	15.2	3.40	161.8	39.00	1484.5	1.74	76.2	5.44	258.8	1996.5
E163-3.5	n.d.	n.d.	4.84	115.3	21.52	1281.7	71.30	3397.2	n.d.	n.d.	0.49	29.2	4823.4
E180-0.5	n.d.	n.d.	7.48	109.6	33.56	1229.3	170.80	5005.3	n.d.	n.d.	3.17	116.1	6460.3
E181-1.5	n.d.	n.d.	1.60	39.0	1.84	112.1	18.40	896.5	n.d.	n.d.	0.24	14.6	1062.1
E200-0.5	n.d.	n.d.	1.32	15.0	8.60	244.4	49.50	1125.6	n.d.	n.d.	n.d.	n.d.	1385.1
E201-1.5	n.d.	n.d.	1.40	13.8	6.28	154.4	56.70	1115.4	n.d.	n.d.	n.d.	n.d.	1283.6
F130-0.5	n.d.	n.d.	4.52	44.4	11.64	285.6	88.00	1727.1	n.d.	n.d.	n.d.	n.d.	2057.1
F131-1.5	n.d.	n.d.	2.48	25.1	8.76	221.9	205.30	4160.9	n.d.	n.d.	n.d.	n.d.	4407.9
F133-3.5	n.d.	n.d.	0.68	7.4	2.24	60.5	56.70	1226.0	n.d.	n.d.	n.d.	n.d.	1293.9
F150-0.5	n.d.	n.d.	1.28	19.5	16.80	640.0	103.00	3138.9	4.32	151.4	0.49	18.7	3968.4
F151-1.5	n.d.	n.d.	1.60	15.8	22.40	551.6	88.00	1733.7	n.d.	n.d.	n.d.	n.d.	2301.1
F153-3.5	n.d.	n.d.	1.40	14.7	13.20	347.4	126.00	2653.1	n.d.	n.d.	0.31	8.2	3023.4
F170-0.5	n.d.	n.d.	0.92	11.5	10.20	319.5	124.20	3112.1	n.d.	n.d.	0.26	8.1	3451.3
F171-1.5	n.d.	n.d.	4.72	50.7	4.92	132.1	47.40	1018.4	n.d.	n.d.	n.d.	n.d.	1201.3

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
F17a3-3.5	n.d.	n.d.	0.96	12.2	2.68	85.4	56.50	1440.3	n.d.	n.d.	n.d.	n.d.	1537.9
F17b3-3.5	n.d.	n.d.	1.08	11.8	3.80	103.9	64.50	1411.3	n.d.	n.d.	n.d.	n.d.	1527.0
F17c3-3.5	n.d.	n.d.	1.04	11.3	4.12	112.2	65.70	1431.6	n.d.	n.d.	n.d.	n.d.	1555.2
F190-0.5	n.d.	n.d.	2.48	27.6	10.04	279.1	165.70	3684.8	0.96	24.6	0.10	2.8	4018.8
F191-1.5	n.d.	n.d.	10.60	111.1	6.80	178.1	187.00	3919.2	n.d.	n.d.	n.d.	n.d.	4208.4
F193-3.5	n.d.	n.d.	4.20	47.2	3.08	86.6	96.40	2167.5	n.d.	n.d.	n.d.	n.d.	2301.3
F210-0.5	n.d.	n.d.	1.04	11.7	3.52	98.8	77.60	1743.1	n.d.	n.d.	n.d.	n.d.	1853.6
F211-1.5	n.d.	n.d.	2.96	29.3	4.76	117.7	129.80	2567.9	n.d.	n.d.	n.d.	n.d.	2714.9
F213-3.5	n.d.	n.d.	4.64	46.5	4.56	114.2	109.10	2185.3	n.d.	n.d.	n.d.	n.d.	2346.0
G140-0.5	n.d.	n.d.	14.16	214.7	104.00	3942.5	97.00	2941.7	n.d.	n.d.	n.d.	n.d.	7098.9
G141-1.5	n.d.	n.d.	1.84	30.3	47.60	1962.3	28.00	923.4	n.d.	n.d.	n.d.	n.d.	2916.1
G143-3.5	n.d.	n.d.	25.08	261.5	9.20	239.9	23.00	479.7	n.d.	n.d.	n.d.	n.d.	981.1
G160-0.5	1.96	118.4	12.48	754.1	8.80	1329.4	7.00	846.0	9.96	1384.2	2.32	350.5	4782.6
G161-1.5	0.32	5.1	21.06	334.3	78.00	3095.8	21.00	666.8	n.d.	n.d.	n.d.	n.d.	4102.0
G163-3.5	1.74	24.8	502.80	7179.2	156.40	5582.8	28.00	799.6	n.d.	n.d.	0.19	6.8	13593.2
G180-0.5	n.d.	n.d.	1.32	15.4	5.52	160.8	63.10	1470.5	n.d.	n.d.	0.08	2.3	1649.0
G181-1.5	n.d.	n.d.	2.32	25.6	2.80	77.4	80.10	1770.3	n.d.	n.d.	n.d.	n.d.	1873.3
G183-3.5	n.d.	n.d.	1.76	18.1	2.52	64.8	73.40	1509.8	n.d.	n.d.	n.d.	n.d.	1592.7
G200-0.5	18.30	220.0	24.48	294.3	17.00	510.9	83.10	1998.1	n.d.	n.d.	n.d.	n.d.	3023.3
G201-1.5	n.d.	n.d.	6.72	70.0	5.28	137.5	161.80	3370.4	n.d.	n.d.	n.d.	n.d.	3577.9
G203-3.5	n.d.	n.d.	1.92	20.7	3.04	81.8	57.00	1227.7	n.d.	n.d.	n.d.	n.d.	1330.2
G220-0.5	n.d.	n.d.	1.52	17.1	10.52	296.2	91.90	2070.2	n.d.	n.d.	n.d.	n.d.	2383.6
G221-1.5	n.d.	n.d.	2.40	26.0	18.92	512.9	57.70	1251.3	n.d.	n.d.	0.20	5.4	1795.7
G223-3.5	n.d.	n.d.	2.20	23.8	13.36	361.7	125.10	2709.3	n.d.	n.d.	n.d.	n.d.	3094.8
H150-0.5	n.d.	n.d.	6.76	127.4	41.60	1959.5	82.00	3090.0	1.22	52.9	0.15	7.1	5236.8

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
H151-1.5	n.d.	n.d.	1.84	30.6	87.20	3623.9	60.00	1994.8	n.d.	n.d.	n.d.	n.d.	5649.2
H153-3.5	0.44	8.1	15.92	292.4	71.60	3287.2	24.00	881.5	n.d.	n.d.	0.13	6.0	4475.1
H170-0.5	n.d.	n.d.	1.20	30.7	5.60	357.7	20.00	1022.0	n.d.	n.d.	n.d.	n.d.	1410.4
H171-1.5	n.d.	n.d.	2.92	140.3	8.40	1009.2	6.00	576.7	0.38	42.0	n.d.	n.d.	1768.2
H173-3.5	1.62	20.9	170.80	2205.4	54.80	1768.9	20.00	516.5	n.d.	n.d.	0.20	6.5	4518.2
H190-0.5	n.d.	n.d.	0.72	10.1	9.28	325.3	130.20	3651.0	8.02	258.6	1.52	53.3	4298.3
H191-1.5	n.d.	n.d.	0.64	13.5	16.84	885.6	123.50	5195.8	14.48	700.6	0.32	16.8	6812.3
H193-3.5	1.94	93.7	25.20	1216.7	42.56	5137.3	89.60	8652.3	6.46	717.4	1.12	135.2	15952.6
H210-0.5	n.d.	n.d.	0.60	5.5	3.00	68.8	50.20	921.0	n.d.	n.d.	n.d.	n.d.	995.3
H211-1.5	0.26	4.8	1.24	22.8	9.32	428.5	109.30	4020.3	2.60	110.0	0.20	9.2	4595.6
H213-3.5	n.d.	n.d.	2.08	21.8	6.88	179.9	61.50	1286.5	n.d.	n.d.	n.d.	n.d.	1488.2
H23a0-0.5	n.d.	n.d.	14.24	171.3	17.56	528.2	85.70	2062.1	n.d.	n.d.	n.d.	n.d.	2761.6
H23b0-0.5	n.d.	n.d.	15.76	173.5	18.52	509.8	90.10	1984.2	n.d.	n.d.	n.d.	n.d.	2667.6
H23c0-0.5	n.d.	n.d.	15.92	193.3	20.08	609.6	95.40	2316.9	n.d.	n.d.	n.d.	n.d.	3119.9
H231-1.5	13.90	109.9	22.20	175.5	11.84	234.0	100.50	1589.3	n.d.	n.d.	0.75	14.8	2123.6
H233-3.5	n.d.	n.d.	0.88	10.1	5.68	163.2	62.40	1434.6	n.d.	n.d.	n.d.	n.d.	1607.9
I200-0.5	n.d.	n.d.	3.24	82.4	7.56	480.8	65.50	3332.8	4.26	249.3	0.63	40.1	4185.5
I201-1.5	0.18	6.8	7.40	278.6	26.44	2488.2	219.50	16525.5	10.70	926.4	1.76	165.6	20391.1
I203-3.5	0.28	17.2	8.36	513.6	4.20	645.1	4.90	602.1	6.46	912.8	34.40	5283.6	7974.5
I220-0.5	1. 6	32.7	4.40	135.8	5.00	385.7	9.40	580.0	n.d.	n.d.	0.18	13.9	1148.1
I221-1.5	0.76	32.9	2.68	115.9	3.56	385.0	4.56	394.5	4.10	407.9	4.11	444.5	1780.7
I223-3.5	n.d.	n.d.	1.24	15.3	3.04	93.6	20.72	510.3	n.d.	n.d.	n.d.	n.d.	619.2
I240-0.5	3.88	51.7	4.68	62.3	15.32	510.0	65.20	1736.3	n.d.	n.d.	n.d.	n.d.	2360.2
I241-1.5	8.70	106.6	4.72	57.9	5.00	153.2	39.20	961.0	n.d.	n.d.	n.d.	n.d.	1278.7
I243-3.5	1.18	13.6	3.08	35.4	9.76	280.7	63.50	1461.2	n.d.	n.d.	n.d.	n.d.	1790.9
I260-0.5	0.16	1.8	1.40	16.0	15.24	435.4	196.40	4489.1	5.68	149.3	1.82	52.0	5143.6

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
I26a1-1.5	n.d.	n.d.	1.48	15.9	28.24	756.8	291.70	6254.0	1.88	46.4	0.23	6.2	7079.2
I26b1-1.5	n.d.	n.d.	1.88	19.5	28.56	739.9	285.40	5914.9	1.92	45.8	0.59	15.3	6735.4
I26c1-1.5	n.d.	n.d.	1.76	19.4	27.72	762.6	272.30	5993.0	0.92	23.3	0.19	5.2	6803.5
J19a0-0.5	0.20	6.7	1.48	49.5	4.56	381.1	122.60	8197.5	3.80	292.2	1.65	137.9	9064.9
J19b0-0.5	0.16	5.2	1.68	54.1	5.84	470.5	139.40	8984.9	3.20	237.2	1.46	117.6	9869.6
J19c0-0.5	0.18	6.3	1.44	50.0	5.08	441.1	132.60	9210.5	4.76	380.2	1.04	90.3	10178.3
J191-1.5	n.d.	n.d.	5.80	198.1	22.80	1947.1	54.90	3750.8	1.10	86.4	0.33	28.2	6010.6
J193-3.5	0.22	7.5	1.96	66.7	2.04	173.5	2.28	155.2	0.30	23.5	0.67	57.0	483.4
J210-0.5	0.14	1.7	2.76	33.6	12.52	380.5	86.50	2103.3	n.d.	n.d.	n.d.	n.d.	2519.1
J211-1.5	13.00	135.8	4.84	50.6	10.56	275.9	64.20	1341.7	n.d.	n.d.	n.d.	n.d.	1803.9
J230-0.5	0.10	6.4	1.48	95.1	2.32	372.8	5.60	719.8	n.d.	n.d.	0.36	57.8	1252.0
J231-1.5	1. 4	48.5	4.28	199.6	8.52	993.2	18.70	1743.9	n.d.	n.d.	1.13	131.7	3116.9
J233-3.5	n.d.	n.d.	0.52	5.4	5.16	134.2	46.80	973.5	n.d.	n.d.	n.d.	n.d.	1113.1
J250-0.5	0.28	4.2	0.52	7.9	17.00	644.3	122.50	3714.2	12.86	448.4	2.15	81.5	4900.6
J251-1.5	n.d.	n.d.	0.12	3.9	2.00	161.9	1.79	115.9	n.d.	n.d.	0.20	16.2	297.9
J253-3.5	n.d.	n.d.	0.68	7.1	6.40	167.4	30.40	636.2	0.00	n.d.	0.14	3.7	814.4
J270-0.5	4.42	56.8	2.24	28.8	8.64	277.5	32.80	842.7	1.26	37.2	0.16	5.1	1248.1
J271-1.5	n.d.	n.d.	0.92	10.1	2.36	64.8	26.10	573.4	n.d.	n.d.	n.d.	n.d.	648.3
K200-0.5	2 .7	1216.4	2.32	136.3	7.84	1151.8	10.50	1234.0	0.94	127.0	0.46	67.6	3933.1
K203-3.5	n.d.	n.d.	17.72	229.0	17.56	567.2	59.00	1524.7	n.d.	n.d.	0.11	3.6	2324.4
K220-0.5	0.32	98.5	0.92	283.3	14.44	11116.9	23.50	14473.5	18.24	12919.0	7.02	5404.5	44295.7
K221-1.5	n.d.	n.d.	2.92	138.1	43.64	5160.1	74.80	7075.6	10.52	1144.4	0.19	22.5	13540.6
K223-3.5	0.28	2.6	5.36	49.6	3.24	74.9	21.50	397.6	n.d.	n.d.	0.06	1.4	526.0
K240-0.5	11.90	487.6	15.12	619.5	24.44	2503.6	56.80	4654.8	2.90	273.3	0.98	100.4	8639.3
K241-1.5	8.70	390.5	2.96	132.8	11.64	1306.0	10.30	924.5	7.38	761.8	10.05	1127.6	4643.2
K243-3.5	4.88	52.3	8.48	90.9	7.64	204.8	37.40	802.2	n.d.	n.d.	0.05	1.3	1151.6

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
K260-0.5	0.22	3.0	1.20	16.2	37.40	1260.6	125.70	3389.5	1.96	60.8	0.88	29.7	4759.7
K261-1.5	n.d.	n.d.	0.64	29.2	16.00	1824.2	26.30	2398.8	6.94	727.9	1.16	132.3	5112.4
K263-3.5	0.86	15.4	1.16	20.7	20.52	917.2	75.20	2689.1	5.76	236.9	1.05	46.9	3926.2
K280-0.5	2.92	66.1	0.76	17.2	12.60	712.7	34.40	1556.6	5.40	281.0	0.36	20.4	2653.9
K281-1.5	4.92	164.0	4.88	162.6	21.44	1786.2	45.10	3005.9	18.62	1427.2	0.79	65.8	6611.8
L210-0.5	n.d.	n.d.	0.32	3.4	37.72	995.8	143.90	3039.3	n.d.	n.d.	0.05	1.3	4039.8
L211-1.5	n.d.	n.d.	3.76	39.6	16.20	426.7	106.90	2252.4	n.d.	n.d.	0.06	1.6	2720.3
L230-0.5	n.d.	n.d.	0.40	27.3	9.84	1676.4	14.40	1962.6	1.14	178.7	0.42	71.6	3916.5
L231-1.5	n.d.	n.d.	1.48	90.8	31.28	4799.4	53.80	6603.8	2.56	361.4	0.42	64.4	11919.9
L233-3.5	7.80	84.0	5.92	63.8	11.56	311.2	52.60	1132.9	n.d.	n.d.	n.d.	n.d.	1591.9
L250-0.5	n.d.	n.d.	7.40	78.3	16.96	448.6	105.60	2234.7	n.d.	n.d.	0.08	2.1	2763.7
L251-1.5	35.60	1380.1	0.44	17.1	7.28	705.6	14.80	1147.5	2.18	194.4	0.25	24.2	3468.9
L25a3-3.5	5.18	196.4	0.92	34.9	10.72	1016.0	32.30	2448.9	6.18	538.8	0.92	87.2	4322.2
L25b3-3.5	4.34	193.9	2.48	110.8	9.04	1009.7	23.60	2108.8	5.18	532.3	17.04	1903.3	5858.9
L25c3-3.5	6.10	218.0	0.88	31.5	11.48	1025.8	37.50	2680.7	6.90	567.2	0.87	77.7	4601.0
L270-0.5	n.d.	n.d.	0.44	22.4	11.52	1463.6	11.40	1158.7	2.28	266.5	1.80	228.7	3139.9
L271-1.5	n.d.	n.d.	0.28	6.6	6.12	360.2	22.90	1078.1	1.88	101.8	0.16	9.4	1556.1
L273-3.5	n.d.	n.d.	6.20	66.5	10.92	292.9	42.60	914.0	n.d.	n.d.	n.d.	n.d.	1273.3
M200-0.5	n.d.	n.d.	1.12	12.8	10.16	291.2	61.30	1405.6	n.d.	n.d.	n.d.	n.d.	1709.6
M201-1.5	2 .9	457.5	0.72	15.8	7.40	405.0	14.50	634.8	2.64	132.9	0.07	3.8	1649.9
M220-0.5	46.80	854.8	18.68	341.2	20.28	926.0	49.40	1804.5	1.00	42.0	0.09	4.1	3972.5
M221-1.5	18.00	263.8	2.68	39.3	9.80	359.1	37.10	1087.5	3.62	122.0	0.07	2.6	1874.2
M223-3.5	3.42	36.3	8.64	91.6	11.44	303.1	50.70	1074.8	n.d.	n.d.	0.03	0.8	1506.6
M240-0.5	4.40	104.0	0.80	18.9	13.04	770.9	27.10	1281.7	8.36	454.7	0.39	23.1	2653.3
M241-1.5	0.32	15.6	0.22	10.7	8.96	1088.7	7.50	729.0	30.52	3411.6	1.28	155.5	5411.1
M243-3.5	0.26	2.9	4.72	53.2	2.32	65.4	17.60	397.0	n.d.	n.d.	n.d.	n.d.	518.6

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
M260-0.5	6.70	153.0	2.24	51.2	24.92	1422.8	96.80	4421.3	9.18	482.2	1.02	58.2	6588.6
M261-1.5	1.46	40.5	0.68	18.9	10.56	732.6	19.40	1076.7	7.70	491.4	0.70	48.6	2408.6
M280-0.5	39.40	860.3	17.44	380.8	53.08	2897.5	81.80	3572.2	3.50	175.8	0.38	20.7	7907.3
M281-1.5	6.00	115.0	11.88	227.7	19.40	929.7	57.10	2189.0	n.d.	n.d.	0.31	14.9	3476.3
M283-3.5	1.82	20.4	9.28	104.2	17.36	487.5	57.50	1291.9	n.d.	n.d.	0.03	0.8	1904.9
N210-0.5	2.00	717.8	9.32	334.5	16.80	1507.5	23.80	1708.5	1.08	89.2	0.25	22.4	4379.9
N211-1.5	1.30	40.1	1.92	59.2	7.20	554.7	9.00	554.7	11.06	783.9	5.58	429.9	2422.5
N230-0.5	41.20	2364.5	5.16	296.1	16.04	2301.4	18.00	2066.1	1.16	153.1	0.68	97.6	7278.8
N231-1.5	5.58	66.2	2.12	25.2	3.56	105.7	13.80	327.6	n.d.	n.d.	0.15	4.5	529.2
N233-3.5	12.90	164.4	6.16	78.5	9.48	302.1	31.10	792.9	n.d.	n.d.	0.09	2.9	1340.8
N250-0.5	24.40	283.8	10.12	117.7	16.32	474.6	50.30	1170.2	n.d.	n.d.	0.27	7.9	2054.2
N251-1.5	13.20	307.4	2.92	68.0	13.48	784.9	20.70	964.3	2.04	109.3	0.36	21.0	2254.9
N253-3.5	4.18	51.0	1.56	19.0	10.96	334.3	51.10	1246.8	n.d.	n.d.	0.61	18.6	1669.7
O220-0.5	n.d.	n.d.	1.28	44.6	8.72	759.7	66.60	4641.5	2.10	168.3	0.26	22.7	5636.7
O22a1-1.5	n.d.	n.d.	8.08	312.1	22.16	2140.0	60.80	4697.2	0.60	53.3	n.d.	n.d.	7202.7
O22b1-1.5	n.d.	n.d.	7.92	305.9	20.56	1985.5	50.00	3862.9	0.22	19.5	n.d.	n.d.	6173.8
O22c1-1.5	n.d.	n.d.	7.88	296.1	23.36	2194.4	53.50	4020.5	0.42	36.3	n.d.	n.d.	6547.3
O223-3.5	n.d.	n.d.	71.80	944.5	27.04	889.2	35.40	931.3	n.d.	n.d.	n.d.	n.d.	2765.1
O240-0.5	15.00	705.3	10.00	470.2	23.44	2755.2	28.00	2632.9	2.08	224.9	0.37	43.5	6832.0
O241-1.5	12.00	258.1	4.36	93.8	7.68	412.9	69.10	2972.1	n.d.	n.d.	0.10	5.4	3742.2
O243-3.5	2.94	40.5	18.16	250.4	22.36	770.7	47.90	1320.8	n.d.	n.d.	0.02	0.7	2383.0
P230-0.5	n.d.	n.d.	3.12	165.3	13.60	1801.5	42.70	4525.0	0.44	53.6	0.66	87.4	6632.9
P231-1.5	n.d.	n.d.	6.92	89.1	7.60	244.6	27.50	707.9	0.16	4.7	0.12	3.9	1050.2
P23a3-3.5	0.94	13.8	20.72	304.9	25.60	941.9	60.70	1786.6	0.18	6.1	n.d.	n.d.	3053.4
P23b3-3.5	1.56	20.6	16.32	215.1	29.08	958.3	61.90	1631.8	0.54	16.4	n.d.	n.d.	2842.2
P23c3-3.5	3.26	45.3	11.84	164.7	28.68	997.1	62.50	1738.4	0.12	3.8	n.d.	n.d.	2949.3

Table 3A-1: continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 Sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
P250-0.5	13.80	833.6	2.52	152.2	9.60	1449.7	21.00	2536.9	2.40	333.4	0.28	42.3	5348.1
P251-1.5	25.80	1210.1	2.88	135.1	8.96	1050.6	22.10	2073.0	n.d.	n.d.	0.54	63.3	4532.1
P253-3.5	3.74	46.7	2.04	25.4	4.56	142.2	12.10	301.9	n.d.	n.d.	0.17	5.3	521.5
Q240-0.5	n.d.	n.d.	1.52	38.9	13.56	867.2	92.90	4753.0	12.06	709.6	1.71	109.4	6478.0
Q24a1-1.5	0.12	3.3	3.60	98.8	11.64	798.3	40.70	2232.9	0.62	39.1	0.45	30.9	3203.2
Q24b1-1.5	0.46	12.3	3.48	93.0	10.96	732.2	40.30	2153.8	0.56	34.4	0.15	10.0	3035.7
Q24c1-1.5	0.50	13.7	4.44	121.8	10.60	726.9	38.10	2090.3	0.34	21.5	0.22	15.1	2989.3
Q243-3.5	n.d.	n.d.	5.12	130.5	12.80	815.5	20.10	1024.5	4.74	277.8	7.08	451.1	2699.5
Q260-0.5	0.68	8.3	96.00	1176.2	133.30	4083.0	145.10	3555.6	3.08	86.8	1.29	39.5	8949.4
R250-0.5	31.20	1106.0	16.36	579.9	27.88	2470.8	65.70	4657.9	3.66	298.4	0.30	26.6	9139.6
R251-1.5	11.00	219.7	2.52	50.3	10.52	525.3	39.80	1589.7	1.00	45.9	0.26	13.0	2443.9
R253-3.5	14.00	169.9	17.40	211.2	20.28	615.3	35.70	866.5	n.d.	n.d.	0.16	4.9	1867.7
R270-0.5	31.00	1175.7	10.40	394.4	13.28	1259.1	30.20	2290.7	0.18	15.7	0.34	32.2	5167.8
R271-1.5	7.30	393.6	5.88	317.0	6.36	857.2	17.80	1919.3	1.74	215.8	0.66	89.0	3791.9
R273-3.5	4.60	154.5	2.36	79.3	12.08	1014.5	28.10	1888.0	2.94	227.2	15.12	1269.9	4633.4
S260-0.5	n.d.	n.d.	1.60	42.1	21.44	1411.8	105.20	5541.7	7.62	461.6	1.00	65.8	7523.1
S261-1.5	21.60	1069.9	3.16	156.5	16.72	2070.5	38.40	3804.2	5.02	571.9	0.13	16.1	7689.1
T270-0.5	n.d.	n.d.	1.40	35.3	16.00	1007.3	75.90	3822.8	4.66	269.9	2.19	137.9	5273.2
T271-1.5	9.80	405.9	2.68	111.0	9.92	1027.1	30.80	2551.1	0.90	85.7	0.34	35.2	4216.0
U260-0.5	n.d.	n.d.	3.48	36.2	6.44	167.4	48.30	1004.3	n.d.	n.d.	0.12	3.1	1210.9
U261-1.5	5.70	64.5	6.28	71.1	14.52	411.0	66.10	1496.6	n.d.	n.d.	0.11	3.1	2046.3
U263-3.5	6.52	74.1	14.56	165.5	13.72	390.0	40.40	918.6	n.d.	n.d.	0.19	5.4	1553.7

Table 3A-2: Replicate Sample Analysis for Iron

sed indicates concentration in sediment (dry weight basis)

AVG indicates the average of thee replicate samples. RSD indicates the relative standard deviation of the three replicates. SRM 2704 is NIST Buffalo River Sediment

Sample Replicate	EX sed	WAS sed	ER sed	MR sed	OX1 sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	Mg/kg
B3a0-0.5	4.25	55.89	211.61	1781.95	n.d.	n.d.	2053.69
B3b0-0.5	4.19	61.31	197.38	1717.99	n.d.	n.d.	1980.87
B3c0-0.5	3.65	57.22	166.10	1580.33	n.d.	n.d.	1807.29
AVG	4.03	58.14	191.69	1693.42	n.d.	n.d.	1947.29
RSD	8.24	4.86	12.14	6.08	--	--	6.50
B9a0-0.5	n.d.	8.43	143.33	4898.43	n.d.	n.d.	5050.19
B9b0-0.5	n.d.	9.28	146.97	5098.65	n.d.	n.d.	5254.90
B9c0-0.5	n.d.	8.78	142.15	5006.45	n.d.	n.d.	5157.37
AVG	n.d.	8.83	144.15	5001.18	n.d.	n.d.	5154.16
RSD	--	4.85	1.74	2.00	--	--	1.99
B13a1-1.5	1.25	73.51	298.62	2027.71	n.d.	n.d.	2401.09
B13b1-1.5	1.35	74.11	298.70	2066.20	n.d.	n.d.	2440.36
B13c1-1.5	2.08	75.81	309.71	2366.76	n.d.	n.d.	2754.36
AVG	1.56	74.48	302.35	2153.56	n.d.	n.d.	2531.94
RSD	29.02	1.60	2.11	8.62	--	--	7.65

Table 3A-2 continued:

Sample Replicate	EX sed	WAS sed	ER sed	MR sed	OX1 sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	Mg/kg
D9a3-3.5	n.d.	13.82	71.31	559.36	n.d.	n.d.	644.49
D9b3-3.5	n.d.	16.60	93.10	650.57	n.d.	n.d.	760.27
D9c3-3.5	n.d.	15.46	80.81	627.74	n.d.	n.d.	724.01
AVG	n.d.	15.29	81.74	612.56	n.d.	n.d.	709.59
RSD	--	9.15	13.36	7.75	--	--	8.35
F17a3-3.5	n.d.	12.24	85.40	1440.27	n.d.	n.d.	1537.90
F17b3-3.5	n.d.	11.82	103.93	1411.27	n.d.	n.d.	1527.02
F17c3-3.5	n.d.	11.33	112.22	1431.62	n.d.	n.d.	1555.17
AVG	n.d.	11.79	100.52	1427.72	n.d.	n.d.	1540.03
RSD	--	3.84	13.66	1.04	--	--	0.92
I26a1-1.5	n.d.	15.87	756.82	6253.98	46.35	6.16	7079.19
I26b1-1.5	n.d.	19.48	739.89	5914.95	45.76	15.28	6735.36
I26c1-1.5	n.d.	19.37	762.61	5993.04	23.29	5.23	6803.53
AVG	n.d.	18.24	753.11	6053.99	38.47	8.89	6872.69
RSD	--	11.27	1.57	2.93	34.19	62.48	2.65
J19a0-0.5	6.69	49.48	381.12	8197.51	292.20	137.91	9064.90
J19b0-0.5	5.16	54.14	470.52	8984.94	237.19	117.63	9869.57
J19c0-0.5	6.25	50.01	441.07	9210.46	380.23	90.30	10178.33
AVG	6.03	51.21	430.90	8797.64	303.20	115.28	9704.27
RSD	13.07	4.98	10.57	6.05	23.80	20.72	5.92

Table 3A-2 continued:

Sample Replicate	EX sed	WAS sed	ER sed	MR sed	OX1 sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
L25a3-3.5	196.37	34.88	1015.97	2448.94	538.84	87.19	4322.20
L25b3-3.5	193.91	110.80	1009.74	2108.84	532.30	1903.32	5858.92
L25c3-3.5	218.03	31.45	1025.83	2680.73	567.24	77.74	4601.03
AVG	202.77	59.04	1017.18	2412.84	546.13	689.42	4927.38
RSD	6.55	75.97	0.80	11.92	3.40	152.49	16.62
O22a1-1.5	n.d.	312.12	2140.02	4697.23	53.31	n.d.	7202.67
O22b1-1.5	n.d.	305.94	1985.51	3862.85	19.55	n.d.	6173.84
O22c1-1.5	n.d.	296.09	2194.38	4020.53	36.30	n.d.	6547.30
AVG	n.d.	304.72	2106.64	4193.54	36.38	n.d.	6641.27
RSD	--	2.65	5.14	10.57	46.40	--	7.84
P23a3-3.5	13.83	304.93	941.88	1786.64	6.09	0.00	3053.38
P23b3-3.5	20.56	215.12	958.28	1631.84	16.37	0.00	2842.17
P23c3-3.5	45.34	164.66	997.12	1738.35	3.84	0.00	2949.30
AVG	26.58	228.24	965.76	1718.94	8.77	0.00	2948.29
RSD	62.42	31.13	2.94	4.61	76.20	--	3.58
Q24a1-1.5	3.29	98.75	798.26	2232.95	39.12	30.86	3203.24
Q24b1-1.5	12.29	92.99	732.19	2153.82	34.42	10.02	3035.74
Q24c1-1.5	13.72	121.80	726.94	2090.30	21.45	15.09	2989.30
AVG	9.77	104.52	752.47	2159.02	31.66	18.66	3076.09
RSD	57.87	14.58	5.28	3.31	28.90	58.26	3.66

Table 3A-2 continued:

Sample Replicate	EX sed	WAS sed	ER sed	MR sed	OX1 sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SRM27042/3/97	1.7	657.2	2661.1	5174.1	n.d.	n.d.	8494.1
SRM27042/17/97	1.4	830.1	2696.5	4644.0	n.d.	n.d.	8171.9
SRM27042/24/97	1.3	1196.6	2266.2	5411.4	n.d.	n.d.	8875.5
SRM27043/10/97	0.6	811.0	2964.9	5758.8	n.d.	n.d.	9535.4
SRM27043/24/97	1.0	875.8	2510.8	5360.6	n.d.	n.d.	8748.2
SRM27044/7/97	0.9	635.1	3077.1	5698.3	n.d.	n.d.	9411.4
AVG	1.13	834.30	2696.10	5341.21	n.d.	n.d.	8872.74
RSD	33.98	24.25	10.98	7.59	--	--	5.92

Table 3B-1:
Sequential Chemical Extraction Data for Copper
sol'n indicates concentration detected in leachate solution, mg/L
sed indicates concentration in sediment, mg/kg (dry weight basis)
nd indicates not detected, -- indicates not measured

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
B30-0.5	--	--	--	--	28.9	0.7	22.5	0.5	--	--	1.7	0.0	1.2
B31-1.5	--	--	n.d.	n.d.	15.60	0.41	5.50	0.12	446.00	10.88	1.00	0.03	11.43
B33-3.5	--	--	n.d.	n.d.	13.10	0.33	9.20	0.19	3.50	0.08	1.00	0.03	0.63
B50-0.5	--	--	n.d.	n.d.	45.20	1.11	8.20	0.16	7.60	0.17	3.00	0.07	1.52
B51-1.5	--	--	n.d.	n.d.	11.70	0.32	6.60	0.14	n.d.	n.d.	2.00	0.05	0.51
B53-3.5	--	--	n.d.	n.d.	24.80	0.73	11.80	0.28	10.10	0.27	3.00	0.09	1.38
B70-0.5	--	--	n.d.	n.d.	30.30	0.72	1.90	0.04	n.d.	n.d.	5.00	0.12	0.88
B71-1.5	--	--	34.40	0.34	23.30	0.58	n.d.	n.d.	n.d.	n.d.	1.00	0.02	0.94
B73-3.5	--	--	27.00	0.30	8.40	0.23	18.80	0.41	n.d.	n.d.	3.00	0.08	1.02
B90-0.5	--	--	19.9	0.2	78.3	2.1	13.0	0.3	n.d.	n.d.	2.5	0.1	2.8
B91-1.5	--	--	17.20	0.18	10.90	0.29	6.70	0.14	n.d.	n.d.	2.42	0.06	0.69
B93-3.5	--	--	n.d.	n.d.	n.d.	n.d.	20.80	0.44	n.d.	n.d.	4.50	0.12	0.56
B110-0.5	--	--	n.d.	n.d.	750.00	22.99	0.00	0.00	441.00	12.44	79.50	2.44	37.86
B111-1.5	--	--	n.d.	n.d.	25.00	0.69	6.50	0.14	7.60	0.19	2.30	0.06	1.09
B113-3.5	--	--	n.d.	n.d.	39.00	1.11	27.90	0.64	5.60	0.15	6.32	0.18	2.08
B130-0.5	--	--	51.30	0.55	250.00	6.70	110.00	2.36	390.00	9.61	46.50	1.25	20.46
B131-1.5	--	--	n.d.	n.d.	5.7	0.2	6.4	0.1	n.d.	n.d.	13.0	0.3	0.4
B133-3.5	--	--	n.d.	n.d.	13.30	0.35	53.00	1.11	4.30	0.10	56.20	1.47	3.02

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
B150-0.5	--	--	51.70	0.56	270.00	7.30	57.60	1.25	413.00	10.28	18.50	0.50	19.89
B151-1.5	--	--	86.60	0.96	100.00	2.78	90.00	2.00	523.00	13.39	27.50	0.77	19.90
B153-3.5	--	--	37.50	0.59	250.00	9.86	110.00	3.47	1415.00	51.35	93.00	3.67	68.95
B170-0.5	--	--	54.50	0.58	330.00	8.79	100.00	2.13	461.00	11.29	55.00	1.46	24.26
B171-1.5	--	--	n.d.	n.d.	33.40	0.84	39.70	0.80	7.40	0.17	5.32	0.13	1.95
B173-3.5	--	--	n.d.	n.d.	27.70	1.45	6.50	0.27	235.00	11.33	4.50	0.24	13.29
C20-0.5	--	--	n.d.	n.d.	104.10	2.76	35.20	0.75	252.00	6.15	7.50	0.20	9.86
C21-1.5	--	--	n.d.	n.d.	15.20	0.36	11.10	0.21	1.30	0.03	n.d.	n.d.	0.61
C23-3.5	--	--	n.d.	n.d.	17.10	0.43	71.60	1.45	4.00	0.09	1.50	0.04	2.01
C40-0.5	--	--	n.d.	n.d.	1882.00	51.08	14.70	0.32	21.60	0.54	5.00	0.14	52.07
C41-1.5	--	--	n.d.	n.d.	19.91	0.51	46.00	0.95	7.20	0.17	0.50	0.01	1.65
C43-3.5	--	--	n.d.	n.d.	28.30	0.68	66.30	1.27	1.80	0.04	0.50	0.01	2.01
C60-0.5	--	--	n.d.	n.d.	8.20	0.20	2.90	0.06	2.56	0.06	1.36	0.03	0.35
C61-1.5	--	--	n.d.	n.d.	13.50	0.33	18.70	0.36	3.40	0.08	3.24	0.08	0.84
C63-3.5	--	--	n.d.	n.d.	9.10	0.22	70.40	1.36	1.40	0.03	0.00	0.00	1.61
C80-0.5	--	--	7310.00	79.61	43492.0	1184.12	9354.00	203.74	67140.00	1681.73	20180.00	549.43	3698.63
C81-1.5	--	--	n.d.	n.d.	0.60	0.02	6.00	0.14	226.00	6.10	60.50	1.77	8.03
C83-3.5	--	--	n.d.	n.d.	9.30	0.24	80.30	1.66	198.00	4.70	1.50	0.04	6.64
C100-0.5	--	--	34.10	0.39	19.80	0.56	14.30	0.33	27.30	0.72	3.60	0.10	2.10
C101-1.5	--	--	27.20	0.27	11.40	0.28	4.60	0.09	157.00	3.57	2.42	0.06	4.27
C103-3.5	--	--	29.50	0.32	17.60	0.47	n.d.	n.d.	2.00	0.05	3.20	0.09	0.92

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
C120-0.5	--	--	n.d.	n.d.	31.50	0.87	6.50	0.14	178.00	4.55	4.92	0.14	5.70
C121-1.5	--	--	n.d.	n.d.	10.10	0.25	29.90	0.59	4.10	0.09	3.00	0.07	1.00
C123-3.5	--	--	n.d.	n.d.	9.80	0.29	84.10	1.97	6.70	0.18	2.74	0.08	2.51
C140-0.5	--	--	51.30	0.61	320.00	9.44	120.00	2.83	495.00	13.44	24.00	0.71	27.03
C141-1.5	--	--	n.d.	n.d.	28.50	0.75	100.00	2.10	25.20	0.61	2.50	0.07	3.52
C143-3.5	--	--	12.80	0.15	18.50	0.52	160.00	3.63	4.80	0.13	4.36	0.12	4.55
C160-0.5	--	--	n.d.	n.d.	128.60	3.79	37.50	0.88	231.00	6.26	9.00	0.26	11.19
D50-0.5	--	--	n.d.	n.d.	40.20	0.98	8.70	0.17	227.00	5.08	6.38	0.16	6.39
D51-1.5	--	--	n.d.	n.d.	8.00	0.21	3.90	0.08	197.00	4.86	n.d.	n.d.	5.15
D53-3.5	--	--	8.10	0.09	24.80	0.71	145.10	3.32	203.00	5.34	3.00	0.09	9.55
D70-0.5	--	--	71.90	0.81	230.00	6.44	17.20	0.39	265.00	6.83	14.50	0.41	14.87
D71-1.5	--	--	n.d.	n.d.	235.30	5.70	10.00	0.19	189.00	4.22	1.50	0.04	10.15
D73-3.5	--	--	n.d.	n.d.	31.30	0.92	51.00	1.20	201.00	5.45	8.40	0.25	7.83
D90-0.5	--	--	n.d.	n.d.	25.50	0.66	4.30	0.09	190.00	4.50	1.00	0.03	5.27
D91-1.5	--	--	n.d.	n.d.	5.60	0.16	11.70	0.26	212.00	5.40	5.58	0.15	5.97
D93-3.5	--	--	n.d.	n.d.	31.5	0.9	52.6	1.2	205.7	5.4	2.3	0.1	7.5
D110-0.5	--	--	n.d.	n.d.	24.70	0.58	67.50	1.28	205.00	4.45	2.54	0.06	6.37
D111-1.5	--	--	6.10	0.06	20.40	0.53	160.00	3.32	184.00	4.39	0.50	0.01	8.31
D113-3.5	--	--	n.d.	n.d.	5.90	0.15	47.20	0.94	189.00	4.33	0.00	0.00	5.41
D130-0.5	--	--	n.d.	n.d.	60.50	1.59	13.70	0.29	45.50	1.10	3.08	0.08	3.07
D131-1.5	--	--	n.d.	n.d.	4.80	0.11	27.30	0.52	n.d.	n.d.	2.40	0.06	0.69
D133-3.5	--	--	n.d.	n.d.	12.10	0.34	65.30	1.46	n.d.	n.d.	3.82	0.11	1.90

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
D150-0.5	--	--	42.10	0.46	120.00	3.29	48.70	1.07	35.20	0.89	9.50	0.26	5.96
D151-1.5	--	--	166.50	1.66	240.00	5.98	150.00	2.99	10.50	0.24	11.50	0.29	11.16
D153-3.5	--	--	20.60	0.21	16.60	0.43	78.80	1.63	n.d.	n.d.	4.92	0.13	2.40
D170-0.5	--	--	232.10	3.61	500.00	19.42	410.00	12.74	2510.00	89.71	174.00	6.76	132.24
D171-1.5	--	--	90.30	1.32	160.00	5.86	240.00	7.03	2220.00	74.74	3.92	0.14	89.09
D173-3.5	--	--	20.00	0.24	47.70	1.42	30.30	0.72	47.10	1.29	21.00	0.62	4.29
D190-0.5	--	--	n.d.	n.d.	820.00	25.24	320.00	7.88	1070.00	30.31	65.00	2.00	65.43
D191-1.5	--	--	147.30	2.79	1100.00	52.13	1490.00	56.49	9880.00	430.80	1495.00	70.86	613.08
D193-3.5	--	--	n.d.	n.d.	470.00	13.98	81.70	1.94	900.00	24.64	43.00	1.28	41.84
E140-0.5	--	--	79.80	0.84	190.00	4.99	53.50	1.12	32.10	0.78	15.50	0.41	8.14
E141-1.5	--	--	n.d.	n.d.	23.80	0.68	11.10	0.25	n.d.	n.d.	3.16	0.09	1.02
E143-3.5	--	--	n.d.	n.d.	19.80	0.54	59.60	1.30	n.d.	n.d.	1.00	0.03	1.86
E160-0.5	--	--	21.00	0.32	66.90	2.52	17.10	0.52	400.00	13.86	17.00	0.64	17.86
E161-1.5	--	--	17.10	0.33	44.90	2.14	15.30	0.58	290.00	12.69	49.00	2.33	18.07
E163-3.5	--	--	115.10	2.74	501.80	29.89	11.50	0.55	360.00	19.73	17.50	1.04	53.94
E180-0.5	--	--	226.90	3.32	660.00	24.18	320.00	9.38	750.00	25.28	501.50	18.37	80.52
E181-1.5	--	--	1940.00	47.26	1050.00	63.95	110.00	5.36	1390.00	77.88	274.00	16.69	211.13
E200-0.5	--	--	n.d.	n.d.	240.00	6.82	20.80	0.47	240.00	6.28	21.50	0.61	14.18
E201-1.5	--	--	n.d.	n.d.	88.70	2.18	18.40	0.36	200.00	4.52	15.50	0.38	7.45
F130-0.5	--	--	9.70	0.10	38.20	0.94	6.00	0.12	6.00	0.14	5.50	0.13	1.42
F131-1.5	--	--	0.00	0.00	9.90	0.25	63.80	1.29	1.80	0.04	3.80	0.10	1.68

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
F133-3.5	--	--	29.00	0.31	23.30	0.63	220.00	4.76	3.10	0.08	3.16	0.09	5.86
F150-0.5	--	--	n.d.	n.d.	370.00	14.09	100.00	3.05	680.00	23.83	10.50	0.40	41.37
F151-1.5	--	--	54.70	0.54	290.00	7.14	36.50	0.72	250.00	5.66	1.00	0.02	14.09
F153-3.5	--	--	49.00	0.52	36.60	0.96	180.00	3.79	4.10	0.10	0.50	0.01	5.38
F170-0.5	--	--	97.50	1.22	470.00	14.72	220.00	5.51	590.00	17.00	5.90	0.18	38.64
F171-1.5	--	--	n.d.	n.d.	n.d.	n.d.	19.50	0.42	n.d.	n.d.	1.76	0.05	0.47
F173-3.5	--	--	n.d.	n.d.	16.0	0.5	69.9	1.6	n.d.	n.d.	1.4	0.0	2.1
F190-0.5	--	--	n.d.	n.d.	83.90	2.33	28.50	0.63	220.00	5.63	4.50	0.13	8.72
F191-1.5	--	--	n.d.	n.d.	10.80	0.28	35.60	0.75	0.00	0.00	0.50	0.01	1.04
F193-3.5	--	--	22.60	0.25	16.00	0.45	170.00	3.82	n.d.	n.d.	2.50	0.07	4.60
F210-0.5	--	--	n.d.	n.d.	21.40	0.60	74.70	1.68	n.d.	n.d.	4.32	0.12	2.40
F211-1.5	--	--	n.d.	n.d.	29.90	0.74	160.00	3.17	4.00	0.09	2.50	0.06	4.06
F213-3.5	--	--	n.d.	n.d.	45.30	1.13	100.00	2.00	13.80	0.32	5.04	0.13	3.58
G140-0.5	--	--	n.d.	n.d.	280.00	10.61	47.10	1.43	85.20	2.97	4.50	0.17	15.18
G141-1.5	--	--	n.d.	n.d.	130.00	5.36	33.10	1.09	410.00	15.55	24.50	1.01	23.01
G143-3.5	--	--	n.d.	n.d.	41.30	1.08	5.90	0.12	13.80	0.33	5.50	0.14	1.67
G160-0.5	--	--	n.d.	n.d.	15.00	2.27	28.20	3.41	390.00	54.20	5.50	0.83	60.71
G161-1.5	--	--	n.d.	n.d.	150.00	5.95	90.00	2.86	640.00	23.37	31.00	1.23	33.41
G163-3.5	--	--	n.d.	n.d.	3.10	0.11	36.20	1.03	420.00	13.79	23.00	0.82	15.76
G180-0.5	--	--	n.d.	n.d.	160.00	4.66	59.20	1.38	310.00	8.31	13.00	0.38	14.73
G181-1.5	--	--	n.d.	n.d.	n.d.	n.d.	190.00	4.20	11.40	0.29	4.00	0.11	4.60

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
G183-3.5	--	--	n.d.	n.d.	24.00	0.62	220.00	4.53	7.20	0.17	3.00	0.08	5.39
G200-0.5	--	--	n.d.	n.d.	31.90	0.96	10.80	0.26	16.50	0.46	3.54	0.11	1.78
G201-1.5	--	--	n.d.	n.d.	52.60	1.37	100.00	2.08	5.20	0.12	2.00	0.05	3.63
G203-3.5	--	--	n.d.	n.d.	13.00	0.35	100.00	2.15	4.30	0.11	1.56	0.04	2.65
G220-0.5	--	--	n.d.	n.d.	160.00	4.51	110.00	2.48	99.50	2.58	7.00	0.20	9.76
G221-1.5	--	--	n.d.	n.d.	100.00	2.71	43.80	0.95	45.20	1.13	8.50	0.23	5.02
G223-3.5	--	--	n.d.	n.d.	16.70	0.45	190.00	4.11	0.00	0.00	2.30	0.06	4.63
H150-0.5	--	--	n.d.	n.d.	400.00	18.84	130.00	4.90	440.00	19.07	5.00	0.24	43.04
H151-1.5	--	--	n.d.	n.d.	320.00	13.30	47.30	1.57	420.00	16.06	21.00	0.87	31.80
H153-3.5	--	--	n.d.	n.d.	110.00	5.05	5.50	0.20	640.00	27.03	23.00	1.06	33.34
H170-0.5	--	--	4410.00	112.68	3440.00	219.73	220.00	11.24	710.00	41.72	15.50	0.99	386.36
H171-1.5	--	--	n.d.	n.d.	210.00	25.23	49.10	4.72	540.00	59.69	9.00	1.08	90.72
H173-3.5	--	--	n.d.	n.d.	45.80	1.48	43.50	1.12	360.00	10.69	13.00	0.42	13.71
H190-0.5	--	--	n.d.	n.d.	450.00	15.77	140.00	3.93	960.00	30.96	52.50	1.84	52.50
H191-1.5	--	--	n.d.	n.d.	800.00	42.07	310.00	13.04	1590.00	76.93	47.50	2.50	134.54
H193-3.5	--	--	n.d.	n.d.	220.00	26.56	120.00	11.59	690.00	76.63	19.50	2.35	117.12
H210-0.5	--	--	n.d.	n.d.	2.30	0.05	190.00	3.49	n.d.	n.d.	2.70	0.06	3.60
H211-1.5	--	--	n.d.	n.d.	160.00	7.36	100.00	3.68	400.00	16.92	7.50	0.34	28.30
H213-3.5	--	--	n.d.	n.d.	17.60	0.46	190.00	3.97	4.20	0.10	3.16	0.08	4.62
H230-0.5	--	--	n.d.	n.d.	76.0	2.2	32.4	0.8	0.8	29.8	11.7	0.3	4.1
H233-3.5	--	--	n.d.	n.d.	36.30	1.04	160.00	3.68	2.30	0.06	1.24	0.04	4.82

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 Sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
I200-0.5	--	--	117.70	2.99	560.00	35.62	380.00	19.34	1020.00	59.69	38.50	2.45	120.08
I201-1.5	--	--	239.70	9.02	910.00	85.64	390.00	29.36	890.00	77.06	133.50	12.56	213.64
I203-3.5	--	--	n.d.	n.d.	13.90	2.13	4.40	0.54	460.00	65.00	34.00	5.22	72.90
I220-0.5	--	--	n.d.	n.d.	13.90	1.07	41.90	2.59	1370.00	97.22	69.00	5.32	106.20
I221-1.5	--	--	n.d.	n.d.	1.10	0.12	27.90	2.41	830.00	82.58	40.00	4.33	89.44
I223-3.5	--	--	18.50	0.23	12.40	0.38	17.80	0.44	5.70	0.16	1.24	0.04	1.25
I240-0.5	--	--	n.d.	n.d.	79.60	2.65	16.00	0.43	70.20	2.15	7.50	0.25	5.48
I241-1.5	--	--	n.d.	n.d.	43.30	1.33	120.00	2.94	17.80	0.50	5.12	0.16	4.93
I243-3.5	--	--	n.d.	n.d.	91.20	2.62	160.00	3.68	11.50	0.30	4.50	0.13	6.74
I260-0.5	--	--	n.d.	n.d.	260.00	7.43	130.00	2.97	730.00	19.19	49.00	1.40	30.99
I261-1.5	--	--	n.d.	n.d.	373.3	10.0	96.7	2.10	405.00	9.90	3.3	0.1	22.0
J190-0.5	--	--	n.d.	n.d.	136.7	11.4	176.7	11.8	510.00	39.20	36.0	3.0	65.8
J191-1.5	--	--	n.d.	n.d.	1070.00	91.38	120.00	8.20	1430.00	112.35	436.40	37.27	249.20
J193-3.5	--	--	n.d.	n.d.	48.80	4.15	0.90	0.06	1840.00	144.00	31.96	2.72	150.94
J210-0.5	--	--	n.d.	n.d.	110.00	3.34	0.00	0.00	330.00	9.23	5.50	0.17	12.74
J211-1.5	--	--	n.d.	n.d.	76.50	2.00	34.10	0.71	300.00	7.21	5.50	0.14	10.06
J230-0.5	--	--	n.d.	n.d.	68.70	11.04	54.50	7.01	1070.00	158.17	72.50	11.65	187.87
J231-1.5	--	--	n.d.	n.d.	3.40	0.40	n.d.	n.d.	3000.00	321.74	851.00	99.20	421.34
J233-3.5	--	--	42.10	0.44	51.20	1.33	20.70	0.43	300.00	7.18	3.14	0.08	9.46
J250-0.5	--	--	n.d.	n.d.	810.00	30.70	180.00	5.46	2233.10	77.86	51.00	1.93	115.95
J251-1.5	--	--	n.d.	n.d.	11.10	0.90	230.00	14.89	123.20	9.17	9.50	0.77	25.74

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
J253-3.5	--	--	n.d.	n.d.	40.30	1.05	0.80	0.02	59.20	1.42	4.50	0.12	2.61
J270-0.5	--	--	n.d.	n.d.	58.70	1.89	510.00	13.10	405.90	11.99	13.00	0.42	27.40
J271-1.5	--	--	n.d.	n.d.	45.80	1.26	60.50	1.33	10.90	0.28	0.50	0.01	2.88
K200-0.5	--	--	n.d.	n.d.	48.50	7.13	350.00	41.13	237.90	32.15	2.50	0.37	80.78
K203-3.5	--	--	n.d.	n.d.	63.50	2.05	250.00	6.46	144.30	4.29	11.50	0.37	13.17
K220-0.5	--	--	n.d.	n.d.	24.70	19.02	410.00	252.52	318.60	225.66	16.04	12.35	509.54
K221-1.5	--	--	10.50	0.50	101.10	11.95	240.00	22.70	143.60	15.62	7.00	0.83	51.60
K223-3.5	--	--	0.00	0.00	19.50	0.45	20.90	0.39	13.20	0.28	3.00	0.07	1.19
K240-0.5	--	--	15.90	0.65	200.00	20.49	170.00	13.93	840.40	79.20	20.50	2.10	116.37
K241-1.5	--	--	n.d.	n.d.	3.10	0.35	39.50	3.55	340.70	35.17	16.00	1.80	40.86
K243-3.5	--	--	43.80	0.47	33.20	0.89	32.90	0.71	17.20	0.42	4.00	0.11	2.60
K260-0.5	--	--	n.d.	n.d.	530.00	17.86	71.00	1.91	337.80	10.48	20.36	0.69	30.94
K261-1.5	--	--	n.d.	n.d.	25.80	2.94	280.00	25.54	192.30	20.17	5.20	0.59	49.24
K263-3.5	--	--	n.d.	n.d.	100.00	4.47	400.00	14.30	333.80	13.73	26.88	1.20	33.70
K280-0.5	--	--	n.d.	n.d.	31.00	1.75	390.00	17.65	314.00	16.34	17.56	0.99	36.73
K281-1.5	--	--	n.d.	n.d.	128.30	10.69	520.00	34.66	451.40	34.60	40.80	3.40	83.35
L210-0.5	--	--	495.20	5.23	790.00	20.86	640.00	13.52	360.00	8.74	29.80	0.79	49.13
L211-1.5	--	--	12.90	0.14	60.50	1.59	20.20	0.43	98.50	2.39	3.82	0.10	4.64
L230-0.5	--	--	5.60	0.38	62.60	10.66	14.40	1.96	159.60	25.02	5.36	0.91	38.94
L231-1.5	--	--	n.d.	n.d.	120.00	18.41	30.10	3.69	260.00	36.70	4.04	0.62	59.43
L233-3.5	--	--	n.d.	n.d.	70.20	1.89	0.00	0.00	24.10	0.60	10.80	0.29	2.78

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
L250-0.5	--	--	n.d.	n.d.	90.00	2.38	41.50	0.88	80.90	1.97	5.68	0.15	5.38
L251-1.5	--	--	n.d.	n.d.	31.70	3.07	15.80	1.23	350.00	31.21	4.20	0.41	35.91
L253-3.5	--	--	n.d.	n.d.	26.6	2.6	11.4	0.9	283.30	25.4	5.1	0.5	29.4
L270-0.5	--	--	n.d.	n.d.	30.50	3.88	5.30	0.54	280.00	32.73	4.24	0.54	37.68
L271-1.5	--	--	n.d.	n.d.	28.80	1.69	11.00	0.52	90.00	4.87	6.68	0.39	7.48
L273-3.5	--	--	n.d.	n.d.	16.56	0.44	237.60	5.10	46.50	1.15	38.04	1.02	7.71
M200-0.5	--	--	10.20	0.12	74.10	2.12	28.40	0.65	41.70	1.10	3.60	0.10	4.09
M201-1.5	--	--	n.d.	n.d.	25.80	1.41	4.50	0.20	75.30	3.79	6.10	0.33	5.73
M220-0.5	--	--	8.80	0.16	77.00	3.52	10.40	0.38	240.00	10.08	6.44	0.29	14.43
M221-1.5	--	--	6.40	0.09	97.90	3.59	83.00	2.43	270.00	9.10	5.88	0.22	15.43
M223-3.5	--	--	3.40	0.04	64.60	1.71	0.00	0.00	37.80	0.92	8.04	0.21	2.88
M240-0.5	--	--	23.50	0.56	100.00	5.91	35.50	1.68	720.00	39.16	25.44	1.50	48.81
M241-1.5	--	--	n.d.	n.d.	32.30	3.92	8.50	0.83	530.00	59.25	8.80	1.07	65.07
M243-3.5	--	--	n.d.	n.d.	12.90	0.36	18.80	0.42	n.d.	n.d.	2.40	0.07	0.86
M260-0.5	--	--	43.50	0.99	250.00	14.27	65.40	2.99	940.00	49.37	49.76	2.84	70.47
M261-1.5	--	--	n.d.	n.d.	86.30	5.99	28.10	1.56	470.00	30.00	16.16	1.12	38.66
M280-0.5	--	--	28.50	0.62	250.00	13.65	49.70	2.17	450.00	22.60	14.08	0.77	39.81
M281-1.5	--	--	13.40	0.26	90.00	4.31	15.80	0.61	87.60	3.86	20.20	0.97	10.01
M283-3.5	--	--	10.80	0.12	61.90	1.74	90.00	2.02	12.20	0.32	6.16	0.17	4.37
N210-0.5	--	--	n.d.	n.d.	50.10	4.50	34.60	2.48	400.00	33.02	15.84	1.42	41.42
N211-1.5	--	--	n.d.	n.d.	18.40	1.42	10.80	0.67	310.00	21.97	32.80	2.53	26.58

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
N230-0.5	--	--	8.90	0.51	72.40	10.39	28.60	3.28	380.00	50.16	5.48	0.79	65.13
N231-1.5	--	--	n.d.	n.d.	49.80	1.48	22.90	0.54	24.20	0.66	7.20	0.21	2.90
N233-3.5	--	--	n.d.	n.d.	42.00	1.34	24.30	0.62	37.30	1.09	8.88	0.28	3.33
N250-0.5	--	--	14.40	0.17	93.90	2.73	14.20	0.33	60.60	1.62	8.36	0.24	5.09
N251-1.5	--	--	n.d.	n.d.	20.40	1.19	3.30	0.15	82.70	4.43	4.00	0.23	6.00
N253-3.5	--	--	n.d.	n.d.	61.70	1.88	20.40	0.50	75.30	2.11	14.32	0.44	4.93
O220-0.5	--	--	5.90	0.21	140.00	12.20	130.00	9.06	610.00	48.89	7.28	0.63	70.99
O221-1.5	--	--	43.2	1.6	396.7	37.9	163.3	12.5	436.70	38.4	13.8	1.3	91.8
O223-3.5	--	--	n.d.	n.d.	36.90	1.21	46.80	1.23	310.00	9.38	22.80	0.75	12.57
O240-0.5	--	--	34.10	1.60	250.00	29.39	63.00	5.92	440.00	47.58	13.08	1.54	86.03
O241-1.5	--	--	17.90	0.38	110.00	5.91	110.00	4.73	440.00	21.76	13.80	0.74	33.54
O243-3.5	--	--	19.90	0.27	90.00	3.10	36.00	0.99	74.80	2.37	12.20	0.42	7.16
P230-0.5	--	--	36.50	1.93	450.00	59.61	150.00	15.90	620.00	75.56	13.52	1.79	154.79
P231-1.5	--	--	n.d.	n.d.	11.40	0.37	8.60	0.22	220.00	6.51	30.52	0.98	8.08
P233-3.5	--	--	--	--	42.1	1.5	32.1	0.9	330.00	10.60	22.3	0.8	13.7
P250-0.5	--	--	n.d.	n.d.	90.00	13.59	30.00	3.62	350.00	48.62	7.00	1.06	66.90
P251-1.5	--	--	5.60	0.26	75.40	8.84	12.80	1.20	320.00	34.52	7.96	0.93	45.76
P253-3.5	--	--	n.d.	n.d.	13.30	0.41	5.80	0.14	21.30	0.61	5.12	0.16	1.33
Q240-0.5	--	--	17.90	0.46	120.00	7.67	100.00	5.12	1120.00	65.90	26.72	1.71	80.85
Q241-1.5	--	--	12.2	0.3	120.0	8.2	45.2	2.5	320.00	20.00	12.1	0.8	31.8
Q243-3.5	--	--	n.d.	n.d.	54.50	3.47	28.80	1.47	470.00	27.55	20.16	1.28	33.77

Table 3B-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	µg/L	mg/kg	mg/kg
Q260-0.5	--	--	n.d.	n.d.	610.00	18.68	32.00	0.78	2120.00	59.74	159.40	4.88	84.09
R250-0.5	--	--	20.30	0.72	170.00	15.07	90.00	6.38	410.00	33.43	7.64	0.68	56.27
R251-1.5	--	--	11.30	0.23	90.00	4.49	90.00	3.59	400.00	18.37	11.56	0.58	27.27
R253-3.5	--	--	10.30	0.12	90.00	2.73	42.80	1.04	250.00	6.98	21.80	0.66	11.53
R270-0.5	--	--	n.d.	n.d.	73.80	7.00	24.20	1.84	540.00	47.10	14.12	1.34	57.27
R271-1.5	--	--	n.d.	n.d.	53.20	7.17	49.70	5.36	450.00	55.80	15.16	2.04	70.37
R273-3.5	--	--	n.d.	n.d.	91.00	7.64	11.70	0.79	260.00	20.09	22.16	1.86	30.38
S260-0.5	--	--	34.40	0.91	280.00	18.44	140.00	7.37	830.00	50.28	17.60	1.16	78.16
S261-1.5	--	--	n.d.	n.d.	30.50	3.78	70.10	6.94	330.00	37.60	4.12	0.51	48.83
T270-0.5	--	--	26.50	0.67	180.00	11.33	130.00	6.55	550.00	31.86	24.04	1.51	51.92
T271-1.5	--	--	13.00	0.54	150.00	15.53	15.30	1.27	450.00	42.86	8.08	0.84	61.04
U260-0.5	--	--	38.10	0.40	82.50	2.14	100.00	2.08	16.60	0.40	7.52	0.20	5.21
U261-1.5	--	--	19.40	0.22	140.00	3.96	110.00	2.49	300.00	7.81	21.40	0.61	15.09
U263-3.5	--	--	n.d.	n.d.	84.80	2.41	90.00	2.05	92.70	2.42	19.16	0.54	7.43

Table 3B-2: Replicate Sample Analysis for Copper

sed indicates concentration in sediment (dry weight basis)
indicates the average of thee replicate samples. RSD indicates the relative standard deviation of the three replicates. SRM 2704 is NIST Buffalo River Sediment

Sample	RX sed mg/kg	WAS sed mg/kg	ER sed mg/kg	MR sed mg/kg	OX1sed mg/kg	OX2 sed mg/kg	Total sed mg/kg
B3a0-0.5	--	n.d.	0.8	0.2	n.d.	0.1	1.1
B3b0-0.5	--	n.d.	0.8	0.4	n.d.	0.0	1.3
B3c0-0.5	--	n.d.	0.6	0.7	n.d.	0.0	1.4
	--	--	0.7	0.5	--	0.0	1.2
RSD	--	--	13.9	55.3	--	30.0	14.0
B9a0-0.5	--	0.3	1.3	0.3	0.2	0.1	2.1
B9b0-0.5	--	0.2	1.2	0.3	0.2	0.1	1.8
B9c0-0.5	--	0.2	3.7	0.3	0.2	n.d.	4.4
	--	0.2	2.1	0.3	0.2	0.1	2.8
RSD	--	35.6	69.8	12.8	13.8	25.1	49.9
B13a1-1.5	--	n.d.	0.2	0.1	n.d.	0.3	0.6
B13b1-1.5	--	n.d.	0.1	0.1	n.d.	n.d.	0.3
B13c1-1.5	--	n.d.	0.1	0.1	n.d.	n.d.	0.3
	--	--	0.2	0.1	--	0.3	0.4
RSD	--	--	10.6	3.7	--	n.d.	50.4

Table 3B-2: Continued

Sample	EX sed	WAS sed	ER sed	MR sed	OX1sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
D9a3-3.5	--	n.d.	1.0	1.1	5.3	0.1	7.5
D9b3-3.5	--	n.d.	0.9	1.1	5.4	0.1	7.5
D9c3-3.5	--	n.d.	0.8	1.3	5.4	0.1	7.6
	--	--	0.9	1.2	5.4	0.1	7.5
RSD	--	--	14.6	7.5	1.5	14.1	0.4
H23a0-0.5	--	n.d.	2.3	0.8	0.7	0.6	4.3
H23b0-0.5	--	n.d.	2.1	0.8	0.9	0.3	4.1
H23c0-0.5	--	n.d.	2.3	0.7	0.8	0.2	4.0
	--	--	2.2	0.8	0.8	0.3	4.1
RSD	--	--	4.1	7.0	9.9	57.9	4.2
I26a1-1.5	--	n.d.	10.2	2.1	10.8	0.1	23.2
I26b1-1.5	--	n.d.	9.6	2.1	10.0	0.1	21.8
I26c1-1.5	--	n.d.	10.2	2.0	8.9	0.1	21.1
	--	--	10.0	2.1	9.9	0.1	22.0
RSD	--	--	3.4	4.0	10.1	18.2	5.0

Table 3B-2: Continued

Sample	EX sed	WAS sed	ER sed	MR sed	OX1sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
J19a0-0.5	--	1.1	10.9	10.7	37.7	2.3	62.6
J19b0-0.5	--	n.d.	12.1	12.9	39.3	3.3	67.6
J19c0-0.5	--	n.d.	11.3	11.8	40.7	3.5	67.3
	--	--	11.4	11.8	39.2	3.0	65.8
RSD	--	--	5.4	9.3	3.9	21.6	4.2
L25a3-3.5	--	n.d.	2.9	0.8	27.0	0.3	31.0
L25b3-3.5	--	n.d.	1.9	0.7	23.6	1.0	27.3
L25c3-3.5	--	n.d.	2.9	1.1	25.5	0.3	29.7
	--	--	2.6	0.9	25.4	0.5	29.4
RSD	--	--	21.0	25.6	6.7	83.6	6.5
O22a1-1.5	--	1.7	35.7	12.4	38.2	1.5	89.5
O22b1-1.5	--	1.3	37.7	12.4	37.3	1.2	89.8
O22c1-1.5	--	2.0	40.4	12.8	39.8	1.2	96.1
	--	1.6	37.9	12.5	38.4	1.3	91.8
RSD	--	21.8	6.2	1.9	3.2	15.1	4.0

Table 3B-2: Continued

Sample	EX sed	WAS sed	ER sed	MR sed	OX1sed	OX2 sed	Total sed
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
P23a3-3.5	--	n.d.	0.8	1.0	10.8	1.0	13.6
P23b3-3.5	--	n.d.	1.4	0.8	10.9	0.5	13.7
P23c3-3.5	--	n.d.	2.1	0.9	9.9	0.8	13.8
	--	--	1.5	0.9	10.6	0.8	13.7
RSD	--	--	43.9	7.1	5.3	31.5	0.4
Q24a1-1.5	--	0.4	8.2	2.6	20.2	1.1	32.6
Q24b1-1.5	--	0.3	8.0	2.1	20.3	0.8	31.5
Q24c1-1.5	--	0.2	8.2	2.7	19.6	0.6	31.3
	--	0.3	8.2	2.5	20.0	0.8	31.8
RSD	--	26.5	1.5	13.5	2.0	31.1	2.2
SRM27042/3/97	--	2.4	35.9	5.7	20.9	0.3	65.2
SRM27042/17/97	--	2.2	36.2	6.4	20.4	0.2	65.4
SRM27042/24/97	--	1.7	32.1	6.0	24.4	0.3	64.4
SRM27043/10/97	--	2.4	36.5	6.0	21.5	0.2	66.6
SRM27043/24/97	--	1.1	35.7	6.9	23.7	0.2	66.6
SRM27044/7/97	--	2.6	39.1	6.0	19.0	0.2	67.0
		2.1	35.9	6.2	21.6	0.2	65.9
RSD		28.0	6.2	6.4	9.4	16.4	1.5

Table 3C-1:
Sequential Chemical Extraction Data for Zinc
sol'n indicates concentration detected in leachate solution, mg/L
sed indicates concentration in sediment, mg/kg (dry weight basis)
nd indicates not detected, -- indicates not measured

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
B3a0-0.5	0.03	0.34	0.01	0.10	n.d.	n.d.	0.44	8.85	0.00	0.00	0.13	3.27	12.66
B3b0-0.5	0.15	1.70	0.04	0.39	n.d.	n.d.	0.10	2.14	0.00	0.00	0.01	0.25	4.58
B3c0-0.5	1.33	12.81	0.01	0.10	n.d.	n.d.	0.16	3.01	0.00	0.00	0.01	0.22	16.13
B31-1.5	1.37	14.57	0.06	0.64	0.30	8.06	0.26	5.45	0.20	4.98	n.d.	n.d.	33.69
B33-3.5	0.01	0.14	0.01	0.10	n.d.	n.d.	0.16	3.19	0.05	1.26	0.02	0.48	5.17
B50-0.5	0.49	4.86	0.06	0.59	0.09	2.31	0.36	7.02	0.01	0.18	0.10	2.43	17.39
B51-1.5	n.d.	n.d.	n.d.	n.d.	0.09	2.55	0.23	4.92	n.d.	n.d.	0.05	1.33	8.79
B53-3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	5.13	n.d.	n.d.	0.03	0.86	5.99
B70-0.5	0.09	0.90	0.19	1.77	n.d.	n.d.	0.04	0.71	0.01	0.18	n.d.	n.d.	3.55
B71-1.5	n.d.	n.d.	0.04	0.35	0.01	0.35	0.02	0.34	n.d.	n.d.	n.d.	n.d.	1.03
B73-3.5	0.13	1.47	0.11	1.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.67
B9a0-0.5	0.05	0.57	n.d.	n.d.	0.19	5.11	0.29	6.05	n.d.	n.d.	n.d.	n.d.	11.73
B9b0-0.5	n.d.	n.d.	n.d.	n.d.	0.19	5.36	0.26	5.68	0.03	0.71	n.d.	n.d.	11.75
B9c0-0.5	0.03	0.36	n.d.	n.d.	0.14	3.76	0.28	5.79	0.19	4.52	n.d.	n.d.	14.43
B91-1.5	0.11	1.22	0.04	0.38	0.03	0.91	0.66	14.10	n.d.	n.d.	n.d.	n.d.	16.61
B93-3.5	0.01	0.15	0.19	1.98	n.d.	n.d.	0.02	0.36	n.d.	n.d.	n.d.	n.d.	2.49
B110-0.5	1.57	19.30	0.36	4.41	0.23	7.17	n.d.	n.d.	0.11	3.21	0.04	1.20	35.29
B111-1.5	n.d.	n.d.	0.11	1.22	n.d.	n.d.	0.04	0.82	0.03	0.71	n.d.	n.d.	2.75

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
B113-3.5	0.03	0.39	0.09	0.97	n.d.	n.d.	0.12	2.67	n.d.	n.d.	n.d.	n.d.	4.03
B130-0.5	n.d.	n.d.	0.14	1.45	0.05	1.45	0.09	1.86	0.16	4.04	n.d.	n.d.	8.80
B13a1-1.5	n.d.	n.d.	0.04	0.37	n.d.	n.d.	0.19	3.91	n.d.	n.d.	n.d.	n.d.	4.27
B13b1-1.5	n.d.	n.d.	0.09	0.95	n.d.	0.11	0.30	6.67	0.01	0.21	n.d.	n.d.	7.94
B13c1-1.5	n.d.	n.d.	0.04	0.40	n.d.	n.d.	0.25	5.71	n.d.	n.d.	n.d.	n.d.	6.11
B133-3.5	n.d.	n.d.	0.09	0.89	0.04	1.15	0.02	0.36	n.d.	n.d.	n.d.	n.d.	2.39
B150-0.5	0.33	3.61	0.22	2.38	0.49	13.36	0.33	7.08	n.d.	n.d.	n.d.	n.d.	26.43
B151-1.5	0.09	1.05	0.77	8.57	1.46	40.73	1.51	33.54	0.07	1.74	0.13	3.59	89.22
B153-3.5	1.75	27.68	32.12	506.84	22.74	896.91	17.95	566.42	0.84	30.63	0.11	4.30	2032.78
B170-0.5	1.23	13.14	1.75	18.59	1.71	45.64	1.70	36.15	0.13	3.28	0.05	1.30	118.11
B171-1.5	n.d.	n.d.	n.d.	n.d.	0.12	3.13	0.10	1.96	0.01	0.19	n.d.	n.d.	5.28
B173-3.5	0.19	4.07	n.d.	n.d.	0.21	11.22	0.15	6.16	0.05	2.31	n.d.	n.d.	23.76
C20-0.5	0.73	7.79	0.16	1.70	0.19	5.15	0.51	10.76	0.01	0.20	0.15	3.95	29.55
C21-1.5	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	0.16	3.01	n.d.	n.d.	n.d.	n.d.	3.11
C23-3.5	n.d.	n.d.	0.19	1.87	0.04	1.11	0.14	2.77	n.d.	n.d.	n.d.	n.d.	5.75
C40-0.5	0.53	5.80	0.06	0.65	0.08	2.28	0.38	8.19	n.d.	n.d.	n.d.	n.d.	16.91
C41-1.5	0.31	3.25	n.d.	n.d.	0.09	2.43	0.13	2.63	n.d.	n.d.	n.d.	n.d.	8.31
C43-3.5	n.d.	n.d.	0.11	1.06	n.d.	0.10	0.03	0.52	n.d.	n.d.	n.d.	n.d.	1.67
C60-0.5	n.d.	n.d.	0.19	1.80	0.07	1.80	0.05	0.92	0.11	2.42	n.d.	n.d.	6.95
C61-1.5	0.27	2.65	0.09	0.82	0.03	0.82	0.27	5.17	0.01	0.18	n.d.	n.d.	9.65
C63-3.5	n.d.	n.d.	0.04	0.34	n.d.	n.d.	0.04	0.72	0.07	1.51	0.02	0.46	3.03
C80-0.5	4.85	52.86	3.51	38.23	1.34	36.59	12.91	281.15	1.93	48.44	1.74	47.35	504.62

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
C81-1.5	0.01	0.16	0.06	0.70	0.04	1.29	0.03	0.63	n.d.	n.d.	n.d.	n.d.	2.79
C83-3.5	n.d.	n.d.	0.01	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10
C100-0.5	0.23	2.67	0.21	2.40	0.07	2.11	0.37	8.38	0.21	5.62	0.01	0.26	21.43
C101-1.5	0.01	0.14	n.d.	n.d.	n.d.	n.d.	0.10	1.92	n.d.	n.d.	n.d.	n.d.	2.05
C103-3.5	0.03	0.36	0.06	0.64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.01
C120-0.5	0.15	1.71	0.06	0.67	0.05	1.50	0.49	10.82	0.12	3.17	n.d.	n.d.	17.86
C121-1.5	0.09	0.92	0.04	0.34	n.d.	n.d.	0.43	8.38	0.01	0.18	n.d.	n.d.	9.83
C123-3.5	0.07	0.86	0.06	0.70	0.03	0.99	0.12	2.73	0.05	1.29	n.d.	n.d.	6.58
C140-0.5	0.07	0.87	2.24	26.38	1.43	42.32	2.40	56.59	0.13	3.64	0.07	2.04	131.83
C141-1.5	0.03	0.36	0.54	5.62	0.04	1.16	0.05	0.99	n.d.	n.d.	n.d.	n.d.	8.12
C143-3.5	n.d.	n.d.	0.54	6.07	0.04	1.25	0.12	2.65	n.d.	n.d.	n.d.	n.d.	9.96
C160-0.5	n.d.	n.d.	n.d.	n.d.	0.11	3.36	0.38	8.88	n.d.	n.d.	n.d.	n.d.	12.24
D50-0.5	0.11	1.11	0.01	0.10	0.11	2.77	0.29	5.59	0.03	0.63	n.d.	n.d.	10.20
D51-1.5	n.d.	n.d.	0.01	0.11	n.d.	n.d.	0.09	1.86	0.07	1.68	n.d.	n.d.	3.65
D53-3.5	n.d.	n.d.	0.01	0.11	n.d.	n.d.	0.14	3.13	0.03	0.74	n.d.	n.d.	3.99
D70-0.5	1.41	15.85	0.31	3.47	0.26	7.40	0.34	7.55	0.03	0.72	0.05	1.37	36.37
D71-1.5	n.d.	n.d.	0.04	0.34	0.03	0.82	0.04	0.72	0.05	1.07	0.01	0.22	3.17
D73-3.5	n.d.	n.d.	0.04	0.41	n.d.	n.d.	0.01	0.17	0.01	0.22	n.d.	n.d.	0.80
D90-0.5	0.23	2.41	0.19	1.90	0.14	3.71	0.12	2.41	0.05	1.14	0.04	1.00	12.57
D91-1.5	n.d.	n.d.	0.09	0.94	0.01	0.39	n.d.	n.d.	0.05	1.22	n.d.	n.d.	2.55
D9a3-3.5	0.13	1.49	0.04	0.39	0.01	0.39	0.03	0.60	0.01	0.21	0.01	0.25	3.33
D9b3-3.5	0.05	0.61	0.29	3.20	n.d.	n.d.	n.d.	n.d.	0.01	0.21	n.d.	n.d.	4.01

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER Sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
D9c3-3.5	n.d.	n.d.	0.09	1.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.00
D110-0.5	n.d.	n.d.	0.06	0.57	0.02	0.57	0.27	5.04	0.05	1.04	n.d.	n.d.	7.22
D111-1.5	0.03	0.35	0.09	0.88	n.d.	n.d.	0.22	4.50	0.03	0.67	n.d.	n.d.	6.40
D113-3.5	n.d.	n.d.	0.06	0.60	0.06	1.59	0.05	0.94	0.03	0.64	0.01	0.22	3.99
D130-0.5	0.09	0.99	n.d.	n.d.	0.08	2.21	0.65	13.64	0.22	5.43	n.d.	n.d.	22.27
D131-1.5	0.19	1.86	0.06	0.57	n.d.	n.d.	0.27	5.11	0.03	0.62	n.d.	n.d.	8.15
D133-3.5	0.07	0.83	0.06	0.67	0.04	1.23	0.13	2.84	0.05	1.23	n.d.	n.d.	6.80
D150-0.5	0.05	0.59	0.36	3.94	0.22	6.13	0.26	5.63	0.01	0.20	n.d.	n.d.	16.50
D151-1.5	0.09	0.94	0.61	6.08	0.24	6.08	0.79	15.69	0.01	0.18	n.d.	n.d.	28.98
D153-3.5	0.07	0.76	0.41	4.23	0.03	0.88	0.27	5.52	0.01	0.19	n.d.	n.d.	11.58
D170-0.5	12.99	201.82	27.82	432.30	21.18	822.65	7.95	247.01	0.69	24.80	0.25	9.67	1738.27
D171-1.5	0.17	2.55	1.27	18.59	2.06	75.24	0.59	17.21	0.17	5.86	n.d.	n.d.	119.45
D173-3.5	0.29	3.50	2.40	28.47	1.40	41.73	1.31	31.08	0.01	0.22	n.d.	n.d.	104.99
D190-0.5	12.82	157.90	7.66	94.33	5.23	161.13	5.62	138.34	0.23	6.63	0.12	3.66	561.99
D191-1.5	4.37	82.92	3.59	67.96	2.86	135.36	0.89	33.63	0.23	10.20	n.d.	n.d.	330.08
D193-3.5	0.01	0.17	2.31	27.49	1.63	48.62	0.42	9.93	0.05	1.31	n.d.	n.d.	87.52
E140-0.5	n.d.	n.d.	n.d.	n.d.	0.15	4.05	0.38	7.92	0.03	0.68	0.01	0.24	12.88
E141-1.5	n.d.	n.d.	n.d.	n.d.	0.14	4.09	0.16	3.57	0.01	0.21	n.d.	n.d.	7.86
E143-3.5	0.01	0.15	0.02	0.22	0.04	1.20	0.11	2.33	0.09	2.20	n.d.	n.d.	6.09
E160-0.5	0.61	9.25	0.07	1.05	0.31	11.83	0.16	4.73	0.05	1.66	n.d.	n.d.	28.53
E161-1.5	0.41	7.88	n.d.	n.d.	0.17	8.28	0.14	5.21	0.12	5.43	n.d.	n.d.	26.80
E163-3.5	0.17	4.15	5.42	129.12	3.30	196.78	0.89	42.26	0.12	6.79	n.d.	n.d.	379.11
E180-0.5	n.d.	n.d.	2.15	31.43	1.92	70.48	2.79	81.67	1.51	51.02	0.33	12.05	246.65

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
E181-1.5	0.09	2.29	0.30	7.19	0.21	13.03	0.56	27.14	0.17	9.75	0.04	2.38	61.77
E200-0.5	0.35	4.02	0.36	4.09	0.37	10.63	0.72	16.30	0.08	2.20	0.07	1.96	39.21
E201-1.5	0.07	0.73	0.19	1.82	0.10	2.56	0.18	3.48	0.07	1.67	0.05	1.20	11.47
F130-0.5	0.13	1.31	0.10	0.93	0.17	4.27	0.38	7.40	0.06	1.44	0.01	0.22	15.58
F131-1.5	0.01	0.14	n.d.	n.d.	0.04	1.11	0.10	1.97	0.07	1.72	n.d.	n.d.	4.95
F133-3.5	0.13	1.45	0.10	1.03	n.d.	n.d.	0.19	4.04	0.04	1.09	n.d.	n.d.	7.61
F150-0.5	0.25	3.87	3.93	59.88	6.22	236.79	3.83	116.63	3.08	108.08	0.27	10.25	535.49
F151-1.5	0.11	1.12	n.d.	n.d.	0.54	13.40	2.41	47.42	0.16	3.72	n.d.	n.d.	65.66
F153-3.5	n.d.	n.d.	n.d.	n.d.	0.04	1.16	0.30	6.25	0.03	0.68	n.d.	n.d.	8.09
F170-0.5	0.19	2.43	4.16	52.12	3.93	123.22	5.75	144.00	0.17	4.84	0.06	1.85	328.46
F171-1.5	1.57	16.91	0.09	0.91	n.d.	n.d.	0.40	8.53	0.11	2.67	n.d.	n.d.	29.02
F17a3-3.5	n.d.	n.d.	0.09	1.08	n.d.	n.d.	0.14	3.49	0.13	3.75	0.02	0.61	8.93
F17b3-3.5	n.d.	n.d.	0.06	0.66	n.d.	n.d.	0.08	1.68	0.17	4.23	0.03	0.79	7.36
F17c3-3.5	n.d.	n.d.	0.06	0.65	n.d.	n.d.	0.07	1.46	0.06	1.60	n.d.	n.d.	3.72
F190-0.5	7.31	81.26	1.74	19.29	0.94	26.24	0.78	17.28	0.08	2.15	0.07	1.92	148.13
F191-1.5	0.03	0.36	0.64	6.65	0.02	0.63	0.36	7.48	n.d.	n.d.	n.d.	n.d.	15.12
F193-3.5	n.d.	n.d.	0.61	6.86	0.03	0.96	0.19	4.20	n.d.	n.d.	n.d.	n.d.	12.02
F210-0.5	0.63	7.12	0.66	7.41	0.18	5.17	0.52	11.61	0.01	0.21	n.d.	n.d.	31.52
F211-1.5	n.d.	n.d.	0.66	6.53	0.05	1.34	0.19	3.70	0.01	0.18	n.d.	n.d.	11.75
F213-3.5	n.d.	n.d.	0.56	5.61	0.11	2.85	0.15	2.94	n.d.	n.d.	n.d.	n.d.	11.41
G140-0.5	n.d.	n.d.	0.99	14.94	3.96	150.27	0.61	18.41	0.15	5.16	0.03	1.10	189.88
G141-1.5	n.d.	n.d.	0.01	0.16	1.27	52.52	0.97	31.89	0.23	8.87	0.03	1.20	94.65

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
G143-3.5	n.d.	n.d.	n.d.	n.d.	0.12	3.23	n.d.	n.d.	0.07	1.77	0.02	0.50	5.50
G160-0.5	n.d.	n.d.	n.d.	n.d.	2.73	413.01	0.00	0.00	1.43	199.30	0.02	2.87	615.17
G161-1.5	n.d.	n.d.	n.d.	n.d.	0.58	22.86	1.83	58.04	0.47	17.31	0.04	1.55	99.76
G163-3.5	n.d.	n.d.	n.d.	n.d.	0.42	14.85	0.43	12.22	0.20	6.70	0.11	3.89	37.66
G180-0.5	1.21	14.15	0.31	3.61	0.31	9.15	1.04	24.17	0.15	4.13	0.01	0.26	55.46
G181-1.5	n.d.	n.d.	0.01	0.11	n.d.	0.11	0.41	9.00	0.17	4.27	n.d.	n.d.	13.49
G183-3.5	0.01	0.14	0.04	0.36	0.04	1.13	0.16	3.23	0.23	5.39	n.d.	n.d.	10.26
G200-0.5	0.43	5.22	0.34	4.03	0.11	3.43	0.63	15.08	0.01	0.22	0.04	1.17	29.14
G201-1.5	n.d.	n.d.	0.14	1.41	0.08	2.19	0.11	2.23	0.15	3.55	n.d.	n.d.	9.37
G203-3.5	0.15	1.66	0.01	0.11	n.d.	n.d.	0.08	1.66	0.05	1.19	0.01	0.24	4.86
G220-0.5	0.43	4.89	1.06	11.94	0.37	10.53	1.06	23.81	0.01	0.21	n.d.	n.d.	51.38
G221-1.5	n.d.	n.d.	0.49	5.26	0.21	5.80	0.22	4.71	n.d.	n.d.	n.d.	n.d.	15.77
G223-3.5	n.d.	n.d.	0.81	8.77	0.03	0.92	0.20	4.27	n.d.	n.d.	n.d.	n.d.	13.96
H150-0.5	0.01	0.26	1.79	33.63	1.26	59.16	0.67	25.17	0.31	13.35	0.05	2.31	133.88
H151-1.5	0.03	0.57	0.34	5.57	1.10	45.55	0.23	7.58	0.31	11.78	0.01	0.37	71.41
H153-3.5	0.01	0.26	n.d.	n.d.	0.46	20.94	0.67	24.53	0.77	32.44	0.04	1.79	79.96
H170-0.5	0.23	5.98	3.37	86.10	2.65	169.53	1.63	83.19	0.07	4.00	0.00	0.00	348.80
H171-1.5	1.05	50.65	2.79	133.84	2.42	290.26	0.63	60.36	0.19	20.78	n.d.	n.d.	555.89
H173-3.5	n.d.	n.d.	n.d.	n.d.	0.40	13.04	0.51	13.12	0.17	4.99	0.02	0.61	31.76
H190-0.5	0.07	0.94	0.91	12.76	1.78	62.53	0.89	24.87	0.35	11.22	n.d.	n.d.	112.33
H191-1.5	n.d.	n.d.	n.d.	n.d.	1.40	73.84	0.64	26.80	0.15	7.16	0.02	1.00	108.79
H193-3.5	0.02	0.82	2.21	106.71	1.69	204.48	0.34	32.54	0.09	9.77	0.08	9.54	363.86

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
H210-0.5	0.03	0.31	0.14	1.24	n.d.	n.d.	0.05	0.86	0.09	1.86	0.02	0.44	4.71
H211-1.5	3.33	61.32	1.04	19.03	0.80	36.97	0.72	26.37	0.31	13.03	n.d.	n.d.	156.72
H213-3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	6.21	0.04	1.06	n.d.	n.d.	7.27
H23a0-0.5	0.06	0.69	0.01	0.12	0.04	1.32	0.64	15.33	0.11	2.99	0.05	1.47	21.92
H23b0-0.5	n.d.	n.d.	0.06	0.66	0.04	1.21	0.63	13.81	0.07	1.72	n.d.	n.d.	17.40
H23c0-0.5	0.05	0.57	0.04	0.43	0.10	3.16	0.54	13.04	0.03	0.78	n.d.	n.d.	17.98
H231-1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	3.43	0.13	2.33	0.04	0.77	6.53
H233-3.5	0.24	2.72	n.d.	n.d.	n.d.	0.11	0.12	2.69	0.03	0.74	n.d.	n.d.	6.27
I200-0.5	n.d.	n.d.	0.49	12.34	0.48	30.78	n.d.	n.d.	1.73	101.11	0.19	12.02	156.26
I201-1.5	4.31	162.13	9.76	367.40	7.86	739.32	4.31	324.26	0.19	16.28	0.07	6.49	1615.88
I203-3.5	n.d.	n.d.	0.06	3.69	0.22	33.18	0.35	42.64	0.35	49.17	n.d.	n.d.	128.68
I220-0.5	n.d.	n.d.	0.31	9.56	2.02	156.12	2.02	124.46	0.61	43.15	0.09	6.86	340.16
I221-1.5	n.d.	n.d.	n.d.	n.d.	2.93	317.30	1.88	162.39	0.19	18.70	0.07	7.46	505.85
I223-3.5	0.14	1.69	0.09	1.05	n.d.	n.d.	0.05	1.16	0.07	2.10	n.d.	n.d.	5.99
I240-0.5	0.12	1.56	0.07	0.93	0.21	7.12	0.51	13.50	0.08	2.57	n.d.	n.d.	25.69
I241-1.5	n.d.	n.d.	0.02	0.25	n.d.	0.12	0.13	3.11	0.06	1.80	n.d.	n.d.	5.29
I243-3.5	n.d.	n.d.	n.d.	n.d.	0.03	0.98	0.19	4.30	0.03	0.90	n.d.	n.d.	6.18
I260-0.5	1.73	19.74	14.48	165.48	8.62	246.17	7.27	166.12	2.75	72.23	0.51	14.54	684.29
I26a1-1.5	0.05	0.58	0.32	3.43	1.12	30.12	1.28	27.38	0.05	1.18	0.04	1.05	63.74
I26b1-1.5	0.09	0.97	0.40	4.09	1.14	29.64	1.32	27.29	0.01	0.19	0.06	1.53	63.72
I26c1-1.5	0.09	1.03	0.37	4.07	0.98	27.07	1.12	24.58	0.03	0.71	0.04	1.07	58.54
J19a0-0.5	--	--	4.05	135.23	1.14	95.62	0.78	51.95	0.15	11.38	0.11	9.11	303.29

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
J19b0-0.5	7.15	230.36	4.77	153.72	1.50	121.17	0.83	53.30	0.13	9.49	0.09	7.17	575.22
J19c0-0.5	6.79	235.75	4.07	141.35	1.32	114.96	0.77	53.28	0.13	10.22	0.15	12.94	568.50
J191-1.5	6.47	220.95	2.72	92.91	1.54	131.86	0.97	66.07	0.07	5.34	0.01	0.77	517.89
J193-3.5	0.01	0.48	n.d.	n.d.	0.38	32.67	6.04	410.85	3.91	305.85	0.03	2.47	752.31
J210-0.5	0.55	6.74	n.d.	n.d.	0.32	9.85	1.48	35.91	0.03	0.78	0.06	1.79	55.07
J211-1.5	0.03	0.36	n.d.	n.d.	0.04	1.15	0.30	6.21	0.03	0.67	n.d.	n.d.	8.38
J230-0.5	0.03	2.19	n.d.	n.d.	0.69	111.51	0.78	99.88	0.21	30.75	0.06	9.48	253.80
J231-1.5	0.27	12.78	5.25	244.57	22.10	2575.79	22.43	2091.60	40.14	4304.90	1.01	117.62	9347.26
J233-3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	2.64	0.01	0.19	n.d.	n.d.	2.83
J250-0.5	n.d.	n.d.	0.65	9.78	1.91	72.54	0.67	20.22	n.d.	n.d.	0.01	0.34	102.88
J251-1.5	n.d.	n.d.	n.d.	n.d.	0.25	20.56	0.05	3.04	n.d.	n.d.	0.03	2.35	25.95
J253-3.5	n.d.	n.d.	0.17	1.78	0.39	10.31	0.28	5.80	0.03	0.67	0.03	0.76	19.32
J270-0.5	n.d.	n.d.	0.10	1.22	2.08	66.93	2.13	54.65	0.47	13.83	0.08	2.54	139.16
J271-1.5	n.d.	n.d.	0.05	0.49	0.09	2.58	0.12	2.57	n.d.	n.d.	n.d.	n.d.	5.65
K200-0.5	0.01	0.82	1.04	60.82	2.30	338.47	0.97	113.65	0.09	11.89	n.d.	n.d.	525.66
K203-3.5	n.d.	n.d.	0.06	0.78	0.22	7.24	0.27	6.90	0.01	0.24	0.01	0.29	15.44
K220-0.5	n.d.	n.d.	0.07	21.56	3.55	2736.11	1.39	854.24	0.09	62.33	0.02	14.63	3688.86
K221-1.5	n.d.	n.d.	0.90	42.33	0.96	113.98	0.23	21.47	0.07	8.05	n.d.	n.d.	185.84
K223-3.5	n.d.	n.d.	n.d.	n.d.	0.03	0.79	0.07	1.24	0.01	0.17	n.d.	n.d.	2.19
K240-0.5	0.19	7.95	0.90	36.67	3.29	337.43	2.48	202.99	0.93	87.46	0.13	13.21	685.72
K241-1.5	n.d.	n.d.	0.32	14.36	7.18	805.14	2.58	231.31	0.31	31.79	0.02	2.13	1084.73
K243-3.5	n.d.	n.d.	0.10	1.02	0.13	3.59	0.14	2.94	0.01	0.20	0.01	0.24	7.99

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
K260-0.5	n.d.	n.d.	0.17	2.29	0.60	20.36	0.26	6.93	0.05	1.49	0.02	0.64	31.71
K261-1.5	n.d.	n.d.	n.d.	n.d.	0.41	47.20	0.11	9.76	0.11	11.33	0.06	6.73	75.02
K263-3.5	0.17	3.11	n.d.	n.d.	0.64	28.79	0.38	13.48	0.03	1.15	0.10	4.43	50.95
K280-0.5	0.09	2.13	n.d.	n.d.	n.d.	n.d.	1.04	46.92	0.37	19.15	0.05	2.77	70.97
K281-1.5	n.d.	n.d.	n.d.	n.d.	0.78	65.32	0.46	30.46	0.11	8.28	n.d.	n.d.	104.05
L210-0.5	n.d.	n.d.	1.57	16.58	2.06	54.49	2.65	55.91	0.03	0.68	0.03	0.77	128.42
L211-1.5	0.27	2.89	n.d.	n.d.	0.09	2.48	0.33	6.89	0.03	0.68	n.d.	n.d.	12.93
L230-0.5	0.21	14.58	0.07	4.77	0.53	90.97	0.23	30.94	0.09	13.79	0.01	1.53	156.59
L231-1.5	0.15	9.45	0.27	16.57	0.45	69.66	0.13	15.59	0.11	15.25	n.d.	n.d.	126.52
L233-3.5	0.01	0.15	0.07	0.75	0.10	2.80	0.18	3.81	n.d.	n.d.	n.d.	n.d.	7.52
L250-0.5	n.d.	n.d.	n.d.	n.d.	0.13	3.54	0.40	8.40	0.01	0.19	n.d.	n.d.	12.14
L251-1.5	n.d.	n.d.	n.d.	n.d.	0.47	45.94	0.15	11.40	0.15	13.20	n.d.	n.d.	70.53
L25a3-3.5	n.d.	n.d.	n.d.	n.d.	0.66	62.93	0.28	21.00	0.15	12.90	n.d.	n.d.	96.84
L25b3-3.5	n.d.	n.d.	n.d.	n.d.	0.49	55.18	0.30	26.54	0.23	23.43	0.00	0.00	105.15
L25c3-3.5	n.d.	n.d.	n.d.	n.d.	0.68	61.12	0.32	22.66	0.23	18.74	0.00	0.00	102.53
L270-0.5	n.d.	n.d.	n.d.	n.d.	0.57	72.93	0.24	24.09	n.d.	n.d.	0.04	4.96	101.97
L271-1.5	n.d.	n.d.	n.d.	n.d.	0.29	17.30	0.11	5.04	0.01	0.43	0.10	5.83	28.60
L273-3.5	n.d.	n.d.	n.d.	n.d.	0.06	1.72	0.15	3.15	n.d.	n.d.	n.d.	n.d.	4.87
M200-0.5	0.29	3.37	n.d.	n.d.	0.18	5.27	0.30	6.81	n.d.	n.d.	n.d.	n.d.	15.45
M201-1.5	0.01	0.31	n.d.	n.d.	0.12	6.79	0.07	2.93	n.d.	n.d.	n.d.	n.d.	10.03
M220-0.5	0.29	5.37	n.d.	n.d.	0.54	24.84	0.33	11.94	n.d.	n.d.	0.02	0.87	43.02
M221-1.5	0.05	0.79	n.d.	n.d.	0.50	18.47	0.34	9.88	n.d.	n.d.	n.d.	n.d.	29.14

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
M223-3.5	0.13	1.42	n.d.	n.d.	0.09	2.49	0.18	3.75	n.d.	n.d.	0.01	0.24	7.90
M240-0.5	n.d.	n.d.	n.d.	n.d.	0.98	58.17	0.61	28.71	0.09	4.79	0.02	1.12	92.79
M241-1.5	0.17	8.46	n.d.	n.d.	0.81	98.90	0.40	38.59	0.09	9.84	n.d.	n.d.	155.79
M243-3.5	0.03	0.38	0.12	1.35	0.01	0.39	0.05	1.06	n.d.	n.d.	0.01	0.25	3.45
M260-0.5	0.05	1.23	n.d.	n.d.	0.79	45.33	0.50	22.70	0.01	0.42	0.03	1.66	71.34
M261-1.5	n.d.	n.d.	n.d.	n.d.	0.60	41.90	0.34	18.70	0.03	1.79	0.02	1.32	63.71
M280-0.5	0.15	3.36	0.52	11.35	1.15	62.99	0.71	30.87	0.05	2.41	0.07	3.77	114.76
M281-1.5	n.d.	n.d.	0.05	0.86	0.21	10.26	0.10	3.72	0.01	0.35	0.03	1.39	16.58
M283-3.5	0.11	1.28	n.d.	n.d.	0.08	2.36	0.16	3.53	n.d.	n.d.	n.d.	n.d.	7.17
N210-0.5	0.73	26.34	0.45	15.97	2.30	206.74	1.01	72.29	0.09	7.26	0.03	2.60	331.21
N211-1.5	0.23	7.21	n.d.	n.d.	1.36	105.09	0.54	33.10	0.61	43.09	0.05	3.78	192.26
N230-0.5	n.d.	n.d.	0.30	16.93	1.61	231.57	0.71	81.15	0.05	6.34	n.d.	n.d.	335.99
N231-1.5	0.05	0.64	0.17	2.02	0.13	3.98	0.06	1.35	n.d.	n.d.	0.01	0.27	8.26
N233-3.5	0.03	0.43	0.12	1.53	0.19	6.18	0.15	3.75	n.d.	n.d.	0.02	0.61	12.50
N250-0.5	n.d.	n.d.	0.02	0.23	0.18	5.35	0.22	5.05	n.d.	n.d.	n.d.	n.d.	10.63
N251-1.5	0.09	2.19	n.d.	n.d.	0.37	21.78	0.17	7.78	0.01	0.43	0.01	0.52	32.70
N253-3.5	0.01	0.17	n.d.	n.d.	0.20	6.22	0.21	5.05	n.d.	n.d.	0.02	0.58	12.02
O220-0.5	0.41	14.43	n.d.	n.d.	0.99	86.59	0.53	36.73	0.03	2.24	0.05	4.27	144.26
O22a1-1.5	0.57	22.17	5.35	206.47	4.37	422.40	2.90	223.81	0.01	0.71	0.07	6.66	882.23
O22b1-1.5	0.45	17.54	4.62	178.46	3.84	371.22	2.77	213.77	0.01	0.71	0.06	5.70	787.40
O22c1-1.5	0.59	22.32	5.47	205.54	4.33	407.13	3.07	230.49	0.25	21.43	0.07	6.48	893.38
O223-3.5	n.d.	n.d.	n.d.	n.d.	0.52	17.23	0.58	15.18	0.85	25.66	0.16	5.23	63.30

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
O240-0.5	0.73	34.51	1.99	93.33	1.44	169.73	0.43	40.15	0.03	3.03	0.09	10.46	351.21
O241-1.5	n.d.	n.d.	0.41	8.82	0.40	21.72	1.85	79.44	n.d.	n.d.	0.03	1.56	111.54
O243-3.5	0.09	1.30	0.51	7.03	0.19	6.69	0.22	5.98	n.d.	n.d.	0.08	2.72	23.72
P230-0.5	1.45	77.04	6.80	360.04	4.70	623.12	2.93	310.18	0.15	18.04	0.15	19.74	1408.16
P231-1.5	0.07	0.95	0.10	1.22	0.95	30.70	0.59	15.11	1.09	32.21	0.17	5.44	85.63
P23a3-3.5	n.d.	n.d.	n.d.	n.d.	0.30	11.18	0.35	10.21	n.d.	n.d.	0.06	2.17	23.57
P23b3-3.5	0.05	0.71	n.d.	n.d.	0.30	10.02	0.32	8.36	n.d.	n.d.	n.d.	n.d.	19.09
P23c3-3.5	0.13	1.86	n.d.	n.d.	0.31	10.92	0.33	9.10	n.d.	n.d.	0.02	0.66	22.54
P250-0.5	0.11	6.89	0.71	42.89	0.81	122.92	0.76	91.45	0.71	98.36	0.04	5.89	368.39
P251-1.5	n.d.	n.d.	0.61	28.61	0.40	47.37	0.32	29.74	n.d.	n.d.	0.02	2.23	107.94
P253-3.5	0.05	0.67	0.17	2.12	0.17	5.43	0.10	2.42	n.d.	n.d.	n.d.	n.d.	10.64
Q240-0.5	1.77	45.38	2.92	74.70	7.02	448.69	4.22	215.75	1.67	98.14	0.19	12.09	894.75
Q24a1-1.5	0.03	0.93	0.50	13.58	0.76	52.39	0.99	54.15	0.15	9.34	0.08	5.42	135.81
Q24b1-1.5	n.d.	n.d.	0.55	14.56	0.73	49.04	0.96	51.15	0.15	9.10	0.03	1.94	125.78
Q24c1-1.5	0.01	0.38	0.42	11.52	0.67	46.22	0.95	51.96	0.11	6.81	0.07	4.73	121.63
Q243-3.5	n.d.	n.d.	0.02	0.51	0.76	48.68	0.73	37.06	2.11	123.57	0.08	5.03	214.84
Q260-0.5	n.d.	n.d.	1.46	17.89	0.83	25.55	0.35	8.50	0.06	1.80	n.d.	n.d.	53.74
R250-0.5	1.05	37.36	3.21	113.79	1.55	137.72	1.09	77.06	0.25	20.22	0.01	0.80	386.95
R251-1.5	0.01	0.28	0.46	9.19	0.59	29.66	0.51	20.25	n.d.	n.d.	n.d.	n.d.	59.38
R253-3.5	0.00	0.00	0.89	10.74	0.14	4.37	0.13	3.08	n.d.	n.d.	0.01	0.27	18.46
R270-0.5	n.d.	n.d.	0.46	17.45	1.03	98.04	1.01	76.38	0.45	39.08	0.02	1.80	232.74
R271-1.5	n.d.	n.d.	0.46	24.80	0.92	124.54	0.69	74.08	1.31	162.19	0.05	6.60	392.22

Table 3C-1:Continued

Sample	EX sol'n	EX sed	WAS sol'n	WAS sed	ER sol'n	ER sed	MR sol'n	MR sed	OX1 sol'n	OX1 sed	OX2 sol'n	OX2 sed	Total sed
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/kg
R273-3.5	n.d.	n.d.	0.74	24.69	0.43	36.45	0.26	17.27	0.11	8.34	0.01	0.76	87.51
S260-0.5	0.91	24.07	1.47	38.72	2.61	172.13	1.15	60.42	0.15	8.97	0.01	0.59	304.90
S261-1.5	n.d.	n.d.	n.d.	n.d.	0.52	64.89	0.27	26.45	n.d.	n.d.	0.04	4.83	96.17
T270-0.5	2.67	67.34	1.82	45.83	2.32	146.31	0.99	49.71	0.09	5.10	0.10	6.23	320.53
T271-1.5	n.d.	n.d.	1.77	73.30	1.97	204.38	1.05	86.72	0.11	10.29	0.14	14.39	389.08
U260-0.5	0.11	1.19	1.01	10.50	0.29	7.64	0.24	4.93	0.27	6.41	0.03	0.75	31.42
U261-1.5	n.d.	n.d.	1.44	16.25	1.37	38.89	1.15	25.97	n.d.	n.d.	0.09	2.52	83.62
U263-3.5	n.d.	n.d.	0.76	8.64	0.55	15.75	0.45	10.16	n.d.	n.d.	0.03	0.82	35.38

Table 3C-2: Replicate Sample Analysis for Zinc

sed indicates concentration in sediment (dry weight basis)
avg indicates the average of thee replicate samples. RSD indicates the relative standard deviation of the three replicates. SRM 2704 is NIST Buffalo River Sediment

Sample	EX sed (mg/kg)	WAS sed (mg/kg)	ER sed (mg/kg)	MR sed (mg/kg)	OX1sed (mg/kg)	OX2 sed (mg/kg)	Total sed (mg/kg)
B3a0-0.5	bdl	bdl	bdl	8.8	bdl	3.3	12.1
B3b0-0.5	1.7	bdl	bdl	2.1	bdl	bdl	3.8
B3c0-0.5	12.8	bdl	bdl	3.0	bdl	bdl	15.8
AVG	7.25	bdl	bdl	4.7	bdl	bdl	10.6
RSD	108.31	--	--	78.1	--	--	57.9
B9a0-0.5	bdl	bdl	5.1	6.0	bdl	bdl	11.2
B9b0-0.5	bdl	bdl	5.4	5.7	bdl	bdl	11.0
B9c0-0.5	bdl	bdl	3.8	5.8	4.5	bdl	14.1
AVG	bdl	bdl	4.74	5.8	bdl	bdl	12.1
RSD	--	--	18.1	3.2	--	--	14.2
B13a1-1.5	bdl	bdl	bdl	3.9	bdl	bdl	3.9
B13b1-1.5	bdl	bdl	bdl	6.7	bdl	bdl	6.7
B13c1-1.5	bdl	bdl	bdl	5.7	bdl	bdl	5.7
AVG	bdl	bdl	bdl	5.4	bdl	bdl	5.4
RSD	--	--	--	25.9	--	--	25.9

Table 3C-2:Continued

Sample	EX sed (mg/kg)	WAS sed (mg/kg)	ER sed (mg/kg)	MR sed (mg/kg)	OX1sed (mg/kg)	OX2 sed (mg/kg)	Total sed (mg/kg)
D9a3-3.5	1.5	bdl	bdl	bdl	bdl	bdl	1.5
D9b3-3.5	bdl	3.2	bdl	bdl	bdl	bdl	3.2
D9c3-3.5	bdl	1.0	bdl	bdl	bdl	bdl	1.0
AVG	bdl	bdl	bdl	bdl	bdl	bdl	1.9
RSD	--	--	--	--	--	--	60.9
F17a3-3.5	bdl	1.1	bdl	3.5	3.8	bdl	8.3
F17b3-3.5	bdl	bdl	bdl	1.7	4.2	bdl	5.9
F17c3-3.5	bdl	bdl	bdl	1.5	1.6	bdl	3.1
AVG	bdl	bdl	bdl	2.2	bdl	bdl	5.8
RSD	--	--	--	50.4	--	--	45.7
H23a0-0.5	bdl	bdl	1.3	15.3	3.0	1.5	21.1
H23b0-0.5	bdl	bdl	1.2	13.8	1.7	bdl	16.7
H23c0-0.5	bdl	bdl	3.2	13.0	bdl	bdl	16.2
AVG	bdl	bdl	1.90	14.1	bdl	bdl	18.0
RSD	--	--	57.59	8.3	--	--	15.0
I26a1-1.5	bdl	3.4	30.1	27.4	1.2	1.0	63.2
I26b1-1.5	1.0	4.1	29.6	27.3	bdl	1.5	63.5
I26c1-1.5	1.0	4.1	27.1	24.6	bdl	1.1	57.8
AVG	bdl	3.87	28.94	26.4	bdl	bdl	61.5
RSD	--	9.7	5.7	6.0	--	--	5.2

Table 3C-2:Continued

Sample	EX sed (mg/kg)	WAS sed (mg/kg)	ER sed (mg/kg)	MR sed (mg/kg)	OX1sed (mg/kg)	OX2 sed (mg/kg)	Total sed (mg/kg)
J19a0-0.5	--	135.2	95.6	52.0	11.4	9.1	--
J19b0-0.5	230.4	153.7	121.2	53.3	9.5	7.2	575.2
J19c0-0.5	235.7	141.4	115.0	53.3	10.2	12.9	568.5
AVG	233.05	143.44	110.58	52.8	bdl	bdl	571.9
RSD	1.64	6.57	12.05	1.5	--	--	0.8
L25a3-3.5	bdl	bdl	62.9	21.0	12.9	bdl	96.8
L25b3-3.5	bdl	bdl	55.2	26.5	23.4	bdl	105.1
L25c3-3.5	bdl	bdl	61.1	22.7	18.7	bdl	102.5
AVG	bdl	bdl	59.74	23.4	18.4	bdl	101.5
RSD	--	--	6.79	12.1	28.7	--	4.2
O22a1-1.5	22.2	206.5	422.4	223.8	bdl	6.7	881.5
O22b1-1.5	17.5	178.5	371.2	213.8	bdl	5.7	786.7
O22c1-1.5	22.3	205.5	407.1	230.5	21.4	6.5	893.4
AVG	20.68	196.82	400.25	222.7	bdl	6.3	853.9
RSD	13.15	8.08	6.56	3.8	--	8.2	6.8
P23a3-3.5	bdl	bdl	11.2	10.2	bdl	2.2	23.6
P23b3-3.5	bdl	bdl	10.0	8.4	bdl	bdl	18.4
P23c3-3.5	1.9	bdl	10.9	9.1	bdl	bdl	21.9
AVG	bdl	bdl	10.71	9.2	bdl	bdl	21.3
RSD	--	--	5.71	10.1	--	--	12.5

Table 3C-2:Continued

Sample	EX sed (mg/kg)	WAS sed (mg/kg)	ER sed (mg/kg)	MR sed (mg/kg)	OX1sed (mg/kg)	OX2 sed (mg/kg)	Total sed (mg/kg)
Q24a1-1.5	bdl	13.6	52.4	54.2	9.3	5.4	134.9
Q24b1-1.5	bdl	14.6	49.0	51.1	9.1	1.9	125.8
Q24c1-1.5	bdl	11.5	46.2	52.0	6.8	4.7	121.2
AVG	bdl	13.22	49.22	52.4	8.4	4.0	127.3
RSD	--	11.74	6.28	3.0	16.5	45.8	5.5
SRM27042/3/97	22.4	51.9	71.9	65.7	15.9	bdl	227.8
SRM27042/17/97	22.7	54.3	71.8	66.9	14.1	2.7	232.4
SRM27042/24/97	22.1	51.4	66.4	73.8	14.8	1.6	230.1
SRM27043/10/97	21.7	50.6	72.8	72.6	12.7	1.2	231.5
SRM27043/24/97	21.7	48.0	75.1	53.8	12.0	1.9	212.5
SRM27044/7/97	--	--	--	--	--	--	--
AVG	22.09	51.27	71.59	66.55	13.90	1.84	226.87
RSD	2.1	4.4	4.5	11.9	11.4	32.5	3.6

Table 3D-1 Calculation of S^{2-} in NaOH Trap for acid volatile sulfide determination

Abs. indicates absorbance of methylene blue produced by MDR solution and S^{2-} liberated from samples
Conc. indicates converted concentration of S^{2-} in trap solution

SampleID	S^{2-} trap Abs. (1:10 dilution)	Conc. (normal range calib.) S (umol/100 ml)	S^{2-} trap Abs. (no dilution)	Conc. (low range calib.) S (umol/100 ml)
J19AVS	0.00	-0.74	0.01	0.01
J23AVS	0.10	3.38	0.92	**3.75**
K22AVS	0.07	2.42	0.71	**2.90**
N23AVS	0.18	**6.93**		
O22aAVS	0.46	**19.19**		
O22cAVS	0.45	**18.84**		
O22dAVS	0.44	**18.49**		
P25AVS	0.01	-0.17	0.11	**0.42**

Table 3D-1 Calculation of acid volatile sulfide (AVS)

SampleID	Ww wet weight (g)	dry weight (g)	S (umol/100ml)	R dry wt./ wet wt.	AVS = S/(R*Ww) (umol/g dry sed)
J19AVS	2.99	1.03	0.01	0.35	0.01
J23AVS	3.06	0.35	3.74	0.12	10.58
K22AVS	3.07	0.43	2.90	0.14	6.69
N23AVS	2.93	0.60	6.93	0.20	11.61
O22aAVS	3.15	1.60	19.19	0.51	12.62
O22cAVS	3.16	1.61	18.84	0.51	11.92
O22dAVS	3.06	1.56	18.49	0.51	11.51
P25AVS	2.99	0.45	0.42	0.15	0.09

Table 3D-2 Concentrations of simultaneously extracted metals (SEM) from AVS/SEM analysis

$[SEM]_x$ (μmol/g) indicates concentration of metal in leachate fluid after acid volatile sulfide liberation
b.d.l. indicates concentration was below detection limit

Sample ID	$[SEM]_{Fe}$ umol/g	$[SEM]_{Mn}$ umol/g	$[SEM]_{Zn}$ umol/g	$[SEM]_{Ni}$ umol/g	$[SEM]_{Cu}$ umol/g	$[SEM]_{Pb}$ umol/g	$[SEM]_{Cd}$ umol/g
J19 AVS	66.96	0.04	0.21	b.d.l.	0.35	32.85	b.d.l.
J23 AVS	33.15	0.64	2.26	0.06	0.13	4.17	0.68
K22 AVS	110.43	5.37	7.04	0.05	0.11	1.17	0.16
N23 AVS	76.10	0.85	2.87	b.d.l.	0.06	1.32	0.01
O22a AVS	26.05	1.15	1.27	0.08	0.03	0.83	b.d.l.
O22c AVS	24.16	1.13	1.28	0.06	0.02	1.07	b.d.l.
O22d AVS	24.65	1.15	1.24	0.08	0.03	1.03	b.d.l.
O22 AVS avg	24.95	1.14	1.26	0.07	0.02	0.98	b.d.l.
P25 AVS	101.70	1.86	1.10	0.09	0.10	0.56	0.01

Table 3E-1:
Pore water data for samples taken on 7/26/97.

Sample	Temp. (C)	pH	Eh	Alkalinity as HCO_3^- (mg/L)	NH_3 (mg/L)	NO_3^- (mg/L)	S^{2-} (mg/L)	SO_4^{2-} (mg/L)	CH_4 (mg/L)
J23 top	17.5	6.49	-100.0	202.60	0.13	0.00	1.45	1.60	8.67
J23 bottom	--	6.85	-148.0	173.93	0.43	0.00	1.44	0.70	2.58
K22 top	14.0	6.97	-15.0	324.93	0.38	0.00	0.19	0.00	3.37
K22 bottom	--	7.06	-22.0	164.37	0.13	0.00	0.19	6.20	0.31
N23 top	16.5	6.54	-51.0	277.14	0.46	0.02	0.23	1.70	11.61
N23 bottom	--	6.58	-48.0	244.65	1.30	0.00	0.24	0.60	20.32
P25 top	17.5	7.32	150.0	91.74	0.12	0.86	0.21	2.40	0.00
P25 bottom	--	--	-35.0	221.71	4.11	0.01	0.21	0.20	12.26

Sample	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Br^- (mg/L)	Cl^- (mg/L)	Fe(total) (mg/L)	Fe^{2+} (mg/L)	$Fe_{tot} - Fe^{2+} = Fe^{3+}$ (mg/L)
J23 top	45.50	12.60	2.25	21.06	bdl	41.60	1.26	1.20	0.06
J23 bottom	43.00	12.45	3.92	19.91	bdl	39.60	1.32	1.20	0.12
K22 top	57.50	14.35	2.87	18.46	bdl	37.40	8.32	3.90	4.42
K22 bottom	40.00	11.23	2.01	19.21	bdl	32.90	3.32	3.00	0.32
N23 top	65.50	14.37	2.02	14.54	bdl	19.10	47.40	50.00	-2.60
N23 bottom	58.50	13.50	1.67	16.00	bdl	23.70	36.36	34.80	1.56
P25 top	25.50	6.55	1.22	14.02	bdl	21.00	7.08	2.15	4.93
P25 bottom	30.00	6.72	1.36	14.20	bdl	19.50	9.72	9.10	0.62

Sample	Cd (ug/l)	Co (ug/l)	Cu (ug/l)	Cr (ug/l)	Mn (ug/l)	Ni (ug/l)	Pb (ug/l)	Zn (ug/L)	
J23 top	--	0.42	0.46	11.54	156.86	3.65	bdl	--	
J23 bottom	--	0.50	1.83	84.84	54.85	3.16	1.61	--	
K22 top	--	0.44	bdl	44.88	496.22	1.06	0.53	--	
K22 bottom	--	0.20	bdl	29.82	245.34	0.84	0.26	--	
N23 top	--	1.48	0.78	137.60	973.35	7.27	0.34	--	
N23 bottom	--	0.68	bdl	164.30	645.66	2.99	3.18	--	
P25 top	--	0.23	0.87	19.20	19.59	2.25	0.12	--	
P25 bottom	--	0.94	0.05	70.00	464.08	3.07	bdl	--	

Table 3E-2:
Pore water data for samples taken on 7/26/97.

Sample	Temp. (C)	pH	Eh	Alkalinity as HCO_3^- (mg/L)	NH_3 (mg/L)	NO_3^- (mg/L)	S^{2-} (mg/L)	SO_4^{2-} (mg/L)	CH_4 (mg/L)
I22	7.1	7.08	-140	160.55	1.11	--	0.79	--	0.27
J23	13.9	6.57	-152	168.20	1.52	--	2.67	--	11.49
K28	10.4	6.59	-101	179.67	0.91	--	0.44	--	0.13
L27	11.9	6.81	-52	374.62	1.14	--	0.24	--	15.3
M28	12.5	6.41	-45	324.93	5.07	--	0.32	--	31.02
N25	15.7	6.6	-71	217.89	1.05	--	0.41	--	2.43
Q26	13.4	6.65	-27	237.01	6.11	--	0.17	--	16.82
S26	14.8	7.5	-10	202.60	1.45	--	0.14	--	4.21

Sample	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Br^- (mg/L)	Cl^- (mg/L)	Fe(total) (mg/L)	Fe^{2+} (mg/L)	$Fe_{tot} - Fe^{2+} = Fe^{3+}$ (mg/L)
I22	42.50	11.84	2.26	19.19	--	--	1.49	1.43	0.06
J23	47.00	12.48	3.70	23.50	--	--	0.71	0.69	0.02
K28	48.00	15.76	3.14	22.16	--	--	5.00	5.02	-0.02
L27	72.50	31.60	1.91	24.39	--	--	2.63	2.88	-0.25
M28	59.50	15.44	3.85	15.94	--	--	29.67	30.62	-0.95
N25	61.00	14.75	1.38	19.24	--	--	5.14	4.80	0.34
Q26	58.50	12.32	5.54	13.49	--	--	17.06	17.49	-0.43
S26	57.00	8.05	1.57	6.83	--	--	1.62	1.44	0.18

Sample	Cd (ug/L)	Co (ug/L)	Cu (ug/L)	Cr (ug/L)	Mn (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	
I22	--	0.22	2.08	25.12	0.03	3.33	--	--	
J23	--	0.21	1.68	11.40	0.09	3.99	--	--	
K28	--	0.52	0.48	2.02	0.15	2.70	--	--	
L27	--	0.48	0.13	3.04	0.51	3.33	--	--	
M28	--	0.31	1.10	40.96	1.20	3.45	--	--	
N25	--	0.29	1.22	6.64	0.21	3.09	--	--	
Q26	--	1.45	5.17	5.72	3.18	3.11	--	--	
S26	--	0.49	0.88	22.60	5.41	1.96	--	--	

Table 3E-3:
Pore water data for samples collected 10/8/97

Sample	Temp. (C)	pH	Eh	Alkalinity as HCO_3^- (mg/L)	NH_3 (mg/L)	NO_3^- (mg/L)	S^{2-} (mg/L)	SO_4^{2-} (mg/L)	CH_4 (mg/L)
J23 top	9.5	6.51	-105	156.73	0.26	bdl	1.67	0.60	3.01
J23 bottom	9.5	6.7	-125	137.62	0.62	0.19	0.89	0.80	2.25
K22 top	9.9	6.76	-188	210.25	0.55	bdl	0.12	0.60	6.34
K22 bottom	9.9	6.99	-157	129.97	0.58	bdl	bdl	5.60	bdl
N23	11	6.24	6	175.84	0.82	0.38	bdl	0.80	9.86
O22	11.7	7.02	-160	424.32	20.42	bdl	0.46	1.60	19.61
P25 top	12.4	6.37	19	91.74	0.86	bdl	bdl	0.10	bdl
P25 bottom	12.4	6.15	21	126.15	3.20	bdl	bdl	0.30	4.61
Q26 barrel	15.2	6.71	-95	137.62	2.44	bdl	bdl	0.80	bdl

Sample	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Br^- (mg/L)	Cl^- (mg/L)	Fe(total) (mg/L)	Fe^{2+} (mg/L)	$Fe_{TOT} - Fe^{2+} = Fe^{3+}$ (mg/L)
J23 top	41.00	4.92	13.00	25.00	bdl	48.80	0.64	0.45	0.19
J23 bottom	42.00	3.32	12.50	25.00	bdl	48.40	0.84	0.69	0.15
K22 top	40.00	4.53	11.00	14.00	bdl	22.20	3.56	3.41	0.15
K22 bottom	50.00	3.23	14.50	20.50	bdl	37.40	3.56	3.31	0.25
N23	32.50	1.20	9.00	13.50	bdl	21.10	11.44	9.54	1.90
O22	135.00	0.39	2.50	5.50	bdl	11.00	0.8	0.61	0.19
P25 top	26.50	1.95	7.50	19.00	bdl	31.80	7.64	9.54	-1.90
P25 bottom	25.50	1.41	6.50	15.00	bdl	22.00	9.36	10.53	-1.17
Q26 barrel	32.50	2.32	8.50	12.00	bdl	29.30	11.36	7.96	3.40

Sample	Cd (ug/L)	Co (ug/L)	Cu (ug/L)	Cr (ug/L)	Mn (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	
J23 top	0.39	0.16	3.01	16.43	70.19	2.14	1.70	2.43	
J23 bottom	1.21	0.16	3.36	40.67	32.24	2.39	0.91	12.14	
K22 top	0.16	0.20	5.08	63.69	270.77	1.90	0.03	55.61	
K22 bottom	0.04	0.18	6.54	26.52	395.47	1.99	0.09	93.63	
N23	0.01	0.35	8.53	96.14	402.94	2.67	1.98	150.68	
O22	0.20	0.39	4.40	43.36	270.15	9.78	0.50	162.19	
P25 top	0.67	0.85	8.76	144.66	361.96	3.74	1.84	242.62	
P25 bottom	0.04	1.26	1.70	167.90	302.84	4.67	0.83	217.78	
Q26 barrel	0.03	0.61	2.27	10.47	1410.10	2.32	3.72	14.40	

Table 3E-4:
Pore Water Data Collected on 11/20/97

Sample	Temp. (C)	pH	Eh	Alk. As HCO_3^- (mg/L)	NH_3 (mg/L)	NO_3^- (mg/L)	S^{2-} (mg/L)	SO_4^{2-} (mg/L)	CH_4 (mg/L)
J23	--	6.8	-82	156.73	0.61	bdl	0.66	12.94	0.07
K22	2.7	6.75	58	141.44	0.61	bdl	bdl	5.23	1.98
N23	1.8	6.43	47	141.44	0.22	bdl	bdl	0.66	1.75
O22	5.6	7.19	-17	428.14	12.99	bdl	0.17	5.72	8.48
P25	1.5	6.57	42	122.33	1.09	bdl	bdl	bdl	1.17

Sample	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Br^- (mg/L)	Cl^- (mg/L)	Fe(total) (mg/L)	Fe^{2+} (mg/L)	Fe_{Tot} - Fe^{2+}= Fe^{3+} (mg/L)
J23	43.50	4.16	13.00	26.50	bdl	49.20	0.32	0.21	0.11
K22	44.00	4.34	14.00	18.00	bdl	26.30	1.98	1.59	0.39
N23	34.50	0.69	9.50	16.50	bdl	24.00	13.66	12.43	1.23
O22	134.50	0.45	4.00	7.00	bdl	12.60	1.56	1.49	0.07
P25	26.50	2.72	7.00	14.00	bdl	31.00	7.44	7.09	0.35

Sample	Cd (ug/L)	Co (ug/L)	Cu (ug/L)	Cr (ug/L)	Mn (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	
J23	3.91	0.11	5.35	3.83	73.48	2.11	0.64	10.82	
K22	1.26	0.22	3.44	35.88	392.61	1.60	bdl	14.05	
N23	1.19	0.42	4.44	124.19	517.20	1.88	0.32	83.51	
O22	1.10	0.31	9.16	41.16	404.66	1.72	0.73	2.34	
P25	1.17	0.63	1.99	122.54	350.16	2.27	1.46	17.87	

Table3F-1: Sequential Chemical Extraction Data for Pure Minerals

-- indicates leachate not measured, * indicates extraction was not performed
Amount added (µmol) indicates amount weighed out for extractions
Sum total, (µmol) indicates calculated sum of individual extractions
%EX, WAS, ER, MR, OX1, OX2 indicate percentages of recovered metals in a particular extraction
Shaded areas indicate the extraction that accounts for the highest percentage of recovered metals.

SampleID	Amount added	Sum total	% Recovered	%EX	%WAS	%ER	%MR	%OX1	%OX2
	(µmol)	(µmol)							
CuSa	198.7	81.4	41.0%	--	0.0%	0.0%	0.1%	91.2%	8.8%
CuSb	73.2	15.4	21.1%	--	0.0%	0.1%	0.2%	75.0%	24.6%
CuSc	188.3	98.1	52.1%	--	0.0%	0.0%	0.1%	97.4%	2.5%
FeSa	238.9	171.9	72.0	0.7%	5.7%	12.4%	62.3%	16.7%	2.1%
FeSb	147.9	99.6	67.3	0.8%	5.3%	6.5%	65.5%	19.5%	2.4%
FeSc	79.6	31.7	39.8	1.7%	5.7%	14.9%	61.0%	13.0%	3.8%
ZnSa	164.2	131.6	80.1%	0.0%	0.1%	24.1%	5.7%	70.1%	0.0%
ZnSb	215.5	202.9	94.1%	0.1%	0.1%	14.3%	4.0%	81.5%	0.0%
ZnSc	82.1	113.1	137.7%	0.0%	0.1%	26.4%	7.5%	65.9%	0.0%
Pyrite a	417.4	15.0	3.6	0.1%	0.2%	0.5%	1.0%	--	98.2%
Pyrite b	160.0	9.5	5.9	0.2%	0.2%	0.8%	6.3%	8.7%	83.8%
Pyrite c	243.5	12.0	4.9	0.2%	0.2%	0.7%	1.0%	15.1%	82.9%

Table3F-1:Continued

SampleID	Amount added (µmol)	Sum total (µmol)	% Recovered	%EX	%WAS	%ER	%MR	%OX1	%OX2
Magnetite a	441.9	8.8	2.0%	0.0%	0.5%	1.4%	92.5%	3.5%	2.0%
Magnetite b	517.0	10.0	1.9%	0.0%	0.4%	1.6%	91.5%	4.9%	1.6%
Magnetite c	966.7	9.0	0.9%	0.0%	0.7%	4.0%	88.9%	3.8%	2.6%
Siderite a	686.4	271.4	39.5%	0.0%	0.4%	6.4%	84.2%	1.9%	7.0%
Siderite b	452.4	217.9	48.2%	0.0%	0.5%	9.4%	81.5%	3.3%	5.3%
Siderite c	557.7	269.1	48.3%	0.0%	0.4%	7.5%	85.7%	0.8%	5.6%
Siderite d	319.43	171.53	*	*	*	*	53.7%	*	*
Siderite e	416.99	265.00	*	*	*	*	63.5%	*	*
Siderite f	151.08	103.49	*	*	*	*	68.5%	*	*
Siderite g	49.21	42.97	*	*	*	*	87.3%	*	*

Note - Shaded areas within the data indicate the extraction that accounts for the highest percentage of the recovered metal.

Appendix 3G:

X-ray Diffraction Peak Interpretations and Mineral Identification

Peak Identification and mineral identification is described in detail for sample D11 1-1-5 prior to a modified sequential chemical extraction (WAS, ER and MR extractions only). Brief comments are given if mineralogy changed after a given extraction within the sequence. All minerals present in the sample prior to extractions were found to be present after extractions with the exception notable exception of calcite not present after the WAS, NaOAc (pH 5) extraction

Sample D11 1-1.5

Quartz is present as evident by several peaks a couple of hkl reflections (112) at 1.82 Å, (200) at 2.12 Å, as well as more common peaks at 3.33 Å, and 4.23 Å.

Calcite is present as evident by a 2.27 Å peak (this disappears after extraction with NaOAc (pH 5), a common extraction to remove carbonates).

Several ***feldspars*** are present. Peaks at 3.12 Å and 3.18 Å are indicative of plagioclases. A peak at 3.23 Å indicates that a potassium feldspar is also present possibly microcline.

An ***Amphibole*** of some kind is present as evident by an 8.38 Å peak.

Mica is present as evident by a (001) peak at 9.81 Å and a broad (002) peak at 4.9 Å. Fe in octahedral sites of mica (biotite) causes the (002) peak to be missing or very weak

relative to the (001) peak. Relatively strong (002) peaks indicate the presence of Mg or Al micas (muscovite). In this case the (002) is relatively weak but still noticeable suggesting the presence of illite which can have Fe substitution in octahedral sites.

Kaolinite may be present as evident by a peak at 7.07 Å (001), and a peak on the shoulder of a broad peak at 3.5 Å. Positive identification of kaolinite is hindered by the presence of chlorite. There appears to be three separate peaks near 3.5 Å which may be vermiculite (004), chlorite (004) at 3.53 Å, and kaolinite (002) at 3.56 Å.

Chlorite is present as evident by a (001) peak at 14.0 Å for Mg-saturated, K-saturated and K 550°C treatments. Also, higher order peaks are found at (002) peak at 7 Å, a (003) peak at 4.7 Å, and a (004) peak at 3.53 Å. The three peaks around 3.5 Å may indicate vermiculite (004), chlorite (004) at 3.53 Å, and kaolinite (002) at 3.56 Å peaks.

Vermiculite may be present as evident by 14 Å peak and an (004) peak at 3.48 Å. The three peaks around 3.5 Å indicate chlorite (004), vermiculite (004), and kaolinite (002) peaks. However, vermiculite collapses to 10Å when K-saturated. The 10 Å/14 Å peak ratios for the K-saturated sample should be larger than that for the Mg saturated sample if vermiculite is present.

HIV may be present as evident by broad intensity between the 10 Å an 14 Å peaks for all treatments and high order peaks of vermiculite around 3.5. The three peaks around 3.5 Å may indicate vermiculite (004) at 3.48 Å, chlorite (004) at 3.53 Å, and kaolinite (002) at 3.56 Å peaks.