THESIS

CHARACTERIZATION AND PREDICTION OF LONG-TERM ARSENIC MOBILITY, DISSOLUTION, AND KINETIC BEHAVIOR IN ARSENIC CONTAMINATED FLOODPLAIN DEPOSITS OF WHITEWOOD CREEK AND THE BELLE FOURCHE RIVER, SOUTH DAKOTA.

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ABSTRACT

CHARACTERIZATION AND PREDICTION OF LONG-TERM ARSENIC MOBILITY, DISSOLUTION, AND KINETIC BEHAVIOR IN ARSENIC CONTAMINATED FLOODPLAIN DEPOSITS OF WHITEWOOD CREEK AND THE BELLE FOURCHE RIVER, SOUTH DAKOTA

From 1877 to 1977, the Homestake Mine discharged over 100 million tons of arsenic-rich minewastes from Lead, South Dakota into Whitewood Creek (WWC), which joins the Belle Fourche River (BFR). Arsenopyrite and other arsenic-bearing minerals were deposited in tailings (containing between 0.12% to 0.35% arsenic) and mixed with uncontaminated alluvium along the floodplains of WWC and the BFR as overbank deposits and filling abandoned meanders. Since it is not feasible to remove millions of tons of contaminated sediments from the area, an understanding of arsenic mobility on long timescales is vital. Many studies have laid the framework for factors controlling arsenic mobility appropriate to fluvial sedimentary systems; investigating mechanisms of arsenic mobilization, adsorption/desorption kinetics, and the effects of pH, changing redox conditions, etc., however, these studies were conducted on relatively short time scales and did not quantify arsenic mass-budget on field-scales.

This study focuses on the long-term retention, dissolution, and kinetic behavior of arsenic from mine tailings. The uniqueness of this site enables arsenopyrite dissolution behavior to be constrained over a 135-year timespan (1877-2012). This allows for the investigation of changes in arsenic's residence sites, its rate of release into the environment, calculation of its transport mass-budget, and elucidation of how natural processes have or have not remediated arsenic contamination over a span of 35 years since the deposition of tailings have ceased (1977-2012). For this investigation, sediment, surface water, and seep water samples were collected along reaches of WWC and the BFR for analysis of arsenic and other geochemical constituents. Sequential extractions of the sediments were performed to determine the mineralogical setting of the arsenic as well as the proportion of arsenic available at different rates of release into the environment. Additionally, various historical data (discharge levels, geochemical analyses

of water and sediment samples) were compiled from the United States Geological Survey database. Regressions were applied to historical data to estimate the rate of physical and chemical arsenic removal from the WWC watershed.

Sediments collected along the floodplains of WWC and the BFR exhibited arsenic concentrations ranging from approximately 100 to 4,000 mg/kg. The results from the sequential extractions applied to the sediments suggest arsenic is predominantly located in residence sites that are not easily accessible, and arsenic is not readily mobilized or released into solution in large quantities under normal environmental conditions seen in WWC and the BFR. An average of 16% of the arsenic is weakly bound to readily exchangeable surface sites, water-soluble secondary minerals and available for rapid release, or is adsorbed to exchange sites that easily exchange PO4³⁻ ions for adsorbed arsenic oxyanions, is weakly bound in amorphous to poorly crystalline fine-grained metal oxides/hydroxides, reducible phases, and easily soluble carbonates. An average of 24% of the arsenic is moderately strongly bound in weakly soluble secondary minerals like clays or crystalline fine-grained metal oxides/hydroxides and will be released relatively slowly with time. The remaining 60% of arsenic is interpreted to be relatively immobile and locked in arsenopyrite in part due to the formation of metal oxyhydroxide coating, which slows down the degradation of the mineral. These interpretations are supported by the elevated but still relatively low total arsenic concentrations (EPA MCL for arsenic is 0.01 mg/L) of in-stream water in WWC (averaging 0.037 mg/L) and in the BFR (averaging 0.021 mg/L), considering that in-stream sediments carried by WWC and the BFR have high arsenic concentrations (264 to 694 mg/kg).

Based on regressions applied to 30 years of historical sediment transport and arsenic concentration in solution and in sediment load (1982-2012), the average annual total arsenic load transported out of WWC during these 30 years was estimated to be between 34 to 71 megagrams (Mg) per year. At this rate, based on the 17,400 to 50,800 Mg of arsenic that remain in storage along the floodplains of WWC, complete arsenic transport out of the floodplains of WWC would range between 250 to 1,500 years. The actual rate of arsenic removal is expected to be longer because the model is based on a uniform movement of uniformly distributed sediment, and historical patterns may not be reflective of

future trends, as evidenced by the decline in suspended arsenic transport rate starting in the early- to mid-1980s. The constant shifting of the stream creates abandoned meanders along WWC that can store contaminated sediment where the stream no longer has access. Conversely, as the meanders shift over time, the once-abandoned meanders could be again accessed by WWC. The majority of suspended sediment transport occurs during flood events; approximately 88% of the total arsenic load moved during the years between 1983 to 2012 occurred in only 3 of the years (1983, 1984, and 1995). Thus, the rate of arsenic transport for the next 30-year period is uncertain and could be lower if the number of flood events remains low.

Although the WWC area once experienced heavy environmental degradation during the period of active mining, natural processes have allowed for relatively stable current environmental conditions. However, the physical transport of arsenic-contaminated sediment and the slow release of arsenic to the environment endures downstream to the BFR into the Cheyenne River and Lake Oahe and will continue for many generations.

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CHAPTER 1. INTRODUCTION

Arsenic contamination of water sources, soils, and sediments could be due to natural geochemical and biogeochemical processes (geogenic) or could be attributable to the disposal and storage of minewastes or tailings from the mining of metals (anthropogenic). High concentrations of dissolved arsenic in ground water, exceeding the maximum concentration limit (MCL) of 0.01 mg/L recommended for drinking water by the World Health Organization (WHO), is usually geogenic, with many areas affected within the United States as well as large regions of Bangladesh, India, China, and Vietnam (Smedley and Kinniburgh, 2002). People who depend on these contaminated groundwater sources face widespread, chronic, and severe health issues such as gastrointestinal, kidney, liver, and skin cancers, as well as reproductive disorders and birth defects (Rahman et al., 2009). Arsenic can also be toxic to plants and aquatic life, having an average phytotoxicity threshold of 40 mg/kg in crop plants (Sheppard, 1992)

Anthropogenically sourced arsenic from historic mining activity degrades the quality of surrounding soils and sediments, thus impairing surface and ground water quality. Additionally, tailings deposited into rivers or streams can be re-entrained and re-deposited along floodplains for tens to hundreds of miles downstream, further spreading the contamination (Marron, 1992). The toxicity and impact of arsenic cannot be assessed only by its total concentration in the sediment. Even more vital is the assessment of arsenic's mobility and retention, which is dependent on arsenic's speciation, its interaction with other metals, the presence and abundance of bacteria and organic matter, and how arsenic is partitioned amongst its residence sites within the sediment. Some terminologies presented in this chapter are defined below and may be interchangeably used:

- Oxide, hydroxide and oxyhydroxide mineral groups comprised of cations such as aluminum, iron, or manganese where the anionic component is either an oxygen (-O), a hydroxyl group (-OH), or an oxygen and a hydroxyl (-OOH), respectively. When addressing these three groups collectively, they will be referred to as (Al, Fe, Mn)–oxyhydroxides.
- Residence sites / settings the location within the sediment/ substrate where arsenic is bound.

 Partitioning / fractionation – the distribution and apportionment of arsenic amongst its residence sites or settings.

1.1. Literature Review

Below is an overview of the literature and knowledge on arsenic transport and mobility. Topics addressed include: 1) arsenic geochemistry overview, 2) arsenic immobilization, 3) arsenic mobilization, 4) detection and characterization of arsenic settings, and 5) kinetics of arsenopyrite dissolution.

1.1.1. Arsenic Geochemistry Overview

Arsenic is a metalloid that is generally associated with iron and sulfide minerals in gold and silver ores. Common primary arsenic-bearing minerals include arsenopyrite (FeAsS), arsenian or arsenical pyrite (Fe(S, As)₂), realgar (AsS), and orpiment (As₂S₃). Because of arsenic's close association with gold and silver, these arsenic-bearing minerals are usually mined, crushed, and milled along with the ore. In soils, arsenic exists in two main oxidation states (3+) and (5+), with As⁵⁺ comprising greater than 90% of total arsenic species in some oxidized soils (Matera, 2003). As a result of arsenic's tendency to bind with O^{2-} and OH^- , it forms oxyanions due to the net negative charge of the complexes it forms. Common complexes for As (V) in aqueous solution include AsO₄³⁻ and H₂AsO₄⁻, while As (III) commonly forms H₃AsO₃°, with other possible complexes including H₄AsO₄⁻ and HAsO₃²⁻.

Arsenite (As (III)) is more mobile and toxic than arsenate (As(V)) because As(V) sorbs more strongly to minerals and other constituents in sediment (Kocar et al., 2006; Tufano et al., 2008). This is in part due to the negatively charged As(V) complexes having a greater affinity for positively charged mineral surfaces (commonly containing Fe³⁺ or Al³⁺) than the neutrally charged As(III) complexes. Arsenite also forms weaker inner-sphere complexes as well as outer-sphere complexes with iron oxyhydroxides, which results in more rapid arsenic desorption (Ona-Nguema et al., 2005).

1.1.2. Arsenic Immobilization in Surficial Environments

The dominant process immobilizing arsenic in near-surface environments is its sorption onto soil particles. Sorption is a general term used to describe the retention of a metal (sorbate) to a surface

(sorbent) through mechanisms like adsorption (arsenic is retained on the surface) and precipitation (arsenic is incorporated into the mineral structure).

Adsorption is a dominant process in arsenic retention and is largely controlled by surface functional groups (molecular units in the structure of the solid or sorbent that have exposed reactive components to attach with metals in solution), which bind with ions or molecules in solution to form surface complexes. The two types of surface complexes are: 1) outer-sphere complexes, where a water molecule is present between the metal ion or molecule and the surface functional group, and 2) innersphere complexes, where the water molecule is not present. The absence of the water molecules allows for inner-sphere complexes to have much stronger bonds with surfaces than outer-sphere complexes.

In many environments, a large proportion of the arsenic adsorbs to clays (kaolinite and montmorillonite) and iron or aluminum oxyhydroxide surfaces as both inner- and outer-sphere complexes (Fendorf et al., 1997; Arai et al., 2001; Catalano et al., 2008). Additionally, arsenate, rather than arsenite, is preferentially adsorbed by aluminum hydroxides and aluminosilicate clay minerals (Manning and Goldberg, 1997 a & b). Arsenic is also known to bind with manganese oxides, where adsorbed arsenite is oxidized to arsenate with reduction of Mn (III or IV) (Manning et al., 2002; Oscarson et al., 1981). Arsenate and arsenite exhibit maximum adsorption onto organic matter at pH 5.5 and 8.0, respectively (Grafe et al., 2001 & 2002; Ko et al., 2004). Yet, the correlation between organic matter and total arsenic is typically poor (Chen et al., 2002), indicating its role in arsenic retention in soils and sediments is limited, possibly due to the incompatibility of negatively charged anions to negatively charged surfaces (Thanabalasingam and Pickering, 1986).

Precipitation is another process governing arsenic retention. As primary arsenic minerals weather, thermodynamically more stable arsenic-bearing secondary minerals form. A common secondary mineral of arsenopyrite is scorodite (FeAsO₄·2H₂O) (Donahue et al., 2000); its formation is presented in (Equation 1.1). Fine-grained secondary ferric oxyhydroxides (e.g., goethite, ferrihydrite) can be markedly arsenic-rich and can form weathering crusts that may obstruct further weathering of the primary arsenic mineral (Bowell, 1994).

$$FeAsS + 14Fe^{3+} + 10H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + FeAsO_4 \cdot 2H_2O + 16H^+$$

Equation 1.1.

Other secondary mineral precipitates include jarosite (KFe₃(SO₄)₂(OH)₆), a weathering product of pyrite where arsenate can substitute for SO₄²⁻ (Savage et al., 2000), hornesite (Mg₃(AsO₄)₂·8H₂O) (Voigt et al., 1996), calcium arsenates (Juillot et al., 1999), in addition to iron arsenic oxides (e.g. FeAsO₄·2H₂O) (Davis et al., 1996). The stability of these secondary arsenic-bearing phases depends on the crystallinity of the mineral structure. For example, amorphous iron oxyhydroxides like ferrihydrite are less stable than the more crystalline goethite. Additionally, the greater the molar iron to arsenic ratio (Fe:As) of the arsenic-bearing secondary phase, the less soluble arsenic is (Krause and Ettel, 1989). Arsenic can be considered relatively insoluble at a molar Fe:As ratio of three or greater (Harris and Monette, 1989). Under certain conditions, carbonates and organic matter are known hosts of arsenic (Larios et al., 2013). For example, arsenate forms outer-sphere complexes with Ca²⁺ forming amorphous iron-calcium arsenate minerals, especially in carbonate-buffered tailings (Walker et al., 2009; Sadiq, 1997; Smith et al., 1998; Harvey et al., 2002).

1.1.3. Arsenic Mobilization

The desorption of arsenic from solid phases can be attributed to three main pathways: (1) changes in pH, (2) competitive exchange by ion displacement, and (3) changes in Eh causing the reduction of arsenate to arsenite or the reductive dissolution of substrate iron and manganese oxyhydroxides.

pH is a major factor controlling the adsorption, desorption, and precipitation of arsenic. Arsenic sorption on clay minerals (kaolinite and montmorillonite) is highly pH dependent (Frost and Griffin, 1997). Maximum As (III) and As (V) sorption onto hydrous metal oxides are in pH ranges of 7 to 10 and 4 to 7, respectively (Pierce and Moore, 1982). For example, the percent of As (V) adsorbed onto a hydrous ferric oxide in typical sediment is close to 100% at pH 4 and decreases to less than 10% at pH 10 (Dixit and Herring, 2003).

Competitive exchange and displacement of arsenic complexes by phosphate ions, which are similar in size and charge, is another mobilization mechanism of surface sorbed arsenic (Manning and

Goldberg, 1996; Dixit and Hering, 2003; Smedley and Kinniburgh, 2002; Violante and Pigna, 2002). Areas with high fertilizer and pesticide runoff are especially prone to this type of arsenic mobilization (Jain and Loeppert, 2000; Peryea and Kammerack, 1997). Carbonates and organic matter can also competitively adsorb onto mineral surfaces and desorb arsenic or inhibit arsenic adsorption (Redman et al., 2002; Van Geen et al., 1994; Villalobos and Leckie, 2001).

Changes in Eh most commonly occur in saturated soils, usually after the depletion of O₂ by bacteria or microbes, which then utilize other electron acceptors either through the reduction of arsenate to arsenite or by the reductive dissolution of Fe (III) phases. It is debated whether arsenic reduction or iron reduction exerts more influence in the destabilization and release of arsenic in soils. The reduction of arsenate to arsenite could play a dominant role since As (III) forms labile complexes with iron oxyhydroxides. However, in soils and sediments total arsenic content generally display strong correlations with iron content (Smedley and Kinniburgh, 2002), thus the reductive dissolution of Fe (III) phases can greatly impact arsenic retention and also reduce the total amount of sorbent available (Fendorf, et al., 2010).

Although iron oxyhydroxide weathering-crust formation around a primary arsenic-bearing mineral can hinder the weathering process, fine-grained amorphous ferrihydrite is thermodynamically unstable and is readily bio-reducible. However, ferrihydrite may not dissolve congruently and can be transformed to more crystalline phases (goethite, hematite, or magnetite) during the reductive dissolution process; decreasing the amount of surface area available for arsenic retention (Appelo et al., 2002). Yet, as mentioned in the section above, these crystalline phases are more thermodynamically stable than amorphous phases. Thus, "while reductive dissolution of ferric (hydr)oxides can lead to arsenic release, under conditions conducive to re-mineralization, arsenic desorption is suppressed rather than promoted" (Fendorf, et al., 2010).

Although iron oxyhydroxides can govern arsenic mobility, it appears that the adsorbed arsenic also impacts iron oxyhydroxide solubility and transformation. Borch (2007) discovered that oxyanions (phosphates & arsenates) sorb to iron oxyhydroxide surfaces, hindering their dissolution and thus

hindering secondary mineral formation like goethite. Similarly, Rancourt et al. (2001) confirms that the structure of ferrihydrite is stabilized by adsorbed arsenic, retarding its transformation to more crystalline phases.

1.1.4. Detection and Characterization of Arsenic Settings

The identification of arsenic-bearing phases is conducted through instrumental techniques such as SEM-EDS (Scanning Electron Microscope with Energy Dispersive Spectroscopy) to conduct morphological analyses of individual grains and mineral surfaces and to examine arsenic association with other elements. XRD (X-ray diffraction) is also used to differentiate crystalline mineral phases within the sediment (Juillot et al., 1999; Larios et al., 2012; Corriveau et al., 2011). Crystalline arsenic mineral phases, however, are usually low in abundance and not detectable due to the instrument's approximate 5% molar detection limit (Matera, 2003). Non-crystalline phases such as fine-grained amorphous ferrihydrite are not detectable with XRD.

Synchrotron-based analytical techniques are a powerful tool that can distinguish the oxidation state of arsenic and other metals through X-ray absorption near-edge structure (XANES) as well as characterize mineral phases, examine atomic bond strengths and geometries of surface complexes through extended X-ray absorption fine structure (EXAFS) (Eiche et al., 2010; Fendorf et al., 1997; Grafe et al., 2008, Savage et al., 2000). For example, synchrotron-based studies have concluded that As (V) is primarily adsorbed on iron or aluminum oxyhydroxides as inner-sphere complexes (Fuller et al., 1993; Fendorf et al., 1997). However, the use of synchrotron instrumentation is costly and still not widely accessible.

Sequential extraction methods provide an alternative due to their cost-effectiveness and less costly instrumental requirements. In this technique, reagents are sequentially applied to sediment samples, with each reagent chosen to selectively dissolve a known mineral phase or attack a known residence site of arsenic. Each of these fractions are operationally defined based on the type and selectivity of the reagents used, the order in which extractants are applied, the extraction time, and re-adsorption or re-distribution phenomena, (Van Herreweghe el at., 2003). Sequential extraction is a useful and well-

recognized technique and is commonly utilized to characterize site-specific arsenic availability. Although it cannot provide information on how and where arsenic is specifically bound within minerals, it can assess the overall mobility of arsenic and how it is distributed amongst classes of mineralogical phases and residence sites.

Inter-study comparisons of data from sequential extractions are difficult owing to the multitude of extraction protocols aimed to extract various types of arsenic-bearing phases. With the establishment of the Tessier (Tessier et al., 1979) and BCR protocols (developed by the Standard Measurements and Testing Program of the European Community; formerly known as BCR) (Ure et al., 1993), extensive usage of these two "standardized" schemes have occurred, but many revisions and modifications to the extraction procedure are still being made (Abollino et al., 2006; Barona et al., 1999; Quevauviller, 2002). The visualization and interpretation of sequential extraction results can be challenging on account of the large amounts of data generated. Many studies incorporate chemometric statistical techniques, such as simple correlations, multivariate linear regression, and principal component analysis, which can provide insight into relationships amongst metals, grouping of samples, pattern recognition, and predictions of arsenic mobility (Abollino et al., 2011; Giacomino et al., 2011).

1.1.5. Kinetics of Arsenopyrite Dissolution

Research on the stability and decomposition of arsenopyrite, a major primary host of arsenic, in natural settings, had not received extensive focus until the study by Craw et al. (2003). This study concluded from field observations, laboratory experiments, and theoretical calculations of new thermodynamic data that arsenopyrite can remain stable if stored under water-saturated, near-surface, and moderately reducing conditions (Craw et al., 2003). Arsenopyrite dissolution rates also decrease with time due to secondary mineral formation such as scorodite on grain surfaces. It was noted that under highly oxidizing conditions, the solubility of scorodite, not that of arsenopyrite, controls dissolved arsenic concentrations (Vink, 1996). Laboratory studies conducted on arsenopyrite decomposition frequently do not reflect natural environmental conditions, for example, using cleaned and cleaved mineral surfaces (Corkhill and Vaughan, 2009) or experiments conducted at very low pH of 1 to 4 (Asta et al., 2010).

Although, these studies support the overall conclusion that highly oxidizing conditions induce a greater rate of arsenopyrite dissolution.

The combination of factors such as pH, presence of iron and phosphate, and dissolved oxygen levels, etc., all affect the dissolution of arsenopyrite and other arsenic-bearing minerals, but the extent of their influences are heavily dependent on time. In a study by Rubinos et al. (2011), it was concluded that "the evaluation of arsenic mobility based merely on short-time experiments, as generally used in most standard leaching test, is unrealistic and may seriously underestimate arsenic mobility". Similarly, O'Reilly et al. (2001) found that initial desorption of arsenic from goethite by phosphate was rapid, but as time went on, phosphate ceased to exert an effect on arsenic desorption. In addition, Craw et al. (2003) concluded that equilibrium cannot be reached even in laboratory experimentation of up to 2 years. Moreover, arsenopyrite dissolution rates may also be affected by complex bio-geochemical relationships in the soil system not considered in laboratory experiments.

In addition to the aforementioned factors, the stability of suspended particulate matter (SPM), which are carriers of arsenic in a river system, are also affected by temporal variations in hydrology and rainfall intensity. In the study conducted by Grosboi et al. (2011), it was revealed that arsenic-bearing phases in SPM, such as clays and iron oxyhydroxides, carried higher levels of arsenic during high flow relative to manganese-oxyhydroxides which carried higher arsenic concentrations during low flow.

1.2. Purpose and Significance of Study

It is clear that our knowledge of the dissolution of arsenopyrite and other arsenic-bearing minerals is incomplete. Arsenic residence sites and stability vary within sediments, but adsorption and precipitation are the dominant sorption mechanisms. Even with the shortcomings associated with sequential extraction methods, it is still a useful tool to assess arsenic mobility. A general weakness recognized in the literature is the short-term basis of experiments and limited consideration of long-term arsenic mobility. There is very little site-specific historical data to support statements and predictions. Especially lacking is the quantification of physical transport of arsenic-bearing sediment.

Many studies have laid the framework for assessing factors controlling arsenic mobility; investigating arsenic mobilization mechanisms, adsorption/desorption kinetics, and the effects of pH, redox, etc. (Al-Abed, 2007; Corkhill and Vaughan, 2009; Craw, 2003; Dixit and Herring, 2003). But these studies were conducted on relatively short time scales without the quantification of arsenic massbudget on field-scales and lack the simultaneous compilation of data on these subjects.

In many areas affected by historical mining, such as the study location (i.e., areas surrounding Whitewood Creek and the Belle Fourche River of South Dakota), millions of tons of arseniccontaminated sediments remain exposed and intermixed with the surrounding environment, making their removal unfeasible. Thus, it is vital to understand site-specific arsenic mobility and retention behavior to determine the transport mechanism and transport rate of arsenic out of the area and the effect this transport will have on downstream locations.

The aim of this study is not to primarily assess microscale components of arsenic mobility, such as its binding mechanisms, rather, these components are coupled with macroscale data to investigate the long-term retention, dissolution, and kinetic behavior of arsenic from mine tailings, with a focus on the chemistry of dissolved arsenic in surface waters, fluvial sediments, and aerobic soils. This study utilizes microscale and meso-scale data (e.g. sediment geochemistry, arsenic partitioning and residence sites) in combination with macroscale empirical and historical data (measured discharge and suspended sediment transport rates) to comprehensively document and assess the complex long-term effects on arsenic storage in the environment.

1.3. Study Objectives

- Assessment of the current environmental conditions of WWC and the BFR with a focus on discerning if there has been significant natural remediation to surface water and sediments.
- Identify the controls on dissolved arsenic concentrations in the stream water.
- Investigate arsenic residence sites within the sediments and how they influence arsenic partitioning in order to evaluate its potential mobility and release into the environment.

- Gain insight into the distribution of arsenic-contaminated sediments in the floodplains and evaluate arsenic mobility in relation to its physical placement in the sediments.
- Quantify arsenic's mass-budget with time to predict and constrain the length of time arsenic will remain in the system and estimate arsenic transport rates out of the system.
- Forecast how environmental changes may impact arsenic mobility and transport in the area.
- Determine the fate of arsenic in contaminated sediments over the next few hundred years.

1.4. Approaches used to Address Study Objectives

Sediment and water samples were collected to evaluate metal concentrations and assess current overall environmental quality. Sequential extractions of the sediments were performed to determine the mineralogical setting of the arsenic and other elements of interest as well as the proportion of arsenic available at different rates of release into the environment. Statistical analyses were applied to sequential extraction data to gain insight into the relationship between arsenic with other metals. Physical and mineralogical characterization of the sediments were observed from sediment samples and compiled from the literature. Historical river discharge and suspended sediment data, in addition to historical water and sediment chemistry data, were compiled from the United States Geological Survey (USGS) databases. Statistical assessments were applied to the historical data in order to provide a 'best possible' estimate of rates of arsenic transport and removal.

CHAPTER 2. STUDY LOCATION AND SITE HISTORY

Homestake Mine is located near the northern edge of the Black Hills, in the town of Lead of Lawrence County, South Dakota (elevation: 1,650 m or 5,400 ft) (Figure 2.1). Operating from 1877 to 2002, its ore bodies were predominantly mined for gold and some silver and the mine was the largest and deepest gold mine in North America during its operation (Smith, 2003). From 1877 to 1977, over 100 million megagrams (Mg) of arsenic-contaminated mine tailings were discharged into Whitewood Creek, and a significant portion is still stored along the floodplains of Whitewood Creek (WWC) and the Belle Fourche River (BFR) (Cherry et al., 1986; Goddard, 1987; Marron, 1992).

2.1. Homestake Mine Geology

The Poorman, Homestake, and Ellison Formations are the oldest to youngest stratigraphic units within the mine, respectively. Gold mineralization occurs within the metamorphosed pelites and sandstones as well as the sideroplesite-quartz schist of the Precambrian Homestake Formation (Noble, 1950). Near the ore body, the sideroplesite ((Fe,Mg) (CO3)), a magnesium-rich variety of siderite, has been partially to completely metamorphosed to cummingtonite ((Mg, Fe)7 Si8O22(OH)2) or is almost completely chloritized (Noble and Harder, 1948; Slaughter, 1968).

The ore bodies at Homestake Mine are composed of 7 to 8% iron sulfides, including arsenopyrite (FeAsS), pyrrhotite (FeS), and pyrite (FeS2) (Noble, 1950), with lesser amounts of chalcopyrite (CuFeS2), galena (PbS), ilmenite (FeTiO3), hematite (Fe2O3), and magnetite (Fe3O4) (Caddey et al., 1991; Slaughter, 1968). Though not in abundance, carbonate minerals are present, including ankerite (Ca(Mg,Fe)(CO3)2), calcite (CaCO3), and dolomite (CaMg(CO2)3) (Slaughter, 1968). Other minerals present in the ore body consist of biotite (K(Mg,Fe)3AlSi3O12), chlorite ((Mg,Fe,Al)3(Si,Al)4O10(OH)2), graphite, and albite (NaAlSi3O8) (Noble, 1950).

Arsenopyrite (FeAsS), the main host of arsenic, is disseminated throughout the Homestake Formation, varying from trace amounts to more than 15% by volume (Noble, 1950; Caddey et al., 1991). Arsenopyrite is generally associated with gold ore grades greater than 4.7 grams per ton (Caddey et al., 1991). Rocks containing arsenopyrite were mined, crushed into fine-grained tailings, and after gold extraction, were discharged into Whitewood Creek, which flows into the Belle Fourche River (Figure 2.1).

2.2. Homestake Mining and Environmental History

Prior to the 1900s, mined ore consisted mostly of oxide and hydroxide minerals from oxidized ore and paleoplacer deposits, including oxidation products of pyrite, pyrrhotite, and arsenopyrite. After the 1900s, ore was mined below the zone of oxidation from the Precambrian Homestake Formation (Wuolo, 1986). By 1976, after nearly 100 years of mining, it is estimated that between 105 to 124.9 million Mg of ore had been processed, extracting between 893 to 1101 Mg of gold (Caddey et al., 1991; Marron, 1992; Homestake Gold Mine, 1976).

On average, the mills processed around 5,000 Mg of ore a day, using mercury amalgamation and cyanide during the gold extraction process (Wuolo, 1986). The use of mercury was discontinued in 1970 (S.D. Dept. of Game, Fish and Parks et al., 2005). Initially, coarse sand-sized particles were produced by stamp mills, but the later usage of rod and ball mills yielded finer particles over time (Marron, 1992). Some sand-sized fractions were used to backfill the mine-workings, while silt-sized fractions were transported down to Deadwood Creek for further cyanide treatment and eventually discharged into Whitewood Creek (Wuolo, 1986). By 1955, fifty percent of all tailings produced were used to backfill the underground tunnels. In 1977, all tailings were directed to the Grizzly Gulch tailings impoundment (4.8 km south of the mine mills near Lead) and discharge of tailings into WWC ceased (U.S. EPA, 2012; Wuolo, 1986). After a century of mining, it is estimated that approximately 110 million Mg of mined material was discharged into Whitewood Creek (Marron, 1992).

Until the implementation of the Clean Water Act during the 1970s, no environmental regulations were in place, and the sanitation district of Lead and Deadwood was discharging untreated raw sewage into WWC. Carrying a mix of sewage and mine-waste, WWC did not support aquatic life (Goddard, 1989; S.D. Dept. of Game, Fish and Parks et al., 2005) and local residents and property owners attested to

the stream flowing black. Issues with arsenic contamination continued with several cases of arsenic toxicosis in cattle fed with corn contaminated by soils with up to 140 ppm arsenic (Wuolo, 1986).

In 1983, under CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act), an 18 mile segment of WWC (Figure 2.2) was determined to be most critically impacted and was declared a Superfund Site on the National Priority List (NPL) (Cherry et al., 1986; Goddard, 1989; U.S. EPA, 1990 and 2012). In 1984, remedial actions made by Homestake included the installation of a wastewater treatment plant to treat mining operations effluent discharging into WWC. (S.D. Dept. of Game, Fish and Parks et al., 2005). Homestake also removed 3,440 cubic meters (4,500 cubic yards) of contaminated sediments from 16 residential yards (U.S. EPA, 2012) and funded several comprehensive environmental studies of the site (Fox Consultants Inc., 1984a and 1984b; Cherry et al., 1986). However, the potential environmental impacts downstream were not addressed (S.D. Dept. of Game, Fish and Parks et al., 2005). These remedial actions were completed in 1994, and the EPA removed WWC from the NPL in 1996. Since the majority of contaminated sediments were left in place, perpetual monitoring of both surface and ground water will continue, with the EPA conducting five-year reviews; the most recent review up to the time of this study was completed in September 2012 (U.S. EPA, 2012).

2.3. Previous Environmental Studies of the Site

Concurrently with Homestake's remedial activities (implemented during the 1980s to early 1990s), a collaboration of entities (U.S. Geologic Survey, U.S.EPA, and South Dakota Geological Survey and Water Resources Division) conducted detailed investigations of the extent of arsenic contamination and its transport within WWC and the BFR. Several key findings are discussed below. The creek, which was grey and opaque from the suspension of fine-grained tailings, flowed clear soon after the cessation of tailings disposal (Marron, 1992 and also supported by discussions with local residents). But the average dissolved arsenic concentrations in the stream fluctuated above and below the 1983 National Primary Drinking Water Limit of 0.05 mg/L (50 μ g/L) (by 2012, standards have tightened to 0.01 mg/L or 10 μ g/L) (U.S. EPA, 1990 and 2009). Maximum dissolved arsenic concentrations in WWC occur in July and August due to the low discharge of the creek, while input from groundwater into

the creek continues, causing a negative correlation between discharge and arsenic concentrations (Goddard and Wuolo, 1987).

The pH and the formation of iron oxyhydroxide coatings on grain surfaces were concluded to be the dominant controls on dissolved arsenic concentrations in the stream (Goddard and Wuolo, 1987; Fuller et al., 1987; Cherry et al., 1986; Goddard, 1989). The dominant arsenic species in the stream water is As(V) (Fuller et al., 1987). Arsenic is immobilized by adsorption onto iron oxyhydroxide surfaces or precipitation into secondary iron-arsenate minerals (Cherry et al., 1986; Fuller et al., 1987). Maximum adsorption of arsenic is predicted to be at pH 6.5, with the desorption of arsenic beginning at pH 8.5 (Goddard and Wuolo, 1987). Arsenic release does not seem to depend on bacterial oxidation of arsenopyrite (Cherry et al., 1986). Most of the arsenic is in the solid phase and not readily soluble (Cherry et al., 1986), thus contaminated sediments are expected to remain in place for hundreds to thousands of years (Cherry, 1986; Marron, 1989; Goddard, 1989).

Arsenic concentrations in groundwater monitoring wells along the alluvial floodplains of WWC ranged from 0.0025 to 2 mg/L (2.5 to 2,000 μ g/L) (Wuolo, 1986); however, groundwater concentrations were generally orders of magnitude lower than the surrounding sediment arsenic concentrations (Goddard, 1987). A ban is in place on developing and using well water within the greater than 100 ppm arsenic zone delineated in Figure 2.3. Water supply wells must be situated away from contaminated sediment and producing only in alluvium that was not overlain with tailings. Arsenic concentrations within these wells were below the 1986 Primary Drinking Water Limit of 0.05 mg/L.

Acid generation was minimal owing to the slow rate of sulfide mineral oxidation and the high buffering capacity of carbonate minerals (Cherry et al., 1986), resulting in groundwater at near neutral pH between 6 to 8 (Fuller et al., 1987). Limestone bedrock is also in contact with the upstream reaches of Whitewood Creek (Goddard, 1987). No major changes to the pH were anticipated at the time of these studies, but a concern for the longevity of carbonate buffering capacity was noted by Wuolo, 1986. Under stable environmental conditions, arsenic levels in the groundwater were also expected to remain at similar concentrations.

2.4. Whitewood Creek

Whitewood Creek is a perennial mountain stream in part originating as springs from the Mississippian Pahasapa Limestone in the northern regions of the Black Hills. From the town of Lead to the town of Whitewood, WWC has a drainage area of 105 km². From the town of Whitewood to WWC's confluence with the BFR, WWC has drainage area of 260 km² (Wuolo, 1986). Between the towns of Lead and Whitewood, WWC's average gradient is 0.0161 and flows over gravels and cobbles in a narrow channel that has incised into Paleozoic limestones and Precambrian bedrock. Downstream of Whitewood, the topography changes to a gentle hilly region, and the average gradient decreases to 0.0086. Here, the meandering and locally braided stream incises into both the alluvial floodplain and the Upper Cretaceous Pierre Shale bedrock (Goddard, 1987; Marron, 1992). Rural developments, livestock grazing, and cultivation of hay are the dominant private land uses of this region (U.S. EPA, 2012). Recreational activities such as fishing, boating, and hiking are popular uses of public lands along the creek (S.D. Dept. of Game, Fish and Parks et al., 2005).

2.4.1. Channel and Floodplain Characterization

The 20.9 km (13 mile) segment of WWC between Lead and Whitewood has a narrow channel width of 3 to 5 m (9.8 to 16.4 ft). Due to the steeper gradient and lack of alluvial floodplain development, storage of arsenic-rich sediment is relatively low along this segment as compared to segments downstream of Whitewood. Although, localized storage of tailings exists in abandoned meanders (Marron, 1992). The segment between the town of Whitewood to the confluence with the Belle Fourche (41.7 km or 26 mi) has abundant tailings deposited as overbank sediment and in abandoned meanders (Marron, 1992). In the upstream half of this segment, the channel is wide, and tailings may, in some cases, extend up to 100 meters from the channel as overbank deposits (U.S. EPA, 2012). In the downstream half of this segment, meander abandonment and channel incision are more prevalent, with arsenic-contaminated sediments filling these abandoned channels. Evidence of channel incision since the start of tailings input can be seen in exposed bank cross-sections revealing streambeds that were up to 3 meters higher than the modern streambed (Marron, 1992). Increased sediment loading from the influx of

mine tailings could be a cause for the rapid channel incision, meander straightening and abandonment, and a change in water input as a result of water diversion (Marron, 1992).

2.4.2. Pre-Mining Alluvium and Mining-Related Sediments

Pre-mining, the sediments deposited by the stream included buff-colored silt, clay, coarse sands, and gravels. This pre-mining alluvium is usually less than 10 meters thick (Goddard, 1987) and is composed of clasts of sandstones, limestones, quartzite, and metamorphic rocks of the Black Hills. Thin, white bands of calcite can be found locally cementing the matrix together (Wuolo, 1986).

Mining-related sediments, which have arsenic concentrations commonly exceeding 2000 mg/kg, are red-brown silts, sands, and lenses of moist gray silty-clay composed of sulfide-bearing tailings (Goddard, 1989; Marron, 1992). Previous studies did not clearly define the thickness of tailings-bearing sediment in WWC, however in some stretches, there is a sharp distinct contact between pre-mining and mining-related alluvium based on color, but in other areas the pre-mining and mining-related alluvium can be mixed down to the Pierre Shale bedrock. It has been observed that arsenic-contaminated sediments usually have an orange-brown color, and the increasing intensity of the color can be loosely correlated with increasing arsenic concentrations in the sediments (Marron, 1992). The mineralogy of the tailings reflects the composition of mined ore deposits (see section 2.1). The presence of amorphous materials such as ferric hydroxides is evidence of considerable oxidation of sulfide minerals present in the tailings (Cherry et al., 1986; Goddard, 1987; Wuolo, 1986). Quartz, chlorite, and gypsum also make up a considerable portion of mineralogical composition. Mining-related sediments containing low arsenic concentrations were usually deposited at times of high stream flow (Marron, 1989).

2.4.3. Quantification of Sediment Supply and Floodplain Storage

Marron's 1992 study (Marron, 1992) estimated that the total amount of tailings produced by Homestake Mine was 127×10^6 Mg, but due to tailings used to backfill mine workings, only 110×10^6 Mg of those tailing were actually discharged into WWC between 1876-1976. Of the 110×10^6 Mg of tailings discharged into the WWC, only about 13% (14.5 x 10⁶ Mg) remain deposited in WWC's floodplains at the time of the study. Another 29% (31.9 x 10⁶ Mg) were delivered to and stored in the floodplains of the BFR, with the remaining portion transported to the Cheyenne River and eventually deposited into Lake Oahe (Figure 2.1). Of the estimated 14.5×10^6 Mg of tailings stored in the floodplains of WWC, less than 1.0×10^6 Mg is stored in the reach between Lead and Whitewood; 5.8×10^6 Mg is stored in the 20 km reach downstream of Whitewood; and 8.7×10^6 Mg is stored in the last 6 km reach before WWC's confluence with the BFR (Marron, 1992).

2.4.4. Discharge Levels

Discharge levels from 1982 to 2011 at four gauging locations along WWC were compiled from the USGS database. On average, high flow occurs during spring to early summer (April - June), with an average discharge between 1.56 to 2.83 m³/s (55-100 ft³/s). Low flow occurs from mid-summer through winter (July - March), with levels fluctuating between 0.34 to 0.71 m³/s (12 to 25 ft³/s). Mean annual floods are about 14.2 m³/s (500 ft³/s), and 8- to 10-year floods are about 56.6 m³/s (2000 ft³/s) (Mussetter Engineering, Inc. et al., 1996). The water table generally stays within the pre-mining alluvium and does not usually rise into the overlying mining-related alluvium (Cherry et al., 1986). But because of higher discharge during a few weeks in the spring, there is flow from the creek into the alluvium as back storage, which then flows back from seeps into the creek after high-flow conditions end (Wuolo, 1986).

2.4.5. Physical and Environmental Changes

Current observations and published reports show that WWC has evolved since the studies in the 1980s. Noticeable physical changes include straightening of meanders and the destabilization of exposed cut-banks. The exposed cut-banks are highly unstable and easily collapsible, hence potentially reintroducing both contaminated and uncontaminated alluvium into the stream water. A property owner along WWC disclosed that up to 40 feet of lateral erosion of the cut-bank can occur within one season (Figure 2.4). Local USGS geologist John Stamm suggested that one contributing cause could be motion of large blocks of ice in the stream during spring, which grind against the bank and de-stabilize the exposed cut-bank walls (personal communication, 2010).

The density and diversity of aquatic life and vegetation have increased (U.S. EPA, 2012; S.D. Dept. of Game, Fish and Parks et al., 2005). In 1965, WWC did not support aquatic bottom organisms

(U.S. EPA, 2012) and some areas were poorly vegetated or completely devoid of vegetation (Wuolo, 1986). After the 1980s, aquatic invertebrate species multiplied, insects, mosses, and algae reappeared, trout was re-introduced into WWC, and riparian vegetation returned to once bare areas (Mussetter et al., 1996; S.D. Dept. of Game, Fish and Parks et al., 2005).

2.5. The Belle Fourche River

WWC joins the BFR near the southern boundary of Butte County with the northwestern boundary of Meade County, South Dakota. The BFR is a tributary of the Cheyenne River, which flows into Lake Oahe and becomes part of the Missouri River. The BFR is a meandering river with a mean annual discharge of 10.2 m³/s (Marron, 1992) and a greater capacity to store mining-related sediments than WWC due to its larger channel dimensions and wider floodplains. Over the same time period, channel abandonment in the BFR has been less frequent compared to WWC, thus 60% of the mine tailings are stored as overbank deposits, with 40% stored as point-bar deposits and very little stored in abandoned channels (Marron, 1992).

The fine sand to silt-sized contaminated sediments are deposited mostly on the insides of meander bends (point bars), whereas high bluffs and terraces form the outsides of meander bends (cut banks) (Figure 2.5), preventing significant overbank deposition (Marron, 1992). Mining-related sediments of the BFR has not been as systematically surveyed as that of the WWC, however, arsenic concentrations in BFR sediments have been found up to 1,722 mg/kg, averaging one meter thick, and extending laterally up to 90 meters from the river channel (Marron, 1992).

CHAPTER 3. METHODS

In this project, multiple analytical tools (sediment petrography, bulk chemistry analysis, and sequential extractions) were applied to stream waters and sediments collected from WWC and the BFR to investigate arsenic mobility on a micro-scale. On a macro- or field- scale, arsenic's transport rate out WWC was estimated through analysis of historical data and arsenic mobility was evaluated on short and long timescales, as well as predictions made about the environmental conditions in the future.

3.1. Water Sample Collection

On WWC, eight water samples were collected between Deadwood, South Dakota and just before WWC's confluence with the BFR. On the BFR, one water sample was collected approximately 7.5 riverkilometers upstream from its confluence with WWC, while three other water samples were collected approximately 70 river-kilometers downstream from the confluence. Sample Locations A to L are presented in Figure 4.1. In total, in-stream water samples were collected at twelve locations (8 from WWC, 4 from the BFR), while seep-water samples were collected at three locations along WWC. GPS coordinates (taken with Garmin Etrex Legend) for all water sample locations and brief site descriptions are listed in Appendix 4-1.

Water samples were collected in the channel approximately 5 feet from the bank using a small bucket attached to a rope. Dissolved oxygen was immediately taken with the DO-600 ExStik II probe from Extech Instruments. Other water quality parameters like pH, specific conductivity, and temperature were also taken at the same time with the PCTestr 35 Multi-Parameter probe from Eutech Instruments.

An aliquot of the water sample was suctioned into a 10ml plastic syringe and expelled directly into a 15mL Nalgene screw-top scintillation vial. The second aliquot of the water sample was also suctioned through the syringe but expelled through a 0.45µm syringe-attachment membrane filter (IC-Millex-LH filter unit from Millipore). Unfiltered samples provide the total concentration of metals, while filtered samples provide the concentration of dissolved metals in the water. Each scintillation vial was pre-acidified with a small drop of ultra-pure nitric acid which prevents the precipitation of metals and
keeps them in solution. The water samples were kept on ice in a cooler until they could be placed under refrigeration upon returning from the field in the evening.

3.2. Sediment Sample Collection

Sediments from the point bars, cut banks, and within the stream bed were collected to characterize the metal concentration distributions and mobility of sediments in contact with stream water. Criteria for their selection included: proximity to previous USGS studies, site accessibility (i.e., landowner permission), and approximate equal sample spacing along the whole reach of the study area (Figure 4.1).

In-stream sediments were collected with co-located in-stream waters from Locations A, D, G, H, K, and L. In-stream sediments were collected from the bottom of the active channel using a trowel and stored with the stream-water accumulated during collection. These samples were placed under refrigeration daily upon returning from the field.

Point-bar sediment samples were collected from the point-bars of WWC (Locations D, G, and H) and the BFR (Location K), along transects positioned perpendicular to the segment of the channel. Sediment samples were collected from four points along the transect (10 to 20 meters spacing). At each point, sediment samples were collected from various depth intervals, from the surface to a max depth of 1.83 meters (6 ft). The exact position of the points along the transect line were chosen based on the ease of auguring, usually in areas without many cobble- to pebble-sized clasts. The sandy to clay-rich areas generally contained the highest amount of tailings. Sediment was extracted using a hand-auger. When a change in sediment composition, size, and/or color was observed, then the core would be split into separate samples. The maximum depth of the auger's reach was six feet. To avoid cross-contamination between sediments at different depths, sediment from the very top and bottom inch or so of each core was discarded. The auguring process could also shift and transport sediment between different depths, but this amount is relatively small when compared to the total volume of sample collected (1.1 to 2.6 liters or 0.3 to 0.7 gallons per sample).

At Locations G and H, cut banks with exposed strata containing both pre- and post-mining alluvium were also sampled (see photo in Figure 3.1). Sediments were extracted from individual layers distinguished by changes in its color, sediment composition and/or grain size. The cut-bank has not been extensively re-worked by the meandering stream system since the onset of the most recent phase of incision. Thus, sediments from these layers should provide a sediment history of aggradation during tailings disposal and a sequence of arsenic mobilization patterns and chemical changes through time since the start of tailings disposal. Sediments collected from these exposed layers in cut-banks were chiseled out using a rock hammer. Around 3 inches of the outer and most weathered sediments were first removed from each layer before sample collection. Care was taken to ensure minimal contamination from other layers, though the mixing of some particles from the adjacent layers could have occurred, the amount is relatively small when compared to the total volume of sample collected (1.1 to 2.6 liters or 0.3 to 0.7 gallons per sample).

All point-bar and cut bank sediments were placed in gallon-sized plastic zip-lock bags and stored at room temperature. Most samples were dry to slightly moist and the moisture was retained in the bags. Once field work was completed (2 weeks total), all sediments were stored under refrigeration to prevent bacterial activity and to preserve the samples in the chemical state at the time of their collection.

3.3. Mineralogical Composition and Physical Characterization of Sediment Samples

The mineralogical composition and physical characteristics of 17 representative sediment samples collected along the floodplains of WWC and the BFR were observed under a reflected light stereo microscope. Their mineralogical modal percentages, especially that of arsenopyrite, were qualitatively assessed to assess whether there were any marked changes relative to the mineralogy recorded in past USGS studies. Any changes in the abundance of arsenopyrite could provide indications as to how long arsenic will persist in the environment.

3.4. Bulk Geochemical Analysis: Sediment and Water Samples

The bulk geochemistry of the sediments is necessary to characterize the current condition of the sediment and the extent of the contamination. A total of 130 sediment samples collected from multiple

transects were condensed down to 77 representative samples by mixing 2 to 3 samples of adjacent depths in equal proportions. Sediments were mixed based on visual inspections of the similarity in sediment color, grain size, and amount of organic material. Sediments collected from exposed cut banks were not mixed because they were sampled based on distinct differences between strata observed in the field.

Sediment samples were oven dried at 55°C for 48 hours, and the percent moisture of each sample was obtained. Dried samples were then crushed to a fine powder using porcelain mortar and pestles. To prevent cross-contamination, all equipment was washed and cleaned with ethyl alcohol between uses.

Following the EPA preparation Method 3050a, 0.2g of each sediment-powder was acid-digested with 3mL of ultra-pure nitric acid (HNO₃) and 1mL of ultra-pure hydrochloric acid (HCl). This protocol was applied to dissolve sulfide minerals, such as arsenopyrite (FeAsS) which is dissolved by nitric acid with the separation of sulfur. The digestions were heated in an oven at 90-95°C for 10 to 12 hours and then brought to a volume of 20 mL by addition of ultra-pure de-ionized water. Any grains that were not digested or dissolved by the acids (mostly silicates) were allowed to settle to the bottom of the tube before the solution was extracted for chemical analysis.

These 77 sediment samples were analyzed for a suite of 33 metals by inductively coupled plasma optical emission spectroscopy (ICP-OES). The analyses were conducted on the Perkins Elmer Optima 7300-DV ICP-OES instrument at Colorado State University's Center for Environmental Medicine Analytical Laboratory. A total of 29 water samples were analyzed by ICP-OES and also by inductively coupled plasma mass spectroscopy (ICP-MS); using the ELAN DRC II instrument from Perkin Elmer SCIEX. Both spectrometric techniques were applied because the ICP-MS is better suited for the analysis of trace to ultra-trace elements due to its lower detection limits. But the ICP-OES is more suitable for major elements, highly concentrated samples, or samples with widely varying concentrations of elements. The detection limits for both instruments and analytical results are reported in Chapters 4 and 5.

3.5. Sequential Extractions

Although the total concentration of trace metals in the soil is an indication of contamination levels, it does not provide insight into the bioavailability and mobility of the metals. Thus, sequential

extractions are used to mimic environmental chemical conditions and to assess the availability of metals and their potential release into the environment. In the sequential extraction procedure, various chemical extractants are applied to sediments to release metals residing on surfaces of minerals or hosted by specific mineral phases into solution (Keon, et al., 2001; Wenzel, et al., 2001; Muller et al., 2007).

Sequential extractions were applied to sediment samples collected along reaches of WWC and the BFR to investigate the residence sites and mineral-hosts of arsenic. Other elements within the sediments were also extracted and which can provide insight on controls of arsenic mobility. Quantifying the amount of arsenic hosted by each type of site will provide a picture of arsenic's mobility over time, as well as how environmental changes can impact arsenic solubility. The sequential extractions protocols set by this study was based on the schemes of prior studies discussed below.

Four different extractants were sequentially applied to each sediment sample. Each extractant is operationally defined to selectively attack one or multiple residence sites, meaning the procedure itself defines from which phases arsenic is extracted (Leinz et al., 2000; Keon, et al., 2001). The residence sites are: (1) deionized water (DI-water) targets weak, electrostatically bound, readily exchangeable analytes on the surfaces of minerals and in readily soluble secondary minerals (Leinz, et al., 2000; Rodriguez, et al., 2003; Muller, et al., 2007); (2) 1M sodium phosphate monobasic (1 M NaH₂PO₄) competitively exchanges PO4³⁻ ions for adsorbed arsenic oxyanions, especially those bound by outer-sphere complexes and bound to organic matter (Larios, et al., 2012; Violante, et al., 2002; O'Reilly, et al., 2001; Lombi, et al., 2000; Rodriguez, et al., 2003; Keon, et al., 2001); (3) 0.2M hydroxylamine HCl (0.2 M NH₂OH·HCl) dissolves soluble carbonates and reductively dissolves amorphous to weakly crystalline fine-grained iron, manganese, and aluminum oxyhydroxides, which are mineral phases with a high affinity to host arsenic (Leinz, et al., 2000; Huang, et al., 2010; Lombi, et al., 2000; Bermond, et al., 1993; Rodriguez, et al., 2003); (4) 1M hydrochloric acid (1M HCl) dissolves less readily soluble secondary minerals (clays, coarse grained oxides), where arsenic may be bound in the minerals' crystal lattice (Huang, et al., 2010; Keon, et al., 2001). The remaining unextractable arsenic (residual fraction) which is assumed to be predominantly bound in arsenopyrite, its original host mineral. All extractant solutions

were prepared using American Chemical Society (ACS) grade reagents from Fisher Scientific (sodium phosphate) and Sigma Aldrich (hydroxylamine HCl and hydrochloric acid).

Sequential extractions were performed on 35 sediment samples collected from two sites along WWC (Locations G and H) and one site along the BFR (Location K). Samples from each site were chosen so that arsenic extraction patterns by depth and by distance from the river could be fully represented. The experimental procedure involved sequentially saturating 4 grams of each sediment sample with 40 mL of each extractant in a plastic 50 mL centrifuge tube. The moisture content of the sediment was taken into account so that each sample contained 4 grams of solid material. The mixtures were shaken for 20 minutes using a Burrell wrist action shaker and then centrifuged at 4000 revolutions per minute (RPM) for 20 minutes to separate solid particles from the solution. The supernatant was decanted into a 60 mL syringe and passed through a 0.45 µm syringe membrane filter with a 0.7 µm glass fiber pre-filter to remove large particulates (Millex-HPF LCR by Millipore). The four extractants were applied sequentially to the same 4 grams of sediment. A total of 140 extractions were performed within one week. Samples were stored at room temperature away from light. All samples were then analyzed by the ICP-OES at the Soil, Water, and Plant Testing Laboratory in the Soils and Crop Science Department at Colorado State University. The samples were divided by extractant type and ran through the ICP-OES in four separate groups. For quality assurance, four duplicate samples and three arsenic-standard solutions (0.1 ppm, 10 ppm, and 100 ppm arsenic) were also analyzed per group (a total of 16 duplicates and 12 arsenic-standards). A matrix correction was applied to correct the analytical results for interference by the constituents forming the extractants.

Since there is a 1:10 ratio of solid to liquid (4 g sediment, 40 ml extractant), a transformation was applied to the raw extraction data (in parts per million) to correct for volume prior to data analyses and the application of statistical tests. The raw data results reflect the concentration of the metals in relation to the volume of the liquid, so in order to ascertain the concentration of metals extracted from the solid, these raw values were multiplied by a factor of ten.

Although the extractants are operationally defined to selectively release metals hosted in specific sites or mineral phases, some extractants applied can be less selective, and the release of metals associated with unintended targeted phases is possible (Bermond et al., 1993; Muller et al., 2007). There are still many uncertainties, and more work is needed in this area to understand how residence sites may be affected by extractants not intended to attack them. For example, coating of Fe-oxyhydroxide by phosphate or phosphate surface complexation on Fe-oxyhydroxides can hinder its dissolution (Borch et al., 2007).

Hydroxylamine-HCl is acidic and reducing, while sodium phosphate is less acidic and weakly oxidizing. One hypothesis is that the application of one extractant may alter the redox state of the sediment sample, which could affect the extraction capabilities of the following extractant and thus produce different sequential extraction results. To understand possible interactions between extractant interactions and targeted sites, a sub-experiment was conducted to investigate the effects of reversing hydroxylamine and sodium phosphate extraction sequences (Appendix 6-1).

Two sediment samples with similar arsenic concentrations (1,881 mg/kg and 1,996 mg/kg) were selected from two WWC sites. The extraction protocol (applying sodium phosphate before hydroxylamine) and then vice versa was applied to separate aliquots of both sediment samples. Results indicate that changing the sodium phosphate and hydroxylamine extraction sequence did not significantly affect the total amount of arsenic extracted. However, it did change the amount of arsenic extracted by each extractant and thus the interpretation of the amount of arsenic hosted by each type of site. See Appendix 6-1 for details.

3.6. Estimating Suspended Sediment Flux and Total Arsenic Transport Rate

Suspended sediment is any solid material (organic or inorganic particles), usually greater than 0.45 µm, that is transported within the water column of a body of water. Suspended sediment has been known to be a major reservoir and significant mode of transport for trace elements in river systems. Understanding suspended sediment transport in WWC is vital in estimating the mobilization and rate of arsenic removal from WWC.

Suspended sediment load data along with discharge and arsenic concentrations in the solid (suspended sediments) and dissolved phases have been collected by the USGS and are available from two USGS gauging stations along WWC. The upstream station (WWC Above Whitewood) is located at an elevation of 1,122 meters (3680 ft), has a drainage area of 146.85 km² (56.7 mi²), and is approximately 30 km from WWC's confluence with the BFR. The downstream station (WWC Above Vale) is located at an elevation of 866 meters (2840 ft), has a drainage area of 264.179 km² (102 mi²), and is approximately 5 km from WWC's confluence with the BFR. All historical data were gathered from these USGS websites: Upstream Station (WWC Above Whitewood, SD):

http://nwis.waterdata.usgs.gov/nwis/dv?site_no=06436180

Downstream Station (WWC Above Vale, SD):

http://nwis.waterdata.usgs.gov/nwis/dv?site no=06436198

Suspended sediment load data was collected periodically from 1982 to 2012. During this period, the upstream station was sampled 256 times, while the downstream station was sampled 239 times. From 1982 to 1995, data was collected at least once during most months. From 1995 to 2012, data collections decreased to about 4 times a year (April-June, September, and December). Discharge was measured multiple times per day at both the upstream and downstream sites, and the average of these discharge values was recorded daily. 10,959 days of mean daily discharge values were collected from each gauging station from November 9, 1982 to November 9, 2012. Since suspended sediment load data were measured only a few times a year, rating-curves were generated to predict daily suspended sediment loads from measured daily discharge values. The rate of suspended-arsenic transport in WWC over a 30-year timespan was also derived from various methods such as raw data averaging, ratings curves, and using percent-arsenic distributions. These methods will be discussed in more detail in Chapter 7.

CHAPTER 4. WHITEWOOD CREEK AND THE BELLE FOURCHE RIVER WATER QUALITY ASSESSMENT

In the summer of 2011 (July 10th through 17th), surface water samples (total and dissolved) were collected from seven points along WWC (Locations B to H) and from four points along the BFR (Locations I to L) (Figure 4.1).

4.1. Sample Location Description

The sample at Location A was collected from Whitetail Creek, situated upgradient and approximately 1.75 kilometers to the southwest of Homestake Mine. Locations B, C, D, and E are in the upstream reaches of WWC, while Locations F, G, and H are in the downstream reaches of WWC. Location L is located on the BFR upstream of the confluence between WWC and the BFR. Locations I, J, and K are located on the BFR downstream of its confluence with WWC. Seep samples were collected from Locations B, G, and H along WWC. Chemical analyses of the water samples were conducted between October 2011 to March 2012 (testing by multiple labs and multiple rounds of analyses with ICP-OES and ICP-MS). Appendix 4-1 presents sample location descriptions, coordinates, elevations, and date of sample collection. Appendix 4-2 presents the geochemical analytical results of the water samples and comparisons to various human health-based standards.

To be cost effective, multiple replicates of samples could not be collected at each location, which would provide a better insight into the range of concentrations present per location. The fluctuations seen in total and dissolved concentrations in the current dataset could reflect a natural range of concentrations present at the sampling locations. Spikes or dips in concentrations seen at one location is not a significant confirmation of a true difference in concentration between reaches and reasons for these changes can only be speculative. Additionally, the sample collection was conducted during the summer and only reflected the hydro-geochemical behavior of the low-flow season. This investigation only focused on broad trends and patterns in concentration and provided insight into the general water quality conditions at the time of sampling.

4.2. Surface Water Quality Field Parameters

Upgradient of Homestake and WWC at Location A, the pH was 8.5. WWC's in-stream pH started at 8.7 (Location B) and slightly declined to 8.3 (Location H) with minimal fluctuations in between (Table 4.1 and Figure 4.2a). Downstream of its confluence with WWC, the pH of the BFR slightly decreased to 8.1 (Location I) and then maintained at pH 8.2 in further downstream reaches (Locations J and K). Upstream of the confluence with WWC, the pH of the BFR Location L (pH 8.2) was similar to values measured downstream. The pH levels of seep waters (pH 6.9 to 7.6) collected from WWC are lower than levels measured in-stream (pH 8.3 to 8.7). This low to neutral pH range suggests the seep water is in contact with more acidic producing minerals or organic matter, most likely sulfides, considering the high amounts of sulfides in the area (Noble, 1950). Additionally, the relatively neutral seep water is further indicative of the high buffering capacity of carbonate minerals like ankerite (Ca(Mg,Fe)(CO3)2), calcite (CaCO3), and dolomite (CaMg(CO2)3) present as gangue minerals in the ore deposit and in the surrounding bedrock (ex: Whitewood Dolomite, Pahasapa Limestone, and the Pierre Shale) (Slaughter, 1968; Appendix 5-2 and 5-4). Due to the small sample size of seep waters, it is unclear if the slight decrease in pH observed in the lower reaches of WWC could be influenced by the contribution of seep waters. In summary, all in-stream pH's were at relatively levels to support aquatic life.

The range of in-stream dissolved oxygen (DO) levels measured in WWC (5.14 to 6.1 mg/L) displayed low variance with minor fluctuations (Locations B to H) (Table 4.1 and Figure 4.2b). The DO concentration of the upgradient sample at Location A measured slightly higher at 6.3 mg/L. DO levels in the BFR waters upgradient of its confluence with WWC started at 5.34 mg/L but decreased to 4.56 and 4.83 mg/L by Locations I and J, respectively, however by Location K, levels rose back to 5.37 mg/L. The generally lower DO measured in the BFR as compared to levels in WWC could reflect the shallower gradient the BFR flows over, causing less turbidity, thus introducing less oxygen into the system. The BFR also flows through a greater area of ranching and farmlands, likely contributing fertilizer and nutrients to the river, thus lowering oxygen levels. The average DO concentration of WWC's seep waters (1.81 mg/L) was about one-third of the average concentration in-stream WWC waters (5.58 mg/L).

Specific conductance levels reflect the amount of dissolved solids in the system. Levels upgradient of Homestake Mine at Location A began at 568 µS/cm and similar levels were maintained downgradient of the Mine at Location B (514μ S/cm) (Table 4.1 and Figure 4.2c). However, by Location C, concentrations more than doubled (1,145 μ S/cm) and continued to steadily increase to 1,459 μ S/cm by Location H. This increase is likely due to the contribution of seep water containing higher levels of dissolved solids ranging from 1,373 µS/cm to 8,010 µS/cm (Table 4.1). This is most evident in the increase in specific conductance levels between Locations B and C, likely due to the high concentration of dissolved solids in the Location B seep (8.010 μ S/cm). Another factor increasing dissolved solids is the dissolution of soluble minerals such as calcite and gypsum (from the Pierre shale and limestone units of the bedrock) in the riverbed and alluvium. The mean specific conductance of the seep waters (4,321 μ S/cm) is about four times greater than the mean specific conductance of WWC waters (1160 μ S/cm). Specific conductance levels in the BFR $(1,465 - 1,574 \mu \text{S/cm})$ did not increase much beyond concentrations seen in WWC at Location H (1,459 µS/cm). Dissolved solids content may also be influenced by the changing topography and land usage types (steeper mountain stream to shallow meanders through ranch and farmlands) as well as being affected by different geological units the river flows through. Since the discharge of WWC is much lower than the BFR, WWC's dissolved solids concentration can be more easily influenced by its seeps contributing high levels of dissolved solids into the stream. The secondary EPA MCL set for aesthetic purposes for total dissolved solids is 500 mg/L, which the in-stream and seep samples from Location C and onward exceeded (after applying a conversion between μ S/cm to mg/L).

The water temperatures upgradient of WWC at Location A (17.9 °C) and the range of water temperatures of WWC from Locations B to G (17.2 to 18.6 °C) were relatively consistent and stable (Table 4.1 and Figure 4.2d). By Location H, temperatures had increased to 26.8 °C and were at similar levels in waters of the BFR (24.1 to 28 °C). The increased temperatures in WWC near the confluence with the BFR could be due to the lowered elevation of the Location, less shading from vegetation, contribution of warmer water from tributaries and anthropogenic discharges, and the changes in ambient

air temperatures between the dates of sample collection (Appendix 4-1). Seep water samples collected at Locations B and G had lower temperatures (13.8°C and 14.5 °C, respectively) than WWC waters, however, the temperature of the seep water sample collected at Location H (27.6 °C) was similar to the temperature of the in-stream water sample at Location H (26.8 °C). This could be due to the slow collection of seep water into the sample container exposed to ambient temperatures, thus not may be not representative of actual seep water temperature.

4.3. Surface Water Quality Geochemistry Overview

The geochemical analytical results of the water samples were compared to various human healthbased standards or average concentration ranges found in surface waters (Appendix 4-2). The details of each type of standard or comparison range is explained in more detail in Appendix 4-2. For some analytes (calcium, magnesium, silicon, tin, and sodium), comparative values were not presented due to the analyte's low toxicity and wide range of naturally occurring concentrations.

4.3.1. Comparison to Water Quality Standards

Of the analytes (arsenic, antimony, barium, beryllium, cadmium, chromium, lead, and selenium) compared to the U.S. Environmental Protection Agency's (USEPA) National Primary Drinking Water Regulations maximum contaminant levels (MCLs), exceedance of their respective MCLs were seen in arsenic, antimony, beryllium, cadmium, and lead (Appendix 4-2).

For arsenic, exceedances of its MCL (0.01 mg/L) were seen in the majority of WWC and BFR samples. The amount by which concentrations exceeded the MCL (a relatively conservative drinking water standard) were relatively low in the upstream reaches of WWC (Locations B, C, and D) with the maximum total arsenic concentration measured at Location D (0.016 mg/L). In the downstream reaches (Locations E to H), exceedances were present at all locations, with the maximum total arsenic concentration G (0.087 mg/L). Arsenic concentrations did not exceed the MCL in the BFR upstream of its confluence with WWC (Location L). Downstream of the confluence, exceedances were present at all locations, with the maximum total arsenic concentration measured at Location L).

Cadmium exceedances were seen in all WWC and BFR samples. The average cadmium concentration of all in-stream WWC and BFR samples (0.0206 mg/L) was nearly four times that of its MCL (0.005 mg/L). According to a USGS geochemical study of soils of the conterminous United States, shale is generally elevated in cadmium and the topsoil (0 to 5 cm) of the Black Hills area is elevated in cadmium (ranging between 0.3 to 6 mg/kg cadmium) (USGS, 2017). The number of MCL exceedances for antimony, beryllium, and lead were few and were either seen in the Location H seep sample and/or in samples where only the results by ICP-OES were available (sometimes at concentrations near the practical quantitation limit).

Of the analytes (aluminum, copper, iron, sulfate (as sulfur), and zinc) compared to the EPA National Secondary Drinking MCLs (a non-enforceable guideline regarding contaminants that may cause cosmetic or aesthetic effects in drinking water), exceedances were seen in aluminum, iron, and sulfur; with Iron displaying the greatest number of exceedances (Appendix 4-2). Of the analytes (boron, manganese, molybdenum, nickel, and strontium) compared to the EPA Health Advisory (HA) Life-time Standard, exceedances of manganese, molybdenum, nickel, and strontium were only seen in WWC seep samples (Appendix 4-2). Of the analytes (cobalt, lithium, and vanadium) compared to average concentration ranges found in surface water, only lithium concentrations in both WWC and BFR waters exceeded the upper bounds of concentrations found in surface waters. Cobalt and vanadium results generally fell within average concentrations found in surface waters (Appendix 4-2).

The overall water quality of WWC and the BFR appears to be in good standing relative to human-health standards. The two major metals of concern were arsenic and cadmium, displaying the greatest number of exceedances. Other analytes of interest (AOIs) include aluminum, calcium, iron, manganese, and sulfur due to the exceedances of their respective comparison values and their association and influence on arsenic mobility. The concentration patterns and trends of these select seven analytes will be further discussed below.

4.4. In-Stream Surface Water Geochemistry of Seven Analytes of Interest

Arsenic – The concentration trends of total and dissolved arsenic generally paralleled that of each other. At Location A, total and dissolved concentrations were elevated (exceeding the MCL of 0.01 mg/L) but fell below the MCL immediately downgradient of Homestake Mine at Location B (Figures 4.3a and 4.3b). Concentrations then steadily peaked around Locations F, G, and H, however, there was a dip in the dissolved concentrations at Location G. From the upstream reaches of WWC to its downstream reaches, there was approximately an order of magnitude increase in arsenic concentrations. Downstream of the WWC's confluence with the BFR, at Locations I, J, and K, there was a general decrease in concentrations compared to peak levels seen in WWC at Locations F, G, and H. Approximately 3.5 km upstream of WWC's confluence with BFR at Location L, concentrations (0.0090 mg/L) were below the MCL and appear to be representative of baseline conditions.

The data suggests the water at Location A may not be representative of baseline conditions of the WWC since it is likely that open-pit gold and silver mining at the Bald Mountain Mine located upgradient to the northwest of Location A could be affecting its water quality. Additionally, Location A is located along Whitetail Creek and downstream from tailings input from the active Wharf Mine, and thus still within the extent of contamination. Concomitantly, pockets of natural background arsenic from mineral deposits containing arsenopyrite and other arsenic-bearing minerals occur throughout the area (Noble, 1950). Water draining from these naturally arsenic-bearing areas can contribute to localized highs in arsenic concentrations in WWC.

The data suggests that there is no major input of arsenic from the tailings pile and other reclaimed waste piles as evidenced by the drop in total and dissolved arsenic concentrations (0.008 and 0.005 mg/L, respectively) to levels below the MCL at Location B. Location B is located along WWC downstream of Gold Run Creek, where Homestake Mine had historically directly discharged untreated mining and milling wastes. Increases in arsenic concentrations are seen further downstream, likely contributed by tailings storage in the alluvial deposits and from seeps. The highest concentrations of total arsenic are observed in the lower elevation, flat, alluvial plain area around Locations F, G, and H (range: 0.047 to 0.087 mg/L). These areas likely allowed for greater deposition and storage of tailings, which through the

development of seeps, continues to mobilize arsenic to WWC. On the BFR, the slight uptick in totalarsenic as well as total- iron and aluminum at Location K, may reflect the continual remobilization of substantial quantities of tailings stored on the banks, contributing to the colloidal metals load. While arsenic concentrations in the BFR are generally lower due to dilution by the greater discharge of the BFR, localized increases in arsenic concentrations in the BFR could be due to storage of tailings in the floodplains re-entering the river, contributing to the elevated dissolved arsenic concentrations.

Aluminum – There was a decreasing trend in total aluminum concentrations from Location A (0.445 mg/L) to Location F (0.015 mg/L) (Table 4.2a and Figure 4.3a). However, concentrations increased to 0.167 mg/L at Location G and continued to increase in downgradient WWC and BFR waters, with max levels seen at Location K (0.511 mg/L). The total concentration in the upgradient BFR water at Location L (0.347 mg/L) was within the range of levels seen in the downgradient waters of the BFR (0.241 to 0.511 mg/L). The average total aluminum concentration in downgradient BFR Locations (0.333 mg/L) was higher than average concentrations in WWC (0.107 mg/L) (Table 4.2a). The increased contribution of aluminum at Location G could be explained by a change in the composition of the bedrock from intrusive rhyolitic rocks and limestones to predominantly silt, clay, and shale deposits (see discussions in Chapter 5). Dissolved aluminum concentrations fluctuated with no apparent trending patterns, ranging from 0.010 to 0.065 mg/L in WWC and 0.002 to 0.101 mg/L in the BFR (Table 4.2b and Figure 4.3b).

Calcium – Total calcium concentrations upgradient of WWC at Location A was 83 mg/L. In WWC there was an increasing trend in total calcium concentrations from Location B (64 mg/L) to Location H (177 mg/L) (Table 4.2a and Figure 4.3a). In the BFR, concentrations continued to increase to 226 mg/L by Location I but then slightly decreased to 203 mg/L by Location K. The total calcium concentration in the upgradient BFR water at Location L (223 mg/L) fell within the range of levels seen in the downgradient BFR waters (203 to 226 mg/L). The average total calcium concentration in downgradient BFR Locations (214 mg/L) was higher than average concentration in WWC (122 mg/L) (Table 4.2a). The increasing levels of total calcium could be explained by dissolution of both calcite and

gypsum from bedrock (limestone and shales) and soils. Dissolved calcium concentrations, in parallel with total concentrations, exhibited a similar increasing trend in WWC and a slightly decreasing trend in the BFR. Dissolved calcium displayed a similar continual rising trend, ranging from 64 to 183 mg/L in WWC and 185 to 224 mg/L in the downgradient waters of BFR (Table 4.2b and Figure 4.3b).

Cadmium – Total cadmium concentrations fluctuated without a discernable trend between 0.005 to 0.034 mg/L in WWC and between 0.01 to 0.036 mg/L in the downgradient reaches of the BFR (Locations I, J, and K) (Table 4.2a and Figure 4.3a). Total cadmium concentrations upgradient of WWC at Location A (0.017 mg/L) and in the upgradient reach of BFR at Location L (0.035 mg/L) fell within the range of concentrations seen in their respective downgradient reaches. On average, total cadmium concentrations in WWC (0.023 mg/L) was similar to average concentrations in downgradient BFR Locations (0.021 mg/L) (Table 4.2a). Dissolved cadmium concentrations also fluctuated without significant trending patterns, ranging from 0.011 to 0.024 mg/L in WWC and 0.017 to 0.024 mg/L in the BFR (Table 4.2b and Figure 4.3b).

Iron – Total iron concentrations upgradient of WWC at Location A was 0.961 mg/L and decreased to 0.535 mg/L at Location B. Further downgradient in WWC, there was an order of magnitude decline in total iron from Location C (1.18 mg/L) to Location F (0.112 mg/L), then followed by the same order of magnitude of increasing total iron from Location F to Location I (1.11 mg/L) on the BFR (Table 4.2a and Figure 4.3a). The total concentration in the upgradient BFR water at Location L (1.07 mg/L) was within the range of levels seen in the downgradient waters of the BFR (0.658 to 1.11 mg/L). On average, total iron concentrations in WWC (0.558 mg/L) was lower than average concentrations in downgradient BFR Locations (0.912 mg/L) (Table 4.2a). Dissolved iron concentrations increased from Location A (0.016 mg/L) to Location D (0.135 mg/L), however, levels fell to 0.028 mg/L at Location E but then rose by nearly two orders of magnitude to 1.66 mg/L by Location I (Table 4.2b and Figure 4.3b). Dissolved concentrations declined to 0.12 and 0.14 mg/L, farther downgradient of the BFR at Locations J and K, respectively. Dissolved iron is much greater in WWC compared to the BFR due to the abundance of iron-

bearing oxides, oxyhydroxides, and sulfide minerals in the bedrock where seep waters emanate, contributing to the dissolved load in WWC.

Manganese – Total manganese concentrations generally paralleled those of total iron concentrations. Total manganese upgradient of WWC at Location A was 0.133 mg/L and declined by an order of magnitude to 0.014 mg/L by Location E, however, concentrations then rose over an order of magnitude by Location I (0.175 mg/L) (Table 4.2a and Figure 4.3a). The total manganese concentration in the upgradient BFR water at Location L (0.158 mg/L) was greater than the range of levels seen in the furthest downgradient reaches of the BFR at Locations J and K (0.08 and 0.07 mg/L). On average, total manganese concentrations in the WWC (0.077 mg/L) was lower than average concentrations in downgradient BFR Locations (0.158 mg/L) (Table 4.2a). Dissolved manganese concentrations also paralleled that of dissolved iron concentration patterns, increasing from Location A (0.018 mg/L) to Location D (0.097 mg/L), but then falling an order of magnitude in concentration at Location E to 0.006 mg/L. Levels then rose more than an order of magnitude to 0.296 mg/L by Location I (Table 4.2b and Figure 4.3b). Dissolved concentrations declined to 0.012 and 0.044 mg/L farther downgradient of the BFR at Locations J and K, respectively. Manganese is strongly associated with the iron-bearing oxides, oxyhydroxides, and sulfide minerals in the bedrock of WWC and its transport geochemistry can be highly similar to that of iron.

Sulfur – Total sulfur concentrations generally paralleled those of total calcium concentrations. Total sulfur upgradient of WWC at Location A was 40 mg/L. In WWC, there was a sharp rise in total sulfur concentrations from Location B (27 mg/L) to Location C (158 mg/L), followed by a plateauing of concentrations until Location G (170 mg/L). Further downstream, concentrations increased to 224 mg/L at Location H and continually rose to 272 mg/L at Location K, the furthest downgradient reach of the BFR (Table 4.2a and Figure 4.3a). The total sulfur concentration in the upgradient BFR water at Location L (211 mg/L) was slightly lower than concentrations seen in the downgradient BFR waters (218 to 272 mg/L) (Table 4.2a). The increasing levels of total sulfur is likely due to the dissolution of gypsum and other easily soluble sulfate minerals found within the bedrock and the alluvial sediments of the area.

Dissolved sulfur displayed a similar continual rising trend, ranging from 27 to 238 mg/L in WWC and 232 to 262 in the downgradient waters of the BFR (Table 4.2b and Figure 4.3b).

4.4.1. Proportion of Analytes in the Dissolved Phase

For each analyte, the proportion of the dissolved phase relative to its total concentration is presented in Figure 4.4. In several samples, the dissolved concentration was greater than the total concentration. This error could be attributed to concentrations being at or near the method detection limit and the general imprecision at low concentrations associated with ICP instrumentation. Although the results are erroneous when the proportion of the analyte in the dissolved phase is greater than 100%, we can still interpret that the majority of the analyte is likely in the dissolved phase. The actual percentage in the dissolved and total phases and individual fluctuations are not as relevant as recognizing broad trends and patterns seen across multiple analytes. In the case of cadmium, too many dissolved concentrations exceeded their respective total concentrations, and the proportion in the dissolved phase could not be reliably interpreted.

The proportion of arsenic in the dissolved phase was at its lowest upgradient of WWC at Location A (51%) and steadily increased until Location F (91%), which suggests most of the input in the lower WWC can be interpreted to be dissolved. This general rise of the proportion of arsenic in the dissolved phase from the upstream to mid-stream reaches of WWC was also generally paralleled by the increasing trends seen in dissolved percentages of aluminum, iron and manganese along the same reach (Figure 4.4). At Location G, the percent of dissolved arsenic dropped to 20%, along with localized dips in percentages of dissolved aluminum, iron, manganese, and aluminum. This could indicate a decrease in the number of seeps or an increase in the total load (as seen in the increases of total arsenic, aluminum, iron, and manganese concentrations shown in Figure 4.3a), thus locally diluting dissolved metals contribution at Location G. The true cause of the decrease in the percent of dissolved metals is difficult to pinpoint from a single water sample per sampling location. Further downstream of Location G, the percent of dissolved arsenic, iron, and manganese generally increased until Location I and then drastically declined in downgradient reaches of the BFR. At the time of sample collection (July 2011), a large proportion of

arsenic in WWC was carried in the dissolved phase (50% or greater), however, the percentage of dissolved arsenic in WWC fluctuated between locations. For calcium and sulfur, the concentrations observed in WWC and the BFR were dominated almost completely by the dissolved phase (greater than 90%) with minimal fluctuations and minimal differences between WWC and BFR stations (Figure 4.4).

4.5. Seep Water Geochemistry of Seven Analytes of Interest

Seep water was collected at Locations B, G, and H, and the results were compared to the colocated in-stream metals concentrations at each Location (Figure 4.5). Seep B was located at the toe of the reclaimed mine dump, while seep G was found emanating from an alluvial bank. Seep H was found emanating from the alluvial bank comprised of a deep red-brown silty clay matrix with well-rounded, poorly-sorted cobbles and pebbles. A gypsum-like precipitant was found on the cobbles and an iridescent film formed on top of the small shallow pool which formed beneath the seep. Seeps water chemistry can provide an indication of what analytes are being reworked and transported from alluvium. Only the total fraction of the seep B sample was analyzed, and dissolved metals concentrations are not available. In general, total arsenic in seep water was lowest at the upstream site Location B (0.0127 mg/L) and greatest at the midstream site Location G (0.395 mg/L). At Location G, the total arsenic concentration of the seep water was 4.5 times greater than the in-stream WWC water, while concentrations were only 1.5 and 1.7 times greater at Locations B and H, respectively (Figure 4.5a). Dissolved arsenic concentrations in seeps are generally more than 1 order of magnitude greater than dissolved concentrations in the stream (Figure 4.5b). For the other analytes of concern, their total concentrations in seep water were greater than their total concentrations in the co-located in-stream sample. The exception being aluminum and cadmium at Locations B and G where their total concentrations were lower in the seep water than their respective instream concentrations (Figure 4.5a).

4.6. Historical Discharge and Arsenic Concentrations in WWC

Paired arsenic concentrations and discharge measurements collected at 15 stations along WWC from 1983 to 2012 (averaging 27 paired samples per year between 1983 to 1994 and 7 samples per year between 1995 to 2012) were compiled from the USGS database and an inventory of the available data

from each gauging station is presented in Appendix 4-3. The paired arsenic concentration and discharge data are presented as annual averages in Table 4.3 and Figure 4.6. Over this 26-year period of data collection, arsenic concentrations have been highly variable, with average annual total arsenic ranging between 0.034 to 0.660 mg/L (averaging 0.125 mg/L) and average annual suspended arsenic concentrations ranging between 0.012 to 0.634 mg/L (averaging 0.098 mg/L). However, average annual dissolved arsenic concentrations have been comparatively stable, ranging between 0.020 to 0.047 mg/L (averaging 0.028 mg/L) and did not appear to be influenced by high discharge years as total and suspended arsenic concentrations were (Figure 4.6). This was most notably illustrated in May of 1995 where a large storm event likely transported large amounts of sediment and colloidal material into WWC and spiking total and suspended arsenic concentrations upwards, however dissolved concentrations did not appear to be affected (Figure 4.6). The 26-year average dissolved arsenic concentration (0.028 mg/L) was comparable to the average dissolved arsenic concentrations in WWC samples (Locations B-H) collected in July 2011 from this study (0.027 mg/L) (Tables 4.2b and 4.3). Based on the historical WWC data, average annual total arsenic concentrations fluctuated around 0.125 mg/L, while average dissolved arsenic concentrations fluctuated around 0.028 mg/L; both were elevated above the current EPA MCL of 0.01 mg/L with little evidence of continuous upward or downward trending concentrations (Table 4.3 and Figure 4.6).

The average annual percent of dissolved arsenic ranged widely between 4% to 66% (Table 4.3 and Figure 4.7). The average dissolved percentage in 2011 (51%) was on the higher end of the spectrum and was a confirmation of the high average percentage of dissolved arsenic detected in WWC samples (Locations B through G) collected in July 2011 from this study (68%) (Figures 4.4 and 4.7). Generally, years with peaks in average annual discharge resulted in the lowest percent of dissolved arsenic (Figure 4.7). This negative correlation between the percent of dissolved arsenic and discharge level is more clearly exhibited in Figure 4.8, where the percent of dissolved arsenic generally decreased with increasing discharge. Excluding the high discharge years (1983, 1984, and 1995), the mean of the average annual percent dissolved arsenic was 48% (Table 4.3). The historical data suggests that under normal flow

conditions, half of the arsenic transported was in the dissolved phase and that the source(s) of this dissolved phase was not readily impacted by large precipitation events or fluctuations in discharge.

CHAPTER 5. WHITEWOOD CREEK AND THE BELLE FOURCHE RIVER SEDIMENT SAMPLES CHARACTERIZATION AND ANALYSIS

Sediment samples were collected at each surface water sample Location along WWC and the BFR, see Figure 4.1 in Chapter 4 for sample Locations map. Sample Locations were chosen to capture data representing each reach of the study area and were also based on accessibility to privately owned land. Location A is located above Homestake's mine waste piles; Locations B through E are in the upstream reaches of WWC; Locations F through H are in the downstream reaches of WWC; Location L is located on the BFR upstream of the confluence between WWC and the BFR; and Locations I to K are located on the BFR downstream of WWC's confluence with the BFR.

5.1. Sample Locations and Sediment Descriptions

Table 5.1 lists all collected sediment samples, their descriptions, and summarizes the types of analyses conducted on the samples as well as any grouping or consolidation of sediments prior to analyses. Due to cost constraints, some samples were combined with other adjacent samples post sample collection (i.e., two or more sample units were mixed or composited together to form a representative sample of a larger unit). A total of six in-stream sediment samples (i.e., sediments collected in the stream bed) were also collected at Locations A, D, G, H, K, and L (Table 5.1). Transect and depth profile sampling on point bars occurred at Locations D, G, H, and K, and these localities are discussed in more detail below. In addition, sediment collection from exposed cut-banks occurred at Locations G and H. The depth profile sample segments or units were selected based on visual inspections of the strata. A sediment layer of similar color, grain size, or mineralogical composition was considered one unit and collected as one sample. Transcribed field notes of sampling activities are presented in Appendix 5-1.

5.1.1. Location D Study Area and Sample Descriptions

Photos of Location D are presented in Figures 5.1 and 5.2. Location D is located in the upper reaches of WWC in a narrow valley with little floodplain development, in a heavily vegetated area of dense grasses, shrubs, and trees. The area is predominately used for recreation and with no agricultural

activity nearby. From measurements taken from aerial photos, the sinuosity of the reach 1 km upstream and 1 km downstream of Location D were 1.2 and 1.0, respectively; the width of the channel ranged from 5.8 to 7.9 meters (5 measurements) (Appendix 5-1). Deposition of materials onto the floodplain was relatively low, as evidenced by the low bank buildup above the surface of the water at the time of sampling (approximately up to 0.5 meters thick). However, in some areas there was evidence of flood terraces (approximately 0.7 meters high) and channel migration. The present-day channel is relatively narrow (approximately 5 meters wide) and not deeply incised into the earlier alluvial sediments, but there was evidence of incision into older bedrock on some cut-banks. The bed load consisted of sub-rounded to sub-angular large cobble (15 cm to <30 cm) to boulder (30 to 60 cm) sized materials. According to the USGS Geological map (Redden and DeWitt 2008), in the area of Location D, WWC was incised into alluvial deposits of mud, silt, sand, and gravel (max thickness of 10 meters). Geologic members in the nearby surrounding area include rhyolitic intrusive rocks, the Minnelusa Formation (sandstone, limestone, and minor shales), Pahasapa Limestone (dolomitic and reef-like limestone), Englewood Limestone (impure limestone), Whitewood Dolomite and Winnipeg Formation (massive dolomite), and Deadwood Formation (glauconitic sandstone, shale, siltstone, and conglomerate) (Appendix 5-2).

At Location D, four samples were selected for geochemical analysis (Table 5.1). These include samples collected 18 meters from the stream on the east bank (or right bank looking downstream) at four depths ranging from the ground surface to a depth of 1.31 meters (each depth is represented by letters at the end of the sample ID). The samples were comprised of organic-rich soils near the surface, followed by sediments with greater silt and clay content at mid-depths, then moist sand and cobbles with greater depths. Small 'metallic' fragments likely to be micas or pyrite and red silty-sand were observed at the lower depths.

5.1.2. Location G Study Area and Sample Descriptions

Photos of Location G are presented in Figures 5.3 to 5.6. Location G is located in the middle reaches of WWC, where the topography is relatively flatter than Location D and the surroundings immediately adjacent to the stream is highly vegetated with dense grasses, shrubs, and trees. Land use in

the area was predominately for farming and ranching. Flood plain development was wider in comparison to Location D. From measurements taken from aerial photos, the sinuosity of the reach 1 km upstream and 1 km downstream of Location G were 2.1 and 1.3, respectively; the width of the channel ranged from 4.1 to 7.2 meters (5 measurements) (Appendix 5-1). The cut banks were incised 4 meters, an indication that high amounts of deposition and incision have occurred in the area. Incision into unstable and slumping exposed cut-banks were observed in several areas in this reach (Figure 5.3). Up to 1 meter of incision into the Pierre Shale bedrock was observed. Evidence of channel migration and abandoned meanders were observed from aerial photos. The channel is generally wider than the channel at Location D and the stream bed was comprised of sub-rounded to sub-angular cobble (16 to <30 cm) sized materials and some silt and clay. According to the USGS Geological map (Strobel, et al., 1999) (Appendix 5-2), WWC in the area of Location G was mostly incised into alluvium comprised of moderately to well-sorted clay, silt, sand, and gravel deposits (max thickness of 50 ft). Geologic members in the nearby surrounding area include the Pierre Shale to Skull Creek Shale sequences (units of shale, limestone, and sandstone) and gravel deposits (moderately sorted, generally stratified, clay, silt, sand, and well-rounded gravel of paleochannels and stream terraces along former flood plains).

At Location G, 24 samples were selected for geochemical analysis (Table 5.1). The samples G2.1 to G2.8 were collected at 8 depth intervals along the face of the exposed cut-bank based on changes in grain-size, color, or material (Figure 5.4). Samples collected near the surface was composed of organic-rich soils, where lenses of deep adobe red silty-clay were observed (Figure 5.5), followed below by bands of light buff to tan and grey to brown units comprised of a mixture of clay-silt-sand sized grains with small calcrete or caliche nodules (<1 cm) found in some bands. Some contacts between bands are gradual, while some are sharp.

The location of sample IDs beginning with G3.1, G3.2, G3.3, and G3.4 were collected on the point bar approximately 100-150 meters downstream and on the opposite bank of the cut-bank samples. These samples were collected at four points along a transect with increasing distance from the stream bank (at 13.5, 21.4, 45, and 60 meters). At each point, depth profile samples were collected from the

surface to depths up to 1.3 meters (each depth is represented by letters at the end of the sample ID). Samples collected closer to the bank were generally comprised of yellow and grey silt to sand sized grains, while samples collected farther from the bank were comprised of dark grey and red clay sized grains.

5.1.3. Location H Study Area and Sample Descriptions

Photos of Location H are presented in Figures 5.7 to 5.10. Location H is located near the mouth WWC and its confluence with the BFR, where the topography is similar to Location G and the surroundings immediately adjacent to the stream are vegetated with dense grasses, shrubs, and trees. Flood plain development was also similar to Location G. From measurements taken from aerial photos, the sinuosity of the reach 1 km upstream and 1 km downstream of Location H are 1.2 and 1.8, respectively; the width of the channel ranged from 4.2 to 7.3 meters (5 measurements) (Appendix 5-1). The cut banks were incised approximately 4.5 meters, an indication that high amounts of deposition and incision have occurred in the area, including up to 1 meter of incision into the shale bedrock. The exposed banks in some areas displayed greater amounts of cobble-sized alluvium than was observed at Location G (Figures 5.8 and 5.9) with local lenses of silt to sand-sized alluvium in some horizons. Evidence of channel migration and abandoned meanders were observed from aerial photos over a width of 70 to 270 meters. The channel was generally similar in width to Location G, and the stream bed was comprised of sub-rounded to sub-angular cobble (16 to <30 cm) sized materials and some silt and clay. According to the USGS Geological map (Strobel, et al., 1999) (Appendix 5-2), WWC in the area of Location H was mostly incised into alluvium comprised of moderately to well-sorted clay, silt, sand, and gravel deposits (max thickness of 50 ft). Geologic members in the nearby surrounding area include the Pierre Shale to Skull Creek Shale sequences (units of shale, limestone, and sandstone) and gravel deposits (moderately sorted, generally stratified, clay, silt, sand, and well-rounded gravel of paleochannels and stream terraces along former flood plains) (Appendix 5-2).

At Location H, 25 samples were selected for geochemical analysis (Table 5.1). The samples H1.1 to H1.7 were collected from 9 depth-intervals along the face of the exposed cut-bank based on changes in

grain size, color, or material (Figure 5.9). These samples are composed of yellowish silt with no vegetation at the surface, followed below by interchanging layers of coarse (cobble and gravel sized) and fine (clay-silt-sand) material and shale bedrock at the bottom. Contacts between layers were smeared in some places but, in general, were relatively well defined. Some features within a layer were collected separately for analysis, such as gypsiferous white irregular nodule growths (H1.2AA) and black angular brittle anthracite-like clasts (H1.5AA). Also, within the H1.5 layer, lenses of grey and dark red/rusty brown silty clay (H1.5A), lenses of grey and yellowish-brown silty clay (H1.5C), both intermixed in a matrix of yellow-orange silty sand (H1.5B), were collected and analyzed separately (Figure 5.10). The average of the results from all three samples was taken to represent the composition of layer H1.5.

Sample IDs beginning with H2.1, H2.2, H2.3, and H2.4 were collected approximately 150 to 200 meters downstream and on the opposite bank of the cut-bank samples. These samples were collected at four points along a transect with increasing distance from the stream bank (at 4, 9, 18, and 35 meters). At each point, depth profile samples were collected from the surface to depths up to 1.37 meters (each depth is represented by letters at the end of the sample ID). The transect appeared to cut across formations of old flood terraces. Sample Location H2.1 was 4 meters from the stream, and its surface was only 0.3 meters higher than the surface of the stream. Sample Location H2.2 was 9 meters from the stream, but its surface level was 0.46 meters higher than the surface level of sample Location H2.1. Sample Locations H2.3 and H2.4 were 18 and 35 meters, respectively, away from the stream, and their surface levels were 0.91 meters higher than the surface level of sample Location H2.2 and 1.68 meters higher than the surface level of sample Location H2.1. Samples collected closer to the stream were generally comprised of sand to cobble sized material, while samples collected farther from the bank were comprised of brown and grey silt to clays, which allowed for augering and sampling to greater depths.

5.1.4. Location K Study Area and Sample Descriptions

Photos of Location K are presented in Figures 5.11 to 5.13. Location K is located on the BFR approximately 60 to 70 river kilometers downstream of its confluence with WWC. The BFR flows through grassy flat plains of low relief in an area of low hills and grass lands. The surroundings

immediately adjacent to the stream were vegetated with tall grasses (Figure 5.11). Flood plain development was much wider than WWC due to the larger size of the river and the flat topography which it flows through. From measurements taken from aerial photos, the sinuosity of the reach 1 km upstream and 1 km downstream of Location K were 2.4 and 1.6, respectively; the width of the channel ranged from 25.7 to 44.4 meters (5 measurements) (Appendix 5-1). The cut banks were 5.4 meters tall in some areas, an indication that high amounts of deposition and incision have occurred in the area, including incision into the shale bedrock. In some areas, down-slumping of banks were observed where a barbed wire fence collapsed and slumped down with the strata it was built on (Figure 5.12). Evidence of channel migration and abandoned meanders were present over a width of 100 to 700 meters. The average channel width (34 meters), was much wider than the average channel width of WWC (5 to 7 meters) (Appendix 5-1). Due to the muddy river water, the bed-load of the BFR was inferred to be comprised of cobble, pebble, and abundant silt and clay based on deposits observed on the bank. The exposed banks revealed strata composed of a vegetated topsoil layer at the surface, followed below by interbanded thin layers of pebble to cobble-sized clasts and thick layers of sand, silts, and clays (see Appendix 5-1 for more detailed descriptions). The contacts between these layers are relatively sharp and well defined (Figure 5.13).

According to the USGS Geological map (Martin, et al., 2004) (Appendix 5-2), The BFR in the area of Location K is mostly incised into alluvium (clay to boulder-sized clasts with locally abundant organic material; thickness up to 23 meters) and Pierre Shale (fissile to block shale with persistent beds of bentonite, black organic shale, light-brown chalky shale, minor sandstone, conglomerate, and abundant carbonate and ferruginous concretions; thickness up to 823 meters). Geologic members in the nearby surrounding area include terrace deposits of clay to boulder-sized clasts deposited as pediments, paleochannels, and terrace fills of former flood plains, with a thickness up to 23 meters (Appendix 5-2).

At Location K, 17 samples were selected for geochemical analysis (Table 5.1). The Location of sample IDs beginning with K1.1, K1.2, K1.3, and K1.4 were collected on the east point bar. These samples were collected at four points along a transect with increasing distance from the stream bank (at 2, 15, 30, and 46 meters). At each point, depth profile samples were collected from the surface to depths up

to 1.42 meters (each depth is represented by letters at the end of the sample ID). Samples collected closer to the river were generally moister and comprised of grey, brown, and red clays, while samples collected farther from the bank were less moist and comprised of buff to tan or yellow clays and fine sands.

5.2. Mineralogical Observations of Samples from WWC and the BFR

A subset of samples collected from Location G (WWC) and Location K (BFR) were selected for detailed mineralogical observations from grain mounts. Mineralogical observations are presented in Appendix 5-3, and a summary of the findings is discussed below. Nine samples from Location G and seven samples from Location K were selected for detailed mineralogical observations through microscopy, which included mineralogical identification and obtaining an approximate visual estimate of modal percentages. Many samples contained an abundance of grains heavily coated in fine particles, up to 80-90% coverage in some cases, which made distinguishing arsenopyrite from other dark colored minerals difficult. These fine-grained particles ranged from orange-amber or bronze in color to yellow, golden-white, or black and were interpreted to be iron oxides.

In general, sediments collected from Location G appeared to have a greater mineralogical variety compared to sediments collected from Location K. Samples at Location K were finer grained, more uniform in grain size and modal composition compared to Location G samples which were generally comprised of larger and more heterogeneous grains. For example, quartz displayed a slightly wider range of grain sizes at Location G (less than 0.1 to 1.0 mm) compared to Location K (less than 0.1 to 0.5 mm). Arsenopyrite grains were generally smaller than quartz grains and displayed a slightly wider range of grain sizes at Location G (less than 0.1 to 0.7 mm) compared to Location K (less than 0.1 to 0.3 mm) and with minimal deviations from this range. Only two samples (G2.4 and K1.4D) reacted strongly to acid, and these samples were buff or dull-yellow-tan and light grey in color. Sample G3.3A, a surface soil, was medium-dark brown colored and displayed a slight reaction to acid. Siderite and other carbonates were not conclusively observed but suspected to be present due to the samples' reaction with acid.

All samples were predominately composed of between 80 to 95% quartz, with little difference in percent abundance between WWC and BFR samples. One exception being sample G3.3F (i.e.,

geochemical analyses sample G3.3D; see Table 5.1), where quartz only comprised 40-50% of this sample. Geochemically, the manganese concentration (3,897 mg/kg) in this sample was the highest concentration in all Location G samples, which could be due to the slightly higher percent abundance of manganese-bearing minerals such as garnets (3-5%). The copper concentration (101.57 mg/kg) of G3.3D was also the highest compared to other Location G samples. Arsenopyrite percent abundances generally range from under 3% to 5%. An arsenopyrite abundance of 15% was observed in sample G3.3F, however, its arsenic concentration (1,116 mg/kg) was similar to the average arsenic concentration across all Location G and K samples (1,084 mg/kg).

Other observable minerals include amphiboles (like hornblende), garnets, micas, gypsum, possibly calcite, and possibly some sulfides (including pyrite or chalcopyrite) where combined percent abundances of these minerals ranged approximately from 10 to 20% in Location G samples and 5 to 10% in Location K samples. Visible grains of sulfates like gypsum were possibly observed in 5 of the 9 Location G samples (G2.4, G2.8, G3.1D, G3.3A, G3.3F) but was not observed in any of the Location K samples. Visible grains of sulfides like pyrite were possibly observed in 2 Location G samples (G3.3F and G3.4E) and 2 Location K samples (K1.1D and K1.2F). Interestingly, these sulfide grains were located in Location G samples which were 45 to 60 meters from the stream bank at a depth between 0.76 to 1 meters (Table 5.1). While at Location K, these grains were observed in samples collected 2 to 15 meters from the stream bank at a depth between 0.61 to 0.79 meters. Although very few visible grains of sulfides were observed, the ultra-fine particles coating the grains were suspected to be comprised of iron oxide reaction products of sulfides.

A detailed account of the mineralogy of the Black Hills was documented in the work of Roberts and Rapp (1965). Sulfate, sulfide, carbonate, arsenate, and oxide/oxyhydroxide minerals listed as occurring in the vicinity of Homestake Mine (located in Lawrence County) or in the vicinity of the catchment below the mine (located in Meade County) are summarized and listed in Appendix 5-4 for reference.

To confirm mineral identification, further in-depth study of the mineralogical composition is recommended using X-ray fluorescence (XRF), scanning electron microscopy (SEM), or other spectroscopic methods. These techniques may provide insight into surface reaction and alteration of mineral grains and formation of secondary arsenic minerals which can attenuate dissolved arsenic during the weathering of primary arsenic minerals. Information about how much dissolution on the surfaces of sulfide minerals (arsenopyrite and pyrite) have occurred and the amount of iron oxyhydroxide formation may support the quantification of arsenopyrite dissolution over time, provide estimates of arsenic transport rate out of the watershed, and illuminate factors affecting arsenic mobility.

5.3. Geochemical Signatures of the Sediments

Analyses of the geochemical signatures of samples collected from cut banks and on point bars will be discussed separately below. All lab-reported geochemical results are presented in Appendix 5-5. Arsenic is used as a measure of the level of contamination based on Marron's 1992 assessment that sediments with less than 200 mg/kg arsenic are considered uncontaminated, while arsenic exceeding 2000 mg/kg are considered sediments that contain mine tailings (Marron 1992). From the complete set of analytes, a subset of analytes of interest (AOI), including arsenic, aluminum, calcium, copper, iron, potassium, magnesium, manganese, phosphorus, silver, sulfur, and strontium, were selected for more indepth assessment. The concentrations of these AOIs were compared to their respective ranges of typical upper continental crust and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database (https://earthref.org/GERMRD/) and (presented in Tables 5.2 to 5.7) and are herein referred to as world background levels. The full dataset gathered from the GERM database are presented in Appendix 5-6. The AOIs were selected because they are either expected to be associated with arsenic-contaminated sediments or may help to explain the evolution of arsenic contamination and its transport on a micro- and macro scale. Aluminum is found in clay minerals, calcium and strontium are generally associated with carbonates which are less abundant in contaminated sediments due to sulfide dissolution, which creates secondary iron hydroxides and sulfates that produce acidity and may leach out carbonate minerals. Magnesium is also associated with clays and carbonates,

while potassium occurs naturally at high concentrations in shales, and phosphorus is associated with organic matter. Iron and manganese occur in ore minerals and in weathering products. Copper, silver, and sulfur are also found in ore minerals and may be closely associated with occurrences of arsenic. Other metals concentrations were not significantly elevated to be of concern.

5.3.1. Cut Bank Sediment Samples

For the cut bank profile at Location G, AOI results are presented in Table 5.2 and Figure 5.14. A high arsenic concentration (1881 mg/kg) is found in the top soil horizon (between 0 to 0.6 m below ground surface) which decreased two orders of magnitude (6 to 20 mg/kg) just 1 meter below the ground surface, comparable to average world background levels (1.5 to 27 mg/kg) (Table 5.2). This suggests that since the commencement of mining activities, approximately 1 meter thick of mining material was deposited on the alluvial plain that was exposed by formation of the cut banks at Location G the cut banks of Location G. Past studies have documented the downcutting of a historic meander of WWC approximately 1 km from its confluence with the BFR which had filled with tailings from Homestake Mine. After the meander filled, WWC "eroded through the meander sediments and into the underlying shale bedrock" (Rees and Ranville 1988). During mining, the high sediment load carried by the WWC did not allow for much erosion. After mining ceased, the energy that used to carry the load of tailings can now be expended on erosion and downcutting through the older alluvial sediments and into the shale bed rock.

For the cut bank profile at Location H, AOI results are presented in Table 5.2 and Figure 5.14. High arsenic concentrations were found near the surface and throughout the depth profile (831 to 2758 mg/kg), until the appearance of shale bedrock starting at 3.5 meters below the surface which had an arsenic concentration (6 mg/kg) that was comparable to world background levels (1.5 to 27 mg/kg). Approximately 3.5 meters of contaminated material was deposited or has been preserved on the cut bank of Location H. This is approximately three times thicker than the deposition that occurred on the cut banks of Location G. Over the period of mining, contaminated sediment stored along the banks around Location G could have been more readily transported. The greater deposition of tailings material at

Location H could be due in part to the flatter slope, changes in energy, and greater accommodation space at Location H. After the cessation of tailings disposal, evidence suggest Location H also went through a period of down cutting, similar to Location G.

Sediments low in arsenic at the Location G cut bank were typically buff, yellow, medium-brown and orange in color, generally poorly sorted, comprised of silt and sand with gravel to cobble-sized clasts (Table 5.2 and Figure 5.14a). While the sediments high in arsenic were a deep rusty-red band approximately 0.3m thick with dark grey-brown to rusty-red toned clay lenses up to 3m wide. Similarly, the high arsenic sediments at the Location H cut bank were grey, brown, and orange-red clay and silt (Table 5.2 and Figure 5.14a). Of note, arsenic concentrations were slightly lower in sample H1.4, which was mainly comprised of gravel to cobble-sized clasts, and also in sample H1.2, which was comprised of silt and sand with a gypsum-like white coating with dark black silt to sand and poorly sorted gravels and cobbles.

At Location G, AOIs which follow a similar pattern to arsenic in the cut bank depth profile samples include copper, iron, manganese, phosphorus, and silver (Figure 5.14). AOIs displaying a weakly inverse relationship to arsenic includes calcium and sulfur, and strontium, while no clear correlation can be discerned between arsenic and aluminum, magnesium, and potassium. At Location H, AOIs which followed a similar pattern to arsenic in the cut bank depth profile samples include copper, iron, and silver, while sulfur and phosphorus displayed a weakly similar pattern to arsenic (Figure 5.14). Aluminum and magnesium patterns mirrored each other but not arsenic. Additionally, no clear correlation could be discerned between arsenic and calcium, manganese, potassium, and strontium. Silver and sulfur concentrations in the depth profile samples were one or two orders of magnitude greater than their respective world background levels, while aluminum and potassium concentrations were below their respective world background levels (Table 5.2).

Due to the heterogeneity of the sediment samples, correlations between the AOIs are not clearly discernible and may be why arsenic correlations with other AOIs at Location G differed from its correlation to other AOIs at Location H. Additionally, Location H is farther downstream, and the

chemical signature of sediments could be different from sediment stored upstream at Location G. Factors could include input from other sediment-carrying sources between Location G and Location H, the reentrainment of contaminated and uncontaminated alluvial sediments from storage, and the sensitivity of metals to redox conditions. For example, manganese is sensitive to oxidation, thus, its concentration in relation to arsenic may vary depending on the redox conditions at Location G and H. Sulfur is found throughout the Pierre Shale (Schultz et al., 1980) and is likely a component of all sediment in the alluvium thus transported downstream in increasing quantities. This may explain why sulfur was found at greater levels at Location H compared to Location G and may explain sulfur's weakly inverse relationship to arsenic at Location G but a weakly similar pattern to arsenic at Location H.

In summary, the cut bank at Location H had a thicker accumulation of contaminated materials as evidenced by the higher average concentrations of arsenic, copper, iron, manganese, sulfur, and silver found in the depth profile samples at Location H (1,503 mg/kg, 56 mg/kg, 83,027 mg/kg, 915 mg/kg, 16,365 mg/kg, and 2 mg/kg, respectively) compared to average concentrations in the depth profile at Location G (279 mg/kg, 35 mg/kg, 37,353 mg/kg, 694 mg/kg, 5,796 mg/kg, and 1 mg/kg, respectively) (Table 5.2). Average concentrations of aluminum, calcium, magnesium, phosphorus, and strontium were generally lower at Location H (8 mg/kg, 248 mg/kg, 11 mg/kg, 843 mg/kg, 4,656 mg/kg, 463 mg/kg, and 54 mg/kg , respectively) than at Location G (12,749 mg/kg, 34,077 mg/kg, 7,977 mg/kg, 576 mg/kg, and 122 mg/kg , respectively) (Table 5.2), which indicate that clays, carbonates, and organics are greater in low-arsenic sediment than in high-arsenic sediments. Strontium and calcium were geochemically lower in contaminated sediments. Only potassium concentrations were similar between the two Locations.

5.3.2. Point Bar Sediment Samples

Location D

Sediment samples collected on the point bar of Location D were highly elevated in arsenic (887 to 1,109 mg/kg) in comparison to world background levels (1.5 to 27 mg/kg); AOI concentrations are presented in Table 5.3 and Figure 5.15. At 18 meters from WWC, sediments were consistently contaminated from the ground surface to a depth of 1.37 meters (arsenic concentrations averaged

approximately 1000 mg/kg). Concentrations for the other AOIs also remained steady throughout the profile, with the exception of calcium and sulfur concentrations which were lower in sample D3.3B (sample depth interval of 0.23 to 0.71 meters) and greater in sample D3.3C (sample depth interval of 0.71 to 1.19 meters) (Figure 5.15). Because calcium and sulfur are components of gypsum, the dip in concentration may indicate that gypsum content is slightly depleted at the 0.23 to 0.71 meters depth interval.

Location G

Arsenic concentrations of sediment samples collected on the point bars of Location G (123 to 4061 mg/kg) were elevated to highly contaminated compared to world background levels (1.5 to 27 mg/kg); AOI concentrations are presented in Table 5.4 and Figure 5.16. At 13.5 meters from WWC (G3.1 samples), the arsenic concentration began at 1128 mg/kg and decreased to 123 mg/kg at a depth range of 1.14-1.30 meters but then increased to 1194 mg/kg at the max depth of 1.83 meters. At 21.4 meters from WWC (G3.2 samples), arsenic remained relatively stable but increased from 1082 mg/kg at the surface to 2236 mg/kg at a depth range of 0.71-0.81 meters. At 45 meters from WWC (G3.3 samples), arsenic increased from 649 mg/kg at the surface to 4061 mg/kg at a depth range of 0.66-0.76 meters but then decreased to 1116 mg/kg at the max depth of 1.01 meters. At 60 meters from WWC (G3.4 samples), arsenic remained relatively stable but decreased from 2194 mg/kg at the surface to 1276 mg/kg at the max depth of 0.76 meters. Arsenic contamination near the surface (0 to 0.23 meters depth) ranged from 649 mg/kg (45 meters from WWC) to 2194 mg/kg (60 meters from WWC). The arsenic concentration (1881 mg/kg) found near the surface (0 to 0.6 meters depth) on the cut bank at Location G fell within this range. These arsenic concentrations indicate that all profiles were contaminated and there was a greater thickness of contaminated sediments in the point bar (up to 1.83 meters) than in the cut bank (up to 0.6 meters) (Tables 5.2 and 5.4). Silver concentrations in point bar sediments were 2 orders of magnitude greater than world background levels, and on average, were greater than concentrations found in the cut bank samples. Sulfur concentrations in point bar samples were on average 17 percent greater than their respective world

background levels, aluminum concentrations were below world background levels, potassium and strontium concentrations were below or near the lower end of their respective world background levels.

Location H

Arsenic concentrations of sediment samples collected on the point bars of Location H (173 to 3890 mg/kg) were elevated to highly contaminated in comparison to world background levels (1.5 to 27 mg/kg); AOI concentrations are presented in Table 5.5 and Figure 5.17. The point bar transect appeared to be positioned across sediments deposited from flood events or from progressive downcutting through alluvium. The ground surface of Location H2.1 (4 meters from WWC) was only slightly higher than the surface of the stream. The ground surface of Location H2.2 (9 meters from WWC) was 0.46 meters higher than the ground surface of Location H2.1. The ground surface of Location H2.4 (18 and 35 meters from WWC, respectively) was 0.91 meters higher than the ground surface of Location H2.2 and 1.68 meters higher than the ground surface of Location H2.1.

At 4 to 9 meters from WWC (H2.1 samples), arsenic concentrations at the near-surface (0 to 0.86 meters) ranged from 652 to 845 mg/kg, indicating a mixture of tailings and alluvium. At 18 meters from WWC (H2.3 samples), arsenic concentrations at the surface started at highly contaminated levels (2634 and 3890 mg/kg) and decreased to 598 mg/kg (sample H2.3D) at the max depth of 1.35 meters. Sample H2.3D was comprised of fine yellow sand with black fragments, suggesting an elevated amount of tailings was mixed with high amounts of alluvium. At 35 meters from WWC (H2.4 samples), arsenic concentrations at the near-surface start at highly contaminated levels (3166 and 1873 mg/kg) and continually decreased to 173 mg/kg at the max depth of 1.37 meters. The lower arsenic levels suggest a mixing zone where the amount of alluvium material was greater than the amount of tailings material, thus diluting arsenic concentrations. Other lines of evidence include the increase in calcium and strontium in conjunction with decreases in copper, silver, sulfur and iron. Arsenic contamination near the surface (0 to 0.76 meters depth) ranged from 652 mg/kg (9 meters from WWC) to 3,890 mg/kg (35 meters from WWC). The arsenic concentration (2,175 mg/kg) found near the surface (0 to 0.5 meters depth) on the cut bank at Location H fell within this range.

At Locations H2.3 and H2.4, the high levels of arsenic (1873 to 3890 mg/kg) found in nearsurface sediments (0 to 0.76 meters) suggest these sediments have experienced a relatively low amount of mixing and dilution with clean alluvium during deposition or since these tailings were deposited. One possible explanation for this could be the flood stage did not reach this part of the point bar easily, possibly because the meanders may have shifted with time (however meander development since 1870 cannot be easily reconstructed). This suggests that pockets of similar highly contaminated sediments are likely to occur at other locations and these pockets are not highly susceptible to remobilization. In general, concentrations of arsenic and other AOIs (Al, Cu, Fe, K, Mg, Mn, S,) were lower near the banks of the WWC compared to samples farther from the bank, suggesting near-bank material experienced higher rates of remobilization and more dilution from the reworking of pre-mining alluvium. Finer grained material, which appeared to contain greater amounts of arsenic (as assessed from the cut bank samples), can be carried farther than coarser-grained material which is usually more readily deposited closer to the banks. This scenario was exhibited at Location H where near-surface samples collected 4 to 9 meters from WWC were comprised of fine to coarse sand, silt, and cobbles, while samples farther from the bank (18 to 35 meters from WWC) contained more clay material (Table 5.1).

Silver concentrations in point bar sediments at Location H were on average 2 orders of magnitude greater than world background levels, and on average, were greater than concentrations in the cut bank samples. Sulfur concentrations in point par samples were on average greater than their respective world background levels, while aluminum concentrations were below world background levels. Potassium and strontium concentrations were below or near the lower end of their respective world background levels.

Location K

Arsenic concentrations of samples collected on the point bars of Location K ranged from near background levels (15 to 48 mg/kg) to elevated or highly contaminated (331 to 2246 mg/kg) in comparison to world background levels (1.5 to 27 mg/kg); AOI concentrations are presented in Table 5.6 and Figure 5.18. At 2 meters from BFR (K1.1 samples), arsenic concentrations at the surface (0 to 0.38 meters) started at 331 mg/kg and increased to 2246 mg/kg at the max depth of 1.14 meters. At 15 meters

from BFR (K1.2 samples), arsenic increased from 335 mg/kg at the surface to 2038 mg/kg at a depth range of 0.36-0.71 meters and then decreased to 1599 mg/kg at the max depth of 1.22 meters. The similar patterns found in samples at 2 and 15 meters from the bank of the BFR suggest that much of the near-bank and near-surface tailings deposits have been covered with post-mining alluvium, which may explain the lower arsenic concentrations in near-surface samples. Concentrations of other AOIs associated with mining (Ag, Cu, Fe, Mg, Mn, S) were also lower near the surface and displayed continuous increasing concentrations with greater depth down to 1.22 meters.

At 30 meters from the BFR (K1.3 samples), arsenic concentrations at the near-surface (0.05-0.25 meters) started at highly contaminated levels (1002 mg/kg) and increased to 2030 mg/kg at the max depth of 1.22 meters. At 46 meters from BFR (K1.4 samples), arsenic concentrations at the near-surface (0.02 to 0.23 meters) started at 476 mg/kg (likely comprised of high amounts of alluvium mixed with tailings) and decreased down to 16 and 15 mg/kg at a depth range of 0.81 to 1.42 meters. These arsenic concentrations were near natural average crustal and river sediment levels (Table 5.6 and Appendix 5-6), which suggests that these were older pre-mining uncontaminated alluvial sediments. Concentrations of other AOIs associated with mining (Ag, Cu, Fe, Mg, Mn, S) were also on average lower in K1.4 compared to other samples collected at Location K. Silver concentrations in point bar sediments were up to 1 to 2 orders of magnitude greater than world background levels, but on average, were less than concentrations found at Location H. Sulfur concentrations were greater than world background levels; aluminum and potassium concentrations were below world background levels.

Highly contaminated sediments (arsenic concentrations greater than 1000 mg/kg) found at Locations K1.1, K1.2, and K1.3 were comprised of mostly clays and fine silt, generally deep red or rusty red-orange, brown-grey, with fine silt-sized particles of a semi-metallic luster. Comparatively, minimally contaminated sediments (arsenic concentrations less than 100 mg/kg) found at Location K1.4 were generally light buff to yellow-grey in color and comprised clays with greater fractions of silt and fine sand (Table 5.1).
In summary, arsenic concentrations from point bar samples at Location G indicate a high degree of arsenic contamination which remained relatively constant with depth. Conversely, point bar samples at Location H indicate a high degree of contamination which generally decreased with depth. While Location K exhibits a relatively lower level of contamination at the surface which generally increased with depth, with the exception of the Location farthest from the bank (46 meters from BFR), where concentrations decreased more than an order of magnitude with depth to relatively uncontaminated levels. Sediments along the BFR were more homogeneous in grain size than sediments along WWC.

5.3.3. In-Stream Sediment Samples

In-stream sediment AOI results are presented in Table 5.7 and Figure 5.19. In-stream sediment sample A1 was collected from Whitetail Creek, a tributary of a reach of WWC above Lead, South Dakota, at a Location approximately 1.75 kilometers upstream and southwest of Homestake Mine. This tributary was sampled to evaluate if other sources besides Homestake Mine contributed to the contamination found in WWC. The in-stream sediment sample from Location A1 suggests that Whitetail Creek was a source of contamination to WWC. Arsenic and silver concentrations (382 and 2.64 mg/kg, respectively) at Location A1 are both at least an order magnitude greater than average background levels (6.87 and 0.053 mg/kg, respectively) (Table 5.7). One potential source of this contamination could be from the Golden Reward Mine, located upstream and approximately 2.5 kilometers southwest of the sample Location. Golden Reward Mine was primarily mined for gold, silver, and tellurium (from the mineral calaverite), being in operation from 1988 to 1996, with final reclamations completed in 2002 (SDDENR 2002 and USGS MRDS 2011). There were numerous other mines in the surrounding area, however, at the time, the Golden Reward Mine was the second-largest gold producer in the Black Hills.

WWC - Arsenic concentrations of in-stream sediments in the downstream reaches of WWC (averaging 669 mg/kg at Locations G and H) increased two-fold compared to in-stream sediment concentrations in the upstream reaches (averaging 323 mg/kg Locations A and D). Conversely, copper, silver, and manganese concentrations steadily declined downstream (Figure 5.19). In the lower reaches at Locations G and H, the declining silver concentrations were still more than an order of magnitude greater

than its world background levels, while copper and manganese concentrations were within the range of their respective background levels (Table 5.7 and Figure 5.19). Aluminum, calcium, potassium, and magnesium displayed similar patterns to one another, where concentrations dipped at Location G but generally increased back to upstream levels. Aluminum and potassium concentrations at all WWC Locations were below their respective minimum world background levels, while calcium, magnesium, and strontium were largely within the range of their background levels (Table 5.7 and Figure 5.19). Iron and phosphorus maintained relatively steady concentrations and were within the range of their background levels, however, phosphorus displayed a slight decrease in concentration at Location H (Table 5.7 and Figure 5.19).

In-stream sediment AOI concentrations were compared to average concentrations of depth-profile sediment samples collected from the point bar (Tables 5.3, 5.4, 5.5, and 5.7). For Location D, calcium, copper, magnesium, manganese, phosphorus, and strontium concentrations of the in-stream sample D1 exceeded the average of Location D point bar samples (average of 4 samples from depth profile D3.3). The calcium concentrations at D1 (37,729 mg/kg) exceeded the point bar average (152 mg/kg) by more than two orders of magnitude. For Location G, phosphorus and strontium concentrations of the in-stream sample G1 exceeded the average of Location G point bar samples (average of 16 samples from depth profiles G3.1, G3.2, G3.3, and G3.4). For Location H, calcium and strontium of the in-stream sample H1 exceed the average of Location H point bar samples (average of 12 samples from depth profiles H2.1, H2.2, H2.3, and H2.4). Arsenic concentrations of in-stream samples collected from Locations D, G, and H were two to three times lower than their respective point bar average arsenic concentrations, which suggests ample dilution from sediment with low arsenic concentrations.

BFR - Location L is located on the BFR approximately 7.5 river kilometers upstream of its confluence with WWC. In-stream sediment concentrations of arsenic (9 mg/kg) was at uncontaminated levels and within the range of world background levels (Table 5.7). However, the copper concentration (124.3 mg/kg) at Location L was greater than WWC sample averages (47.7 mg/kg) and greater than the max world background concentration of 89 mg/kg. Although the cause is unknown, the slightly elevated

levels suggest natural copper concentrations could be higher in the upper reaches of the Belle Fourche, or man-made copper contamination could have occurred. Along with copper, concentrations of calcium, sulfur, and strontium were also greater at Location L compared to the WWC sample averages. These latter three analytes are associated with shale and carbonate materials, which are dominant components of the Pierre Shale found in abundance along the BFR (Martin et al., 2004). From observations made along the BFR and from geologic maps, it appears the overall availability and exposure of the Pierre Shale to erosion was relatively more abundant in the BFR than in the WWC.

At Location K (located on the BFR approximately 60 to 70 river kilometers downstream of its confluence with WWC), arsenic, silver, aluminum, iron, potassium, magnesium, manganese and phosphorus concentrations of the in-stream sample K1 were greater than their respective concentrations of the in-stream sample at Location L (Table 5.7). For Location K, only strontium slightly exceeded the average of Location K point bar samples (average of 16 samples from depth profiles K1.1, K1.2, K1.3, and K1.4). This suggests sediment input associated with mining from WWC contributed to the increase in analyte concentrations of BFR in-stream sediments while dilution from uncontaminated alluvium was also present.

5.4. Relationship between Arsenic and Iron Concentrations in Sediments

The relationship between arsenic to iron in the sediments collected from the cut bank and point bar is a positive curvilinear one (Figures 5.20 a, b, c). The relationship between arsenic and iron are grouped by 1) sediments with relatively low contamination (region of box A), 2) sediments with elevated arsenic but high iron (region of box B), and 3) sediments with high-arsenic and high iron (region of box C). In general, iron is an indicator of arsenic contamination because of its positive correlation. Sediments collected from Locations G, H, and K with greater than 50,000 mg/kg iron always contain greater than 200 mg/kg arsenic. Sediment with low iron concentrations (less than the GERM average of 50,000 mg/kg) is generally sediments with low arsenic contamination (less than 200 mg/kg). These low arsenic and low iron sediments are found at Location G in the lower cut bank samples, at Location H in the bedrock Pierre Shale sample and in the sub-surface sample (1.17 to 1.37 meters deep) 35 meters from WWC, and at Location K in all samples 46 meters from the bank of the BFR. At Locations G and H, sediments with greater than 200 mg/kg arsenic generally contain iron levels greater than 50,000 mg/kg, with the exception of G3.3A. Sediments with greater than 2,000 mg/kg arsenic generally contain iron levels greater than 80,000 mg/kg, with the exception of G3.4A (Figures 5.20 a, b).

At Location K, three out of the four surface samples (K1.1A, K1.2A, and K1.4A) contain arsenic levels at moderately contaminated levels (between 300 to 500 mg/kg) and iron concentration under 42,000 mg/kg (Figure 5.20c). The surface sample (K1.3A) with the highest arsenic concentration (1,002 mg/kg) also had the highest iron content (67,311 mg/kg). All samples collected the farthest distance from the bank (46 meters) and into the subsurface (K1.4B, K1.4C, K1.4D, and K1.4E), contain very low arsenic (<50 mg/kg) and very low iron (<23,000 mg/kg); plotting the in region of box A. Sediments with low arsenic but high iron concentrations (region of box B) are not present in samples collected at Location K (Figure 5.20c). Sediments collected between 2 to 30 meters from the bank and into the subsurface contain high levels of arsenic (>1,500 mg/kg) and iron (89,000 mg/kg); plotting in the region of box C. This grouping of samples based on distance from the bank was not observed in Location G and H samples.

5.5. Summary

In summary, there is not a single tailings horizon, instead, the thickness, geometry and lateral extent of contaminated sediment varies between all Locations. At Location G, the bulk of the contaminated material on the cut banks were stored in a relatively thin upper section. While at Location H the whole thickness of the cut bank was comprised of contaminated sediments. Sediments on the point bars of Locations G and H were generally highly contaminated throughout the entirety of each profile with relatively consistent concentrations with changing distances from the WWC. At Location K, sediments near the bank of the BFR and near the ground surface are less contaminated than sediments farther from the bank and at deeper depths in the profile. The size, geometry, and gradient of the river produce different capacities for transport, storage, and deposition of contaminated sediments. At Locations G and H, more sediments are deposited and stored on the banks, possibly due to the lower

gradient, which produces flatter and wider flood plains as compared to area in the vicinity of Location D. The flood events which produce the sediment sequence on the BFR (Location K) may not all be not all related to flood events on WWC, because more tributaries introduce other sources of sediment to the BFR. Arsenic is diluted near the surface and at Locations close to bank of the BFR, indicating postmining deposition events introduced uncontaminated alluvium which have diluted arsenic concentrations. With the exception of iron, silver, and sulfur, the other AOIs were generally consistent and uniform in concentrations with depth and distance from the bank, signifying a homogenization of sediments from multiple sources in addition to WWC's contribution.

CHAPTER 6. SEQUENTIAL EXTRACTION OF SEDIMENT SAMPLES RESULTS AND ANALYSES

The main objectives of sequential extractions are: 1) to determine the residence sites or mineral hosts of arsenic, which are factors that control arsenic mobility and retention; 2) to establish relationships between the setting of arsenic and other metals in the sediments; 3) to examine arsenic mobility trends by depth and distance downstream. Examination of correlations and simple descriptive statistics were applied to supplement the investigation of these objectives.

6.1. Sequential Extraction Procedure

The extraction methods were based on and modified from the protocols in the literature which are discussed in more detail in Chapter 3. Methods. The first extractant (E1) applied, DI-water, targets weakly bound readily exchangeable surface sites and water-soluble secondary minerals. The second extractant (E2), sodium phosphate monobasic (1M NaH₂PO₄), targets exchange sites and analytes bound to organics. The third extractant (E3), hydroxylamine HCl (0.2M NH₂OH·HCl), targets weakly crystalline fine-grained metal oxides/hydroxides or reducible phases and soluble carbonates. The fourth extractant (E4), hydrochloric acid (1M HCl), targets weakly soluble minerals (E4). The sum of E1, E2, E3, and E4 represents the total amount of extractable analytes (ET), which will also interchangeably be referred to as the mobile fraction in the text. The remaining un-extractable or residual fraction (ER) represents the amount of analyte remaining in the sediment or (i.e., the difference between a metal's total sediment concentration and its total extracted concentration). An alternative sequence of the E2 and E3 extractants (i.e., applying hydroxylamine prior to sodium phosphate) was tested to explore how the interaction of an initial extractant with the sediment may affect the extraction capabilities of subsequent extractants. The results and discussions for this sub-experiment can be found in Appendix 6-1.

The sequential extractions were applied to cut bank and point bar sediments collected from Locations G, H, and K (see Figure 4.1) for sample locations map. Table 5.1 in Chapter 5 lists all collected sediment samples, their descriptions, and summarizes the types of analyses conducted on the

samples as well as any grouping or consolidation of sediments prior to sequential extractions (i.e., two or more samples were composited together to form a representative sample of a larger unit).

The raw lab ICP-OES results from the leachate or supernatant included concentrations for a suite of 36 metals and a total of 32 samples (Appendix 6-2). A majority of these metals were eliminated from further analysis because: 1) the majority of their concentrations were below the detection limit; or 2) these metals were considered unlikely to be relevant to arsenic mobility and correlations with arsenic are not apparent or expected. Six analytes (As, Al, Ca, Fe, Mn, S) remained, and within this reduced analyte pool, results below detection were replaced with a value one-half of the analyte's detection limit (Appendix 6-3). These leachate concentrations (in mg/L) were converted into the extracted solid concentrations (in mg/kg) (Appendix 6-4) that was converted to extraction percentages (Tables 6.1 and 6.2). Extraction percentages are calculated by dividing the analyte's extracted solid concentration by its total sediment concentration and multiplying by one hundred. Each table presents results from the four extractions (E1, E2, E3, E4), the ET and ER fractions, and the total sediment concentrations for each of the 32 samples. In cases where the total extracted analyte concentration was greater than their respective sediment concentration (found in the datasets of arsenic, calcium, and sulfur), the result was excluded from the pool of data presented in graphical representations (Figures 6.1 through 6.4).

6.2. Sequential Extraction Results

In the sections below, results for each of the six analytes are presented. Extraction patterns between extractants and between sample locations are discussed. Correlations between sediments concentrations and amount of analyte extracted are considered, as well as correlations between arsenic and other extracted analyte percentages. The concentration of an analyte extracted by each extractant is an estimation of the amount of that analyte residing on the residence site targeted by the extractant.

6.2.1. Arsenic

Arsenic extraction results are presented in Tables 6.1a, 6.2a, and Figure 6.1a. The average percentage (over all samples depths at each location) of total extractable or mobile arsenic tend to increase downstream. Location G (WWC) samples contain the lowest average percentage of total

extractable arsenic (29%), followed by Location H (WWC) (38%), and Location K (BFR) (50%) (Table 6.2a and Figure 6.2a). The higher amount of mobile arsenic at Location K was driven by higher average arsenic extraction percentages seen in all four extractions compared to average levels in Locations G and H samples (Figure 6.2a). Additionally, on average, the greatest amount of arsenic weakly bound to E1 surface sites were samples from Location K. This suggests that arsenic in sediments found along the Belle Fourche were generally more mobile compared to WWC sediments.

Although the percentage of total extractable arsenic varied between samples (Figure 6.1a), the extraction behavior of each sample (ER > E4 > E2 > E3 > E1) was relatively consistent between samples (Figures 6.1a and 6.2a). And of the weakly bound arsenic (E1, E2, or E3 extractions), arsenic residing on the E2 site was dominant. The similar extraction behavior between all samples may suggest that similar physio-chemical sediment characteristics and mineralogy, acting as the dominant control on arsenic mobility, is persistent throughout all samples at all depths and along the whole distance downstream. For example, the sediments may have undergone similar types of chemical and physical weathering for a similar period of time which has caused comparable weathering conditions at all sample Locations, resulting in arsenic mobilization to and from each residence site in similar proportions.

Any distinct arsenic extraction differences between samples collected at the ground surface and samples collected at greater depth is not clearly discernible. Approximately 20% to 30% of the arsenic was extractable in 3 out of 8 surface samples (G3.1A, H1.7, and K1.3A), while the remaining 5 surface samples contained approximately 40% to 60% extractable arsenic (Table 6.1a and Figure 6.1a). For the point bar samples of Location G, profile G3.1 (located 13.5 meters from WWC) displayed total extractable arsenic percentages, which initially decreased from the surface but then increased at the deepest interval of the profile. The opposite pattern was seen at profile G3.3 (located 45 meters from WWC), where total extractable arsenic was greatest near the ground surface and generally declined with depth. For the point bar samples at Location H, profile H2.4 (located 35 meters from WWC) displayed a similar down-profile decrease in total arsenic extraction to that of profile G3.3 (Table 6.1a and Figure 6.1a). Location K point bar samples, profile K1.1 (located 2 meters from the BFR) also displayed a

similar down-profile decrease in total arsenic extraction similar to that of profile G3.3 and H2.4 (Table 6.1a and Figure 6.1a). The extraction patterns at profile K1.3 (located 30 meters from the BFR) did not noticeably change much down-profile. At profile K1.4 (located 46 meters from the BFR), total arsenic extraction percentages increased down-profile similar to that of profile G3.1, possibly in conjunction with the decrease in arsenic concentrations in the sediments down-profile seen in the samples of both profiles.

For the cut-bank samples at Location H, there was a general down-profile increase in total extractable arsenic percentage (from 24% at H1.7 to 66% at H1.2B), coincident with the general decline in sediment arsenic concentrations down-profile (from 2,175 mg/kg at H1.7 to 995 mg/kg at H1.2B) (Table 6.1a and Figure 6.1a). Sample H1.2A did not conform to the extraction pattern of other Location H cut-bank samples, possibly as a result of the unusual chemistry of this sample. Sample H1.2A displayed low arsenic extractability, having a total extractable arsenic percentage of 17% compared to that 66% of H1.2B even though sediment arsenic concentration of sample H1.2A (667 mg/kg) was similar to that of sample H1.2B (995 mg/kg) (Table 6.1a). However, the sediment manganese concentration of H1.2A (4,347 mg/kg) was almost twice that of H1.2B (2,343 mg/kg) and approximately nine times greater than the average manganese concentration of the other Location H cut bank samples (198 to 774 mg/kg; averaging 468 mg/kg). The high amount of manganese in the H1.2A sample could be one factor in the relatively low amounts of total extractable arsenic from that sample. Although iron and aluminum hydroxides are typically the main host phases for arsenate adsorption in sediments, manganese hydroxides have a good retention capacity for arsenate, especially if few efflorescent precipitates (e.g., aluminum and iron hydroxides, calcite, organic matter coating) are present, which could inhibit the reactivity of manganese hydroxides (Gorny et al., 2015).

There appeared to be a correlation between lower total arsenic sediment concentrations and increased arsenic mobility observed amongst the point bar samples collected at Locations G and K. At Location G, samples G3.1D and G3.3A had the lowest total arsenic contents (123 and 649 mg/kg, respectively) and the highest total extraction percentages (30% and 61%) compared to other samples within their respective depth profiles (Table 6.1a and Figure 6.1a). At Location K, samples K1.1A,

K1.3A, and K1.4B had the lowest total arsenic contents (193, 1002, and 39 mg/kg) and produced the highest total extraction percentages (55%, 31%, and 83%) compared to the other samples within their respective depth profiles (Table 6.1a and Figure 6.1a). The two most arsenic-poor samples, K1.4B (39 mg/kg) and K1.4C (48 mg/kg) contained the greatest percentage of total extractable arsenic of all samples due to a noticeably larger fraction of arsenic residing in the E2, E3, and E4 fractions and very little in the residual fraction (i.e., presumably arsenopyrite) (Table 6.1a and Figure 6.1a). The low arsenic content in these two samples could be due to the sample containing a greater portion of pre-mining alluvial sediment mixed with post-mining contaminated sediment. Additionally, as both samples were collected below more strongly contaminated sediment, some of the arsenic above expected average background concentrations (1.5 to 27 mg/kg; Appendix 5-5) may be due to leaching and migration downward from the strongly contaminated layer above since sediment deposition. The combination of these two scenarios could account for the low amount of arsenic contained in the interpreted arsenopyrite fraction and the high amount of arsenic present in less stable forms in these two samples.

The opposite pattern is observed at Location H, where lower total sediment concentrations in samples H1.2A and H2.4D (667 and 894 mg/kg, respectively) yielded lower total arsenic extraction percentages (17% and 18%, respectively) compared to other samples within their respective depth profiles (Table 6.1a and Figure 6.1a). As discussed earlier, the high manganese concentrations in sample H1.2A could hinder arsenic mobility. For sample H2.4D, the sediment aluminum concentration (25,716 mg/kg) was approximately 10,000 mg/kg greater than the average aluminum concentration of the other samples in its respective depth profile (15,301 mg/kg; range: 10,169 to 18,941 mg/kg). Iron and aluminum hydroxides have been known to have the highest affinity for arsenate and are the main host phases for arsenate adsorption in sediments (Gorny et al., 2015). Since sample H2.4D had relatively high sediment concentrations of aluminum and iron, these conditions appeared favorable for the high retention and low mobility of arsenic.

An interesting pattern appeared when observing the relationship between arsenic extraction concentrations and arsenic sediment concentrations (Figure 6.3a). Extracted arsenic concentrations in E1

remained relatively constant (between 0.117 to 2.90 mg/kg)¹ regardless of arsenic sediment concentrations. Conversely, extracted arsenic concentrations in E2, E3, and E4 increased with increasing arsenic sediment concentrations. These patterns suggest the amount of arsenic residing on weakly bound surface sites(E1) does not change with the degree of contamination and could indicate the capacity of this residence site is similar in sediments across all upstream to downstream locations. For the other extractable sites (E2, E3, and E4), the positive correlation seems to suggest the amount of these other residence sites increases as the degree of contamination increases.

Although on average, arsenic is most mobile at location K, no general patterns appear to correlate any single attribute to increased arsenic mobility. In point-bar samples at locations G and H, the highest amount of mobile arsenic belonged to samples near the surface (G3.3a and H2.4a), while at location K it belonged to a sample collected at greater depths (K1.4c) (Figure 6.1a). The above-mentioned three samples varied in their original arsenic sediment concentrations (649, 3166, and 48 mg/kg, respectively) and were all located between 35 to 46 meters from the riverbank. Arsenic's susceptibility to mobilization appear to vary depending on the physical and geochemical makeup of the sediments as well as by depth and distance from the stream, suggesting the rate of arsenic dissolution is varied across the study area.

On average, 61% of arsenic in the sediments are likely tightly bound in in the residual phase, interpreted to largely be arsenopyrite; 24% are bound in secondary minerals; 11% are bound to exchange sites; 4.8% are bound in reducible phases, and 0.37% are weakly bound to surface sites (i.e., ER > ET: E4 > E2 > E3 > E1) (Table 6.2a). The results of the sequential extractions suggest arsenic is predominantly located in residence sites that are not easily accessible and would not be easily released under normal environmental conditions.

¹ The range of concentrations were calculated excluding results from sample H1.3B (43.55 mg/kg) and samples with possible erroneous results (G2.6, G2.5, and K1.4D; see Appendix 6-4). It is suspected the high concentration found in E1 of sample H1.3B could be from solid particles that were not properly filtered out.

6.2.2. Aluminum

Aluminum extraction results are presented in Tables 6.1b and 6.2b; Figures 6.1b and 6.2b. Total aluminum content in the sediment ranged between 5,545 to 25,716 mg/kg. The extraction pattern of aluminum was similar to that of arsenic and iron (i.e., on average, Residual > ET: E4 > E2 > E3 > E1) (Table 6.2b). On average, 12% of aluminum was mobile (ET), which is predominantly hosted in the E4 fraction (11%) (Table 6.2b). However, the total extracted aluminum percentages in individual samples can fluctuate between 4.98 to 41.4% (556 to 3,055 mg/kg; averaging 1,369 mg/kg) (Tables 6.1b and 6.2b). The average percent of mobile aluminum was greatest at Location H (16%) and lowest at Location G (8.7%) (Table 6.2b and Figure 6.2b). On average, very little of the mobile aluminum (0.80%) belonged to the water-soluble fraction (E1), except for five samples in Location H (2.9% to 8.3%), which were two to three orders of magnitude greater than all other E1 extraction percentages (Tables 6.1b and 6.2b). Mobile aluminum is predominantly associated with fine-grained clay minerals as evidenced by the high aluminum content in E4 which can be explained by the break-down of clay minerals by the hydrochloric acid (1 M HCl).

There appears to be little correlation between total extracted aluminum concentrations and its sediment concentrations (slope = 0.01; $R^2 = 0.48$). As expected, there is a strong correlation between residual concentrations and sediment concentrations (slope = 0.90; $R^2 = 0.99$) (Figure 6.3b). Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) do not appear to be strongly associated with the solubilization of aluminum-bearing minerals as demonstrated by their weak linear correlations (Figure 6.4a). The correlation patterns between extracted arsenic and aluminum concentrations was similar to that of extracted arsenic and iron (of all four extractions), however, the correlation between extracted arsenic and iron is stronger than between extracted arsenic and aluminum (Figures 6.4a and 6.4c). This suggests that iron and aluminum may be associated with the same fine-grained clay minerals (E4) however, a greater proportion of arsenic may be bound to iron-bearing fine-grained minerals rather than aluminum-bearing ones. Ultimately on average

across all three locations, 88% of aluminum and 94% of iron was immobile in the residual fraction (Table 6.2b).

6.2.3. Calcium

Calcium extraction results are presented in Tables 6.1c and 6.2c; Figures 6.1c and 6.2c. Total calcium content in the sediment ranged between 2,703 to 46,280 mg/kg. The extraction pattern of calcium (i.e., $ET > Residual: E4 \approx E2 \approx E1 > E3$) was different from that of arsenic, aluminum, and iron (i.e., Residual > ET: E4 > E2 > E3 > E1). On average, 75% of calcium was mobile (ET), which on average is predominantly hosted in the E1, E2, and E4 fractions (each between 20 to 23%) (Table 6.2c). The average percent of mobile calcium was highly similar between Locations G, H and K (73%, 75%, and 76%, respectively (Table 6.2c and Figure 6.2c). However, the total extracted calcium percentages in individual samples fluctuated between 37 to 100% (1,797 to 29,241 mg/kg; averaging 9,889 mg/kg) (Tables 6.1c and 6.2c; Appendix 6-4c).

In Location H samples, the majority of the calcium appears to be bound in the E1 and E2 fractions, while at Locations G and K, the majority is bound in the E2 and E4 fractions (Figure 6.1c). This is interpreted to indicate multiple hosts of calcium, where one source contains easily soluble calcium such as in gypsum, while the other sources are more strongly bound, such as carbonates like calcite and dolomite from the Pahasapa Limestone or Pierre Shale that is present within the study area (Appendix 5-2). Gypsum solubility in pure water at 25 °C is approximately 2,000 mg/L and calcium is approximately 30% by weight. If gypsum was present, calcium in the supernatant extracted by E1 would be expected to range approximately between 500 to 700 mg/L. E1 extracted calcium concentrations in the E1 supernatant of individual samples fluctuated between 4.2 to 551 mg/L, averaging 249 mg/L (Appendix 6-4c). These supernatant calcium concentrations at the higher end of the range are within the order of magnitude of what would be expected from gypsum dissolution. The sequential extraction methodology performed in this study may not be able to fully dissolved gypsum in the E1 extraction (by DI water) in the 20 minute-extraction as stipulated by the protocol.

As expected, there was a strong positive linear correlation between total extracted calcium concentrations and its sediment concentrations (slope = 0.59; $R^2 = 0.93$) (Figure 6.3c). Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) do not appear to be strongly associated with the release of calcium-bearing minerals, as demonstrated by their weak linear correlations (Figure 6.4b).

6.2.4. Iron

Iron extraction results are presented in Tables 6.1d and 6.2d; Figures 6.1d and 6.2d. The extraction pattern of total extracted iron is similar to that of total extracted arsenic (i.e., Residual > ET: E4 > E2 > E3 > E1). On average, only 6.2% of iron is mobile (ET) and predominantly hosted in the E4 fraction (averaging 6.0%), which corresponds to an average ET concentration of 4545 ppm (average iron content in the sediment is 77,466 ppm) (Table 6.2d). Iron is predominately immobile in the residual fractions (89 to 99%) (Table 6.2d). The average percent of mobile iron is greatest at Location K (8.6%) and lowest at Location G (4.8%) (Figure 6.2d). Total extracted iron percentages are relatively consistent throughout all sediment samples (2.5 - 11%), while total iron content in the sediment fluctuates greatly (19,861 - 115,664 ppm) with no correlations between total extracted percentages and total sediment concentrations (Figure 6.3d). Iron was the least extractable metal, followed by aluminum < arsenic < sulfur < manganese, and calcium exhibiting the highest mobility (Table 6.2(a-f)).

There does not appear to be a strong association between the dissolution of iron-bearing minerals and the release of arsenic residing on surface sites (E1), exchange sites (E2), and reducible sites (E3), and from secondary minerals (E4) as demonstrated by the low to weak linear correlations between extracted arsenic and extracted iron concentrations (Figure 6.4c). For E1, the slope (0.02) is flat, and although the R² (0.80) of the linear regression is relatively strong, the value is highly influenced by one anomalously high arsenic extraction concentration (43.6 mg/kg) seen in sample H1.3B. E1 iron concentrations in select Location H cut-bank samples (H1.5B, H1.5A, H1.4, H1.3B, and H1.3A) were atypically high (47.8 to 1495 mg/kg) compared to E1 iron concentrations seen in all other samples (0.05 to 4.54 mg/kg) (Appendix 6-4). The significant iron concentrations extracted by E1 suggests the presence of easily soluble secondary iron-sulfate minerals such as melanterite present in the vicinity of Deadwood (Appendix 5-4), which are typically very soluble in pure water. However, the E1 arsenic concentrations of these Location H cut-bank samples, (0.465 to 2.55 mg/kg; excluding sample H1.3B) were within the range of E1 arsenic concentrations of all other samples (0.117 to 2.89 mg/kg) (Appendix 6-4). This appears to suggest similar amounts of readily available surface-bound and soluble arsenic are released regardless of the amount of surface-bound and soluble iron, and thus surface-bound arsenic is likely not associated with or controlled by surface-bound and soluble iron.

For E2 and E3, the slopes of extracted arsenic versus extracted iron concentrations (2.63 and 6.18, respectively) are positive, however, the R² (0.40 and 0.28) of the linear regressions are relatively weak (Figure 6-4c). It is worth noting that the amount of iron extracted from the E2 (11.1 to 110 mg/kg) and E3 (0.05 to 14.1 mg/kg) extractions are clearly defined, and there is minimal overlap in extracted iron concentrations (Figure 6.4c). However, there is considerable overlap in the range of extracted arsenic concentrations in E2 (9.51 to 392 mg/kg) compared to E3 (4.64 to 180 mg/kg) (Figure 6.4c). The extraction pattern for E4 and ET are closely aligned to one another with decidedly similar flat slopes (0.06 and 0.09) and weak R² (0.35 and 0.42), respectively (Figure 6.4c). Excluding sample G2.7, the highly similar range of extracted iron concentrations between E4 (612 to 8625 mg/kg) and ET (624 to 8723 mg/kg) and the relatively similar range of extracted arsenic concentrations between E4 (17 to 910 mg/kg) and ET (32 to 1482) indicate the majority of mobile arsenic and iron resides in the E4 fraction (Appendix 6-4).

Each extractant appears to perform well at targeting specific iron residence sites, as evidenced by the partitioning of extracted iron into distinct concentration groups (Figure 6.3c). However, reducible arsenic (E3) and arsenic bound in secondary minerals (E4) do not appear to have a strong association with Fe-oxyhydroxides or other iron-bearing amorphous or fine-grained minerals due to the weak correlations between extracted arsenic and extracted iron seen in Figure 6.4c. Possible interpretations based on these results include: 1) arsenic released in these extractions may be bound in other non-iron-bearing secondary minerals that are not greatly affected by reductive dissolution of iron-bearing minerals; 2) the limited

amount of iron extracted in E3 suggest concentrations of amorphous to poorly crystalline Feoxyhydroxides in the sediments may be low.

6.2.5. Manganese

Manganese extraction results are presented in Tables 6.1e and 6.2e; Figures 6.1e and 6.2e. Total manganese content in the sediment ranged between 286 to 4,347 mg/kg. The extraction pattern of manganese (i.e., on average, Residual > ET: E3 > E4 > E1 > E2) was unique and more variable than that of all other analytes (Table 6.2(a-f)). On average, 47% of manganese was mobile (ET), and predominantly hosted in the E3 and E4 fractions (24% and 20%, respectively) (Table 6.2e). The total extracted manganese percentages in individual samples can fluctuate between 4.56 to 85.5% (22.7 to 3140 mg/kg; averaging 654 mg/kg) (Tables 6.1e and 6.2e). The average percent of mobile manganese was greatest at Locations G and K (60 and 64%, respectively) and lowest at Location H (23%) (Table 6.2e and Figure 6.2e). There appeared to be a modest positive linear correlation between total extracted manganese concentrations and its sediment concentrations (slope = 0.56; $R^2 = 0.70$) (Figure 6.3e).

However, the percentage of manganese extracted from weakly bound surface sites (E1) in the cut bank samples at Location H was much greater than the point bar samples at Location H and greater than in all samples from Locations G and K (Table 6.1e and Figure 6.1e). The cut bank samples at Location H with the greatest extractability from E1 sites were generally comprised of a dark grey, sometimes black, to dark red-brown color. Compared to low-E1 extractability sediments that were more yellow-orange in color. Due to the low extractions from the E3 and E4 fractions, the percentage of mobile (ET) manganese from cut bank samples at Location H was much lower compared to the total extracted manganese in samples from other locations.

As evidenced by the high manganese content in E3 and E4 at Locations G and K, mobile manganese is interpreted to be predominantly associated with less readily dissolvable fine-grained manganese oxyhydroxides (e.g., manganite and pyrolusite), manganese carbonates (e.g., rhodochrosite) and other secondary minerals noted within the study area (Appendix 5-2). However, in the cut bank samples of Location H (samples H1.6 to H1.2B), mobile manganese is predominantly hosted in easily

dissolvable fractions as evidenced by the relatively high manganese content in E1 and E2 in comparison to the percentages found in E1 and E2 of H2.4 samples (Table 6.1e and Figure 6-1e). This implies that within all the samples collected, Mn is likely present in a relatively stable form (e.g., manganese carbonates such as rhodochrosite, or manganese oxyhydroxides such as manganite, pyrolusite) as well as in highly soluble form (e.g., manganese sulfates and secondary manganese hydroxides). A portion of the samples where Mn is water-soluble (H1.5B, H1.5A H1.4, H1.3B, and H1.3A) are also samples where aluminum is also water-soluble (Figures 6.1b and 6.1e). Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) do not appear to be strongly associated with the solubilization of manganese-bearing minerals as demonstrated by the weak linear correlations between extracted arsenic and extracted manganese (Figure 6.4d).

6.2.6. Sulfur

Sulfur extraction results are presented in Tables 6.1f and 6.2f; Figures 6.1f and 6.2f. Total sulfur contents in the sediment ranged between 619 to 25,650 mg/kg. The extraction pattern of sulfur (i.e., on average, Residual > ET: E1 > E2 > E3 > E4) was different from that of arsenic, aluminum, and iron (i.e., for these three analytes, on average, E1 extracted the least and E4 extracted greatest concentrations of the targeted analyte) (Table 6.2f). On average, 43% of sulfur was mobile (ET), and predominantly hosted in the E1 fraction (24.9%) (Table 6.2f). However, the total extracted sulfur percentages in individual samples can fluctuate between 1.49 to 89.7% (31 to 14,092 mg/kg; averaging 5,368 mg/kg) (Tables 6.1f and 6.2f). The average percent of mobile sulfur was greatest at Locations H and K (49% and 50%, respectively) and lowest at Location G (25%) (Table 6.2f and Figure 6.2f). There appears to be a modest positive linear correlation between total extracted sulfur concentrations and its sediment concentrations (slope = 0.55; $R^2 = 0.84$) (Figure 6.3f).

Mobile sulfur is predominantly associated with easily dissolvable minerals, as evidenced by the high sulfur content in E1 and E2. Although sulfur is always present in the E1 fraction, it is not always strongly detectable in the E2, E3, and E4 fractions, especially in many surface/near surface samples (Table 6.1f). This is interpreted to indicate: 1) the formation of an easily dissolvable sulfur-based

precipitant on the surfaces of minerals or formation of gypsum in the sediment; and 2) multiple sources of sulfur, where one source contains easily soluble sulfur (most likely to be gypsum and/or other less likely sulfates such as chalcanthite, epsomite, goslarite, melanterite, and potash alum, found throughout Lawrence county [Appendix 5-4]), while the other sources contain more strongly bound sulfur (sulfides such as arsenopyrite, galena, marcasite, pyrite, and sphalerite, found throughout Lawrence county [Appendix 5-4]). As discussed previously, gypsum solubility in pure water at 25 °C is approximately 2,000 mg/kg and sulfur is approximately 24% by weight. If gypsum was present, sulfur in the supernatant extracted by E1 would be expected to range approximately between 370 to 570 mg/L. E1 extracted sulfur concentrations in the E1 supernatant of individual samples fluctuated between 1.65 to 570.8 mg/L, averaging 272.3 mg/L (Appendix 6-4f). The supernatant sulfur concentrations are within the order of magnitude of what would be expected from gypsum dissolution. Presumably, the presence of other sulfate salts (e.g., highly soluble iron-sulfate salts) may be limited or are only locally present. The low amount of E1 extractable iron (Figure 6.1d) supports the minor presence of iron-sulfate salts. However, E1 extractable iron in several location H samples (H1.5B, H1.5A, H1.4, H1.3B, and H1.3A) were distinctly higher than all other samples (Table 6.1D and Appendix 6-4D) and could be an indication of iron-sulfate salt formation there.

Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) do not appear to be strongly associated with the release of sulfur-bearing minerals as demonstrated by the weak linear correlations between extracted arsenic and extracted sulfur (Figure 6.4e).

6.3. Summary

On average, across all collected samples, 39% of arsenic was mobile (ET), which was greater than the percentage of extractable iron (6%) and aluminum (12%), but less than sulfur (43%), manganese (47%) and calcium (75%) (Table 6.2(a-f)). Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) do not appear to be strongly associated with the release of aluminum-, calcium-, manganese-, or sulfur-bearing minerals as demonstrated by their weak linear correlations. Only iron appeared to display stronger but not-definitive signs of being associated with the release of arsenic (Figure 6.4(a-e)). Arsenic is not clearly tied to one mineral but to a mixture of insoluble minerals (arsenopyrite, etc.), oxides, hydroxides, and fine-grained clays. Evidence suggests that arsenic could be recycled in-situ (released from more strongly bound sites but then retained on less strongly bound surface or exchange sites). The majority of the arsenic is not strongly associated with easily soluble minerals and thus is not easily transported further downstream in solution.

CHAPTER 7. ESTIMATING ANNUAL SUSPENDED SEDIMENT FLUX AND ARSENIC TRANSPORT RATES BASED ON HISTORICAL DATA

Arsenic is transported out of WWC as suspended-arsenic (arsenic carried by suspended sediment) and dissolved-arsenic; the rates of both transport mechanisms were calculated and summed to estimate the total-arsenic transport rate. Through three difference methods, including regression analysis, estimates of the suspended sediment flux over a period of 30 years was established, providing a range of where the true arsenic transport rate lies. Dissolved-arsenic transport rates compiled from USGS historical database were summed with the estimated suspended-arsenic transport rate to arrive at the total-arsenic removal rate over a period of 30 years. The calculated total-arsenic transport rate was applied to data from the literature on total arsenic storage along WWC, and an estimation of the time needed for complete arsenic removal from WWC was established.

7.1. Dataset Descriptions and User-Defined Terminology

Thirty years (1982 - 2012) of discharge and suspended sediment data were compiled from the USGS database² from two different gauging stations on WWC (Upstream and Downstream sites -see definitions below). Discharge data were measured values collected by the USGS (a total of 21,918 results across two sites), but only a relatively small number of suspended sediment flux data (a total of 495 results across two sites) were collected.

Suspended sediment samples were composited from subsamples collected at either equal width increments (EWI), equal discharge increments (EDI) from an entire fluvial cross-section, or the sample was collected as a point sample. The sample collection method depended on the flow stage and discharge conditions during sample collection, but the specific set of protocols for each methodology did not change over the period of record for the site. The suspended sediment concentrations were analyzed using the ASTM Method D 3977-97 from the American Society for Testing and Materials, Standard Test Method

² The USGS surface water database can be accessed at https://waterdata.usgs.gov/nwis/sw.

for Determining Sediment Concentration in Water Sample (American Society for Testing and Materials, 2000). The analytical method did not change over the period of record at the Whitewood Creek sites. The USGS dataset and some user-defined terminology used in subsequent sections of the text are described below:

Whole-population (whole-pop.) = 30 years (1982 to 2012) of measured mean-daily discharge values at two sites on WWC:

- Upstream Site = USGS gauge and sampling location on WWC located upstream of the town of Whitewood, South Dakota. USGS Station # 06436180, Whitewood Creek Above Whitewood, SD. The site is 1122 meters (3,680 feet) above the NGVD (National Geodetic Vertical Datum) of 1929 and has a drainage area of 146.8 square kilometers (56.7 square miles). 30 years of data (November 1982 to November 2012) were downloaded from the USGS database, which contained 10,959 measured mean daily discharge results (Figure 4.1; location E).
- Downstream Site = USGS gauge and sampling location on WWC located upstream of the town of Vale, South Dakota. USGS Station # 06436198, Whitewood Creek Above Vale, SD. The site is 866 meters (2,840 feet) above the NGVD (National Geodetic Vertical Datum) of 1929 and has a drainage area of 264.2 square kilometers (102 square miles). 30 years of data (November 1982 to November 2012) were downloaded from the USGS database, which contained 10,959 measured mean daily discharge results (Figure 4.1; approximately 4 river kilometers (2.5 miles) upgradient and southwest of location H).

Sub-population (sub-pop.) = a subset of the whole-population for which a measured mean-daily discharge is paired with its respective measured suspended sediment concentration:

- Upstream Site = 256 paired mean-daily discharge and suspended sediment concentration results from January 1983 to October 2012 were downloaded from the USGS database.
- Downstream Site = 239 paired mean-daily discharge and suspended sediment concentration results from January 1983 to October 2012 were downloaded from the USGS database.

SSC = Suspended Sediment Concentration; units = milligram per liter (mg/L). Measured by USGS as described above, data downloaded from USGS database.

SSF = Suspended Sediment Flux: a rate calculated by USGS from SSC measurements based on discharge. Original units = tons per day (tons/day) but converted by user to Mg per day (Mg/day). Data downloaded from USGS database.

- Actual or Measured SSF = suspended sediment concentrations (SSC) measured and converted to suspended sediment flux (tons per day) by the USGS. Each measured SSF value is paired with a measured mean-daily discharge value. This dataset was downloaded from the USGS database.
- Predicted or Estimated SSF = suspended sediment flux that was calculated from measured mean-daily discharge values, based on regressions / rating curves derived from the sub-population dataset where a relationship between measured mean-daily discharge was established.

This dataset was calculated in this study by the author and discussed in more detail below.

Log = log-transformed data

7.2. Assessment of Discharge and Suspended Sediment Flux Distributions

The suspended-arsenic transport rate covering the period between 1982 to 2012 can be estimated using regressions applied to the above datasets. However, the population distributions of these datasets should first be examined to assess the quality of the regression and rating-curve estimation accuracy.

The distribution of whole-population and sub-population discharges at both upstream and downstream sites were examined primarily for how well the sub-population represented its respective whole-population. The sub-population should capture the same range and distribution of discharges as the whole population, and the maximum of the sub-population should account for the high discharge events of the whole population. Both whole- and sub-population distributions were also assessed for a unimodal distribution to confirm that the dataset came from a single population. The distribution of the measured-SSF data from both sites were similarly evaluated. The discharge and SSF distributions at both sites were also examined for differences in discharge levels and suspended sediment transport behavior between the upstream and downstream locations in order to determine which site best captured suspended sediment transport behavior out of WWC.

7.2.1. Discharge Population – Distribution Analysis

For the whole-population discharge distributions, the upstream site's log-discharge values (log m^3 /sec) were more right-skewed towards higher discharges than the downstream site's log-discharge values which were more left-skewed towards lower values. (Figures 7.1 and 7.2). Maximum discharges were in a similar range at both sites, but the downstream site experienced more low-flow conditions. Log-discharges ranged from -1.55 to 1.83 (0.028 to 67.11 m³/sec) for the upstream site and -5.55 to 1.92 (2.8x10⁻⁶ to 82.69 m³/sec) for the downstream site.

Comparing the upstream site's whole-population with its sub-population, both population distributions were slightly right-skewed (Figures 7.1 and 7.3). However, 95% of log-discharges in the sub-population fell between -1.02 to 0.7661 (0.096 to 5.84 m³/s), while 95% of the log-discharges in the whole-population fell between -1.0825 to 0.4587 (0.0827 to 2.88 m³/s). This indicated that the upstream site's sub-population discharges were more concentrated at higher flows and may not fully represent the upstream site's whole-population discharges.

Comparing the downstream site's whole-population with its sub-population, both population distributions were slightly left-skewed (Figures 7.2 and 7.4). Additionally, 95% of log-discharges in the sub-population (-1.52 to 1.04 [0.030 to 10.96 m³/s]) was within the range of 95% of log-discharges in the whole-population (-1.87 to 1.06 [0.013 to 11.48 m³/s]). This indicated that the downstream site's sub-population discharges reflected the magnitude and range of the downstream site's whole-population discharges. Additionally, the maximum of the sub-population captured the high discharge events of the whole population.

7.2.2. Suspended Sediment Flux Population – Distribution Analysis

Next, the sub-population of suspended sediment flux (SSF) distributions were reviewed. The distribution of measured log-SSF values for both upstream and downstream sites (Figures 7.5 and 7.6) were right-skewed towards higher measured log-SSF values. The lowest log-SSF value for both sites was

-2.042 log-SFF (i.e., 0.009 Mg per day), but the downstream site's maximum log-SSF of 5.122 (i.e.,
132,449 Mg per day) was about 41 times greater than the upstream site's maximum log-SSF of 3.51 (i.e.,
3,239 Mg per day). Overall, the median discharges were similar at both sites, but the median SSF were higher at the downstream site than at the upstream site.

Goodness-of-fit tests (Shapiro-Wilk and Lilliefors tests) were applied to the whole-population discharge, the sub-population discharge, and the measured-SSF populations using the statistical program ProUCL version 5.1. The results demonstrated that none of the above upstream or downstream populations (discharge and SSF whole- and sub-populations) fit a normal distribution. The distribution of the variables used to create the rating curve does not need to be normally distributed for a regression to function properly. Statistical tests applied to the dataset in subsequent sections such as T-tests assumes a normal population distribution, however, the T-test could be valid even when the populations are not normally distributed because of the central limit theorem (i.e., with repeated sampling, the sample distributions converge to a normal distribution, regardless of the distribution of the initial sample population). If the sample size is sufficiently large, as in the case of the discharge dataset (n > 10,900) and SSF dataset (n > 230) datasets, then the T-test will be robust to non-normality and still valid even when the dataset does not follow a normal distribution.

7.2.3. Rationale for Establishing Regressions or Rating Curves

In the upstream reaches, there was evidence of down cutting of the WWC channel and lateral breakdown of its banks. Much of this eroded material could be transported down to the downstream site, which was only 5.1 kilometers (3.2 miles) from its confluence with the BFR. Thus, the downstream site best captured suspended sediment transport behavior out of WWC. This is also supported by the analyses in the previous sections, which demonstrated that the downstream location had a greater amount of high SSF values than the upstream location, thus better capturing how much sediment is being transported out of the catchment, the effect discharge had on SSF, and the rate of suspended sediment removal from WWC.

Additionally, as demonstrated in the previous section, in comparison to the upstream site's dataset, the distribution of the downstream site's sub-population discharge data was in closer alignment with the distribution of its whole-population discharge data. Since the downstream site's sub-population dataset was representative of its whole population dataset, a rating curve or regression can be established based on the relationship between sub-population discharges and their respective measured-SSF.

Applying a regression to the downstream site's sub-population data would produce a more suitable regression to model the relationship between discharge and suspended sediment carried out of WWC. Therefore, regression or rating-curves were applied to downstream datasets only to predict SSF removal rates. Unless stated otherwise, all discussions below pertain to data from the downstream site only.

7.3. Regression and Fit

To predict SSF for the whole-population discharges that do not have a paired measured SSF value, rating-curves were generated from the downstream site's sub-population discharge and measured-SSF data. Previous studies have shown that in the absence of actual continuous SSF data, discharge is a good predictor or proxy for SSF (Asselman, 2000; Horowitz, 2002; and Horowitz, 2008). Rating curves were developed to relate SSF (dependent variable) and discharge (independent variable) values. SSF and discharge data were log-transformed prior to analysis.

7.3.1. Regression Application and Selection

Linear and polynomial regressions were tested and the statistics from each regression's predicted SSF dataset are presented in Table 7.1. Applying a single linear fit to the downstream log-discharge vs. log-SSF data (Table 7.1 column A) could severely under-predict both low and high SSF values (Figure 7.7). As seen in the residual plot, at very low and very high measured actual-log-SSF's, the residuals cluster above the zero line (Figure 7.8). Amongst the other regressions tested, the top two performing regressions were the 2-linear and 4th order polynomial ratings curves (Table 7.1). Their predicted SSF means were relatively close to the actual SSF means, and the sum of the 239 predicted SSF values from these two ratings curves were the closest to the sum of the actual 239 SSF values with a percent

difference around 14% (linear) and 27% (4th order polynomial) (Table 7.1, columns C and H). The individual percent errors between actual and predicted SSF ranged between -175% and +175% (averaging 9.06%) for the 2 linear regressions, and percent errors ranged between -180% to +174% (averaging 0.23%) for the 4th order polynomial regression. These ranges were comparable to the percent errors for daily values (-76% to +205%) determined by Horowitz (2008). Based on these preliminary assessments and evaluations of the scatter of their residuals (discussed in subsequent sections), these two ratings curves were determined to provide the best fit to the sub-population dataset and which will result in the best predicted SSF values.

The first selected regression comprises of 2-linear rating-curves; one linear fit for \leq -0.925 logdischarge (m³/s) values, and one linear fit for > -0.925 log-discharge (m³/s) values (Figure 7.9). The second regression is a 4th-order polynomial rating curve (Figure 7.10) where all predicted log-SSF values fall in the middle portion of the polynomial curve because measured log-discharge values never fall outside of the -3.0 to 2.0 range (Figure 7.9 and 7.10). Both rating curves are most suitable for estimating SSF from log-discharges that fall between -3.0 to 2.0. As a general principle, rating curves should be applied to data that fall within the fitted range (i.e., interpolation). The analysis from the previous sections have demonstrated that the downstream site's sub-population discharges reflect the magnitude and range of the downstream site's whole-population discharges and captures the high discharge events of the whole population.

For the regression comprised of 2-linear rating curves (Figure 7.9), when log-discharges are less than or equal to -0.925, there is a weak positive relationship ($R^2=0.20$) between log-discharge and log-SSF, indicating log-SSF is not very responsive to changes at low log-discharge. When log-discharges are greater than -0.925, there is a stronger positive relationship ($R^2=0.85$), indicating the variation in log-SSF is a stronger function of the variation in log-discharge. At log-discharges larger than -0.925, SSF becomes more responsive to increases in discharge. The cutoff at -0.925 was chosen by inspection so that both linear fits meet and connect while providing the best fit to their dataset.

For the 4th-order polynomial rating curve (Figure 7.10), there is a strong positive curvilinear relationship (R^2 =0.88) between log-discharge and log-SSF. The curve closely overlies the two linear regressions and captures the scatter of the data, especially in the mid-log-discharges (-0.5 to 0.5), where the scatter is tighter about the curve. But the regression may not provide the best estimations of log-SSF at very low or very high log-discharges (< -1.0 or > 1.0). However, the curve is a closer fit visually to the shape of the scatter at the lower and higher ends compared to the fit of the 2-linear fit regressions.

7.3.2. Regression Fit Assessment

A caveat with using R^2 as a measure of the regression's goodness of fit is that this value is likely inflated due to discharge being the X-variable and also present in the calculation of the Y-variable (i.e., SSF is the product of discharge and suspended sediment concentration). Instead of solely relying on R^2 as a measure of goodness of fit, other methods were employed and discussed below.

Residual plots were produced to examine how well the rating curves fit the data. It is important that the residual variation is randomly scattered, does not display a trend, and in the most optimal cases, fit tightly about the zero-line. In cases where the rating curve is not optimal or not accounting for all the variables, the distribution of the residuals may deviate from normal. However, rating curves may still be the best model available, and it has been argued that the normality of the distribution of residuals may not be as important as the random scatter of the residuals (Wheeler 2013).

A measure of model fit is displayed in the residual plot for the 2-linear rating curves (combining both linear-fits) (Figure 7.11). At low log-discharges (< -0.9), the residuals cluster around the zero line but display greater variance, with several log-SSF residuals greater than 0.5. At mid-range log-discharges (-0.9 to 1.0), the log-SSF residuals cluster randomly about the zero line with many log-SSF residuals plotting below -0.5. While at very high log-discharges (> 1.0), the majority of log-SFF residuals are above 0.5, with one slightly below zero. This indicates that, in general, the model makes accurate predictions but can tend to underpredict SSFs at very low discharges, overpredict SSFs at low to mid-range discharges, and underpredict SSFs at very high discharges. Previous studies have encountered similar results where the rating-curve "underestimates high and overestimates lows" (Horowitz 2002), but

"the longer the period of interest, the greater the chance for over- and underestimates to balance each other out"(Horowitz 2002). Additionally, the residual distribution is unimodal, with a mean near zero (Figure 7.12), and the results from the Shapiro-Wilk and Lilliefors goodness-of-fit test tests (conducted in the ProUCL v5.1 statistical program) concluded the dataset fell under an approximately normal distribution. This indicates that although the linear fit does not account for all the variation in log-SSF, it is still a good model (Figure 7.9).

The 4th order polynomial regression log-SSF residual plot (Figure 7.13) is very similar to the 2linear regression residual plot (Figure 7.11). However, comparatively, the 4th order polynomial log-SFF residuals in the 0.5 to 1.5 range at log-discharges between -0.925 to 1.0 are slightly more abundant, and at very high discharges, the residuals plot slightly lower (Figure 7.13). The 4th order polynomial model equally under- and over predicts SSF at very low discharges (< -0.9), over predicts SSF at low to midrange discharges (-0.9 to 1.0), and underpredict SSFs at very high discharges (> 1.0) to a lesser degree than the 2-linear regression. The residual distribution is unimodal, with a mean near zero (Figure 7.14), and the dataset is normally distributed (results from Shapiro-Wilk and Lilliefors goodness-of-fit tests conducted in ProUCL v5.1 statistical program). This indicates that although the 4th order polynomial fit does not account for all the variation in log-SSF, it is still a good model (Figure 7.10).

7.3.3. Comparison of Measured and Predicted Suspended Sediment Flux

Figure 7.15 presents a comparison of actual SSF measurements (239 sampled days) and ratings curve-derived SSF predictions (239 predictions). The figure confirms that although the predicted SSF values of the 2-linear and 4th order polynomial ratings curves may fall short or over-shoot some of low and high discharges, in general, the predicted values align relatively well with the actual SSF fluctuations.

Horowitz (2008) argued that a good regression does not need to fit each individual data point but should average out the scatter in the data. "Estimation accuracy depends on the number of paired data points available to develop (calibrate) the rating curves, and how well they represent the ranges of discharge and SSF at the site" (Horowitz 2008). In the case of the sub-population dataset, there was a sufficient amount of paired data points (n=239), and they represented the range of the whole-population

discharges and SSF at the site. Corrections based on percent-error values were applied to the regression to further ensure accuracy and will be discussed in more detail in later sections.

7.4. Average Annual Suspended Sediment Flux Calculations

The whole-population mean-daily discharge data (collected from 1982 through 2012; n = 10,959) were input into the two rating curves (2-linear and 4th-order polynomial), which produced two different sets of predicted-SSF values. The sum of each set of predicted-SSF values produced two different estimates of the 30-year (10,959 days) total-SSF. Dividing each of the two predicted total-SSF by 30 years provided two estimates of the average annual rate of suspended sediment transport (Mg/year) out of WWC in the past 30 years (Table 7.2).

In order to refine the predicted 30-year total-SSF, an adjustment was applied based on the percent error between the sum of rating-curve derived 239 average daily SSF values and the sum of 239 actual field measured average daily SSF values (Table 7.1). This percent difference represents the amount of over- or under-prediction by the ratings curves and calculated using Equation 7.1.

% Error =
$$\left(\frac{\text{Predicted Sum SSF} - \text{Measured Sum SFF}}{\text{Average of Predicted and Measured Sum SSF}}\right) x 100$$

Equation 7.1.

As presented in Table 7.1, the sum of 239 measured daily SSF values was 210,096 Mg; the raw 2-linear ratings curve derived sum-SSF (239,906 Mg) over predicted the actual SSF by 14.19%, while the raw 4th order polynomial ratings curve derived sum-SSF (266,834 Mg) over-predicted the actual SSF by 27.01%. These percent errors were applied to Equation 7.2 and used as a calibration tool to determine the adjusted 30-year total-SSF estimate. Each raw (i.e., unadjusted) 30-year total-SSF estimate (linear and polynomial rating-curve derived from 10,959 measured-discharge values) was entered into the "Raw 30 Year Total SSF Estimate" variable in Equation 7.2.

Adjusted 30 Year Total SSF Estimate

 $= Raw 30 Year Total SSF - (Raw 30 Year Total SSF \times |\%Difference|)$

Equation 7.2.

The rounded estimate of the 30-year total-SSL (before a percent-difference adjustment) derived by 2 linear rating curves is 1,000,000 Mg, while the 4th-order polynomial rating curve generates a raw 30-year total-SSL estimate of 1,450,000 Mg (Tables 7.2 and 7.3). Adjustments of -14.19% and -27.01% were applied to the 2 linear rating curves and the 4th order polynomial derived 30-year total SSLs, respectively. The best estimate constraining where the actual 30-year total SSF lies falls between 861,000 Mg to 1,060,000 Mg (Table 7.2). Thus, on average, the annual SSF transported out of WWC over the last 30 years, factoring in years of extreme drought or flood years, likely falls between 28,000 to 35,000 Mg per year (Table 7.2).

The adjustments were applied to account for possible unrecognized biases in the model fits because neither model fit is exact. A few extreme observations not appropriately captured by the rating curve may be exerting a disproportionate influence on the final estimates, and the adjustment is an attempt to counterbalance these disproportionate influences. No precedent has been set for this type of adjustment approach, but other correction approaches have been used with mixed results (Duan 1983, Ferguson 1986, Horowitz 2008). Some such as the Ferguson (1986) method have been contested by authors replying to his work (Koch and Smillie 1986, Miller 1988), with the main weakness being this approach can inflate the estimated SSF. The Duan (1983) smearing correction approach has also seen mixed results. Horowitz (2008) found in some cases, the smearing correction can over predict the total flux. The author found that if the priority of the regression is the accuracy of the total-SSF prediction (and not the accuracy of the SSF fluctuation through time), then "an uncorrected linear regression provides the most accurate results" (Horowitz 2008). In view of the fact the smearing correction results have been variable and contested in the literature, it was decided that a simple correction based on percent errors could sufficiently provide a range of where the actual 30-year total SSF lies.

Horowitz (2008) found percent errors between actual and rating-curved derived total SSF values (based on different types of regressions) ranges from -33% to +20% when the SSF sampling frequency was once every 2 months. WWC sampling frequency was more sporadic and on average greater than every 2 months, with errors of 14% (2 linear regression) and 27% (4th order polynomial regression),

which is comparable to findings by Horowitz (2008). The effects of sampling error must also be considered when evaluating the differences between actual and predicted SSF calculations (Horowitz 2008). A replicate of the SSF data for a particular day may yield a slightly different value due to short-term spatial and temporal variability of the suspended sediment concentration. Horowitz (2008) found that errors associated with discharge measurements can range between 2 to 20% while errors in suspended sediment concentration measurements is on the order of \pm 10%. Hence, differences between actual and rating-curve derived SSF estimates between 15-20% are within the normal range of measurement and estimation error.

7.4.1. Estimated Thirty-Year Suspended Sediment Flux Patterns (1982 - 2012)

As displayed in Table 7.3 and Figure 7.16, the estimated annual total suspended sediment loads derived by 2-linear rating curves, and one 4th order polynomial rating curve were similarly aligned. The variability of estimated total annual suspended loads generally spanned across 3 orders of magnitude between 100 to 100,000 Mg per year, except for loads in 1995 and 2008 where both rating curves predicted the total annual loads to be greater than 100,000 Mg. The combined estimated annual totals in 1995 and 2008 comprised more than half (about 58%) of the total 30-year suspended sediment load (Table 7.3). The high SSF values in 1995 and 2008 corresponded with some of the highest discharges of the entire 30-year period. This is evidence that a few large flood events control a great proportion of suspended sediment transport out of WWC.

The maximum daily SSF value of each year plotted in Figure 7.16 depicts how suspended sediment transport in just a single day can, in many cases, dominate the total load of that entire year. It has been found that a large percentage of annual sediment loads are transported during a small number of floods over relatively short time periods. In a study of 27 small and medium streams in Illinois, the total sediment transport from the top four highest flow events can form 68% percent of the annual load (Markus and Demissie 2006). As a comparison, the estimated daily total sediment load from the top four highest discharges in 1995 (319,000 and 420,000 Mg; 2 linear and 4th order polynomial, respectively) made up 91% and 89% of the estimated total annual load (352,000 and 472,000 Mg, respectively). While

the suspended sediment load from the top four highest discharges in 2008 (202,000 and 291,000 Mg) made up 83% and 82% of the total annual load (242,000 and 353,000 Mg, respectively).

7.4.2. Historical Suspended Sediment Transport Analysis

The sub-population measured SSF's were split between 1983-1994 and 1996-2012 to examine changes in the suspended sediment transport behavior over time. Since a large flood event occurred in 1995, it was chosen as the dividing year and data from that year was not included in the analyses.

For the upstream site, the log-SSF versus log-discharge graph (Figure 7.17) and t-test statistical results (Table 7.4a) indicate that SSF values during the periods 1983-1994 and 1996-2012 were from two statistically different populations. The log-SFF t-statistic of 4.085 was greater than the two-tail t-critical value of 1.978, and the two-tail p-value of 7.56×10^{-5} was significant at the 95% confidence level. The log-discharge t-test results (Table 7.4a) indicated discharges were not statistically different between the two time-periods. The t-statistic of 1.367 was less than the two-tail t-critical value of 1.984, and the two-tail p-value of 0.175 was not significant at the 95% confidence level.

The slope of the best-fit log-SSF vs. log-discharge line was steeper for 1983-1994 dataset (Figure 7.17), indicating that during this time period, high discharges carried more suspended sediment than high discharges during the 1996-2012 time period. This suggests that between 1983-1994 there was a readily transportable bedload of tailings leftover in the upper WWC, which at least in part has since been flushed out along this reach.

For the downstream site, the log-SSF versus log-discharge graph (Figure 7.18) and their t-test statistical results table (Table 7.4b) indicated that SSF values were not statistically different between the 1983-1994 and 1996-2012 periods. The t-statistic of 0.686 was less than the two-tail t-critical value of 1.979, and the two-tail p-value of 0.494 was not significant at the 95% confidence level. The log-discharge t-test results (Table 7.4b) indicated that discharges were also not statistically significant different between the two time periods. The t-statistic of 0.457 was less than the two-tail t-critical value of 1.986, and the two-tail p-value of 0.649 was not significant at the 95% confidence level.

The downstream site did not exhibit the same patterns as the upstream site, possibly because the downstream reach of WWC was heavily affected by agricultural activities and irrigation practices. The abundance of tributaries and distributaries near the downstream site could also smear any sediment flux patterns between the past and recent time periods. Although the readily transportable bedload of tailings leftover in the upper reaches of WWC could be at least in part depleted, there could still be plenty of reworking of the sediments in the lower reaches of the WWC. As observed during site reconnaissance and sample collection, erosion features appeared to be more extensive in the lower reaches of WWC, downstream of the town of Whitewood (Chapter 5). This supports the use of a single rating curve on the entire 30-year downstream location dataset to generate estimated suspended sediment fluxes because the relationship between discharge and SSF appears to be stable and from the same statistical population.

7.5. Calculation of Suspended-Arsenic Transport Rate

There are additional uncertainties when calculating suspended-arsenic transport rate because although discharge was measured daily, far fewer surface water samples were collected and analyzed for both total and dissolved arsenic concentrations in conjunction with suspended-sediment concentrations during the period between 1982 to 2012 at the downstream site (sample count = 150). Discrete water samples collected by the USGS at the downstream site on WWC were analyzed for total and dissolved arsenic concentrations. Sample collection frequencies ranged from 1 to 10 or more times per year, with gaps in the data for several months or even several years (e.g., 1986-1989). Three methods were developed and tested to compare and evaluate the accuracy of the resultant suspended-arsenic transport rates.

Method #1 investigates if a reasonable estimate of the annual rate of arsenic transport during the 30-year period between 1982 and 2012 can be achieved by calculating the average of all available daily arsenic flux per year, multiplying each of these values by 365 as a rough estimate of the total annual arsenic load, and then taking the mean of all the annual arsenic loads. The weakness of this method is that the scarcity of arsenic data creates data gaps that raw-data-averaging cannot account for, such as periods without sampling (1986-1989) and arsenic concentrations during flooding events. One cannot rely on

arsenic concentrations measured a few times a year to fully capture the true range of transported arsenic load of that year. Method #2 attempts to fill in these data gaps by establishing a relationship between suspended arsenic concentration and discharge in the sub-population dataset and applying the regression to the 30-year dataset (the same method applied to estimate suspended sediment load in Section 7.4). Method #3 is a more novel approach to calculate arsenic transport rates because it makes use of percentarsenic distribution data within the suspended fraction of the water samples and proportionally applies it to the suspended sediment load estimations from Table 7.2. This method was developed to ameliorate the potential for error caused by data gaps and to provide a means for estimating a range of transport rates. This method also accounts for the fact that higher discharges may carry more arsenic-rich sediments and that arsenic concentrations could in part be dependent on SSF and discharge levels.

7.5.1. Method #1: Raw Data Averaging

Each dissolved arsenic concentration (compiled from USGS database from 1983 to 2012) was subtracted from its respective total arsenic concentration. The resulting set of suspended-arsenic concentrations were multiplied by its corresponding instantaneous discharge and converted to Mg per day, resulting in a set of suspended arsenic flux which acts as a substitute estimate for the daily suspended arsenic load. The average of all estimated daily arsenic loads in a single year multiplied by 365 days would then provide a rough estimate of the average annual arsenic load.

Calculated average annual suspended-arsenic loads from 1983-2012 ranged from 0.17 to 637 Mg per year, with an average calculated suspended-As flux of 52 Mg per year (Table 7.5). A large flooding event occurred in 1995, peaking between May 8th to 14th of that year; the instantaneous discharge (86 m³/s) recorded on May 9, 1995, was up to an order of magnitude larger than the upper limit of discharges of non-flood days in that year (0.11 to 12.31 m³/s). Only three samples were collected and analyzed for arsenic concentrations in 1995, and one was during the flood-event. The suspended-arsenic flux during the flood event on May 9, 1995 (23 Mg per day) was three to five orders of magnitude greater than the suspended-arsenic flux on May 24th (0.012 Mg per day) and August 30th (0.00059 Mg per day) of that year. Since there were only three samples collected in 1995, it would be more appropriate to calculate a

weighted average based on the number of flood days in 1995, so as not to skew the results, refer to Equation 7.3 below.

Arsenic Load for 1995

= (Daily Fux #1 measured during flood event x 7days)
+ (Daily Flux #2 measured during non flood days x 179 days)
+ (Daily Flux #3 measured during non flood days x 179 days)

Equation 7.3.

The weakness of this Method #1 is that is heavily dependent on timing and frequency of sampling and potential errors can be introduced when peak flow events are not captured as in the case of 2008. The peak high flow recorded on June 5, 2008 (72 m³/s) was comparable to the peak flow high flow on May 9, 1995 (86 m³/s), however, water samples were not analyzed for arsenic concentrations during the 2008 peak event. Thus, there is a potential for underestimation or overestimation of the annual suspended-arsenic loads, but given the dominance of high flow events, underestimation is more critical.

7.5.2. Method #2: Rating Curves

The same rating-curve approach used in Section 7.4 was applied to predict suspended arsenic concentrations in water for the whole-population discharge measurements (collected from 1982-2012) that did not have a paired suspended arsenic value (the difference between total and dissolved arsenic concentrations in the water). A rating curve was generated using the downstream site's subset of measured sub-population discharge data, which had paired suspended arsenic concentrations in the water. Previous studies have shown that in the absence of actual continuous metals concentration data, the rating curve approach was found to be suitable for estimating dissolved metals concentrations (Goolsby et al. 2001, Vanni et al. 2001, Stelzer and Likens 2006) Some studies, however, found weak correlations ($R^2 < 0.20$) between discharge and suspended metals concentration levels (Horowitz, 1995, Horowitz et al., 2001a). For the purpose of this study, it is postulated that since discharge controls suspended sediment concentrations, and so long as there is a relationship between suspended sediment concentrations and suspended arsenic concentrations in water, discharge is likely to influence suspended arsenic concentrations in water.

In the case of the WWC downstream location dataset, a second-order polynomial rating curve provided a good model ($R^2 = 0.68$) of the positive relationship between log suspended arsenic concentrations (dependent variable) and log discharge (independent variable) (Figure 7.19). This moderately strong positive relationship could be due to higher discharges being able to carry more arsenic-rich sediments which are generally denser than arsenic-poor sediments (due to arsenic residing in denser minerals such as arsenopyrite). If arsenic concentrations in the suspended fraction were of a similar range, then during high discharges the increased amount of suspended material would dilute suspended arsenic concentrations, and a weakly positive or negative relationship would be expected. However, at the WWC downstream location, high discharges picked up more arsenic-rich sediments, which produced the moderately strong positive relationship.

The curvilinear relationship ($R^2=0.68$) between log-discharge and log-suspended arsenic concentrations (Figure 7.19) captured the scatter of the data, especially in the mid-log-discharges where the scatter is tighter about the curve. However, the regression appeared to both underestimate and overestimate log-suspended arsenic concentrations at very high log-discharges, which could result in the balance out the over- and under- estimations. The goal of the rating curve in the context of this study is not to ensure the accuracy of predictions on an individual basis, but to ensure the curve is a suitable representation of the entire dataset so that it can be applied to the whole population dataset.

The predicted median concentration (0.030 mg/L) was similar to the measured median (0.034 mg/L), which is an error of -11%. However, the predicted average concentration (0.44 mg/L) was higher than the measured average (0.30 mg/L), which is an error of 38%. This indicates that the regression has overpredicted a few values, thus skewing the average to the higher values, but the regression is better at matching to measured values in the mid ranges. The percent errors between each measured and predicted pair ranged from -176% to 152%, with an average error of -0.3%. The range in the errors signal that there are other unknown factors besides discharge that control suspended arsenic concentrations. The low
average of the errors also implies that in sufficiently large datasets, the over-predictions are generally balanced out by the under-predictions.

A measure of model fit is displayed in the residual plot (Figure 7.20). At low to mid-range logdischarges (less than -1.0 to 0) the residuals scatter randomly, with the majority concentrated between -0.5 and +0.5. At higher log-discharges (great than 0 to 2.0), the spread of the residuals is greater but remain randomly scattered and relatively evenly distributed between over predictions (negative values) and under predictions (positive values). This indicates that, in general, the model makes accurate predictions but can under-predict and over-predict at very high discharges. Additionally, the residual distribution (Figure 7.21) is unimodal, with a mean near zero, and a normal distribution (results from Shapiro-Wilk and Lilliefors goodness-of-fit tests conducted in ProUCL v5.1 statistical program). This indicates that although the 2nd order polynomial fit does not account for all the variation in log-suspended arsenic concentrations, it is still a good model (Figure 7.19).

Figure 7.22 presents a comparison of actual suspended arsenic concentration measurements (153 sampled days), and rating-curve derived suspended arsenic concentration predictions (153 predictions). This graph further confirms that there is both over prediction and underprediction of low and high peaks, yet in general, the predicted values align relatively well with the actual suspended arsenic concentration fluctuations. Based on these preliminary assessments and evaluations of the scatter of their residuals, the second-order polynomial rating curve provides a good fit to the sub-population dataset and will provide a good estimation of the predicted suspended arsenic values.

The whole-population mean-daily discharge data (collected from 1982 through 2012) were input into the 2nd order polynomial regression. Since the log-discharges of the sub-population calibration dataset ranged only from -2.7 to 1.93 and the whole population log-discharges ranged from -5.5 to 1.92, log-discharges less than -2.7 (n=147) were removed prior to the application of the regression. Since the magnitude of these discharges is very small, their removal from the calculation is not anticipated to have a significant impact on the end result. The resultant 10,812 predicted mean-daily suspended arsenic concentrations (mg/L) was converted to mean-daily suspended arsenic loads (Mg/day) and their sum

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provided an estimate of the 30 year (10,959 days) total suspended arsenic load carried out of WWC between 1982 and 2012. Dividing this value by 30 years provides an estimate of the average annual rate of suspended arsenic transport out of WWC during those 30 years.

The estimate of the 30-year suspended arsenic load derived by the 2nd order polynomial rating curves is 980 Mg. Thus, on average, the annual suspended arsenic load transported out of WWC over the last 30 years, factoring in years of extreme drought or flood years, would be approximately 33 Mg per year.

7.5.3. Method #3: Using percent Arsenic Distribution

The distribution of 150 arsenic concentrations in the suspended sediment (data compiled from the Downstream Site on WWC) is plotted on Figure 7.23. The percentages were calculated by taking each suspended arsenic concentration in water (mg/L) and dividing by their respective suspended sediment concentration (mg/L). The distribution is strongly right-skewed, ranging from 0.0049% to 2.33% arsenic, with a median of 0.08% and a mean of 0.2% arsenic and a tail of more extreme values (Tables 7.6 and 7.7). The mean of 0.2% arsenic is within the range of percent arsenic in tailings reported by the South Dakota Department of Health in 1960 (0.12% arsenic) and by Noble in 1950 (0.35% arsenic) as summarized in the publication by Goddard (1989).

Estimation of average arsenic particulate concentrations in major world rivers range from 3.8 ppm (0.00038%) to 27 ppm (0.0027%) (data compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database). As depicted in Table 7.8, approximately 19% of suspended sediments contain between 0.0049 to 0.05 percent arsenic (averaging 0.03% arsenic); in comparison to the GERM database, this is interpreted to be the portion of uncontaminated to mildly contaminated alluvial sediments. Approximately 40% of suspended sediments contain between greater than 0.05 to 0.1 percent arsenic (averaging 0.07% arsenic); this is considered moderately contaminated sediments comprised of alluvial sediments mixed with some tailings. Approximately 28% of suspended sediments contain between > 0.1 to 0.35 percent arsenic (averaging 0.22% arsenic); this is predominantly the tailings portion (as summarized in the publication by Goddard (1989); see discussion in the previous paragraph about the

0.35 percent-arsenic cut-off). Approximately 13% of suspended sediments contain between > 0.35 to 2.33 percent arsenic (averaging 0.8% arsenic); this is considered the more concentrated, possibly arsenopyrite-enriched tailings portion. Arsenopyrite has been documented as one of the primary sources of arsenic in the literature and was observed in sediment samples collected for this study, refer to Chapter 1 and Chapter 5 for details.

Based on calculations in Section 7.4, the lower and upper bounds of the estimated total 30-year suspended sediment load (860,680 to 1,055,327 Mg; see 'Calculated Value' from Table 7.2) was multiplied by the proportion of suspended sediment load containing each average arsenic percentage, resulting in a range of suspended sediment loads containing their respective average arsenic percentages (Table 7.8, Column 5). To find the suspended arsenic load in each percent-arsenic range, this value was then multiplied by the average percent-arsenic within each range (Table 7.8, Column 6). The sum of all proportionally weighted suspended arsenic loads provides the 30-year suspended arsenic load (Table 7.8, Column 7).

Over 30 years, it is estimated that between 166,398 and 204,030 Mg of sediment contained arsenic levels ranging between 0.0049 to 0.05 percent (totaling 50 to 62 Mg of suspended arsenic); between 344,272 to 422,131 Mg of sediment contained arsenic levels ranging between >0.05 to 0.1 percent (totaling 30.78 to 37.08 Mg of suspended arsenic); between 240,990 to 295,492 Mg of sediment contained arsenic levels ranging between >0.1 to 0.35 percent (totaling 436 to 534 Mg of suspended arsenic); and between 109,019 to 133,675 Mg of sediment contained arsenic levels ranging between >0.35 to 2.33 percent (totaling 969 to 1188 Mg of suspended arsenic). In summation, between 1,700 to 2,100 Mg of suspended arsenic has been transported out of the WWC over a 30-year time span (i.e., averaging about 57 to 70 Mg of suspended arsenic per year) (Table 7.8).

7.5.4. Comparison of the Suspended-Arsenic Transport Calculation Methods #1, #2, and #3)

The 30-year suspended arsenic transport rate is presumed to fall within the range of the results from all three methods of calculation, which were all within the same order of magnitude, as summarized in Table 7.9. Method #1 provides a mid-range estimate of the annual average suspended arsenic load (52

Mg per year). This estimation is likely influenced by missing data that raw averaging cannot account for and may cause the mean to be skewed low. However, the lack of data points may also cause high flow events with greater suspended arsenic transport to skew the mean high, especially if more samples were collected during flood times than non-flood times. Method #2 provides the lowest estimate of the annual average suspended arsenic load (33 Mg per year). This could be due to the fit of the rating curve not adequately capturing the relationship between discharge and arsenic concentrations at high flows (Figure 7.19). Method #3 provides the highest range of estimations (57 to 70 Mg per year) but is still comparable to Method #1 and Method #2 estimates. This supports that the calculation procedures of Method #3 are within reason and a suitable alternative method to estimating historic arsenic transport rates.

The annual average suspended arsenic load is a representation of the estimated average annual transport rate over the 30-year period between 1982 to 2012. The actual transport rate each year differs greatly from this average depending on weather conditions and precipitation amounts during that year. Additionally, the estimated annual averages could change in future 30-year periods depending on local climate changes. However, this average is a good substitute when applied to longer timescales for estimating how long the WWC will be transporting arsenic-contaminated sediments.

7.6. Calculation of Dissolved-Arsenic and Total-Arsenic Transport Rate

The distribution of measured dissolved arsenic concentrations at the downstream site is slightly right-skewed towards higher measured concentrations (Figure 7.24). The range of concentrations is between 0.014 to 0.13 mg/L, with about 90% of the concentrations residing between 0.014 to 0.06 mg/L. The linear relationship between dissolved arsenic concentrations and discharge is a relatively weak ($R^2 = 0.33$) negative one; as discharge increases, dissolved arsenic concentrations tend to decrease (Figure 7.25). This effect could be largely due to dilution of arsenic concentrations during high discharges and indicates that higher discharges do not cause more arsenic to go into solution. In scenarios where seeps draining contaminated sediment make a major contribution to dissolved metals concentrations, we would expect to see increasing dissolved concentrations with increasing discharge. But this was not the case at WWC, which supports the fact that there is minimal groundwater contribution to arsenic in the WWC.

Since the relationship between dissolved arsenic concentration and discharge is relatively weak (Figure 7.25), the regression method implemented in Method #2 would not provide a rating curve that could adequately capture the relationship between discharge and dissolved arsenic concentrations and would not necessarily provide a better estimate than raw data averaging. Additionally, since the estimated suspended arsenic transport rate was comparable between the three methods as discussed in Section 7.5, then there is more confidence in the accuracy of applying Method #1's raw data averaging to estimate the dissolved arsenic transport rate directly from the incomplete USGS dataset. Additionally, dissolved arsenic only accounts for a very small fraction of the total arsenic load transported out of WWC (Table 7.5), thus small errors in its estimation would not greatly affect the estimation of the total arsenic transport rate.

Each dissolved arsenic concentration was multiplied by its corresponding instantaneous discharge and converted to Mg per day, resulting in a set of dissolved arsenic loads that act as substitute estimates for the daily dissolved arsenic load. The average of all estimated daily dissolved arsenic loads in a single year multiplied by 365 days provides a rough estimate of the dissolved average annual arsenic load (Table 7.5).

Average annual dissolved arsenic loads in the 30-year period (1983-2012) ranged from 0.33 to 3.89 Mg, with an average dissolved-arsenic load of 1.24 Mg per year (Table 7.10). Compared to the average suspended-arsenic estimations (33-70 Mg per year; Table 7.9), dissolved arsenic was not a major contributor to total arsenic transport. However, it appears that in low-flow years dissolved arsenic can dominate the total-arsenic load, while in high flow years suspended-arsenic dominates the total-arsenic load, while in high flow years suspended-arsenic flux in WWC is carried in the suspended load, especially during high flow or flood events.

The estimated average annual total arsenic load range between 34 to 71 Mg per year (Table 7.10). Using these estimates, the total load over the 30-year period between 1983 to 2012 was estimated to range between 1,020 to 2,130 Mg.

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7.7. Estimation of Timeframe for Complete Arsenic Removal from Whitewood Creek

As discussed in Chapter 2, it was estimated that 14.5 million Mg of arsenic contaminated sediments remain in storage along the alluvial floodplain of WWC during the early 1990's (Marron 1992). Applying the range of percent arsenic in tailings (0.12% to 0.35%), as discussed in Section 7.5.3, to 14.5 million Mg results in an estimated range of amount of arsenic stored in contaminated sediment along WWC in 1990 (17,400 to 50,800 Mg). Applying the estimated range of annual total arsenic transport rate out of WWC (Table 7.10), the estimated total timespan for arsenic removal from WWC would range between 250 to 1,500 years. These calculations are summarized in Table 7.11.

CHAPTER 8. DISCUSSIONS AND SUMMARY

During Homestake Mine's first 100 years of operation (1877 to 1977), over 100 million tons of tailings were discharged into WWC. Since the commencement of mining activities, up to 4 meters of tailings were deposited in some areas along WWC's floodplain. The tailings contained an abundant amount of arsenopyrite and other arsenic-bearing minerals (containing between 0.12% to 0.35% arsenic) (South Dakota Department of Health, 1960; Noble, 1950) and introduced arsenic-bearing sediment to the river system. Much of these tailings were carried further downstream and deposited in the floodplains of the BFR. However, during the early 1990's, it was estimated that 14.5 million Mg of contaminated sediments remain in storage along the alluvial floodplain of WWC (Marron, 1992). The results from sediments collected during this study along the alluvial floodplains of WWC confirmed some of the historical findings. The sequential extraction experiments and historical data analyses provided further insights into the current state of arsenic mobility and offer predictions about the future of arsenic transport in the WWC watershed.

8.1 Geometry, Quantity, and Concentration of Arsenic Contaminated Storage in Floodplains

At the upgradient Location G, arsenic-contaminated sediments (519 to 1,881 mg/kg) were observed in the upper 0.6 meters of the 4 meters thick exposed cut bank, while pre-mining alluvial sediments (9 to 20 mg/kg arsenic) occupied the next 2.4 meters and the shale bedrock (6 mg/kg arsenic) underlaid the bottom 1 meter of the strata. At downgradient Location H, arsenic-contaminated sediments (831 to 2,758 mg/kg) were observed throughout the 3.5 meters of the 4.5 meters thick exposed cut bank with the shale bedrock (6 mg/kg arsenic) occupying the bottom 1 meter of the total thickness. Contaminated sediments were dark, fine-grained, and concentrated as a relatively thin layer at the top of the cut bank at the upgradient Location G. However, at the downgradient Location H, the sediments appear to have been reworked, leaving only contaminated sediments present while no pre-mining alluvial strata was exposed. The sediments are also relatively lighter in color, coarser-grained, and more heterogenous than that of Location G. This suggests rapid erosion and re-deposition of an estimated 3.5

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meters of sediment since 1877 at Location H. On the BFR at Location K, samples were not collected from the 5.4 meters tall cut bank, which included exposed shale bedrock. The tall cut bank is an indication that high amounts of deposition and incision have occurred in the area, including incision into the shale bedrock.

On the point bars of WWC, between 0.76 to 1.83 meters of arsenic-contaminated sediments (123 to 4,061 mg/kg) were observed, extending at least 60 meters into the floodplain at Location G, and between 0.86-1.37 meters of arsenic-contaminated sediments (173 to 3,890 mg/kg) were observed extending at least 35 meters into the floodplain at Location H. On the point bars of the BFR at Location K (located approximately 60 to 70 river kilometers downstream of its confluence with WWC), up to 1.22 meters thick of arsenic-contaminated sediments (331 to 2,246 mg/kg) extended at least 46 meters into the floodplain. Sediments on the point bars of Locations G and H were generally highly contaminated throughout the entirety of each depth profile with relatively consistent concentrations with increasing distance from the WWC. At Location K, sediments near the bank of the BFR and near the ground surface are less contaminated than sediments farther from the bank and at deeper depths in the profile. Arsenic is lower near the surface and at locations close to bank of the BFR, indicating post-mining deposition events introduced uncontaminated alluvium that diluted arsenic concentrations.

Arsenic and iron concentrations in the sediments appeared to be correlated at all locations (Figure 5.20). Sediments with low iron concentrations (less than the GERM average of 50,000 mg/kg) were generally sediments with low arsenic contamination (less than 200 mg/kg). These low arsenic and low iron sediments were found at Location G in the lower cut bank samples; at Location H in the shale sample and in the sub-surface sample (1.17 to 1.37 meters deep) 35 meters from WWC; and at Location K in all samples 46 meters from the bank of the BFR. At Locations G and H, sediments with greater than 200 mg/kg arsenic generally contained iron levels greater than 50,000 mg/kg, while sediments with greater than 2,000 mg/kg arsenic generally contained iron levels greater than 80,000 mg/kg. Both metals were present in the sediments at high concentrations, as expected in the study area which has high amounts of iron-bearing sulfide minerals like arsenopyrite.

In summary, there is not a single tailings horizon, instead the thickness, geometry and lateral extent of contaminated sediment varies between all locations. The size, sinuosity, and gradient of the river produce different capacities for transport, storage, and deposition of contaminated sediments. There is significant spatial variability of the distribution of contaminated sediments in the WWC, which has implications for any modeling of future flood plain erosion. These data support the large extent of highly contaminated sediments still in storage and available for transport along both river systems. Unstable and slumping exposed cut-banks that have collapsed, introducing large masses of likely contaminated sediment into the river channel were observed in several areas along WWC and the BFR.

8.2 Residence Sites of Arsenic and Factors Controlling Arsenic Mobility and Retention

Based on sequential extraction experiments performed on Locations G, H, and K sediments, it can be concluded that on average about 40% of the arsenic is labile while 60% remains relatively immobile. Of the labile arsenic, an average of 0.37% is weakly bound to readily exchangeable surface sites and water-soluble secondary minerals and available for rapid release (results of DI water extraction (E1)); an average of 11% is weakly bound to organics or is adsorbed to exchange sites which easily exchanges PO43- ions for adsorbed arsenic oxyanions and also available for quick release (results of 1M sodium phosphate monobasic extraction (E2)); an average of 4.8% is weakly bound in amorphous to weakly crystalline fine-grained metal oxides/hydroxides, reducible phases, other surface site, or easily soluble carbonates and available for slower release (results of 0.2M hydroxylamine HCl extraction (E3)); and an average of 24% is moderately strongly bound in weakly soluble secondary minerals like clays or crystalline fine-grained metal oxides/hydroxides and will be released even more slowly (results of 1 M hydrochloric acid extraction (E4)) (Table 6.2a). Therefore, of the labile arsenic, only up to about 16% (E1, E2, and E3) is available for relatively rapid release when in contact with water, and the other 24% is more strongly bound and will be mobilized very slowly over time. The 60% of immobile arsenic (interpreted to be in arsenopyrite) is likely locked in the arsenopyrite due to formation of metal oxyhydroxide coating which slows down the degradation of the mineral (Larios, et al., 2012; Matera et al., 2003). Although, arsenopyrite grains were not readily visible in the sediment.

The results of the sequential extractions suggest arsenic is predominantly located in residence sites that are not easily accessible, and arsenic is not readily mobilized or released into solution in large quantities under normal environmental conditions seen in WWC and the BFR. These interpretations are supported by the elevated but still relatively low total arsenic concentrations (EPA MCL for arsenic is 0.01 mg/L) of in-stream water in WWC (Locations B to H) ranging between 0.008 to 0.087 mg/L (averaging 0.037 mg/L) and in the BFR (Locations I to K) ranging between 0.012 to 0.033 mg/L (averaging 0.021 mg/L) (Table 4.2a), considering that in-stream sediments carried by WWC and the BFR have high arsenic concentrations (264 to 694 mg/kg) (Table 5.7).

The following correlation between sediments with relatively low arsenic concentrations (39 to 48 mg/kg) above background levels (1.5 to 27 mg/kg; Appendix 5-5) and increased arsenic mobility was observed at two point bar samples collected from Location K. These samples were collected below more strongly contaminated sediment (476 mg/kg) and contained the greatest proportion of arsenic residing in mobile fractions compared to all other samples (Figure 6.1). This could be due to leaching, downward migration and reprecipitation from the strongly contaminated layer above and suggests that a minor amount of secondary mobilization of arsenic can produce a higher proportion of arsenic that is present in less stable forms and can be more readily mobilized.

Interestingly, the concentration of arsenic residing on weakly bound surface sites (E1) did not change with increasing sediment arsenic concentrations and indicates the capacity of this residence site is similar in sediments across all locations (Figure 6.3a). For the other extractable sites (E2, E3, and E4), a positive correlation between sediment arsenic concentration and extracted arsenic concentration was present, suggesting the amount of these other residence sites increased as the degree of contamination increased.

Arsenic's susceptibility to mobilization did not clearly correlate to any physical attributes of the sediment (i.e., grain size, color, etc.) nor to depth or distance from the bank. Arsenic mobility and its relationship with geochemical makeup of the sediments is complex, requiring a larger dataset to fully gain insight. The rate of arsenic dissolution may be highly varied locally and across the study area.

8.3 Relationship Between Extracted Arsenic, Extracted Iron, and Other Extracted AOIs

Iron and aluminum hydroxides have been known to have the highest affinity for arsenate and are commonly the main host phases for arsenate in sediments (Gorny et al., 2015; Huang, et al., 2010; Larios, et al., 2012; Lombi, et al., 2000; Muller, et al., 2007). However, the results of the sequential extractions did not demonstrate a strong association between the dissolution of iron-bearing minerals and the release of arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), or from secondary minerals (E4) as demonstrated by the low to weak linear correlations between extracted arsenic released in these extracted iron concentrations (Figure 6.4c). Possible interpretations include: 1) the arsenic released in these extracted by the reductive dissolution of iron-bearing minerals, and arsenic release is not greatly affected by the reductive dissolution of iron-bearing minerals; 2) the limited amount of iron extracted in E3 suggest that the amount of amorphous to poorly crystalline iron oxyhydroxides in the sediments could be low or that more crystalline iron oxyhydroxides could be more prevalent; 3) the molal concentration of the hydroxylamine HCl was not strong enough to be effective, especially when its application comes after the sodium phosphate extraction. Presumably, the source of the arsenic in E4 is, in part, bound within these crystalline iron oxyhydroxides and secondary aluminum minerals such as clays.

As discussed in Appendix 6-1, changing the extraction sequence between 1M sodium phosphate monobasic and 0.2M hydroxylamine HCl affected the results of which weakly bound sites arsenic was mobilized from but did not greatly affect the total amount of arsenic extracted by these two extractants (Appendix 6-1). In other words, the sum of E2 and E3 extracted arsenic (estimated proportion of relatively weakly bound arsenic) was not greatly altered by the sequence of the extractions and did not alter the main conclusions of this study. Arsenic reprecipitation during sequential extractions is well documented (Bermond et al., 1993; Rodriguez et al., 2003; Wenzel et al., 2001; Hudson-Edwards et al., 2004; Van Herreweghe et al., 2003; Muller et al., 2007). It is likely that when sodium phosphate was applied first, arsenic was competitively exchanged from the surface by phosphate ions, including arsenic residing on surfaces of iron oxyhydroxides. However, a portion of the recently mobilized arsenic did not remain in solution and quickly re-precipitated or re-adsorbed onto freshly exposed mineral surfaces. The application of hydroxylamine HCl following sodium phosphate removed the surface-bound arsenic that was not fully removed by sodium phosphate. In other words, when hydroxylamine HCl is applied after sodium phosphate, the source of arsenic extracted by hydroxylamine HCl can be interpreted to be from the dissolution of amorphous iron oxyhydroxides containing arsenic and also from weakly bound arsenic released from all other surface sites. Additionally, although hydroxylamine HCl is known for its effectiveness in dissolving cryptocrystalline iron oxyhydroxides (Leinz et al., 2000; Huang et al., 2010; Lombi et al., 2000; Bermond et al., 1993; Rodriguez et al., 2003), only a small portion of the iron is available for dissolution because phosphate ions (from E2) coating mineral surfaces may be inhibiting their reductive dissolution (Borch et al., 2007). All scenarios discussed above may explain why hydroxylamine HCl extracted-iron decreased up to two-orders of magnitude while hydroxylamine HCl was applied after sodium phosphate (Appendix 6-1).

Arsenic residing on surface sites (E1), exchange sites (E2), reducible sites (E3), and fine-grained clay minerals (E4) also do not appear to be strongly correlated with the release of aluminum-, calcium-, manganese-, or sulfur-bearing minerals as demonstrated by their weak linear correlations (Figure 6.4). In the E1 extraction, similar amounts of readily available surface-bound arsenic were released over a wide range of released aluminum, calcium, iron, manganese, and sulfur concentrations. Thus, surface bound arsenic is likely not associated with or controlled by easily soluble minerals of these above-mentioned elements.

Mobile arsenic is not clearly associated with one mineral but is tied to a mixture of insoluble and weakly soluble minerals such as oxides, hydroxides, and fine-grained clays. Evidence suggests that arsenic could be recycled in-situ (released from more strongly bound sites but then retained on less strongly bound surface or exchange sites). The majority of the arsenic is not strongly associated with easily soluble minerals or leachable sites and thus is not easily transported further downstream in solution.

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8.4 Arsenic Transport on the Watershed Level and its Historical Patterns

The historical (1983 to 2012) median dissolved arsenic concentration measured from the downstream site on WWC was 0.03 mg/L (Figure 7.24) and supports sequential extraction findings that arsenic did not easily mobilize into solution from the sediments. Dissolved arsenic concentrations and the ratio between dissolved to total arsenic load decreased with increasing discharge (Figures 7.25 and 7.26), while suspended arsenic became the dominant proportion of the arsenic transported during high discharges (Figures 4.6 and 4.7). This effect is largely attributed to the dilution of dissolved arsenic concentrations during high discharges and indicates that higher discharges do not cause more arsenic to go into solution. In scenarios where seeps and tributaries are large contributors to dissolved metals concentrations, one would expect to see increasing dissolved concentrations with increasing discharge, but this was not the case at WWC. Although dissolved arsenic can dominate the total-arsenic load in low-flow years, the totalarsenic load in these years is only a fraction compared to high flow years where a much higher suspended-arsenic load dominated the total-arsenic load (Tables 7.5 and 7.10). Averaged over high and low-flow years, the majority of arsenic transport in WWC has been carried in the suspended load and occurs predominantly during the occasional high flow or flood event. Based on the calculations from this study, over the period of 30 years (1982-2012), annual suspended arsenic load is estimated to range between 33 to 70 Mg per year while annual dissolved arsenic load is estimated to be 1.2 Mg per year, resulting in a total arsenic annual load to be approximately between 34 to 71 Mg per year.

8.5 Estimation of Arsenic Removal from WWC Watershed

As presented in Chapter 7 based on regressions applied to 30 years of historical data (1982-2012) and also based on concentrations of arsenic in the suspended- and in the dissolved-load over the same time period, the average annual total arsenic load transported out of WWC during these 30 years were estimated to be between 34 to 71 Mg per year (Table 7.10). Applying this estimated range of total arsenic transport rate to the approximately 17,400 to 50,800 Mg of arsenic that remain in storage along the floodplains of during the early 1990's (Table 7.11) resulted in an estimated total timespan for arsenic removal from WWC ranging between 250 to 1,500 years.

The actual rate of arsenic removal is expected to be longer than the above estimates because the model is based on a uniform movement of uniformly distributed sediment, however, the real-world scenario is more complicated. Actual arsenic removal time could vary, as evidenced by the decline in suspended arsenic transport rate at the downstream site starting in the early- to mid-1980's which then flattened after 1990 to 2012 (Figure 7.22). Although this decline is reflected in calculations of the estimated annual rate of total arsenic transport by WWC, historical patterns may not be reflective of future trends, especially given the complications of climate change. The constant shifting of the stream creates abandoned meanders along WWC that can store contaminated sediment where the stream no longer has access. Conversely, as the meanders shift over time, the once abandoned meanders could be again accessed by WWC. As discussed, the majority of suspended sediment transport occurs during flood events. Based on the annual average total arsenic load data from Table 7.5, approximately 88% of the total arsenic load moved between the years of 1983 to 2012 occurred in only 3 of the years (1983, 1984, and 1995). Thus, the rate of arsenic transport for the next 30-year period is uncertain and could be lower if the number of flood events remains low. Additionally, arsenopyrite dissolution rates may decrease with time due to weakly soluble secondary mineral formation such as scorodite on grain surfaces.

Although the WWC area once experienced heavy environmental degradation during the period of active mining, its current overall environmental condition has been relatively stable. Acid generation is still minimal owing to the slow rate of sulfide mineral oxidation and the high buffering capacity of carbonate minerals (Cherry et al., 1986) resulting in WWC surface water pH to range from 8.3 to 8.7 and WWC seep water to maintain near neutral pH between 6.9 to 7.6 (which is within the pH range of 6 to 8 as reported by Fuller et al., 1987). However, the slow release of arsenic from contaminated sediments to the environment endures and the continual transport of arsenic-contaminated suspended sediment downstream to the BFR and beyond will continue for many generations.

CHAPTER 9. CONCLUSIONS AND RECOMMENDATIONS

Based on the study objectives listed in Chapter 1.3, the main conclusions from the study are summarized as follows:

- 1. What are the current environmental conditions along WWC and the BFR? Has there been significant natural remediation to surface water and sediments?
 - Total arsenic concentrations of in-stream water collected from WWC and the BFR during the summer of 2010 ranged between 0.008 to 0.09 mg/L, which are generally still above the EPA MCL of 0.01 mg/L. Arsenic concentrations found in floodplain sediments collected along WWC and the BFR during this study (6 to 4,000 mg/kg) are still much greater than the range found in background crustal and river particulates (1.5 to 27 mg/kg). As expected, since arsenic dissolution and physical transport rates are slow, there has been little change in arsenic concentrations, and arsenic contamination of water and sediments continues to dominate the region. However, the overall environmental quality of the area has improved due to implementation of environmental regulations and institutional controls, allowing for the return of aquatic life and recreational use of WWC.
- 2. What controls dissolved arsenic concentrations in the stream water of WWC?
 - Dissolved arsenic concentrations in WWC decreases with increasing discharge, which indicates
 that higher discharges do not cause more arsenic to go into solution. The slow and minimal
 dissolution of arsenic into the environment is largely due to the relatively low amounts of
 breakdown products which hosts less stable arsenic and the dominance of arsenopyrite where the
 majority of arsenic is hosted in a relatively stable state.
- 3. How is arsenic partitioned within the sediments and how does its residence sites affect its mobility and release into the environment?
 - About 40% of the arsenic is labile, while 60% remains relatively immobile. Of the labile arsenic, on average, 0.37% is weakly bound to readily exchangeable surface sites and water-soluble

secondary minerals and available for rapid release; 11% is weakly bound to organics or is adsorbed to exchange sites which easily exchanges PO₄³⁻ ions for adsorbed arsenic oxyanions and also available for quick release; 4.8% is weakly bound in amorphous to weakly crystalline finegrained metal oxides/hydroxides, reducible phases, other surface site, or easily soluble carbonates and available for slower release; and 24% is moderately strongly bound in weakly soluble secondary minerals like clays or crystalline fine-grained metal oxides/hydroxides and will be released even more slowly. The 60% of immobile arsenic (interpreted to be in arsenopyrite) is likely locked in the arsenopyrite due to formation of metal oxyhydroxide coating which slows down the degradation of the mineral.

- 4. How are arsenic-contaminated sediments in the floodplains distributed and are there any relationships between arsenic mobility to its physical placement in the sediments?
 - There is not a single tailings horizon, instead the thickness, geometry and lateral extent of contaminated sediment varies between all locations. Arsenic's susceptibility to mobilization did not clearly correlate to any physical attributes of the sediment (like grain size) nor to depth or distance from the bank. However, a larger dataset may be required to gain insight into any possible correlations.
- 5. What is the estimated transport rate for arsenic out of WWC and how long will arsenic remain in the WWC system?
 - The total arsenic transport rate over the period of 30 years (between 1982 to 2012) is estimated to be between 34 to 71 Mg per year. At this uniform rate of removal, the total timespan for arsenic removal from the WWC system would take approximately 250 to 1,500 years. The actual rate of arsenic removal is expected to be longer because the prediction is based on a uniform movement of uniformly distributed sediment, however, the real-world scenario is more complex.
- 6. Are there any environmental changes that may impact arsenic's mobility and transport in the area?
 - Large physical disturbances and movement of sediments may alter the relative stability of arsenic in the sediments. If any changes to the pH or redox conditions within the sediments occur, like

exposing buried sediments to the surface or saturating sediments under the water table, then increased dissolution of arsenic out of the sediments could occur.

- 7. What will be the fate of arsenic in contaminated sediments over the next few hundred years?
 - Arsenic concentrations in the surface sediment of point bars may decrease with time due to dilution by clean alluvium. If regional climatic conditions remain relatively stable, then arsenic will remain strongly chemically bound within the sediments and surface water quality should continue to be stable. However, bank instability and failures will continue to introduce and spread contaminated sediments to areas downstream of WWC and the BFR.

Recommendations for additional research and continual management of the area include the following:

- The potential for chemical remobilization of arsenic on a regional level and on longer time scales will need to be better understood. If changes to the future climatic conditions of the study area occur, could they impact the geochemical conditions (e.g., pH and redox) of the sediments and thus the mobility of arsenic?
- There is significant spatial variability of the distribution of contaminated sediments in the WWC. Modeling of future flood plain erosion and changes to the meanders of the WWC and the BFR could be better understood to predict future physical movement of contaminated sediments.
- To minimize further input and transport of contamination downstream, areas of high erosion can be identified and monitored, while structures can be developed to stabilize the banks.
- Surface water, groundwater quality, and aquatic habitat monitoring, as well as periodic assessment of anthropogenic impacts and alterations to the region should continue to be implemented.

TABLES

Chapter 4. - Tables

				Dissolve	d Oxvgen	Specific Co	nductance	Water		
Locat	tion	pl	4	(m	g/L)	(μS/	cm)	Temperat	ure (°C)	
		Stream	Seep	Stream	Seep	Stream	Seep	Stream	Seep	
A		8.5		6.3		568		17.9		
	В	8.7	7	5.5	0.2	514	8,010	18.4	13.8	
	С	8.7		6.1		1,145		18.4		
U	D	8.5		5.7		1,288		17.2		
C D M M F G	Е	8.6		5.14		1,171		17.5		
5	F	8.3		5.33		1,276		17.5		
	G	8.4	7.6	5.96	1.84	1,270	1,373	18.6	14.5	
	н	8.3	6.9	5.33	3.38	1,459	3,580	26.8	27.6	
	Ι	8.1		4.56		1,472		27.7		
Ř	J	8.2		4.83		1,535		27		
B	К	8.2		5.73		1,574		28		
	L	8.2		5.34		1,465		24.1		

Table 4.1. Field parameters collected from in-stream and seep samples in WWC and the BFR.

Locat	tion	Sample Type	As	AI	Са	Cd	Fe	Mn	S
Α		In Stream	0.025	0.445	83	0.017	0.961	0.133	40
	Р	In Stream	0.008	0.197	64	0.025	0.535	0.107	27
	В	Seep	0.013	0.012	506	0.010	15.5	15.4	1662
	С	In Stream	0.012	0.101	101	0.005	1.175	0.143	158
	D	In Stream	0.016	0.067	106	0.025	0.655	0.062	168
Ň	Ε	In Stream	0.028	0.065	104	0.033	0.340	0.014	155
ž	F	In Stream	0.061	0.015	150	0.010	0.112	0.028	169
	G	In Stream *	0.087	0.167	152	0.034	0.458	0.052	170
	G	Seep	0.395	0.009	191	0.017	1.576	1.024	201
	ы	In Stream	0.047	0.138	177	0.027	0.628	0.131	224
	п	Seep *	0.080	0.176	513	0.045	3.389	9.316	713
	Ι	In Stream	0.018	0.248	226	0.010	1.108	0.175	218
¥	J	In Stream	0.012	0.241	214	0.016	0.658	0.080	233
B	К	In Stream *	0.033	0.511	202	0.036	0.971	0.070	272
	L	In Stream	0.004	0.347	223	0.035	1.069	0.158	211
In	WWC (Loc. B-H) In-Stream Average:		0.037	0.107	122	0.023	0.558	0.077	153
In	BFR (Loc. I-K) In-Stream Average:			0.333	214	0.021	0.912	0.108	241

Table 4.2a. Total analyte concentrations (mg/L) of in-stream and seep water samples collected from WWC and the BFR. A star * denotes that ICP-OES results are reported for that sample (i.e., not enough sample was left to be analyzed by ICP-MS). All other results are by ICP-MS.

Locat	tion	Sample Type	As	AI	Ca	Cd	Fe	Mn	s
Α		In Stream	0.013	0.006	79	0.016	0.016	0.018	38
	D	In Stream	0.005	0.031	64	0.023	0.042	0.095	27
	D	Seep							
	С	In Stream	0.008	0.021	99	0.011	0.053	0.057	148
	D	In Stream	0.014	0.034	108	0.015	0.135	0.097	170
۸C	Ε	In Stream	0.024	0.011	104	0.018	0.028	0.006	155
ž	F	In Stream	0.055	0.010	151	0.020	0.074	0.026	169
	G	In Stream *	0.018	0.065	150	0.024	0.144	0.039	167
	G	Seep	0.451	0.006	191	0.012	1.45	0.872	201
	ы	In Stream	0.063	0.010	183	0.011	0.684	0.236	238
	п	Seep *	1.650	0.210	526	0.070	46.4	9.565	745
	I	In Stream	0.047	0.101	224	0.018	1.66	0.296	233
Ř	J	In Stream	0.009	0.002	210	0.023	0.014	0.021	232
B	К	In Stream *	0.010	0.017	185	0.017	0.012	0.012	262
	L	In Stream	0.009	0.019	217	0.024	0.143	0.044	207
	WWC (Loc. B-H)		0.027	0.026	122	0.017	0 166	0.070	152
In	In-Stream Average:		0.027	0.026	123	0.017	0.100	0.079	123
In	BFR (Loc. I-K) In-Stream Average:			0.040	207	0.020	0.562	0.110	242

Table 4.2b. Dissolved analyte concentrations (mg/L) of in-stream and seep water samples collected from WWC and the BFR. A star * denotes that ICP-OES results are reported for that sample (i.e., not enough sample was left to be analyzed by ICP-MS). All other results are by ICP-MS.

Table 4.3. USGS historical average annual arsenic concentrations and discharge collected from all USGS gauging locations along WWC between 1983-2012 (n = 346). Only samples with paired discharge and arsenic concentrations were compiled to compute annual averages. The proportion (in percent) of analytes in the dissolved or suspended phase were derived from taking dissolved or suspended concentrations and dividing by the total concentration. Annual averages reflect the average of percentages over the number of samples of collected per one year period and captures the effects of samples collected during flooding (ex: 1995).

Year	Number of Samples	Avg Discharge (ft ³ /s)	Avg Total Arsenic (mg/L)	Avg Suspended Arsenic (mg/L)	Avg Dissolved Arsenic (mg/L)	Avg Suspended Arsenic Percentage	Avg Dissolved Arsenic Percentage
1983	60	87.4	0.492	0.464	0.028	94%	6%
1984	42	107.5	0.627	0.598	0.029	95%	5%
1985	16	12.0	0.072	0.025	0.047	35%	65%
1990	17	19.4	0.060	0.022	0.037	37%	63%
1991	21	22.7	0.051	0.022	0.029	43%	57%
1992	21	15.4	0.060	0.028	0.032	46%	54%
1993	20	45.5	0.078	0.054	0.024	69%	31%
1994	18	45.6	0.076	0.052	0.024	69%	31%
1995	5	650.4	0.660	0.634	0.026	96%	4%
1996	12	53.9	0.062	0.042	0.021	67%	33%
1997	8	84.2	0.077	0.056	0.021	73%	27%
1998	8	35.0	0.037	0.013	0.024	35%	65%
1999	8	47.5	0.088	0.065	0.023	74%	26%
2000	6	83.6	0.117	0.090	0.027	77%	23%
2001	10	23.1	0.040	0.016	0.024	39%	61%
2002	7	12.4	0.052	0.018	0.034	34%	66%
2003	8	23.3	0.049	0.017	0.032	35%	65%
2004	8	11.7	0.075	0.032	0.043	43%	57%
2005	7	40.8	0.095	0.070	0.024	74%	26%
2006	8	53.7	0.120	0.090	0.030	75%	25%
2007	6	64.0	0.055	0.028	0.028	50%	50%
2008	6	59.5	0.035	0.014	0.021	41%	59%
2009	8	53.1	0.038	0.017	0.020	46%	54%
2010	8	54.2	0.059	0.035	0.024	59%	41%
2011	6	60.0	0.042	0.021	0.021	49%	51%
2012	2	30.0	0.034	0.012	0.022	35%	65%
26-Y	ear Average:	69.1	0.125	0.098	0.028	57%	43%
	Min:	11.7	0.034	0.012	0.020	34%	4%
	Max:	650.4	0.660	0.634	0.047	96%	66%

Chapter 5. - Tables

Table 5.1. Summary of sample collection and samples selected for 1) geochemical analyses, 2) mineralogical observations, and 3) sequential extractions. Some samples selected for geochemical analyses were grouped and mixed (two or more samples were composited together to form a representative sample of a larger unit). na = sample not geochemically analyzed.

Loc	Orig. Field Sample ID	Geo- chemical Analyses Sample ID	Mineral- ogical Obser- vations	Bulk Chem. & Sequen- tial Extrac- tions	Sediment Description	Dist. from Stream (m)	Depth MIN (m)	Depth MAX (m)
	2.1	na				0.3	0	0.15
	2.2	na				0.5	0	0.13
	2.3	na				1	0	0.05
	3.1	na				7	0	0.22
	3.2A	na				11	0	0.08
	3.2B	na				11	0.08	0.30
	3.3A	D3.3A				18	0	0.23
	3.3B	D3 3B				18	0.23	0.46
	3.3C	50.05				18	0.46	0.71
_	3.3D	D2 2C			Metallic specs, possible pyrite,	18	0.71	0.91
	3.3E	D3.3C			grades to sandy texture	18	0.91	1.19
	3.3F	D3.3D			Red, sandy, hit cobbles, more moist	18	1.19	1.37
	3.4	na				26	0	0.38
	4.1	na			Rocky, hard to auger	2	0	0.25
	4.2A	na			Rocky (igneous, shale), angular, subangular, rounded	12	0	0.15
	4.2B	na			Large cobble 8in diameter	12	0.15	0.25
	4.3	na			Too hard to dig	22	0	0.08
	4.4	na			Cobbles (7.5-15 cm)	32	0	0.08
	1.1A	na			Very pebbly, gravel rich	3	0	0.38
	1.2A	na			Clay	10	0	0.20
	1.2B	na			Silty, yellow grains, hit cobbles	10	0.20	0.35
	1.3A	na			Clay, more red	18	0	0.18
	1.3B	na	x		More silty than G1.3A. Light brown to medium brown w/ dull orange. Fine sandy-silt, moderately well sorted.	18	0.18	0.41
G	1.3C	na			Moist, hit cobbles	18	0.40	0.56
	1.4A	na			Clay, silty	28	0	0.20
	1.4B	na			Moist, pebbly	28	0.20	0.35
	2.8	G2.8	x		Dark lenses in G2.7, up to 3m wide. Medium-brown w/ rusty red tones, metallic specs. Mostly clay, well sorted.	3	0	0.60
	2.7	G2.7		x	A-horizon soil, includes a deep rusty-red band ~0.3m thick intermixed with dark grey layers.	3	0	0.60

2.6	G2.6		x	Light buff orange-brown (1 shade lighter than G2.4). Fine sand texture with 10cm dark grey nodules.	3	0.60	1.20
2.5	G2.5		x	Band of dark grey-brown subtlety grading into a lighter layer in between. Old twigs and calcareous pieces (1.25cm) present in ~5% of the layer.	3	1.20	1.60
2.4	G2.4	x		Light-medium brown mixed with dull orange, fine sand to silt, small vesicles, and splotches of adobe rusty-red present in ~2% of layer. Sharp contact with G2.3.	3	1.60	2.00
2.3	G2.3			Medium brown, sharp contact with G2.4. Silty with pebbles (<2.5cm) present in ~20% of the layer.	3	2.00	2.20
2.2	G2.2			Medium-brown upper portion, gradational contact with layer below consisting of poorly sorted gravel to cobble sized (15cm) clasts, sub- round to sub-angular clasts, white coating on light brown-buff matrix.	3	2.20	3.00
2.1	G2.1			Shale- dark to light grey. White coating, small patches of brown- crumbly pebble sized inclusions. Weathered shale is sticky.	3	3.00	4.00
3.1A	G3.1A		х	Weathered shale is sticky. X Red sandy silt		0	0.23
3.1B	G3.1B		х		13.5	0.23	0.41
3.1C				Medium-dark brown w/ rusty red,	13.5	0.41	0.61
3.1D	G3.1C	X	x	yellow. Mix of clay and fine silt.	13.5	0.61	0.76
3.1E				Similar to G2.8, but more metallic specs.	13.5	0.76	1.04
3.1F	G3 1D		¥	More dark grey clay, some orange	13.5	1.04	1.14
3.1G	00.10		~	with yellow	13.5	1.14	1.30
3.1H	G3.1E			Moist, muddy, silt, dark grey chunks	10	1.52	1.75
3.11				and root material.	10	1.75	1.83
3.2A	G3.2A			Lower down-dipped area	21.4	0	0.20
3.2B	G3.2B			Dark brown with metallic red	21.4	0.20	0.35
3.2C					21.4	0.35	0.51
3.2D	G3.2C	X		Moist, hit cobble. Rusty orange to light brown mixed w/ buff-grey. Fine		0.51	0.71
3.2E				silt & clay.	21.4	0.71	0.81
3.3A	G3.3A	x	x	Medium-dark brown. Mostly very fine silt and clay, poorly sorted (<1 to 4 mm grains).	45	0	0.23
3.3B	G3 3B		¥		45	0.23	0.35
3.3C	00.05		^		45	0.35	0.46
						•	•
3.3D	G3.3C		x	Hard cohesive clays of red, dark	45	0.46	0.66

	3.3F	G3.3D	x	x	Dark metallic sparkles, mix of medium-brown, dull orange-turmeric, grey. Silt, clay, 25% fine sand. Similar to G3.2D, but darker brown, less orange.	45	0.76	1.01
	3.4A	G3.4A			Grasses show rust stain spots	60	0	0.15
	3.4B	G3.4B			Dark clay	60	0.15	0.35
	3.4C	00.40			Deale al second the second second second	60	0.35	0.51
	3.4D	G3.4C			Dark clay with metallic sparkles	60	0.51	0.66
	3.4E	G3.4D	x		Rusty-orange, light brown w/silver metallic grey. Fine silt and clay, well sorted. Similar to G3.2D, more silver-grey, less orange.	60	0.66	0.76
	1.7	H1.7		x	Silt: buff to light grey, tan-yellow, no	2	0	0.50
	1.6	H1.6		x	Silt/gravel/cobble: red, orange, yellow matrix w/ poorly sorted, well rounded, pebble-cobble clasts (<2.5cm to 10cam). Sharp contact w/ unit below	2	0.50	0.90
	1.5C	H1.5C		x	Silt-clay: grey lenses w/ yellow brown intermixed	2	0.90	1.20
	1.5B	H1.5B		X	Silt-sand: yellow orange	2	0.90	1.20
	1.5A	H1.5A		x	Silt-clay: grey lens w/ dark red intermixed, rusty brown	2	0.90	1.20
	1.5AA	H1.5AA			Black angular brittle, glassy sheen, anthracite-like pieces (~5mm)	2	0.90	1.20
	1.4	H1.4		х	Gravel/cobble: poorly sorted (<1cm to 15cm)	2	1.20	1.50
	1.3B	H1.3B		х	Silt: dark grown w/ light yellow	2	1.50	2.30
	1.3A	H1.3A		x	Fine silt: dark brown-red, finer grained than H1.3B	2	1.50	2.30
н	1.2B	H1.2B		x	Silt-sand: yellow, orange, red mix	2	2.30	3.50
	1.2A	H1.2A		x	Silt-sand: same as H1.2B but w/ gypsum-like white coating/growths	2	2.30	3.50
	1.2AA	H1.2AA			Silt-sand: similar to H1.2A but w/ dark black sandy silt and poorly sorted gravel/cobble (<1cm to 10cm)	2	2.30	3.50
	1.1	H1.1			Shale: dark grey-black	2	3.50	4.50
	2.1A	H2 1A			Sandy brown moist fine grained	4	0	0.23
	2.1B	112. IA			Sandy brown, moist, lifte grained	4	0.23	0.33
	2.1C	H2 1P			Coarse yellow sand, hit cobbles &	4	0.33	0.76
	2.1D	112.10			water	4	0.76	0.86
	2.2A					9	0	0.23
	2.2B	H2.2			Fine sand-silt, moist, hit cobbles	9	0.23	0.56
	2.2C					9	0.56	0.76
	2.3A	H2 3A			Yellow-huff brown	18	0	0.20
	2.3B					18	0.20	0.35

	2.3C					18	0.35	0.51
	2.3D	H2.3B			Grey clay lens, metallic sparkles	18	0.51	0.76
	2.3E					18	0.76	0.94
	2.3F	H2.3C			Dark grey and black chunks, moist	18	0.94	1.07
	2.3G					18	1.07	1.22
	2.3H	H2.3D			Fine yellow sand, black chunks	18	1.22	1.35
	2.4A	H2.4A		x	Orange brown	35	0.05	0.23
	2.4B	H2.4B		x	Dull yellow, light grey	35	0.23	0.43
	2.4C	H2 4C		~	Dark grav, golden en oko	35	0.43	0.61
	2.4D	п2.40		^	Dark grey, golden specks	35	0.61	0.79
	2.4E					35	0.79	1.01
	2.4F	H2.4D		X	Dark black chunks, moist	35	1.01	1.17
	2.4G	H2.4E			Muddy / moist	35	1.17	1.37
	1.1A	K1 1A		¥	Clay rich arey brown	2	0	0.23
	1.1B			~	Ciay hon, gicy brown	2	0.23	0.38
	1.1C			v	Sticky cohesive clay, grey and red chunks. medium-dark grey w/ rusty	2	0.38	0.61
	1.1D	K1.1B	x	X	orange brown. Mostly clay w/ fine silt, well sorted.	2	0.61	0.79
	1.1E	K1 1C	x	x	Deep red & grey, metallic specs, rusty orange-red brown w/ light	2	0.79	0.99
	1.1F	KIIIO		~	turmeric yellow & grey. Mostly clay, some fine silt, well sorted.	2	0.99	1.14
	1.1G	na				2	1.14	1.22
	1.2A	na			Sandy area	15	0	0.05
	1.2B	K1 2A			Sandy area, vegetation changes	15	0.05	0.20
	1.2C	N1.2A			flowers.	15	0.20	0.35
	1.2D	K1 2B			Red brown and vellow clay	15	0.35	0.61
	1.2E	N1.20				15	0.61	0.71
к	1.2F	K1 2C	X		Moist, medium dark grey w/ rust	15	0.71	0.79
	1.2G				some fine silt, well sorted.	15	0.79	0.91
	1.2H	K1 2D			Moist, similar to K1.2C but more	15	0.91	1.04
	1.21		X		grey streaks	15	1.04	1.22
	1.3A	K1.3A	x	x	Adobe deep red clay, brown-grey, fine metallic sparkles. Fine silt and clay, well sorted.	30	0.05	0.25
	1.3B	K1.3B		х	Red clay, easy to auger	30	0.25	0.61
	1.3C	K4 20		Y	Rusty red orange, some turmeric	30	0.61	0.76
	1.3D	K1.3C	Х	X	yellow, light brown & grey. Fine silt and clay, well sorted.	30	0.76	0.96
	1.3E				Moist, similar to K1.3C, possibly	30	0.96	1.12
	1.3F	K1.3D			shale	30	1.12	1.22
	1.4A	K1.4A		x	All buff-brown w/ hint of dull yellow	46	0.02	0.23
	1.4B			Y		46	0.23	0.43
	1.4C	K1.4B		Ă		46	0.43	0.63

	1.4D	K1.4C	x	x	Light grey yellow buff, less moist. Mostly fine silt, some clay, well sorted. Similar to K1.1D but lighter.	46	0.63	0.81
	1.4E	K1.4D		х	More clay mixed in	46	0.81	1.01
	1.4F					46	1.01	1.24
	1.4G	K1.4E				46	1.24	1.42
	Loc A	A1				0	NA	NA
nent	Loc D	D1				0	NA	NA
tream Sedir	Loc G	G1			Mix of light tan-yellow to brown- black. Medium-coarse grained sand (~1mm), some 2 -3mm grains, sub angular to angular.	0	NA	NA
S-ul	Loc H	H1				0	NA	NA
MC	Loc K	К1				0	NA	NA
	Loc L	L1				0	NA	NA

Table 5.2. Analytes of interest (AOIs) concentrations (mg/kg) of sediment samples collected from the cut bank profiles of Locations G and H. Some results listed in Location H are the average of 2 to 3 individual samples (presented in *light grey italics*). The ranges of typical upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database are presented for comparison (Appendix 5-6).

Upper Co	ntinental Cru	st	Min:	1.5	0.050	43,000	3,000	12.7	23,000	4,649	4,000	270	480	62	40
and River Pa	articulates W	orld	Max:	27	0.055	156,000	92,053	89	108,000	35,300	40,160	1,700	2,000	1,037	380
Background	d Levels (mg/	'kg)	Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225
Sample ID	Dist. from Strm (m)	Depth MIN (m)	Depth MAX (m)	As	Ag	AI	Ca	Cu	Fe	к	Mg	Mn	Ρ	S	Sr
G2.8	~3	0	0.6	519	2.36	15,325	11,587	69.73	95,651	3,834	9,531	1,626	583	457	44.48
G2.7	~3	0	0.6	1,881	2.07	18,838	2,956	81.17	103,572	4,084	9,752	1,865	784	1,341	22.69
G2.6	~3	0.6	1.2	9	0.39	8,084	42,360	15.22	18,514	1,959	8,685	416	464	4,820	101.50
G2.5	~3	1.2	1.6	9	0.61	15,021	46,280	27.68	24,274	3,338	8,677	465	664	15,898	194.84
G2.4	~3	1.6	2.0	13	0.87	10,316	40,093	25.64	27,617	2,291	10,181	571	632	2,012	95.49
G2.3	~3	2.0	2.2	14	1.02	15,108	15,503	30.02	28,257	3,289	6,054	546	687	3,008	94.54
G2.2	~3	2.2	3.0	20	1.20	8,617	64,443	33.74	40,276	1,513	6,882	906	527	1,877	145.41
G2.1	~3	3.0	4.0	6	0.46	13,256	26,905	33.75	18,963	2,611	5,609	87	274	11,618	197.70
			Average:	279	1	12,749	34,077	35	37,353	2,726	7,977	694	576	5,796	122
H1 7	~2	0.00	0.50	2 175	1.62	8 153	6 5 1 5	13 78	02 107	3 054	3 834	/08	300	11 3/3	21.40
H1 6	~2	0.00	0.00	2,173	2.02	5 545	17 103	98.06	00 788	2 526	2 /01	430	563	17 0/1	64.02
	~2	0.00	1 20	2,750	2.30	9,545	0.818	70.80	01 003	2,320	4 380	370	311	16 07/	22.14
нт.5 (д. b, c avg)	~2	1.20	1.20	1,903	2.40	6 150	7 731	17.38	102 650	2,020	3 003	860	227	25 200	22.14
H13(ABava)	~2	1.20	2.30	1,024	2.05	6,462	8 646	51.28	102,039	2,347	3 163	752	481	22,230	36.84
H1 2 (A B avg)	~2	2.30	3.50	831	2.12	6 302	14 707	53.61	71 547	1 386	5 127	3 345	687	13 940	66 10
H1 1	~2	3.50	4 50	6	0.90	15 527	18 290	24.33	21 675	3 739	10 685	141	579	6 4 1 2	136 59
	-	0.00	Average:	1,503	2	8,248	11,843	56	83,027	2,601	4,656	915	463	16,365	54
H1 5C	~2	0.00	1.20	1.056	1.92	11 460	7 991	71.04	70.028	2 271	5 275	286	191	10 567	20.74
H1.50	~2	0.90	1.20	1,950	2.03	6 762	6 702	20 20	100 140	2,377	0,370	200	225	16,628	19.65
H1 5A	~2	0.90	1.20	2 038	2.07	10 289	14 872	51.65	96 812	3 707	4 977	432	220	23 728	27.05
H1.5AA	~2	0.90	1.20	485	1 40	12 568	6 260	566 52	36 721	1 598	4 240	198	273	9 310	29.95
H1.3B	~2	1.50	2.30	1.429	1.63	5.737	8,519	49.36	104.457	2,165	2.867	774	400	25.650	32.90
H1.3A	~2	1.50	2.30	2,063	2.62	7,186	8,772	53.21	98,203	2,510	3,459	729	563	19,663	40.77
H1.2B	~2	2.30	3.50	995	2.76	6,485	14,579	62.78	70,699	1,255	4,144	2,343	700	15,072	70.74
H1.2A	~2	2.30	3.50	667	2.23	6,298	14,835	44.45	72,395	1,518	6,110	4,347	673	12,808	61.45
H1.2AA	~2	2.30	3.50	255	2.63	35,954	2,385	512.51	15,550	252	41,264	11,534	622	130,677	9.06

Table 5.3. Analytes of interest (AOIs) concentrations (mg/kg) of sediment samples collected on the point bar of Location D. The ranges of typical upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database are presented for comparison (Appendix 5-6).

Upper Cor	Upper Continental Crust		Min:	1.5	0.050	43,000	3,000	12.7	23,000	4,649	4,000	270	480	62	40
and River Pa	and River Particulates World			27	0.055	156,000	92,053	89	108,000	35,300	40,160	1,700	2,000	1,037	380
Background Levels (mg/kg)		Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225	
Sample ID	Dist. from	Depth	Depth	Δe	٨a	۵	Ca	Cu	F۵	ĸ	Ma	Mn	P	G	Sr
	Strm (m)	MIN (m)	MAX (m)	~	~9	~	Ua	ou	10	ĸ	ing		•	U	01
D3.3A	18	0.00	0.23	999	2.54	12,096	281	40.59	97,488	3,405	5,975	833	325	4,109	7.91
D3.3B	18	0.23	0.71	887	2.23	16,769	41	64.06	95,856	3,872	7,962	856	312	1,881	8.42
D3.3C	18	0.71	1.19	1,109	3.89	15,470	81	72.01	108,889	3,722	7,193	711	403	4,148	21.82
D3.3D 18 1.19		1.37	1,020	3.51	12,236	204	71.59	100,316	2,682	5,543	738	453	3,847	24.39	

Upper Cor	ntinental Cru	st	Min:	1.5	0.050	43,000	3,000	12.7	23,000	4,649	4,000	270	480	62	40
and River Pa	articulates W	orld	Max:	27	0.055	156,000	92,053	89	108,000	35,300	40,160	1,700	2,000	1,037	380
Background	Levels (mg/	′kg)	Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225
Sample ID	Dist. from Strm (m)	Depth MIN (m)	Depth MAX (m)	As	Ag	AI	Ca	Cu	Fe	к	Mg	Mn	Р	S	Sr
G3.1A	13.5	0.00	0.23	1,128	5.39	11,148	2,704	62.25	103,119	3,028	6,064	1,122	931	2,112	25.94
G3.1B	13.5	0.23	0.41	805	4.51	7,742	694	82.79	110,814	2,633	3,441	1,211	514	3,815	14.65
G3.1C	13.5	0.41	1.04	530	3.77	8,230	3,184	62.65	84,136	2,296	4,404	2,023	415	619	26.75
G3.1D	13.5	1.04	1.30	123	2.41	8,633	26,717	33.07	38,675	2,672	9,903	660	547	3,067	44.33
G3.1E	10	1.52	1.83	1,194	3.72	10,511	33,334	63.74	61,681	2,460	9,865	1,102	685	2,880	62.05
G3.2A	21.4	0.00	0.20	1,082	3.99	15,424	4,550	66.69	80,196	6,127	7,837	1,360	601	5,254	61.05
G3.2B	21.4	0.20	0.51	1,199	5.54	22,470	12,295	79.18	101,040	6,366	11,557	760	505	8,819	19.01
G3.2C	21.4	0.51	0.81	2,236	5.44	8,684	7,885	49.05	86,897	3,341	4,151	531	472	10,240	37.37
G3.3A	45	0.00	0.23	649	2.17	10,335	9,618	29.09	36,129	3,051	5,643	649	534	886	23.74
G3.3B	45	0.23	0.46	960	4.27	22,597	11,254	59.64	85,675	5,142	11,660	1,312	448	5,036	21.23
G3.3C	45	0.46	0.76	4,061	6.76	10,505	14,211	35.74	115,664	3,687	5,036	470	498	20,036	34.09
G3.3D	45	0.76	1.01	1,116	6.08	20,264	9,535	101.57	110,637	3,763	8,651	3,897	619	9,409	33.60
G3.4A	60	0.00	0.15	2,194	3.08	10,032	2,885	41.28	58,168	3,062	3,704	760	502	2,120	20.77
G3.4B	60	0.15	0.36	2,442	3.81	18,913	1,956	60.28	92,542	4,928	8,810	1,048	500	3,168	20.63
G3.4C	60	0.36	0.66	2,141	5.99	11,301	14,561	58.13	110,172	4,898	5,277	519	482	16,966	45.22
G3.4D	60	0.66	0.76	1,276	6.99	22,113	21,087	65.78	109,772	4,500	10,128	2,295	525	19,112	30.73

Table 5.4. Analytes of interest (AOIs) concentrations (mg/kg) of sediment samples collected on the point bar of Location G. The ranges of typical upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database are presented for comparison (Appendix 5-6).

Upper Cor	ntinental Cru	st	Min:	1.5	0.050	43,000	3,000	12.7	23,000	4,649	4,000	270	480	62	40
and River Particulates World Background Levels (mg/kg)		Max:	27	0.055	156,000	92,053	89	108,000	35,300	40,160	1,700	2,000	1,037	380	
		Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225	
Sample ID	Dist. from	Depth	Depth	As	Ag	А	Са	Cu	Fe	к	Mg	Mn	Р	s	Sr
-	Strm (m)	MIN (m)	MAX (m)		-						-				
H2.1A (4m)	4	0.33	0.63	731	3.46	4,566	12,830	30.84	62,655	1,001	3,757	807	776	3,336	50.83
H2.2 (9m)	9	0.00	0.76	652	3.02	5,153	12,383	29.70	52,245	1,078	3,553	693	558	2,035	46.50
H2.1B (4m)	4	0.63	0.86	845	3.54	4,344	12,539	29.56	60,264	914	3,434	860	577	3,701	59.85
H2.3A	18	0.00	0.36	2,634	5.66	6,819	10,353	35.07	122,580	3,978	3,212	800	233	20,784	24.36
H2.3B	18	0.36	0.76	3,890	6.36	11,854	15,154	52.56	114,983	3,875	5,357	561	585	21,074	29.46
H2.3C	18	0.76	1.07	910	6.83	21,412	17,249	115.20	106,568	4,731	9,617	1,518	464	15,291	25.36
H2.3D	18	1.07	1.35	598	4.66	21,443	21,589	101.39	67,746	3,478	7,293	2,912	623	15,063	44.16
H2.4A	35	0.05	0.23	3,166	5.37	18,941	2,703	93.53	108,013	4,687	8,853	802	562	6,616	22.88
H2.4B	35	0.23	0.43	1,873	6.41	10,169	11,698	29.15	112,213	3,625	4,736	655	294	19,925	24.95
H2.4C	35	0.43	0.79	979	6.88	16,792	18,734	106.02	101,514	3,620	7,814	4,069	392	14,573	36.77
H2.4D	35	0.79	1.17	894	7.96	25,716	15,869	100.02	115,559	4,888	12,331	2,912	502	11,394	51.52
H2.4E	35	1.17	1.37	173	3.24	12,370	25,689	31.44	40,989	2,878	9,201	1,589	575	4,368	64.32

Table 5.5. Analytes of interest (AOIs) concentrations (mg/kg) of sediment samples collected on the point bar of Location H. The ranges of typical upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database are presented for comparison (Appendix 5-6).

Upper Co	ntinental Cru	ist	Min:	1.5	0.050	43,000	3,000	12.7	23,000	4,649	4,000	270	480	62	40
and River Pa	articulates W	orld	Max:	27	0.055	156,000	92,053	89	108,000	35,300	40,160	1,700	2,000	1,037	380
Background	d Levels (mg	/kg)	Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225
Sample ID	Dist. from Strm (m)	Depth MIN (m)	Depth MAX (m)	As	Ag	AI	Ca	Cu	Fe	к	Mg	Mn	Ρ	S	Sr
K1.1A	2	0.00	0.38	331	2.74	15,783	12,419	32.64	41,618	2,569	7,122	847	609	2,520	74.53
K1.1B	2	0.38	0.79	1,731	6.52	19,140	22,063	68.25	93,735	2,525	9,955	1,699	488	13,014	70.78
K1.1C	2	0.79	1.14	2,246	8.17	32,000	18,924	128.13	120,158	3,624	23,741	2,658	657	12,251	96.41
K1.2A	15.0	0.05	0.36	335	2.93	14,131	11,861	32.64	40,757	2,373	6,878	740	697	1,510	68.24
K1.2B	15.0	0.36	0.71	2,038	6.14	17,223	15,408	74.31	92,847	2,999	9,190	2,180	618	6,438	71.30
K1.2C	15.0	0.71	0.91	1,894	6.93	23,224	18,327	71.33	111,091	3,373	13,543	2,319	510	8,432	67.64
K1.2D	15.0	0.91	1.22	1,599	6.19	23,595	16,418	71.57	98,404	3,243	13,213	2,298	616	6,781	66.15
K1.3A	30.0	0.05	0.25	1,002	2.87	12,637	6,912	44.89	67,311	2,250	7,642	1,504	442	2,165	49.99
K1.3B	30.0	0.02	0.61	1,821	4.80	16,522	19,944	71.76	89,064	3,219	8,696	1,818	442	12,071	69.47
K1.3C	30.0	0.61	0.97	2,148	4.27	16,156	15,510	78.33	100,045	2,950	8,605	2,023	390	10,070	56.66
K1.3D	30.0	0.97	1.22	2,030	4.28	18,209	16,643	71.95	98,281	2,343	13,294	2,358	342	8,666	57.43
K1.4A	46	0.02	0.23	476	1.72	10,358	10,534	36.29	37,508	1,925	5,947	809	440	1,515	41.16
K1.4B	46	0.23	0.63	39	0.93	10,643	16,183	18.64	22,949	1,884	4,884	523	467	1,672	58.43
K1.4C	46	0.63	0.81	48	0.81	6,516	15,395	13.17	19,861	1,223	3,425	443	375	2,095	53.16
K1.4D	46	0.81	1.01	16	0.80	7,975	17,793	13.95	18,464	1,557	4,726	395	415	3,156	85.55
K1.4E	46	1.01	1.42	15	0.65	5,481	14,884	10.23	15,567	1,122	4,131	350	358	1,844	64.83

Table 5.6. Analytes of interest (AOIs) concentrations (mg/kg) of sediment samples collected on the point bar of Location K. The ranges of typical upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database are presented for comparison (Appendix 5-6).

u a Upper Continental Crust and River Particulates World 40 380 Min: 0.050 43,000 3,000 23,000 4,649 4,000 1.5 12.7 270 480 62 Max.

Table 5.7. Analytes of interest (AOIs) concentrations (mg/kg) of in-stream sediment samples from WWC and the BFR. The ranges of typical
upper continental crustal and river particulate concentrations compiled from the Geochemical Earth Reference Model (GERM) Reservoir Database
are presented for comparison (Appendix 5-6).

		iviax.	21	0.055	150,000	92,000	09	100,000	55,500	40,100	1,700	2,000	1,037	300	
Background Levels (mg/kg)		Mean:	6.87	0.053	88,763	26,224	39.43	49,982	22,374	15,351	930	937	597	225	
Sample ID	Dist. from Strm (m)	Depth MIN (m)	Depth MAX (m)	As	Ag	AI	Ca	Cu	Fe	к	Mg	Mn	Р	S	Sr
A1	0	NA	NA	382	2.64	7,809	23,897	52.51	49,102	1,624	5,316	1,489	730	623	99.74
D1	0	NA	NA	264	2.46	11,082	37,726	67.23	41,642	2,641	8,396	1,247	790	1,063	71.24
G1	0	NA	NA	694	1.56	4,340	9,402	39.91	52,956	940	3,092	730	775	1,692	48.80
H1	0	NA	NA	643	1.61	8,197	17,518	31.23	44,886	1,777	5,905	513	483	3,092	70.97
K1	0	NA	NA	424	1.64	12,121	12,060	35.51	43,292	1,742	6,341	1,069	471	2,219	76.76
L1	0	NA	NA	9	0.71	7,181	41,853	124.30	19,697	1,484	3,611	475	451	4,191	156.76

Chapter 6. - Tables

Table 6.1a. Arsenic

Percentage of (a) arsenic, (b) aluminum, (c) calcium, (d) iron, (e) manganese, and (f) sulfur extracted from the sediment. See Appendix 6-4 for extracted concentrations from the from the sediment and in the supernatant. E1 = readily exchangeable surface sites; E2 = exchange sites; E3 = fine grained Feoxyhydroxides & carbonates; E4 = weakly soluble minerals. Samples with greater than 100% recovery in extraction relative to that analyzed in the total content of the sediment sample (i.e., Total Extracted > 100%) was likely due to instrumentation or precision error. These samples (italicized with grey highlight) were excluded from statistical analyses and graphical representation.

Sample ID	E1	F2	E3	E/	Total Extracted	Posidual	Sediment
Sample ID	LI	LZ	LJ	L4		Residual	(mg/kg)
G2.7	0.035%	6.11%	4.93%	32.0%	43.0%	57.0%	1,881
G2.6	4.44%	76.5%	5.3%	62.1%	148%	-48.4%	8.51
G2.5	8.34%	74.4%	19.1%	44.6%	146%	-46.4%	9.43
G3.1A	0.091%	5.69%	2.72%	13.9%	22.4%	77.6%	1,128
G3.1B	0.037%	2.61%	1.40%	5.9%	9.93%	90.1%	805
G3.1C	0.132%	4.64%	2.29%	9.9%	17.0%	83.0%	530
G3.1D	0.667%	8.81%	4.00%	16.9%	30.4%	69.6%	123
G3.3A	0.446%	12.3%	6.77%	41.3%	60.8%	39.2%	649
G3.3B	0.073%	9.72%	4.83%	20.8%	35.4%	64.6%	960
G3.3C	0.024%	5.09%	2.58%	12.1%	19.8%	80.2%	4,061
G3.3D	0.089%	6.60%	3.26%	16.2%	26.2%	73.8%	1,116
H1.7	0.077%	5.82%	2.80%	15.4%	24.1%	75.9%	2,175
H1.6	0.033%	5.29%	2.54%	17.0%	24.9%	75.1%	2,758
H1.5C	0.081%	10.9%	4.31%	24.4%	39.7%	60.3%	1,956
H1.5B	0.040%	14.1%	5.59%	25.8%	45.6%	54.4%	1,962
H1.5A	0.023%	10.1%	5.18%	22.4%	37.8%	62.2%	2,038
H1.4	0.171%	13.6%	5.10%	26.0%	44.9%	55.1%	1,024
H1.3B	3.05%	18.4%	6.68%	26.3%	54.5%	45.5%	1,429
H1.3A	0.123%	14.9%	5.60%	26.9%	47.5%	52.5%	2,063
H1.2B	0.106%	14.4%	4.43%	47.0%	65.9%	34.1%	995
H1.2A	0.105%	4.56%	1.67%	10.7%	17.0%	83.0%	667
H2.4A	0.037%	12.4%	5.68%	28.7%	46.8%	53.2%	3,166
H2.4B	0.052%	9.79%	5.17%	20.2%	35.2%	64.8%	1,873
H2.4C	0.063%	11.1%	5.13%	17.5%	33.7%	66.3%	979
H2.4D	0.092%	5.97%	2.94%	8.9%	17.9%	82.1%	894
K1.1A	1.00%	17.6%	7.36%	29.3%	55.3%	44.7%	193
K1.1B	0.371%	11.7%	5.62%	26.1%	43.8%	56.2%	331
K1.1C	0.017%	8.95%	4.11%	25.2%	38.3%	61.7%	1,731
K1.3A	0.035%	8.18%	3.70%	19.2%	31.1%	68.9%	1,002
K1.3B	0.071%	8.09%	3.67%	22.5%	34.3%	65.7%	1,821
K1.3C	0.005%	8.11%	3.57%	20.3%	32.0%	68.0%	2,148
K1.4A	0.190%	13.3%	5.03%	33.9%	52.4%	47.6%	476
K1.4B	3.92%	24.5%	12.0%	42.5%	82.9%	17.1%	39
K1.4C	0.732%	24.5%	11.4%	46.7%	83.4%	16.6%	48
K1.4D	0.161%	50.7%	9.50%	77.5%	138%	-37.9%	15.56

	11001111110011						
Sample ID	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)
G2.7	0.008%	0.208%	0.012%	5.20%	5.43%	94.6%	18,838
G2.6	0.006%	0.432%	0.006%	7.44%	7.89%	92.1%	8,084
G2.5	0.003%	0.361%	0.005%	7.40%	7.77%	92.2%	15,021
G3.1A	0.004%	0.174%	0.007%	4.80%	4.98%	95.0%	11,148
G3.1B	0.006%	0.574%	0.046%	8.77%	9.40%	90.6%	7,742
G3.1C	0.006%	0.537%	0.020%	8.25%	8.81%	91.2%	8,230
G3.1D	0.006%	0.436%	0.006%	7.78%	8.23%	91.8%	8,633
G3.3A	0.029%	0.797%	0.028%	8.03%	8.88%	91.1%	10,335
G3.3B	0.002%	0.234%	0.009%	11.0%	11.3%	88.7%	22,597
G3.3C	0.005%	0.388%	0.025%	9.39%	9.80%	90.2%	10,505
G3.3D	0.052%	0.458%	0.025%	12.4%	12.9%	87.1%	20,264
H1.7	0.350%	0.656%	0.039%	9.9%	10.9%	89.1%	8,153
H1.6	0.225%	1.007%	0.056%	14.0%	15.3%	84.7%	5,545
H1.5C	0.509%	0.499%	0.034%	25.6%	26.6%	73.4%	11,469
H1.5B	2.87%	0.399%	0.030%	11.5%	14.8%	85.2%	6,763
H1.5A	3.76%	0.575%	0.042%	5.56%	9.93%	90.1%	10,289
H1.4	6.67%	0.635%	0.042%	6.14%	13.5%	86.5%	6,150
H1.3B	8.34%	0.650%	0.044%	6.39%	15.4%	84.6%	5,737
H1.3A	4.73%	0.525%	0.043%	8.20%	13.5%	86.5%	7,186
H1.2B	0.141%	1.100%	0.074%	40.1%	41.4%	58.6%	6,485
H1.2A	0.008%	0.841%	0.035%	14.7%	15.6%	84.4%	6,298
H2.4A	0.003%	0.222%	0.012%	12.6%	12.9%	87.1%	18,941
H2.4B	0.067%	0.397%	0.030%	8.84%	9.34%	90.7%	10,169
H2.4C	0.003%	0.353%	0.025%	8.98%	9.36%	90.6%	16,792
H2.4D	0.002%	0.623%	0.028%	11.1%	11.8%	88.2%	25,716
K1.1A	0.003%	0.342%	0.003%	8.48%	8.82%	91.2%	14,820
K1.1B	0.003%	0.357%	0.007%	9.43%	9.80%	90.2%	15,783
K1.1C	0.003%	0.117%	0.003%	11.9%	12.0%	88.0%	19,140
K1.3A	0.004%	0.304%	0.004%	11.3%	11.6%	88.4%	12,637
K1.3B	0.003%	0.152%	0.003%	13.8%	13.9%	86.1%	16,522
K1.3C	0.003%	0.120%	0.003%	10.7%	10.8%	89.2%	16,156
K1.4A	0.005%	0.514%	0.005%	10.6%	11.1%	88.9%	10,358
K1.4B	0.005%	0.436%	0.005%	8.85%	9.30%	90.7%	10,643
K1.4C	0.008%	0.568%	0.008%	9.57%	10.2%	89.8%	6,516
K1.4D	0.006%	0.457%	0.006%	7.58%	8.05%	92.0%	7,975

Table 6.1b. Aluminum

I able 6.1C. Calciu	m

Sample ID	E1	F2	E2	E/	Total Extracted	Posidual	Sediment
Sample ID	C1	EZ.	ES	C4	TOTAL EXTLACTED	Residual	(mg/kg)
G2.7	3.45%	42.4%	10.5%	31.2%	87.5%	12.5%	2,956
G2.6	8.16%	3.52%	6.03%	41.9%	59.6%	40.4%	42,360
G2.5	10.2%	4.47%	5.60%	42.9%	63.2%	36.8%	46,280
G3.1A	1.56%	39.1%	9.19%	28.9%	78.7%	21.3%	2,704
G3.1B	11.5%	30.2%	6.29%	60.8%	109%	-8.72%	694
G3.1C	2.42%	19.5%	6.53%	49.2%	77.7%	22.3%	3,184
G3.1D	5.99%	14.4%	9.12%	44.8%	74.2%	25.8%	26,717
G3.3A	0.772%	21.8%	7.75%	44.9%	75.2%	24.8%	9,618
G3.3B	17.0%	22.2%	6.60%	20.9%	66.7%	33.3%	11,254
G3.3C	38.3%	42.6%	14.7%	7.90%	103%	-3.49%	14,211
G3.3D	42.4%	16.7%	5.02%	14.2%	78.3%	21.7%	9,535
H1.7	70.3%	20.4%	3.73%	3.95%	98.4%	1.58%	6,515
H1.6	32.1%	29.9%	10.7%	8.56%	81.2%	18.8%	17,193
H1.5C	61.2%	21.5%	9.39%	7.43%	99.5%	0.499%	7,881
H1.5B	40.1%	29.6%	13.9%	8.60%	92.2%	7.84%	6,702
H1.5A	26.4%	28.0%	11.4%	7.91%	73.8%	26.2%	14,872
H1.4	34.6%	21.2%	13.7%	11.3%	80.7%	19.3%	7,731
H1.3B	31.7%	27.1%	20.7%	13.7%	93.2%	6.82%	8,519
H1.3A	34.9%	26.7%	15.7%	12.2%	89.5%	10.5%	8,772
H1.2B	19.4%	6.08%	1.29%	10.1%	36.9%	63.1%	14,579
H1.2A	17.2%	15.7%	11.6%	26.6%	71.1%	28.9%	14,835
H2.4A	12.8%	34.1%	8.02%	11.5%	66.5%	33.5%	2,703
H2.4B	34.8%	23.6%	7.06%	3.30%	68.8%	31.2%	11,698
H2.4C	23.6%	15.3%	4.17%	2.17%	45.2%	54.8%	18,734
H2.4D	23.9%	14.4%	5.72%	7.56%	51.6%	48.4%	15,869
K1.1A	1.04%	23.2%	9.65%	34.0%	67.8%	32.2%	14,800
K1.1B	1.56%	24.5%	8.38%	34.6%	69.0%	31.0%	12,419
K1.1C	19.3%	17.5%	14.8%	16.2%	67.7%	32.3%	22,063
K1.3A	4.52%	33.9%	10.1%	49.0%	97.5%	2.51%	6,912
K1.3B	23.4%	22.1%	13.7%	12.2%	71.4%	28.6%	19,944
K1.3C	29.0%	21.0%	13.5%	13.4%	76.9%	23.1%	15,510
K1.4A	1.06%	29.0%	12.5%	44.5%	87.0%	13.0%	10,534
K1.4B	5.93%	25.8%	11.9%	35.9%	79.6%	20.4%	16,183
K1.4C	9.35%	22.1%	13.5%	33.7%	78.6%	21.4%	15,395
K1.4D	8.37%	20.0%	11.2%	29.2%	68.7%	31.3%	17,793

Sample ID	E1	E2	E3	E4	Total Extracted	Residual	Sediment
	.	0.0070/			0.40004		(mg/kg)
G2.7	0.004%	0.097%	0.014%	0.014%	0.128%	99.9%	103,572
G2.6	0.0003%	0.062%	0.003%	3.31%	3.37%	96.6%	18,514
G2.5	0.0002%	0.046%	0.001%	3.62%	3.66%	96.3%	24,274
G3.1A	0.004%	0.075%	0.007%	4.11%	4.20%	95.8%	103,119
G3.1B	0.0000%	0.081%	0.004%	2.44%	2.52%	97.5%	110,814
G3.1C	0.001%	0.086%	0.002%	3.14%	3.23%	96.8%	84,136
G3.1D	0.0001%	0.089%	0.001%	5.33%	5.42%	94.6%	38,675
G3.3A	0.007%	0.116%	0.005%	5.69%	5.82%	94.2%	36,129
G3.3B	0.00006%	0.048%	0.002%	5.96%	6.01%	94.0%	85,675
G3.3C	0.00004%	0.070%	0.004%	4.17%	4.24%	95.8%	115,664
G3.3D	0.00005%	0.064%	0.001%	5.46%	5.53%	94.5%	110,637
H1.7	0.00011%	0.099%	0.005%	3.89%	4.00%	96.0%	92,197
H1.6	0.00005%	0.076%	0.005%	4.42%	4.51%	95.5%	99,788
H1.5C	0.001%	0.113%	0.010%	10.9%	11.0%	89.0%	79,028
H1.5B	0.048%	0.106%	0.008%	8.55%	8.71%	91.3%	100,140
H1.5A	0.081%	0.100%	0.006%	5.24%	5.43%	94.6%	96,812
H1.4	0.669%	0.100%	0.008%	5.08%	5.86%	94.1%	102,659
H1.3B	1.43%	0.104%	0.009%	5.66%	7.21%	92.8%	104,457
H1.3A	0.403%	0.112%	0.009%	6.86%	7.38%	92.6%	98,203
H1.2B	0.001%	0.127%	0.012%	11.0%	11.2%	88.8%	70,699
H1.2A	0.00007%	0.076%	0.000%	4.55%	4.63%	95.4%	72,395
H2.4A	0.00005%	0.070%	0.004%	7.56%	7.63%	92.4%	108,013
H2.4B	0.00004%	0.078%	0.003%	3.24%	3.32%	96.7%	112,213
H2.4C	0.00005%	0.079%	0.003%	3.45%	3.53%	96.5%	101,514
H2.4D	0.00004%	0.033%	0.000%	3.30%	3.34%	96.7%	115,559
K1.1A	0.002%	0.119%	0.002%	8.49%	8.61%	91.4%	35,869
K1.1B	0.002%	0.119%	0.002%	8.39%	8.51%	91.5%	41,618
K1.1C	0.0001%	0.062%	0.001%	8.83%	8.89%	91.1%	93,735
K1.3A	0.0001%	0.094%	0.002%	8.20%	8.29%	91.7%	67,311
K1.3B	0.0001%	0.071%	0.001%	9.03%	9.11%	90.9%	89,064
K1.3C	0.00005%	0.060%	0.001%	7.45%	7.51%	92.5%	100,045
K1.4A	0.003%	0.137%	0.002%	9.13%	9.27%	90.7%	37,508
K1.4B	0.0002%	0.179%	0.002%	8.81%	8.99%	91.0%	22,949
K1.4C	0.0003%	0.267%	0.002%	8.08%	8.35%	91.6%	19,861
K1.4D	0.0003%	0.238%	0.003%	7.99%	8.23%	91.8%	18,464

Table 6.1d. Iron
Sample ID	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)
G2.7	0.003%	0.198%	22.3%	36.0%	58.5%	41.5%	1,865
G2.6	0.012%	1.80%	37.7%	23.7%	63.2%	36.8%	415.76
G2.5	0.011%	1.53%	39.1%	31.7%	72.3%	27.7%	464.63
G3.1A	0.004%	0.348%	20.4%	26.2%	46.9%	53.1%	1,122
G3.1B	0.160%	1.05%	40.3%	36.5%	78.0%	22.0%	1,211
G3.1C	0.002%	0.212%	53.2%	32.0%	85.5%	14.5%	2,023
G3.1D	0.008%	0.864%	24.9%	31.1%	56.9%	43.1%	660
G3.3A	0.008%	0.596%	37.7%	33.6%	71.8%	28.2%	649
G3.3B	0.004%	0.309%	13.5%	19.8%	33.6%	66.4%	1,312
G3.3C	0.560%	0.627%	19.7%	11.0%	31.9%	68.1%	470
G3.3D	2.06%	0.765%	36.6%	22.8%	62.2%	37.8%	3,897
H1.7	0.668%	0.191%	0.605%	3.10%	4.6%	95.4%	498
H1.6	1.62%	0.494%	9.49%	6.57%	18.2%	81.8%	437
H1.5C	3.29%	0.712%	0.475%	8.73%	13.2%	86.8%	286
H1.5B	4.50%	0.477%	0.124%	3.88%	9.0%	91.0%	391
H1.5A	7.42%	0.838%	0.182%	2.15%	10.6%	89.4%	432
H1.4	8.95%	1.08%	0.196%	1.40%	11.6%	88.4%	860
H1.3B	16.5%	1.56%	0.282%	1.52%	19.8%	80.2%	774
H1.3A	15.2%	1.49%	0.332%	2.23%	19.2%	80.8%	729
H1.2B	4.43%	0.829%	12.0%	10.8%	28.1%	71.9%	2,343
H1.2A	0.006%	0.634%	53.1%	18.5%	72.2%	27.8%	4,347
H2.4A	0.006%	0.237%	15.1%	22.2%	37.6%	62.4%	802
H2.4B	0.411%	0.205%	1.70%	2.46%	4.78%	95.2%	655
H2.4C	0.012%	0.063%	7.61%	5.48%	13.2%	86.8%	4,069
H2.4D	0.002%	0.232%	36.3%	28.9%	65.5%	34.5%	2,912
K1.1A	0.007%	0.843%	31.3%	30.5%	62.6%	37.4%	713
K1.1B	0.006%	0.537%	27.1%	26.7%	54.4%	45.6%	847
K1.1C	0.003%	0.170%	41.1%	32.2%	73.5%	26.5%	1,699
K1.3A	0.003%	0.249%	24.7%	20.3%	45.2%	54.8%	1,504
K1.3B	0.003%	0.145%	38.6%	24.7%	63.5%	36.5%	1,818
K1.3C	0.002%	0.123%	40.1%	34.7%	75.0%	25.0%	2,023
K1.4A	0.006%	0.527%	32.5%	27.9%	60.9%	39.1%	809
K1.4B	0.010%	0.987%	38.6%	32.5%	72.1%	27.9%	523
K1.4C	0.011%	1.53%	38.1%	26.9%	66.5%	33.5%	443
K1.4D	0.013%	2.44%	38.8%	27.7%	69.0%	31.0%	394.91

Table 6.1e. Manganese

Table 6.1f. Sulfur

Sample ID	F1	F2	F3	F4	Total Extracted	Residual	Sediment
oumpre in							(mg/kg)
G2.7	2.48%	0.373%	0.373%	0.373%	3.60%	96.4%	1,341
G2.6	75.0%	4.98%	1.07%	22.5%	103%	-3.50%	4,820
G2.5	37.9%	4.28%	7.83%	81.5%	132%	-31.5%	15,898
G3.1A	0.78%	0.237%	0.237%	0.237%	1.49%	98.5%	2,112
G3.1B	2.61%	4.80%	1.31%	0.131%	8.86%	91.1%	3,815
G3.1C	7.31%	0.808%	0.808%	0.808%	9.73%	90.3%	619
G3.1D	65.45%	4.29%	5.79%	41.9%	117%	-17.5%	3,067
G3.3A	2.64%	0.564%	0.564%	0.564%	4.33%	95.7%	886
G3.3B	34.33%	5.06%	0.532%	0.099%	40.0%	60.0%	5,036
G3.3C	26.17%	25.1%	8.03%	4.47%	63.7%	36.3%	20,036
G3.3D	44.85%	16.1%	4.00%	1.26%	66.2%	33.8%	9,409
H1.7	37.79%	9.60%	1.39%	0.107%	48.9%	51.1%	11,343
H1.6	28.43%	24.4%	7.47%	7.03%	67.4%	32.6%	17,941
H1.5C	43.01%	21.8%	5.62%	4.71%	75.1%	24.9%	10,567
H1.5B	20.78%	18.2%	4.94%	8.11%	52.1%	47.9%	16,628
H1.5A	21.24%	16.2%	5.86%	7.03%	50.3%	49.7%	23,728
H1.4	18.75%	7.52%	3.51%	10.8%	40.6%	59.4%	25,290
H1.3B	22.25%	9.41%	5.48%	17.8%	54.9%	45.1%	25,650
H1.3A	24.94%	14.0%	5.98%	12.5%	57.4%	42.6%	19,663
H1.2B	21.27%	10.2%	1.26%	3.21%	36.0%	64.0%	15,072
H1.2A	21.11%	8.41%	8.20%	4.13%	41.9%	58.1%	12,808
H2.4A	5.37%	5.80%	0.647%	0.076%	11.9%	88.1%	6,616
H2.4B	21.36%	11.3%	2.85%	1.82%	37.3%	62.7%	19,925
H2.4C	31.52%	14.8%	3.15%	0.071%	49.6%	50.4%	14,573
H2.4D	40.54%	13.1%	4.61%	0.044%	58.3%	41.7%	11,394
K1.1A	7.21%	0.279%	0.279%	0.279%	8.05%	91.9%	1,792
K1.1B	6.58%	0.198%	0.198%	0.198%	7.18%	92.8%	2,520
K1.1C	35.96%	17.4%	17.6%	18.7%	89.7%	10.3%	13,014
K1.3A	11.76%	0.231%	0.231%	0.231%	12.5%	87.5%	2,165
K1.3B	36.68%	22.1%	15.4%	4.05%	78.2%	21.8%	12,071
K1.3C	45.99%	19.5%	14.3%	7.12%	86.8%	13.2%	10,070
K1.4A	3.87%	0.330%	0.330%	0.330%	4.86%	95.1%	1,515
K1.4B	55.47%	3.57%	1.34%	0.299%	60.7%	39.3%	1,672
K1.4C	63.11%	5.20%	2.64%	0.239%	71.2%	28.8%	2,095
K1.4D	50.71%	4.24%	3.93%	20.4%	79.3%	20.7%	3,156

Table 6.2a. Arsenic

	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)
Loc. G (G2.5	& G2.6 exclu	ded)	_		Count=	9	
Avg	0.18%	6.8%	3.6%	19%	29%	71%	1250
Median	0.089%	6.11%	3.26%	16.2%	26.2%	73.8%	960
Std. Dev	0.225%	2.94%	1.66%	11.2%	15.4%	15.4%	1160
Min	0.024%	2.61%	1.40%	5.89%	9.9%	39.2%	123
Max	0.667%	12.3%	6.77%	41.3%	60.8%	90.1%	4061
Loc. H Count= 14							
Avg	0.29%	11%	4.5%	23%	38%	62%	1713
Median	0.079%	11.0%	5.11%	23.4%	38.8%	61.2%	1914
Std. Dev	0.795%	4.20%	1.45%	9.34%	14.0%	14.0%	742
Min	0.023%	4.56%	1.67%	8.86%	17.0%	34.1%	667
Max	3.05%	18.4%	6.68%	47.0%	65.9%	83.0%	3166
Loc. K (K1.4D	excluded)				Count=	9	
Avg	0.70%	14%	6.3%	30%	50%	50%	865
Median	0.190%	11.7%	5.03%	26.1%	43.8%	56.2%	476
Std. Dev	1.25%	6.79%	3.30%	9.7%	20.4%	20.4%	834
Min	0.005%	8.09%	3.57%	19.2%	31.1%	16.6%	39
Max	3.92%	24.5%	12.0%	46.7%	83.4%	68.9%	2148
All Locations	(G2.5, G2.6,	& K1.4D e>	cluded)		Count=	32	
Avg	0.37%	11%	4.8%	24%	40%	60%	1344
Median	0.085%	9.75%	4.63%	22.5%	36.6%	63.4%	1070
Std. Dev	0.854%	5.37%	2.34%	10.5%	17.8%	17.8%	943
Min	0.005%	2.61%	1.40%	5.89%	9.93%	16.6%	39
Max	3.92%	24.5%	12.0%	47.0%	83.4%	90.1%	4061

Statistical summary of (a) arsenic, (b) aluminum, (c) calcium, (d) iron, (e) manganese, and (f) sulfur extraction percentages from the point bar and cut bank samples on Table 6.1, grouped by sample location.

	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)	
Loc. G					Count=	11		
Avg	0.01%	0.42%	0.02%	8.2%	8.7%	91%	12854	
Median	0.006%	0.432%	0.012%	8.03%	8.81%	91.2%	10505	
Std. Dev	0.015%	0.180%	0.013%	2.22%	2.29%	2.29%	5415	
Min	0.002%	0.174%	0.005%	4.80%	4.98%	87.1%	7742	
Max	0.052%	0.797%	0.046%	12.4%	12.9%	95.0%	22597	
Loc. H Count= 14								
Avg	2.0%	0.61%	0.04%	13%	16%	84%	10407	
Median	0.288%	0.599%	0.037%	10.5%	13.5%	86.5%	7670	
Std. Dev	2.84%	0.245%	0.015%	9.26%	8.56%	8.56%	6037	
Min	0.002%	0.222%	0.012%	5.56%	9.34%	58.6%	5545	
Max	8.34%	1.10%	0.074%	40.1%	41.4%	90.7%	25716	
Loc. K					Count=	10		
Avg	0.004%	0.34%	0.005%	10%	11%	89.4%	13055	
Median	0.004%	0.350%	0.004%	10.1%	10.5%	89.5%	13729	
Std. Dev	0.002%	0.163%	0.002%	1.82%	1.71%	1.71%	4097	
Min	0.003%	0.117%	0.003%	7.58%	8.05%	86.1%	6516	
Max	0.008%	0.568%	0.008%	13.8%	13.9%	92.0%	19140	
All Locat	ions				Count=	35		
Avg	0.80%	0.47%	0.02%	11%	12%	88%	11933	
Median	0.006%	0.436%	0.020%	9.39%	10.8%	89.2%	10358	
Std. Dev	2.01%	0.231%	0.018%	6.29%	6.35%	6.35%	5348	
Min	0.002%	0.117%	0.003%	4.80%	4.98%	58.6%	5545	
Max	8.34%	1.10%	0.074%	40.1%	41.4%	95.0%	25716	

Table 6.2b. Aluminum

Table 6.2c. Calcium

	E1	E2	E3	E4	Total Extracted	Residual	Sediment	
	B 8. C2 2C (voludod)			Count-	0	(IIIg/Kg)	
100. 0 (03.1						9		
Avg	10%	20%	7.4%	35%	73%	27%	17179	
Median	5.99%	19.5%	6.60%	41.9%	75.2%	24.8%	9618	
Std. Dev	13.1%	13.4%	1.86%	12.2%	8.77%	8.77%	17067	
Min	0.772%	3.52%	5.02%	14.2%	59.6%	12.5%	2704	
Max	42.4%	42.4%	10.5%	49.2%	87.5%	40.4%	46280	
Loc. H Count= 14								
Avg	33%	22%	9.8%	9.6%	75%	25%	11186	
Median	31.9%	22.5%	10.0%	8.58%	77%	23%	10235	
Std. Dev	16.0%	7.60%	5.26%	5.94%	20%	20%	4831	
Min	12.8%	6.08%	1.29%	2.17%	37%	0.499%	2703	
Max	70.3%	34.1%	20.7%	26.6%	100%	63%	18734	
Loc. K					Count=	10		
Avg	10%	24%	12%	30%	76%	24%	15155	
Median	7.15%	22.6%	12.2%	33.8%	74.2%	25.8%	15452	
Std. Dev	10.0%	4.73%	2.07%	12.6%	9.78%	9.78%	4419	
Min	1.04%	17.5%	8.38%	12.2%	67.7%	2.51%	6912	
Max	29.0%	33.9%	14.8%	49.0%	97.5%	32.3%	22063	
All Location	s (G3.1B &	G3.3C exc	luded)		Count=	33		
Avg	20%	22%	9.77%	23%	75%	25%	14023	
Median	17.2%	22.1%	9.65%	16.2%	75.2%	24.8%	12419	
Std. Dev	17.5%	8.73%	4.05%	15.3%	14.4%	14.4%	9722	
Min	0.772%	3.52%	1.29%	2.17%	36.9%	0.499%	2703	
Max	70.3%	42.4%	20.7%	49.2%	100%	63.1%	46280	

	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)
Loc. G					Count=	11	
Avg	0.002%	0.08%	0.004%	3.9%	4.0%	96%	75564
Median	0.0002%	0.075%	0.003%	4.11%	4.20%	95.8%	85675
Std. Dev	0.002%	0.021%	0.004%	1.74% 1.73		1.73%	38212
Min	0.00004%	0.046%	0.001%	0.014% 0.128%		94.0%	18514
Max	0.007%	0.116%	0.014%	5.96%	6.01%	99.9%	115664
Loc. H Count= 14							
Avg	0.188%	0.09%	0.006%	6.0%	6.3%	94%	96691
Median	0.0004%	0.099%	0.006%	5.16%	5.64%	94.4%	99964
Std. Dev	0.409%	0.024%	0.004%	2.64% 2.68%		2.68%	13773
Min	0.00004%	0.033%	0.000%	3.24%	3.24% 3.32%		70699
Max	1.43%	0.127%	0.012%	11.0%	11.2%	96.7%	115559
Loc. K					Count=	10	
Avg	0.001%	0.13%	0.002%	8.4%	8.6%	91%	52642
Median	0.0002%	0.119%	0.002%	8.44%	8.56%	91.4%	39563
Std. Dev	0.001%	0.073%	0.001%	0.525%	0.518%	0.518%	32031
Min	0.00005%	0.060%	0.001%	7.45%	7.51%	90.7%	18464
Max	0.003%	0.267%	0.003%	9.13%	9.27%	92.5%	100045
All Locat	ions				Count=	35	
Avg	0.076%	0.10%	0.004%	6.0%	6.2%	94%	77466
Median	0.0002%	0.089%	0.003%	5.66%	5.86%	94.1%	92197
Std. Dev	0.269%	0.048%	0.003%	2.60%	2.63%	2.63%	33289
Min	0.00004%	0.033%	0.0001%	0.01%	0.128%	88.8%	18464
Max	1.43%	0.267%	0.014%	11.0%	11.2%	99.9%	115664

Table 6.2d. Iron

	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)
Loc. G					Count=	11	
Avg	0.26%	0.75%	31%	28%	60%	40%	1281
Median	0.008%	0.627%	36.6%	31.1%	62.2%	37.8%	1122
Std. Dev	0.621%	0.530%	11.9%	7.81%	17.2%	17.2%	1031
Min	0.002%	0.198%	13.5%	11.0%	31.9%	14.5%	416
Max	2.06%	1.80%	53.2%	36.5%	85.5%	68.1%	3897
Loc. H					Count=	13	
Avg	4.5%	0.65%	9.8%	8.4%	23%	77%	1395
Median	2.46%	0.564%	1.15%	4.68%	15.7%	84.3%	752
Std. Dev	5.60%	0.475%	16.0%	8.72%	21.2%	21.2%	1413
Min	0.002%	0.063%	0.124%	1.40%	4.56%	27.8%	286
Max	16.5%	1.56%	53.1%	28.9%	72.2%	95.4%	4347
Loc. K					Count=	10	
Avg	0.006%	0.75%	35%	28%	64%	36%	1077
Median	0.006%	0.532%	38.3%	27.8%	65.0%	35.0%	828
Std. Dev	0.004%	0.742%	5.78%	4.24%	9.21%	9.21%	619
Min	0.002%	0.123%	24.7%	20.3%	45.2%	25.0%	395
Max	0.013%	2.44%	41.1%	34.7%	75.0%	54.8%	2023
All Locat	ions				Count=	34	
Avg	1.9%	0.71%	24%	20%	47%	53%	1268
Median	0.011%	0.596%	24.9%	23.7%	56.9%	43.1%	802
Std. Dev	4.10%	0.563%	16.9%	12.1%	25.6%	25.6%	1093
Min	0.002%	0.063%	0.124%	1.40%	4.56%	14.5%	286
Max	16.5%	2.44%	53.2%	36.5%	85.5%	95.4%	4347

 Table 6.2e.
 Manganese

Table 6.2f. Sulfur

	E1	E2	E3	E4	Total Extracted	Residual	Sediment (mg/kg)	
Loc. G (G2.	6, G2.5, &	G3.1D exclu	uded)		Count=	8		
Avg	15%	6.6%	2.0%	0.99%	25%	75%	5407	
Median	4.97%	2.81%	0.686%	0.468%	9.29%	90.71%	2963	
Std. Dev	17.4%	9.15%	2.73%	1.46%	27.7%	27.67%	6584	
Min	0.779%	0.237%	0.237%	0.099%	1.49%	33.76%	619	
Max	44.9%	25.1%	8.03%	4.47%	66.2%	98.51%	20036	
Loc. H Count= 14								
Avg	26%	13%	4.4%	5.5%	49%	51%	16514	
Median	21.8%	12.2%	4.773%	4.42%	50.0%	50.0%	15850	
Std. Dev	9.94%	5.46%	2.31%	5.40%	15.3%	15.3%	5831	
Min	5.37%	5.80%	0.647%	0.044%	11.9%	24.9%	6616	
Max	43.0%	24.4%	8.20%	17.8%	75.1%	88.1%	25650	
Loc. K					Count=	10		
Avg	32%	7.3%	5.6%	5.2%	50%	50%	5007	
Median	36.3%	3.91%	1.99%	0.31%	65.9%	34.1%	2343	
Std. Dev	22.5%	8.79%	7.15%	7.93%	36.8%	36.8%	4708	
Min	3.87%	0.198%	0.198%	0.198%	4.86%	10.3%	1515	
Max	63.1%	22.1%	17.6%	20.4%	89.7%	95.1%	13014	
All Location	ns (G2.6, G	2.5, G3.1D	excluded)		Count=	32		
Avg	25%	9.7%	4.2%	4.3%	43%	57%	10141	
Median	21.8%	8.91%	3.00%	1.03%	49.2%	50.8%	10318	
Std. Dev	17.2%	7.98%	4.55%	5.89%	27.9%	27.9%	7944	
Min	0.779%	0.198%	0.198%	0.044%	1.49%	10.3%	619	
Max	63.1%	25.1%	17.6%	20.4%	89.7%	98.5%	25650	

Chapter 7. - Tables

Table 7.1. General statistics of untransformed predicted SSF data derived from various linear and polynomial ratings curves (columns A through H) compared to the general statistics of actual SSF data compiled from the USGS database (column J).

	Α	С	E	F	G	Н	J
Predicted SSF (Mg/d)	1 Linear	2 Linear	1 Linear 1 Poly.	2nd Order Poly.	3rd Order Poly.	4th Order Poly.	Actual SSF (Mg/d)
Min	0.00005	0.01336	0.00366	0.00933	0.01251	0.00601	0.00907
Max	23,725	209,582	223,200	2,845,832	908,964	217,424	132,449
Mean	136	1,004	1,129	12,175	4,000	1,116	879
Median	1.79	1.46	1.10	1.18	1.20	1.08	1.45
St. Dev	1,545	13,586	14,535	184,090	58,818	14,184	8,997
Sum (n=239)	32,514	239,906	269,772	2,909,905	955,974	266,834	210,096
% Difference							
Between Predicted	-84.52%	14.19%	28.40%	1285%	355%	27.01%	
and Actual Sum							

Table 7.2. Estimate of the total amount of suspended sediment removed over 30 years and the annual removal rate from WWC.

		2-Linear Fits Regression	4th-Order Polynomial Regression	
Raw 30-Vear Total SSI	Calculated Value:	1,002,991 Mg	1,445,773 Mg	
	(Rounded Estimate)	(1,000,000 Mg)	(1,450,000 Mg)	
Percent Difference Adjustments	Calculated Value:	-14.19%	-27.01%	
Adjusted 30-Year Total SSL	Calculated Value:	860,680 Mg	1,055,327 Mg	
30-Year Total SSL Range	Rounded Estimate:	861,000 to 1,060,000 Mg		
Average Annual Total SSL Range	Rounded Estimate:	timate: 28,000 to 35,000 Mg/yea		

	Predicte	ed Total Annual	Suspended Sediment	: Loads (Mg)	
Year	2 Linear	4th Order Polynomial	Year	2 Linear	4th Order Polynomial
1982	288	197	1998	50,956	90,258
1983	16,181	19,590	1999	19,740	26,368
1984	20,427	27,067	2000	5,106	5,340
1985	260	205	2001	1,616	1,245
1986	6,705	7,411	2002	225	182
1987	2,571	2,037	2003	2,597	2,256
1988	1,423	1,143	2004	139	117
1989	1,574	1,293	2005	953	810
1990	1,387	1,074	2006	9,356	10,568
1991	4,141	4,418	2007	32,754	57,472
1992	319	249	2008	242,063	353,147
1993	12,857	17,713	2009	56,946	95,543
1994	8,920	9,420	2010	14,855	16,631
1995	351,636	472,167	2011	79,579	141,492
1996	32,643	50,360	2012	234	173
1997	24,541	29,828	30-Yr Total: (Rounded estimate)	1,002,991 1,000,000	1,445,773 1,450,000

Table 7.3. Estimated annual total suspended sediment loads (Mg) derived by (a) 2-linear ratings curves and (b) one 4th order polynomial ratings curve.

Table 7.4a. T-test for population differences between 1983-1994 and 1996-2012 time periods at the upstream site. Statistically significant differences were detected in log-SSF populations, but not between log-discharge populations.

Log-SSF	1983-1994	1996-2012	Log-Discharge	1983-1994	1996-2012
Mean	0.298	-0.321	Mean	-0.103	-0.197
Variance	1.378	1.042	Variance	0.179	0.255
Observations	187	67	Observations	187	67
Hyp. Mean Diff.	0		Hyp. Mean Diff.	0	
df	133		df	101	
t Stat	4.085		t Stat	1.367	
P(T<=t) two-tail	7.56E-05		P(T<=t) two-tail	0.175	
t Critical two-tail	1.978		t Critical two-tail	1.984	

Table 7.4b. T-test for population differences between 1983-1994 and 1996-2012 time periods at the downstream site. Statistically significant differences were not detected in either log-SSF populations or log-discharge populations.

Log-SSF	1983-1994	1996-2012	Log-Discharge	1983-1994	1996-2012
Mean	0.318	0.192	Mean	-0.239	-0.287
Variance	1.702	1.548	Variance	0.314	0.599
Observations	170	66	Observations	170	66
Hyp. Mean Diff.	0		Hyp. Mean Diff.	0	
df	124		df	93	
t Stat	0.686		t Stat	0.457	
P(T<=t) two-tail	0.494		P(T<=t) two-tail	0.649	
t Critical two-tail	1.979		t Critical two-tail	1.986	

Year	Annual Average Total- Arsenic Load (Mg)	Annual Average Dissolved- Arsenic Load (Mg)	Annual Average Suspended- Arsenic Load (Mg)	# of Samples Collected per Year
1983	401.39	3.48	397.91	15
1984	640.52	3.89	636.63	14
1985	0.58	0.33	0.25	7
1986-1989	NA	NA	NA	NA
1990	1.28	0.65	0.63	9
1991	1.49	0.71	0.78	10
1992	1.40	0.47	0.93	11
1993	6.58	1.12	5.47	10
1994	13.86	1.02	12.84	8
1995°	165.07	2.12	162.96	3
1996	14.83	1.20	13.63	5
1997	21.56	1.48	20.08	4
1998	1.63	0.91	0.72	4
1999	9.83	1.32	8.50	4
2000	30.36	2.18	28.18	3
2001	1.22	0.58	0.64	5
2002	0.72	0.40	0.32	4
2003	1.64	0.72	0.92	4
2004	0.71	0.41	0.31	4
2005	11.65	0.85	10.79	4
2006	12.91	1.27	11.63	4
2007	4.02	1.03	2.99	4
2008	9.77	1.84	7.92	4
2009	3.55	1.07	2.48	4
2010	8.88	1.11	7.77	4
2011	3.34	1.23	2.11	4
2012	1.44	0.85	0.59	1
Min:	0.58	0.33	0.25	1
Max:	640.52	3.89	636.63	15
Average:	53	1.2	52	Sum: 153

Table 7.5. Annual suspended arsenic load by year over the 30-year period between 1983 to 2012 as calculated by Method #1 (raw data averaging). Data not available from 1986 to 1989.

^a A weighted average was applied to data in 1995 to calculate the annual average arsenic loads, see Equation 7.3 for details.

%-As Ranges	Average %-As Within Each Range	Cumulative Percent	Count
0.0049 - 0.05%	0.03%	19%	29
>0.05 - 0.1%	0.07%	59%	60
>0.1 - 0.15%	0.13%	72%	19
>0.15 - 0.2%	0.16%	79%	10
>0.2 - 0.25%	0.23%	81%	4
>0.25 - 0.3%	0.28%	85%	6
>0.3 - 0.35%	0.31%	87%	3
>0.35 - 0.4%	0.39%	89%	3
>0.4 - 0.45%	0.42%	92%	4
>0.45 - 0.6%	0.54%	94%	3
>0.6 - 1%	0.74%	97%	4
>1 - 2.33%	1.89%	100%	5

Table 7.6. Cumulative percentages of percent-arsenic in suspended sediment (dataset from Figure 7.23).

Table 7.7. Descriptive statistics of the	e percent-arsenic in suspended sediment	(dataset from Figure 7.23).

Mean	0.196%
Median	0.081%
Minimum	0.0049%
Maximum	2.33%
Std. Error	0.029
Std. Dev	0.356
Variance	0.127
25th Percentile	0.05%
50th Percentile	0.08%
75th Percentile	0.16%
Kurtosis	19.597
Skewness	4.244
Count	150

Colu	ımn 1	Column 2	Column 3	Column 4	Colu	mn 5	Colu	mn 6	Colu	mn 7
Range c Average S Sediment (See 'Ca Value' fr 7	of 30 Year Suspended Load (Mg) alculated rom Table .2)	%-As Ranges (Downstream Site Data)	Average %-As Within Each Range	Proportion of Suspended Sediment Load Containing Each Average %-As	Rang Suspe Sedime (Mg) Co Respe Averag [Col 1] >	ge of ended nt Load ntaining ective ge %-As k [Col 4]	Rang Propor Weig Suspen Load [Col 3] >	ge of tionally hted ded-As (Mg) < [Col 5]	Range o Suspen Load (Mg Co	f 30 Year Ided-As g) [Sum of l 6]
Min	Max	(See Table	e 7.6 and Fig	ure 7.23)	Min	Max	Min	Max	Min	Мах
860,680	1,055,327	$\begin{array}{c} 0.0049\% - 0.05\% \\ > 0.05 - 0.1\% \\ > 0.1 - 0.15\% \\ > 0.15 - 0.2\% \\ > 0.2 - 0.25\% \\ > 0.25 - 0.3\% \\ > 0.3 - 0.35\% \\ > 0.35 - 0.4\% \\ > 0.4 - 0.45\% \\ > 0.45 - 0.6\% \\ > 0.6 - 1\% \end{array}$	0.03% 0.07% 0.13% 0.16% 0.23% 0.28% 0.31% 0.39% 0.42% 0.54% 0.74%	0.1933 0.4000 0.1267 0.0667 0.0267 0.0400 0.0200 0.0200 0.0267 0.0200 0.0267	166,398 344,272 109,019 57,379 22,951 34,427 17,214 22,951 17,214 22,951	204,030 422,131 133,675 70,355 28,142 42,213 21,107 21,107 28,142 21,107 28,142	50.66 244.33 136.57 94.16 53.32 97.94 53.91 66.95 96.75 92.28 170.13	62.12 299.58 167.45 65.37 120.09 66.10 82.09 118.64 113.15 208.60	1,700 (57 Mg per year)	2,100 (70 Mg per year)

Table 7.8. Using calculated suspended sediment loads and percent-arsenic in suspended sediments to estimate the amount of suspended-arsenic transported out of WWC, weighted by mass using historical data compiled from 1982-2012.

Table 7.9. Summary of 30-year and annual calculated average suspended arsenic loads by three methodologies. The 30-year suspended arsenic load was not calculated under Method #1 because data is not available from 1986-1989 to calculate the 30-year sum.

	Calculated Average Suspended Arsenic Load (Mg)			
Method	30-Year	Annual		
#1 Raw Data Averaging	N/A	52		
#2 Ratings Curve / Regression	980	33		
#3 Data Extrapolation	1,700 - 2,100	57 - 70		

Table 7.10. Estimated suspended-arsenic, dissolved-arsenic, and total-arsenic transport rates out of WWC.

Estimated Rate of Annual Arsenic Transport (Mg/year)				
Estimated Range Annual Suspended-Arsenic (see Table 7.9):	33 to 70			
Estimated Average Annual Dissolved-Arsenic (see Table 7.5):	1.2			
Estimated Range of Annual Total-Arsenic Transport Rate:	34 to 71			

 Table 7.11. Estimated timespan for complete arsenic removal from WWC.

Estimated amount of contaminated sediment stored along WWC in 1990 as reported by the literature ¹ :	14,500,000 Mg
Estimated range of arsenic percentages in tailings as reported by the literature ² :	0.12% to 0.35%
Estimated range of amount of arsenic stored in contaminated sediment along WWC in 1990:	17,400 to 50,800 Mg
Estimated annual rate of total arsenic transport by WWC (see Table 7.10):	34 to 71 Mg/year
Estimated total timespan for arsenic removal from WWC:	250 to 1,500 years

¹ Marron, 1992.

² South Dakota Department of Health, 1960 (0.12% arsenic) and Noble, 1950 (0.35% arsenic) as summarized in the publication by Goddard, 1989.

FIGURES





Figure 2.1. Map of study area (WWC in red and the BFR in blue), the surrounding region, and connections between the main water bodies of the region. Source: Cherry et al., 1986.



Figure 2.2. Flow paths of WWC (in red) and the BFR (in blue). WWC's drainage basin is delineated by the long, dashed lines. Location of Homestake Mine (in yellow) and the extent of the Superfund Site (in green). Source: Cherry et al., 1986.



Figure 2.3. Boundary of the 100-year flood zone along WWC assumed to have high arsenic concentrations. Development and well-water usage in this region are banned. Source: U.S. EPA, 2012.



Figure 2.4. Whitewood Creek on the Berger property between the town of Whitewood and its confluence with the Belle Fourche River (i.e., sample location G – see sample location map on Figure 4.1). Evidence of bank instability and lateral erosion into the cut-banks.



Figure 2.5. The Belle Fourche River at the intersection with State Highway 34, facing upstream (i.e., sample location K – see sample location map on Figure 4.1). An example of high bluffs and terraces forming the cut banks along the BFR.

Chapter 3. - Figures



Figure 3.1. Exposed cut-bank with evidence of erosion and visible color changes in the sediment along WWC at the Berger Site (Location G). See field personnel in photo for scale.

Chapter 4. - Figures



Figure 4.1. Stream water, seep water, and sediment sampling locations along Whitewood Creek and the Belle Fourche River, South, Dakota



Figure 4.2. Field parameters: a) pH, b) dissolved oxygen, c) specific conductance, and d) temperature; data collected from in-stream waters of Whitewood Creek and the Belle Fourche River and in three seep waters collected from Whitewood Creek.





Figure 4.3. Analytes of Interest (AOIs): (a) total and (b) dissolved concentrations of in-stream surface water samples collected from Whitewood Creek and the Belle Fourche River. A star * denotes that ICP-OES results are reported for that sample (i.e., not enough sample was left to be analyzed by ICP-MS). All other results are by ICP-MS.



Figure 4.4. The proportion (in percent) of analytes of interest (AOIs) in the dissolved phase (i.e., dissolved concentration divided by total concentration x 100). Only in-stream samples are presented. A star * denotes that ICP-OES results are reported for that sample (i.e., not enough sample was left to be analyzed by ICP-MS). All other results are by ICP-MS.





Figure 4.5. a) Total and b) dissolved analyte concentrations in seep samples compared to their co-located in-stream sample concentrations.



Figure 4.6. Average annual total, suspended, and dissolved arsenic concentrations and discharge data collected from 15 USGS gauging locations along WWC from 1983 to 2012. The EPA Maximum Contaminant Level (MCL) is provided for comparison. There is not a peak in arsenic levels during 2008 because arsenic concentrations were not analyzed for during the 2008 peak flow event.



Figure 4.7. Trends of average annual dissolved and suspended arsenic percentages compared to average annual discharge collected from 15 USGS gauging locations along WWC from 1983 to 2012. Annual averages reflect the average of percentages over the number of samples of collected per one year period and captures the effects of samples collected during flooding (ex: 1995).



Figure 4.8. A negative correlation between percent of dissolved arsenic and its paired-discharge values collected in WWC between 1983 and 2012 (n = 346).

Chapter 5. - Figures



Figure 5.1. Location D: general overview of sample location. WWC flowing through bedrock canyons with banks formed with coarse sized sand to large cobbles and heavily vegetated surroundings.



Figure 5.2. Location D: banks with abundant cobble-sized clasts and low deposition of fine material on the floodplains.



Figure 5.3. Location G: general overview of sample location. WWC is incised into unstable and slumping exposed cut-banks on the right, the flood plain can be seen on the far right, and cobble sized bed load in the center.



Figure 5.4. Location G: sample IDs G2.1 to G 2.8. Exposed bank (4m tall) with shale bedrock at the bottom then grading from the coarser material (cobble to pebble sized) to finer material (sand to clay sized) towards the top. Contact with the shale bedrock is not shown but is below the view of the photo.



Figure 5.5. Location G: lenses of deep adobe red silty-clay intermixed with dark gray layers approximately 0.3 meters from the top.



Figure 5.6. Location G: exposure of point bar sediment, evidence of multiple flooding events re-working alluvial sediments and depositing sand to cobble sized alluvial sediments and finer grained grey lenses (interpreted to be tailings).



Figure 5.7. Location H: general overview of sample location. WWC incised into unstable exposed sediment, cut banks on the left.



Figure 5.8. Location H: a portion of the sampled exposed cut bank with high amounts of cobble and gravel sized material.



Figure 5.9. Location H: samples H1.1 to H 1.7 collected from exposed cut-bank (4.5m tall) with shale bedrock at the bottom and interbedded layers of coarse (cobble and gravel sized) and fine (clay-silt-sand) material on top.



Figure 5.10. Location H: lenses of grey fine-grained sandy silt intermixed with dark red/rusty brown clay (H1.5A) and lenses of grey and yellowish brown silty clay (H1.5C) in a matrix of yellow-orange silty sand (H1.5B).



Figure 5.11. Location K: general overview of sample location (point bar). This photo is oriented facing downstream on the BFR towards the point bar comprised of grassy flat plains.



Figure 5.12. Location K: an unstable exposed cut-bank (opposite bank to Figure 5.11) with incision into shale bedrock. Down slumping of material from above can be seen in the foreground of the lower left corner.



Figure 5.13. Location K: exposed cut-bank composed of a vegetated topsoil layer at the surface, followed below by interbedded thin layers of pebble to cobble sized clasts and thick layers of sand, silts, and clays.



Figure 5.14a, b, c. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected on the cut bank profiles of Locations G and H. Samples H1.5, H1.3, and H1.2 are comprised of the average of 2 to 3 individual samples (see Table 5.2 for details). Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample H1.7 is plotted on the Y-axis at 0.5 m, which is representative of the 0 to 0.5 m depth interval from which the sample was collected.


Figure 5.14d, e, f. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected on the cut bank profiles of Locations G and H. Samples H1.5, H1.3, and H1.2 are comprised of the average of 2 to 3 individual samples (see Table 5.2 for details). Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample H1.7 is plotted on the Y-axis at 0.5 m, which is representative of the 0 to 0.5 m depth interval from which the sample was collected.



Figure 5.14g, h, i. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected on the cut bank profiles of Locations G and H. Samples H1.5, H1.3, and H1.2 are comprised of the average of 2 to 3 individual samples (see Table 5.2 for details). Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample H1.7 is plotted on the Y-axis at 0.5 m, which is representative of the 0 to 0.5 m depth interval from which the sample was collected.



Figure 5.14j, k, l. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected on the cut bank profiles of Locations G and H. Samples H1.5, H1.3, and H1.2 are comprised of the average of 2 to 3 individual samples (see Table 5.2 for details). Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample H1.7 is plotted on the Y-axis at 0.5 m, which is representative of the 0 to 0.5 m depth interval from which the sample was collected.



Figure 5.15. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected 18 meters from the bank of WWC on the point bar of Location D. Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample D3.3B is plotted on the Y-axis at 0.71 m, which is representative of the 0.23 to 0.71 m depth interval from which the sample was collected.





Figure 5.16a, b. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of WWC on the point bar of Location G. Each point is plotted at the maximum depth interval from which the sample was collected from. For example, sample G3.1C is plotted on the Y-axis at 1.04 m, which is representative of the 0.41 to 1.04 m depth interval from which the sample was collected.





Figure 5.16c, d. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of WWC on the point bar of Location G. For example, sample G3.3D is plotted on the Y-axis at 1.01 m, which is representative of the 0.76 to 1.01 m depth interval from which the sample was collected.





Figure 5.17a, b. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of WWC on the point bar of Location H. For example, sample H2.3A is plotted on the Y-axis at 0.35 m, which is representative of the 0 to 0.35 m depth interval from which the sample was collected.



Figure 5.17c. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of WWC on the point bar of Location H. For example, sample H2.4B is plotted on the Y-axis at 0.43 m, which is representative of the 0.23 to 0.43 m depth interval from which the sample was collected.





Figure 5.18a, b. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of the BFR on the point bar of Location K. For example, sample K1.1C is plotted on the Y-axis at 1.14 m, which is representative of the 0.79 to 1.14 m depth interval from which the sample was collected.





Figure 5.18c, d. Concentrations of analytes of interest (AOIs) by depth from sediment samples collected at various distances from the bank of the BFR on the point bar of Location K. For example, sample K1.4D is plotted on the Y-axis at 1.01 m, which is representative of the 0.81 to 1.01 m depth interval from which the sample was collected.



Figure 5.19. Concentrations of analytes of interest (AOIs) of in-stream sediment samples collected from the active channel of WWC and the BFR.



Figure 5.20a. Relationship between arsenic and iron concentrations in sediment samples collected from the cut-bank and point bar of Location G. Vertical red dashed lines denote 200 mg/kg and 2,000 mg/kg arsenic; horizontal red dashed line denotes 50,000 mg/kg iron. The black dashed trendline is based on all samples collected from Locations G, H, and K. The green solid trendline is based on Location G samples. Samples generally plot in the three corners of the triangle elucidated by the orange dashed lines. Sediments with relatively low contamination plots in the region of box A, sediments with elevated arsenic but high iron plot in the region of box B, and sediments with high-arsenic and high iron plot in the region of box C.



Figure 5.20b. Relationship between arsenic and iron concentrations in sediment samples collected from the cut-bank and point bar of Location H. Vertical red dashed lines denote 200 mg/kg and 2,000 mg/kg arsenic; horizontal red dashed line denotes 50,000 mg/kg iron. The black dashed trendline is based on all samples collected from Locations G, H, and K. The green solid trendline is based on Location H samples. Samples generally plot in the three corners of the triangle elucidated by the orange dashed lines. Sediments with relatively low contamination plots in the region of box A, sediments with elevated arsenic but high iron plot in the region of box B, and sediments with high-arsenic and high iron plot in the region of box C.



Figure 5.20c. Relationship between arsenic and iron concentrations in sediment samples collected from the point bar of Location K. Vertical red dashed lines denote 200 mg/kg and 2,000 mg/kg arsenic; horizontal red dashed line denotes 50,000 mg/kg iron. The black dashed trendline is based on all samples collected from Locations G, H, and K. The green solid trendline is based on Location K samples. Samples generally plot in the three corners of the triangle elucidated by the orange dashed lines. Sediments with relatively low contamination plots in the region of box A, sediments with elevated arsenic but high iron plot in the region of box C.





Figure 6.1a. Percentage of (a) arsenic, (b) aluminum, (c) calcium, (d) iron, (e) manganese, and (f) sulfur extracted by each extractant (E1, E2, E3, and E4) relative to its total sediment concentration. Samples are ordered upstream to downstream and grouped from surface to subsurface (left to right). Samples with greater than 100% recovery in the extraction relative to that analyzed in the total content of the sediment sample (shown in black lines) was likely due to instrumentation or precision error and were excluded from graphical representation. See Table 6.1 for dataset.



Figure 6.1b.



Figure 6.1c.



Figure 6.1d.



Figure 6.1e.



Figure 6.1f.



Figure 6.2a. Comparison of average extraction percentages of (a) arsenic, (b) aluminum, (c) calcium, (d) iron, (e) manganese, and (f) sulfur by each extractant (E1, E2, E3, E4) grouped by samples collected from upstream (locations G and H) and downstream (location K) locations. See Table 6.2 for dataset.



Figure 6.2b.



Figure 6.2c.



Figure 6.2d.



Figure 6.2e.



Figure 6.2f.



Figure 6.3a. Extractions (E1, E2, E3, and E4) performed on all sediment samples (collected from locations G, H, and K) comparing the analyte's concentration [(a) arsenic, (b) aluminum, (c) calcium, (d) iron, (e) manganese, and (f) sulfur] in the sediment to its extracted concentrations from the sediment. See Appendix 6-4 for dataset.

	<u>Slope</u>	$\underline{\mathbf{R}^2}$		<u>Slope</u>	<u>R²</u>
E1:	0.0001	0.0002	Total:	0.31	0.70
E2:	0.08	0.61	Residual:	0.69	0.92
E3:	0.04	0.72			
E4:	0.19	0.70			



E3: 0.00005 0.020 E4: 0.10 0.51







_	<u>Slope</u>	<u>R</u> ²		<u>Slope</u>	<u>R</u> ²		
E1:	0.0026	0.0065	Total:	0.56	0.70		
E2:	0.0035	0.32	Residual:	0.44	0.60		
E3:	0.36	0.67					
E4:	0.19	0.61					



E4: 0.10

0.56



Figure 6.4a. Relationship between extracted aluminum and extracted arsenic concentrations.

0		1			
	<u>Slope</u>	<u>R²</u>		<u>Slope</u>	<u>R²</u>
E1:	0.03	0.33	Total:	0.1	0.05
E2:	-0.86	0.055	Residual:	0.0044	0.00
E3:	4.80	0.037			
E4:	0.06	0.04			







Figure 6.4c. Relationship between extracted iron and extracted arsenic concentrations.

0		-			
	<u>Slope</u>	<u>R²</u>		<u>Slope</u>	<u>R²</u>
E1:	0.023	0.8	Total:	0.094	0.42
E2:	2.63	0.4	Residual:	0.016	0.44
E3:	6.18	0.28			
E4:	0.06	0.35			





	<u>Slope</u>	<u>R²</u>		<u>Slope</u>	<u>R²</u>
E1:	0.11	0.31	Total:	-0.16	0.12
E2:	-2.82	0.043	Residual:	-0.08	0.01
E3:	-0.03	0.14			
E4·	-0.21	0.07			



	Slope	<u>R²</u>		<u>Slope</u>	<u>R²</u>
E1:	0.0009	0.064	Total:	0.036	0.25
E2:	0.04	0.32	Residual:	0.043	0.07
E3:	0.03	0.17			
E4:	0.07	0.11			

Chapter 7. - Figures



Figure 7.1. A slightly right-skewed distribution of whole-population log-transformed discharge values collected from November 1982 to November 2012 at WWC Above Whitewood (upstream site).



Figure 7.2. A left-skewed distribution of whole-population log-transformed discharge values collected from November 1982 to November 2012 at WWC Above Vale (downstream site). A zero discharge is represented by a log-discharge value of less than -5.5.



Figure 7.3. A right-skewed distribution of sub-population log-transformed discharge values collected from January 1983 to October 2012 at WWC Above Whitewood (upstream site).



Figure 7.4. A slightly left-skewed distribution of sub-population log-transformed discharge values collected from January 1983 to October 2012 at WWC Above Vale (downstream site).



Figure 7.5. A right-skewed distribution of sub-population log-transformed SSF values collected from January 1983 to October 2012 at WWC Above Whitewood (upstream site).



Figure 7.6. A right-skewed distribution of sub-population log-transformed SSF values collected from January 1983 to October 2012 at WWC Above Vale (downstream site).



Figure 7.7. One linear regression fitting log-transformed discharge and log-transformed SSF data at the downstream site.



Figure 7.8. The residual plot (difference between actual and predicted log-SSF versus actual log-discharge) of the one linear regression from Figure 7.7.



Figure 7.9. Two linear regressions fitting log-transformed discharge and log-transformed SSF data at the downstream site.



Figure 7.10. 4th-order polynomial regression fitting log-transformed discharge and log-transformed SSF data at the downstream site.



Figure 7.11. The residual plot (difference between actual and predicted log-SSF versus actual log-discharge) of the two linear regressions from Figure 7.9.



Figure 7.12. A unimodal, approximately normal distribution of residuals with a mean near zero for the 2 linear regression fit of downstream site SSF.



Figure 7.13. The residual plot (difference between actual and predicted log-SSF versus actual log-discharge) of the 4th order polynomial regression from Figure 7.10.



Figure 7.14. A unimodal, normal distribution of residuals with a mean near zero for the 4th order polynomial regression fit of downstream site SSF.


Figure 7.15. Comparison of actual daily SSF measurements (239 sampled days) against ratings curve derived SSF predictions calculated from 2-linear ratings curves and one 4th order polynomial ratings curve.



Figure 7.16. Comparison of annual totals of estimated daily SSFs over 30 years of data (10,959 samples), derived by 2-linear ratings curve and one 4th order polynomial ratings curve. The predicted daily max SSF value per year is plotted to show how the annual SSF in some years can be dominated by even one day of high flow and high suspended sediment transport.



Figure 7.17. Populations of SSF's between the 1983-1994 and 1996-2012 time periods at the upstream site.



Figure 7.18. Populations of SSF's between the 1983-1994 and 1996-2012 time periods at the downstream site.



Figure 7.19. A second-order polynomial regression fitting log-transformed discharge and log-transformed suspended-arsenic concentration data at the downstream site.



Figure 7.20. The residual plot (difference between actual and predicted log-suspended arsenic concentrations versus actual log-discharge) of the second order polynomial regression from Figure 7.19.



Figure 7.21. A unimodal, normal distribution of residuals with a mean near zero for the second order polynomial regression fit of suspended arsenic concentrations at the downstream site.



Figure 7.22. A comparison of actual suspended arsenic concentration measurements (153 sampled days) and ratings curve derived suspended arsenic concentration predictions (153 predictions) at the downstream site.



Figure 7.23. A frequency plot displaying a right-skewed distribution of percent arsenic in suspended sediment. Data compiled from the WWC Above Vale station (downstream site).



Figure 7.24. A right-skewed distribution of dissolved arsenic concentrations collected between January 1983 to October 2012 at WWC Above Vale (downstream site).



Figure 7.25. Scatterplot of the negative relationship between dissolved arsenic concentrations and logdischarge at WWC Above Vale (downstream site) between 1983 to 2012.



Figure 7.26. The inverse exponential relationship between the dissolved/total arsenic load ratio and annual average discharge. The data from this graph was tabulated from the dataset displayed in Table 7.5.

REFERENCES

- Abollino, O., Giacomino, A., Malandrino, M., Mentasti, E., Aceto, M., Barberis, R., 2006. Assessment of Metal Availability in a Contaminated Soil by Sequential Extraction. Water, Air, and Soil Pollution, vol. 137, p. 315-338.
- Abollino, O., Malandrino, M., Giacomino, A., Mentasti, E., 2011. The role of chemometrics in single and sequential extraction assays: A review, Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition. Analytica Chimica Acta, vol. 688, p. 104-121.
- Al-Abed, S.R., Jegadeesan, G., Purandare, J., Allen, D., 2007. Arsenic release from iron rich mineral processing waste: Influence of pH and redox potential. Chemosphere, vol. 66, p. 775-782.
- American Society for Testing and Materials (ASTM), 2000, Standard test methods for determining sediment concentration in water samples: D 3977-97, vol. 11.02, Water (II), p. 395-400.
- Appelo, C.A.J., Van der Weiden, M.J.J., Tournassat, C., and Charlet, L., 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environmental Science and Technology, vol. 36: p. 3096-3103.
- Arai, Y., Elzinga, E.J., Sparks, D.L., 2001. X-ray absorption spectroscopic investigation of arsenite and arsenate adsorption at the aluminum oxide-water interface. Journal of Colloid and Interface Science, vol. 235, p. 80-88.
- Asta, M.P., Cama J., Ayora, C., Acero, P., Giudici G., 2010. Arsenopyrite dissolution rates in O2-bearing solutions. Chemical Geology, vol. 273, p. 272-285.
- Asselman, N.E.M. 2000. Fitting and interpretation of sediment rating curves. Journal of Hydrology, 234, p. 228-248.
- Barona, A., Aranguiz, I., Elias, A., 1999. Zinc and copper distribution in soils and their removal by chelating extraction. Journal of Chemical Technology & Biotechnology, vol. 74, p. 700–708.
- Bermond, A.P., Eustache, S., 1993. Hydoxylamine extraction of trace metals in soils; kinetic aspects. Environmental Technology, vol. 14, pg. 359-365.
- Borch, T., Masue, Y., Kukkadapu, R.K., Fendorf, S., 2007. Phosphate imposed limitations on biological reduction and alteration of Ferrihydrite. Environmental Science and Technology, vol. 41, p. 166-172.
- Bowell, R.J., 1994. Sorption of arsenic by iron oxides and hydroxides in soils. Applied Geochemistry, vol. 9, p. 279-286.
- Caddey, S.W., Bachman, R.L., Campbell, T.J., Reid, R.R., Otto, R.P., 1991. The Homestake gold mine, an early Proterozoic iron-formation-hosted gold deposit, Lawrence County, South Dakota. U.S. Geological Survey Bulletin, vol. 1857, Ch. J.

- Catalano, J. G., C. Park, Fenter, P., Zhang, Z., 2008. Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. Geochimica et Cosmochimica Acta, vol. 72, p. 1986-2004.
- Chen, M., Ma, L.Q., Harris, W.G., 2002. Arsenic concentrations in Florida surface soils: influence of soil type and properties. Soil Science Society of America Journal, vol. 66, p. 632-640.
- Cherry, J.A., Morel, F.M.M., Rouse, J.V., Schnoor, J.L., Wolman, M.G., 1986. Hydrogeochemistry of sulfide and arsenic-rich tailings and alluvium along Whitewood Creek, South Dakota. Colorado School of Mines, Mineral and Energy Resources, v.29, no. 4, 5, 6.
- Corkhill, C.L., Vaughan, D.J., 2009. Arsenopyrite oxidation A review. Applied Geochemistry, vol. 24, p. 2342-2361.
- Corriveau, M.C., Jamieson, H.E. Parsons, M.B., Hall, G.E.M, 2011. Mineralogical characterization of arsenic in gold mine tailings from three sites in Nova Scotia. Geochemistry Exploration, Environment, Analysis, vol. 11, p. 179-192.
- Craw, D., Falconer, D., Youngson, J.H., 2003. Environmental arsenopyrite stability and dissolution: theory, experiment, and field observations. Chemical Geology, vol. 199, p. 71-82.
- Davis, A., Ruby, M.V., Bloom, M., Schoof, R., Freeman, G., Bergstrom, P.D., 1996. Mineralogic constraints on the bioavailability of arsenic in smelter-impacted soils. Environmental Science and Technology, vol. 30, p. 392-399.
- Dixit, S., Hering, J.G., 2003. Comparison of Arsenic(V) and Arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environmental Science Technology, vol. 37, p. 4182-4189.
- Donahue, R., Hendry, M.J., Landine, P., 2000. Distribution of arsenic and nickel in uranium mill tailings, Rabbit Lake, Saskatchewan, Canada. Applied Geochemistry, vol. 15, p. 1097-1119.
- Duan, Naihua. 1983. Smearing Estimate: A Nonparametric Retransformation Method. Journal of American Statistical Association, 78, p. 605–610.
- Eiche, E., Kramar, U., Berg, M., Berner, Z., Norra, S., Neumann, T., 2010. Geochemical changes in individual sediment grains during sequential arsenic extractions. Water Research, vol. 44, p. 5545-5555.
- Fendorf, S.E., Eick, M.J., Grossl, P.R., Sparks, D.L., 1997. Arsenate and chromate retention mechanisms on goethite. Environmental Science and Technology, vol. 31, p. 315-320.
- Fendorf, S., Nico, P.S., Kocar, B.D., Masue, Y., Tufano, K.J., 2010. Chapter 12 Arsenic Chemistry in Soils and Sediments, vol. 34, p. 357-378.
- Ferguson, R.I. 1986. River Loads Underestimated by Rating Curves. Water Resources Research, 22, No.1, p. 74–76.
- Fox Consultants, Inc. 1984a. Whitewood Creek Study, Phase I. Prepared for the South Dakota Department of Water and Natural Resources Office of Air Quality and Solid Waste. April 16, 1984.

- Fox Consultants, Inc. 1984b. Whitewood Creek Study, Phase II. Prepared for the South Dakota Department of Water and Natural Resources Office of Air Quality and Solid Waste, Homestake Mining Company and the United States Environmental Protection Agency. November 1984.
- Frost, R.R., Griffin, R.A., 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Science Society of America Journal, vol. 41, p. 53-57.
- Fuller C.C., Davis, J.A., Claypool-Frey, R.G., 1987. Partitioning of arsenic by iron oxides in Whitewood Creek, South Dakota, in Mallard, G.E., ed., U.S. Geological Survey Toxic Substances Hydrology Program: Surface-Water Contamination: Proceedings of the technical meeting, Denver, Colorado, February 2-4, 1987: U.S. Geological Survey Open File Report 87-764, p. 19-21.
- Fuller, C.C., Davis, J.A., Waychunas, G.A., 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochimica et Cosmochimica Acta, vol. 57, p. 2271-2282.
- Geochemical Earth Reference Model (GERM) Reservoir Database. www.EarthRef.org.
- Giacomino, A., Abollino, O., Malandrino, M., Mentasti, E., 2011. The role of chemometrics in single and sequential extraction assays: A review, Part II. Cluster analysis, multiple linear regression, mixture resolution, experimental design and other techniques. Analytica Chimica Acta, vol. 688, p. 122-139.
- Goddard, K.E., 1987. Gold-mill-tailings contamination of the Cheyenne River system, western South Dakota, in Mallard, G.E., ed., U.S. Geological Survey Toxic Substances Hydrology Program. Surface-Water Contamination: Proceedings of the technical meeting, Denver, Colorado, February 2-4, 1987. U.S. Geological Survey Open File Report 87-764, p. 1-10.
- Goddard, K.E., 1989. Composition, distribution, and hydrological effects of contaminated sediments resulting from the discharge of gold-mining wastes to Whitewood Creek at Lead and Deadwood, South Dakota. U.S. Geological Survey Water Resources Investigation Report 87-4051.
- Goddard, K.E. and Wuolo, R.W., 1987. Processes controlling the concentration of dissolved arsenic in Whitewood Creek, South Dakota, in Mallard, G.E., ed., U.S. Geological Survey Toxic Substances Hydrology Program: Surface-Water Contamination: Proceedings of the technical meeting, Denver, Colorado, February 2-4, 1987: U.S. Geological Survey Open File Report 87-764, p. 23-25.
- Goolsby D.A., Battaglin, W.A., Aulenbach, B.T., Hooper, R.P. 2001. Nitrogen Input to the Gulf of Mexico. Journal of Environmental Quality, 30, p. 329–336.

Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Made, B., Noiriel, C., 2015. Arsenic behavior in river sediments under redox gradients: A review. Science of the Total Environment, v. 505, p. 423-434.

- Grafe, M., Eick, M.J., and Grossl, P.R., 2001. Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon. Soil Science Society of America Journal, vol. 65, p. 1680-1687.
- Grafe, M., Eick, M.J., Grossl, P.R., and Saunders, A.M., 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. Journal of Environmental Quality, vol. 31, p. 1115-1123.

- Grafe, M., Tappero, R.V., Marcus, M.A., 2008. Arsenic speciation in multiple metal environments: II. Micro-spectroscopic investigation of a CCA contaminated soil. Journal of Colloid and Interface Science, vol. 321, p. 1-20.
- Grosbois, C., Courtin-Nomade, A., Robin, E., Bril, H., Tamura, N., Schafer, J., Blanc, G., 2011. Fate of arsenic-bearing phases during the suspended transport in a gold mining district (Isle river Basin, France). Science of the Total Environment, vol. 409, p. 4986-4999.
- Harris, G.B., Monette, S., 1989. The disposal of arsenical residues. In: Proceedings of Productivity and Technology in the Metallurgical Industries, Cologne, West Germany.
- Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science, vol. 298, p. 1602-1606.
- Hass, A., Fine, P., 2010. Sequential selective extraction procedures for the study of heavy metals in soils, sediment, and waste materials - a critical review. Critical Reviews in Environmental Science and Technology, vol. 40, p. 365-399.
- Homestake Gold Mine, 1976. 1876 Homestake Centennial 1976, Homestake Mining Company, Lead, South Dakota.
- Horowitz A.J., 1995. The Use of Suspended Sediment and Associated Trace Elements in Water Quality Studies. IAHS Press. IAHS Special Publication No. 4, p. 58.
- Horowitz, A.J., Elrick, K.A., Smith, J.J. 2001. Estimating Suspended Sediment and Trace Element Fluxes in Large River Basins: Methodological Considerations as Applied to the NASQAN Program. Hydrological Process, 15, p. 1107–1132.
- Horowitz, A.J. 2002. The Use of Rating (Transport) Curves to Predict Suspended Sediment Concentration: A Matter of Temporal Resolution. Turbidity and Other Sediment Surrogates Workshop, April 30 - May 2, 2002, Reno, NV.
- Horowitz, A.J. 2008. Determining Annual Suspended Sediment and Sediment-Associated Trace Element and Nutrient Flux. Science of the Total Environment, 400, p. 315-343.
- Huang, J.H., Kretzschmar, R., 2010. Sequential extraction method for speciation of arsenate and arsenite in mineral soils. Analytical Chemistry, vol. 82, pg. 5534-5540.
- Hudson-Edwards, K.A., Houghton, S.L., Osborn, A., 2004. Extraction and analysis of arsenic in soils and sediments. Trends in Analytical Chemistry, vol. 23, p. 745-752.
- Jain, A., and Loeppert, R.H., 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. Journal of Environmental Quality, vol. 29, p. 1422-1430.
- Juillot, F., Ildefonse, Ph., Morin, G., Calas, G., De Kersabiec, A.M., Benedetti, M., 1999. Remobilization of arsenic from buried wastes at an industrial site: mineralogical and geochemical control. Applied Geochemistry, vol. 14, p. 1031-1048.

- Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. Environmental Science Technology, vol. 35, p. 2778-2784.
- Ko, I., Kim, J.Y., Kim, K.W., 2004. Arsenic speciation and sorption kinetics in the Ashematite-humic acid system. Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 234, p. 43-50.
- Kocar, B. D.; Herbel, M. J.; Tufano, K. J.; Fendorf, S., 2006. Contrasting effects of dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport. Environmental Science and Technology, vol. 40, p. 6715-6721.
- Koch, Roy W., Smillie, Gary M. 1986. Comment on "River Loads Underestimated by Rating Curves" by R.I. Ferguson. Water Resources Research, 22, No. 13, p. 2121–2122.
- Krause, E., Ettel, V.A., 1989. Solubilities and stabilities of ferric arsenate compounds. Hydrometall, vol. 22, p. 311–337.
- Larios, R., Martinez, R.F., Alvarez, R., Rucandio, I., 2012. Arsenic pollution and fractionation in sediments and mine waste samples from different mine sites. Science of the Total Environment, vol. 431, p. 426-435.
- Larios, R., Martinez, R.F., Silva, V., Rucandio, I., 2013. Chemical availability of arsenic and heavy metals in sediments from abandoned cinnabar mine tailings. Environmental Earth Science, vol. 68, p. 535-546.
- Leinz, R.W., Sutley, S.J., Desborough, George A., Briggs, P.H., 2000. An investigation of partitioning of metals in mine wastes using sequential extractions. ICARD 2000 Proceedings, vol. I and II, pg. 1489-1499.
- Lombi, E., Sletten, R.S., Wenzel, W.W., 2000. Sequentially extracted arsenic from different size fractions of contaminated soils. Water, Air, and Soil Pollution, vol. 124, pg. 319-332.
- Manning, B.A., and Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Science Society of America Journal, vol. 60, p. 121-131.
 Manning, B.A., and Goldberg, S., 1997a. Arsenic (III) and arsenic (V) absorption on three California soils. Soil Science, vol. 162, p. 886-895.
- Manning, B.A., and Goldberg, S., 1997b. Adsorption and stability of arsenic (III) at the clay mineralwater interface. Environmental Science and Technology, vol. 31, p. 2005-2011.
- Manning, B.A., Fendorf, S., Bostick, B.C., and Suarez, D.L., 2002. Arsenic (III) oxidation and arsenic (V) adsorption reactions on synthetic birnessite. Environmental Science and Technology, vol. 36, p. 976-981.
- Markus, Momcilo; Demissie, Misganaw. 2006. Predictability of Annual Sediment Loads Based on Flood Events. Journal of Hydrologic Engineering, 11, v4. P. 354-361.
- Marron, D.C., 1989. The transport of mine tailings as suspended sediment in the Belle Fourche River, west-central South Dakota, USA. Sediment and the Environment, Proceedings of the Baltimore Symposium, May 1989, p. 19-26.

- Marron, D.C., 1992, Floodplain storage of mine tailings in the Belle Fourche River system: A sediment budget approach: Earth Surface Processes and Landforms, v. 17, p. 675-685.
- Martin, James E., Sawyer, J. Foster, Fahrenbach, Mark D., Tomhave, Dennis W., Schulz, Layne D. 2004. Geologic Map of South Dakota. https://ngmdb.usgs.gov/ngmdb/ngmdb_home.html. (Loc K: USGS Map)
- Matera, V., Le Hecho, I., Laboudigue, A., Thomas, P., Tellier, S. Astruc, M., 2003. A methodological approach for the identification of arsenic bearing phases in polluted soils. 2003. Environmental Pollution, vol. 126, p. 51-64.
- Miller, Theodore K. 1988. Comment on "River Loads Underestimated by Rating Curves" by R.I. Ferguson. Water Resources Research, 24, No. 7, p. 1217-1219.
- Muller, K., Daus, B., Morgenstern, P., 2007. Mobilization of antimony and arsenic in soil and sediment samples - evaluation of different leaching procedures. Water Air Soil Pollution, vol. 183, p. 427-436.
- Mussetter Engineering, Inc., Owen Ayres and Associates, Inc., Harner and Associates, Inc., Chadwick Ecological Consultants, Inc., 1996, Reclamation Plan for the Redex Mine Reach of Whitewood Creek, South Dakota: Prepared for Homestake Mining Company, Inc.
- Noble, J.A., 1950. Ore mineralization in the Homestake gold mine, Lead, South Dakota. Geological Society of America Bulletin, vol. 61, p. 221-251.
- Noble, J.A., and Harder, J.O., 1948. Stratigraphy and metamorphism in a part of the northern Black Hills and the Homestake mine, Lead, South Dakota. Geological Society of America Bulletin, vol. 59, p. 941-975.
- Ona-Nguema, G., Morin, G., Juillot, F., Calas, G., and Brown, G.E.J., 2005. EXAFS analysis of arsenite adsorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite. Environmental Science and Technology, vol. 39, p. 9147-9155.
- O'Reilly, S.E., Strawn, D.G., Sparks, D.L., 2001. Residence Time Effects on Arsenate Adsorption/Desorption Mechanisms on Goethite. Soil Science Society of America Journal, vol. 65, p. 67-77.
- Oscarson, D.W., Huang, P.M., Liaw, W.K., 1981. Role of manganese in the oxidation of arsenite by freshwater lake sediments. Clays and Clay Minerals, vol. 29, p. 219-225.
- Peryea, F.J., and Kammerack, R., 1997. Phosphate-enhanced movement of arsenic out of a lead arsenatecontaminated topsoil and through uncontaminated subsoil. Water Air Soil Pollution, vol. 93, p. 243-254.
- Pierce, M.L., Moore, C.B., 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Research, vol. 16, p. 1247-1253.
- Quevauviller P., 2002. Methodologies in Soil and Sediment Fractionation Studies, Royal Society of Chemistry, Cambridge.

- Rahman, M.M., Ng, J.C., Naidu, R., 2009. Chronic exposure of arsenic via drinking water and its adverse health impacts on humans. Environmental Geochemistry and Health, vol. 31, p. 189-200.
- Rancourt, D.G., Fortin, D., Pichler, T., Thibault, P., Laflamme, G., Morris, R.V., Mercier, P.H.J., 2001. Mineralogy of a natural As-rich hydrous ferric oxide coprecipitate formed by mixing of hydrothermal fluid and seawater: Implications regarding surface complexation and color banding in ferrihydrite deposits. American Mineralogist, vol. 86, p. 834–851.
- Redden, Jack A., DeWitt, Ed. 2008. Maps Showing Geology, Structure, and Geophysics of the Central Black Hills, South Dakota. https://ngmdb.usgs.gov/ngmdb/ngmdb_home.html. (Loc D: USGS Map)
- Redman, A.D., Macalady, D.L., and Ahmann, D., 2002. Natural organic matter affects arsenic speciation and adsorption on hematite. Environmental Science and Technology, vol. 36, p. 2889-2896.
- Rees, T.F., and Ranville, J.F, 1988, Colloids in Seeps and Springs along Whitewood Creek. In: (ed. Goddard, K.E.), U.S. Geological Survey Applied Research Studies of the Cheyenne River System, South Dakota: Description and Collation of Data, Water Years 1985-86 U.S. Geological Survey. Open-File Report 88-484, p. 125-139.
- Roberts, Willard L., Rapp Jr, George. Mineralogy of the Black Hills. 1965. South Dakota School of Mines and Technology. Bulletin; no. 18.
- Rodriguez, R.R., Basta, N.T., Casteel, S.W., Armstrong, F.P., Ward, D.C., 2003. Chemical extraction methods to access bioavailable arsenic in soil and solid media. Journal of Environmental Quality, vol. 32, pg. 876-884.
- Rubinos, D.A., Iglesias, L., Diaz-Fierros, F., Barral, M.T., 2011. Interacting Effect of pH, Phosphate and Time on the Release of Arsenic from Polluted River Sediments (Anllo'ns River, Spain). Aquat Geochem, vol. 17, p. 281-306.
- Sadiq M. Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations, 1997. Water Air Soil Pollution, vol. 93, p.117-136.
- Savage, K.S., Tingle, T.N., O'Day, P.A., Waychunas, G.A., Bird, D.K., 2000. Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California. Applied Geochemistry, vol. 15, p. 1219–1244.
- Schultz, Leonard G., Tourtelot, Harry A., Gill, James R., Boerngen, Josephine G. 1980. Composition and Properties of the Pierre Shale and Equivalent Rocks, Northern Great Plains Region. Geochemistry of the Pierre Shale and Equivalent Rocks of the Late Cretaceous Age. US Geological Survey Professional Paper 1064-B.
- Sheppard, S.C., 1992. Summary of phytotoxic levels of soil arsenic. Water Air Soil Pollution, vol. 64, p. 539–550.
- Slaughter, A.L., 1968. Homestake Mine. Wyoming Geological Association 20th Field Conference Guidebook, p. 157-171.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemisty, vol. 17, p. 517-568.

- Smith, D.A., 2003. Here's to low-grade ore and plenty of it, the Hearsts and the Homestake Mine. Mining Engineering, vol. 55, p. 10-14.
- Smith, E., Naidu, R., Alston, A.M., 1998. Arsenic in the soil environment: a review. Advances in Agronomy, vol. 64, p. 149-195.
- South Dakota Department (S.D. Dept.) of Game, Fish and Parks, S.D. Dept. of Environment and Natural Resources, U.S. Dept. of Interior Fish and Wildlife Service, U.S. Dept. of Interior Bureau of Land Management, U.S. Dept. of Interior Bureau of Reclamation, 2005. Final conceptual restoration and compensation plan for Whitewood Creek and the Belle Fourche and Cheyenne River watersheds, South Dakota.
- South Dakota Depart of Environment and Natural Resources (SDDENR), The Minerals and Mining Program, 2002. Summary of The Mining Industry in South Dakota 2001.
- Stelzer, R.S., Likens, G.E. 2006. Effects of Sampling Frequency on Estimates of Dissolved Silica Export by Streams: The Role of Hydrological Variability and Concentration–Discharge Relationships. Water Resources Research, 42, WO7415. doi:10.1029/2005WR004615.
- Strobel, Michael L., Jarrell, Gregory J., Sawyer, J. Foster, Schleicher, John R. 1999. Distribution of Hydrogeologic Units in the Black Hills Area, South Dakota. https://ngmdb.usgs.gov/ngmdb/ngmdb_home.html. (Loc G and H: USGS Map)
- Thanabalasingam, P., and Pickering, W.F., 1986. Arsenic sorption by humic acids. Environmental Pollution, vol. 12, p. 233-246.
- Walker, S.R., Parsons, M.B., Jamieson, H.E., Lanzirotti, A., 2009. Arsenic mineraology of near-surface tailings and soils: influences on arsenic mobility and bioaccessibility in the Nova Scotia gold mining districts. The Canadian Mineralogist, vol. 47, p. 533-556.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, vol. 51, p. 844-851.
- Tufano, K.T., Reyes C.W., Saltikov, C., Fendorf, S., 2008. Reductive processes controlling arsenic retention: Revealing the relative importance of iron and arsenic reduction. Environmental Science and Technology, vol. 42, p. 8283-8289.
- Ure, A.M., Quevauviller, P., Muntau, H., Griepink, B., 1993. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken Under the Auspices of the BCR of the Commission of the European Communities. International Journal of Environmental Analytical Chemistry, vol. 51, p. 135-151.
- U.S. EPA, 1990. EPA Superfund Record of Decision, Whitewood Creek. EPA ID: SDD980717136, OU1, Whitewood SD, March 30, 1990.
- U.S. EPA, 2009. National Primary Drinking Water Regulations: EPA 816-F-09-004.
- U.S. EPA, 2012. Five-year review report for Whitewood Creek Superfund Site, Lawrence, Meade and Butte Counties, South Dakota. EPA ID: SDD980717136.

USGS Mineral Resources Data System (MRDS). 2011. https://mrdata.usgs.gov/mrds

- USGS, 2017. Geochemical and Mineralogical Maps, with Interpretation, for Soils of the Conterminous United States. USGS Scientific Investigations Report 2017-5118.
- Vanni, M.J., Renwick, W.H., Headworth, J.L., Auch, J., Schaus, M.H. 2001. Dissolved and Particulate Nutrient Flux from Three Adjacent Agricultural Watersheds: A Five-Year Study. Biogeochemistry, 54, p. 85–114.
- Van Geen, A., Robertson, A.P., and Leckie, J.O., 1994. Complexation of carbonate species at the geothite surface: Implications for adsorption of metal ions in natural waters. Geochimica et Cosmochimica Acta, vol. 58, p. 2073-2086.
- Van Herreweghe, S., Swennen, R., Vandecasteele, C., Cappuyns, V., 2003 Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environmental Pollution, vol. 122, p. 323-342.
- Villalobos, M., and Leckie, J.O., 2001. Surface complexation modeling and FTIR study of carbonate adsorption to goethite. Journal of Colloid and Interface Science, vol. 235, p. 15-32.
- Vink, B.W., 1996. Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams. Chemical Geology, vol. 130, p. 21– 30.
- Violante, A., and Pigna, M., 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Science Society of America Journal, vol. 66, p. 1788-1796.
- Violante, A., Pigna, M., Ragusa R., 2002. Factors affecting arsenate adsorption / desorption on/from variable charge minerals and soils. 17th WCSS, Thailand, Symposium no. 47, Paper no. 133.
- Voigt, D.E., Brantle, S.L., Hennet, R.J., 1996. Chemical fixation of arsenic in contaminated soils. Applied Geochemistry, vol. 11, p. 633-643.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica Chimica Acta, vol. 436, p. 309-323.
- Wheeler. 2013. Should the Residuals Be Normal? Quality Digest. November 4, 2013 http://www.qualitydigest.com/inside/quality-insider-article/should-residuals-be-normal.html#
- Wuolo, R.W., 1986. Laboratory studies of arsenic adsorption in alluvium contaminated with gold-mine tailings along Whitewood Creek, Black Hills, South Dakota [M.S. thesis]. South Dakota School of Mines, 159 pages.

APPENDICES

Location		Sample Location Description	NAD 83 (N)	NAD 83 (W)	Elevation (m)	Elevation (ft)	Sample Date
	А	Kirk Road near Lead: above tailings hill (stream upgradient of WWC)	44°20.584'	103°46.686′	1,598	5244	7/10/2011
	P	Kirk Road near Lead: below tailings hill	44°21.067'	103°44.643′	1,480	4856	7/10/2011
	В	<u>Seep</u> Kirk Road near Lead: below tailings hill	44°21.067'	103°44.643′	1,480	4856	7/10/2011
	С	Deadwood Park: by old height gauge (USGS 06436170)	44°22.798'	103°43.421′	n/a	n/a	7/10/2011
eek	D	WWC Rd, North of Deadwood: in a small valley	44°23.949'	103°42.089′	1,340	4397	7/11/2011
od Cr	E	Crook Mtn. Rd, Crook City: (USGS Station 06436180)	44°26.540'	103°37.779′	1,135	3725	7/13/2011
tewo	F	North of Whitewood City: (USGS Station 06436190)	44°32.505′	103°34.297′	982	3222	7/13/2011
Whi	G	Berger Site, downstream of bridge (USGS study location)	44°'33.054	103°'32.860'	957	3140	7/13/2011
		Seep Berger Site, upstream of bridge (USGS study location)	44°33.022′	103°32.957′	950	3116	7/13/2011
		WWC near confluence with BFR: (near USGS study location)	44°38.224'	103°27.422′	858	2814	7/16/2011
		Seep WWC near confluence with BFR: (near USGS study location)	44°38.190'	103°27.417′	849	2784	7/16/2011
liver	I	BFR intersection with HWY 79; NW bank	44°38.205'	103°25.686′	849	2787	7/16/2011
rche F	J	BFR intersection with Bismark Trail; upstream of bridge	44°37.605′	103°15.401'	813	2667	7/16/2011
e Four	К	BFR intersection with HWY 34; NE bank	44°30.813'	103°08.121′	783	2569	7/17/2011
Belle	L	BFR upstream of its confluence with WWC; Vale Cutoff Rd.	44°40.254'	103°29.259′	856	2809	7/14/2011

Appendix 4-1. Sample Location Description and Collection Dates

NOTE:

Locations highlighted in light yellow indicate alluvial sediment sampling locations, as discussed in Chapter 5.

Location		Samala Tuna	Total or	Α	s	A		E	\$	Ва	Be	2	Са	C	d	С	0
	JCation	Sample Type	Dissolved	MS	OES	MS	OES	MS	OES	OES	MS	OES	OES	MS	OES	MS	OES
			MDL:	2.6E-05	0.02	1.0E-05	0.005	1.0E-05	0.01	0.0005	5.0E-06	0.0002	0.05	2.0E-06	0.001	1E-06	0.005
		Ca	lculated PQL:	7.8E-05	0.06	0.00003	0.015	0.00003	0.03	0.0015	0.000015	0.0006	0.15	6E-06	0.003	3E-06	0.015
			1/2 MDL:	1.3E-05	0.01	5E-06	0.0025	5E-06	0.005	0.00025	2.5E-06	0.0001	0.025	1E-06	0.0005	5E-07	0.0025
	Comparison Values			0.0	01	0.2		6.	0	2.0	0.0	04	n/a	0.005		0.0022 - 0.0029	
	۵	In Stream	Dissolved	0.0129		0.0061		0.0228		0.086	1.1E-05		79.38	0.0156		0.0010	
	~	motream	Total	0.0250		0.4450		0.0250		0.102	1.4E-04		83.47	0.0168		0.0020	
		In Stroom	Dissolved	0.0048		0.0311		0.0279		0.081	1.5E-05		64.36	0.0227		0.0009	
	В	in stream	Total	0.0082		0.1974		0.0284		0.083	4.1E-05		63.92	0.0253		0.0011	
		Seep	Total	0.0127		0.0120		0.0902		0.032	2.3E-04		506.15	0.0104		0.0298	
	C	In Stroom	Dissolved	0.0077		0.0212		0.0741		0.069	1.6E-05		98.67	0.0114		0.0007	
	J	in stream	Total	0.0117		0.1014		0.0704		0.067	6.5E-05		101.31	0.0046		0.0008	
	5	In Stroom	Dissolved	0.0139		0.0337		0.0787		0.071	4.6E-05		108.12	0.0147		0.0006	
<u>×</u>	U	mstream	Total	0.0160		0.0666		0.0746		0.074	2.0E-05		106.32	0.0245		0.0005	
ree	F	In Stroom	Dissolved	0.0236		0.0112		0.0714		0.075	3.6E-05		104.14	0.0176		0.0003	
Οp	E	mstream	Total	0.0280		0.0645		0.0715		0.076	6.6E-05		103.82	0.0326		0.0003	
õ	F	In Stroom	Dissolved	0.0554		0.0098		0.0799		0.053	4.5E-05		150.86	0.0204		0.0003	
tew		mstream	Total	0.0608		0.0154		0.0862		0.052	3.0E-05		150.25	0.0100		0.0003	
Vhit	6	In Stroom *	Dissolved		0.018		0.065		0.016	0.050		0.002	149.58		0.024		-0.014
5		III Stream	Total		0.087		0.167		-0.006	0.053		0.002	152.01		0.034		-0.008
	G	Seen	Dissolved	0.4506		0.0062		0.0808		0.024	5.6E-05		190.86	0.0123		0.0009	
		seeh	Total	0.3953		0.0089		0.0691		0.026	3.6E-05		191.38	0.0167		0.0008	
		In Stroom	Dissolved	0.0629		0.0105		0.1484		0.043	4.5E-05		182.66	0.0109		0.0009	
		mstream	Total	0.0472		0.1380		0.1119		0.045	4.5E-05		177.19	0.0273		0.0004	
	п	Soon *	Dissolved		1.650		0.210		0.172	0.020		0.004	526.48		0.070		0.032
		Seeh	Total		0.080		0.176		0.150	0.024		0.006	512.75		0.045		0.015
		In Stroom	Dissolved	0.0467		0.1008		0.2366		0.054	6.5E-05		224.42	0.0183		0.0032	
ver		mstream	Total	0.0176		0.2478		0.1952		0.053	8.1E-05		226.42	0.0100		0.0012	
e Ri		In Stroom	Dissolved	0.0089		0.0024		0.2112		0.049	3.1E-05		210.33	0.0232		0.0002	
çþ	J	mstream	Total	0.0124		0.2410		0.2145		0.050	9.3E-05		214.18	0.0165		0.0003	
oni	v	In Stroom *	Dissolved		BDL		0.02		0.17	0.043		BDL	185.48		0.02		BDL
le Ε	ĸ	in Stream.	Total		0.033		0.511		0.129	0.046		0.001	202.47		0.036		-0.018
Bel		In Stroom	Dissolved	0.0090		0.0185		0.1945		0.054	1.0E-05		217.18	0.0235		0.0005	
	L	instream	Total	0.0040		0.3472		0.1761		0.058	1.2E-04		223.23	0.0352		0.0005	

Appendix 4-2. Analytical Results of Water Samples (ICP-MS and ICP-OES)

	cation		Total or	C	r	C	u	Fe	L	i	Mg	Mn	М	0	Na	N	i	Р	b
	cation	Sample Type	Dissolved	MS	OES	MS	OES	OES	MS	OES	OES	OES	MS	OES	OES	MS	OES	MS	OES
			MDL:	1.3E-05	0.005	6E-06	0.005	0.01	1.0E-05	0.01	0.01	0.002	2E-06	0.005	0.01	4E-06	0.002	1E-06	0.02
		Ca	lculated PQL:	3.9E-05	0.015	1.8E-05	0.015	0.03	0.00003	0.03	0.03	0.006	6E-06	0.015	0.03	1.2E-05	0.006	3E-06	0.06
			1/2 MDL:	6.5E-06	0.0025	3E-06	0.0025	0.005	5E-06	0.005	0.005	0.001	1E-06	0.0025	0.005	2E-06	0.001	5E-07	0.01
Comparison Values		0.	1	1.	0	0.3	0.001 -	0.003	n/a	0.3	0.0	4	n/a	0.1		0.015			
	^	In Stroom	Dissolved	0.0007		0.0012		0.016	0.0055		16.57	0.018	0.0005		10.78	0.0024		0.0000	
	A	in Stream	Total	0.0037		0.0082		0.961	0.0074		18.22	0.133	0.0002		10.96	0.0066		0.0106	
		In Stroom	Dissolved	0.0006		0.0020		0.042	0.0072		25.81	0.095	0.0004		6.40	0.0042		0.0001	
	В	in Stream	Total	0.0011		0.0028		0.535	0.0077		25.60	0.107	0.0004		6.36	0.0048		0.0006	
		Seep	Total	0.0009		0.0118		15.488	0.0518		1250.09	15.440	0.0020		96.96	0.0834		0.0003	
	c	In Stroom	Dissolved	0.0009		0.0026		0.053	0.0284		74.19	0.057	0.0010		34.58	0.0074		0.0000	
	C	in Stream	Total	0.0011		0.0045		1.175	0.0276		79.86	0.143	0.0011		35.14	0.0084		0.0087	
	п	In Stream	Dissolved	0.0010		0.0053		0.135	0.0267		88.19	0.097	0.0014		37.99	0.0083		0.0034	
¥	U	in Stream	Total	0.0009		0.0033		0.655	0.0251		84.21	0.062	0.0014		38.79	0.0077		0.0005	
ree	F	In Stream	Dissolved	0.0008		0.0036		0.028	0.0245		80.94	0.006	0.0017		36.36	0.0062		0.0002	
ЧC	L	in Stream	Total	0.0010		0.0038		0.340	0.0244		80.60	0.014	0.0015		36.06	0.0072		0.0007	
00/	F	In Stream	Dissolved	0.0006		0.0043		0.074	0.0241		73.60	0.026	0.0015		34.56	0.0058		0.0055	
tev		in Stream	Total	0.0005		0.0033		0.112	0.0257		73.18	0.028	0.0013		34.57	0.0059		0.0003	
vhi		In Stream *	Dissolved		0.010		-0.003	0.144		0.260	72.73	0.039		0.031	35.04		0.018		0.095
>	G	G	Total		0.013		0.016	0.458		0.219	73.95	0.052		0.038	35.13		0.018		0.077
	J	Seen	Dissolved	0.0005		0.0020		1.447	0.0216		74.01	0.872	0.0020		39.79	0.0087		0.0025	
		Seep	Total	0.0005		0.0018		1.576	0.0186		74.01	1.024	0.0018		39.43	0.0077		0.0004	
		In Stream	Dissolved	0.0006		0.0053		0.684	0.0458		94.82	0.236	0.0026		51.09	0.0083		0.0004	
	н	moticam	Total	0.0013		0.0046		0.628	0.0368		91.53	0.131	0.0022		50.48	0.0068		0.0004	
		Seen *	Dissolved		0.072		-0.028	46.386		0.533	283.04	9.565		0.210	98.53		0.102		0.464
		эсер	Total		0.072		-0.074	3.389		0.328	286.61	9.316		0.110	96.83		0.080		0.292
L		In Stream	Dissolved	0.0022		0.0154		1.661	0.0657		68.99	0.296	0.0082		56.57	0.0133		0.0038	
ive		moticam	Total	0.0015		0.0067		1.108	0.0578		66.97	0.175	0.0065		57.03	0.0097		0.0018	
e R		In Stream	Dissolved	0.0005		0.0040		0.014	0.0668		66.00	0.021	0.0081		70.53	0.0069		0.0000	
rch	,	in Stream	Total	0.0012		0.0045		0.658	0.0697		67.68	0.080	0.0067		72.22	0.0080		0.0008	
no:	к	In Stream *	Dissolved		BDL		BDL	0.0116		0.06	66.16	0.0118		0.01	79.22		0.003		BDL
le F	ĸ	in stream	Total		0.010		-0.011	0.971		0.064	67.09	0.070		0.006	81.57		0.003		0.072
Bel		In Stream	Dissolved	0.0007		0.0050		0.143	0.0587		58.52	0.044	0.0094		51.75	0.0084		0.0016	
	-	in Stream	Total	0.0016		0.0054		1.069	0.0540		58.87	0.158	0.0074		57.23	0.0101		0.0014	

Appendix 4-2. Analytical Results of Water Samples (ICP-MS and ICP-OES)

Location			Total or	S	S	b	S	e	Si	S	n	Sr	v	1	Z	n
		Sample Type	Dissolved	OES	MS	OES	MS	OES	OES	MS	OES	OES	MS	OES	MS	OES
			MDL:	0.05	2E-06	0.02	0.00007	0.02	0.01	1E-06	0.02	0.005	5E-06	0.005	1.0E-05	0.001
		Ca	Iculated PQL:	0.15	6E-06	0.06	0.00021	0.06	0.03	3E-06	0.06	0.015	1.5E-05	0.015	0.00003	0.003
			1/2 MDL:	0.025	1E-06	0.01	3.5E-05	0.01	0.005	5E-07	0.01	0.0025	2.5E-06	0.0025	5E-06	0.0005
	Comparison Values:		250	0.0	06	0.0	05	n/a	n/	a	4.0	0.00004	- 0.22	5.0		
	Δ	In Stream	Dissolved	37.85	0.0004		0.0018		7.68	0.0000		0.292	0.0005		0.0367	
	~		Total	39.57	0.0005		0.0017		8.47	0.0000		0.311	0.0045		0.0888	
		In Stream	Dissolved	27.39	0.0003		0.0009		6.34	0.0000		0.168	0.0008		0.0323	
	В	moticam	Total	26.87	0.0003		0.0009		6.42	0.0000		0.168	0.0015		0.0413	
		Seep	Total	1661.79	0.0001		0.0008		10.02	0.0000		2.260	-0.0015		0.0901	
	c	In Stream	Dissolved	147.80	0.0002		0.0010		5.79	-0.0001		0.405	0.0005		0.0143	
	C	motream	Total	157.78	0.0002		0.0011		6.04	0.0000		0.414	0.0014		0.0225	
	р	In Stream	Dissolved	169.61	0.0003		0.0012		6.03	0.0001		0.413	0.0006		0.0494	
¥	U	in Stream	Total	167.58	0.0003		0.0012		6.18	0.0000		0.416	0.0012		0.0474	
ree	F	In Stream	Dissolved	155.34	0.0003		0.0012		5.51	0.0000		0.404	0.0005		0.0247	
р	-	moticam	Total	155.48	0.0003		0.0010		5.63	0.0000		0.400	0.0010		0.0329	
00	E	In Stroom	Dissolved	169.47	0.0003		0.0016		4.73	0.0000		0.770	0.0002		0.0279	
tev	•	in stream	Total	169.26	0.0003		0.0017		4.73	0.0000		0.771	0.0003		0.0127	
vhi	c	In Stream *	Dissolved	166.79		0.081		0.001	4.87		0.006	0.789		-0.014		-0.102
>		moticam	Total	169.64		0.100		-0.010	5.11		-0.048	0.769		0.053		-0.078
	J	Soon	Dissolved	201.08	0.0001		0.0001		4.92	0.0000		0.762	-0.0001		0.0163	
		зеер	Total	200.88	0.0001		0.0001		4.92	0.0000		0.757	-0.0001		0.0153	
		In Stream	Dissolved	237.67	0.0004		0.0020		4.54	0.0001		1.033	0.0002		0.0251	
	u	in Stream	Total	224.38	0.0003		0.0017		4.66	0.0001		0.980	0.0027		0.0255	
	п	Seen *	Dissolved	745.44		0.472		-0.102	11.97		-0.273	4.127		-0.021		-0.579
		Зеер	Total	712.89		0.602		-0.081	7.92		0.045	3.880		-0.338		-0.681
		In Stream	Dissolved	233.21	0.0004		0.0022		5.57	0.0005		2.580	0.0019		0.1563	
vel	•	in Stream	Total	217.50	0.0003		0.0019		5.71	0.0001		2.658	0.0032		0.0576	
e Ri		In Stream	Dissolved	231.86	0.0003		0.0022		4.45	0.0000		2.430	0.0010		0.0178	
ç	,	in Stream	Total	232.70	0.0003		0.0021		5.08	0.0000		2.476	0.0032		0.0231	
ino	ĸ	In Stream *	Dissolved	262.24		BDL		BDL	4.21		BDL	2.6164		0.00		0.02
lе F	ĸ	in Stream	Total	271.93		0.134		-0.024	4.79		-0.045	2.706		0.003		0.030
Bel		In Stroom	Dissolved	206.90	0.0002		0.0021		5.20	0.0000		2.634	0.0016		0.1191	
	L L	in sueall	Total	210.75	0.0002		0.0019		6.13	0.0000		2.689	0.0056		0.2926	

Appendix 4-2. Analytical Results of Water Samples (ICP-MS and ICP-OES)

Appendix 4-2. Analytical Results of Water Samples (ICP-MS and ICP-OES)

Notes:

Analytes of Concern (AOCs) are highlighted in light yellow and are discussed in depth in the text.

Concentrations are reported in milligram per liter (mg/L)

Total samples were collected directly into the containter; dissolved samples were filtered through a 0.45µm syringe-attachment membrane filter.

In-stream * or Seep * = Only ICP-OES results are reported (i.e., not enough sample was left to be analyzed by ICP-MS).

Negative results = concentration is below the method detection limit

ICP-MS = inductively coupled plasma mass spectroscopy

ICP-OES = inductively coupled plasma optical emissions spectroscopy

BDL = below detection limit; concentration is below the method detection limit.

MDL = method detection limit

PQL = practical quantitation limit (set to 3x the MDL)

Comparison Values:

U.S. Environmental Protection Agency's (USEPA) National Primary Drinking Water Regulations maximum contaminant level (MCL) = the highest level of a contaminant that is allowed in drinking water; these analytes include: arsenic, antimony, barium, berylium, cadmium, chromium, lead, and selenium.

Results exceeding the EPA Primary MCL are highlighted in light green.

The EPA National Secondary Drinking MCLs = non-enforceable guidelines regarding contaminants that may cause cosmetic or aesthetic effects in drinking water; these analytes include: aluminum, copper, iron, sulfate (as sulfur), and zinc. Results exceeding the comparison value are highlighted in grey.

Results exceeding the EPA Secondary MCL are highlighted in grey.

EPA Health Advisory (HA) Life-time Standard = non-enforeable estimates of acceptable drinking water levels for a chemical substance based on health effects information; these analytes include: boron, manganese, molybdenum, nickel, and strontium. Results exceeding the comparison value are highlighted in light green.

Results exceeding the EPA HA standard are highlighted in light blue.

0.001 - 0.003 (concentration ranges) = Average concentrations found in surface water. Human health based drinking water ingestion comparison values not established by EPA. Average surface water concentration ranges reported in the literature are presented; these analytes include: colbalt, lithium, and vanadium. See References below for source documentation.

Exceedances of these *concentration ranges* are not highlighted.

n/a = comparison value is not available due to the analyte's low toxicity; these analytes include: calcium, magnesium, silicon, tin, and sodium.

References:

EPA MCL and HA standards:

U.S. Environmental Protection Agency (USEPA) 2018. Drinking Water Standards and Health Advisories. Office of Water USEPA. EPA 822-F-18-001. Washington, DC. March 2018. Colbalt:

Cobalt and inorganic cobalt compounds. James H. Kim, Herman J. Gibb, Paul D. Howe. Concise international chemical assessment document; 69. World Health Organization. 2006. Lithium:

Oram, Brian, P.G. Date Unknown. Lithium in Groundwater, Drinking Water Marcellus Shale Water Testing. Water Research Center. Pennsylvania. Accessed online 12/21/2019. Vanadium:

Agency for Toxic Substances and Disease Registry (ATSDR). Date Unknown. Public Health Statement - Vanadium.

http://waterdata.usgs.gov/nwis

WHITEWOOD CREEK USGS GAUGE LOCATIONS

1) USGS 442134103441901 WHITEWOOD CREEK ABOVE GOLD RUN

Latitude 44°21'34", Longitude 103°44'19" NAD27 Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-24	1987-08-13	5
Field/Lab water-quality samples	1983-10-24	1986-03-13	5

2) USGS 06436170 WHITEWOOD CREEK AT DEADWOOD

Latitude 44°22'48", Longitude 103°43'25" NAD27 Lawrence County, South Dakota, Hydrologic Unit 10120202 Drainage area: 40.7 square miles Contributing drainage area: 40.7 square miles,

Datum of gage: 4,500.00 feet above NGVD29.

Data Type	Begin Date	End Date	Count
Daily Data			
Discharge, cubic feet per second	1981-10-01	1995-09-30	5113
Daily Statistics			
Discharge, cubic feet per second	1981-10-01	1995-09-30	5113
Monthly Statistics			
Discharge, cubic feet per second	1981-10	1995-09	
Annual Statistics			
Discharge, cubic feet per second	1982	1995	
Peak streamflow	1982-05-15	1995-05-08	14
Field measurements	1982-05-13	1998-08-04	135
Field/Lab water-quality samples	1981-11-06	1998-08-04	146
Additional Data Sources	Begin Date	End Date	Count
Instantaneous-Data Archive **offsite**	1990-10-01	1995-09-30	167072

3) USGS 442314103424101 WHITEWOOD CREEK AB SEWAGE TREATMENT PLANT

Latitude 44°23'14", Longitude 103°42'41" NAD27 Lawrence County, South Dakota, Datum of gage: 4,480 feet above NGVD29.

Data Type	Begin Date	End Date	Count
Field measurements	1986-03-13	1986-03-13	1
Field/Lab water-quality samples	1986-03-13	1986-03-13	1

4) USGS 442330103421501 WHITEWOOD CREEK BELOW ALT HWY 14

Latitude 44°23'30", Longitude 103°42'15" NAD27 Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-25	1984-04-09	2
Field/Lab water-quality samples	1983-10-25	1984-04-09	5

5) USGS 442500103413501 WHITEWOOD CREEK BEL SLAUGHTERHOUSE GULCH

Latitude 44°25'00", Longitude 103°41'35" NAD27

Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-25	1984-04-19	2
Field/Lab water-quality samples	1983-10-25	1984-04-09	5

6) USGS 06436180 WHITEWOOD CR ABOVE WHITEWOOD,SD

Latitude 44°26'32", Longitude 103°37'44" NAD27 Lawrence County, South Dakota, Hydrologic Unit 10120202 Drainage area: 56.7 square miles Contributing drainage area: 56.7 square miles,

Datum of gage: 3,680.00 feet above NGVD29.

Data Type	Begin Date	End Date	Count
Real-time	Pr	evious 120 days	
Daily Data			
Discharge, cubic feet per second	1982-10-26	2011-11-03	10601
Daily Statistics			
Discharge, cubic feet per second	1982-10-26	2011-02-14	10339
Monthly Statistics			
Discharge, cubic feet per second	1982-10	2011-02	
Annual Statistics			
Discharge, cubic feet per second	1983	2011	
Peak streamflow	1983-05-07	2010-08-03	28
Field measurements	1983-09-29	2011-09-08	342
Field/Lab water-quality samples	1983-01-06	2011-09-08	500
Additional Data Sources	Begin Date	End Date	Count
Instantaneous-Data Archive **offsite**	1990-10-01	2010-09-30	504277
Annual Water-Data Report (pdf) **offsite**	2006	2010	5

7) USGS 442740103371001 WHITEWOOD CREEK ABOVE 1-90

Latitude 44°27'40", Longitude 103°37'10" NAD27

Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-26	1984-04-10	2
Field/Lab water-quality samples	1983-10-26	1984-04-10	5

8) USGS 442825103373001 WHITEWOOD CREEK BEL WHITEWOOD

Latitude 44°28'25", Longitude 103°37'30" NAD27 Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-07-14	1984-04-10	3
Field/Lab water-quality samples	1983-07-14	1984-04-10	6

9) USGS 442940103371501 WHITEWOOD CREEK IN SEC 10

Latitude 44°29'40", Longitude 103°37'15" NAD27 Lawrence County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-26	1984-04-10	2
Field/Lab water-quality samples	1983-10-26	1984-04-10	5

6

10) USGS 06436190 WHITEWOOD CREEK NEAR WHITEWOOD,SD

Latitude 44°32'30.38", Longitude 103°34'17.46" NAD27 Lawrence County, South Dakota, Hydrologic Unit 10120202 Drainage area: 77.5 square miles

Contributing drainage area: 77.5 square miles, Datum of gage: 3,175.00 feet above NGVD29.

Data Type	Begin Date	End Date	Count	
Real-time	Previous 120 days			
Daily Data	•			
Discharge, cubic feet per second	1981-09-22	2011-11-03	11000	
Daily Statistics				
Discharge, cubic feet per second	1981-09-22	2011-01-02	10695	
Monthly Statistics				
Discharge, cubic feet per second	1981-09	2011-01		
Annual Statistics				
Discharge, cubic feet per second	1981	2011		
Peak streamflow	1982-05-20	2010-08-03	29	
Field measurements	1983-09-29	2011-08-09	294	
Field/Lab water-quality samples	1981-11-06	2010-08-04	338	
Additional Data Sources	Begin Date	End Date	Count	
Instantaneous-Data Archive **offsite**	1990-10-01	2010-09-30	647998	
Annual Water-Data Report (pdf) **offsite**	2006	2010	5	

11) USGS 443300103325501 WHITEWOOD CRK AT BERGER RANCH

Latitude 44°33'00", Longitude 103°32'55" NAD27 Meade County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-07-15	1984-04-11	3
Field/Lab water-quality samples	1983-07-15	1984-04-11	11

12) USGS 443355103315001 WHITEWOOD CRK AT SEC 17 AB CROW CRK TRIB

Latitude 44°33'55", Longitude 103°31'50" NAD27 Meade County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-10-27	1984-04-11	2
Field/Lab water-quality samples	1983-10-27	1984-04-11	4

13) USGS 443525103311001 WHITEWOOD CREEK AT MARTIN RANCH

Latitude 44°35′25″, Longitude 103°31′10″ NAD27 Meade County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-07-15	1984-04-11	3
Field/Lab water-quality samples	1983-07-15	1984-04-11	8

14) USGS 443620103305001 WHITEWOOD CREEK AT SEC 33

Latitude 44°36'20", Longitude 103°30'50" NAD27 Butte County, South Dakota,

Data Type	Begin Date	End Date	Cour
Field measurements	1983-10-28	1984-04-12	
Field/Lab water-quality samples	1983-10-28	1984-04-12	

2

15) USGS 06436198 WHITEWOOD CR ABOVE VALE,SD

Latitude 44°37'03.00", Longitude 103°28'49.00" NAD27 Butte County, South Dakota, Hydrologic Unit 10120202 Drainage area: 102 square miles Contributing drainage area: 102 square miles, Datum of gage: 2,840.00 feet above NGVD29.

Data Type **Begin Date End Date** Count Real-time -- Previous 120 days --Daily Data Discharge, cubic feet per second 1982-11-05 10591 2011-11-03 Daily Statistics Discharge, cubic feet per second 1982-11-05 2011-02-17 10332 Monthly Statistics Discharge, cubic feet per second 1982-11 2011-02 Annual Statistic Discharge, cubic feet per second 1983 2011 1983-05-07 Peak streamflow 2010-08-08 28 **Field measurements** 1983-09-29 2011-09-08 350 Field/Lab water-quality samples 1983-01-06 2011-09-08 495 End Date **Additional Data Sources** Begin Date Count 1990-10-01 2010-09-30 499637 Instantaneous-Data Archive **offsite** Annual Water-Data Report (pdf) **offsite** 2006 2010 5

16) USGS 443815103272501 WHITEWOOD CREEK AT MOUTH

Latitude 44°38'15", Longitude 103°27'25" NAD27

Butte County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-07-13	1984-04-12	3
Field/Lab water-quality samples	1983-07-13	1984-04-12	8

BELLE FOURCHE RIVER USGS GAUGE LOCATIONS

1) USGS 444020103282001 BELL FOURCHE RV AB WHITEWOOD CRK TRIB

Latitude 44°40'20", Longitude 103°28'20" NAD27 Butte County, South Dakota,

Data Type	Begin Date	End Date	Count
Field measurements	1983-07-12	1984-04-13	2
Field/Lab water-quality samples	1983-07-12	1984-04-13	6

2) USGS 06436250 BELLE FOURCHE RIVER AT VALE SD

Latitude 44°38'10", Longitude 103°25'37" NAD27 Butte County, South Dakota, Hydrologic Unit 10120202 Drainage area: 4,964 square miles Contributing drainage area: 4,957 square miles,

Data Type	Begin Date	End Date	Count
Field measurements	1982-11-01	2002-11-13	37
Field/Lab water-quality samples	1983-01-05	2002-11-13	67

3) USGS 443753103152300 BELLE FOURCHE RIVER NR VALE, SD

Latitude 44°37'53", Longitude 103°15'23" NAD27 Butte County, South Dakota, Hydrologic Unit 10120202 Datum of gage: 2,660.00 feet above NGVD29.

Data Type	Begin Date	End Date	Count
Field measurements	2001-03-29	2002-11-13	13
Field/Lab water-quality samples	2001-03-29	2002-11-13	10

4) USGS 443738103152000 BELLE FOURCHE RIVER NEAR VALE, SD

Latitude 44°37'38", Longitude 103°15'20" NAD27 Butte County, South Dakota, Hydrologic Unit 10120202 Datum of gage: 2,650.00 feet above NGVD29.

Data Type	Begin Date	End Date	Count
Field measurements	2001-03-29	2002-06-25	8
Field/Lab water-quality samples	2001-03-29	2002-06-25	10

5) USGS 06437000 BELLE FOURCHE R NEAR STURGIS,SD (Hwy 34 and BF)

Latitude 44°30'47", Longitude 103°08'11" NAD27 Meade County, South Dakota, Hydrologic Unit 10120202 Drainage area: 5,821 square miles Contributing drainage area: 5,814 square miles, Datum of gage: 2,526.13 feet above NGVD29.

Data Type	Begin Date	End Date		Count
Real-time	Previous 120 d	lays		
Daily Data				
Discharge, cubic feet per second	1945-11-07		2011-11- 03	24103
Suspended sediment concentration, milligrams per liter	1955-10-01		1958-09- 30	1074
Suspended sediment discharge, tons per day	1955-10-01		1958-09- 30	1096
Daily Statistics	r	1		1
Discharge, cubic feet per second	1945-11-07	2010-10-28		23732
Suspended sediment concentration, milligrams per liter	1955-10-01	1958-09-30		1074
Suspended sediment discharge, tons per day	1955-10-02	1958-09-30		1095
Monthly Statistics		•		
Discharge, cubic feet per second	1945-11	2010-10		
Suspended sediment concentration, milligrams per liter	1955-10	1958-09		
Suspended sediment discharge, tons per day	1955-10	1958-09		
Annual Statistics	•	*		
Discharge, cubic feet per second	1946	2011		
Suspended sediment concentration, milligrams per liter	1956	1958		
Suspended sediment discharge, tons per day	1956	1958		
Peak streamflow	1946-05-24	2010-05-13		65
Field measurements	1946-05-02	2011-10-12		490
Field/Lab water-quality samples	1954-08-09	2010-08-11		1405
Additional Data Sources	Begin Date	End Date		Count
Instantaneous-Data Archive **offsite**	1990-10-01	2010-09-30		479096
Annual Water-Data Report (pdf) **offsite**	2006	2010		5

Appendix 5-1. Transcribed Field Notes

7/10/2011 (WWC: 7 water, 3 solid)

- A. Kirk Rd ABOVE mine waste pile/hill or Yates Shaft [10:00AM] (1unfiltered, 1filtered; 1stream sediment)
- **B.** Kirk Rd BELOW mine waste pile/hill or Yates Shaft [10:30AM] (1unfiltered, 1filtered; 1unfiltered seep, 1stream sediment)
- C. <u>USGS 06436170</u> Deadwood park, by old height gauge [12:40PM] (1unfiltered, 1filtered; 1unfiltered seep, 1stream sediment)

7/11/2011 (WWC: 2 water, 19 solid)

D. Whitewood Creek Road, North of Deadwood [10:30AM] (1unfiltered, 1filtered; 1unfiltered seep, 1stream sediment)

Location 2: (Sketch on Pg. 113 in field notebook) East bank of WWC, 20-30m east of WWC Rd.

	Depth	Description
2.1	6in into surface	Closest to active channel, vegetated
2.2	5in into bank	0.5m from active channel, 1.8ft high
2.3	2in into soil horizon	1 ft below top of bank terrace

Location 3: [12:40pm] (sunny, partly cloudy)

	Depth from surface	Description
3.1	0-8.5in	7m from active bank, smeltered/volcanic looking rock
3.2A	0-3in	11m from active bank, inside old channel
3.2B	3-12in	Change to clay rich from silt, lighter yellow brown color
3.3A	0-9in	18m from active bank, east of old channel
3.3B	9-18in	
3.3C	18-28in	
3.3D	28-36in	Occurrence of pyrite?
3.3E	36-45in	Occurrence of sandy texture on bottom core
3.3F	45-52in	Red, sandy, hit rocks on bottom, more moist
3.4	0-15in	26m from active bank, on gentle hill east of old channel

Location 4: Further north on WWC Rd. Homestake property with public entrance. [3:00pm]

(Started to rain around 4:20pm)

	Depth from surface	Distance from Bank	Description
4.1	0-10in	2m	Rocky, hard to auger
4.2A	0-6in	12m	Very rocky, igneous intrusive, shale,
			subangular to angular, some rounded
4.2B	6-10in		Large cobble 8in diameter
4.3	0-3in	22m	Too hard to dig, raining more
4.4	0-3in	32m	Many cobbles (3-6in)

<u>7/13/2011</u>

- E. <u>USGS 06436180</u> Cook City and Crook Mountain Road, south of Whitewood City (site #5). [9:20am] (1unf, 1F, 1sedim.)
- F. <u>USGS 06436190</u> North of Whitewood City (site #9). [10:30am] (1unf, 1F, 1sedim.)
- G. Berger Bridge (site #10). [10:30am]

(N.W bank: 1unf, 1F, 1sedim., 1seep)

	0		, 0
	Depth from surface	Distance from Bank	Description
1.1A	0-1ft3in	3m	Very pebbly, gravel rich
1.2A	0-8in	10m	Clay
1.2B	8-1ft2in	10m	Silty, yellow grains, hit cobbles
1.3A	0-7in	18m	Clay, more red
1.3B	7-1ft4in	18m	More silty
1.3C	1.4-1.10	18m	Moist, hit cobbles
1.4A	0-8in	28m	Clay, silty
1.4B	8in-1ft2in	28m	Moist, pebbly

-Transect of auger holes taken perpendicular to WWC on SE bank, 50m from bridge:

Stratigraphic column of downcut/exposed SE bank, 200-300m from bridge (refer to pg. 117 of field notebook for sketch). [N 44°33.038 W 103°32.678 Elev: 3138ft]

Label	Thickness	Height	Description
		above	
		stream	
2.7	60cm	3.4-4.0m	A-horizon soil, lenses within layer 2.8. Some areas show lenses up to
			3m wide, 1ft thick max of deep rusty-adobe red with dark gray
			layers. Usually 6-8in below top of land.
2.6	60cm	2.8-3.4m	Light buff orange brown. Similar to layer 2.4, but 1 shade lighter.
			Finer sand texture with nodules 4in of darker grey.
2.5	40cm	2.4-2.8m	Band of dark grey brown with lighter layer in between. Subtle
			grading into change in colors. Old twigs and limestone pieces <0.5in
			found 5% throughout layer.
2.4	40cm	2.0-2.4m	Light orange-brown, sharp contact with layer below. Fine sand/silty,
			small vesicles, splotches of adobe-rust red 2%.
2.3	20cm	1.8-2.0m	Medium brown, sharp contact with layer above. Silty, less pebbles
			<1in, 20% of layer
2.2	80cm	1.0-1.8m	Cobble, gravel, sub-rounded to sub-angular clasts, white coating on
			light brown-buff matrix. Poorly sorted, gravel to cobble (6in).
			Gradational contact with upper medium brown layer.
2.1		0-1.0m	Shale: Light grey to dark, white coating, small patches of brown
			crumbly pebble sized inclusions. Weathered shale is sticky.

7/14/2011

L. Belle Fourche above WWC confluence: east of Nisland on Vale Cutoff Rd. [11:00am]

(BF 1.1 unf, BF 1.2 F, BF 1.0 sedim)

G. Berger NE bank, more east (20m) than previous strat column:

(Sketch pg. 121)

Depth	Label	Dist from	Description
(ft.in)		stream (m)	
0.0-0.9	3.1A	13.5	red sandy silt
0.9-1.4	3.1B	13.5	
1.4-2.0	3.1C	13.5	some yellow silt
2.0-2.6	3.1D	13.5	
2.6-3.5	3.1E	13.5	
3.5-3.9	3.1F	13.5	more dark grey clay
3.9-4.3	3.1G	13.5	
5.0-5.9	3.1H	10	muddy, silt, top may not match above
5.9-6.0	3.11	10	
0.0-0.8	3.2A	21.4	lower down dip area
0.8-1.2	3.2B	21.4	darker stuff with red
1.2-1.8	3.2C	21.4	more darker-brown metallic red
1.8-2.4	3.2D	21.4	
2.4-2.8	3.2E	21.4	moist, hit cobble
0.0-0.9	3.3A	45	
0.9-1.2	3.3B	45	
1.2-1.6	3.3C	45	
1.6-2.2	3.3D	45	bits of dark grey
2.2-2.6	3.3E	45	more dark grey clay
2.6-3.4	3.3F	45	lots of dark metallic; pyrite?
0.0-0.6	3.4A	60	grasses show slight stains, some also have no stains
0.6-1.2	3.4B	60	more dark clay
1.2-1.8	3.4C	60	
1.8-2.2	3.4D	60	darker clay with shiny sparkles
2.2-2.6	3.4E	60	dark red (very tired, stopped)
-	-	75	Shady, cottonwood area, very cobblely, pebbly, cannot dig far

I. Belle Fourche and Hwy 79; NW bank 7/16/2011 [10:00am]

(BF: 1unf, 1F, 1sedim)

J. Belle Fourche and Bismark Trail (Upstream of bridge; figure Pg. 122) 7/16/2011 [10:40am]

(BF: 1unf, 1F, 1sedim)

H. WWC below confluence on River Loop Rd (Trohkimoinen property) 7/16/2011 [11:50am]

(BF: 1unf, 1F, 1sedim)

Depth	Thickness	Label	Sequence	Description
(meters)	(meters)			
0-0.5	0.5	1.7	Silt	-Buff, light grey-buff, tan-yellow
			(Top soil)	-Silty, no vegetation growing ontop
0.5-0.9	0.4	1.6		-Red, orange, yellow silt matrix with poorly sorted, well
			Cobbles	rounded, small cobble pebble (<1in to 4in) clasts.
				-Sharp contrast with unit below (distinct and clear contact
				line)
0.9-1.2	0.3	1.5	Silt	-1.5C: slime grey lenses with yellow brown intermixed
				-1.5B: yellow orange silty sand
				-1.5A: slime grey lenses with darker red intermixed, rusty
				brown
				-1.5AA: black chunks/pieces (~5mm) in the grey lenses
1.2-1.5	0.3	1.4	Cobbles	 -Very poorly sorted, small pebble-gravels (<1cm) to large
				cobbles (~6in)
1.5-2.3	0.8	1.3	Silt	-1.3B: dark brown with light yellow
				-1.3A: dark brownish-red, finer grained silt than 1.3B
2.3-3.5	1.2	1.2	Cobbles	-1.2B: sandy silt, yellow, orange and red mix
				-1.2A: same as 1.2B, but with gypsum-like white
				stains/growths
				-1.2AA: same as above, but with dark black sandy silt and
				very poorly sorted cobbles (<1cm to 10in *units?*)
3.5-4.5	1.0	1.1	Shale	-Shale, dark grey-black

H. WWC below confluence on River Loop Rd (Trohkimoinen property) 7/18/2011 [9:40am]

(no water samples collected)

Depth	Label	Dist from	Description
(ft.in)		stream (m)	
0.0-0.9	2.1A	4	Sandy brown
0.9-2.1	2.1B	4	Very moist
2.1-2.6	2.1C	4	
2.6-2.10	2.1D	4	Hit cobble and water
0.0-0.9	2.2A	9	Finer sandy silt
0.9-1.10	2.2B	9	
1.10-2.6	2.2C	9	Moist, hit cobble
0.0-0.8	2.3A	18	Yellow buff brown
0.8-1.2	2.3B	18	
1.2-1.8	2.3C	18	Hit clay lens, grey
1.8-2.6	2.3D	18	Pyrite?
2.6-3.1	2.3E	18	Moist, darker grey?
3.1-3.6	2.3F	18	Dark black chunks
3.6-4.0	2.3G	18	
4.0-4.5	2.3H	18	More dark blacks
			(Tall grasses and reeds in this area)
0.2-0.9	2.4A	35	
0.9-1.5	2.4B	35	
1.5-2.0	2.4C	35	
2.0-2.7	2.4D	35	Dark grey, pyrite?
2.7-3.4	2.4E	35	Moist, dark black chunks
3.4-3.10	2.4F	35	
3.10-4.6	2.4G	35	Moist. muddy

K. Belle Fourche: HWY 34, NE Bank; near Volunteer (Poss Ranch) 7/17/2011 [10:12am]

(BF: 1unf, 1F, 1sedim)

60m North of the bridge, NE bank:

Depth	Label	Dist from	Description
(ft.in)		stream (m)	
0.0-0.9	1.1A	2	Clay-rich, grey brown
0.9-1.3	1.1B	2	Similar
1.3-2.0	1.1C	2	Very sticky cohesive clay-rich
2.0-2.7	1.1D	2	Chunks of grey w/red
2.7-3.3	1.1E	2	Deep red + grey (pyrite? Shiny)
3.3-3.9	1.1F	2	Chunks of grey slime
3.9-4.0	1.1G	2	Hit cobble, moist/wet, large grey chunks-shale?
0.0-0.2	1.2A	15	Opening of conductions upgetation changes from tall grosses to
0.2-0.8	1.2B	15	Opening of sandy area; vegetation changes from tail grasses to
0.8-1.2	1.2C	15	weeds + smail nowers.
1.2-2.0	1.2D	15	Red w/brown yellow
2.0-2.4	1.2E	15	Red w/yellow clay
2.4-2.8	1.2F	15	Moist, deep red w/yellow, some grey
2.8-3.0	1.2G	15	Moist red w/grey
3.0-3.5	1.2H	15	More grey than above
3.5-4.0	1.21	15	More grey streaks
0.2-	1.3A	30	
0.10			
0.10-	1.3B	30	Red clay, easy to auger
2.0			
2.0-2.6	1.3C	30	More yellow, pyrite?
2.6-3.2	1.3D	30	Darker bits, pyrite?
3.2-3.8	1.3E	30	Same
3.8-4.0	1.3F	30	Moist, shale?
0.1-0.9	1.4A	46	Top soil
0.9-1.5	1.4B	46	
1.5-2.1	1.4C	46	
2.1-2.8	1.4D	46	More silty, fine sandy
2.8-3.4	1.4E	46	More clay mixed in
3.4-4.1	1.4F	46	
4.1-4.8	1.4G	46	

K. Belle Fourche: HWY 34, NE Bank; near Volunteer (Poss Ranch) 7/17/2011 [10:12am]

NW Bank:

Shale: ~2.5m thick, light grey, crumbly

Lenses of indurated dark mudstone (purple-black-brown), ~2in thick; weathers to orange-yellow

Depth (meters)	Thickness (meters)	Sequence	Description
0.0-0.4	0.4		Topsoil
0.4-0.6	0.2		Pebbles <0.5-3.0 inches
0.6-1.1	0.5		Greyish buff-yellow clay, grading up to coarse sand; muddy shale pieces the size of the coarse sand
1.1-1.3	0.2		Pebbles <0.5-3.0 inches; medium coarse sand matrix w/shale
1.3-2.6	1.3		Cross bedded, sandy silt, shale Clay lens, oxidizes red
			Shalely mudstone silt
2.6-2.8	0.2		Cobbles + pebbles: poorly sorted, well rounded
2.8-5.4	2.6		Shale w/ lenses of <0.5in-6in of limestone, metamorphics, and igneous
			(BF River)
River Sinuosity Measurements

	Upstream Reach	Downstream Reach		
Location D				
River Length (km)	1	1		
Valley Length (km)	0.83	0.98		
Sinuosity	1.2	1.0		
Location G				
River Length (km)	1	1		
Valley Length (km)	0.47	0.77		
Sinuosity	2.1	1.3		
Location H				
River Length (km)	1	0.9		
Valley Length (km)	0.82	0.5		
Sinuosity	1.2	1.8		
Location K				
River Length (km)	5	5		
Valley Length (km)	2.08	3.12		
Sinuosity	2.4	1.6		

Channel Width Measurements

	Width 1 (m)	Width 2 (m)	Width 3 (m)	Width 4 (m)	Width 5 (m)	Average
Loc. D	9.07	5.75	6.38	8.98	7.83	7.0
Loc. G	4.11	5.68	7.18	5.29	4.22	5.3
Loc. H	5.35	7.32	5.22	5.17	4.16	5.4
Loc. K	44.39	32.21	33.56	37.09	25.74	34.6

Notes:

- Measurements taken from Google Earth

- Width measurements taken from the reach 1 river kilometer upstream and 1 river kilometer downstream of each sample location.

Unit	Color	Name	Description
Location D)		
Qal	light beige yellow	Alluvial deposits (Holocene and Pleistocene)	Stream-laid deposits of mud, silt, sand, and gravel. Narrow deposits not shown. Max thickness 10m.
Tr	light red	Rhyolitic intrusive rocks (Eocene to Paleocene)	Tan to ivory containing sparse phenocrysts of quartz, feldspar, and biotite. Forms dikes, sills, and laccolithic bodies, including probable feeder pipes.
P[Pm	light blue	Minnelusa Formation (Lower Permian and Pennsylvanian)	Sandstone, limestone, and minor shale. Thickness 120-350m.
Мр	mid blue	Pahasapa Limestone (Lower Mississippian)	Mainly thick-bedded dolomitic limestone. Reef-like, bluish limestone in uppermost part. Includes Englewood Limestone in areas of steep terrain. Thickness 80-210m.
MDe	darker purple	Englewood Limestone (Lower Mississippian and Upper Devonian)	Lavender, impure limestone. Shown in combination with Pahasapa Limestone in areas of steep terrain. Thickness 10-20m.
Oww	lightest purple	Whitewood Dolomite (Upper Ordovician) and Winnipeg Formation (Middle Ordovician), undivided Whitewood Dolomite	Gray to tan, massive dolomite. Thickness 0-45m.
OCd	mid purple	Deadwood Formation (Lower Ordovician and Uppder Cambrian)	Glauconitic sandstone, shale, siltstone, and conglomerate. Thickness 0-200m.

Appendix 5-2. Descriptions of Exposed Geological Units at Locations D, G, H, and K

Unit	Color	Name	Description
Location G	i & H		
Qa	light beige yellow	Alluvium	Moderately to well-sorted clay, silt, sand, and gravel deposited by streams. Thickness ranges from 0-50 ft. A local aquifer where saturated.
Qg	yellow w/ red dots	Gravel deposits	Moderately sorted, heterogeneous, generally stratified, clay, silt, sand, and well-rounded gravel of paleochannels, pediments, and stream terraces along former flood plains. Three Quaternary terraces are identifiable in the northern portion of the study area and between 6 & 8 terraces in the southern portion. Thickness 0-60 ft. A local aquifer where saturated.
Kps	mid green Pierre Shale to Skull Creek Shale, undifferentiated (Cretaceous sequence) Pierre Shale 1200-2700; Niobrara Formation 80-300; C Formation 225-380; Belle Fourche Shale 150-850; Mor Sandstone 0-150 (local aquifer where saturated); and		Confining unit of shale, limestone, and sandstone containing the following formations listed with their thickness in feet: Pierre Shale 1200-2700; Niobrara Formation 80-300; Carlile Shale 350-750; Greenhorn Formation 225-380; Belle Fourche Shale 150-850; Mowry Shale 125-230; Newcastle Sandstone 0-150 (local aquifer where saturated); and Skull Creek Shale 150-270.
Location K		•	
Qal	light yellow	Alluvium (Quaternary)	Clay to boulder sized clasts with locally abundant organic material. Thickness up to 75ft (23m).
Qt	light brown	Terrace deposits (Quaternary)	Clay to boulder sized clasts deposited as pediments, paleochannels, and terrace fills of former flood plains. Thickness up to 75ft (23m).
Кр	wintergreen	Pierre Shale(Uppder Cretaceous)	Blue-gray to dark-gray, fissile to blocky shale with persistent beds of bentonite, black organic shale, and light-brown chalky shale. Contains minor sandstone, conglomerate, and abundant carbonate and ferruginous concretions. Thickness up to 2700st (823m).

A	ppendix	5-2	. Descri	ptions o	of Ex	posed	Geolog	gical	Units at	Locations	D, (э, н ,	, and	Κ
		-												

Notes:

Sources are listed in the Reference section of the text. https://ngmdb.usgs.gov/ngmdb/ngmdb_home.html

Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
		Arsenopyrite	< 5%	0.1 - 0.5	Subangular-subrounded	Vitreous iridescent black	
	- Silt - fine sand. Poorly	Quartz	80 - 85%	<0.1 - 0.8	Angular-subrounded, some prisms	Clear-opaque, some tinted slight yellow-amber	
G1.3B	- No reaction w/ acid. - Grains coated w/	Amphiboles	5 - 7%	0.2 - 0.5	Subangular	Black-green, golden iridescent	Garnets- Light of microscope interferes w/ colors
	(5-10% coverage).	Garnets / Chalcopyrite or Fe-oxides (?)	1 - 2%	<0.1	Angular, irregular	Red-amber, orange bronze-gold	
		Micas / Schist	< 3%	0.2 - 0.8	Platy sheets & pieces	Brown golden, reflective	
		Arsenopyrite	5-7%	<<0.1 - 0.1	Subangular-subrounded	Iridescent black, some with golden sheen	Golden luster on occassional grains of arsenopyrite. Siderite was not observed, but suspected to be present due to sample reaction with acid.
		Quartz	90%	<0.1 - 0.3	Angular-subangular	Clear-opaque, yellowish	
	- Fine Sitt. - Moderately well sorted. - Mild to strong	Micas	<3%	<0.3 - 1	Angular, platy, some elongate	Golden and silver iridescent sparkles	
G2.4	reaction w/ acid. - Grains coated w/ ultra fine grained yellow	Gypsum	<3%	0.1 - 0.5	Angular, platy	Pearly to clear	
	golden-white tint (50- 80% coverage) and ultra fine dark particles	Hematite (?)	<1%	<0.1 - 0.4	Subrounded	Bright rusty metallic red-orange, fine golden sparkles	
	(5% coverage).	Amphiboles (?)	<<1%	~0.5	Platy, angular striation	Dark greenish with blakc sheen	
		Deep green grains (?)	<<1%	<<0.1 - 0.2	Subrounded	Deep forest to emerald green crystalline sparkes	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes	
		Arsenopyrite	8-10%	<<0.1 - 0.1	Subangular	Iridescent black, vitreous		
	- Mostly clay. - Well sorted. - No reaction w/ acid	Quartz	80%	<<0.1 - 0.2 (avg 0.1)	Angular-subangular, some subrounded	Clear, some w/ orange-brown tint		
	Grains coated w/ ultra fine grained orange- yellow-brown tint and	Gypsum / micas (?)	5-8%	<<0.1 - 0.5	Angular, platy, thin	Pearly clear, vitreous / golden pearly, iridescent	ID b/c similar to biotite and interferences by	
G2.8 redi part cove fine part cove	redish metallic amber particles (50-80% coverage) and ultra	Hematite (?)	5-8%	<0.1 - 0.1	Subrounded	Rusty metallic shine, red-orange bronze	Difficult to distinguish between gypsum and	
	fine clay sized black particles (30-40% coverage).	Biotite (?)	<5%	0.1 - 0.5	Subangular, platy, thick	Dark but not as vitreous as arsenopyrite	- micas -	
		Deep green grain (?)	<<0.5%	~0.1	Subrounded	Deep forest to emerald green crystalline sparkes		
		Arsenopyrite	<5%	<0.1 - 0.2	Angular-subangular, good crystal faces	Vitreous iridescent black		
	- Mix of fine silt to clay.	Quartz	80%	<0.1 - 0.7	Angular-subangular	Clear, orange-yellow tint	Some grains covered w/ bronze-orange ultra fine grains.	
63.10	- Moderately well sorted. - No reaction with acid.	Schist	10%	~1	Subangular-subrounded	Black-green, brown-green, metallic		
63.10	- Grains coated w/ fine grained orange-bronze particles (10-30%	Gypsum / micas (?)	3%	0.5 - 1	Subangular-angular	Pearly iridescent		
	coverage).	Hematite (?)	1%	<0.1	Subrounded	Bright rusty metallic red-orange		
		Deep green grain (?)	<<0.5%	0.2 - 0.4	Subrounded	Forest emerald green, crystalline sparkle		

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID ¹	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
	- Fine silt and clay.	Arsenopyrite	<3-5%	<0.1 - 0.4	Subangular	Vitreous iridescent black	
	 Moderately well sorted. No reaction w/ acid. Grains coated w/ ultra 	Quartz	90%	<0.1 - 0.5	Angular-subangular elongate fragments	Clear, w/ orange tint	
G3.2D	fine yellow-orange brown particles (25- 50% coverage).	Glaucophane schist (?)	<3-5%	0.2 - 0.5 (1 max)	Subangular-platy	Green-blue black	-
	- Clear, thin needle to platy pieces w/ striations, more abundant in this	Garnet (?)	<3%	<0.1 - 0.1	Subangular	Deep red vitreous	-
	sample.	Clear rhombus prisms (calcite?)	<3%	0.2 - 0.5	Angular, perfect euhedral rhombus crystal faces	Clear	
		Arsenopyrite	3-4%	<0.1 - 0.3	Subangular-angular	Iridescent pearly black	
		Quartz	80-85%	<0.1 - 0.5	Angular-subrounded	Clear-opaque, orange-yellow tint	
	- Fine silt and clay with	Garnet (?)	3%	<0.1 - 0.3	Angular-subangular, no distinct crystal faces	Dark amber-red	
	a few large grains. - Moderately well	Glaucophane schist (?)	<3%	0.2 - 0.5	Angular-subangular, platy	Black-green	
G3.3A	- Slight reaction with acid.	Micas	<3%	0.2 - 0.5	Angular, platy	Golden brown	
	fine particles of clear and orange-yellow and	Hematite (?)	1-2%	<0.1 - 0.2	Subangular	Rusty sub-metallic red crystalline sparkles	
	black grains.	Gypsum	1-2%	0.2 - 0.5	Angular, thin platy	Iridescent, transparent	
		Elongate clear fibers	1-2%	0.3 - 0.5	Thin elongate, striations	Clear, yellow tinted	
		Chloritic green grains	<1%	0.1 - 0.3	Subangular-subrounded	Deep chloritic green, granular crystalline particles	

Appendix 5-3. Mineralogical O	bservations of Select	Sediment Samples
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Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
		Arsenopyrite	10-15%	<0.1 - 0.7	Subangular-angular	Iridescent vitreous black	
		Quartz	40-50%	<0.1 - 1	Subangular-angular, some prisms	Clear-opaque, yellow tinted	
		Amphiboles	5-8%	0.2 - 0.5	Angular	Pearly black, dark green	_
	- Silt with some clay, 25% fine sand. - Poorly sorted.	Glaucophane schist (?)	5-8%	0.3 - 0.5	Angular, platy	Dark brown to pearly black	
G3.3F	- No reaction w/ acid. Grains coated w/ ultra fine rusty orange-	Garnet (?)	3-5%	0.1 - 0.3	Angular-subangular, no distinct crystal faces	Dark amber-red	Pyrite / gold(?) are mostly associated w/ arsenopyrite grains.
	yellow particles. - Heavily coated, hard to ID grains.	Micas	3-5%	0.3 - 0.5	Angular, thin platy	Pearly, brown greenish grey	
		Gypsum (?)	1-2%	0.2 - 0.4	Angular, thin platy	Iridescent, transparent	-
		Elongate clear fibers	1-2%	0.2 - 0.7	Thin elongate, striations	Clear, yellow tinted	
		Pyrite / gold (?)	<0.5%	<0.05	Angular, very fine grain	Deep golden bright shine	_
		Arsenopyrite	7-10%	<0.1 - 0.2	Subangular	Vitreous iridescent black	
	 Fine silt and clay. Well sorted, very fine grained 	Quartz	80-85%	<0.1 - 0.3	Angular-subangular	Transparent-opaque, orange- yellow tint	_
00.45	 No reaction w/ acid. Grains coated w/ fine 	Elongate clear fibers	10-15%	0.1 - 0.5	Angular, fragments of needles, shards	Clear, slightly yellow tinted	>90% of quartz found in grey clusters. Pyrite / chalcopyrite / gold(?) are mostly associated w/ arsenopyrite grains.
G3.4E	crystalline fine particles (80-90% coverage).	Micas	7-10%	0.1 - 0.4	Subangular, irregular flakes	Golden brownish yellow or dark iridescent black	
	- Abundance of grey, brown, rusty orange- red, golden clumps.	Schist	3%	0.2 - 0.4	Angular-subangular, platy	Greyish black, green iridescent	
		Pyrite / chalcopyrite / gold (?)	<0.8%	<0.05	Irregular to cubic, tiny specs on occasional grains	Golden bright	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
		Arsenopyrite	3-5%	<0.1	Subangular-angular	Vitreous iridescent black	
	- Moderately well sorted.	Quartz	85-90%	<0.1 - 0.5	Subangular-angular	Clear-opaque, a few tinted amber colored grains	Arsenopyrite grains are
K1 1D	 No reaction w/ acid. Ultra fine powdery, clear, white, and 	Hematite / Fe-oxide grains	5-7%	<0.1 - 0.3	Subangular, granular	Deep organge rusty red, organge- yellow, golden	associated with tiny patches of deep bright red or golden orange
KI.ID	orange-gold, or crystalline metallic deep orange particles	Micas	3-5%	0.2 - 0.7	Subangular, irregular, platy, curved	Golden brown pearly dark silver	fibers or grains. Pyrite / chalcopyrite / gold(?) are mostly associated
	(80-90% coverage). Ultra fine black	Schist	<3%	0.3 - 0.5	Angular	Black and green	w/ arsenopyrite grains.
		Pyrite / chalcopyrite / gold (?)	<<1%	<0.05	Too small to tell, possibly cubic	Small tiny flecks, bright golden sparkles	
K1.1E	- Clay and fine silt.	Arsenopyrite	3-8%	<0.1 - 0.3	Subangular-subrounded	Vitreous iridescent black	
	sorted. - No reaction w/ acid. - Heavily coated w/	Quartz	85-95%	<0.1 - 0.3	Angular, very irregular shattered, fragmental	Clear-opaque, w/ orange tint	
	brown bronze particles. - Forms clumps, each clum having vastly different modal percentages.	Micas	5-8%	0.2 - 0.4	Subangular, platy, flaky	Yellow, brown, golden reflective iridescent	
		Amphiboles (?)	1-3%	0.1 - 0.4	Semi-elongate w/ striations	Hard to distinguish from arsenopyrite, green black	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
	- Clay and fine silt. - Moderately well to	Arsenopyrite	5-8%	<0.1 - 0.3	Subangular, irregular faces	Vitreous iridescent black, deep brone-red coating	
K1 25	poorly sorted. - No reaction w/ acid. - Grains coated by ultra	Quartz	80-85%	0.1 - 0.4 (0.8 max)	Angular-subangular	Clear, tinted w/ rusty orange	
K1.2F	particles (30-90% coverage). - Different modal	Schist or micas	5-8%	0.1 - 0.4	Platy flaky	Black, golden yellow brown	
	percentages for different clumps.	Gold or pyrite / chalcopyrite	<0.5%	<<0.05	Too small to see shape	Bright metallic golden	
	- Clay and fine silt. - Moderately poor	Arsenopyrite	<3%	0.1 - 0.2	Subangular-subrounded	Vitreous irridescent black	
		Quartz	80-90%	<0.1 - 0.4	Subangular-angular	Clear-opaque	Ultra fine grained particles could be micas, pryite, or gold.
K1 21	sorting. - No reaction w/ acid. - Heavily forms hard	Micas	5-7%	<<0.1 - 0.2	Platy	Irridescent, golden silver	
NI.21	clumps, ~90% of grain surfaces covered by ultra fine particles,	Fe-oxides	2-3%	<0.1	Subrounded flakes or pieces	Orange-red golden luster	
	obstructing view of larger particles.	Ultra fine grained particles	80-90%	<0.01	Sugar-like granules (quartz?)	white to light orange	
		Ultra fine grains w/ gold luster	1%	<<0.01	Finely disseminated throughout	Bright golden luster	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID 1	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
	- Clay and fine silt.	Arsenopyrite	<3%	0.1 - 0.3	Subangular	Irridescent vitreous black	
K1 24	- Moderately well sorted. - No reaction w/ acid.	Quartz	85-90%	<0.1 - 0.4	Subangular-angular	Clear-opaque, some yellow tint	Elongate striated shards (unknown composition) with dusting of rusty
KI.3A	grained light orange- yellow to rusty red- bronze particles (10-	Amphiboles	<3%	0.2 - 0.4	Elongate w/ striations	Black w/ iridescent luster	luster ultra-fines (5-10% coverage), possilby Fe- oxide grains.
	30% coverage).	Schist (Glauconitic?)	<2%	0.2 - 0.4	Platy	Black w/ green hues, vitreous	
		Arsenopyrite	~5%	<0.1 - 0.3	Subangular	Black vitreous iridescent	
	- Clay and fine silt. - Moderately well	Quartz	85-90%	<0.1 - 0.3	Angular to sub-angular, fragmented/broken	Clear-opaque, some orange tinting	Some arsenopyrite grains have weathered
K1.3D	sorted. - No reaction w/ acid. - Coated w/ white &	Micas	3-5%	0.2 - 0.4	Subangular, platy	Golden brown to black, silver- green iridescent	roun indentation pockets filled with fine powdery-grannular
p	orange fine grained particles.	Amphiboles	<3%	0.2 - 0.4	Black irredescent luster	Black iridescent luster	possibly Fe-oxides (red- orange bronze luster).
	U	Ultra fine golden grains	<<1%	<0.05	Too small to tell	Bright golden luster	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

Sample ID ¹	Description	Minerals	Abundance	Size (mm)	Shape/Form	Color	Notes
	 Fine silt with clay. Moderately well sorted. Strong reaction with acid. Coated w/ white-clear fine grained particles and finely disseminated ultra fine grained black particles 	Arsenopyrite	<3%	<0.1 - 0.2	Subangular	Vitreous, iridescent black	
		Quartz	95%	<0.1 - 0.4	Subangular-angular	Clear white-opaque	
		Micas	1%	0.2 - 0.5	Subangular, platy	Golden brown & silver, iridescent, reflective	
K1.4D		Calcite (?)	1-2%	0.3 - 0.4	Rhombohedral, clean faces	Milky clear, rainbow colors, light pearly	
		Fe-oxides	1-3%	<0.1 - 0.1	Subangular-subrounded	Golden rusty to deep rusty-red luster	
		Ultra fine golden-bronze grains (on quartz & arsenopyrite grains)	<<0.5%	<<0.05	Too small to tell	Bright golden luster	

Appendix 5-3. Mineralogical Observations of Select Sediment Samples

¹ The Sample ID matches the "Original Field Notes Sample ID" field from Table 5.1.

Mineral Type ¹	Mineral Name	Chemical Composition	Solubility	Occurance	Select Relevant Counties	Select Relevant Locations	Pg # ²
	Azurite	Cu ₃ (OH) ₂ (CO ₃) ₂	effervesces in HCl	very sparingly in pegmatites and vein deposits, associated with malachite	Lawrence	WWC, Lead, Deadwood	31
	Calcite	CaCO3	dissolve in dilute HCl	widely distributed (Pahasapa limestone), implanted on pyrite & dolomite crystals	Lawrence Meade	Homestake	45
	Cerussite	PbCO ₃	effervesces in nitric	several locations & mines (important Pb ore)	Lawrence	Lead, Galena	56
	Dolomite/ Ankerite	Ca(Mg,Fe,Mn)(CO ₃) ₂	powdered, effervesces in acids	gangue mineral in veins and ore desposits, associated w/ calcite, quartz, pyrite.	Lawrence	Homestake, WWC, Deadwood	74, 19
Carbonates	Magnesite	MgCO ₃	soluble in HCl	occurs sparingly as gangue mineral in gold and carbonate ore deposits.	Lawrence	Homestake	128
Carbonates	Malachite	Cu ₂ (OH) ₂ (CO ₃)	effervesces in acids	observed in pegmatites, insignificant amounts in several vein deposits, incrustations in cracks of slate	Lawrence	Homestake	130
	Rhodochrosite	MnCO ₃	soluble in warm acids	small pockets in mineralized zones 2 miles SW of Lead, minor amounts in calcite-pyrite veins at Homestake	Lawrence	Lead, Homestake	173
	Siderite	FeCO ₃	soluble in HCl	very common gangue mineral, in quartz geodes from the Englewood Formation	Lawrence Meade	Homestake, WWC, Deadwood	182
	Smithsonite	ZnCO3	effervecess in acids	alteration product along fractur/cleavage planes in sphalerite	Lawrence	Galena	185
	Strontianite	SrCO ₃	soluble in HCl	radial-fibrous aggregates up to 2 inches thick collected at the 5450 ft level at Homestake	Lawrence	Homestake	196

Appendix 5-4.	Mineralogy of t	he Black Hills	 Select Summary 	of Minerals
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Mineral Type	Mineral Name	Chemical Composition	Solubility	Occurance	Select Relevant Counties	Select Relevant Locations	Pg # 1
	Arsenolite	As ₂ O ₃	n/a	probably present at many localities where arsenopyrite was exposed to weathering, but only reported in 2 localities	Custer, Pennington	Custer, Keystone	26
	Cassiterite	SnO ₂	soluble in HCl	found in abundance in well-weathered exposures of the Sharon Spring member of the Pierre Shale and in pegmatites	Lawrence	Tinton	51
	Goethite	HFeO ₂	soluble in HCl	after hematite, most common ferric oxide, widespread, occurs as fibrous veinlets in quartzite or stalactitic masses	Lawrence, Meade	Roubaix, Sturgis	95
	Hematite	Fe ₂ O ₃	soluble in concentrated HCl	widespread occurrence, mined for ore, deposited as banded beds	Lawrence	WWC, Deadwood, Homestake	107
Oxides and	Ilmenite	FeTiO ₃	n/a	found sparingly in pegmatites and metamorphic rocks	Lawrence	Nemo, Roubaix	114
Oxy-	Lepidocrocite	FeO(OH)	n/a	present in much of the material that is commonly classed as limonite	n/a	n/a	122
hydroxides	Limonite	$Fe_2O_3 - nH_2O$	soluble in HCl	name given to mixtures of goethite, hematite, and other hyrdrous Fe-oxides	Lawrence, Meade	WWC, Deadwood, Homestake	125
	Magnetite	FeFe ₂ O ₄	soluble in HCl	many known localities, minor constituent of many igneous, metamorphic, and sedimentary rocks	Lawrence	Homestake, Nemo, Lead	129
	Manganite	MnO(OH)	soluble in HCl	possibly numerous occurrences in deposits of Mn-oxides, difficult to ID without X-ray methods	Lawrence	Deadwood	131
	Pyrolusite	MnO ₂	soluble in HCl	component of concretions in pockets / layers / dendrites of Pahasapa and other limestones	Lawrence	Lead, Deadwood	161
	Rutile	TiO ₂	insoluble in acids	occurs sparingly in certain igneous and metamorphic rocks as microscopic accessory mineral	Lawrence	Little Elk Creek, Nemo	174

Appendix 5-4. Mineralogy of the Black Hills - Select Summary of Minerals

Mineral Type	Mineral Name	Chemical Composition	Solubility	Occurance	Select Relevant Counties	Select Relevant Locations	Pg # 1
	Argentite	Ag ₂ S	n/a	mircroscopic inclusions in argentiferous galena (mined for Ag), major silver mineral at Galena	Lawrence	Galena	25
	Arsenopyrite	FeAsS	decomposes by nitric	great abundance in ores at Homestake, in disseminated grains, compact masses, & crystals (occasionally coated in gold). Crystals often quite well developed when found in chlorite or quartz, occasionally coated with bright plates of gold or inclusions of gold	Lawrence	Homestake, Deadwood	27
	Chalcopyrite	FeCuS ₂	n/a	most widespread of Cu-ores, scattered but not abudant	Lawrence	Homestake, Deadwood	59
	Covellite	CuS	n/a	found sparingly associated with bornite, chalcocite, chalcopyrite in veinlets of oxidized materials	Lawrence	Galena	72
	Galena	PbS	dissolves in nitric (forms Pb-sulfate)	widespread in ore veins	Lawrence	Homestake, Deadwood	90
Sulfides	Loellingite	FeAs ₂	n/a	observed in 1 vein deposit in Black Hills area, abundant in small grains associated with galena and pyrite	Lawrence	Galena	127
	Marcasite	FeS ₂	easily decomposes in dilute nitric	occurs in slates and schists, accessory mineral in several ore deposits, found as thin flaments fillings cracks in Pierre shale and other sedimentary rocks	Lawrence Meade Butte	WWC, Deadwood	132
	Molybdenite	MoS ₂	decomposes by nitric	very sparingly in qtz veins, small flakes	Lawrence	Maitland	143
	Pyrite	FeS ₂	insolube in HCl, but fine powder is completely soluble in strong nitric	most abundant sulfide mineral, associated with calcite, dolomite, quartz crystals at Homestake	Lawrence	Homestake	158
	Pyrrhotite	Fe _(1-x) S	dissolves in HCl	widespread in vein deposits, constituent of gold ore, in small irregular masses enclosed in arsenopyrite	Lawrence	Homestake, Deadwood	166
	Sphalerite	ZnS	dissolves in HCl	widely distributed but in small amounts iin pegmatites and vein deposits	Lawrence	Deadwood	187
	Stibnite	Sb ₂ S ₃	solube in HCl	found sparingly in vugs in gold ores	Lawrence	Deadwood	195

Appendix 5-4. Mineralogy of the Black Hills - Select Summary of Minerals

Mineral Type	Mineral Name	Chemical Composition	Solubility	Occurance	Select Relevant Counties	Select Relevant Locations	Pg # 1
	Alunite	KAl ₃ (SO ₄) ₂ (OH) - 3H ₂ O	insoluble in HCl	abundant in gold ores at bottom of Strawbery gulch	Lawrence	Deadwood	9
	Anglesite	PbSO ₄	slightly soluble in nitric acid	constituent of Pb-carbonate ores containing galena	Lawrence	Carbonate, Galena	18
	Barite	BaSO ₄	insoluble in acids	widespread in South Dakota, found in cavities in Pierre shale and as gangue mineral in vein deposits	Meade, Lawrence	Homestake, Lead, Sturgis, Belle Fourche River	33
	Celestite	SrSO ₄	insoluble in acids	found in flourite bearing vein (only occurrence)	Lawrence	Lead	55
	Chalcanthite	CuSO4 - 5H ₂ O	in water	in mine tailing, from oxidation of Cu-sulfides (decomposition of chalcopyrite)	Lawrence	Deadwood	58
	Epsomite	MgSO ₄ - 7H ₂ O	in water	efflorescences as thick white crust where pyrite/sulfides are decomposing in the presecence of magensian rocks	Lawrence	Homestake	76
Sulfates	Goslarite	ZnSO ₄ - 7H ₂ O	easily in water	formed through decompostion of sphalerite, found on mine walls	Lawrence	Galena	97
	Gypsum	$CaSO_4 - 2H_2O$	dilute HCl	wide spread, sometimes in thick beds, occurs in abundance as the mineral selenite in Pierre Shale	Meade Lawrence	Lead, Whitewood, Sturgis	102
	Jarosite	KFe ₃ (OH) ₆ (SO ₄) ₂	Insoluble in water soluble in HCl	secondary mineral, widespread as yellowish crusts and coating in cracks and seams in iron- rich ores and rocks	Lawrence	Lead	117
	Melanterite	FeSO ₄ - 7H ₂ O	easily in water	common alteration product of pyrite/marcasite, found as coating on marcasite nodules in Pierre Shale	Lawrence	Deadwood	133
	Natrojarosite	NaFe ₃ (SO ₄) ₂ (OH) ₆	slowly soluble in HCl	coating in and sometimes partly filling cavities in auriferous quartzite	Lawrence	Lead	149
	Potash Alum (Kalinite)	KAI(SO4) ₂ - 12H ₂ O	easily in water	efflorescence on slates, formed by action of sulfuric acid, liberated in the oxidation of pyrite, on aluminum compounds	Lawrence	Lead	157

Appendix 5-4. Mineralogy of the Black Hills - Select Summary of Minerals

Notes:

¹ Select known Black Hills mineral species observed in Butte, Lawrence, and Meade counties by type

² Source: Roberts, Willard L., Rapp Jr, George. Mineralogy of the Black Hills. 1965. South Dakota School of Mines and Technology. Bulletin ; no. 18. n/a = information not available

	Αα	AI	As	в	Ba	Be	Са	Cd	Ce	Co	Cr	Cu
· וח M	0 002	0.05	0.02	0.01	0.0005	0.0002	0.05	0.0005	0.05	0.005	0.005	0.005
62.9	2 364	15324 036	510.256	11 022	205 595	0.906	11597.076	< 0.049	21 794	12 106	24 751	60 722
G2.0 G2.7	2.304	19927 622	1990 673	10.200	164 020	0.000	2056 195	< 0.040	20 /07	10 337	24.731	91 172
G2.7	0.2012	0004 402	0 511	6.024	104.920	0.507	40060.050	0.040	29.491	6 6 2 7	10 075	15 216
G2.0 C2.5	0.365	15020 019	0.011	10.934	121.427	0.524	42300.330	0.291	24 171	0.037	12.075	15.210
G2.5	0.000	10020.910	9.434	12.710	1/9.330	0.703	40279.700	0.329	34.171	0.324	20.013	27.002
G2.4	0.808	10310.393	12.715	8.002	144.209	0.000	40093.135	0.201	37.901	9.803	17.338	25.640
G2.3	1.017	10108.104	13.991	8.676	204.390	0.898	15503.065	0.351	43.980	9.933	20.770	30.015
G2.2	1.202	8617.048	20.370	8.599	310.755	1.101	64442.516	0.739	39.291	16.636	11.400	33.739
G2.1	0.461	13250.303	0.020	9.466	128.107	0.571	20904.545	0.382	30.031	2.300	13.990	33.753
H1./	1.624	8152.780	21/5.211	5.257	135.613	0.173	6515.279	< 0.05	18.448	3.323	12.555	43.783
H1.6	2.983	5545.050	2/5/.515	7.152	167.452	0.345	17193.386	< 0.05	22.746	5.083	10.077	98.064
H1.5C	1.832	11468.533	1955.545	5.612	147.562	0.244	7880.726	< 0.05	18.139	1.397	18.486	/1.939
H1.5B	2.866	6762.518	1961.741	6.395	134.915	0.144	6701.785	< 0.05	16.239	1.999	10.437	88.804
H1.5A	2.670	10288.847	2037.891	7.057	163.242	0.168	148/2.042	< 0.049	16.185	6.354	14.553	51.651
H1.5AA	1.398	12568.081	484.764	14.527	228.708	1.403	6260.431	0.119	22.478	3.481	11.592	566.520
H1.4	2.045	6150.332	1023.537	8.030	160.543	0.321	//30.94/	< 0.05	30.815	6.488	9.184	47.382
H1.3B	1.631	5/3/.325	1429.299	7.431	145.661	0.311	8518.894	< 0.05	16.143	5.037	10.025	49.364
H1.3A	2.616	7186.229	2062.778	6.581	153.331	0.360	8772.197	< 0.051	19.416	14.619	12.113	53.205
H1.2B	2.757	6485.282	994.564	4.977	190.805	0.834	14578.714	0.205	26.264	22.787	10.654	62.775
H1.2A	2.231	6297.899	667.260	5.457	146.067	0.570	14835.038	0.169	33.931	22.168	10.730	44.452
H1.2AA	2.631	35953.746	254.618	< 0.972	13.439	6.269	2385.050	3.011	108.808	166.538	3.490	512.507
H1.1	0.897	15527.203	5.641	15.601	370.305	0.674	18290.463	< 0.048	28.545	11.294	22.982	24.330
G3.1A	5.391	11147.769	1128.156	8.926	149.231	0.370	2703.949	< 0.055	22.097	5.314	16.903	62.251
G3.1B	4.510	7742.111	805.079	8.113	112.476	0.358	693.787	< 0.048	20.988	9.002	14.436	82.786
G3.1C	3.770	8230.249	530.142	7.500	149.548	0.650	3184.144	< 0.049	28.037	14.454	19.935	62.645
G3.1D	2.414	8633.270	122.814	7.093	126.011	0.649	26717.095	< 0.05	33.463	8.821	18.037	33.067
G3.1E	3.719	10511.184	1193.657	8.491	180.109	0.630	33334.001	< 0.051	32.027	11.437	18.638	63.738
G3.2A	3.988	15423.977	1081.942	10.061	156.772	0.535	4550.459	< 0.049	29.237	7.795	19.195	66.685
G3.2B	5.544	22469.770	1199.347	10.013	208.712	0.433	12295.015	< 0.049	16.428	4.188	25.127	79.179
G3.2C	5.437	8683.888	2235.862	6.349	127.306	0.347	7885.399	< 0.05	26.307	3.772	13.528	49.050
G3.3A	2.167	10335.198	648.641	6.088	107.522	0.629	9618.105	< 0.05	38.446	8.820	15.569	29.090
G3.3B	4.272	22597.308	959.974	7.422	197.635	0.444	11254.158	< 0.05	22.136	7.077	25.925	59.641
G3.3C	6.761	10504.775	4061.116	5.560	145.520	0.228	14210.714	< 0.049	12.692	1.839	15.903	35.737
G3.3D	6.082	20263.827	1116.464	7.595	190.437	1.046	9535.202	< 0.05	35.782	24.066	22.986	101.573
G3.4A	3.082	10032.048	2194.072	4.706	105.905	0.540	2884.811	< 0.049	33.992	9.496	15.106	41.283
G3.4B	3.813	18912.834	2442.285	5.158	184.120	0.539	1956.148	< 0.048	25.702	8.311	23.214	60.283
G3.4C	5.990	11301.232	2141.004	5.136	149.985	0.272	14560.999	< 0.049	14.692	3.734	15.956	58.127
G3.4D	6.986	22113.251	1276.307	6.264	181.410	0.747	21087.334	< 0.05	15.360	12.943	24.648	65.782
H2.1A	3.459	4566.027	731.087	4.445	249.329	0.543	12830.469	< 0.048	24.381	7.029	10.730	30.840
H2.1B	3.538	4343.899	845.317	4.148	258.807	0.592	12538.511	< 0.048	27.378	7.471	9.975	29.555
H2.2	3.024	5153.412	651.856	3.358	181.933	0.452	12383.212	< 0.048	30.000	6.187	9.656	29.695
H2.3A	5.664	6818.914	2633.561	4.988	131.007	< 0.019	10353.248	< 0.049	15.145	< 0.498	11.408	35.073
H2.3B	6.355	11853.558	3889.577	7.547	151.901	0.084	15153.671	< 0.05	16.486	1.651	19.134	52.556
H2.3C	6.825	21412.394	910.166	7.899	160.875	0.577	17248.961	< 0.05	22.793	16.676	25.938	115.196
H2.3D	4.656	21443.090	598.130	6.872	153.502	1.203	21589.055	< 0.048	34.122	25.336	19.633	101.386
H2.4A	5.373	18940.861	3165.782	7.110	177.684	0.165	2703.490	< 0.052	23.936	3.210	25.865	93.531
H2.4B	6.413	10169.213	1872.543	5.512	137.118	0.031	11698.019	< 0.05	18.223	< 0.501	13.809	29.147
H2.4C	6.878	16792.232	979.439	8.698	160.371	0.506	18733.833	< 0.05	24.522	33.245	21.739	106.020
H2.4D	7.956	25715.623	893.554	11.420	199.083	0.993	15868.742	< 0.05	30.425	16.590	27.117	100.020
H2.4E	3.241	12370.007	173.169	9.879	180.313	0.670	25688.863	< 0.049	31.119	8.295	17.786	31.435
K1.1A	2.362	14819.797	193.161	10.508	315.674	0.609	14800.199	< 0.049	32.144	9.834	17.886	28.085
K1.1B	2.743	15782.674	331.093	11.653	241.266	0.615	12419.114	< 0.049	32.325	10.643	19.045	32.639
K1.1C	6.519	19139.669	1731.340	15.215	146.282	0.362	22062.972	< 0.05	22.071	8.195	24.035	68.253
K1.1D	8.171	31999.666	2245.859	15.008	171.235	0.404	18923.580	< 0.049	24.591	7.157	39.131	128.133
K1.2A	2.929	14131.062	334.809	9.450	257.132	0.618	11861.028	< 0.048	31.685	9.862	17.585	32.636
K1.2B	6.136	17222.997	2037.674	13.195	177.289	0.385	15408.168	< 0.049	23.098	9.224	21.951	74.305

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

	Fe	к	Li	Μα	Mn	Мо	Na	Ni	Р	Pb	s
MDL:	0.1	0.01	0.01	0.01	0.002	0.005	0.01	0.002	0.05	0.02	0.05
G2.8	95650,956	3834,214	12,596	9530.831	1626.376	1.323	72,742	26,738	582,694	14.846	456,915
G2.7	103572.259	4083.569	10.603	9752.169	1864.827	1.159	51,189	18.064	783.687	19.932	1341.058
G2.6	18513.851	1959.035	8.117	8685.354	415.755	3.018	104.282	19.020	463.578	10.725	4820.470
G2.5	24273.719	3338.125	15.281	8677.434	464.631	4.003	397.053	29.161	663.649	14.376	15897.800
G2.4	27617.048	2290.983	10.292	10181.158	570.581	3.614	402.946	31.373	631.985	13.623	2011.681
G2.3	28256.916	3288.502	12.286	6054.479	546.441	2.852	468.251	33.678	686.519	17.000	3008.099
G2.2	40276.344	1512.801	6.843	6881.570	906.011	6.010	345.785	48,466	526.654	15.933	1877.396
G2.1	18963.204	2611.050	13.092	5608.666	87.099	5.896	331.098	25.925	273.841	20.486	11617.599
H1.7	92196.553	3054.307	2.545	3834.161	497,726	0.692	92.680	9.613	389.844	14.108	11343.340
H1.6	99787.536	2525.935	1.801	2401.206	437.306	5.367	168.013	13.622	563.288	27.261	17940.591
H1.5C	79027.537	2370.740	5.101	5375.466	286,125	0.622	63.068	6.528	480.911	15.122	10566.667
H1.5B	100140.214	2380,789	3.019	2787.086	391.376	0.692	76.330	6.520	224.828	21.228	16628.289
H1.5A	96811.616	3707.013	4.417	4976.559	431.657	< 0.499	107.897	11.559	228.530	15.976	23728.489
H1.5AA	36720.532	1598.279	5.844	4240.193	197.982	1.328	61.519	13.047	273.066	11.447	9309.919
H1.4	102659.457	2347.030	2.595	3002.505	860.103	0.912	83.447	10.956	227.410	20.099	25289.521
H1.3B	104457.477	2164.801	2.683	2866.935	773.844	1.193	77.588	10.745	400.041	20.669	25650.391
H1.3A	98203.156	2510.170	2.769	3458.917	729.306	1.007	81.892	15.527	562.955	19.679	19662.980
H1.2B	70699.337	1255.294	3.221	4143.811	2342.938	3.744	67.350	30,715	700.255	23.579	15071.627
H1.2A	72395.145	1517.698	2.444	6110.110	4347,120	2.463	51.341	34.451	673.427	20.257	12807.522
H1.2AA	15550,107	251.930	27.197	41263.536	11533.820	0.549	86.235	227.682	621.888	2.460	130677.462
H1.1	21675.312	3738.736	26.061	10685.463	140.703	0.688	242.243	33.706	578.996	17.991	6411.588
G3.1A	103118.902	3027.988	4.173	6064.359	1122.248	2.030	27.020	11.086	930.991	16.336	2112.059
G3.1B	110813.916	2633.411	2,192	3440.867	1210.889	1.081	22.030	13.219	514.359	13.056	3814.909
G3.1C	84135.828	2295.753	5.459	4404.090	2023.105	1.606	34.627	23.271	414.973	11.509	618.612
G3.1D	38674.949	2671.920	6.200	9902.549	660,100	2.095	87.919	26.274	546.728	12.827	3066.637
G3.1E	61680 520	2459 790	7 116	9864 534	1102 271	2 396	107 453	29 206	684 954	22 928	2880 453
G3.2A	80195 674	6127 199	9 223	7836 564	1359 728	1 001	156 631	16,966	601 113	12 952	5254 345
G3.2B	101040 202	6366 426	12 292	11557 144	759 639	< 0.49	42 196	8 499	504 618	11 386	8818 919
G3.2C	86897.367	3341.481	3.714	4150.902	530.913	1.201	88.760	8.823	472.208	17.222	10239.992
G3.3A	36128.598	3051.405	5.263	5643.272	648.752	1.484	42.260	23.272	533.840	15.530	886.462
G3.3B	85675.380	5141.607	11.409	11660.414	1311.730	< 0.504	50.478	11.071	448.262	12.398	5035.772
G3.3C	115664.215	3687.014	3.250	5035.889	469.664	0.829	411.167	6.161	497.658	21.159	20036.453
G3.3D	110636.571	3762.926	11.013	8650.848	3896,560	0.768	49.270	26,799	618.500	17.585	9408.510
G3.4A	58168,480	3062,295	4.071	3704.457	760.098	1,796	45,461	21,713	502.340	15.809	2119.854
G3.4B	92541.944	4927.868	8.919	8809.639	1048.440	0.893	44.603	14.131	499.577	16.209	3168.121
G3.4C	110172.129	4897.963	3.735	5276.700	518,546	0.813	107.122	8.081	481.739	15.050	16965.609
G3.4D	109772.248	4500.319	10.709	10127.945	2294.752	0.982	35.686	8.452	525.213	12.934	19111.848
H2.1A	62654.970	1001.004	1.124	3756.859	806.671	2.731	254.335	17.405	776.407	11.699	3336.047
H2.1B	60263.560	913.825	1.252	3434.451	860.180	3.236	245.454	18.701	576.670	12.634	3700.969
H2.2	52244.864	1078.177	1.754	3552.583	693.174	2.986	177.063	16.707	557.678	12.096	2034.509
H2.3A	122579.566	3977.550	< 0.997	3212.125	799.925	0.524	200.004	4.028	232.524	12.010	20784.336
H2.3B	114983.436	3875.360	3.662	5356.901	560.956	0.756	200.033	6.615	585.317	13.344	21073.704
H2.3C	106567.891	4730.567	11.902	9616.557	1517.893	0.750	123.342	16.769	463.688	13.626	15291.205
H2.3D	67745.724	3477.795	15.614	7292.912	2911.678	1.796	182.520	33.676	623.061	14.368	15063.372
H2.4A	108013.247	4687.302	6.882	8853.272	802.108	0.680	112.895	6.441	561.949	14.552	6616.343
H2.4B	112213.061	3624.523	3.357	4735.848	655.389	< 0.501	199.865	4.529	294.157	11.813	19924.581
H2.4C	101514.421	3620.461	8.655	7813.518	4068.846	1.090	298.746	18.976	392.441	15.818	14572.894
H2.4D	115559.339	4888.366	22.745	12330.885	2911.629	0.594	446.904	19.765	502.093	16.059	11394.241
H2.4E	40989.470	2877.614	9.046	9200.961	1589.460	2.023	513.326	28.262	574.711	13.874	4367.976
K1.1A	35868.823	2568.602	14.433	7101.223	713.369	1.156	212.283	26.423	637.458	15.183	1792.475
K1.1B	41617.751	2525.336	15.523	7122.189	846.829	1.111	225.643	29.612	609.165	15.410	2520.274
K1.1C	93735.342	3624.020	13.039	9954.543	1698.821	0.817	335.901	18.016	487.572	13.011	13014.364
K1.1D	120157.767	6199.323	17.777	23740.762	2658.436	0.500	584.575	13.760	656.915	16.287	12251.349
K1.2A	40757.367	2372.637	13.763	6878.319	739.623	1.519	216.082	25.834	696.550	14.744	1509.624
K1.2B	92847.285	2998.770	12.029	9190.114	2180.267	1.158	150.855	20.008	618.136	16.161	6437.677

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

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	Sb	Se	Si	Sn	Sr	Ti	TI	v	Zn
MDL:	0.02	0.02	0.01	0.02	0.0001	0.001	0.02	0.005	0.001
G2.8	2.350	3.522	771.990	< 1.924	44.482	195.992	< 1.924	42.184	83.621
G2.7	2.044	6.118	879.833	< 1.947	22.688	273.073	< 1.947	42.626	90.339
G2.6	3.762	2.471	851.550	< 2.074	101.502	42.136	< 2.074	17.040	41.896
G2.5	3.038	2.951	1045.979	< 1.976	194.840	28.587	< 1.976	30.813	70.763
G2.4	3.251	3.062	763.150	< 2.062	95.494	39.375	< 2.062	23.928	70.543
G2.3	3.221	< 2.024	826.629	< 2.024	94.540	28.971	< 2.024	29.953	90.801
G2.2	3.093	4.277	933.853	< 2.023	145.410	11.609	< 2.023	31.762	94.086
G2.1	4.241	2.779	996.019	< 2.017	197.696	10.454	< 2.017	15.001	53.360
H1.7	3.785	5.582	538.499	< 2.01	21.493	286.136	< 2.01	22.094	41.575
H1.6	7.371	8.701	477.591	< 2.03	64.918	172.498	< 2.03	28.353	51.082
H1.5C	3.423	6.124	570.673	< 2.015	20.741	357.606	< 2.015	28.000	35.423
H1.5B	3.243	9.208	533.553	< 2.006	18.647	242.573	< 2.006	24.476	53.326
H1.5A	3.524	4.876	587.963	< 1.999	27.045	330.670	< 1.999	27.859	97.140
H1.5AA	2.558	5.984	377.420	< 1.953	29.949	310.613	< 1.953	22.838	32.720
H1.4	3.829	8.133	350.540	< 2.01	28.317	186.664	< 2.01	24.137	56.087
H1.3B	4.608	7.280	374.217	< 2.004	32.902	153.752	< 2.004	24.831	55.415
H1.3A	6.519	5.365	484.620	< 2.042	40.772	195.919	< 2.042	26.852	69.662
H1.2B	7.159	3.231	426.530	< 1.965	70.739	105.365	< 1.965	29.791	70.000
H1.2A	7.754	3.898	504.245	< 1.988	61.454	155.573	< 1.988	33.116	65.825
H1.2AA	3.070	2.059	257.932	3.483	9.061	25.115	< 1.944	8.266	215.049
H1.1	3.300	< 1.95	771.298	< 1.95	136.588	18.949	< 1.95	44.984	96.035
G3.1A	< 2.2	4.605	841.926	< 2.2	25.943	239.342	< 2.2	29.449	62.802
G3.1B	< 1.949	4.947	679.869	< 1.949	14.654	187.667	2.504	26.566	47.760
G3.1C	2.034	3.537	667.453	< 1.962	26.753	163.489	< 1.962	28.308	57.218
G3.1D	2.227	3.031	681.407	< 2.018	44.331	68.494	< 2.018	22.841	63.201
G3.1E	2.374	3.986	616.247	< 2.059	62.052	130.120	< 2.059	26.728	92.886
G3.2A	< 1.977	4.675	/02.776	< 1.977	61.051	303.239	< 1.977	26.246	/6.2/8
G3.2B	< 1.96	3.631	875.927	< 1.96	19.011	559.555	< 1.96	35.841	/3.05/
G3.2C	3.585	6.013	619.108	< 2.01	37.369	236.486	< 2.01	21.756	49.775
G3.3A	2.690	2.048	814.841	< 2.003	23.743	54.091	< 2.003	21.996	63.218
G3.3B	< 2.018	2.921	843.628	< 2.018	21.227	460.026	< 2.018	38.047	65.055
G3.3C	3.943	10.439	491.014	< 1.900	34.087	370.302	< 1.900	27.000	50.007
C2 44	4.034	5.234	903.307	< 1.000	20.770	410.079	< 1.000	21 507	60.05/
G3.4A	2.340	3.022	906 101	< 1.900	20.770	272.645	> 1.900	21.507	70.400
G3.4D	3.637	5 530	618 7/1	< 1.929	45 221	335 176	< 1 00	27 320	50 326
G3.40	4 608	3 566	893.675	< 2 008	30 727	506 769	< 2 008	37 946	92.076
H2 1A	3 307	3 424	469 870	< 1 932	50.826	87 911	< 1 932	20 282	60 797
H2.1B	3 736	3 448	460 428	< 1.931	59 852	78 073	< 1.931	22 747	58 710
H2.2	3.795	3.053	505.598	< 1.959	46.499	77.389	< 1.959	18.565	54.249
H2.3A	2.950	7.696	607.153	< 1.995	24.363	347.773	< 1.995	18.392	25.184
H2.3B	2.804	6.091	738.732	< 2.01	29.459	323.201	< 2.01	23.813	42.997
H2.3C	2.680	2.966	755.565	< 2.024	25.357	441,488	< 2.024	32.654	86.697
H2.3D	4.920	3.516	891.358	< 1.942	44.156	222.254	< 1.942	32.288	118.705
H2.4A	< 2.086	5.736	859.123	< 2.086	22.878	406.379	< 2.086	33.050	52.771
H2.4B	2.934	6.370	639.773	< 2.005	24.954	359.515	< 2.005	20.463	37.724
H2.4C	4.296	3.780	805.872	< 2.014	36.767	344.096	< 2.014	29.849	80.408
H2.4D	4.230	2.389	1054.276	< 2.008	51.516	543.884	< 2.008	40.669	127.606
H2.4E	2.442	< 1.982	899.455	< 1.982	64.319	75.031	< 1.982	27.920	77.082
K1.1A	2.024	2.352	1092.892	< 1.981	74.529	34.639	< 1.981	29.869	76.442
K1.1B	< 1.988	< 1.988	1075.058	< 1.988	70.777	34.316	< 1.988	32.584	78.023
K1.1C	2.366	3.631	867.860	< 2.035	96.414	171.861	< 2.035	30.220	61.718
K1.1D	< 1.977	< 1.977	1043.702	< 1.977	56.683	398.224	< 1.977	53.804	95.547
K1.2A	2.654	3.307	1070.213	< 1.956	68.235	32.450	< 1.956	28.979	76.347
K1.2B	< 1.984	4.206	1018.274	< 1.984	71.302	133.820	< 1.984	31.134	70.504

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

	Ag	AI	As	в	Ва	Be	Ca	Cd	Ce	Co	Cr	Cu
MDL:	0.002	0.05	0.02	0.01	0.0005	0.0002	0.05	0.0005	0.05	0.005	0.005	0.005
K1.2C	6.933	23223.911	1894.083	13.626	143.238	0.308	18326.872	< 0.049	18.393	7.107	26.686	71.332
K1.2D	6.193	23594.818	1599.315	13.533	149.438	0.431	16418.258	< 0.047	23.834	8.562	26.834	71.573
K1.3A	2.868	12637.311	1001.659	8.696	211.118	0.326	6912.071	< 0.05	28.267	8.952	17.458	44.890
K1.3B	4.797	16522.368	1821.290	10.817	168.574	0.304	19944.389	< 0.05	22.790	8.965	22.180	71.764
K1.3C	4.267	16156.303	2148.169	12.094	160.782	0.204	15509.665	< 0.048	17.914	8.348	20.217	78.332
K1.3D	4.281	18209.090	2029.761	10.833	147.623	0.189	16642.917	< 0.048	15.423	6.307	21.297	71.945
K1.4A	1.717	10357.742	475.648	5.903	265.911	0.434	10533.972	< 0.05	30.476	8.278	13.815	36.285
K1.4B	0.926	10642.756	38.816	6.846	313.346	0.506	16183.424	< 0.05	31.593	8.513	13.752	18.642
K1.4C	0.810	6516.419	47.970	4.706	283.671	0.388	15395.058	< 0.049	25.689	6.529	9.183	13.169
K1.4D	0.799	7974.690	15.560	6.347	223.222	0.446	17793.218	< 0.05	30.406	6.583	10.647	13.950
K1.4E	0.646	5480.672	15.497	4.374	200.382	0.380	14884.458	0.057	28.230	4.891	7.881	10.227
D3.3A	2.538	12096.029	999.048	3.110	176.378	0.090	281.111	< 0.051	18.332	2.168	18.286	40.593
D3.3B	2.228	16768.555	887.158	2.471	209.140	0.234	40.909	< 0.051	19.702	3.632	24.436	64.060
D3.3C	3.889	15470.301	1108.848	3.785	192.939	0.192	81.199	< 0.049	16.913	3.248	22.079	72.014
D3.3D	3.511	12236.175	1019.768	3.997	198.409	0.276	203.557	< 0.05	17.022	3.661	18.263	71.590
A1	2.642	7809.009	382.280	3.700	290.436	1.109	23896.802	< 0.049	50.579	15.019	44.845	52.509
D1	2.456	11082.414	263.577	5.911	268.528	0.710	37725.809	0.179	47.684	12.315	22.069	67.234
G1	1.556	4340.048	694.179	2.790	134.917	0.564	9401.653	< 0.049	29.073	8.096	11.249	39.907
H1	1.611	8196.955	643.050	7.185	149.980	0.491	17517.677	< 0.049	26.804	7.321	14.355	31.229
K1	1.641	12120.631	424.174	6.877	254.757	0.455	12060.335	< 0.048	32.429	8.637	15.988	35.514
K2	3.609	15495.603	1362.428	8.072	153.992	0.108	12913.018	< 0.049	15.423	22.625	19.281	60.462
L1	0.706	7181.110	9.379	5.985	318.012	0.542	41853.043	1.246	31.885	8.439	10.804	124.303

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

	Fe	к	Li	Mg	Mn	Мо	Na	Ni	Р	Pb	S
MDL:	0.1	0.01	0.01	0.01	0.002	0.005	0.01	0.002	0.05	0.02	0.05
K1.2C	111091.367	3372.686	13.263	13542.537	2319.229	< 0.496	121.757	14.600	510.179	10.545	8432.096
K1.2D	98403.778	3242.651	15.632	13213.201	2298.136	0.615	144.386	20.459	616.211	12.214	6781.051
K1.3A	67311.064	2250.464	8.438	7641.707	1503.601	0.601	111.105	19.853	442.303	12.544	2165.117
K1.3B	89063.655	3218.627	10.092	8696.377	1818.100	1.003	98.660	17.526	442.215	13.619	12070.719
K1.3C	100045.186	2950.249	7.032	8604.614	2022.504	< 0.485	137.641	12.305	390.459	13.647	10069.796
K1.3D	98281.247	2343.490	9.197	13294.456	2357.824	< 0.489	286.060	10.772	342.428	9.663	8665.790
K1.4A	37508.120	1925.144	6.581	5946.844	808.672	1.150	92.951	19.746	440.366	14.026	1514.699
K1.4B	22949.145	1884.394	8.042	4884.071	523.335	1.266	149.812	21.529	467.171	12.775	1671.949
K1.4C	19860.811	1222.779	3.400	3424.822	442.941	1.455	98.080	15.493	375.405	10.559	2094.904
K1.4D	18463.857	1557.134	6.170	4726.248	394.910	1.150	138.426	16.676	414.719	11.301	3156.202
K1.4E	15566.680	1122.286	3.061	4131.416	349.567	1.325	137.684	12.717	357.972	9.180	1844.264
D3.3A	97488.136	3404.844	2.134	5975.472	832.806	< 0.512	33.449	7.355	324.903	9.170	4108.925
D3.3B	95855.765	3872.084	4.483	7961.993	855.976	< 0.515	24.623	7.617	312.489	11.886	1881.408
D3.3C	108888.608	3721.824	3.000	7193.453	711.178	< 0.492	37.293	5.295	403.233	11.791	4148.203
D3.3D	100315.814	2681.542	1.206	5542.661	737.852	1.193	31.662	5.399	452.737	13.894	3847.225
A1	49102.383	1624.182	3.938	5315.894	1489.374	2.636	129.650	41.196	729.814	46.953	623.096
D1	41641.636	2641.267	5.721	8396.167	1247.480	2.307	160.519	33.493	790.421	62.277	1063.413
G1	52956.009	940.247	< 0.99	3092.496	730.340	2.394	78.362	19.562	775.284	16.661	1692.023
H1	44886.495	1777.318	6.701	5904.847	513.428	1.282	137.056	19.752	482.991	13.147	3091.680
K1	43291.685	1741.506	7.795	6341.433	1069.198	0.979	206.044	20.276	470.657	13.810	2218.787
K2	95818.060	1986.633	3.684	7929.389	5396.067	< 0.496	941.316	5.673	310.638	9.371	12228.887
L1	19697.115	1483.543	4.306	3610.686	475.411	4.218	187.697	26.612	451.444	10.743	4191.491

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

	Sb	Se	Si	Sn	Sr	Ti	TI	٧	Zn
MDL:	0.02	0.02	0.01	0.02	0.0001	0.001	0.02	0.005	0.001
K1.2C	< 1.987	3.337	1072.491	< 1.987	67.643	234.663	< 1.987	35.358	74.346
K1.2D	< 1.916	2.607	986.162	< 1.916	66.154	122.861	< 1.916	36.433	86.830
K1.3A	< 2.013	3.856	932.067	< 2.013	49.993	76.409	< 2.013	23.337	53.843
K1.3B	< 2.014	3.504	923.842	< 2.014	69.474	194.634	< 2.014	29.354	56.784
K1.3C	< 1.943	3.931	823.378	< 1.943	56.656	228.827	< 1.943	26.786	49.815
K1.3D	< 1.958	4.493	890.749	< 1.958	57.434	297.227	< 1.958	29.906	57.305
K1.4A	2.618	2.307	787.935	< 2.025	41.155	41.489	< 2.025	23.035	60.052
K1.4B	2.920	2.503	906.439	< 2.032	58.432	28.219	< 2.032	24.180	56.522
K1.4C	3.460	< 1.975	752.128	< 1.975	53.162	25.381	< 1.975	15.598	42.180
K1.4D	2.814	< 2.006	807.537	< 2.006	85.548	26.725	< 2.006	16.592	45.069
K1.4E	3.050	< 1.901	602.693	< 1.901	64.829	24.378	< 1.901	11.102	35.289
D3.3A	< 2.05	5.217	705.432	< 2.05	7.911	422.530	< 2.05	26.025	41.127
D3.3B	< 2.062	4.579	942.002	< 2.062	8.422	477.397	< 2.062	34.556	56.769
D3.3C	2.290	5.050	915.135	< 1.97	21.821	439.313	2.495	37.072	53.830
D3.3D	3.427	5.488	874.872	< 2.013	24.388	317.238	2.431	48.234	59.240
A1	4.419	2.365	595.538	< 1.97	99.739	133.299	2.199	38.477	155.239
D1	2.168	3.477	728.531	28.068	71.244	222.764	< 2.048	27.233	178.924
G1	3.551	3.157	482.785	< 1.98	48.802	77.110	< 1.98	20.828	59.562
H1	2.178	2.762	649.463	< 1.996	70.971	32.609	< 1.996	26.430	62.003
K1	2.237	2.536	727.013	< 1.955	76.761	38.904	< 1.955	23.577	60.567
K2	< 1.984	2.882	679.031	< 1.984	41.011	212.347	< 1.984	26.338	51.020
L1	3.056	5.439	686.522	< 2.048	156.756	12.655	< 2.048	39.620	67.109

Appendix 5-5. Analytical Results of Sediment Samples (ICP-OES)

Notes: Dry Weight Concentrations are presented in mg/kg

MDL = maximum detection limit

< Lab qualifier for results below the Practical Quantitation Limit

		Converted	Original						
Reservoir ¹	Element	Concentration	Concentration -	Original	Corrected	Computation ¹	Reference		
incici voli		$(mg/kg)^2$	Analytes of	Unit	Unit ³	computation			
		(116/16)	Concern						
Upper Continental Crust	Ag	0.053	53	ng/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	Ag	0.055	55	ng/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	Ag	0.055	55	ng/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	Ag	0.05	50	ng/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	Ag	0.053	53	ng/g		Average	Rudnick & Gao 2004		
Congo River Particulates	Ag	38	38	µg/g		Measurement	Martin & Meybeck 1979		
Mississippi River Particulates	Ag	0.7	0.7	μg/g		Measurement	Martin & Meybeck 1979		
Ob River Particulates	Ag	14	14	μg/g		Measurement	Martin & Meybeck 1979		
St. Lawrence River Particulates	Ag	60	60	μg/g		Measurement	Martin & Meybeck 1979		
Yemissei River Particulates	Aq	29	29	µq/q		Measurement	Martin & Meybeck 1979		
Amazon River Particulates	Al	115,000	115000	μg/g		Measurement	Martin & Meybeck 1979		
Colorado River Particulates	Al	43,000	43000	μg/g		Measurement	Martin & Meybeck 1979		
Congo River Particulates	Al	117.000	117000	ug/g		Measurement	Martin & Mevbeck 1979		
Danube River Particulates	Al	63.000	63000	ug/g		Measurement	Martin & Mevbeck 1979		
Ganges River Particulates	Al	77.000	77000	ug/g		Measurement	Martin & Meybeck 1979		
Garonne River Particulates	Al	118.000	118000	110/0		Measurement	Martin & Meybeck 1979		
MacKenzie River Particulates	Al	78,000	78000	110/0		Measurement	Martin & Meybeck 1979		
Mekong River Particulates	Al	112,000	112000	110/0		Measurement	Martin & Meybeck 1979		
Mississippi River Particulates		88,000	88000	110/0		Measurement	Martin & Meybeck 1979		
Narbada River Particulates		79,000	79000	110/0		Measurement	Martin & Meybeck 1979		
Niger River Particulates		156,000	156000	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979		
Nile River Particulates		98,000	98000	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979		
Orinoco River Particulates		112,000	112000	με/ε		Measurement	Martin & Moybeck 1979		
Darana River Particulates	Al 115,000 115000 µg/g Measurement		Maggurement	Martin & Maybeck 1979					
Paralla River Particulates	AI			Ivieasurement	Martin & Maybeck 1979				
River Particulates	AI	94,000	94000	μg/g		Average	Martin & Mayback 1979		
St. Lawrence River Particulates	AI	78,000	78000	µg/g			Martin & Meybeck 1979		
Upper Continental Crust	AI	82,200	15.53	wt%oxide		Composite Average	Hart et al. 1999		
Upper Continental Crust	AI	82,835	15.65	Wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	AI	80,824	15.27	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	AI	81,512	15.4	Wt%	wt% oxide	Estimate	Rudnick & Gao 2004		
Upper Continental Crust	AI	/9,660	15.05	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	81,512	15.4	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	80,295	15.17	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	82,200	15.53	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	85,217	16.1	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	83,841	15.84	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	88,023	16.63	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	79,660	15.05	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	80,136	15.14	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	75,002	14.17	wt%	wt% oxide	Average	Rudnick & Gao 2004		
Upper Continental Crust	Al	84,688	16	wt%oxide		Averages	Shaw et al. 1986		
Upper Continental Crust	Al	77,807	14.7	wt%oxide		Composite Average	Wedepohl 1995		
Amazon River Particulates	As	5.3	5.3	μg/g		Measurement	Martin & Meybeck 1979		
Congo River Particulates	As	3.8	3.8	μg/g		Measurement	Martin & Meybeck 1979		
Magdalena River Particulates	As	7.1	7.1	μg/g		Measurement	Martin & Meybeck 1979		
Mekong River Particulates	As	27	27	μg/g		Measurement	Martin & Meybeck 1979		
Mississippi River Particulates	As	14.6	14.6	μg/g		Measurement	Martin & Meybeck 1979		
Parana River Particulates	As	3.9	3.9	μg/g		Measurement	Martin & Meybeck 1979		
River Particulates	As	5	5	μg/g		Average	Martin & Meybeck 1979		
Upper Continental Crust	As	4.8	4.8	μg/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	As	2	2 2 μg/g		Estimate	te Rudnick & Gao 2004			
Upper Continental Crust	As	4.4	4.4	μg/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	Continental Crust As 5.1 5.1 µg/g			Estimate	Rudnick & Gao 2004				
Upper Continental Crust	As	1.5	1.5	μg/g		Estimate	Rudnick & Gao 2004		
Upper Continental Crust	As	4.8	4.8	μg/g		Average	Rudnick & Gao 2004		

		Converted	Original				
Provincia ¹	Flomont	Concentration	Concentration -	Original	Corrected	6	Poforonco
Reservoir	ciement		Analytes of	Unit	Unit ³	Computation	Reference
		(mg/kg)	Concern				
Amazon River Particulates	Ca	16,000	16000	μg/g		Measurement	Martin & Meybeck 1979
Colorado River Particulates	Ca	34,000	34000	μg/g		Measurement	Martin & Meybeck 1979
Congo River Particulates	Ca	8,400	8400	μg/g		Measurement	Martin & Meybeck 1979
Danube River Particulates	Ca	45,000	45000	μg/g		Measurement	Martin & Meybeck 1979
Ganges River Particulates	Ca	26,500	26500	μg/g		Measurement	Martin & Meybeck 1979
Garonne River Particulates	Ca	19,500	19500	μg/g		Measurement	Martin & Meybeck 1979
MacKenzie River Particulates	Ca	35,800	35800	μg/g		Measurement	Martin & Meybeck 1979
Magdalena River Particulates	Ca	10,000	10000	μg/g		Measurement	Martin & Meybeck 1979
Mekong River Particulates	Ca	5,900	5900	μg/g		Measurement	Martin & Meybeck 1979
Niger River Particulates	Ca	3,300	3300	μg/g		Measurement	Martin & Meybeck 1979
Nile River Particulates	Са	40,000	40000	μg/g		Measurement	Martin & Meybeck 1979
Orinoco River Particulates	Са	3,000	3000	μg/g		Measurement	Martin & Meybeck 1979
Parana River Particulates	Са	5,900	5900	μg/g		Measurement	Martin & Meybeck 1979
River Particulates	Ca	21.500	21500	ug/g		Average	Martin & Meybeck 1979
St. Lawrence River Particulates	Ca	23.000	23000	ug/g		Measurement	Martin & Meybeck 1979
Upper Continental Crust	Ca	92.053	12.88	wt%oxide		Composite Average	Hart et al. 1999
Upper Continental Crust	Ca	37.021	5.18	wt%	wt% oxide	Average	Rudnick & Gao 2004
Upper Continental Crust	Ca	38.951	5.45	wt%	wt% oxide	Average	Rudnick & Gao 2004
Upper Continental Crust	Са	30,303	4.24	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust	Ca	24,300	3.4	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust	Ca	27,945	3 91	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust	Ca	23,085	3.21	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust	Ca	30 303	303 4.24 wt% wt% oxide Average		Average	Budnick & Gao 2004	
Upper Continental Crust	Ca	26.015	3.64	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust	Ca	20,015	3.04	wt%	wt% oxide	Average	Budnick & Gao 2004
Upper Continental Crust		24,380	2 5	w/t%	wt% oxide	Average	Rudnick & Gao 2004
Upper Continental Crust		25,015	J.J / 10	w/t%	wt% oxide	Average	Rudnick & Gao 2004
Upper Continental Crust	Ca	25,540	3.59	w/t%	wt% oxide	Average	Rudnick & Gao 2004
Upper Continental Crust		25,058	2.59	VVL/0	wt% oxide	Ectimato	Rudnick & Gao 2004
Upper Continental Crust		25,058	3.35	wt% oxido	wt/o Uxide	Avoragos	Show of al 1986
Upper Continental Crust	Ca	29,013	3.J 4 1	wt%ovido		Composito Averago	Wedepeel 1980
Amour River Particulates	Cu	25,505		wt/outide		Moosurement	Martin & Mayback 1070
Dapuba Biyar Darticulates	Cu	79	/9	μg/g		Measurement	Martin & Moybeck 1979
Cangos Biver Particulates	Cu	69	89	μg/g		Measurement	Martin & Moybeck 1979
Gariges River Particulates	Cu	50	50	μg/g		Measurement	Martin & Moybeck 1979
Garonne River Particulates	Cu	51	51	µg/g		Measurement	Martin & Meybeck 1979
Leria River Particulates	Cu	12.7	12.7	µg/g		Measurement	Martin & Meybeck 1979
Mackenzie River Particulates	Cu	42	42	µg/g		Massurement	Martin & Meybeck 1979
Niger Biver Particulates	Cu	42	42	µg/g		Massurement	Martin & Meybeck 1979
Niger River Particulates	Cu	60	60	µg/g		Measurement	Martin & Meybeck 1979
Nile River Particulates	Cu	39	39	µg/g		Measurement	Martin & Meybeck 1979
Unner Centinertel Crust	CU	/3	/3	μg/g		ivieasurement	Iviartin & Ivieybeck 1979
Upper Continental Crust	Cu	28	28	µg/g		Average	Rudnick & Gao 2004
Upper Continental Crust	Cu	14	14	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Cu	14	14	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Cu	26	26	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Cu	32	32	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Cu	25	25	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Cu	28	28	µg/g		Estimate	Rudnick & Gao 2004
Opper Continental Crust	Cu	25	25	ppm		Average	laylor et al. 1983
Amazon River Particulates	Cu	266	266	μg/g		Measurement	Martin & Meybeck 1979
Mekong River Particulates	Cu	107	107	µg/g		Measurement	Martin & Meybeck 1979
Narbada River Particulates	Cu	127	127	μg/g		Measurement	Martin & Meybeck 1979
Ob River Particulates	Си	227	227	μg/g		Measurement	Martin & Meybeck 1979
River Particulates	Cu	100	100	µg/g		Average	Martin & Meybeck 1979
St. Lawrence River Particulates	Cu	130	130	µg/g		Measurement	Martin & Meybeck 1979
Yemissei River Particulates	Си	298	298	μg/g		Measurement	Martin & Meybeck 1979
Yukon River Particulates	Си	416	416	μg/g		Measurement	Martin & Meybeck 1979

Reservoir ¹	Element	Converted Concentration	Original Concentration -	Original	Corrected	Computation ¹	Reference	
		(mg/kg) ²	Analytes of Concern	Unit	Unit			
Amazon River Particulates	Fe	55.000	55000	ug/g		Measurement	Martin & Mevbeck 1979	
Colorado River Particulates	Fe	23.000	23000	ug/g		Measurement	Martin & Meybeck 1979	
Congo River Particulates	Fe	71.000	71000	11g/g		Measurement	Martin & Meybeck 1979	
Danube River Particulates	Fe	55,000	55000	110/0		Measurement	Martin & Meybeck 1979	
Ganges River Particulates	Fe	37,000	37000	110/0		Measurement	Martin & Meybeck 1979	
Garonne River Particulates	Fe	58,000	58000	11g/g		Measurement	Martin & Meybeck 1979	
MacKenzie River Particulates	Fe	36,500	36500	11g/g		Measurement	Martin & Meybeck 1979	
Magdalena River Particulates	Fe	52,000	52000	<u>με/ε</u> μσ/σ		Measurement	Martin & Meybeck 1979	
Mekong River Particulates	Fo	56,000	56000	μα/σ		Measurement	Martin & Meybeck 1979	
Mississippi River Particulates	Fo	47,400	47400	<u>με/ε</u> μα/σ		Measurement	Martin & Meybeck 1979	
Narbada River Particulates	Ге	68,000	47400 68000	μg/g		Measurement	Martin & Mayback 1979	
Nigor Diver Particulates	ге	08,000	08000	μg/g		Massurement	Martin & Mayback 1979	
Niger River Particulates	ге	92,000	92000	μg/g		Massurement	Martin & Meybeck 1979	
Oringes Diver Particulates	Fe	108,000	108000	μg/g		Measurement	Martin & Mayback 1979	
Darana River Particulates	ге	38,000	58000	μg/g		Massurement	Martin & Mayback 1979	
Paralla River Particulates	ге	48,000	48000	μg/g		Ivieasurement	Martin & Meybeck 1979	
Ct. Lourspace Diver Derticulates	ге	48,000	48000	μg/g		Average	Martin & Meybeck 1979	
St. Lawrence River Particulates	Fe	48,500	48500	µg/g		Measurement	Martin & Meybeck 1979	
Yukon River Particulates	Fe	63,000	63000	µg/g		Measurement	Martin & Meybeck 1979	
Upper Continental Crust	Fe	/0,112	9.02	wt%oxide		Composite Average	Hart et al. 1999	
Upper Continental Crust	Fe	52,079	6.7	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	56,432	7.26	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	31,792	4.09	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	39,176	5.04	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	34,901	4.49	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	38,399	4.94	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	41,430	5.33	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	36,999	4.76	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	31,792	4.09	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	54,333	6.99	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	44,928	5.78	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	34,201	4.4	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Fe	39,176	5.04	wt%	wt% oxide	Estimate	Rudnick & Gao 2004	
Upper Continental Crust	Fe	34,979	4.5	wt%oxide		Averages	Shaw et al. 1986	
Upper Continental Crust	Fe	34,271	4.409	wt%oxide		Composite Average	Wedepohl 1995	
Amazon River Particulates	К	18,000	18000	μg/g		Measurement	Martin & Meybeck 1979	
Colorado River Particulates	К	15,000	15000	μg/g		Measurement	Martin & Meybeck 1979	
Congo River Particulates	К	12,000	12000	μg/g		Measurement	Martin & Meybeck 1979	
Danube River Particulates	К	20,500	20500	μg/g		Measurement	Martin & Meybeck 1979	
Ganges River Particulates	К	21,000	21000	µg/g		Measurement	Martin & Meybeck 1979	
Garonne River Particulates	К	34,000	34000	μg/g		Measurement	Martin & Meybeck 1979	
MacKenzie River Particulates	К	35,300	35300	μg/g		Measurement	Martin & Meybeck 1979	
Mekong River Particulates	К	24,000	24000	μg/g		Measurement	Martin & Meybeck 1979	
Niger River Particulates	К	10,800	10800	μg/g		Measurement	Martin & Meybeck 1979	
Nile River Particulates	К	19,000	19000	μg/g		Measurement	Martin & Meybeck 1979	
Ob River Particulates	К	20,800	20800	μg/g		Measurement	Martin & Meybeck 1979	
Orinoco River Particulates	К	27,000	27000	μg/g	Measurem		Martin & Meybeck 1979	
Parana River Particulates	К	18,000 18000 µg/g Measurer		Measurement	Martin & Meybeck 1979			
River Particulates	tes K 20,000 20000 µg/g			Average Martin & Meybeck 1979				
St. Lawrence River Particulates	К	25,500	25500	μg/g		Measurement	Martin & Meybeck 1979	

		Converted	Original	Orisiaal	Corrected			
Reservoir ¹	Element	Concentration	Concentration -	Original	Corrected	Computation ¹	Reference	
		(mg/kg) ²	Concern	Unit	Unit			
Upper Continental Crust	К	4,805	4805	ppm		Composite Average	Hart et al. 1999	
Upper Continental Crust	К	4,649	0.56	wt%oxide		Composite Average	Hart et al. 1999	
Upper Continental Crust	К	26,483	3.19	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	24,823	2.99	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	26,483	3.19	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	28,144	3.39	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	23,246	2.8	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	24,989	3.01	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	22,249	2.68	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	К	24,159	2.91	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	к	24,989	3.01	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	к	34.287	4.13	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	к	26.483	3.19	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	к	22.914	2.76	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	к	23.246	2.8	wt%	wt% oxide	Estimate	Rudnick & Gao 2004	
Upper Continental Crust	К	27.397	3.3	wt%oxide		Averages	Shaw et al. 1986	
Upper Continental Crust	К	25.736	3.1	wt%oxide		Composite Average	Wedepohl 1995	
Amazon River Particulates	Mø	11,200	11200	11p/p		Measurement	Martin & Meybeck 1979	
Colorado River Particulates	Mø	10,400	10400	110/0		Measurement	Martin & Meybeck 1979	
Congo River Particulates	Mø	5,800	5800	110/0		Measurement	Martin & Meyheck 1979	
Danube River Particulates	Mg	21 000	21000	11g/g		Measurement	Martin & Meybeck 1979	
Ganges River Particulates	Mg	12 400	12400	11g/g		Measurement	Martin & Meybeck 1979	
Garonne River Particulates	Mg	17 300	17300	11g/g		Measurement	Martin & Meybeck 1979	
MacKenzie River Particulates	Mσ	4 000	4000	11g/g		Measurement	Martin & Meybeck 1979	
Mekong River Particulates	Mσ	13 500	13500	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979	
Niger River Particulates	Mσ	9 300	9300	μσ/σ		Measurement	Martin & Meybeck 1979	
Nile River Particulates	Mσ	18 500	18500	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979	
Orinoco River Particulates	Mσ	5 800	5800	μ6/6 μσ/σ		Measurement	Martin & Meybeck 1979	
Parana River Particulates	Mσ	10,900	10900	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979	
River Particulates	Mσ	11 800	10500	μ <u>σ</u> /σ			Martin & Meybeck 1979	
St Lawrence River Particulates	Mσ	24 500	24500	μ <u>σ</u> /σ		Measurement	Martin & Meybeck 1979	
Upper Continental Crust	Ma	40 160	£4300	46/6 wt%ovide			Hart et al 1999	
Upper Continental Crust	Mg	40,100	0.00	wt/ouxide	wt% oxido		Pudpick & Goo 2004	
Upper Continental Crust	Ma	21,407	3.50	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	13 860	4.55	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	11,809	2.3	vv L/0	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Mg	13 266	2.40	VV L/0	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	12,200	2.2	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	15 700	2.1	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	14 774	2.02	vv L/0	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	13 860	2.43	WL/0	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	20 924	2.5	wt%	wt% ovide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Ma	18 150	2.01	wt%	wι/> Oxide Average % wt% oxide Δverage		Rudnick & Gao 2004	
Upper Continental Crust	Ma	13 266	3.01	wt%	wt% oxide		Rudnick & Gao 2004	
Upper Continental Crust	Ma	14 954	2.2	W/+%	wt% ovido	Estimate	Rudnick & Gao 2004	
Upper Continental Crust	Ma	12 860	2.40	wt%ovido			Shaw et al 1026	
Upper Continental Crust	Ma	14 472	2.3	wt%ovido		Composite Average	Wedenchl 1005	
opper continental crust	IVIS	17,472	2.4	wit/ouxide		composite Average	wedepoin 1993	

Reservoir ¹	Element	Converted Concentration (mg/kg) ²	Original Concentration - Analytes of Concern	Original Unit	Corrected Unit ³	Computation ¹	Reference	
Amazon River Particulates	Mn	1,030	1030	μg/g		Measurement	Martin & Meybeck 1979	
Colorado River Particulates	Mn	430	430	μg/g		Measurement	Martin & Meybeck 1979	
Congo River Particulates	Mn	1,400	1400	µg/g		Measurement	Martin & Meybeck 1979	
Danube River Particulates	Mn	600	600	µg/g		Measurement	Martin & Meybeck 1979	
Ganges River Particulates	Mn	1,000	1000	μg/g		Measurement	Martin & Meybeck 1979	
Garonne River Particulates	Mn	1,700	1700	µg/g		Measurement	Martin & Meybeck 1979	
MacKenzie River Particulates	Mn	600	600	μg/g		Measurement	Martin & Meybeck 1979	
Mekong River Particulates	Mn	940	940	µg/g		Measurement	Martin & Meybeck 1979	
Mississippi River Particulates	Mn	1,300	1300	µg/g		Measurement	Martin & Meybeck 1979	
Narbada River Particulates	Mn	1,200	1200	µg/g		Measurement	Martin & Meybeck 1979	
Niger River Particulates	Mn	650	650	μg/g		Measurement	Martin & Meybeck 1979	
Orinoco River Particulates	Mn	740	740	µg/g		Measurement	Martin & Meybeck 1979	
Parana River Particulates	Mn	270	270	µg/g		Measurement	Martin & Meybeck 1979	
River Particulates	Mn	1,050	1050	µg/g		Average	Martin & Meybeck 1979	
St. Lawrence River Particulates	Mn	700	700	μg/g		Measurement	Martin & Meybeck 1979	
Yukon River Particulates	Mn	1,270	1270	μg/g		Measurement	Martin & Meybeck 1979	
Amazon River Particulates	Р	1,650	1650	μg/g		Measurement	Martin & Meybeck 1979	
Colorado River Particulates	Р	540	540	μg/g		Measurement	Martin & Meybeck 1979	
Congo River Particulates	Р	1,500	1500	µg/g		Measurement	Martin & Meybeck 1979	
Danube River Particulates	Р	680	680	μg/g		Measurement	Martin & Meybeck 1979	
Ganges River Particulates	Р	560	560	µg/g		Measurement	Martin & Meybeck 1979	
Garonne River Particulates	Р	1,300	1300	µg/g		Measurement	Martin & Meybeck 1979	
Mekong River Particulates	Р	2,000	2000	µg/g		Measurement	Martin & Meybeck 1979	
Niger River Particulates	Р	1,600	1600	μg/g		Measurement	Martin & Meybeck 1979	
Parana River Particulates	Р	1,300	1300	μg/g		Measurement	Martin & Meybeck 1979	
River Particulates	Р	1,150	1150	μg/g		Average	Martin & Meybeck 1979	
Upper Continental Crust	Р	480	0.11	wt%oxide		Composite Average	Hart et al. 1999	
Upper Continental Crust	Р	698	0.16	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	698	0.16	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	1,004	0.23	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	655	0.15	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	524	0.12	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	698	0.16	wt%	wt% oxide	Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	655	0.15	wt% wt% oxide		Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	873	0.2	wt% wt% oxide		Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	655	0.15	wt% wt% oxid		Average	Rudnick & Gao 2004	
Upper Continental Crust	Р	655	0.15	0.15 wt%		Estimate	Rudnick & Gao 2004	
Upper Continental Crust	r Continental Crust P 742 0.17 wt		wt%oxide		Composite Average	Wedepohl 1995		

Appendix 5-6. Geochemical Composition of in River Particulates and Upper Continental Crust	-
Analytes of Concern	

Reservoir ¹	Element	Converted Concentration (mg/kg) ²	Original Concentration - Analytes of Concern	Original Unit	Corrected Unit ³	Computation ¹	Reference
Upper Continental Crust	S	62	62	μg/g		Average	Rudnick & Gao 2004
Upper Continental Crust	S	621	621	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	S	309	309	μg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	S	953	953 953			Estimate	Rudnick & Gao 2004
Upper Continental Crust	S	600	600	μg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	S	1,037	1037	ppm		Average	Wedepohl & Hartmann 1994
Amazon River Particulates	Sr	309	309	μg/g		Measurement	Martin & Meybeck 1979
Congo River Particulates	Sr	61	61	µg/g		Measurement	Martin & Meybeck 1979
Garonne River Particulates	Sr	164	164	μg/g		Measurement	Martin & Meybeck 1979
Mekong River Particulates	Sr	92	92	µg/g		Measurement	Martin & Meybeck 1979
Niger River Particulates	Sr	40	40	µg/g		Measurement	Martin & Meybeck 1979
Orinoco River Particulates	Sr	83	83	µg/g		Measurement	Martin & Meybeck 1979
Parana River Particulates	Sr	150	150	μg/g		Measurement	Martin & Meybeck 1979
River Particulates	Sr	150	150	µg/g		Average	Martin & Meybeck 1979
St. Lawrence River Particulates	Sr	70	70	µg/g		Measurement	Martin & Meybeck 1979
Upper Continental Crust	Sr	118	117.5	ppm		Composite Average	Hart et al. 1999
Upper Continental Crust	Sr	320	320	µg/g		Average	Rudnick & Gao 2004
Upper Continental Crust	Sr	316	316	μg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	350	350	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	266	266	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	320	320	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	316	316	μg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	380	380	µg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	Sr	289	289	μg/g		Estimate	Rudnick & Gao 2004
Upper Continental Crust	l Crust Sr 350 3		350	ppm		Averages	Shaw et al. 1986
Upper Continental Crust	Sr	350	350	ppm		Average	Taylor et al. 1983

Notes:

mg/kg = milligram per kilogram ng/g = nanogram per gram ppm = parts per million ug/g = microgram per gram wt% = weight percent

The data was compiled from the Geochemical Earth Reference Model (GERM) reservoir database (https://earthref.org/GERMRD/). Only portions of the complete GERM dataset were used in the calculation of background geochemical levels. This process is discussed in more detail below.

¹ Under the Reservoir field, only river particulates and upper continental crust data was selected to provide meaningful comparisons to cocentrations found in alluvial and fluvial sediments. Under the Computation field, only averages, estimates, and measurements were selected.

² These GERM concentration ranges were compared to averages and ranges reported from other sources (Rudnick and Gao 2004; Viers et al 2009). Any anomalous concentrations in the GERM dataset were excluded from the reported summary statistics of naturally occuring concentrations.

Ag and Cu grey and italicised data entries = up to two orders of magnitude in variability was reported in the Martin and Meybeck 1979 paper with no discussion or commentary on whether it may be an analytical problem or real variability. There is extreme uncertainty with these values and are excluded from the reported summary statistics of naturally occuring concentrations.

³ Units in the GERM database were listed incorrectly as wt% and corrected to wt% oxide, as presented in the source paper (Rudnick & Gao 2004) References:

Martin, J.M., Meybeck, M. 1979. Elemental Mass-Balance of Material Carried by Major World Rivers. Marine Chemistry 7(3): 173-206.

Rudnick, R.L., Gao, S. 2004. Composition of the Continental Crust. In: Treatise on Geochemistry. Holland, H.D. and Turekian, K.K. (Editors), Elsevier, Amsterdam. 3: Viers, J., Dupre, B., Gaillardet J. 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. Science of the Total Environment 407: 853-868.

Appendix 6-1. Supplemental Experiment to Test the Effects of Different Extraction Sequences

A supplemental experiment was conducted to investigate the effects of reversing the order of sodium phosphate (1M NaHPO₄) and hydroxylamine (0.2M NH₂OH·HCl) application. The extraction sequences were applied to two sediment samples (G2.7 and H1.5C) with similar arsenic concentrations (1,881 and 1,956 mg/kg, respectively), collected from exposed cut banks at two WWC sites. Aluminum, iron, manganese, and sulfur extraction patterns were evaluated in addition to arsenic in this investigation because these metals are closely associated with minerals controlling arsenic mobility. Data for the supplemental experiment are presented in Attachments 1 and 2.

In both samples G2.7 and H1.5C, the percentage of sodium phosphate extractable arsenic, aluminum, iron, and sulfur did not change significantly whether sodium phosphate was applied before or after hydroxylamine. Only manganese in sample G2.7 displayed approximately two-orders of magnitude increase in extraction percentages by sodium phosphate when it was applied after hydroxylamine (Attachments 1, 2a, 2c). The sediment manganese concentration of sample G2.7 was approximately 6.5 times greater than the sediment manganese concentration in sample H1.5C (Attachment 1).

In both samples G2.7 and H1.5C, the percentage of hydroxylamine extractable manganese and sulfur did not change significantly whether hydroxylamine was applied before or after sodium phosphate. However, the percentage of hydroxylamine extracted iron decreased up to two-orders of magnitude while hydroxylamine extracted arsenic increased nearly two-orders of magnitude when hydroxylamine was applied after sodium phosphate in both samples (Attachments 1, 2b, 2d). Aluminum displayed differences in extraction patterns between the two samples whereby the percentage of hydroxylamine extracted aluminum did not change significantly in sample G2.7 but decreased by nearly 1.5 orders of magnitude in sample H1.5C. The percentage of hydroxylamine extracted aluminum under either extraction sequence in both samples were very low (0.01 to 1.21%) (Attachments 1, 2b, 2d).

Applying hydroxylamine after sodium phosphate appeared to greatly alter the extractability of arsenic. In samples G2.7 and H1.5C, only a negligible amount of arsenic (0.04% and 0.03%, respectively) was extracted by hydroxylamine when it was applied before sodium phosphate. However, when hydroxylamine was applied after sodium phosphate, arsenic extraction percentages increased by approximately two-orders of magnitude (3.53% and 4.83%, respectively) (Attachment 1). Arsenic residing on exchangeable sites (extractable by sodium phosphate) does not seem to be affected by initial contact with hydroxylamine, however, arsenic hosted in reducible mineral phases (extractable by hydroxylamine) does appear to be affected by initial contact with sodium phosphate. Plausible explanations for this phenomenon are discussed below.

One possibility is that hydroxylamine is not able to effectively attack arsenic host-sites or reducible minerals unless sodium phosphate interacts with them first. The application of sodium phosphate may expose arsenic residence sites that hydroxylamine is not able to reach on its own. Thus, when hydroxylamine is applied first, it could only remove 0.03-0.04% of the arsenic, but when it is applied second, it can remove 3.53-4.83% of the arsenic (Attachment 1).

Another possibility can be explained by the well documented issue of arsenic reprecipitation during sequential extractions (Bermond, et al., 1993; Rodriguez, et al., 2003; Wenzel, et al., 2001; Hudson-Edwards, et al., 2004; Van Herreweghe, et al., 2003; Muller, et al., 2007). When sodium phosphate is applied first, it removes arsenic residing on surface sites (including on the surfaces of Feand Mn- oxides). But a portion of the arsenic does not remain in solution and re-precipitates or re-adsorbs back onto fresh mineral surfaces, especially Fe- and Mn- oxide surfaces which are known to be strong adsorption sites for arsenic (Huang, et al., 2010]; Larios, et al., 2012; Lombi, et al., 2000; Muller, et al., 2007). The application of hydroxylamine following sodium phosphate then dissolves Fe- and Mn- oxides thus releasing the newly and weakly re-adsorbed arsenic that were residing on their surfaces. Although hydroxylamine is known for its effectiveness in dissolving Fe- and Mn oxide surfaces (Huang, et al., 2010), only a small portion of the Fe- and Mn- oxides are able to dissolve because phosphate ions coating their surfaces may be inhibiting their reductive dissolution (Borch et al., 2007). This explains the greater percentage of Fe and Mn extracted when hydroxylamine was applied prior to sodium phosphate (Attachment 1). Regardless of the sequence, sodium phosphate and hydroxylamine extracted greater percentages of Mn than Fe (Attachments 1 and 2).

In the other scenario when hydroxylamine is applied first, the very low percentage of extracted arsenic (0.04% and 0.03%) indicates either there is very little arsenic is associated with residence sites associated with Fe- and Mn- oxides or that the molal concentration of the solution may not be strong enough for the effective dissolution arsenic-associated minerals. The application of sodium phosphate following hydroxylamine, competitively exchanges and removes the arsenic bound on surface sites.

Regardless of the sequence, the sum of total percentage of arsenic extracted by both reagents is similar (Attachment 1) and represents the amount of weakly bound arsenic. Changing the extraction sequence did not greatly alter the total amount of arsenic extracted, but due to reprecipitation, the P1-H2 sequence results seemingly extracted arsenic from different residences sites than the H1-P2 sequence.

One main purpose of applying sequential extractions is to assess the higher end of the possible range of extractable arsenic hosted by each type of residence site. Applying hydroxylamine after sodium phosphate appears to meet this objective. Additionally, this sub-experiment suggests that when hydroxylamine is applied after sodium phosphate, the percentage of arsenic extracted by hydroxylamine could be interpreted to be from both surfaces of dissolved Fe- and Mn- oxyhydroxides and from weakly bound arsenic released from all other surface sites. **Attachment 1.** Percent of metals extracted by sodium phosphate and hydroxylamine from sediment sample G2.7 (a) and sample H1.5C (b) under two different extraction sequences:

P1 - sodium phosphate extraction applied before hydroxylamine

H2 - hydroxylamine extraction applied after sodium phosphate

H1 - hydroxylamine extraction applied before sodium phosphate

P2 - sodium phosphate extraction applied after hydroxylamine

(a)	Extraction	1 Sequence:	To Extrac	otal cted %	Extra Sequ	nction ence:	Composition of Unextracted
G2.7	P1 %	H2 %	(P Extrac	+ H ctions)	H1 %	P2 %	Sediment (mg/kg)
As	4.34	3.53	7.87	6.79	0.04	6.75	1,881
Al	0.18	0.02	0.19	0.16	0.01	0.15	18,838
Fe	0.10	0.01	0.12	0.26	0.15	0.10	103,572
Mn	0.26	24.13	24.38	48.46	34.52	13.94	1,865
S	2.09	0.49	2.59	1.96	0.81	1.14	1,341

(b)	Extraction	Sequence:	To Extra	otal cted %	Extra Sequ	action ence:	Composition of Unextracted
Sample H1.5CC	P1 %	H2 %	(P Extrac	+ H ctions)	H1 %	P2 %	Sediment (mg/kg)
As	12.70	4.83	17.53	13.45	0.03	13.42	1,956
Al	0.49	0.03	0.52	1.54	1.21	0.32	11,469
Fe	0.09	0.01	0.10	0.46	0.35	0.11	79,028
Mn	1.07	0.55	1.62	1.61	1.21	0.40	286
S	20.97	5.80	26.77 28.48		16.75	11.73	10,567



Attachment 2. The effects on percent of metals extracted from sediment sample G2.7 (a,b) and H1.5C (c,d) by reversing sodium phosphate and hydroxylamine sequences; P1- sodium phosphate extraction applied <u>before</u> hydroxylamine; P2- sodium phosphate extraction applied <u>after</u> hydroxylamine; H1- hydroxylamine extraction applied <u>before</u> sodium phosphate; H2- hydroxylamine extraction applied <u>after</u> sodium phosphate

Run	Extraction	Sample	Ag	Al	As	Au	В	Ва	Ве	Ca	Cd	Со	Cr	Cu	Fe
		MDL:	0.01	0.1	0.005	0.1	0.01	0.01	0.001	0.1	0.005	0.01	0.01	0.01	0.01
	Calcul	ated PQL:	0.03	0.3	0.015	0.3	0.03	0.03	0.003	0.3	0.015	0.03	0.03	0.03	0.03
		1/2 MDL:	0.005	0.05	0.0025	0.05	0.005	0.005	0.0005	0.05	0.0025	0.005	0.005	0.005	0.005
1	E1	G2.7	<.0000	0.2421	0.1286	<.0000	1.452	1.601	<.0000	10.83	<.0000	0.0003	<.0000	0.0071	0.4394
2	E1	G2.7	<.0000	0.0285	<.0000	<.0000	1.448	1.475	<.0000	9.582	0.0093	<.0000	<.0000	0.0047	0.402
1	E1	G2.6	<.0000	0.0308	0.0731	<.0000	1.382	0.0483	<.0000	355.6	<.0000	<.0000	<.0000	0.0034	0.0004
2	E1 E1	G2.6	<.0000	<.0000	<.0000	<.0000	1.294	0.0297	0.0002	335.b	0.0107	0.0045	<.0000	<.0000	<.0000
2	E1 F1	G2.5	< 0000	< 0000	< 0000	< 0000	1.566	0.0303	< 0000	490.5	0.0011	< 0000	< 0000	0.0041	< 0000
1	F1	G3.1A	<.0000	0.099	0.1023	<.0000	1.403	1.442	<.0000	4,221	<.0000	<.0000	<.0000	0.0010	0.4538
1	E1	G3.1B	<.0000	0.0255	0.0294	<.0000	1.327	0.3708	<.0000	7.944	0.0001	<.0000	<.0000	0.0035	0.0028
1	E1	G3.1C	<.0000	0.0474	0.0702	<.0000	1.397	1.472	<.0000	7.721	<.0000	<.0000	<.0000	0.006	0.1066
1	E1	G3.1D	<.0000	0.0308	0.0819	<.0000	1.43	0.1193	<.0000	160.1	<.0000	<.0000	<.0000	0.0025	<.0000
1	E1	G3.3A	<.0000	0.2983	0.2894	<.0000	1.489	1.458	<.0000	7.425	<.0000	<.0000	0.0086	0.01	0.2574
1	E1	G3.3B	<.0000	0.0278	0.0702	<.0000	1.309	0.0904	<.0000	191.6	<.0000	<.0000	<.0000	0.0057	<.0000
1	E1	G3.3C	<.0000	0.0041	0.0994	<.0000	1.324	0.0367	<.0000	543.8	<.0000	<.0000	<.0000	<.0000	<.0000
1	E1	G3.3D	<.0000	1.044	0.0993	<.0000	1.356	0.0295	<.0000	404.3	0.0066	0.0047	0.0183	0.0093	<.0000
1	E1	H1.7	<.0000	2.857	0.1666	<.0000	1.472	0.0371	<.0000	458.3	0.0051	<.0000	<.0000	0.0157	0.0105
1	E1	H1.6	<.0000	1.247	0.0906	<.0000	1.334	0.0315	<.0000	551.1	0.0021	<.0000	<.0000	0.0165	<.0000
1	E1	H1.5C	<.0000	5.843	0.1578	<.0000	1.441	0.0532	<.0000	482.5	0.0051	0.0085	<.0000	0.0855	0.0542
1	E1	H1.5B	<.0000	19.39	0.0788	<.0000	1.325	0.0532	<.0000	269	0.0009	0.0289	0.0061	0.2529	4.778
1	E1	H1.5A	<.0000	38.68	0.0465	<.0000	1.361	0.047	<.0000	392.8	0.005	0.0828	<.0000	0.5766	7.829
1	E1	H1.4	<.0000	41.02	0.1755	<.0000	1.402	0.0643	<.0000	267.2	0.0011	0.0836	0.0231	0.6059	68.64
1	E1 E1	H1.3D	<.0000	47.80	4.355	<.0000	1.504	0.1851	< 0000	270.1	0.0468	0.0815	<.0000	0.7474	20 55
1	E1 F1	П1.5A H1 2B	< 0000	0.0126	0.2547	< 0000	1.552	0.0755	< 0000	282.1	< 0000	0.0756	< 0000	0.4622	0.050
1	F1	H1 20	< 0000	0.9120	0.1032	< 0000	1.275	0.0318	< 0000	255.3	< 0000	< 0000	<.0000	0.0028	0.000
1	F1	H2.4A	<.0000	0.0195	0.1169	<.0000	1.176	0.0727	<.0000	34.73	0.0019	0.0023	<.0000	0.0029	0.0017
1	E1	H2.4B	<.0000	0.6861	0.0965	<.0000	1.241	0.0267	<.0000	407.6	<.0000	0.0018	<.0000	0.0069	0.0024
1	E1	H2.4C	<.0000	0.0535	0.0614	<.0000	1.25	0.0285	<.0000	441.5	0.0013	<.0000	<.0000	0.0039	0.0012
1	E1	H2.4D	<.0000	0.0216	0.0819	<.0000	1.235	0.0271	<.0000	379.7	<.0000	<.0000	<.0000	0.0029	0.0099
1	E1	K1.1A	<.0000	0.0154	0.1928	<.0000	1.263	1.409	<.0000	15.39	0.0012	<.0000	<.0000	0.001	0.0667
1	E1	K1.1B	<.0000	0.0216	0.1228	<.0000	1.271	1.5	<.0000	19.38	<.0000	0.0005	<.0000	0.0046	0.0637
1	E1	K1.1C	<.0000	0.0051	0.0294	<.0000	1.254	0.0494	<.0000	425.3	0.0002	<.0000	<.0000	0.0069	0
1	E1	K1.3A	<.0000	0.034	0.0351	<.0000	1.256	0.2442	<.0000	31.24	<.0000	0	<.0000	0.0013	0.0089
1	E1	K1.3B	<.0000	<.0000	0.1286	<.0000	1.301	0.0356	<.0000	467.2	0	0.0009	<.0000	0.0025	0.0003
1	E1	K1.3C	<.0000	0.0102	0.0117	<.0000	1.344	0.058	<.0000	449.9	<.0000	0.0038	<.0000	0.0001	<.0000
1	E1	K1.4A	<.0000	0.0625	0.0906	<.0000	0.2081	0.1019	<.0000	11.19	<.0000	<.0000	0.0061	0.0038	0.0951
1	E1	K1.4B	<.0000	0.0411	0.152	<.0000	0.156	0.1743	<.0000	95.94	<.0000	0.0011	<.0000	0.0032	<.0000
1	E1	K1.4C	<.0000	0.0607	0.0351	<.0000	0.1457	0.1688	<.0000	144	<.0000	<.0000	<.0000	<.0000	0.0018
2	E1 E1	K1.4D	< 0000	0.0504	< 00001	< 0000	0.185	0.1072	<.0000	101	0.0019	<.0000	<.0000	0.0013	< 0000
1	F2	62.7	< 0000	3 128	11.6	<.0000	1 001	0.1084	< 00007	140.7	0.0047	0.0154	1.078	<.0000 0 1/123	<.0000 0 853
2	F2	G2.7	<.0000	4.427	11.38	<.0000	1.119	0.4917	<.0000	125.7	0.245	<.0000	0.5148	0.0991	10.27
1	E2	G2.6	<.0000	3.09	0.5031	<.0000	1.025	1.263	<.0000	173	0.0049	0.0103	1.09	0.0139	1.152
2	E2	G2.6	<.0000	3.893	0.7991	<.0000	1.046	1.137	0.0018	125.1	0.0066	<.0000	0.5369	<.0000	1.132
1	E2	G2.5	<.0000	4.794	0.49	<.0000	1.255	1.066	<.0000	227.9	0.0089	0.0094	1.026	0.0186	1.21
2	E2	G2.5	<.0000	6.046	0.9143	<.0000	1.326	0.858	0.0027	185.5	0.008	0.0056	0.4783	0.0074	1.003
1	E2	G3.1A	<.0000	1.791	6.279	<.0000	1.162	0.8666	<.0000	106.3	0.0704	0.0082	1.057	0.0587	8.048
2	E2	G3.1A	<.0000	2.084	6.556	<.0000	1.172	0.6503	<.0000	105.2	0.1368	0.0137	0.5603	0.0239	7.34
1	E2	G3.1B	<.0000	4.444	2.101	<.0000	1.096	1.169	<.0000	20.97	0.0219	0.0089	1.053	0.0168	9.027
1	E2	G3.1C	<.0000	3.921	2.298	<.0000	1.147	1.15	<.0000	62.34	0.0242	0.0119	1.106	0.0279	7.951
2	E2	G3.1C	<.0000	4.917	2.617	<.0000	1.175	0.7791	<.0000	62.1	0.0419	<.0000	0.6308	0.0109	6.554
1	E2	G3.1D	<.0000	3.761	1.082	<.0000	1.099	0.5454	<.0000	383.8	0.0138	0.0115	1.109	0.0332	3.461
	EZ	G3.3A	<.0000	8.237	7.947	<.0000	1.146	1.067	<.0000	209.9	0.0928	0.0142	1.021	0.0243	4.2
	E2	G3.3B	<.0000	5.289	9.332	<.0000	1.048	0.8846	<.0000	250.4	0.1125	0.01/3	1.003	0.0415	4.15
1	E2	03.30	<.0000	4.076	20.6/	<.0000	0.9905	0.9356	<.0000	159.0	0.24/4	0.0133	1.032	0.0525	8.049 7.126
1	E2 E2	U3.3U	< 0000	5 240	1.3/2	< 00028	1.004	1 000	<.0000	122.0	0.0906	0.0104	1.054	0.0779	7.120 0.1 <i>1</i> 1
1	F2	H1 6		5.549	14 59	< 0000	0.9561	1.008	< 0000	132.9 51 <i>1</i>	0.1435	0.0114	1.034	0.0138	5.141 7.577
	F2	H1.5C	< 0000	5 722	21 2	< 0000	0.9501	0.9031	< 0000	169 1	0.2458	0.0110	1.032	0.0260	8 966
1	E2	H1.5B	<.0000	2.699	27.64	<.0000	0.9828	0.9835	<.0000	198.1	0.3163	0.0114	1.122	0.0194	10.63

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Extraction	Sample	к	Li	Mg	Mn	Мо	Na	Ni	Р	Pb	Rb	S	Sb	Se
		MDL:	0.1	0.01	0.1	0.01	0.01	0.1	0.01	0.01	0.005	0.1	1	0.01	0.005
	Calcul	ated PQL:	0.3	0.03	0.3	0.03	0.03	0.3	0.03	0.03	0.015	0.3	3	0.03	0.015
		1/2 MDL:	0.05	0.005	0.05	0.005	0.005	0.05	0.005	0.005	0.0025	0.05	0.5	0.005	0.0025
1	E1	G2.7	7.498	0.0007	5.351	0.0073	<.0000	8.268	<.0000	0.061	<.0000	<.0000	2.528	<.0000	<.0000
2	E1	G2.7	7.363	0.0024	5.669	0.0055	0.063	7.983	0.0068	<.0000	<.0000	0.0201	4.118	0.0168	0.2937
1	E1	G2.6	0.226	0.0196	25.21	0.0004	<.0000	7.964	0.0042	0.0279	<.0000	<.0000	343.7	<.0000	<.0000
2	E1	G2.6	0.18//	0.0155	23.9	0.0029	0.0429	7.353	0.0155	0.1436	<.0000	<.0000	378.9	0.0042	0.1803
1	E1 51	G2.5	3.261	0.0547	/1.45	0.0013	<.0000	30.54	<.0000	0.0944	<.0000	<.0000	5/3.5	<.0000	<.0000
2	E1 E1	G2.5	3.14	0.0456	1 622	0.0014	0.0022	27.55	0.0051	<.0000	0.0387	< 0000	1 646	< 0000	0.0789
1	E1 E1	G3.1A	1.250	<.0000	2 102	0.0009	< 0000	0.404	< 0000	0.0124	< 0000	< 0000	0.040	< 0000	< 0000
1	F1	G3.10	3 024	0.0037	3 201	0.134	< 0000	7 767	< 0000	0.0017	< 0000	< 0000	4 521	< 0000	< 0000
1	F1	G3.1D	15.74	0.0061	47.9	<.0000	<.0000	11.63	0.0039	0.0993	<.0000	<.0000	200.7	<.0000	<.0000
1	E1	G3.3A	2.556	0.0001	2.605	0.0036	<.0000	7.961	<.0000	0.0555	<.0000	<.0000	2.338	<.0000	<.0000
1	E1	G3.3B	3.762	0.0032	17.23	0.0006	<.0000	8.294	<.0000	0.1553	<.0000	<.0000	172.9	<.0000	<.0000
1	E1	G3.3C	1.521	0.0074	13.83	0.2632	<.0000	8.175	0.0076	0.0357	<.0000	<.0000	524.3	<.0000	<.0000
1	E1	G3.3D	3.713	0.0219	37.02	8.034	<.0000	9.567	0.1434	0.0043	<.0000	<.0000	422	<.0000	<.0000
1	E1	H1.7	1.202	0.0057	1.88	0.3324	<.0000	9.247	<.0000	0.0382	<.0000	<.0000	428.7	<.0000	<.0000
1	E1	H1.6	0.7155	0.0069	4.367	0.7106	<.0000	8.627	0.0026	0.0609	<.0000	<.0000	510	<.0000	<.0000
1	E1	H1.5C	1.309	0.0183	8.286	0.9402	<.0000	8.706	0.0083	<.0000	<.0000	<.0000	454.5	<.0000	<.0000
1	E1	H1.5B	1.676	0.0389	13.2	1.761	<.0000	9.325	0.0742	<.0000	<.0000	<.0000	345.5	<.0000	<.0000
1	E1	H1.5A	1.764	0.0765	23.48	3.202	<.0000	9.563	0.1333	<.0000	<.0000	<.0000	503.9	<.0000	<.0000
1	E1	H1.4	1.777	0.0552	34.06	7.694	<.0000	9.304	0.1524	<.0000	<.0000	<.0000	474.3	<.0000	<.0000
1	E1	H1.3B	1.719	0.0559	50.73	12.75	<.0000	9.258	0.1266	0.2143	<.0000	<.0000	570.8	<.0000	<.0000
1	E1	H1.3A	1.948	0.0575	45.4	11.05	<.0000	9.892	0.1022	<.0000	<.0000	<.0000	490.3	<.0000	<.0000
1	E1	H1.2B	0.8397	0.0284	31.52	10.39	<.0000	8.965	0.1106	<.0000	<.0000	<.0000	320.6	<.0000	<.0000
1	E1	H1.2A	0.4538	0.0074	27.69	0.0256	<.0000	7.153	<.0000	<.0000	<.0000	<.0000	270.4	<.0000	<.0000
1	E1	H2.4A	0.41	0.0012	5.798	0.0068	0.0007	7.047	<.0000	0.0815	<.0000	<.0000	35.56	<.0000	<.0000
1	E1	H2.4B	2.048	0.0074	5.077	0.2694	<.0000	10.61	<.0000	<.0000	<.0000	<.0000	425.6	<.0000	<.0000
1	E1	H2.4C	2.463	0.0104	22.22	0.049	<.0000	21.21	<.0000	<.0000	<.0000	<.0000	459.4	<.0000	<.0000
1	E1	H2.4D	6.034	0.0359	30.85	0.0007	<.0000	35.92	0.0003	0.0406	<.0000	<.0000	461.9	<.0000	<.0000
1	E1	K1.1A	1.699	0.0096	5.159	0.0024	<.0000	13.92	<.0000	0.0475	<.0000	<.0000	12.93	<.0000	<.0000
1	E1	K1.1B	1.313	0.0118	7.511	0.0009	<.0000	13.67	<.0000	0.0457	<.0000	<.0000	16.59	<.0000	<.0000
1	E1	K1.1C	5.585	0.0255	39.29	0.0015	<.0000	27.56	<.0000	<.0000	<.0000	<.0000	468	<.0000	<.0000
1	E1	K1.3A	2.406	0.0092	8	0.0007	0.0066	10.38	<.0000	0.0686	<.0000	<.0000	25.47	<.0000	<.0000
1	E1	K1.3B	5.521	0.0143	15.29	0.0006	<.0000	10.03	<.0000	0.079	<.0000	<.0000	442.8	<.0000	<.0000
1	E1 F1	K1.3C	3.9	0.0142	29.58	0.0009	<.0000	13.12	0.0039	0.0688	<.0000	<.0000	403.1	<.0000	<.0000
1	E1 E1	K1.4A	2.015	0.0055	5.14Z	0.0001	< 0000	4.922	< 0000	0.1090	< 0000	< 0000	02 74	< 0000	< 0000
1	E1 E1	K1.4D	2.577	0.0072	6 765	< 0000	< 0000	7.090	< 0000	0.1222	< 0000	< 0000	92.74	< 0000	< 0000
1	F1	K1.4C	2.114	0.0004	19.07	< 0000	< 0000	7 164	< 0000	0.013	< 0000	< 0000	154.5	< 0000	< 0000
2	F1	K1.4D	3.441	0.0117	19.07	<.0000 0.0027	<.0000 0.0225	6 5 5 1	<.0000 0.0153	< 0000	< 0000	< 0000	165.6	< 0000	<.0000 0 5876
1	F2	G2.7	35 74	0.0029	29 54	0.355	< 0000	1858	0.0782	15230	< 0000	< 0000	< 0000	< 0000	< 0000
2	E2	G2.7	32.55	0.0017	28.77	0.3851	<.0000	1287	0.0634	16010	<.0000	<.0000	<.0000	0.1294	<.0000
1	E2	G2.6	11.32	0.0346	21.6	0.7294	<.0000	1895	0.0265	15490	<.0000	<.0000	20.34	<.0000	<.0000
2	E2	G2.6	9.121	0.0279	21.05	0.7698	<.0000	1294	0.043	16220	0.8562	<.0000	27.69	0.1529	<.0000
1	E2	G2.5	17.01	0.0756	51.51	0.6846	<.0000	1841	0.0354	15270	<.0000	<.0000	58.06	<.0000	<.0000
2	E2	G2.5	14.6	0.0652	49.56	0.7352	<.0000	1329	0.0081	15960	0.1386	<.0000	77.95	0.1819	0.3371
1	E2	G3.1A	28.92	0.0015	21.47	0.3775	<.0000	1873	0.0278	15620	<.0000	<.0000	<.0000	<.0000	<.0000
2	E2	G3.1A	25.87	<.0000	20.76	0.4038	<.0000	1263	0.0046	16220	<.0000	<.0000	<.0000	0.0768	<.0000
1	E2	G3.1B	17.05	0.0051	6.342	1.272	<.0000	1874	0.0487	15770	<.0000	<.0000	18.33	<.0000	<.0000
1	E2	G3.1C	24.42	0.0076	14.76	0.4135	<.0000	1885	0.0304	15820	<.0000	<.0000	<.0000	<.0000	<.0000
2	E2	G3.1C	21.88	0.0041	14.49	0.4434	<.0000	1254	0.0283	16290	<.0000	<.0000	<.0000	0.1628	<.0000
1	E2	G3.1D	28.24	0.0151	36.8	0.5703	<.0000	1895	0.0514	15490	<.0000	<.0000	13.15	<.0000	<.0000
1	E2	G3.3A	33.37	0.0029	32.74	0.3864	<.0000	1783	0.0455	15640	<.0000	<.0000	<.0000	<.0000	<.0000
1	E2	G3.3B	37.31	0.0139	15.63	0.4051	<.0000	1802	0.041	15580	<.0000	<.0000	25.5	<.0000	<.0000
1	E2	G3.3C	14.41	0.008	2.29	0.2943	<.0000	1858	0.0371	15850	<.0000	<.0000	502.1	<.0000	<.0000
1	E2	G3.3D	27.68	0.0228	7.043	2.981	<.0000	1835	0.0871	15890	<.0000	<.0000	151.8	<.0000	<.0000
1	E2	H1.7	9.899	0.0007	0.5119	0.095	<.0000	1852	0.0395	15870	<.0000	<.0000	108.9	<.0000	<.0000
	E2	H1.6	9.776	0.0048	0.9368	0.2162	<.0000	1838	0.0336	15630	<.0000	<.0000	438.6	<.0000	<.0000
	E2	H1.5C	10.3	0.0041	1.505	0.2036	<.0000	1860	0.04	15490	<.0000	<.0000	230.3	<.0000	<.0000
1 1	E2	IUTT'2D	0.104	0.0046	1.540	0.1902	<.UUUU	1004	0.0302	10000	<.UUUU	<.0000	5U3.2	<.0000	<.0000

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run Extraction Sample			Si	Sn	Sr	Th	Ti	Tİ	U	V	w	Zn
		MDL:	0.01	1	0.01	1	0.01	0.1	10	0.01	0.1	0.01
	Calculated PQL:		0.03	3	0.03	3	0.03	0.3	30	0.03	0.3	0.03
		1/2 MDL:	0.005	0.5	0.005	0.5	0.005	0.05	5	0.005	0.05	0.005
1	E1	G2.7	4.341	<.0000	0.0622	<.0000	0.0012	0.1745	<.0000	0.0055	<.0000	1.28
2	E1	G2.7	7.976	0.0702	0.0546	0.4001	<.0000	0.1797	<.0000	<.0000	0.0941	0.9212
1	E1	G2.6	3.28	<.0000	2.912	<.0000	0.0019	<.0000	<.0000	0.0636	0.0311	1.332
2	E1	G2.6	5.62	<.0000	2.52	0.0514	0.0069	<.0000	0.0224	0.0377	0.0931	1.132
1	E1	G2.5	3.353	<.0000	4.879	<.0000	0.0045	<.0000	<.0000	0.308	0.0027	1.249
2	E1	G2.5	5.145	0.0644	4.188	0.0142	0.0011	<.0000	0.0397	0.2111	0.2197	1.352
1	E1	G3.1A	4.565	<.0000	0.0356	<.0000	0.0016	0.14	<.0000	0.0011	0.0622	0.7916
1	E1	G3.1B	4.018	<.0000	0.0518	<.0000	0.0007	0.0998	<.0000	0.0086	0.0516	1.113
1	E1	G3.1C	2.881	<.0000	0.0516	<.0000	0.0008	0.1399	<.0000	0.0106	<.0000	0.8756
1	E1	G3.1D	3.231	<.0000	0.4994	<.0000	0.0026	<.0000	<.0000	0.1777	0.0311	1.361
1	E1	G3.3A	5.565	<.0000	0.0325	<.0000	0.0062	0.0633	<.0000	<.0000	<.0000	1.03
1	E1	G3.3B	3.138	<.0000	0.2157	<.0000	0.0011	<.0000	<.0000	0.0543	<.0000	1.556
1	E1	G3.3C	4.653	<.0000	0.3174	<.0000	0.0038	<.0000	<.0000	0.0538	0.0419	2.101
1	E1	G3.3D	4.861	<.0000	0.2167	<.0000	0.0032	<.0000	<.0000	0.0658	0.0046	2.477
1	E1	H1.7	3.707	<.0000	0.1628	<.0000	0.0036	<.0000	<.0000	<.0000	<.0000	2.28
1	E1	H1.6	3.955	<.0000	0.3221	<.0000	0.0053	<.0000	<.0000	<.0000	0.0204	2.058
1	E1	H1.5C	4.34	<.0000	0.2575	<.0000	0.0022	<.0000	<.0000	<.0000	<.0000	2.078
1	E1	H1.5B	3.298	<.0000	0.2494	<.0000	0.0036	<.0000	<.0000	<.0000	<.0000	1.94
1	E1	H1.5A	4.649	<.0000	0.2215	<.0000	0.0047	<.0000	<.0000	<.0000	<.0000	1.955
1	E1	H1.4	3.808	<.0000	0.2424	<.0000	0.0035	<.0000	<.0000	<.0000	<.0000	1.986
1	E1	H1.3B	3.399	<.0000	0.294	<.0000	0.007	0.1234	<.0000	<.0000	<.0000	2.053
1	E1	H1.3A	3.52	<.0000	0.3069	<.0000	0.0053	<.0000	<.0000	<.0000	<.0000	2.173
1	E1	H1.2B	3.071	<.0000	0.3253	<.0000	0.0021	<.0000	<.0000	0.0538	<.0000	1.832
1	E1	H1.2A	1.901	<.0000	0.3361	<.0000	0.0009	<.0000	<.0000	0.1065	<.0000	1.111
1	E1	H2.4A	3.892	<.0000	0.0471	<.0000	0.0001	<.0000	<.0000	0.026	<.0000	1.131
1	E1	H2.4B	3.874	<.0000	0.3268	<.0000	0.0053	<.0000	<.0000	<.0000	<.0000	1.846
1	E1	H2.4C	3.913	<.0000	0.5864	<.0000	0.0034	<.0000	<.0000	0.0865	0.0109	1.431
1	E1	H2.4D	1.775	<.0000	1.008	<.0000	0.0036	<.0000	<.0000	0.1231	0.0163	1.435
1	E1	K1.1A	2.474	<.0000	0.1576	<.0000	0.0083	<.0000	<.0000	0.0226	0.0112	0.7498
1	E1	K1.1B	2.078	<.0000	0.1891	<.0000	0.0184	0.2936	<.0000	0.0286	<.0000	0.981
1	E1	K1.1C	1.008	<.0000	2.246	<.0000	0.0042	<.0000	<.0000	0.142	0.0233	1.449
1	E1 54	K1.3A	1.859	<.0000	0.2353	<.0000	0.0024	<.0000	<.0000	0.0317	<.0000	0.8441
1	E1 E1	K1.3D	1.435	<.0000	1.327	<.0000	0.0017	< 0000	< 0000	0.0462	<.0000	1.591
1	E1 E1	K1.5C	1.505	< 0000	1.212	< 0000	0.0029	<.0000	< 0000	0.0981	0.0592	1.441
1	E1 E1	K1.4A	2.57	< 0000	0.0515	< 0000	0.0081	0.0228	< 0000	0.0099	< 0000	0.0564
1	E1 E1	K1.4D	2.455	< 0000	0.5674	< 0000	0.0031	< 0000	< 0000	0.0472	< 0000	0.1557
1	F1	K1.4C	2.582	< 0000	1 202	< 0000	0.0013	< 0000	< 0000	0.0271	< 0000	0.1045
2	F1	K1.4D	2.337	< 0000	1.202	<.0000 0.2738	< 0000	<.0000 0 3/171	<.0000 0 1268	0.001	<.0000 0 1031	0.0923
1	F2	62.7	J.802	< 0000	0.458	< 0000	<.0000 0.0122	< 0000	0.1200	< 0000	0.1031	1 5 8 9
2	F2	G2.7	7 318	< 0000	0.438	< 0000	0.0122	< 0000	0.1031	< 0000	< 0000	1.585
1	F2	G2.6	8 36	< 0000	1 635	< 0000	0.0137	< 0000	0.253	< 0000	0.0211	1 391
2	F2	G2.6	14.21	<.0000	1.466	<.0000	0.0159	0.3637	0.3456	<.0000	<.0000	1.448
1	F2	G2.5	16.14	<.0000	3.129	<.0000	0.0137	<.0000	0.2992	<.0000	0.0396	1.442
2	F2	G2.5	32.22	<.0000	2,749	<.0000	0.0143	0.2531	0.3263	<.0000	<.0000	1.478
1	E2	G3.1A	10.58	<.0000	0.4887	<.0000	0.017	<.0000	0.1949	<.0000	0.0389	1.575
2	E2	G3.1A	19.61	0.1355	0.4505	<.0000	0.0137	0.0834	0.3666	<.0000	<.0000	1.609
1	E2	G3.1B	5.157	<.0000	0.1074	<.0000	0.0173	<.0000	0.1806	<.0000	0.0604	1.611
1	E2	G3.1C	9.003	<.0000	0.3203	<.0000	0.0133	<.0000	0.1914	<.0000	0.0112	1.612
2	E2	G3.1C	16.34	<.0000	0.2948	<.0000	0.011	<.0000	0.4887	<.0000	<.0000	1.68
1	E2	G3.1D	10.65	<.0000	0.8193	<.0000	0.0142	<.0000	0.24	<.0000	0.0641	1.485
1	E2	G3.3A	12.63	<.0000	0.3264	<.0000	0.0162	<.0000	0.2979	<.0000	0.0956	1.543
1	E2	G3.3B	20.83	<.0000	0.3526	<.0000	0.015	<.0000	0.2151	<.0000	0.091	1.418
1	E2	G3.3C	4.206	<.0000	0.3476	<.0000	0.0373	<.0000	0.2068	<.0000	0.0803	1.408
1	E2	G3.3D	12.57	<.0000	0.0895	<.0000	0.0145	<.0000	0.2151	<.0000	0.0373	1.503
1	E2	H1.7	1.915	<.0000	0.0724	<.0000	0.0454	<.0000	0.2092	<.0000	<.0000	1.436
1	E2	H1.6	2.54	<.0000	0.3146	<.0000	0.0266	<.0000	0.1784	<.0000	0.0895	1.353
1	E2	H1.5C	3.329	<.0000	0.1005	<.0000	0.0192	<.0000	0.1724	<.0000	0.0404	1.314
1	E2	H1.5B	2.28	<.0000	0.1339	<.0000	0.0281	<.0000	0.157	<.0000	<.0000	1.399

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Run Extraction Sample		Ag	AI	As	Au	В	Ва	Be	Ca	Cd	Со	Cr	Cu	Fe
		MDL:	0.01	0.1	0.005	0.1	0.01	0.01	0.001	0.1	0.005	0.01	0.01	0.01	0.01
	Calculated PQL:		0.03	0.3	0.015	0.3	0.03	0.03	0.003	0.3	0.015	0.03	0.03	0.03	0.03
		1/2 MDL:	0.005	0.05	0.0025	0.05	0.005	0.005	0.0005	0.05	0.0025	0.005	0.005	0.005	0.005
1	E2	H1.5A	<.0000	5.919	20.66	<.0000	1.108	1.085	<.0000	417	0.2381	0.0157	1.057	0.0515	9.699
1	E2	H1.4	<.0000	3.905	13.95	<.0000	0.961	0.9072	<.0000	163.8	0.1614	0.0206	1.003	0.0563	10.24
1	E2	H1.3B	<.0000	3.73	26.34	<.0000	0.9384	0.8464	<.0000	230.6	0.3145	0.0211	1.081	0.063	10.83
1	E2	H1.3A	<.0000	3.//6	30.8	<.0000	0.9406	0.9319	<.0000	234.3	0.3617	0.01/3	1.061	0.0387	11 8 072
1	F2	H1.20	< 0000	5 299	3 045	< 0000	0.350	0.9408	< 0000	232.6	0.105	0.024	1.090	0.0227	5 531
1	E2	H2.4A	<.0000	4.214	39.17	<.0000	0.971	0.9417	<.0000	92.22	0.4625	0.012	1.032	0.0352	7.562
1	E2	H2.4B	<.0000	4.041	18.33	0.0041	0.9512	0.8959	<.0000	275.6	0.2102	0.0105	1.042	0.0164	8.705
1	E2	H2.4C	<.0000	5.924	10.84	<.0000	0.3239	0.202	<.0000	285.9	0.1249	0.012	1.071	0.0377	7.976
1	E2	H2.4D	<.0000	16.02	5.336	<.0000	0.3627	0.195	<.0000	228.1	0.0617	0.0117	1.054	0.03	3.832
1	E2	K1.1A	<.0000	4.455	3.117	<.0000	0.3632	0.1432	<.0000	343.2	0.0369	0.0093	1.059	0.0312	4.801
2	E2	K1.1A	<.0000	5.691	3.692	<.0000	0.4275	0.0728	<.0000	343.2	0.0776	0.0062	0.5631	0.0007	3.731
1	E2	K1.1B	<.0000	5.63	3.885	<.0000	0.3908	0.1914	<.0000	303.7	0.0425	0.0076	1.055	0.0248	4.941
1	E2	K1.1C	<.0000	2.233	15.49	<.0000	0.4415	0.1711	<.0000	385.1	0.1673	0.0151	1.138	0.0287	5.776
1	E2	K1.3A	<.0000	3.836	8.192	<.0000	0.3717	0.1558	<.0000	234	0.088	0.0102	1.132	0.0291	6.298
1	E2	K1.3B	<.0000	2.514	14.74	<.0000	0.3781	0.1567	<.0000	440.5	0.164	0.0131	1.088	0.0435	6.322
1	E2 E2	K1.3C	< 0000	5 3 2 1	634	< 0000	0.3075	0.174	< 0000	325.1	0.1978	0.0085	1.096	0.0211	5.997
1	F2	K1.4R	< 0000	4 639	0.54	< 0000	0.3400	0.3284	< 0000	417.2	0.0713	0.0143	1.150	0.0237	4 113
1	E2	K1.4C	<.0000	3.699	1.177	<.0000	0.3252	0.1759	<.0000	340	0.0096	0.0111	1.137	0.0048	5.297
1	E2	K1.4D	<.0000	3.281	0.7518	<.0000	0.3748	0.1552	<.0000	357.4	0.0096	0.0114	1.096	0.0073	5.072
2	E2	K1.4D	<.0000	4.009	0.8268	<.0000	0.4185	0.0765	<.0000	352.6	0.0021	0.0051	0.3806	<.0000	3.735
1	E3	G2.7	<.0000	0.0068	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000	0.0063	<.0000	0.0006	<.0000	<.0000
2	E3	G2.7	<.0000	0.2188	9.269	<.0000	1.16	1.642	<.0000	30.91	0.2084	0.072	0.0906	0.027	1.413
1	E3	G2.6	<.0000	0.0146	0.1043	<.0000	0.0026	<.0000	<.0000	<.0000	0.0065	<.0000	0.0134	<.0000	<.0000
2	E3	G2.6	<.0000	0.0208	0.0449	<.0000	0.9065	1.352	0.0009	255.6	0.0058	0.0897	0.0178	0.0019	0.0522
1	E3	G2.5	<.0000	0.1134	0.3572	<.0000	1.02	1.337	<.0000	264.6	0.0106	0.0783	0.061	0.0067	0.0202
2	E3	G2.5	<.0000	0.0835	<.0000	<.0000	0.9467	1.25	0.0005	253.5	0.0002	0.0593	<.0000	0.0069	0.0277
2	E3	G3.1A	<.0000	0.1159	3.325	<.0000	1.006	1.77	<.0000	25.5	0.0363	0.0432	0.0315	0.0163	0.6698
1	E3 F3	G3.1A G3.1B	< 0000	0.034	1 1 2 5	< 0000	1 145	1.007	< 0000	4 366	0.0080	0.0238	<.0000 0.0148	0.0090	0.0920
1	E3	G3.10	<.0000	0.2281	1.341	<.0000	0.9657	2.087	<.0000	21.71	0.0114	0.5781	0.0065	0.0105	0.1647
2	E3	G3.1C	<.0000	0.1059	1.091	<.0000	0.9118	1.946	<.0000	19.89	0.0124	0.5323	<.0000	0.0129	0.233
1	E3	G3.1D	<.0000	0.0608	0.4913	<.0000	1.008	1.315	<.0000	243.6	0.0098	0.0484	0.0314	0.0095	0.0567
1	E3	G3.3A	<.0000	0.2915	4.389	<.0000	0.9737	1.824	<.0000	74.54	0.0506	0.0791	0.0473	0.0084	0.1913
1	E3	G3.3B	<.0000	0.2025	4.638	<.0000	0.9395	1.459	<.0000	74.28	0.0472	0.0521	0.0277	0.0132	0.1375
1	E3	G3.3C	<.0000	0.2605	10.48	<.0000	0.9156	1.242	<.0000	209.1	0.1026	0.0198	0.0625	0.0181	0.4114
1	E3	G3.3D	<.0000	0.5036	3.644	<.0000	0.9143	1.289	<.0000	47.91	0.0412	0.8492	0.0474	0.0343	0.0661
1	E3	H1.7	<.0000	0.3207	6.082	<.0000	0.9587	1.293	<.0000	24.31	0.0553	0.0022	0.0421	0.011	0.4984
1	E3	H1.6	<.0000	0.3121	7.007	<.0000	0.9202	1.23	<.0000	183.3	0.0683	0.0238	0.0352	0.0158	0.511
1	E3 F3	H1.5C	< 0000	0.3855	10.419	< 0000	0.8381	1.200	< 0000	92.91	0.080	<.0000	0.039	0.0174	0.8220
1	E3	H1.5D	<.0000	0.4323	10.57	<.0000	0.9302	1.265	<.0000	170.2	0.1070	0.0043	0.0443	0.0097	0.6219
1	E3	H1.4	<.0000	0.2605	5.218	<.0000	0.8964	1.205	<.0000	105.6	0.0492	<.0000	0.0239	0.0177	0.7737
1	E3	H1.3B	<.0000	0.2547	9.551	<.0000	0.7804	1.078	<.0000	176.2	0.1007	0.0009	0.0269	0.0186	0.9144
1	E3	H1.3A	<.0000	0.3062	11.55	<.0000	0.9745	1.235	<.0000	138.1	0.1172	0.005	0.0458	0.0164	0.8367
1	E3	H1.2B	<.0000	0.4821	4.41	<.0000	0.9077	1.261	<.0000	18.8	0.0453	0.3952	0.0057	0.0753	0.8673
1	E3	H1.2A	<.0000	0.2213	1.113	<.0000	0.8908	1.334	<.0000	172.1	0.0236	0.9887	0.0019	0.0457	<.0000
1	E3	H2.4A	<.0000	0.2248	17.97	<.0000	0.9234	1.278	<.0000	21.69	0.1822	0.069	0.0572	0.0128	0.3896
1	E3	H2.4B	<.0000	0.3101	9.677	<.0000	0.9533	1.241	<.0000	82.6	0.1011	0.006	0.0231	0.0116	0.3734
1	E3	H2.4C	<.0000	0.4206	5.021	<.0000	0.1/34	0.3118	<.0000	/8.14	0.0512	0.3082	0.0639	0.0169	0.2618
1	E3 E2	112.4U	< 0000	0.7106	2.03	< 0000	0.218/	0.3008	< 0000	90.81 145 5	0.0333	0.3082	0.0557	0.03	0.0302
2	F3	K1.1A	0.0000	< 0000	1.392	< 0000	0.1254	0.3003	<.0000 0.0004	145.5	0.02	0.1093	< 0000	< 00000	0.0554
1	E3	K1.1B	<.00002	0.1108	1.86	<.0000	0.1275	0.3542	<.0000	104.1	0.0266	0.1265	0.0299	0.0082	0.0654
1	E3	K1.1C	<.0000	0.0701	7.116	<.0000	0.186	0.2791	<.0000	326.3	0.0814	0.285	0.0473	0.019	0.1106
1	E3	K1.3A	<.0000	0.0976	3.708	<.0000	0.1727	0.3541	<.0000	69.69	0.0417	0.1632	0.0451	0.0065	0.1221
1	E3	K1.3B	<.0000	0.0912	6.684	<.0000	0.1637	0.2924	<.0000	273.3	0.0755	0.2787	0.0625	0.0236	0.1317
1	E3	K1.3C	<.0000	0.0991	7.666	<.0000	0.1655	0.2858	<.0000	208.9	0.0794	0.2861	0.0572	0.0166	0.0922

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2
Run	Extraction	Sample	К	Li	Mg	Mn	Мо	Na	Ni	Р	Pb	Rb	S	Sb	Se
_		MDL:	0.1	0.01	0.1	0.01	0.01	0.1	0.01	0.01	0.005	0.1	1	0.01	0.005
	Calcul	ated PQL:	0.3	0.03	0.3	0.03	0.03	0.3	0.03	0.03	0.015	0.3	3	0.03	0.015
		1/2 MDL:	0.05	0.005	0.05	0.005	0.005	0.05	0.005	0.005	0.0025	0.05	0.5	0.005	0.0025
1	E2	H1.5A	8.181	0.0138	2.792	0.3616	<.0000	1858	0.0528	15540	<.0000	<.0000	385	<.0000	<.0000
1	E2	H1.4	7.575	0.0132	4.9	0.925	<.0000	1834	0.0538	15530	<.0000	<.0000	190.1	<.0000	<.0000
1	E2	H1.3B	7.828	0.0119	6.453	1.207	<.0000	1820	0.0443	15760	<.0000	<.0000	241.4	<.0000	<.0000
1	E2	H1.3A	8.09	0.011	5.748	1.086	<.0000	1865	0.0489	15590	<.0000	<.0000	274.8	<.0000	<.0000
1	E2	H1.2B	13.17	0.0448	5.133	1.943	<.0000	1819	0.1019	16090	<.0000	<.0000	154.1	<.0000	<.0000
1	E2	H1.2A	22.05	0.0511	17.88	2.758	<.0000	1853	0.0912	15910	<.0000	<.0000	107.7	<.0000	<.0000
1	E2	H2.4A	17.03	0.0019	11	0.1902	<.0000	1893	0.0386	15/50	<.0000	<.0000	38.36	<.0000	<.0000
1	E2	HZ.4B	11.47	0.0019	1.097	0.1343	<.0000	1809	0.0358	15540	<.0000	<.0000	225.2	<.0000	<.0000
1	E2 E2		22.09	0.0075	4.705	0.2509	< 0000	1095	0.059	15250	< 0000	< 0000	215.0	< 0000	< 0000
1	F2	K1.1Δ	26.49	0.3001	46 22	0.5799	< 0000	1863	0.0452	15670	< 0000	< 0000	< 0000	< 0000	< 0000
2	F2	K1.1A	23.12	0.0251	45.11	0.6231	<.0000	1290	0.0527	16080	0.1388	<.0000	<.0000	0.1626	<.0000
1	E2	K1.1B	24.49	0.0421	53.33	0.4548	<.0000	1836	0.0405	15410	<.0000	<.0000	<.0000	<.0000	<.0000
1	E2	K1.1C	29.21	0.066	22.88	0.2889	<.0000	1846	0.0437	15070	<.0000	<.0000	226.7	<.0000	<.0000
1	E2	K1.3A	28.24	0.0304	33.28	0.3748	<.0000	1871	0.0462	15050	<.0000	<.0000	<.0000	<.0000	<.0000
1	E2	K1.3B	31.12	0.0302	8.75	0.2643	<.0000	1897	0.0405	15340	<.0000	<.0000	266.8	<.0000	<.0000
1	E2	K1.3C	24.18	0.0319	14.55	0.2484	<.0000	1871	0.0444	14920	<.0000	<.0000	196	<.0000	<.0000
1	E2	K1.4A	24.65	0.017	35.2	0.4261	<.0000	1935	0.0364	15000	<.0000	<.0000	<.0000	<.0000	<.0000
1	E2	K1.4B	20.66	0.0195	24.32	0.5164	<.0000	1783	0.0363	14700	<.0000	<.0000	5.971	<.0000	<.0000
1	E2	K1.4C	16.99	0.0154	10.09	0.6769	<.0000	1873	0.0275	14890	<.0000	<.0000	10.89	<.0000	<.0000
1	E2	K1.4D	17.97	0.025	20.42	0.9426	<.0000	1924	0.0349	15310	<.0000	<.0000	13.05	<.0000	<.0000
2	E2	K1.4D	15.43	0.018	20.23	0.9807	<.0000	1263	0.052	16210	<.0000	<.0000	13.73	0.1007	0.6096
1	E3	G2.7	0.064	<.0000	<.0000	<.0000	0.0112	<.0000	<.0000	1.281	<.0000	<.0000	0.8596	<.0000	<.0000
2	E3	G2.7	11.62	0.0011	6.611	41.55	0.0334	904.4	0.0537	2470	<.0000	<.0000	<.0000	<.0000	0.2159
2	E3 E2	G2.6	0.1173	0.0004	<.0000	<.0000	0.0004	<.0000	<.0000	1.211	<.0000	<.0000	0.5732	< 0000	< 0000
1	E3 F3	G2.6	7 364	0.0009	16 73	13.07	0.0071	042.7	0.1302	< 0000	< 0000	< 0000	5.15 117 7	< 0000	< 0000
2	F3	G2.5	6 747	0.0230	15.99	18.00	< 0000	933.3	0.1210	2587	< 0000	< 0000	131.3	< 0000	< 0000
1	F3	G3.1A	7.688	0.0023	5.281	22.56	<.0000	937.6	0.0096	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
2	E3	G3.1A	6.801	<.0000	5.263	23.13	<.0000	762.9	0.0154	1987	<.0000	<.0000	<.0000	<.0000	<.0000
1	E3	G3.1B	4.816	0.0123	1.229	48.83	<.0000	734.6	0.058	<.0000	<.0000	<.0000	5.012	<.0000	<.0000
1	E3	G3.1C	7.029	0.0156	6.399	107.3	<.0000	881	0.2942	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
2	E3	G3.1C	6.016	0.0108	6.147	108	<.0000	728.2	0.2467	1871	<.0000	<.0000	<.0000	<.0000	<.0000
1	E3	G3.1D	7.202	0.0066	9.848	16.44	<.0000	868.6	0.0365	<.0000	<.0000	<.0000	17.75	<.0000	<.0000
1	E3	G3.3A	10.44	0.0026	9.906	24.43	<.0000	984.8	0.0391	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
1	E3	G3.3B	13.43	0.0068	6.981	17.68	<.0000	861.9	0.025	<.0000	<.0000	<.0000	2.68	<.0000	<.0000
1	E3	G3.3C	4.238	0.0033	0.6548	9.242	<.0000	879.8	0.0299	<.0000	<.0000	<.0000	160.9	<.0000	<.0000
1	E3	G3.3D	10.29	0.012	2.54	142.6	<.0000	991.6	0.4036	<.0000	<.0000	<.0000	37.63	<.0000	<.0000
1	E3 E2	п1.7 Ц1 6	2.095	0.0001	0.2209	0.5012	< 0000	890.7 844 5	0.0002	< 0000	< 0000	< 0000	12/1	< 0000	< 0000
1	F3	H1.5C	3 78	0.0018	0.3733	0 1358	<.0000	879 5	0.0090	< 0000	< 0000	< 0000	59 41	< 0000	< 0000
1	E3	H1.5B	2.003	0.0012	0.426	0.0485	0.0148	952.2	0.0246	<.0000	<.0000	<.0000	82.07	<.0000	<.0000
1	E3	H1.5A	2.396	0.003	0.7265	0.0784	0.0022	1010	0.0149	<.0000	<.0000	<.0000	139	<.0000	<.0000
1	E3	H1.4	2.325	0.0034	1.121	0.1683	<.0000	891.3	0.0135	<.0000	<.0000	<.0000	88.83	<.0000	<.0000
1	E3	H1.3B	1.907	0.0035	1.205	0.2185	0.0001	977.3	0.0181	<.0000	<.0000	<.0000	140.5	<.0000	<.0000
1	E3	H1.3A	2.227	0.0029	1.143	0.2422	0.0005	971.5	0.0218	<.0000	<.0000	<.0000	117.6	<.0000	<.0000
1	E3	H1.2B	4.257	0.0332	1.704	28.08	<.0000	794.2	0.1153	<.0000	<.0000	<.0000	18.92	<.0000	<.0000
1	E3	H1.2A	7.512	0.0329	12.45	230.8	<.0000	700.3	1.635	<.0000	<.0000	<.0000	105	<.0000	<.0000
1	E3	H2.4A	5.23	0.0015	2.478	12.12	0.0026	1005	0.0183	<.0000	<.0000	<.0000	4.278	<.0000	<.0000
1	E3	H2.4B	3.132	0.0012	0.3848	1.117	<.0000	978	0.0264	<.0000	<.0000	<.0000	56.82	<.0000	<.0000
1	E3	H2.4C	5.467	0.0032	1.187	30.96	0.0076	1042	0.0344	<.0000	<.0000	<.0000	45.94	<.0000	<.0000
1	E3	H2.4D	11.91	0.2116	7.021	105.8	0.0001	1032	0.3044	<.0000	<.0000	<.0000	52.54	<.0000	<.0000
1	E3	K1.1A	7.349	0.0115	10.07	21.8/	0.0018	937.2	0.0944	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
2	E3 F2	K1.1A	7 051	0.0089	14.97	22.79	< 0000	707.9 915.9	0.0784	1020	< 0000	< 0000	< 0000	< 0000	
1	FR	K1.1C	10 95	0.0302	8 5 8 5	69.81	<.0000	987.2	0.4655	<.0000	<.0000	<.0000	229.2	<.0000	<.0000
1	E3	K1.3A	9.035	0.0112	10.38	37.18	<.0000	894.7	0.1464	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
1	E3	K1.3B	11.13	0.0167	5.505	70.15	<.0000	948.3	0.364	<.0000	<.0000	<.0000	186	<.0000	<.0000
1	E3	K1.3C	9.021	0.0292	6.165	81.13	0.0072	944.3	0.3737	<.0000	<.0000	<.0000	143.6	<.0000	<.0000

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Extraction	Sample	Si	Sn	Sr	Th	Ti	Tİ	U	v	w	Zn
		MDL:	0.01	1	0.01	1	0.01	0.1	10	0.01	0.1	0.01
	Calcul	ated PQL:	0.03	3	0.03	3	0.03	0.3	30	0.03	0.3	0.03
		1/2 MDL:	0.005	0.5	0.005	0.5	0.005	0.05	5	0.005	0.05	0.005
1	E2	H1.5A	2.874	<.0000	0.2135	<.0000	0.0529	<.0000	0.1499	<.0000	0.0657	1.506
1	E2	H1.4	2.181	<.0000	0.155	<.0000	0.0209	<.0000	0.189	<.0000	0.032	1.37
1	E2	H1.3B	1.529	<.0000	0.2231	<.0000	0.0155	<.0000	0.1961	<.0000	0.0465	1.326
1	E2	H1.3A	1.558	<.0000	0.2151	<.0000	0.0195	<.0000	0.1321	<.0000	0.0565	1.344
1	E2	H1.2B	3.382	<.0000	0.1017	<.0000	0.0156	<.0000	0.1831	<.0000	0.0143	1.379
1	E2	H1.2A	6.611	<.0000	0.3772	<.0000	0.0153	<.0000	0.1725	<.0000	0.0449	1.493
1	E2	H2.4A	9.205	<.0000	0.091	<.0000	0.0183	<.0000	0.2719	<.0000	<.0000	1.351
1	E2	H2.4B	3.135	<.0000	0.3061	<.0000	0.0539	<.0000	0.1831	<.0000	0.0228	1.356
1	E2	H2.4C	4.288	<.0000	0.2977	<.0000	0.0175	<.0000	0.233	<.0000	0.0872	0.3372
1	E2	H2.4D	18.96	<.0000	0.5446	<.0000	0.0138	<.0000	0.2032	<.0000	0.0664	0.3328
1	E2	K1.1A	17.37	<.0000	2.185	<.0000	0.0154	<.0000	0.2246	<.0000	0.0918	0.4291
2	E2	K1.1A	33.44	0.0893	1.995	<.0000	0.0154	0.1701	0.365	<.0000	<.0000	0.4618
1	E2	K1.1B	17.29	<.0000	2.11	<.0000	0.0158	<.0000	0.2198	<.0000	0.0564	0.3954
1	E2	K1.1C	15.36	<.0000	1.716	<.0000	0.0151	<.0000	0.2008	<.0000	0.0412	0.3084
1	E2	K1.3A	14.12	<.0000	1.537	<.0000	0.0143	<.0000	0.2271	<.0000	0.0749	0.3445
1	E2	K1.3B	12.86	<.0000	1.133	<.0000	0.0132	<.0000	0.1855	<.0000	0.0227	0.3153
1	E2	K1.3C	13.46	<.0000	0.9222	<.0000	0.014	<.0000	0.1843	<.0000	0.0472	0.3077
1	E2	K1.4A	12.83	<.0000	1.16	<.0000	0.0163	<.0000	0.2589	<.0000	0.0234	0.3703
1	E2	K1.4B	13.32	<.0000	1.432	<.0000	0.0152	<.0000	0.1997	<.0000	0.068	0.3507
1	E2	K1.4C	9.059	<.0000	1.176	<.0000	0.0194	<.0000	0.1926	<.0000	0.0519	0.3525
1	E2	K1.4D	9.097	<.0000	1.827	<.0000	0.0173	<.0000	0.1831	<.0000	<.0000	0.3562
2	E2	K1.4D	15.7	0.036	1.678	<.0000	0.0175	0.4189	0.4486	<.0000	0.0045	0.3905
1	E3	G2.7	0.0547	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000	0.0279	<.0000	0.0036
2	E3	G2.7	11.57	0.0178	0.1616	<.0000	0.0014	0.2343	0.4177	0.0096	<.0000	2.064
1	E3	G2.6	0.0508	<.0000	<.0000	<.0000	0.0007	<.0000	<.0000	0.0425	<.0000	0.0058
2	E3	G2.6	6.754	<.0000	0.6217	<.0000	<.0000	0.1107	0.4498	0.0199	<.0000	1.552
1	E3	G2.5	10.81	<.0000	1.25	<.0000	0.01	<.0000	<.0000	0.0835	<.0000	1.543
2	E3	G2.5	22.42	<.0000	1.19	<.0000	0.0055	<.0000	0.3154	0.0413	<.0000	1.531
1	E3	G3.1A	8.254	<.0000	0.2329	<.0000	0.0053	<.0000	<.0000	0.0229	<.0000	1.666
2	E3	G3.1A	16.11	<.0000	0.2202	<.0000	0.0067	<.0000	0.4654	0.0201	0.0143	1.661
1	E3	G3.1B	3.557	<.0000	0.1181	<.0000	0.0046	<.0000	<.0000	<.0000	<.0000	1.807
1	E3	G3.1C	5.92	<.0000	0.3038	<.0000	0.0059	<.0000	<.0000	0.0158	<.0000	1.689
2	E3	G3.1C	10.41	0.0235	0.2851	<.0000	0.0014	<.0000	0.408	0.0056	<.0000	1.678
1	E3	G3.1D	7.888	<.0000	0.3599	<.0000	0.0085	<.0000	<.0000	0.0472	<.0000	1.536
1	E3	G3.3A	8.977	<.0000	0.1203	<.0000	0.0049	<.0000	<.0000	0.0231	<.0000	1.587
1	E3	G3.3B	12.18	<.0000	0.1514	<.0000	0.007	<.0000	<.0000	0.0182	<.0000	1.495
1	E3	G3.3C	3.540	<.0000	0.1523	<.0000	0.0074	<.0000	<.0000	<.0000	<.0000	1.447
1	E3 E2	U3.3D	8.953	< 0000	0.00	<.0000	0.0068	<.0000	< 0000	<.0000	< 0000	1.0/1
1	E3 E2	п1.7 U1 с	2 105	< 0000	0.0300	< 0000	0.0039	< 0000	< 0000	< 0000	< 0000	1.550
1	E3 F2	H1 5C	2.105	< 0000	0.1001	< 0000	0.0003	< 0000	< 0000	<.0000	< 0000	1.455
1	E3	H1 5B	2.055	< 0000	0.0035	< 0000	0.0001	< 0000	< 0000	0.0003	< 0000	1.41
1	F3	H1.54	3.11	<.0000	0.1092	<.0000	0.009	<.0000	<.0000	<.0000	<.0000	1.496
1	F3	H1.4	2,494	<.0000	0.114	<.0000	0.0048	<.0000	<.0000	0.0019	<.0000	1.439
1	F3	H1.3B	2.111	<.0000	0.1798	<.0000	0.0073	<.0000	<.0000	<.0000	<.0000	1.255
1	E3	H1.3A	2.018	<.0000	0.1491	<.0000	0.005	<.0000	<.0000	<.0000	<.0000	1.472
1	E3	H1.2B	1.976	<.0000	0.0604	<.0000	0.0039	<.0000	<.0000	<.0000	<.0000	1.502
1	E3	H1.2A	3.025	<.0000	0.284	<.0000	0.0045	<.0000	<.0000	0.0355	<.0000	1.714
1	E3	H2.4A	6.082	<.0000	0.0497	<.0000	0.006	<.0000	<.0000	0.0018	<.0000	1.503
1	E3	H2.4B	3.199	<.0000	0.1445	<.0000	0.008	<.0000	<.0000	<.0000	<.0000	1.515
1	E3	H2.4C	3.03	<.0000	0.121	<.0000	0.0059	<.0000	<.0000	<.0000	<.0000	0.4064
1	E3	H2.4D	8.325	<.0000	0.2437	<.0000	0.0063	<.0000	<.0000	<.0000	<.0000	0.4312
1	E3	K1.1A	9.66	<.0000	0.5826	<.0000	0.0072	<.0000	<.0000	0.0406	<.0000	0.3283
2	E3	K1.1A	19.01	0.035	0.5561	<.0000	0.0027	0.0544	0.3832	0.0302	<.0000	0.3337
1	E3	K1.1B	9.429	<.0000	0.5188	<.0000	0.0073	<.0000	<.0000	0.0445	<.0000	0.3629
1	E3	K1.1C	8.627	<.0000	1.05	<.0000	0.0103	<.0000	<.0000	0.0199	<.0000	0.3603
1	E3	K1.3A	8.304	<.0000	0.4124	<.0000	0.006	<.0000	<.0000	0.0285	<.0000	0.3516
1	E3	K1.3B	7.493	<.0000	0.631	<.0000	0.0056	<.0000	<.0000	0.0147	<.0000	0.381
1	E3	K1.3C	7.492	<.0000	0.568	<.0000	0.0064	<.0000	<.0000	0.0224	<.0000	0.3968

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Extraction	Sample	Ag	Al	As	Au	В	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe
		MDL:	0.01	0.1	0.005	0.1	0.01	0.01	0.001	0.1	0.005	0.01	0.01	0.01	0.01
	Calcul	ated POL:	0.03	0.3	0.015	0.3	0.03	0.03	0.003	0.3	0.015	0.03	0.03	0.03	0.03
		1/2 MDL:	0.005	0.05	0.0025	0.05	0.005	0.005	0.0005	0.05	0.0025	0.005	0.005	0.005	0.005
1	E3	K1.4A	<.0000	0.0721	2.394	<.0000	0.1165	0.5302	<.0000	132	0.0282	0.1595	0.0299	0.008	0.0602
1	E3	K1.4B	<.0000	0.0804	0.4641	<.0000	0.1335	0.3452	<.0000	193	0.0097	0.1284	0.0678	0.0051	0.0423
1	E3	K1.4C	<.0000	0.0466	0.5477	<.0000	0.1296	0.3232	<.0000	208.3	0.0133	0.1248	0.0405	0.0058	0.0467
1	F3	K1.4D	<.0000	0.0814	0.2932	<.0000	0.1454	0.3164	<.0000	204.6	0.0108	0.1082	0.0428	0.004	0.0515
2	E3	K1.4D	<.0000	0.0307	<.0000	<.0000	0.1375	0.2886	<.0000	193	0.0072	0.0806	<.0000	0.0098	0.0527
1	F4	G2.7	< 0000	102.4	62.7	0.1023	3,494	8,785	<.0000	97.59	1.212	0.3701	<.0000	1.682	665.6
2	E4	G2.7	<.0000	93.69	57.49	<.0000	3.038	7.92	<.0000	86.81	0.9725	0.3471	<.0000	1.499	622.8
1	E4	G2.6	<.0000	63.26	0.7413	0.1816	2.023	4,748	<.0000	1880	0.0215	0.1023	<.0000	0.265	64.01
2	E4	G2.6	<.0000	57.11	0.3165	<.0000	1.819	4.227	<.0000	1666	0.0083	0.1019	0.0056	0.2343	58.4
1	E4	G2.5	<.0000	116.6	0.5521	0.0229	2.02	1.119	<.0000	2124	0.0292	0.1825	0.0428	0.7894	92.09
2	E4	G2.5	0.0079	105.6	0.2895	<.0000	1.746	0.6851	<.0000	1844	0.0168	0.1521	0.1675	0.7213	83.53
1	E4	G3.1A	<.0000	56.38	16.75	0.1266	2.91	8.065	<.0000	85.02	0.3261	0.113	<.0000	0.5944	448.3
2	E4	G3.1A	<.0000	50.61	14.61	<.0000	2.451	7.265	<.0000	71.22	0.2494	0.1301	<.0000	0.5194	400.2
1	E4	G3.1B	<.0000	67.93	4.742	0.1694	2.358	5.842	<.0000	42.15	0.0846	0.13	0.0863	0.2701	270.2
1	E4	G3.1C	<.0000	72	5.652	0.4378	2.409	9.046	<.0000	170	0.1024	0.3074	<.0000	0.5544	278
2	E4	G3.1C	0.0079	63.8	4.874	<.0000	2.077	7.969	<.0000	143.2	0.076	0.2859	0.0199	0.479	249.9
1	E4	G3.1D	<.0000	67.2	2.075	0.1755	2.132	6.753	<.0000	1196	0.0528	0.1384	0.0303	0.7717	206
1	E4	G3.3A	<.0000	82.96	26.78	0.145	2.31	6.321	<.0000	431.8	0.5132	0.2413	<.0000	0.7863	205.6
1	E4	G3.3B	<.0000	263.3	20.77	<.0000	2.947	9.908	<.0000	253.2	0.4057	0.1701	<.0000	0.8562	535.6
2	E4	G3.3B	<.0000	235.1	19.16	<.0000	2.516	8.877	<.0000	216.5	0.3247	0.1463	0.0151	0.7454	486
1	E4	G3.3C	<.0000	98.6	49.18	<.0000	2.881	3.268	<.0000	112.3	0.9433	0.009	0.0621	0.4875	482.5
1	E4	G3.3D	<.0000	251.1	18.14	0.2608	3.241	9.949	<.0000	135.4	0.3458	0.3865	<.0000	1.188	604.1
1	E4	H1.7	<.0000	80.45	33.42	<.0000	2.693	2.663	<.0000	25.72	0.6327	0.0028	<.0000	0.0631	359.1
1	E4	H1.6	<.0000	77.85	46.89	<.0000	2.759	3.314	<.0000	147.2	0.8836	<.0000	<.0000	0.1324	441.5
1	E4	H1.5C	<.0000	293.5	47.81	<.0000	4.335	3.691	<.0000	58.56	0.8981	0.0146	0.1924	0.9316	862.5
1	E4	H1.5B	<.0000	77.56	50.69	<.0000	4.065	2.793	<.0000	57.66	0.9513	<.0000	0.049	0.1162	855.9
1	E4	H1.5A	<.0000	57.18	45.72	<.0000	2.992	4.662	<.0000	117.7	0.9141	<.0000	<.0000	0.1185	507.5
1	E4	H1.4	<.0000	37.78	26.59	<.0000	3.041	3.012	<.0000	87.06	0.5108	0.009	<.0000	0.1246	521.7
1	E4	H1.3B	<.0000	36.68	37.61	0.0473	3.287	2.605	<.0000	116.9	0.7478	<.0000	0.0863	0.1224	591.5
1	E4	H1.3A	<.0000	58.92	55.4	<.0000	1.865	1.22	<.0000	106.8	1.066	<.0000	<.0000	0.1203	673.3
1	E4	H1.2B	<.0000	260.1	46.7	<.0000	3.886	5.484	<.0000	147.9	0.9223	0.3123	<.0000	1.707	778.4
1	E4	H1.2A	<.0000	92.41	7.148	0.3708	2.384	5.384	<.0000	394.2	0.1507	0.2724	<.0000	0.4779	329.6
1	E4	H2.4A	<.0000	239.5	90.97	<.0000	3.974	3.191	<.0000	31.07	1.747	0.0916	<.0000	0.6505	816.7
1	E4	H2.4B	<.0000	89.94	37.9	0.1145	2.561	2.523	<.0000	38.57	0.7155	0.0096	<.0000	0.1423	363.2
1	E4	H2.4C	<.0000	160.1	17.85	0.0229	1.194	5.575	<.0000	43.99	0.3333	0.1718	0.0428	0.7373	371.5
2	E4	H2.4C	<.0000	141.4	16.35	<.0000	0.9805	4.933	<.0000	37.17	0.2726	0.1479	<.0000	0.6556	329.2
1	E4	H2.4D	<.0000	286.1	7.914	0.4257	1.236	7.564	<.0000	119.9	0.1593	0.2639	<.0000	1.346	381.7
1	E4	K1.1A	<.0000	131.6	5.986	0.1755	1.238	7.407	<.0000	542.3	0.1184	0.1905	<.0000	0.9088	318.8
2	E4	K1.1A	<.0000	119.6	5.352	<.0000	1.07	6./	<.0000	463	0.0769	0.1/6/	<.0000	0.8059	290.1
1	E4	K1.1B	<.0000	148.9	8.634	0.15/2	1.31	7.716	<.0000	429.8	0.168	0.2068	<.0000	0.9805	349
1	E4	K1.1C	<.0000	227.3	43.7	0.1633	2.761	5.182	<.0000	357.5	0.8668	0.1895	<.0000	1.632	827.5
1	£4	K1.3A	<.0000	142.8	19.22	0.0412	1./26	7.427	<.0000	338.9	0.35/9	0.2097	<.0000	1.152	551.9
	E4	K1.3B	<.0000	172.4	40.97	0.04/3	2.568	5.618	<.0000	243.9	0.7677	0.1589	<.0000	1.919	804.5
	E4	K1.3L	<.0000	1/3.1	45.64	0.206	2.293	4.867	<.0000	208.0	0.8082	0.13/8	<.0000	1.007	745.4
1	E4	K1.4A	<.0000	109.7	16.11	0.0961	1.185	8.083	<.0000	408.3	0.2967	0.2125	0.0241	0.9338	342.3
	E4	K1.4D	<.0000	94.21	2.425	0.2182	0.849	7.127	<.0000	201.2	0.0403	0.2052	<.0000	0.0222	202.2
2	E4	K1.4C	<.0000	50.04	2.435	0.1388	0.7848	5.385	<.0000	209.5	0.0538	0.1288	<.0000	0.3901	151 1
1	E4 E4		< 0000	62.24	2.049	<.0000 0.0472	0.0747	4.004	< 0000	400.0 561 /	0.0304	0.11/1	0.1403	0.3030	155.2
2	E4 E4	K1 /D	< 0000	57.54	1.433	< 0000	0.7662	3 806	< 0000	476.9	0.035	0.1205	< 0000	0.3621	130.5
	L.4	1.1.40	<.0000	57.54	0.2000	~.0000	0.7147	5.000	~.0000	4/0.0	0.0114	0.1223	~.0000	0.552	132.0

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Extraction	Sample	к	Li	Mg	Mn	Мо	Na	Ni	Р	Pb	Rb	S	Sb	Se
		MDL:	0.1	0.01	0.1	0.01	0.01	0.1	0.01	0.01	0.005	0.1	1	0.01	0.005
	Calcula	ated PQL:	0.3	0.03	0.3	0.03	0.03	0.3	0.03	0.03	0.015	0.3	3	0.03	0.015
		1/2 MDL:	0.05	0.005	0.05	0.005	0.005	0.05	0.005	0.005	0.0025	0.05	0.5	0.005	0.0025
1	E3	ќ1.4А	6.949	0.0067	8.825	26.27	<.0000	857.8	0.156	<.0000	<.0000	<.0000	<.0000	<.0000	<.0000
1	E3	K1.4B	6.073	0.0079	7.129	20.2	<.0000	915.1	0.1385	<.0000	<.0000	<.0000	2.235	<.0000	<.0000
1	E3	K1.4C	4.306	0.0072	4.859	16.86	<.0000	849	0.1346	<.0000	<.0000	<.0000	5.536	<.0000	<.0000
1	E3	K1.4D	4.406	0.0091	6.712	15.16	<.0000	825.8	0.139	<.0000	<.0000	<.0000	12.22	<.0000	<.0000
2	E3	K1.4D	3.861	0.0068	6.489	15.51	0.0549	701.6	0.1302	1670	<.0000	<.0000	12.6	<.0000	<.0000
1	E4	G2.7	23.17	0.0297	19.1	70.36	<.0000	273.3	0.4081	586.9	<.0000	0.1655	<.0000	<.0000	<.0000
2	E4	G2.7	20.65	0.0275	17.75	63.79	0.0201	243.8	0.3756	579	<.0000	0.1318	<.0000	<.0000	<.0000
1	E4	G2.6	5.773	0.0653	137.2	10.39	0.0168	152	0.3341	1182	<.0000	<.0000	153.4	<.0000	<.0000
2	E4	G2.6	5.095	0.0591	125.6	9.335	0.0562	133.7	0.3239	1157	<.0000	<.0000	63.49	<.0000	0.1597
1	E4	G2.5	10.13	0.1526	118.7	15.61	<.0000	243.4	0.6974	1344	<.0000	<.0000	1864	<.0000	<.0000
2	E4	G2.5	8.815	0.1351	104.8	13.83	0.0314	219.2	0.6017	1299	<.0000	<.0000	726.5	<.0000	1.286
1	F4	G3.1A	15.97	0.0234	18.73	31.33	<.0000	137.6	0.2343	306.3	<.0000	0.0993	< 0000	< 0000	<.0000
2	F4	G3.1A	13.96	0.0204	16.24	27.53	0.0404	122.3	0.1784	291.3	<.0000	0.0814	<.0000	< 0000	0.0659
1	E4	G3.1B	9.86	0.0171	9.015	44.17	<.0000	78.56	0.1538	229.6	<.0000	0.0541	<.0000	<.0000	<.0000
1	E4	G3.1C	12.3	0.034	61.53	68.93	<.0000	110.9	0.3367	266.7	<.0000	0.0655	<.0000	<.0000	<.0000
2	E4	G3.1C	10.96	0.0303	55.13	60.75	<.0000	98.55	0.3055	264.1	<.0000	0.0238	<.0000	<.0000	<.0000
1	F4	G3.1D	7.621	0.0368	145	20.52	<.0000	133.6	0.6527	269.9	< 0000	< 0000	128.6	< 0000	<.0000
1	E4	G3.3A	12.57	0.0168	105	21.77	<.0000	183.3	0.7149	288.7	<.0000	<.0000	<.0000	<.0000	<.0000
1	 F4	G3.3B	29.34	0.0969	87.26	27.57	0.003	161.6	0.3472	363.1	<.0000	0.1451	<.0000	<.0000	<.0000
2	F4	G3.3B	26.05	0.0879	80.15	24.36	0.0404	138.7	0 3467	365.7	< 0000	0 1198	< 0000	< 0000	< 0000
1	F4	G3.3C	9.876	0.0185	17.14	5.168	< 0000	133.7	0.0496	370.3	<.0000	0.108	89.57	<.0000	<.0000
1	F4	G3.3D	24 51	0.0941	48 53	88 84	< 0000	189.4	0 3043	558.9	< 0000	0 1769	11 81	< 0000	< 0000
1	F4	H1.7	5,259	0.0035	4,241	1.543	<.0000	137.8	0.083	329.8	<.0000	0.0723	1,213	<.0000	<.0000
1	F4	H1.6	3.544	0.0042	3.616	2.875	<.0000	146	0.0786	382.5	< 0000	0.1269	126.2	< 0000	<.0000
1	E4	H1.5C	8.234	0.0611	52.8	2.497	<.0000	146.3	0.032	604.5	<.0000	0.2533	49.78	<.0000	<.0000
1	F4	H1.5B	4.97	0.0066	2.955	1.52	<.0000	147.5	<.0000	669.7	<.0000	0.2315	134.9	< 0000	<.0000
1	E4	H1.5A	4.567	0.0063	3.732	0.9261	<.0000	194.4	0.0724	510.5	<.0000	0.1067	166.7	<.0000	<.0000
1	E4	H1.4	11.02	0.0211	9.438	1.204	<.0000	138.3	0.0566	411.7	<.0000	0.1087	272.8	<.0000	<.0000
1	E4	H1.3B	8.656	0.0252	7.227	1.179	<.0000	126.6	0.0698	396.2	<.0000	0.1884	456.5	<.0000	<.0000
1	E4	H1.3A	6.001	0.0192	9.349	1.626	<.0000	137.3	0.0356	513	<.0000	0.1434	245.7	<.0000	<.0000
1	E4	H1.2B	11.58	0.0666	26	25.41	<.0000	97.72	0.2783	584.7	<.0000	0.2111	48.44	<.0000	<.0000
1	E4	H1.2A	13.85	0.0452	75.7	80.4	<.0000	86.89	0.5565	258.2	<.0000	0.0177	52.94	<.0000	<.0000
1	E4	H2.4A	8.218	0.0357	44.57	17.83	<.0000	219.3	0.054	645.5	<.0000	0.1178	<.0000	<.0000	<.0000
1	E4	H2.4B	7.798	0.0098	12.71	1.611	<.0000	164.4	0.097	366	<.0000	0.0427	36.27	<.0000	<.0000
1	E4	H2.4C	11	0.0524	37.36	24.05	<.0000	172.9	0.1109	383	<.0000	0.0746	<.0000	<.0000	<.0000
2	E4	H2.4C	10.09	0.0466	33.27	20.57	0.0065	152.5	0.0995	385.1	<.0000	0.0958	1.568	<.0000	0.3005
1	E4	H2.4D	35.74	0.2641	51.78	84.11	<.0000	188	0.3341	479.4	<.0000	0.1542	<.0000	<.0000	<.0000
1	E4	K1.1A	9.952	0.0978	104.5	23.22	<.0000	204.8	0.7578	334.9	<.0000	0.0541	<.0000	<.0000	<.0000
2	E4	K1.1A	9.077	0.0915	93.55	20.23	0.011	182	0.7017	338.3	<.0000	<.0000	<.0000	<.0000	0.5117
1	E4	K1.1B	9.89	0.1109	93.1	22.64	<.0000	243.1	0.7446	375.7	<.0000	0.0404	<.0000	<.0000	<.0000
1	E4	K1.1C	24.06	0.1844	75.1	54.76	<.0000	170.5	0.3765	531.4	<.0000	0.2192	243.5	<.0000	<.0000
1	E4	K1.3A	14.86	0.1058	93.8	30.47	<.0000	176.8	0.5827	356.6	<.0000	0.1223	<.0000	<.0000	<.0000
1	E4	K1.3B	26.8	0.1899	78.17	44.97	<.0000	158.7	0.393	463.9	<.0000	0.2133	48.93	<.0000	<.0000
1	E4	K1.3C	19.29	0.1304	52.53	70.27	<.0000	152.5	0.3184	471.4	<.0000	0.1496	71.72	<.0000	<.0000
1	E4	K1.4A	10.62	0.064	98.69	22.53	<.0000	161.7	0.6563	260.9	<.0000	0.0154	<.0000	<.0000	<.0000
1	E4	K1.4B	7.301	0.0645	102.3	17.03	<.0000	193	0.6965	282.7	<.0000	<.0000	<.0000	<.0000	<.0000
1	E4	K1.4C	5.675	0.0484	91.78	12.79	0.0282	132.9	0.4724	218.1	<.0000	<.0000	<.0000	<.0000	<.0000
2	E4	K1.4C	5.462	0.0435	82.79	11.02	0.0562	115	0.4457	225.6	<.0000	<.0000	<.0000	<.0000	0.2536
1	E4	K1.4D	5.895	0.0545	94.75	11.63	0.0488	132.4	0.4573	219	<.0000	<.0000	83.55	<.0000	<.0000
2	E4	K1.4D	5.453	0.0525	84.82	10.27	0.0314	121.3	0.442	223.7	<.0000	<.0000	45.4	<.0000	0.2538

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Run	Extraction	Sample	Si	Sn	Sr	Th	Ti	TI	U	v	w	Zn
		MDL:	0.01	1	0.01	1	0.01	0.1	10	0.01	0.1	0.01
	Calcul	ated POL:	0.03	3	0.03	3	0.03	0.3	30	0.03	0.3	0.03
		1/2 MDL:	0.005	0.5	0.005	0.5	0.005	0.05	5	0.005	0.05	0.005
1	E3	K1.4A	6.324	<.0000	0.3597	<.0000	0.0071	<.0000	<.0000	0.0345	<.0000	0.3612
1	E3	K1.4B	6.884	<.0000	0.4657	<.0000	0.0065	<.0000	<.0000	0.0286	<.0000	0.3252
1	E3	K1.4C	4.555	<.0000	0.4683	<.0000	0.0062	<.0000	<.0000	0.023	<.0000	0.2979
1	E3	K1.4D	4.608	<.0000	0.592	<.0000	0.007	<.0000	<.0000	0.028	<.0000	0.3317
2	E3	K1.4D	7.986	0.035	0.5658	<.0000	0.004	0.0474	0.3096	0.0285	0.0593	0.3549
1	E4	G2.7	205.2	<.0000	0.6968	<.0000	0.9867	<.0000	<.0000	<.0000	<.0000	3.809
2	E4	G2.7	97.87	<.0000	0.6309	<.0000	0.8985	5.625	<.0000	<.0000	<.0000	3.478
1	E4	G2.6	106.8	<.0000	2.912	<.0000	0.1738	<.0000	<.0000	<.0000	<.0000	2.599
2	E4	G2.6	50.12	0.0786	2.551	<.0000	0.1542	0.0203	<.0000	<.0000	<.0000	2.416
1	E4	G2.5	206.8	<.0000	5.852	<.0000	0.2234	<.0000	<.0000	<.0000	<.0000	2.747
2	E4	G2.5	95.67	<.0000	5.329	0.2931	0.1905	0.5077	0.003	<.0000	<.0000	2.461
1	E4	G3.1A	189.2	<.0000	0.7527	<.0000	1.076	<.0000	<.0000	<.0000	<.0000	3.098
2	E4	G3.1A	86.43	0.0174	0.6682	0.0366	0.9791	2.183	<.0000	<.0000	<.0000	2.763
1	E4	G3.1B	88.43	<.0000	0.4756	<.0000	0.7477	<.0000	<.0000	<.0000	<.0000	2.815
1	E4	G3.1C	112	<.0000	0.7018	<.0000	0.5236	<.0000	<.0000	<.0000	<.0000	3.031
2	E4	G3.1C	51.91	0.0551	0.6183	0.0259	0.4504	1.939	<.0000	<.0000	<.0000	2.695
1	E4	G3.1D	132.1	<.0000	1.334	<.0000	0.2279	<.0000	<.0000	<.0000	<.0000	2.999
1	E4	G3.3A	156.9	<.0000	0.4771	<.0000	0.3825	<.0000	<.0000	<.0000	<.0000	3.104
1	E4	G3.3B	590.4	<.0000	0.808	<.0000	3.656	<.0000	<.0000	<.0000	<.0000	3.108
2	E4	G3.3B	267.3	<.0000	0.7218	0.0366	3.282	3.888	<.0000	<.0000	<.0000	2.73
1	E4	G3.3C	168.9	<.0000	0.3692	<.0000	3.275	<.0000	<.0000	<.0000	<.0000	2.778
1	E4	G3.3D	515.3	<.0000	0.9473	<.0000	3.584	<.0000	<.0000	<.0000	<.0000	4.479
1	E4	H1.7	60.28	<.0000	0.1734	<.0000	1.923	<.0000	<.0000	<.0000	<.0000	2.747
1	E4	H1.6	53.01	<.0000	0.3767	<.0000	1.051	<.0000	<.0000	<.0000	<.0000	2.653
1	E4	H1.5C	496.9	<.0000	0.2087	<.0000	11.98	<.0000	<.0000	<.0000	<.0000	3.04
1	E4	H1.5B	56.15	<.0000	0.1904	<.0000	2.264	<.0000	<.0000	<.0000	<.0000	2.749
1	E4	H1.5A	46.3	<.0000	0.2776	<.0000	2.756	<.0000	<.0000	<.0000	<.0000	2.671
1	E4	H1.4	56.88	<.0000	0.3682	<.0000	1.912	<.0000	<.0000	<.0000	<.0000	2.64
1	E4	H1.3B	49.44	<.0000	0.4579	<.0000	1.073	<.0000	<.0000	<.0000	<.0000	2.691
1	E4	H1.3A	63.13	<.0000	0.4798	<.0000	1.375	<.0000	<.0000	<.0000	<.0000	0.4746
1	E4	H1.2B	167.8	<.0000	0.9161	<.0000	2.269	<.0000	<.0000	<.0000	<.0000	3.365
1	E4	H1.2A	241.8	<.0000	1.432	<.0000	2.6	<.0000	<.0000	<.0000	<.0000	3.603
1	E4	H2.4A	308.7	<.0000	0.2974	<.0000	6.128	<.0000	<.0000	<.0000	<.0000	2.973
1	E4	H2.4B	112.1	<.0000	0.3448	<.0000	3.529	<.0000	<.0000	<.0000	<.0000	2.641
1	E4	H2.4C	320.8	<.0000	0.5687	<.0000	2.642	<.0000	<.0000	<.0000	<.0000	1.376
2	E4	H2.4C	148.2	0.0645	0.5025	0.1221	2.34	1.3	<.0000	<.0000	<.0000	1.173
1	E4	H2.4D	538.3	<.0000	1.316	<.0000	3.928	<.0000	<.0000	<.0000	<.0000	2.327
1	E4	K1.1A	264	<.0000	1.98	<.0000	0.7722	<.0000	<.0000	<.0000	<.0000	2.306
2	E4	K1.1A	120.2	<.0000	1.784	<.0000	0.6775	1.908	<.0000	<.0000	<.0000	2.055
1	E4	K1.1B	298.9	<.0000	2.015	<.0000	0.9051	<.0000	<.0000	<.0000	<.0000	2.196
1	E4	K1.1C	678.9	<.0000	2.44	<.0000	4.446	<.0000	<.0000	<.0000	<.0000	2.133
1	E4	K1.3A	364.4	<.0000	1.63	<.0000	1.863	<.0000	<.0000	<.0000	<.0000	1.982
1	E4	K1.3B	706.2	<.0000	1.584	<.0000	5.345	<.0000	<.0000	<.0000	<.0000	2.076
1	E4	K1.3C	454.3	<.0000	1.65	<.0000	2.671	<.0000	<.0000	<.0000	<.0000	1.872
1	E4	K1.4A	230	<.0000	1.265	<.0000	1.079	<.0000	<.0000	<.0000	<.0000	2.098
1	E4	K1.4B	153.1	<.0000	1.621	<.0000	0.4239	<.0000	<.0000	<.0000	<.0000	1.835
1	E4	K1.4C	119.4	<.0000	1.473	<.0000	0.4239	<.0000	<.0000	<.0000	<.0000	1.779
2	E4	K1.4C	53.69	0.0173	1.3	0.1435	0.3844	1.086	<.0000	<.0000	<.0000	1.515
1	E4	K1.4D	110.7	<.0000	1.588	<.0000	0.3695	<.0000	<.0000	<.0000	<.0000	1.664
2	E4	K1.4D	51.37	0.0456	1.404	0.2611	0.3307	<.0000	<.0000	<.0000	<.0000	1.487

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Appendix 6-2. Sequential Extractions: Analytical Results of the Supernatant - Run 1 and Run 2

Notes:

Results reported in mg/L

ICP-OES used at Soils Testing Lab at Colorado State: Jarrell-Ash Model 975 ICP AtomComp

MDL = method detection limit

- PQL = practical quantitation limit (set to 3x the MDL)
- E1 = 1st extractant: DI-water
- E2 = 2nd extractant: sodium phosphate monobasic (1 M NaH2PO4)
- E3 = 3rd extractant: hydroxylamine HCl (0.2 M NH2OH·HCl)
- E4 = 4th extractant: hydrochloric acid (1 M HCl)
- ET = total extracted: sum of E1, E2, E3, and E4 concentrations

ER = residual / un-extracted fraction, amount of analyte remaining in the sediment

Run	Extraction	Sample	As	AI	Ca	Fe	Mn	S
		MDL:	0.005	0.1	0.1	0.01	0.01	1
		Calculated PQL:	0.015	0.3	0.3	0.03	0.03	3
		1/2 MDL:	0.0025	0.05	0.05	0.005	0.005	0.5
1&2 Avg	E1	G2.7	0.06555	0.14605	10.206	0.4207	0.005	3.323
1&2 Avg	E1	G2.6	0.0378	0.05	345.6	0.005	0.005	361.3
1&2 Avg	E1	G2.5	0.0787	0.05	474.35	0.005	0.005	603.05
1	E1	G3.1A	0.1023	0.05	4.221	0.4538	0.005	1.646
1	E1	G3.1B	0.0294	0.05	7.944	0.005	0.194	9.946
1	E1	G3.1C	0.0702	0.05	7.721	0.1066	0.005	4.521
1	E1	G3.1D	0.0819	0.05	160.1	0.005	0.005	200.7
1	E1	G3.3A	0.2894	0.2983	7.425	0.2574	0.005	2.338
1	E1	G3.3B	0.0702	0.05	191.6	0.005	0.005	172.9
1	E1	G3.3C	0.0994	0.05	543.8	0.005	0.2632	524.3
1	E1	G3.3D	0.0993	1.044	404.3	0.005	8.034	422
1	E1	H1.7	0.1666	2.857	458.3	0.0105	0.3324	428.7
1	E1	H1.6	0.0906	1.247	551.1	0.005	0.7106	510
1	E1	H1.5C	0.1578	5.843	482.5	0.0542	0.9402	454.5
1	E1	H1.5B	0.0788	19.39	269	4.778	1.761	345.5
1	 F1	H1.5A	0.0465	38.68	392.8	7 829	3 202	503.9
1	F1	H1 4	0 1755	41.02	267.2	68 64	7 694	474.3
1	F1	H1 3B	4 355	47.86	270.1	149 5	12 75	570.8
1	E1	L1 2A	0.2547	32.08	306.3	20 55	11.05	490.3
1	E1		0.2047	0.9126	282.1	0.059	10.30	320.6
1	F1	H1 2A	0.1032	0.05	255.3	0.005	0.0256	270.4
1	F1	H2 4A	0.0702	0.05	34 73	0.005	0.0250	35 56
1	E1	H2.4A	0.0965	0.6861	407.6	0.005	0.2694	425.6
1	F1	H2 4C	0.0505	0.05	407.0	0.005	0.2054	429.0
1	F1	H2 4D	0.0014	0.05	379.7	0.005	0.045	461.9
1	F1	K1.1Δ	0.1928	0.05	15 39	0.0667	0.005	12.93
1	F1	K1.1B	0.1228	0.05	19.35	0.0637	0.005	16 59
1	E1	K1.1C	0.0294	0.05	425.3	0.005	0.005	468
1	E1	K1.3A	0.0351	0.05	31.24	0.005	0.005	25.47
1	E1	K1.3B	0.1286	0.05	467.2	0.005	0.005	442.8
1	E1	K1.3C	0.0117	0.05	449.9	0.005	0.005	463.1
1	E1	K1.4A	0.0906	0.05	11.19	0.0951	0.005	5.862
1	E1	K1.4B	0.152	0.05	95.94	0.005	0.005	92.74
1	E1	K1.4C	0.0351	0.05	144	0.005	0.005	132.2
1&2 Avg	E1	K1.4D	0.0025	0.05	148.85	0.005	0.005	160.05
1&2 Avg	E2	G2.7	11.49	3.9275	125.45	10.0615	0.37005	<u>0.5</u>
1&2 Avg	E2	G2.6	0.6511	3.4915	149.05	1.142	0.7496	24.015
1&2 Avg	E2	G2.5	0.70215	5.42	206.7	1.1065	0.7099	68.005
1&2 Avg	E2	G3.1A	6.4175	1.9375	105.75	7.694	0.39065	<u>0.5</u>
1	E2	G3.1B	2.101	4.444	20.97	9.027	1.272	18.33
1&2 Avg	E2	G3.1C	2.4575	4.419	62.22	7.2525	0.42845	0.5
1	E2	G3.1D	1.082	3.761	383.8	3.461	0.5703	13.15
1	E2	G3.3A	7.947	8.237	209.9	4.2	0.3864	0.5
1	E2	G3.3B	9.332	5.289	250.4	4.15	0.4051	25.5
1	E2	G3.3C	20.67	4.076	605.4	8.049	0.2943	502.1
1	E2	G3.3D	7.372	9.284	158.9	7.126	2.981	151.8
1	E2	H1.7	12.65	5.349	132.9	9.141	0.095	108.9
1	E2	H1.6	14.58	5.584	514	7.577	0.2162	438.6

Appendix 6-3. Sequential Extractions: Analytical Results of the Supernatant - Final Dataset Selection

MDL: 0.005 0.1 0.1 Calculated PQL: 0.015 0.3 0.3	0.01	0.01	1
Calculated PQL: 0.015 0.3 0.3	0.03		
		0.03	3
1/2 MDL: 0.0025 0.05 0.05	0.005	0.005	0.5
1 E2 H1.5C 21.3 5.722 169.1	8.966	0.2036	230.3
1 E2 H1.5B 27.64 2.699 198.1	10.63	0.1865	303.2
1 E2 H1.5A 20.66 5.919 417	9.699	0.3616	385
1 E2 H1.4 13.95 3.905 163.8	10.24	0.925	190.1
1 E2 H1.3B 26.34 3.73 230.6	10.83	1.207	241.4
1 E2 H1.3A 30.8 3.776 234.3	11	1.086	274.8
1 E2 H1.2B 14.36 7.133 88.68	8.973	1.943	154.1
1 E2 H1.2A 3.045 5.299 232.6	5.531	2.758	107.7
1 E2 H2.4A 39.17 4.214 92.22	7.562	0.1902	38.36
1 E2 H2.4B 18.33 4.041 275.6	8.705	0.1343	225.2
1 E2 H2.4C 10.84 5.924 285.9	7.976	0.2569	215.8
1 E2 H2.4D 5.336 16.02 228.1	3.832	0.6767	149.4
1&2 Avg E2 K1.1A 3.4045 5.073 343.2	4.266	0.6015	0.5
1 E2 K1.1B 3.885 5.63 303.7	4.941	0.4548	0.5
1 E2 K1.1C 15.49 2.233 385.1	5.776	0.2889	226.7
1 E2 K1.3A 8.192 3.836 234	6.298	0.3748	0.5
1 E2 K1.3B 14.74 2.514 440.5	6.322	0.2643	266.8
1 E2 K1.3C 17.42 1.932 325.1	5.997	0.2484	196
1 E2 K1.4A 6.34 5.321 305.2	5.126	0.4261	0.5
1 E2 K1.4B 0.9505 4.639 417.2	4.113	0.5164	5.971
1 E2 K1.4C 1.177 3.699 340	5.297	0.6769	10.89
1&2 Avg E2 K1.4D 0.7893 3.645 355	4.4035	0.96165	13.39
2 E3 G2.7 9.269 0.2188 30.91	1.413	41.55	0.5
2 E3 G2.6 0.0449 <u>0.05</u> 255.6	0.0522	15.67	5.15
1&2 Avg E3 G2.5 0.17985 <u>0.0817</u> 259.05	0.02395	18.145	124.5
1&2 Avg E3 G3.1A 3.0655 <u>0.08295</u> 24.84	0.6812	22.845	<u>0.5</u>
1 E3 G3.1B 1.125 0.3598 4.366	0.4826	48.83	5.012
1&2 Avg E3 G3.1C 1.216 0.167 20.8	0.19885	107.65	<u>0.5</u>
1 E3 G3.1D 0.4913 <u>0.05</u> 243.6	0.0567	16.44	17.75
1 E3 G3.3A 4.389 0.2915 74.54	0.1913	24.43	<u>0.5</u>
1 E3 G3.3B 4.638 0.2025 74.28	0.1375	17.68	2.68
1 E3 G3.3C 10.48 0.2605 209.1	0.4114	9.242	160.9
1 E3 G3.3D 3.644 0.5036 47.91	0.0661	142.6	37.63
1 E3 H1.7 6.082 0.3207 24.31	0.4984	0.3012	15.73
1 E3 H1.6 7.007 0.3121 183.3	0.511	4.149	134.1
1 E3 H1.5C 8.419 0.3855 73.98	0.8226	0.1358	59.41
1 E3 H1.5B 10.97 0.2051 92.91	0.7887	0.0485	82.07
1 E3 H1.5A 10.56 0.4323 170.2	0.6219	0.0784	139
1 E3 H1.4 5.218 0.2605 105.6	0.7737	0.1683	88.83
1 E3 H1.3B 9.551 0.2547 176.2	0.9144	0.2185	140.5
1 E3 H1.3A 11.55 0.3062 138.1	0.8367	0.2422	117.6
1 E3 H1.2B 4.41 0.4821 18.8	0.8673	28.08	18.92
1 E3 H1.2A 1.113 0.2213 172.1	0.005	230.8	105
1 E3 H2.4A 17.97 0.2248 21.69	0.3896	12.12	4.278
1 E3 H2.4B 9.677 0.3101 82.6	0.3734	1.117	56.82
1 E3 H2.4C 5.021 0.4206 78.14	0.2618	30.96	45.94
1 E3 H2.4D 2.63 0.7106 90.81	0.0302	105.8	52.54

Appendix 6-3. Sequential Extractions: Analytical Results of the Supernatant - Final Dataset Selection

Run	Extraction	Sample	As	Al	Ca	Fe	Mn	S
	-	MDL:	0.005	0.1	0.1	0.01	0.01	1
		Calculated PQL:	0.015	0.3	0.3	0.03	0.03	3
		1/2 MDL:	0.0025	0.05	0.05	0.005	0.005	0.5
1&2 Avg	E3	K1.1A	1.421	0.05	142.8	0.0561	22.33	<u>0.5</u>
1	E3	K1.1B	1.86	0.1108	104.1	0.0654	22.99	<u>0.5</u>
1	E3	K1.1C	7.116	0.05	326.3	0.1106	69.81	229.3
1	E3	K1.3A	3.708	0.05	69.69	0.1221	37.18	<u>0.5</u>
1	E3	K1.3B	6.684	0.05	273.3	0.1317	70.15	186
1	E3	K1.3C	7.666	0.05	208.9	0.0922	81.13	143.6
1	E3	K1.4A	2.394	0.05	132	0.0602	26.27	<u>0.5</u>
1	E3	K1.4B	0.4641	<u>0.05</u>	193	0.0423	20.2	2.235
1	E3	K1.4C	0.5477	<u>0.05</u>	208.3	0.0467	16.86	5.536
1&2 Avg	E3	K1.4D	0.14785	<u>0.05</u>	198.8	0.0521	15.335	12.41
1&2 Avg	E4	G2.7	60.095	98.045	92.2	644.2	67.075	<u>0.5</u>
1&2 Avg	E4	G2.6	0.5289	60.185	1773	61.205	9.8625	108.445
1&2 Avg	E4	G2.5	0.4208	111.1	1984	87.81	14.72	1295.25
1&2 Avg	E4	G3.1A	15.68	53.495	78.12	424.25	29.43	<u>0.5</u>
1	E4	G3.1B	4.742	67.93	42.15	270.2	44.17	<u>0.5</u>
1&2 Avg	E4	G3.1C	5.263	67.9	156.6	263.95	64.84	<u>0.5</u>
1	E4	G3.1D	2.075	67.2	1196	206	20.52	128.6
1	E4	G3.3A	26.78	82.96	431.8	205.6	21.77	<u>0.5</u>
1&2 Avg	E4	G3.3B	19.965	249.2	234.85	510.8	25.965	<u>0.5</u>
1	E4	G3.3C	49.18	98.6	112.3	482.5	5.168	89.57
1	E4	G3.3D	18.14	251.1	135.4	604.1	88.84	11.81
1	E4	H1.7	33.42	80.45	25.72	359.1	1.543	1.213
1	E4	H1.6	46.89	77.85	147.2	441.5	2.875	126.2
1	E4	H1.5C	47.81	293.5	58.56	862.5	2.497	49.78
1	E4	H1.5B	50.69	77.56	57.66	855.9	1.52	134.9
1	E4	H1.5A	45.72	57.18	117.7	507.5	0.9261	166.7
1	E4	H1.4	26.59	37.78	87.06	521.7	1.204	272.8
1	E4	H1.3B	37.61	36.68	116.9	591.5	1.179	456.5
1	E4	H1.3A	55.4	58.92	106.8	673.3	1.626	245.7
1	E4	H1.2B	46.7	260.1	147.9	778.4	25.41	48.44
1	E4	H1.2A	7.148	92.41	394.2	329.6	80.4	52.94
1	E4	H2.4A	90.97	239.5	31.07	816.7	17.83	0.5
1	E4	H2.4B	37.9	89.94	38.57	363.2	1.611	36.27
1&2 Avg	E4	H2.4C	17.1	150.75	40.58	350.35	22.31	1.034
1	E4	H2.4D	7.914	286.1	119.9	381.7	84.11	0.5
1&2 Avg	E4	K1.1A	5.669	125.6	502.65	304.45	21.725	<u>0.5</u>
1	E4	K1.1B	8.634	148.9	429.8	349	22.64	0.5
1	E4	K1.1C	43.7	227.3	357.5	827.5	54.76	243.5
1	E4	K1.3A	19.22	142.8	338.9	551.9	30.47	<u>0.5</u>
1	E4	K1.3B	40.97	227.2	243.9	804.5	44.97	48.93
1	E4	K1.3C	43.64	173.1	208.6	745.4	70.27	71.72
1	E4	K1.4A	16.11	109.7	468.3	342.3	22.53	0.5
1	E4	K1.4B	1.651	94.21	581.5	202.2	17.03	0.5
1&2 Avg	E4	K1.4C	2.242	62.355	518.05	160.55	11.905	0.5
1&2 Avg	E4	K1.4D	1.20665	60.44	519.1	147.55	10.95	64.475

Appendix 6-3. Sequential Extractions: Analytical Results of the Supernatant - Final Dataset Selection

Appendix 6-3. Sequential Extractions: Analytical Results of the Supernatant - Final Dataset Selection

Notes:

Results reported in mg/L

Values = Results less than the PQL

Run 1 and Run 2 results were averaged to arrive at the final result. With the exception of two cases (E3 extraction of G2.7 and G2.6) where there was a magnitude or greater difference between Run 1 and Run 2 results. Run 2 results were selected because Run 1 results for these two samples appeared to be anomolous compared to the results of other samples (e.g., Ca, Fe, and Mn concentrations were below the detection limit, however, the majority of E3 results in other samples were greater than the detection limit and in many case, orders of magnitude greater than the PQL).

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	0.6555	114.9	92.69	600.95	809.1955	1,071	1,881	G2.7	0.06555	11.49	9.269	60.095	80.92
G2.6	0.378	6.511	0.449	5.289	12.627	-4.116	8.51	G2.6	0.0378	0.6511	0.0449	0.5289	1.26
G2.5	0.787	7.0215	1.7985	4.208	13.815	-4.381	9.43	G2.5	0.0787	0.70215	0.17985	0.4208	1.38
G3.1A	1.023	64.175	30.655	156.8	252.653	876	1,128	G3.1A	0.1023	6.4175	3.0655	15.68	25.27
G3.1B	0.294	21.01	11.25	47.42	79.974	725	805	G3.1B	0.0294	2.101	1.125	4.742	8.00
G3.1C	0.702	24.575	12.16	52.63	90.067	440	530	G3.1C	0.0702	2.4575	1.216	5.263	9.01
G3.1D	0.819	10.82	4.913	20.75	37.302	86	123	G3.1D	0.0819	1.082	0.4913	2.075	3.73
G3.3A	2.894	79.47	43.89	267.8	394.054	255	649	G3.3A	0.2894	7.947	4.389	26.78	39.41
G3.3B	0.702	93.32	46.38	199.65	340.052	620	960	G3.3B	0.0702	9.332	4.638	19.965	34.01
G3.3C	0.994	206.7	104.8	491.8	804.294	3,257	4,061	G3.3C	0.0994	20.67	10.48	49.18	80.43
G3.3D	0.993	73.72	36.44	181.4	292.553	824	1,116	G3.3D	0.0993	7.372	3.644	18.14	29.26
H1.7	1.666	126.5	60.82	334.2	523.186	1,652	2,175	H1.7	0.1666	12.65	6.082	33.42	52.32
H1.6	0.906	145.8	70.07	468.9	685.676	2,072	2,758	H1.6	0.0906	14.58	7.007	46.89	68.57
H1.5C	1.578	213	84.19	478.1	776.868	1,179	1,956	H1.5C	0.1578	21.3	8.419	47.81	77.69
H1.5B	0.788	276.4	109.7	506.9	893.788	1,068	1,962	H1.5B	0.0788	27.64	10.97	50.69	89.38
H1.5A	0.465	206.6	105.6	457.2	769.865	1,268	2,038	H1.5A	0.0465	20.66	10.56	45.72	76.99
H1.4	1.755	139.5	52.18	265.9	459.335	564	1,024	H1.4	0.1755	13.95	5.218	26.59	45.93
H1.3B	43.55	263.4	95.51	376.1	778.56	651	1,429	H1.3B	4.355	26.34	9.551	37.61	77.86
H1.3A	2.547	308	115.5	554	980.047	1,083	2,063	H1.3A	0.2547	30.8	11.55	55.4	98.00
H1.2B	1.052	143.6	44.1	467	655.752	339	995	H1.2B	0.1052	14.36	4.41	46.7	65.58
H1.2A	0.702	30.45	11.13	71.48	113.762	553	667	H1.2A	0.0702	3.045	1.113	7.148	11.38
H2.4A	1.169	391.7	179.7	909.7	1482.269	1,684	3,166	H2.4A	0.1169	39.17	17.97	90.97	148.23
H2.4B	0.965	183.3	96.77	379	660.035	1,213	1,873	H2.4B	0.0965	18.33	9.677	37.9	66.00
H2.4C	0.614	108.4	50.21	171	330.224	649	979	H2.4C	0.0614	10.84	5.021	17.1	33.02
H2.4D	0.819	53.36	26.3	79.14	159.619	734	894	H2.4D	0.0819	5.336	2.63	7.914	15.96
K1.1A	1.928	34.045	14.21	56.69	106.873	86	193	K1.1A	0.1928	3.4045	1.421	5.669	10.69
K1.1B	1.228	38.85	18.6	86.34	145.018	186	331	K1.1B	0.1228	3.885	1.86	8.634	14.50
K1.1C	0.294	154.9	71.16	437	663.354	1,068	1,731	K1.1C	0.0294	15.49	7.116	43.7	66.34
K1.3A	0.351	81.92	37.08	192.2	311.551	690	1,002	K1.3A	0.0351	8.192	3.708	19.22	31.16
K1.3B	1.286	147.4	66.84	409.7	625.226	1,196	1,821	K1.3B	0.1286	14.74	6.684	40.97	62.52
K1.3C	0.117	174.2	76.66	436.4	687.377	1,461	2,148	K1.3C	0.0117	17.42	7.666	43.64	68.74
K1.4A	0.906	63.4	23.94	161.1	249.346	226	476	K1.4A	0.0906	6.34	2.394	16.11	24.93
K1.4B	1.52	9.505	4.641	16.51	32.176	7	39	K1.4B	0.152	0.9505	0.4641	1.651	3.22
K1.4C	0.351	11.77	5.477	22.42	40.018	8	48	K1.4C	0.0351	1.177	0.5477	2.242	4.00
K1.4D	0.025	7.893	1.4785	12.0665	21.463	-5.903	15.56	K1.4D	0.0025	0.7893	0.14785	1.20665	2.15

Appendix 6-4a. Arsenic Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

	mstrumenta
Ar	senic (ppm)
MDL:	0.005
Calculated PQL:	0.015
1/2 MDL:	0.0025

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	1.4605	39.275	2.188	980.45	1023.3735	17,814	18,838	G2.7	0.14605	3.9275	0.2188	98.045	102.34
G2.6	0.5	34.915	0.5	601.85	637.765	7,447	8,084	G2.6	<u>0.05</u>	3.4915	0.05	60.185	63.78
G2.5	0.5	54.2	0.817	1111	1166.517	13,854	15,021	G2.5	<u>0.05</u>	5.42	0.0817	111.1	116.65
G3.1A	0.5	19.375	0.8295	534.95	555.6545	10,592	11,148	G3.1A	<u>0.05</u>	1.9375	0.08295	53.495	55.57
G3.1B	0.5	44.44	3.598	679.3	727.838	7,014	7,742	G3.1B	<u>0.05</u>	4.444	0.3598	67.93	72.78
G3.1C	0.5	44.19	1.67	679	725.36	7,505	8,230	G3.1C	<u>0.05</u>	4.419	0.167	67.9	72.54
G3.1D	0.5	37.61	0.5	672	710.61	7,923	8,633	G3.1D	<u>0.05</u>	3.761	<u>0.05</u>	67.2	71.06
G3.3A	2.983	82.37	2.915	829.6	917.868	9,417	10,335	G3.3A	0.2983	8.237	0.2915	82.96	91.79
G3.3B	0.5	52.89	2.025	2492	2547.415	20,050	22,597	G3.3B	<u>0.05</u>	5.289	0.2025	249.2	254.74
G3.3C	0.5	40.76	2.605	986	1029.865	9,475	10,505	G3.3C	<u>0.05</u>	4.076	0.2605	98.6	102.99
G3.3D	10.44	92.84	5.036	2511	2619.316	17,645	20,264	G3.3D	1.044	9.284	0.5036	251.1	261.93
H1.7	28.57	53.49	3.207	804.5	889.767	7,263	8,153	H1.7	2.857	5.349	0.3207	80.45	88.98
H1.6	12.47	55.84	3.121	778.5	849.931	4,695	5,545	H1.6	1.247	5.584	0.3121	77.85	84.99
H1.5C	58.43	57.22	3.855	2935	3054.505	8,414	11,469	H1.5C	5.843	5.722	0.3855	293.5	305.45
H1.5B	193.9	26.99	2.051	775.6	998.541	5,764	6,763	H1.5B	19.39	2.699	0.2051	77.56	99.85
H1.5A	386.8	59.19	4.323	571.8	1022.113	9,267	10,289	H1.5A	38.68	5.919	0.4323	57.18	102.21
H1.4	410.2	39.05	2.605	377.8	829.655	5,321	6,150	H1.4	41.02	3.905	0.2605	37.78	82.97
H1.3B	478.6	37.3	2.547	366.8	885.247	4,852	5,737	H1.3B	47.86	3.73	0.2547	36.68	88.52
H1.3A	339.8	37.76	3.062	589.2	969.822	6,216	7,186	H1.3A	33.98	3.776	0.3062	58.92	96.98
H1.2B	9.126	71.33	4.821	2601	2686.277	3,799	6,485	H1.2B	0.9126	7.133	0.4821	260.1	268.63
H1.2A	0.5	52.99	2.213	924.1	979.803	5,318	6,298	H1.2A	0.05	5.299	0.2213	92.41	97.98
H2.4A	0.5	42.14	2.248	2395	2439.888	16,501	18,941	H2.4A	0.05	4.214	0.2248	239.5	243.99
H2.4B	6.861	40.41	3.101	899.4	949.772	9,219	10,169	H2.4B	0.6861	4.041	0.3101	89.94	94.98
H2.4C	0.5	59.24	4.206	1507.5	1571.446	15,221	16,792	H2.4C	0.05	5.924	0.4206	150.75	157.14
H2.4D	0.5	160.2	7.106	2861	3028.806	22,687	25,716	H2.4D	<u>0.05</u>	16.02	0.7106	286.1	302.88
K1.1A	0.5	50.73	0.5	1256	1307.73	13,512	14,820	K1.1A	<u>0.05</u>	5.073	0.05	125.6	130.77
K1.1B	0.5	56.3	1.108	1489	1546.908	14,236	15,783	K1.1B	<u>0.05</u>	5.63	0.1108	148.9	154.69
K1.1C	0.5	22.33	0.5	2273	2296.33	16,843	19,140	K1.1C	<u>0.05</u>	2.233	0.05	227.3	229.63
K1.3A	0.5	38.36	0.5	1428	1467.36	11,170	12,637	K1.3A	<u>0.05</u>	3.836	<u>0.05</u>	142.8	146.74
K1.3B	0.5	25.14	0.5	2272	2298.14	14,224	16,522	K1.3B	<u>0.05</u>	2.514	0.05	227.2	229.81
K1.3C	0.5	19.32	0.5	1731	1751.32	14,405	16,156	K1.3C	0.05	1.932	0.05	173.1	175.13
K1.4A	0.5	53.21	0.5	1097	1151.21	9,207	10,358	K1.4A	0.05	5.321	0.05	109.7	115.12
K1.4B	0.5	46.39	0.5	942.1	989.49	9,653	10,643	K1.4B	0.05	4.639	0.05	94.21	98.95
K1.4C	0.5	36.99	0.5	623.55	661.54	5,855	6,516	K1.4C	0.05	3.699	0.05	62.355	66.15
K1.4D	0.5	36.45	0.5	604.4	641.85	7,333	7,975	K1.4D	<u>0.05</u>	3.645	<u>0.05</u>	60.44	64.19

Appendix 6-4b. Aluminum Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

	in our annented							
Alum	Aluminum (ppm)							
MDL:	0.1							
Calculated PQL:	0.3							
1/2 MDL:	0.05							

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	102.06	1254.5	309.1	922	2587.66	369	2,956	G2.7	10.206	125.45	30.91	92.2	258.77
G2.6	3456	1490.5	2556	17730	25232.5	17,128	42,360	G2.6	345.6	149.05	255.6	1773	2523.25
G2.5	4743.5	2067	2590.5	19840	29241	17,039	46,280	G2.5	474.35	206.7	259.05	1984	2924.10
G3.1A	42.21	1057.5	248.4	781.2	2129.31	575	2,704	G3.1A	4.221	105.75	24.84	78.12	212.93
G3.1B	79.44	209.7	43.66	421.5	754.3	-61	694	G3.1B	7.944	20.97	4.366	42.15	75.43
G3.1C	77.21	622.2	208	1566	2473.41	711	3,184	G3.1C	7.721	62.22	20.8	156.6	247.34
G3.1D	1601	3838	2436	11960	19835	6,882	26,717	G3.1D	160.1	383.8	243.6	1196	1983.50
G3.3A	74.25	2099	745.4	4318	7236.65	2,381	9,618	G3.3A	7.425	209.9	74.54	431.8	723.67
G3.3B	1916	2504	742.8	2348.5	7511.3	3,743	11,254	G3.3B	191.6	250.4	74.28	234.85	751.13
G3.3C	5438	6054	2091	1123	14706	-495	14,211	G3.3C	543.8	605.4	209.1	112.3	1470.60
G3.3D	4043	1589	479.1	1354	7465.1	2,070	9,535	G3.3D	404.3	158.9	47.91	135.4	746.51
H1.7	4583	1329	243.1	257.2	6412.3	103	6,515	H1.7	458.3	132.9	24.31	25.72	641.23
H1.6	5511	5140	1833	1472	13956	3,237	17,193	H1.6	551.1	514	183.3	147.2	1395.60
H1.5C	4825	1691	739.8	585.6	7841.4	39	7,881	H1.5C	482.5	169.1	73.98	58.56	784.14
H1.5B	2690	1981	929.1	576.6	6176.7	525	6,702	H1.5B	269	198.1	92.91	57.66	617.67
H1.5A	3928	4170	1702	1177	10977	3,895	14,872	H1.5A	392.8	417	170.2	117.7	1097.70
H1.4	2672	1638	1056	870.6	6236.6	1,494	7,731	H1.4	267.2	163.8	105.6	87.06	623.66
H1.3B	2701	2306	1762	1169	7938	581	8,519	H1.3B	270.1	230.6	176.2	116.9	793.80
H1.3A	3063	2343	1381	1068	7855	917	8,772	H1.3A	306.3	234.3	138.1	106.8	785.50
H1.2B	2821	886.8	188	1479	5374.8	9,204	14,579	H1.2B	282.1	88.68	18.8	147.9	537.48
H1.2A	2553	2326	1721	3942	10542	4,293	14,835	H1.2A	255.3	232.6	172.1	394.2	1054.20
H2.4A	347.3	922.2	216.9	310.7	1797.1	906	2,703	H2.4A	34.73	92.22	21.69	31.07	179.71
H2.4B	4076	2756	826	385.7	8043.7	3,654	11,698	H2.4B	407.6	275.6	82.6	38.57	804.37
H2.4C	4415	2859	781.4	405.8	8461.2	10,273	18,734	H2.4C	441.5	285.9	78.14	40.58	846.12
H2.4D	3797	2281	908.1	1199	8185.1	7,684	15,869	H2.4D	379.7	228.1	90.81	119.9	818.51
K1.1A	153.9	3432	1428	5026.5	10040.4	4,760	14,800	K1.1A	15.39	343.2	142.8	502.65	1004.04
K1.1B	193.8	3037	1041	4298	8569.8	3,849	12,419	K1.1B	19.38	303.7	104.1	429.8	856.98
K1.1C	4253	3851	3263	3575	14942	7,121	22,063	K1.1C	425.3	385.1	326.3	357.5	1494.20
K1.3A	312.4	2340	696.9	3389	6738.3	174	6,912	K1.3A	31.24	234	69.69	338.9	673.83
K1.3B	4672	4405	2733	2439	14249	5,695	19,944	K1.3B	467.2	440.5	273.3	243.9	1424.90
K1.3C	4499	3251	2089	2086	11925	3,585	15,510	K1.3C	449.9	325.1	208.9	208.6	1192.50
K1.4A	111.9	3052	1320	4683	9166.9	1,367	10,534	K1.4A	11.19	305.2	132	468.3	916.69
K1.4B	959.4	4172	1930	5815	12876.4	3,307	16,183	K1.4B	95.94	417.2	193	581.5	1287.64
K1.4C	1440	3400	2083	5180.5	12103.5	3,292	15,395	K1.4C	144	340	208.3	518.05	1210.35
K1.4D	1488.5	3550	1988	5191	12217.5	5,576	17,793	K1.4D	148.85	355	198.8	519.1	1221.75

Appendix 6-4c. Calcium Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

	motramenta							
Calcium (ppm)								
MDL:	0.1							
Calculated PQL:	0.3							
1/2 MDL:	0.05							

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	4.207	100.615	14.13	14.13	133.082	103,439	103,572	G2.7	0.4207	10.0615	1.413	1.413	13
G2.6	0.05	11.42	0.522	612.05	624.042	17,890	18,514	G2.6	0.005	1.142	0.0522	61.205	62
G2.5	0.05	11.065	0.2395	878.1	889.4545	23,384	24,274	G2.5	0.005	1.1065	0.02395	87.81	89
G3.1A	4.538	76.94	6.812	4242.5	4330.79	98,788	103,119	G3.1A	0.4538	7.694	0.6812	424.25	433
G3.1B	0.05	90.27	4.826	2702	2797.146	108,017	110,814	G3.1B	0.005	9.027	0.4826	270.2	280
G3.1C	1.066	72.525	1.9885	2639.5	2715.0795	81,421	84,136	G3.1C	0.1066	7.2525	0.19885	263.95	272
G3.1D	0.05	34.61	0.567	2060	2095.227	36,580	38,675	G3.1D	0.005	3.461	0.0567	206	210
G3.3A	2.574	42	1.913	2056	2102.487	34,026	36,129	G3.3A	0.2574	4.2	0.1913	205.6	210
G3.3B	0.05	41.5	1.375	5108	5150.925	80,524	85,675	G3.3B	<u>0.005</u>	4.15	0.1375	510.8	515
G3.3C	0.05	80.49	4.114	4825	4909.654	110,755	115,664	G3.3C	<u>0.005</u>	8.049	0.4114	482.5	491
G3.3D	0.05	71.26	0.661	6041	6112.971	104,524	110,637	G3.3D	0.005	7.126	0.0661	604.1	611
H1.7	0.105	91.41	4.984	3591	3687.499	88,509	92,197	H1.7	0.0105	9.141	0.4984	359.1	369
H1.6	0.05	75.77	5.11	4415	4495.93	95,292	99,788	H1.6	0.005	7.577	0.511	441.5	450
H1.5C	0.542	89.66	8.226	8625	8723.428	70,304	79,028	H1.5C	0.0542	8.966	0.8226	862.5	872
H1.5B	47.78	106.3	7.887	8559	8720.967	91,419	100,140	H1.5B	4.778	10.63	0.7887	855.9	872
H1.5A	78.29	96.99	6.219	5075	5256.499	91,555	96,812	H1.5A	7.829	9.699	0.6219	507.5	526
H1.4	686.4	102.4	7.737	5217	6013.537	96,646	102,659	H1.4	68.64	10.24	0.7737	521.7	601
H1.3B	1495	108.3	9.144	5915	7527.444	96,930	104,457	H1.3B	149.5	10.83	0.9144	591.5	753
H1.3A	395.5	110	8.367	6733	7246.867	90,956	98,203	H1.3A	39.55	11	0.8367	673.3	725
H1.2B	0.59	89.73	8.673	7784	7882.993	62,816	70,699	H1.2B	0.059	8.973	0.8673	778.4	788
H1.2A	0.05	55.31	0.05	3296	3351.41	69,044	72,395	H1.2A	0.005	5.531	0.005	329.6	335
H2.4A	0.05	75.62	3.896	8167	8246.566	99,767	108,013	H2.4A	0.005	7.562	0.3896	816.7	825
H2.4B	0.05	87.05	3.734	3632	3722.834	108,490	112,213	H2.4B	0.005	8.705	0.3734	363.2	372
H2.4C	0.05	79.76	2.618	3503.5	3585.928	97,928	101,514	H2.4C	0.005	7.976	0.2618	350.35	359
H2.4D	0.05	38.32	0.302	3817	3855.672	111,704	115,559	H2.4D	0.005	3.832	0.0302	381.7	386
K1.1A	0.667	42.66	0.561	3044.5	3088.388	32,780	35,869	K1.1A	0.0667	4.266	0.0561	304.45	309
K1.1B	0.637	49.41	0.654	3490	3540.701	38,077	41,618	K1.1B	0.0637	4.941	0.0654	349	354
K1.1C	0.05	57.76	1.106	8275	8333.916	85,401	93,735	K1.1C	0.005	5.776	0.1106	827.5	833
K1.3A	0.05	62.98	1.221	5519	5583.251	61,728	67,311	K1.3A	<u>0.005</u>	6.298	0.1221	551.9	558
K1.3B	0.05	63.22	1.317	8045	8109.587	80,954	89,064	K1.3B	0.005	6.322	0.1317	804.5	811
K1.3C	0.05	59.97	0.922	7454	7514.942	92,530	100,045	K1.3C	0.005	5.997	0.0922	745.4	751
K1.4A	0.951	51.26	0.602	3423	3475.813	34,032	37,508	K1.4A	0.0951	5.126	0.0602	342.3	348
K1.4B	0.05	41.13	0.423	2022	2063.603	20,886	22,949	K1.4B	0.005	4.113	0.0423	202.2	206
K1.4C	0.05	52.97	0.467	1605.5	1658.987	18,202	19,861	K1.4C	0.005	5.297	0.0467	160.55	166
K1.4D	0.05	44.035	0.521	1475.5	1520.106	16,944	18,464	K1.4D	0.005	4.4035	0.0521	147.55	152

Appendix 6-4d. Iron Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

	instrumenta
	Iron (ppm)
MDL:	0.01
Calculated PQL:	0.03
1/2 MDL:	0.005

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	0.05	3.7005	415.5	670.75	1090.0005	775	1,865	G2.7	0.005	0.37005	41.55	67.075	109.00
G2.6	0.05	7.496	156.7	98.625	262.871	153	416	G2.6	0.005	0.7496	15.67	9.8625	26.29
G2.5	0.05	7.099	181.45	147.2	335.799	129	465	G2.5	0.005	0.7099	18.145	14.72	33.58
G3.1A	0.05	3.9065	228.45	294.3	526.7065	596	1,122	G3.1A	0.005	0.39065	22.845	29.43	52.67
G3.1B	1.94	12.72	488.3	441.7	944.66	266	1,211	G3.1B	0.194	1.272	48.83	44.17	94.47
G3.1C	0.05	4.2845	1076.5	648.4	1729.2345	294	2,023	G3.1C	<u>0.005</u>	0.42845	107.65	64.84	172.92
G3.1D	0.05	5.703	164.4	205.2	375.353	285	660	G3.1D	0.005	0.5703	16.44	20.52	37.54
G3.3A	0.05	3.864	244.3	217.7	465.914	183	649	G3.3A	<u>0.005</u>	0.3864	24.43	21.77	46.59
G3.3B	0.05	4.051	176.8	259.65	440.551	871	1,312	G3.3B	<u>0.005</u>	0.4051	17.68	25.965	44.06
G3.3C	2.632	2.943	92.42	51.68	149.675	320	470	G3.3C	0.2632	0.2943	9.242	5.168	14.97
G3.3D	80.34	29.81	1426	888.4	2424.55	1,472	3,897	G3.3D	8.034	2.981	142.6	88.84	242.46
H1.7	3.324	0.95	3.012	15.43	22.716	475	498	H1.7	0.3324	0.095	0.3012	1.543	2.27
H1.6	7.106	2.162	41.49	28.75	79.508	358	437	H1.6	0.7106	0.2162	4.149	2.875	7.95
H1.5C	9.402	2.036	1.358	24.97	37.766	248	286	H1.5C	0.9402	0.2036	0.1358	2.497	3.78
H1.5B	17.61	1.865	0.485	15.2	35.16	356	391	H1.5B	1.761	0.1865	0.0485	1.52	3.52
H1.5A	32.02	3.616	0.784	9.261	45.681	386	432	H1.5A	3.202	0.3616	0.0784	0.9261	4.57
H1.4	76.94	9.25	1.683	12.04	99.913	760	860	H1.4	7.694	0.925	0.1683	1.204	9.99
H1.3B	127.5	12.07	2.185	11.79	153.545	620	774	H1.3B	12.75	1.207	0.2185	1.179	15.35
H1.3A	110.5	10.86	2.422	16.26	140.042	589	729	H1.3A	11.05	1.086	0.2422	1.626	14.00
H1.2B	103.9	19.43	280.8	254.1	658.23	1,685	2,343	H1.2B	10.39	1.943	28.08	25.41	65.82
H1.2A	0.256	27.58	2308	804	3139.836	1,207	4,347	H1.2A	0.0256	2.758	230.8	80.4	313.98
H2.4A	0.05	1.902	121.2	178.3	301.452	501	802	H2.4A	<u>0.005</u>	0.1902	12.12	17.83	30.15
H2.4B	2.694	1.343	11.17	16.11	31.317	624	655	H2.4B	0.2694	0.1343	1.117	1.611	3.13
H2.4C	0.49	2.569	309.6	223.1	535.759	3,533	4,069	H2.4C	0.049	0.2569	30.96	22.31	53.58
H2.4D	0.05	6.767	1058	841.1	1905.917	1,006	2,912	H2.4D	0.005	0.6767	105.8	84.11	190.59
K1.1A	0.05	6.015	223.3	217.25	446.615	267	713	K1.1A	0.005	0.6015	22.33	21.725	44.66
K1.1B	0.05	4.548	229.9	226.4	460.898	386	847	K1.1B	0.005	0.4548	22.99	22.64	46.09
K1.1C	0.05	2.889	698.1	547.6	1248.639	450	1,699	K1.1C	0.005	0.2889	69.81	54.76	124.86
K1.3A	0.05	3.748	371.8	304.7	680.298	823	1,504	K1.3A	<u>0.005</u>	0.3748	37.18	30.47	68.03
K1.3B	0.05	2.643	701.5	449.7	1153.893	664	1,818	K1.3B	0.005	0.2643	70.15	44.97	115.39
K1.3C	0.05	2.484	811.3	702.7	1516.534	506	2,023	K1.3C	<u>0.005</u>	0.2484	81.13	70.27	151.65
K1.4A	0.05	4.261	262.7	225.3	492.311	316	809	K1.4A	<u>0.005</u>	0.4261	26.27	22.53	49.23
K1.4B	0.05	5.164	202	170.3	377.514	146	523	K1.4B	0.005	0.5164	20.2	17.03	37.75
K1.4C	0.05	6.769	168.6	119.05	294.469	148	443	K1.4C	0.005	0.6769	16.86	11.905	29.45
K1.4D	0.05	9.6165	153.35	109.5	272.5165	122	395	K1.4D	0.005	0.96165	15.335	10.95	27.25

Appendix 6-4e. Manganese Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

	motramenta								
Manganese (ppm)									
MDL:	0.01								
Calculated PQL:	0.03								
1/2 MDL:	0.005								
1/2 MDL:	0.005								

Solid (mg/kg)	E1	E2	E3	E4	ET	Residual	Unextracted Sedim.	Supernatant (mg/L)	E1	E2	E3	E4	ET
G2.7	33.23	5	5	5	48.23	1,293	1,341	G2.7	3.323	<u>0.5</u>	0.5	0.5	4.82
G2.6	3613	240.15	51.5	1084.45	4989.1	-169	4,820	G2.6	361.3	24.015	5.15	108.445	498.91
G2.5	6030.5	680.05	1245	12952.5	20908.05	-5,010	15,898	G2.5	603.05	68.005	124.5	1295.25	2090.81
G3.1A	16.46	5	5	5	31.46	2,081	2,112	G3.1A	1.646	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	3.15
G3.1B	99.46	183.3	50.12	5	337.88	3,477	3,815	G3.1B	9.946	18.33	5.012	0.5	33.79
G3.1C	45.21	5	5	5	60.21	558	619	G3.1C	4.521	<u>0.5</u>	0.5	0.5	6.02
G3.1D	2007	131.5	177.5	1286	3602	-535	3,067	G3.1D	200.7	13.15	17.75	128.6	360.20
G3.3A	23.38	5	5	5	38.38	848	886	G3.3A	2.338	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	3.84
G3.3B	1729	255	26.8	5	2015.8	3,020	5,036	G3.3B	172.9	25.5	2.68	<u>0.5</u>	201.58
G3.3C	5243	5021	1609	895.7	12768.7	7,268	20,036	G3.3C	524.3	502.1	160.9	89.57	1276.87
G3.3D	4220	1518	376.3	118.1	6232.4	3,176	9,409	G3.3D	422	151.8	37.63	11.81	623.24
H1.7	4287	1089	157.3	12.13	5545.43	5,798	11,343	H1.7	428.7	108.9	15.73	1.213	554.54
H1.6	5100	4386	1341	1262	12089	5,852	17,941	H1.6	510	438.6	134.1	126.2	1208.90
H1.5C	4545	2303	594.1	497.8	7939.9	2,627	10,567	H1.5C	454.5	230.3	59.41	49.78	793.99
H1.5B	3455	3032	820.7	1349	8656.7	7,972	16,628	H1.5B	345.5	303.2	82.07	134.9	865.67
H1.5A	5039	3850	1390	1667	11946	11,782	23,728	H1.5A	503.9	385	139	166.7	1194.60
H1.4	4743	1901	888.3	2728	10260.3	15,029	25,290	H1.4	474.3	190.1	88.83	272.8	1026.03
H1.3B	5708	2414	1405	4565	14092	11,558	25,650	H1.3B	570.8	241.4	140.5	456.5	1409.20
H1.3A	4903	2748	1176	2457	11284	8,379	19,663	H1.3A	490.3	274.8	117.6	245.7	1128.40
H1.2B	3206	1541	189.2	484.4	5420.6	9,651	15,072	H1.2B	320.6	154.1	18.92	48.44	542.06
H1.2A	2704	1077	1050	529.4	5360.4	7,447	12,808	H1.2A	270.4	107.7	105	52.94	536.04
H2.4A	355.6	383.6	42.78	5	786.98	5,829	6,616	H2.4A	35.56	38.36	4.278	0.5	78.70
H2.4B	4256	2252	568.2	362.7	7438.9	12,486	19,925	H2.4B	425.6	225.2	56.82	36.27	743.89
H2.4C	4594	2158	459.4	10.34	7221.74	7,351	14,573	H2.4C	459.4	215.8	45.94	1.034	722.17
H2.4D	4619	1494	525.4	5	6643.4	4,751	11,394	H2.4D	461.9	149.4	52.54	0.5	664.34
K1.1A	129.3	5	5	5	144.3	1,648	1,792	K1.1A	12.93	0.5	0.5	0.5	14.43
K1.1B	165.9	5	5	5	180.9	2,339	2,520	K1.1B	16.59	0.5	0.5	0.5	18.09
K1.1C	4680	2267	2293	2435	11675	1,339	13,014	K1.1C	468	226.7	229.3	243.5	1167.50
K1.3A	254.7	5	5	5	269.7	1,895	2,165	K1.3A	25.47	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	26.97
K1.3B	4428	2668	1860	489.3	9445.3	2,625	12,071	K1.3B	442.8	266.8	186	48.93	944.53
K1.3C	4631	1960	1436	717.2	8744.2	1,326	10,070	K1.3C	463.1	196	143.6	71.72	874.42
K1.4A	58.62	5	5	5	73.62	1,441	1,515	K1.4A	5.862	<u>0.5</u>	0.5	0.5	7.36
K1.4B	927.4	59.71	22.35	5	1014.46	657	1,672	K1.4B	92.74	5.971	2.235	0.5	101.45
K1.4C	1322	108.9	55.36	5	1491.26	604	2,095	K1.4C	132.2	10.89	5.536	0.5	149.13
K1.4D	1600.5	133.9	124.1	644.75	2503.25	653	3,156	K1.4D	160.05	13.39	12.41	64.475	250.33

Appendix 6-4f. Sulfur Extraction Concentrations in the Solid and Supernatant

Italicized Values = Lab-reported results that were less than the MDL (originally reported as <.0000) was converted to 1/2 the MDL

Values = Results less than the PQL

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Sulfur (ppm)								
MDL:	1							
Calculated PQL:	3							
1/2 MDL:	0.5							