

THE EFFECTS OF SIMULATED DREDGING AND  
FLOODING ON TRACE-ELEMENT RICH  
SEDIMENTS IN LAKE COEUR D'ALENE AND  
THE COEUR D'ALENE RIVER, IDAHO.

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THESIS

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## ABSTRACT

Lake Coeur d' Alene (Lake CDA) and both Main Stem (MSCDR) and South Fork of the Coeur d' Alene River (SFCDR) are contaminated with heavy metals from numerous years of mining. Possible environmental management plans in the region may include dredging and bank stability projects. Two different studies were initiated to look at potential contaminant release from proposed dredging of Lake CDA and from natural flooding events in the MSCDR and SFCDR.

In the first study, an ex-situ experiment was conducted to determine how dredging releases heavy metals from contaminated lake sediments. The procedure used is as follows: 1) pore water total metal concentration, 2) total metal abundance in the organic, amorphous, crystalline and sulfidic fractions of the solid phase, 3) simulated dredging while measuring pH, Eh, and contaminant release over time, and 4) comparison of experimental data with results predicted from the MINTEQA2 speciation program. To simulate dredging operations, cores taken by gravity drilling were placed into a reaction vessel and mixed while being oxygenated for 800 hours. During the 800 h, solution As and Pb concentrations were found to be higher (0.0838 and 0.57 ppm, respectively) than the maximum contaminant levels allowed for drinking water and therefore would be detrimental to water quality within the lake. Zinc contaminant levels are of concern because they remain consistently high throughout the dredging simulation (8.3 ppm). The sediments remaining from the two dredging trials were also analyzed by selective dissolution analysis; partitioning of contaminants after dredging shifted from the organic fraction to the amorphous and crystalline metal-oxide fraction. The results suggest that management efforts that include dredging could have short-term impact on water quality in the Coeur d' Alene Basin.

An environmental remediation plan is necessary to control the release of heavy metals as flooding occurs in this region. In order to address the environmental ramifications of flooding, water quality in the river system was assessed, contaminates in the riverbank sediments were geochemically phase partitioned, and their release were measured under simulated laboratory flooding experiments. To simulate flooding experiments, 18 columns were constructed allowing the sediment-water interface to be monitored for pH, Eh and

dissolved concentrations of As, Fe, Mn, Pb, and Zn. These columns were subjected to two flooding events. The first event involved the addition of  $N_{2(g)}$  and  $O_{2(g)}$  purged river water to the columns and the second event also had a nutrient source (D-glucose) added to the solution in the columns. During the first event Zn was released at an average concentration of 10.41 mg/L into solution from sediment taken along the MSCDR at Cataldo, ID. For the second event, nutrient loading stimulated microbial activity which in turn increased contaminant levels drastically at all three sites; mean values of trace element contaminants from the three sites are As = 1.54, Pb = 7.57, and Zn = 79.29 mg/L. The release of contaminants due to flooding is degrading water quality in the river system and proving to be extremely detrimental to the aquatic biota. Results indicate that sediments currently situated in the riverbanks are releasing contaminants into the river system as flooding occurs and a remediation plan is necessary to eliminate this problem. In particular, extreme precaution must be used in the region to limit nutrient additions into the river system.

## ACKNOWLEDGMENTS

Yiew, this is the last thing I hope to write. I never thought I would see the day where I would write my acknowledgments. Finally, I can speak with non-scientific words.

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“Lately it occurs to me,

**WHAT A LONG STRANGE TRIP ITS BEEN.....”**

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## 1.1 INTRODUCTION

### 1.1.1 Purpose/Problem Statement

Lake Coeur d' Alene (Lake CDA), the Main Stem (MSCDR), and South Fork of the Coeur d'Alene River (SFCDR) are contaminated with heavy metals from numerous years of mining. Two different studies were initiated to look at potential contaminant release from proposed dredging of Lake CDA and from natural flooding events in the MSCDR and SFCDR. For the latter study, three sampling sites were chosen: (i) MSCDR near the inlet to Lake CDA, (ii) MSCDR at Cataldo, and (iii) SFCDR at Smeltonville. These sites were chosen based on previous research in the area. The contaminants were chosen based on the following criteria:

1. They are constituents of the rocks found in the district, i.e. galena (PbS) sphalerite (ZnS), siderite (FeCO<sub>3</sub>), arsenopyrite (FeAsS).
2. Iron and manganese oxides have high surface areas and act as principle sorbents of contaminants.
3. These contaminants have been studied in previous experiments in the region.
4. Their concentration and distribution in the area is well documented by previous researchers.

### 1.1.2 Purpose/Objectives

Study I: The Release of As, Fe, Pb, Mn, and Zn Upon Oxygenation of Contaminated Sediments from Lake CDA.

The purpose of the first study was to: analyze the release of arsenic (As), iron (Fe), lead (Pb), manganese (Mn), and zinc (Zn) upon oxygenation of contaminated sediments from Lake CDA.

The specific objectives of the first study were to:

1. Simulate dredging of sediments and analyze contaminant release over time.
2. Characterize the pre- and post-dredged core sediment using selective dissolution analysis (SDA).
3. Analyze the pore water from the core for its metal content.
4. Use x-ray diffraction (XRD) to characterize the sediment.
5. Use Minteqa2 speciation program to predict  $\text{Fe}^{+3}/\text{Fe}^{+2}$ ,  $\text{AsO}_3^{-3}/\text{AsO}_4^{-3}$  ratios and saturation indices.

Study II: Mobility of Trace Element Contaminants Upon Flooding of Sediments in the Coeur d'Alene River System, Idaho.

The purpose of the second study was to: quantify As, Fe, Mn, Pb, and Zn, as they are released from the MSCDR and SFCDR bank sediments under simulated extreme and minor flooding events and measuring the release of contaminants when a supplemental nutrient source (i.e., septic tanks and sewage) leaches into the Coeur d'Alene River system.

The specific objectives of the second study were to:

1. Analyze contaminant release from bank sediments under simulated extreme and minor flooding events.
2. Characterize the bank sediments using selective dissolution procedures.
3. Use scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and XRD to analyze the sediment.
4. Assess water quality in the river system over the last 25 years.

## 1.2 DESCRIPTION OF THE STUDY AREA

### 1.2.1 Location

Lake CDA is situated due west of the Bunkerhill Superfund Site (Figure 1.1) in the northern panhandle of Idaho approximately 10 km east of the WA/ID border. Lake CDA is dimictic. The lake undergoes two periods of thermal stratification and a fall and spring overturn (Wyman, 1994). The lake is roughly 64 m deep and covers approximately 130 km<sup>2</sup> with  $9.6 \times 10^{12}$  m<sup>3</sup> of water (Wyman, 1994). The surface elevation is 652 m above sea level with a maximum fluctuation of 1.84 m annually (Minter, 1970). Tributaries include the Spokane River to the north, the CDA River to the east, and the St. Joe River to the south.

The SFCDR is entirely in Shoshone, County, Idaho and has a drainage of 699 km<sup>2</sup>, whereas the MSCDR has a drainage area of about 414 km<sup>2</sup> (Mink, 1971). The SFCDR flows from its headwaters in the Bitterroot Mountains to where it meets the North Fork of the Coeur d'Alene River 4.8 km above Cataldo at Enaville and then continues as the MSCDR for 48.2 km reaching Lake CDA (Bender, 1991). The South Fork is a relatively shallow and swift-moving stream with a gradient of about 14.7 m per km, whereas the MSCDR is relatively deep and slow moving (Norbeck, 1974). The MSCDR flows through a valley which averages 1.2 km to 1.65 km wide (Mink, 1971). The area of the entire basin that both rivers flow through is roughly 3,574 km<sup>2</sup>.

Mine tailings from previous milling operations have formed a veneer of silt over large valley areas (Mink, 1971). Along the SFCDR, deposits of jig tailings from early operations are exposed along the river banks and in places reach a thickness of 3.04 m (Norton, 1980). Approximately 65,317 kg of mine wastes were released to the SFCDR from 1884 to the 1960's (Bennett, 1994). Large quantities of tailings in the valley have covered the natural river alluvium over large areas and have created unstable channel conditions over much of the SFCDR and its tributaries (Ioannou, 1979).

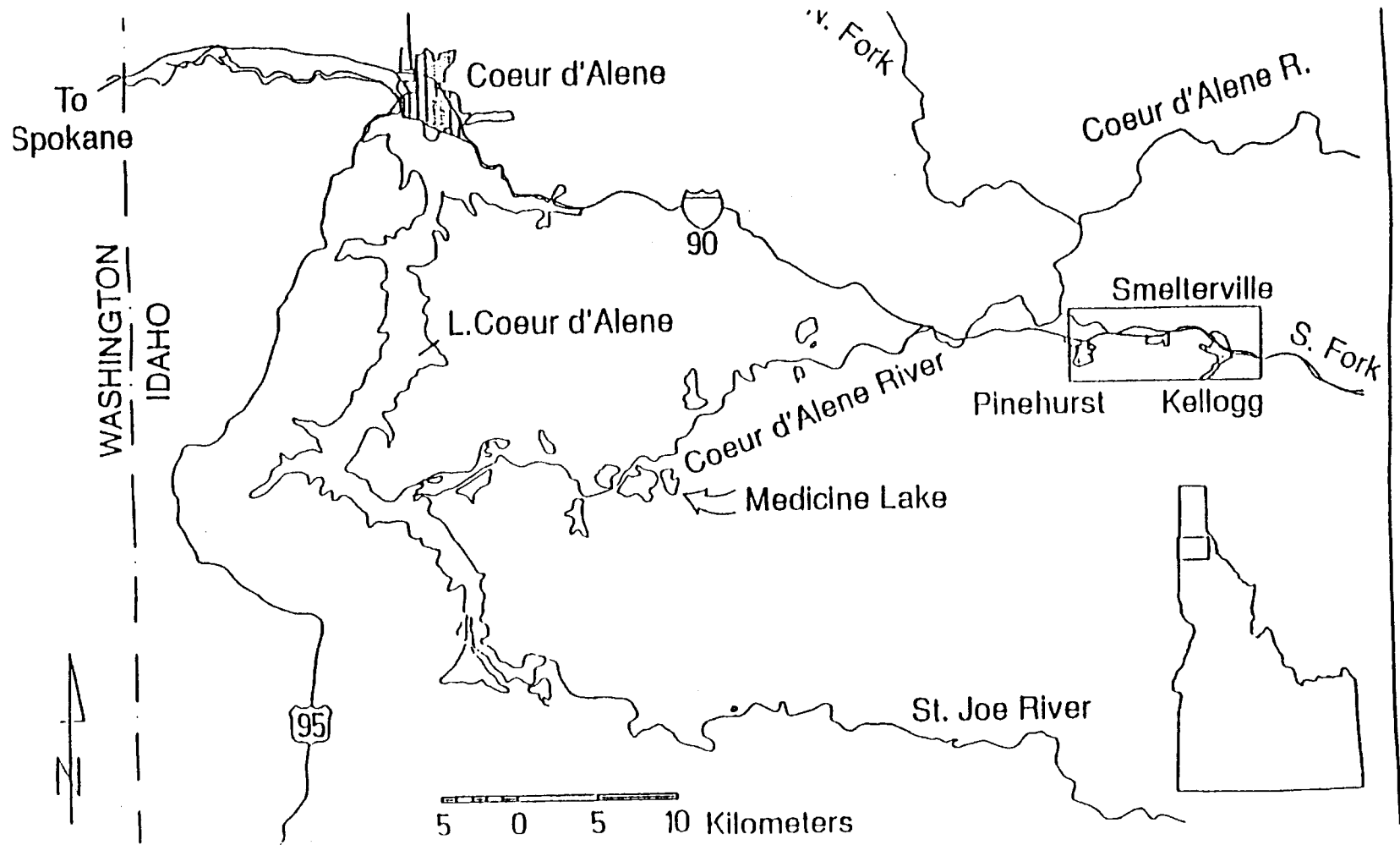


Figure 1.1 Location map of research area (Rember et al., 1993).

Ellis (1932), found no fish fauna, bottom fauna, or plankton living in the MSCDR, SFCDR or in Lake CDA near the inlet of the MSCDR. In the summer of 1973, Rainbow trout placed in live boxes at several locations in the Coeur d'Alene River died within 48 hours (Funk et al., 1975). Today, fish and other aquatic life are returning to the MSCDR.

### **1.2.2 Flood Stages in the MSCDR and SFCDR**

In general, the MSCDR and SFCDR have high-flow rates from late February through May and low-flow periods throughout the remainder of the year. Flooding occurs during late winter and spring when precipitation and snow melt are high in the region. Water levels in the MSCDR and SFCDR respond rapidly to large precipitation events which in turn causes flooding. Historical flow rates for a United States Geological Survey gauging station along the SFCDR at Smeltonville (site iii) which existed from 1972 - 1974, ranged from 1.98 m<sup>3</sup>/sec in October, 1972, to 261 m<sup>3</sup>/sec in February, 1974. The average, minimum, and maximum discharges for the MSCDR at Cataldo (site ii) are 135, 3.45 (in 1929) and 2,237 (January 1974) m<sup>3</sup>/sec (Rabbi, 1994). The MSCDR at Cataldo had low-flow periods from September through December 1992, and peak flows of 283 m<sup>3</sup>/sec from March through May 1993. In more recent times, the MSCDR at Cataldo had a flow rate of 413 m<sup>3</sup>/sec on February, 2, 1996 and peaked at 1932 m<sup>3</sup>/sec in late February, 1996.

### **1.2.3 Geography**

Kootenai County has a land surface which gradually varies from wide, flat floodplains at the western end (Lake CDA) to a fairly steep valley at the eastern (Shoshone County) end. The valley floor at the boundary of Kootenai and Shoshone counties is roughly 1.6 km wide and narrows to 0.4 km near Wallace, Idaho. The CDA mining district is located in the Silver Valley and includes the towns of: Kellogg, Pinehurst, Silverton, Wallace, Kingston, Cataldo, and Mullan. The smelter located in Kellogg ceased production in 1985. On May 26, 1996 the stacks from the smelters were demolished.

### 1.3 GEOLOGIC SETTING

The oldest rocks in the CDA region compose the Precambrian Belt Supergroup. They formed as a result of a large marine basin roughly 850 to 1,450 million years ago (Maley, 1987). During this time, regional metamorphism occurred which morphosed the sediments to form quartzite, siltite, and argillite. Deep-water environments are represented by carbonate rocks, pure quartzites, and thick argillites lacking shallow-water sedimentary structures (Wotruba, 1983). The primary economic minerals mined in the district are galena, sphalerite, and tetrahedrite. Gangue minerals include quartz, siderite, pyrite, and pyrrhotite (Bennett, 1984).

The Belt Supergroup rocks are divided into two groups (Ravalli and Missoula) and six formations (Pritchard, Burke, Revett, St. Regis, Wallace, and Striped Peak) based on their compositions, grain size, and color (Hobbs et al, 1965). The changes in sedimentation between Belt series units are probably related to changes in the tectonics of the basin or in the source area, or in both with 6,096 m having been eroded before the Paleozoic era (Bennett, 1984; Connors, 1976). The vitreous quartzite bedding makes the Revett Formation distinctive and because it is the host gangue rock, it gives the allochthonous mine tailings in the lateral lakes a light greyish color (personal communication, Rember, 1996).

#### *Gem Stocks/Columbia River Basalts*

The Gem stocks are zoned, monzonitic to syenitic intrusions situated northeast of Wallace, Idaho. The Gem stocks are roughly 100 million years old (Cretaceous in age) and intrude lower Belt Supergroup strata belonging to the Pritchard and Burke Formations (Bennett, 1984). Furthermore, during Cretaceous time, batholithic masses intruded to the west of the CDA mining district.

The Columbia River Basalt Group covers an area approximately 199,422 square km in Oregon, Washington, and Idaho. It forms the largest Cenozoic basalt field in North America and has an estimated volume of 375,138 km<sup>3</sup> (Maley, 1987). The basalt flows range in age from 6 million to 17 million years old. In the CDA district, Tertiary Columbia



River Basalt extends from Lake CDA ten miles up the MSCDR with the main basalt flows around the mouth of the river (Hobbs et. al, 1965; Mink, 1971). Alluvial material found in the region was deposited during damming of the ancient CDA River by Columbia River Basalts and by glacial activity 15 million years later. The Columbia River Basalts dammed the ancient Coeur d'Alene River causing interbeds of alluvial material (Latah Formation, 244-335 m) in the CDA valley (Hobbs et al., 1965; Norton, 1980).

### *Glaciation*

During the Pleistocene, continental and alpine glaciers were located in different areas near the CDA district. Three glacial lakes (glacial Lake CDA, glacial Lake Columbia I, and glacial Lake Missoula) occupied regions near the CDA district during Pleistocene time (Dort, 1962; Hobbs et al., 1965; Connors 1976; Waitt and Thorson, 1983; Breckenridge, 1989). These glacial lakes were impounded by different lobes of the Cordilleran ice sheet.

Dort, 1962, proposed glacial Lake CDA formed as a result of lobes of the Cordilleran ice sheet advancing southward to dam the CDA River near Coeur d'Alene, Idaho. This southern most extent of ice has not been fully accepted. Therefore, the existence of glacial Lake CDA is not well documented in the stratigraphy of the region and further mapping needs to be conducted to determine its extent and existence.

The most prominent ancient lake affecting the CDA region was glacial Lake Missoula. The lake formed when the Cordilleran ice sheet moved down the Purcell trench (19,000 years ago) and pinched off or dammed the Clark Fork River at the north end of the Bitterroot Mtns. (Breckenridge, 1989). The lake had a maximum surface elevation of 1260 m, a maximum depth of 670 m, with 2,514 km<sup>3</sup> of water in it, and drained at a rate of 15 km<sup>3</sup>/hr (Connors, 1976; Waitt and Thorson, 1983; Breckenridge, 1989). Periodic breakage of the dam released huge amounts of water and sediment that back-flooded the CDA district. These sediments were deposited in the form of ripple marks (high-energy) near the northern end of Lake CDA and as silts and sands (low-energy) in backwaters extending up the CDA valley (personal communication, Breckenridge, 1996).

## 1.4 MINING HISTORY

Mining in the CDA region started between 1879-1884 when A.J. Pritchard discovered gold in the Murray-Eagle mining district. The main base metal strike in the area occurred in 1885 at Bunker Hill; it is this strike that is responsible for the area's mining riches. The CDA mining district has operated since that time. The district is known for producing lead, zinc, antimony, and silver. From 1884 to 1991, silver production was 1 billion troy ounces, 187,815 tons of copper, 8,014,041 tons of lead, 3,243,269 tons of zinc, and 518,552 troy ounces of gold. Since 1884, the CDA mining district has yielded approximately 5.2 billion dollars in precious metals (Bennett, 1984; Hoffman, 1995).

### *Jig Tailings*

Early hand-picked ores were crushed (25.4-1.4 mm) so that galena (PbS) could be gravity separated by a jig. The jig cell contained a mixture of ore and water. The water separated the light minerals from the heavy galena and the light material was discarded as waste. This procedure was roughly 50-75 % efficient; therefore these early wastes (called jig tailings) that were typically dumped into waterways contained elevated levels of heavy metals and were a source of river contamination (Bennett, 1994).

### *Selective Flotation*

In 1916, selective flotation started replacing jigging as the standard ore recovery practice. The selective flotation process uses various chemical agents (such as copper sulphate, zinc sulphate, and potassium dichromate) to separate the ore from crushed waste rock powder (Ellis, 1932). Furthermore, the selective flotation process is based on the premise that if air is blown through a mixture of finely ground ore, water, and xanthates (chemical flotation agents including tar oil, croesilis acid, and potassium xanthate) sulfide minerals will cling to the froth. Flotation increases the effectiveness of ore recovery to 92 % for Pb and 60 % Zn (Ellis, 1932; Bennett, 1994). An advantage of selective flotation was

that it allowed for the re-mining of jig tailings that were dispersed throughout the mining district. However, the heavy machinery used for excavation of jig tailings mixed the tailings with the upper layer of alluvium (Norbeck, 1974). The flotation procedure required that the rocks be finely ground (0.295-0.044 mm); therefore, the wastes from this procedure easily moved downstream, reaching Lake CDA (Bennett, 1994). Selective flotation made mining lower grade ore profitable. The trade off was that fine powdered mine wastes (along with their chemical agents) were deposited directly into the adjacent waterways. Settling ponds were installed to null this contamination issue in 1968.

### *Smeltonville Flats*

Smeltonville Flats is an area where mine wastes have been deposited on the alluvial flood plain of the SFCDR (Swanson, 1992). The Flats are approximately 13 km<sup>2</sup> in area and are located 62.3 km east of Spokane Washington and 1.2 km west of Kellogg, Idaho (Towatana, 1990). They occurred as a result of a pile and plank dam built about 0.81 km east of the confluence of Pine Creek and the SFCDR to limit the impact of mine wastes on agriculture (Ioannou, 1979; Swanson, 1992). Apparently, the dam was built in 1901 to prevent downriver migration and destroyed in a 1934 flooding event (Ioannou, 1979).

### *Cataldo/Mission Flats*

Cataldo Misson is about 22.5 km southeast of Coeur d'Alene, Idaho. Dates vary on when a dredge was set up at Cataldo (1920s-1934) to remove tailings from the MSCDR and SFCDR and transport them to the Cataldo Flats. Furthermore, a pipeline was recommended (its installation remains to be a question) as a transport for the slime wastes from the mines directly to the Cataldo Flats instead of placing them into waterways (Bennett, 1994).

## 1.5 PREVIOUS INVESTIGATIONS

### *Mink, 1971*

The study was initiated to look at 1) the effect of mining and domestic wastes on the quality of water in the SFCDR, 2) use the North Fork as a comparison based on its natural unaltered state, 3) report on the quality of the MSCDR, 4) provide recommendations on how to improve water quality in the basin. The water quality at three sites used in this investigation are shown in Table 1.1.

**Table 1.1: Metal concentrations in the MSCDR and SFCDR (Mink, 1971).**

Location	Date	pH	As	Fe	Mn	Pb	Zn
			----- mg/L -----				
MSCDR	5/21/69	6.70	-	0.8	0.3	-	0.4
MSCDR	5/21/69	6.70	-	0.9	0.3	-	0.4
SFCDR	5/21/69	9.00	-	0.8	0.5	-	1.2
MSCDR	6/12/69	6.30	<10.0	0.5	0.1	-	0.2
MSCDR	6/12/69	6.60	<10.0	0.0	0.2	-	0.2
SFCDR	6/12/69	5.85	<10.0	1.0	0.4	-	1.1
MSCDR	7/15/69	6.40	-	0.3	0.1	-	1.6
MSCDR	7/15/69	6.40	-	0.3	0.4	-	3.0
SFCDR	7/15/69	6.25	-	0.3	<0.1	-	8.9
MSCDR	8/19/69	7.20	-	0.2	0.5	-	2.6
MSCDR	8/19/69	7.60	-	0.1	0.6	-	2.0
SFCDR	8/19/69	6.55	-	0.1	2.0	-	6.5

Zinc concentrations in the SFCDR averaged 1.4 ppm in the winter, 0.4 in the spring, and 3.4 ppm in the summer. During flooding events, river waters contain elevated levels of Zn. These new sources of Zn are associated with remains of old mine tailings found throughout the valley floor.

### *Galbraith et al., 1972*

At Cataldo Mission Flats, via augering, 35 tailings samples were collected at a depth of 0.9 m, and 4 samples were collected at a 1.8 m depth.. The results on the samples atomic absorption spectrophotometry are presented in Table 1.2 below.

**Table 1.2: Average metal concentration in Cataldo Mission Flats (Galbraith et al., 1972).**

Location	Fe	Mn	Pb	Zn
	----- (%) -----			
Cataldo	11.79	0.79	0.46	0.41

Groundwater sampling was also conducted at the Cataldo Flats. High metal concentrations (50 ppm Zn and 0.8 ppm Pb) were found to be entering the Coeur d'Alene River via groundwater passing through the tailings. Additionally, they hypothesized that during higher ground water flow periods (spring melt), more leached metals reach the river system.

*Maxfield et al., 1974*

A geochemical analysis was performed on 107 cores (1,000 samples) at the delta of Lake CDA. The cores (typically associated with mine tailings) were mainly silt and contained 60-80% quartz, with some sulfides, carbonates, silicates, and oxides. Lead concentration was greatest in the clay fraction followed by organic matter, silt, and sand. Zinc concentrations were greatest in the following size fractions: clay>silt>organic matter>sand. In general, metal concentrations were evenly distributed down to a 52 cm depth. The digestions were done with nitric acid and analyzed using an atomic absorption instrument; the results are shown in Table 1.3:

**Table 1.3: Metal concentration in top layer of dry delta sediments of Lake CDA (Maxfield et al., 1974).**

Element	Minimum	Maximum	Mean	Median
Mn (ppm)	6,200	12,500	8,000	1,740
Pb (ppm)	3,000	6,300	3,700	910
Zn (ppm)	3,200	4,700	3,800	430

*Norbeck, 1974*

The extent of mine tailings and alluvium were mapped from aerial photography in the CDA region. The author conducted a seismic and resistivity survey, and a ground water quality assessment. The surveys indicate that depth to bedrock in the CDA region ranges from 8.2 m-126 m. Based on water-level contours, the MSCDR west of Cataldo is gaining (ground-water gradient is to the river). Furthermore, most of the ground water flow toward the MSCDR is ground water from tributary valleys. A Zn mass transport model was used to quantify Zn contamination in the Smeltonville Flats region. There was approximately 150 kg/day of Zn flowing at a rate of 12,301,250 l/day in late August, 1971.

*Rabe and Bauer, 1977*

This experiment incorporated water quality, sediment geochemical characteristics, and fish toxicity of the CDA drainage district (lateral lakes, and the MSCDR). In 1973, there were roughly 1.1 ppm Zn in the MSCDR, but Zn values decreased to below detection limits in 1974 due to a high flood year. Metal concentrations were above background (Bells Lake) in the cores sampled. Zinc concentrations present in the lakes in the spring are probably not toxic to warm water species but are toxic to trout. Furthermore, Brown bullhead species contained the most Zn out of the 5 fish genus sampled.

*Reece et al., 1978*

An analysis of the bank sediments of the MSCDR and SFCDR to determine metal content was conducted (Table 1.4). A series of laboratory leaching experiments were also carried out where 100 g of sediment was placed in a 1 liter bottle with 400 ml distilled water and the pH was adjusted (3.3-6.7) with sulfuric acid. At pH 6.7, the concentration of Mn increased from 0.6 ppm to 2.5 ppm over a 250 hour time span. Zinc concentrations were 0.7 ppm to 2.1 ppm and also increased over a 250 hour period. Their results indicate that the concentration of metals released at pH 3.3 are higher than at pH 6.7.

**Table 1.4: Elemental concentrations in surface bank sediments of MSCDR and SFCDR (Reece et al., 1978).**

Location	No. Sample	mg/L		
		Mn	Pb	Zn
Delta-the River's mouth	9	7,344 (6,280-8,000)	3,374 (2,460-4,320)	3,007 (2,250-3,480)
Main Stem - 5 km up from delta	2	5,852 (3,160-7,060)	3,677 (2,710-4,740)	3,245 (1,730-6,650)
Main Stem-Cataldo Flats	12	7,650 (3,700-10,600)	3,352 (2,610-4,180)	3,069 (1,960-3,860)
South Fork-Smelterville	32	5,073 (3,180-8,420)	4,797 (1,670-11,400)	3,912 (2,080-7,550)

*Ioannou, 1979*

A depth-integrating hand-line sampler was used with a 3/16 inch nozzle to measure suspended sediment in the SFCDR and a 3-inch pressure difference portable sampler to measure bedload during the snowmelt runoff period of April-June 1978. At the Smelterville bridge on 5/17/78, stream discharge was 55.5 m<sup>3</sup>/s, the suspended sediment concentration was 15.7 mg/L, and the bedload was 260 kg/hr. Analysis of the bedload material revealed that mine tailings are being removed from the riverbanks and are being carried by the river downstream. The volume of erosion was estimated for a one-foot width from each cross section. Near the bridge on Shoshone county airport road, the riverbank had 0.651 cubic meters of sediment eroded and 0.566 cubic meters deposited; nearby, 67.92 cubic meters of stream bank had been eroded. The conclusion was that the SFCDR is dynamic, tailing deposits along the stream are being eroded and deposited in an uncontrolled manner, most of the heavy metals from the bedload samples are associated with the small size grain fractions, and concentrations in suspended sediments are high.

*Keely, 1979*

An examination was conducted of 1) the rate of solubilization and the equilibrium concentrations of solubilized trace metals from riverbank sediments; 2) the effects of agitated (stream simulation) and static (aquifer simulation) soil solutions on the solubilization process; 3) the effect of soil characteristics (e.g. organic content) on the solubilization

process and 4) the effect of oven drying the sediment like Osburn and Cataldo soils on the solubilization process (a sample pre-treatment concern).

Contamination by mine tailings in sediments along the MSCDR appears to be limited to the riverbanks and floodplains. In general, metal concentrations decreased with depth and distance from the Coeur d'Alene River. Metal concentration in soils were determined by atomic absorption spectrophotometer. The metal concentration in Shoshone and Kootenai counties along with the riverbank/floodplains are presented in Table 1.5.

**Table 1.5: Average heavy metal concentrations in Shoshone and Kootenai counties and in the Riverbank/Floodplains of the MSCDR (Keely, 1979).**

Location	Depth (cm)	Cd	Cu	Pb	Zn
----- ug/g -----					
Shoshone	0-5	3.73	21	241	201.97
	5-10	2.60	20	166	163.36
	10-15	2.41	17	116	139.18
Kootenai	0-5	1.67	13	74	92.41
	5-10	1.15	13	50	83.46
	10-15	0.96	13	38	67.86
Riverbank/ Floodplain	0-5	20.09	101	3465	2,451.73
	5-10	19.16	99	3,413	2,380.88
	10-15	18.65	101	3,614	2,477.19

A contaminant release experiment from sediments under agitated and static conditions was also conducted. At Smelterville, the high solubility or dissolution of Zn is attributed to the oxidized layer on the surfaces of soil grains. Furthermore, zinc sulfide may be oxidizing to highly soluble zinc sulphate. Manganese solubility curves follow first-order kinetics fairly well; iron concentrations (2.03 mg/L) were explained as dependant on the oxygenation of organic matter which in turn can form a soluble Fe(III)-organic complex rather than a precipitated Fe(III) hydroxide. An important side effect is that the net pH of solution is not lowered. This explanation works well for mildly acidic soils pH 5-6. In the Cataldo solutions, no soluble iron was detected, Zn values were attributed to adsorption and ion-exchange phenomena in clays. The pH of tailing solutions were 7.74 and 7.78 indicating that acid forming iron redox reactions are neutralized by calcite or dolomite.



*Mok and Wai, 1990*

Samples were collected at depths 15.24 cm below surface (and a core from the delta) and analyzed for As and Sb with instrumental neutron activation analysis (INAA) whereas, Zn, Mn, Fe were analyzed with XRF (Table 1.6). Leaching experiments were carried out by placing 60 g of sediment with 800 ml DI water in a plastic bottle and mixed with a metallic stir bar. The mixture was monitored for pH and metal release over time.

**Table 1.6: Vertical distribution of contaminants from a core of the Delta area, Lake CDA (Mok and Wai, 1990).**

Depth (cm)	As -- (ug/g) --	Fe --- (%) ---	Mn ----- (%) -----
0.5	196.96	11	0.97
4.5	146.63	9	1.00
8.5	7.84	2	0.00
14.5	7.37	2	0.00
18.0	6.21	2	0.02
21.5	5.65	2	0.00

**Table 1.7: Average elemental concentrations and pH in the SFCDR and MSCDR (Mok and Wai, 1990).**

Location	Date	pH	As(III) -- (ug/L) --	As(III) +As(V) -- (ug/L) --	Fe - (mg/L) -	Mn - (mg/L) -	Zn - (mg/L) -
SFCDR	12/86- 6/87	7.53	0.484	0.67	0.02	0.16	1.48
SFCDR	12/86- 6/87	7.36	0.816	0.902	0.23	0.98	2.73
MSCDR	12/86- 6/87	7.70	0.135	0.247	0.07	0.34	0.75
MSCDR	12/86- 6/87	7.70	0.127	0.22	0.07	0.23	0.47
MSCDR	12/86- 6/87	7.44	0.237	0.29	0.11	0.30	0.52
MSCDR	12/86- 6/87	7.39	0.253	0.379	0.12	0.29	0.53
MSCDR	12/86- 6/87	7.53	0.354	0.63	0.11	0.17	0.25

Leaching of As and Sb species from the contaminated MSCDR sediments depends on the pH values of the water as well as the free iron oxides and manganese oxides present in

the sediments. Results from the leaching test indicate that at lower pH values more metals are released into solution. The authors also concluded that As(III) was the predominant form of inorganic As in the SFCDR and MSCDR, whereas the North Fork generally had higher As(V) concentrations (Table 1.7). In general, trace elements were found to be higher in the low flow of winter and lower in the high flow during the spring.

*Towatana, 1990*

A geochemical analysis of 6 backhoe trenches (samples collected every 30.5 cm) in the Smeltonville Flats region was conducted. The contaminants were phase partitioned into the exchangeable, carbonate, Fe-Mn oxide, organic and residual species and their release was measured from sediments in the upper aquifer system. Arsenic, Cu, and Sb were partitioned in the residual species, Cd in the organic fraction, Zn in the Fe-Mn oxide and residual species, and Pb in the Fe-Mn oxide and carbonate fractions. The factors that governed metal solubility in the aquifer system were the pH of water, the buffering capacity of the carbonates in the sediment, and the low solubility of gangue minerals.

*Bender, 1991*

A distribution of contaminants with depth from piston and freezer box cores was determined for Killarney and Bells Lake. In the cores, there was a layering of metallic silt (which was gray in color and had a metallic odor) and black organic matter. The metallic silt was deposited during flooding, and the black organic matter was probably deposited during winter when organisms died. In Killarney Lake the top 80 cm of sediments are contaminated with mining wastes. In a core from Killarney Lake metal concentrations were compared to crustal averages. Arsenic was one to two orders of magnitude higher than the crustal average, Fe was 2 times the crustal average, Mn was 3 times the crustal average, Pb was 3 orders of magnitude greater than the crustal average, and Zn was 1.8-3.4 % by weight in the sediment samples. The values of metal concentration in Killarney Lake are shown in Table 1.10.

*Horowitz et. al., 1992*

Approximately 172 surface (2 cm) bed sediment cores (1 per square kilometer) from Lake CDA and adjacent areas were collected. Each sample was then homogenized using an acid-rinsed glass rod and sieved through a 2000-um polyester screen to remove large material and then freeze dried. Grain-size and heavy mineral separations were made on selected samples to help determine the phase associations of the trace elements in Lake CDA. Geochemical phase determinations were used to partition the trace elements into an Fe oxide phase (0.25 M HCL heated at 50°C for 30 min) and an organic/sulfide phase (30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2 with HNO<sub>3</sub> heated at 85°C for 5 h followed by treatment with 3.2 M ammonium acetate in 20% v/v HNO<sub>3</sub> and shaken for 30 minutes) (Table 1.8).

**Table 1.8: Percentages of oxide and organic/sulfide fractions in Lake CDA (Horowitz et al., 1992).**

Location	Extraction	As	Pb	Zn	Fe	Mn
		----- mg/L -----			----- (%) -----	
Near mouth of CDR						
	Oxides	77	95	76	39	59
	Organic/ Sulfides	2	3	7	25	28
Farther into Lake from mouth of CDR						
	Oxides	71	95	89	37	82
	Organic/ Sulfides	4	4	8	14	9

According to Horowitz et al., some of the highest concentrations (Ag, As, Cd, Cu, Hg, Pb, Sb, Zn) are found in sediments deposited in and around Harrison Slough (north of the right bank of the CDA River and after it enters Lake CDA). Secondary highs were found south of Harlow Point (As, Hg, Pb, Zn). Some of the highest trace element concentrations in the lake are found adjacent to the CDA River delta (Harrison Slough). High concentrations of elements near the CDA river can be associated with varying current direction and velocity associated with losses in sediment transporting capacities of the river as it enters the lake. This explanation, however, does not validate high elemental concentrations in areas perpendicular to current flow (Windy, Rockford, Mica bays) which are not near the inlet of

the CDA river. The results of geochemical analysis of the bank sediments are shown in Table 1.9.

**Table 1.9: Elemental concentrations in surface bank sediments of MSCDR and SFCDR (Horowitz et al., 1992).**

Location	As	Pb	Zn	Fe	Mn
	----- mg/L -----			-- (%) --	-- (%) --
SFCDR					
Smelterville					
Bulk	90	63,000	12,000	17.1	0.62
Light	30	8,100	3,700	4.9	0.14
Heavy	120	80,000	16,000	24.3	0.83
MSCDR at					
Cataldo					
Bulk	160	3,800	7,800	8.8	0.89
Light	80	2,600	5,400	3.8	0.33
Heavy	420	8,600	14,000	36.8	3.00

Based on descriptions of the CDR bank deposits, Horowitz et al. hypothesized that the reddish material (a few mm) found in Lake CDA may have been fine-grained mining and ore-processing waste eroded from the banks. It is also possible that mineral grains coated with authigenic Fe and Mn oxides that were formed from postdepositional dissolution, remobilization, and reprecipitation due to anoxic conditions in the sediment column of the lake.

Galena (PbS), sphalerite (ZnFeS), and tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) are common ore minerals in the CDA mining district. Concentrations of Ag, Cu, Hg, Pb, Sb, and Zn in the lake may indicate: 1) that the CDA mining district is a major source for enriched trace elements, 2) correlation's between these metals and Fe indicates high percentages of Fe sulfides, 3) enriched trace elements are associated with or concentrated by Fe oxides.

*Galbraith, M. 1992*

Six sites near Kellogg, ID where mining and smelting wastes are located were sampled. Contaminants in the sediment were phase partitioned into the exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions. Sediment collected from the SFCDR contained contaminants bound in the Fe-Mn oxide and residual fractions of the

sediment. Furthermore, a comparison of three EPA regulatory leach tests were conducted to determine their effectiveness for mine waste remediation. Each test was effected by the buffering capacity, redox potential, ionic strength, and pH of the sediment.

*Rember et al. 1993*

Flooding in the past century has deposited heavy metals from mine tailings into Medicine Lake. Contamination in the lake is from well-stratified heavy metal contaminated silts on the lake bottom which contain several percent Pb and Zn. The lake bottom sediment was described as being varve like in appearance with the dark portions being autochthonous organic material and the light material was allochthonous fine-grain mine tailings. Based on the stratigraphy of the varves, flooding occurred annually and with no great hiatus in the lake system. Furthermore, cesium-137 was used to determine sedimentation rates in Medicine Lake. Contaminated sediment was deposited at a rate of 1.1 cm/yr between 1951 and 1964 and has been greatly reduced since the installation of tailings ponds in 1968.

*Horowitz et al., 1993*

A geochemical analysis of 12 gravity cores was conducted along with Cs<sup>137</sup> dating to determine sedimentation rates. The sedimentation rates were 2.1 cm/yr (1980-1990), 1.7 cm/yr (1965-1980), 1.3 cm/yr (1959-1965), 1.4 cm/yr (1954-1959). From core interpretation, the thickness of the trace element-rich sediments range from 17 to 119 cm indicating that a major source of the trace element contamination is the Coeur d'Alene River. It is estimated that 75 million metric tons of trace element rich sediments have been deposited on/in the lakebed.

*Wyman, 1994*

Wyman looked at the possibilities for metal contamination from Lake CDA to infiltrate into the Rathdrum Prairie aquifer. Wells around the lake were monitored for metal concentration. There were four shallow monitoring wells in the surface water/groundwater

interface zone that exceeded EPA Secondary Maximum Contaminant Levels (SMCL's) for Fe and Mn in 1989 and 1992, three that exceeded MCL for Se, and one well that exceeded MCL's for As, Cd, and Pb, in December 1992.

*Rabbi, 1994*

Core sampling by a Huttenen Freeze Box was conducted on Porters Lake, Rose Lake, Bull Run Lake, Medicine Lake, Cave Lake, Swan Lake, Black Lake, and Blue Lake. The sediment was phase partitioned into the exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions. Zinc, Pb, and Cu are concentrated in the oxide > organic >= carbonate > exchangeable > residual fractions, whereas Fe, Mn, and As concentrate in the oxide and organic fractions. In all the lateral lakes studied, the concentrations of Pb and Zn were the highest in lake bottom sediments. Furthermore, Pb and Zn were highest in Bull Run Lake and Medicine Run Lake. It was determined that trace metals were stable in lake bottom sediments and that the lateral lakes are acting as sinks for heavy metals transported by the MSCDR.

*Hoffman, 1995*

Contamination in Medicine Lake and Thompson Lake were studied while Bells Lake was used (80 cm depth) as a non-contaminated reference source. A freezer box was used to collect samples and Cs<sup>137</sup> was performed to determine sedimentation rates. The upper 10 cm of sediments yielded an average sedimentation rate of 0.4 cm/yr over a 25 year period; however, before the installation of settling ponds (1968) the sedimentation rate was 1.1 cm/yr. Based on a grain size analysis, Cd, Cu, Pb, Zn concentrations were highest in the least abundant fractions of the samples. Table 1.10 gives a list of values (from freezer box collection) for a 1:1 HNO<sub>3</sub> and a 30% H<sub>2</sub>O<sub>2</sub> digestion for Hoffman and Bender values (Method 3050, EPA) whereas, Rabe and Bauer used a nitric acid digestion.

**Table 1.10: Heavy metal concentrations in Bells, Medicine, Thompson, and Killarney Lakes (Hoffman, 1995; [Bender, 1991]; {Rabe and Brauer, 1974}).**

Location	As	Fe	Mn	Pb	Zn
	----- mg/L -----				
Bells Lake	12-32	3,900-31,600 {5,000-39,000}	120-1107	<2-30 {30-<300}	100-570 {52-110}
Medicine Lake	16-30	17,900-22,000 {65,000-87,000}	249-518	122-518 {2,650-3,000}	140-496 {2,550-2,950}
Thompson Lake	15-25	11,600-13,500 {25,000-70,000}	359-503	56-181 {2,600-3,700}	77-207 {2,150-3,250}
Killarney Lake	[46-376]	[45,000-103,000]	[390-12,450]	[600-37,400]	[3,200-20,250]

*Horowitz et al, 1995.*

The results for the bulk chemical analysis for a few elements analyzed from the gravity cores (Horowitz et al., 1993) and surface grab samples (Horowitz et al., 1992) analyzed with 0.5 g digested with HF/HClO<sub>4</sub>/aqua regia at 200°C are presented in Table 1.11.

**Table 1.11: Elemental concentrations in surface and core sediments of Lake CDA (Horowitz et al., (Part II) 1992, 1995).**

Element	Location	Minimum	Maximum	Mean	Median
As (ppm)	surface	2.40	660	151	56
	core	3.50	845	151	120
Fe (Wt. %)	surface	1.90	16	5	4.9
	core	2.60	14	5	4.9
Mn (Wt. %)	surface	0.01	2	0.67	0.65
	core	0.01	7	0.45	0.26
Pb (ppm)	surface	14	7700	1900	1800
	core	12	27500	3200	1250
Zn (ppm)	surface	63	9100	3600	3500
	core	59	14,000	2,400	2,100

Total contamination was estimated from cores taken in the middle of 12 zones of the lake and multiplied by the density of the sediment and the area in each zone, and then summed. These calculations indicate that 75 million metric tons of trace element-rich

sediments (Ag, Cu, Pb, Zn, Cd, Hg, As, Sb) cover roughly 85% of the lake bottom, with the greatest amount being 470,000 metric tons of Pb.

*Pedersen, 1996*

A critical review of the work by Horowitz et al., 1993 showed that the extractions used were not sufficient for phase partitioning of contaminants; the oxidation of anaerobic sediments significantly skewed any interpretation; and sample handling was done improperly. It was concluded that eutrophication of Lake CDA poses a greater threat to the aquatic biota than does the release of contaminants from Fe and Mn oxides.

*Woods and Beckwith, 1996*

The effects of eutrophication and its potential to mobilize trace elements stored in lake bed sediment of lake CDA was investigated. To assess eutrophication, water quality in the limnetic and littoral zones of the lake were assessed, quantification of hydrologic and nutrient budgets were analyzed coupled with development of a nutrient load/lake response model, and trace-elements in surficial and subsurface lake bed sediments were characterized.

Lake CDA was determined to be oligotrophic during 1991-1992. However, during late summer, in the shallow southern portions of the lake, anoxic conditions existed. The median concentrations of Cu, Pb, and Zn in the water column exceeded water-quality criteria for the protection of freshwater biota, while dissolved concentrations of Zn inhibited phytoplankton growth in the lake. Lake bed contaminants are mainly associated with iron oxides and are available for release as an anoxic hypolimnion develops. Metal concentrations in lake bed sediments (when compared with sediment-quality guidelines) indicate that severe pollution exists which in turn can significantly affect benthic organisms. The nutrient load/lake model indicated that lake CDA has a large assimilative capacity for nutrients thus, the lake is unlikely to develop an anoxic hypolimnion.



## 1.6 BACKGROUND LITERATURE ON CONTAMINANTS

The CDA mining district is contaminated with mine tailings and other mine effluent. It is imperative to quantify the amount of contamination in the regions surface water, ground water, and soil. Therefore, the following section lists background values for As, Fe, Mn, Pb, and Zn in water and soils and discusses there effects on aquatic biota in the region.

### Arsenic

Arsenic concentrations range from 1.8-5.0 mg/kg in the Earth's crust (Moore, 1991). In general, no guidelines are currently in effect for arsenic concentration in aquatic environments. The maximum contaminant level allowed in drinking water is 0.05 mg/L As (U.S. EPA, 1994). Inorganic forms of arsenic include formal oxidation states As(V), arsenate, and As(III), arsenite, with primary aqueous species at neutral pHs being anionic:  $H_xAsO_4^{3-x}$  (arsenate) or  $H_xAsO_3^{3-x}$  (arsenite) (Anderson and Bruland, 1991). In waters containing dissolved oxygen (high Eh), arsenate (AsV) is the dominant species but arsenite (AsIII) may be present in significant amounts. Whereas in anoxic basins or in the pore water of sediments (low Eh), arsenite is found at greater concentrations than arsenate (Seyler and Martin, 1989). In the CDA district, the bioreduction of arsenic is dependant on microorganism populations which in turn are dependant on temperature, ambient light levels, and nutrient availability.

When anaerobic sediments are subjected to short term mixing, such as hydraulic dredging operations or prop wash from passing boats, As(III) will be the major As species released (Brannon and Patrick, 1987). This situation exists in the hypolimnion found in Lake CDA. If dredged sediment in Lake CDA are placed into an aerobic environment (i.e. landsurface) substantial changes in As speciation can occur along with release over time. Over a prolonged period, As(V) will probably be the major constituent released, although release of As(III) will predominate initially (Brannon and Patrick, 1987).

Arsenic is largely associated with Fe oxyhydroxides in oxic sediments and is released to the interstitial water when Fe(III) is reduced to Fe(II) upon burial of the sediments

(Belzile and Tessier, 1989). Subsequently, As can diffuse upwards to the sediment water interface where, under oxic conditions, it becomes associated with newly formed Fe oxyhydroxides or under anoxic conditions it can be released into the hypolimnion (Belzile and Tessier, 1990). This adsorption/desorption mechanism for arsenic interaction with iron oxyhydroxides is the principle controlling force for arsenic mobility in the CDA district.

### Iron

Iron is the fourth most abundant element in the Earth's crust. Freshly precipitated iron oxides have surface areas of 200-500 m<sup>2</sup>g<sup>-1</sup>, this high surface area can sorb inorganic anions, organic anions, and cations such as Zn and Pb. Iron is cycled in the aquatic environment through microbial reduction of iron oxides forming Fe(II). The reduction of Fe(III) releases contaminants whereas, the oxidation of Fe(II) to Fe(III) can sorb newly precipitating contaminants (i.e. arsenic). Iron oxides in the CDA district may have formed as a result of smelting operations. Currently, Fe oxides are found along channel banks of the MSCDR and have been transported into Lake CDA. According to Horowitz et al. (1992), the presence of authigenic Fe oxides in Lake CDA could be due to deposition and burial of detrital Fe oxides in the lake, followed by remobilization under reducing conditions, upward diffusion in the pore waters, and reprecipitation once the fluids have passed through the anoxic/oxic boundary. Regardless of the source, the majority of the enriched trace elements in the surface sediments of Lake CDA appear to be associated with Fe oxides, rather than sulfide. When these surface elements are buried and subjected to anoxic conditions, the Fe oxides and associated trace elements may be solubilized and made bioavailable (Horowitz et al., 1992).

### Manganese

Manganese concentrations are 960 mg/kg in the Earth's crust, whereas in freshwater concentrations vary from 0.002 to 4 mg/L (Moore, 1991). Manganese oxides that precipitate at the anoxic/oxic boundary have surface areas on the order of 200 m<sup>2</sup>g<sup>-1</sup> (Stumm, 1985). For

aquatic chemistry purposes, manganese's oxidation-reduction reactions are imperative. The production of a seasonally anoxic hypolimnion (such as is found Lake CDA) creates a depletion of oxygen which reduces  $Mn^{+4}$  to soluble  $Mn^{+2}$  (at a higher potential than  $Fe^{+3}$  to  $Fe^{+2}$ ) and in the process may release contaminants to the overlying water (Moore, 1991). The rate of oxygenation of manganese oxides is enhanced by manganese oxidizing-bacteria. In general, manganese oxides oxidize slower than iron oxides. In the hypolimnion, Mn concentrations increased dramatically with the development of anoxic conditions. In addition, because Mn is readily reduced, elevated concentrations of Mn were observed with the onset of oxygen depletion and occurred throughout oxygen-depleted hypolimnions (Anderson and Bruland, 1991).

### Lead

Lead contamination has received the greatest media attention in the CDA district. Lead blood level concentrations in children of the CDA district were extremely high in the late 1970's and early 1980's. The concentrations were a major factor contributing to the designation of the Bunkerhill Superfund Site. Lead is generally found in the Earth's crust at 16 mg/kg and in the Earth's soils from 10 to 40 mg/kg dry weight (Merian, 1991). It is found in river waters from 0.1 to 10 mg/L, and its drinking water standards are 0.015 mg/L (U.S. EPA, 1994). In aqueous systems, lead is usually in the +2 oxidation state, and is low in solubility when it forms complexes with hydroxides, carbonates, and sulfides. In fish, the 96 hr  $LC_{50}$  is roughly 0.5 to 10  $mgL^{-1}$  depending on the species (Moore, 1991).

### Zinc

In aquatic systems zinc is generally found in the divalent oxidation state and is available for sorption onto suspended colloids (iron, manganese, aluminum) and organic matter (Moore, 1991). Zinc concentration averages 70 mg/kg in the Earth's crust and 0.005 to 0.015 mg/L in freshwater. The drinking water standard for zinc is 5 mg/L (U.S. EPA, 1994).

In the CDA district, the acute toxicity  $TL_{50}$  96 hour (toxic limit for 50 percent within 96 hours), is from 0.10 mg/L - 0.91 mg/L depending on the physical parameters of the fish and the chemical characteristics of the river water (Norton, 1980).

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## **STUDY ONE: THE RELEASE OF AS, FE, MN, PB, AND ZN UPON OXYGENATION OF CONTAMINATED SEDIMENTS FROM LAKE CDA.**

### **2.0 SUMMARY**

Lake Coeur d' Alene in northern Idaho is contaminated with heavy metals from numerous years of mining. Accordingly, a possible environmental management plan may include dredging. A systematic study on the dredging of heavy metals from lakes sediments was conducted. The procedure used in this study is as follows: 1) pore water total metal concentration, 2) total metal abundance in the organic, amorphous, crystalline and sulfidic fractions of the solid phase, 3) simulated dredging while measuring pH, Eh, and contaminant release over time, and 4) comparison of experimental data with results predicted from the MINTEQA2 speciation program. To simulate dredging operations, cores taken by gravity drilling were placed into a reaction vessel and mixed while being oxygenated for 800 hours. During the 800 h, solution As and Pb concentrations were found to be higher (0.0838 and 0.57 ppm, respectively) than the maximum contaminant levels allowed for drinking water and therefore would be detrimental to water quality within the lake. Zinc contaminant levels are of concern because they remain consistently high throughout the dredging simulation (8.3 ppm). The sediments remaining from the two dredging trials were also analyzed by selective dissolution analysis; partitioning of contaminants after dredging shifted from the organic fraction to the amorphous and crystalline metal-oxide fraction. The results suggest that management efforts that include dredging could have short-term impact on water quality in the Coeur d' Alene Basin.

## 2.1 INTRODUCTION

Historically, in the United States, the Coeur d'Alene Mining District has been one of the major silver, lead, and zinc producing areas. Over the years, numerous environmental studies carried out in the Coeur d'Alene (CDA) region have shown that large amounts of mining, milling, and ore-processing wastes have been deposited in the lower CDA River and Lake CDA (Wai et al., 1985; Horowitz et al., 1992; Horowitz et al., 1993).

Mine tailings and other mine effluent have been deposited in the Coeur d'Alene basin for nearly 100 years. Determining the best management practices for these areas is essential for maintaining environmental quality. Dredging contaminated sediments is one possible environmental clean-up plan proposed for Lake Coeur d'Alene. Dredging is a process by which subsurface sediments are agitated, removed, transported, and discharged to land or water (Brannon and Patrick, 1987). When sediments contaminated with heavy metals or other trace elements are agitated, certain contaminants may sorb or mobilize at the sediment-freshwater interface. Furthermore, dredging and disposal operations may also involve a change in the sediment environment, i.e., a transition from anaerobic to aerobic conditions (Brannon and Patrick, 1987).

Arsenic in aquatic environments has been studied extensively (Wai and Mok, 1985; Brannon and Patrick, 1987; Moore et al. 1988; Seyler and Martin, 1989; Belzile and Tessier, 1990; Mok and Wai, 1990; Anderson and Bruland 1991; Cornett et al., 1992; Driehaus et al., 1995). Seyler and Martin (1989) state that based on thermodynamic calculations As(V) is mainly found in oxic waters, whereas in anoxic systems As(III) should be the stable (soluble) form. Both Pb and Zn are present as divalent cations in aquatic systems; Pb has a tendency to form compounds of low solubility with major anions of natural waters, while Zn is usually more soluble (Hem, 1976; Vymazal, 1985; McKee, 1989; Tessier et al., 1989; Marani et al., 1995). Manganese and iron are redox active, with reduced divalent species being soluble and higher oxidation states, Fe(III), Mn(III), and Mn(IV), being comparatively insoluble in natural waters (Murray, 1975; McKenzie, 1979; Wilson, 1980; Tessier et al., 1985; Sigg, 1987; Matsunga et al. 1993).

By understanding how heavy metals are released into solution during dredging, it is possible to decipher whether dredging can be included in a viable environmental management plan. Understanding the bioavailability and mobility of As, Pb, and Zn caused by dredging in Lake Coeur d'Alene is critical for these practices. If contaminants are readily mobilized, then special precautions must be taken when dredging and disposing of contaminated sediments (Brannon and Patrick, 1987). This study quantifies how contaminants are released upon oxygenation and agitation of a reduced Lake CDA sediment over 800 h incubation periods. Such contaminants may have a substantial impact on the sediment geochemistry, water quality, and biota of Lake CDA.

## **2.2 MATERIALS AND METHODS**

### **2.2.1 Site Characteristics and Sampling Procedure**

Lake Coeur d'Alene (CDA) is situated due west of the Bunkerhill Superfund Site (Fig. 2.1) in northern Idaho approximately 10 km east of the WA/ID border. Lake CDA is dimictic; it undergoes two periods of thermal stratification and a fall and spring overturn (Wyman, 1994). The lake is roughly 64 m deep and covers approximately 130 km<sup>2</sup> (Wyman, 1994).

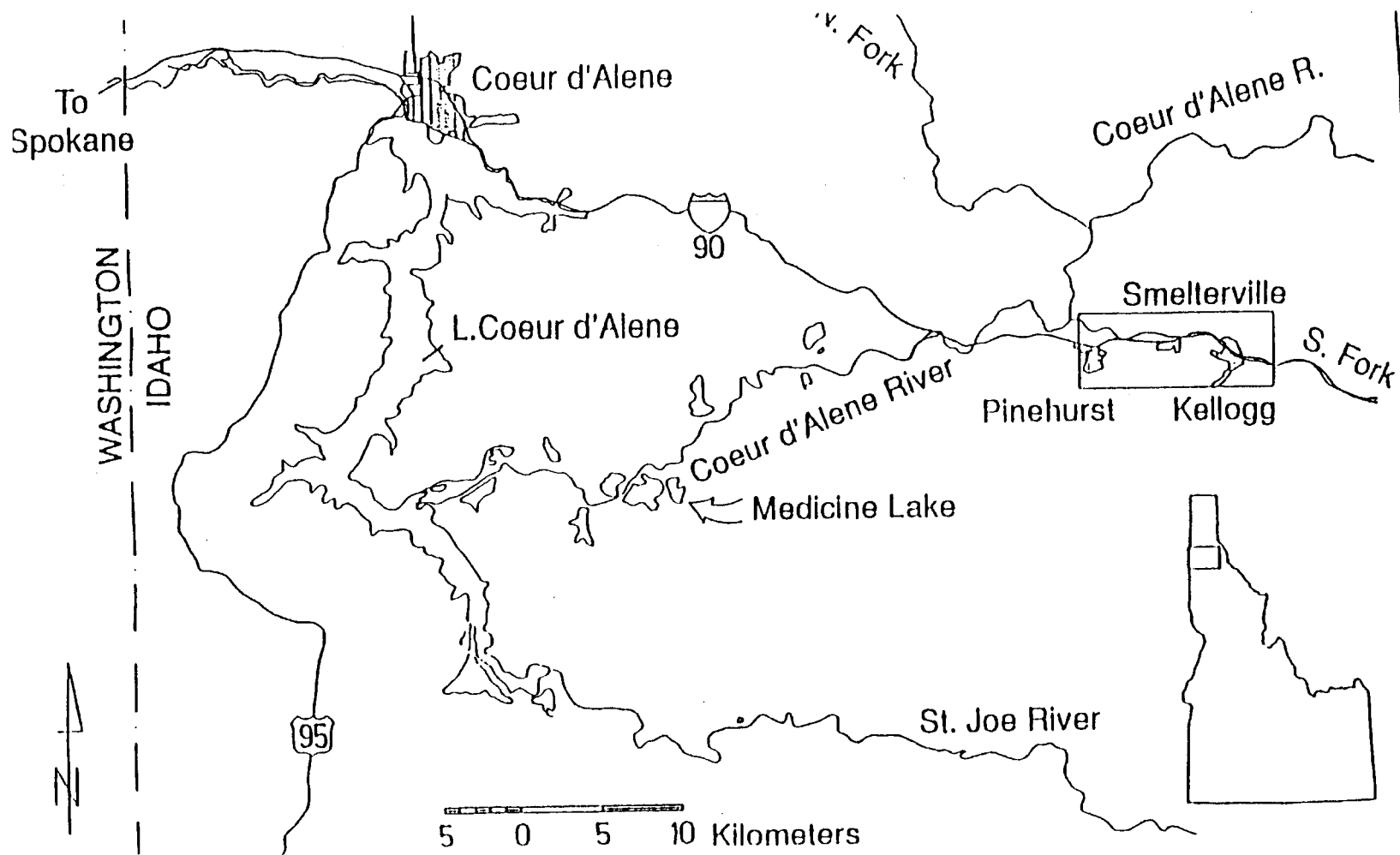


Figure 2.1 Location map of Lake Coeur d'Alene; note, box below Smeltermville is the Bunker Hill Superfund Site (Rember et al., 1993).

The sediment samples used for this study were collected from cores of Lake CDA using a gravity core drilling technique. The cores were collected on June 27, 1995 and purged with nitrogen until the laboratory work began 2 days later. Traverses were made from Harlow point to Harrison, where core samples were collected. Based on previous sampling by Horowitz et al. (1992), it was determined that an ideal sample for this study could be obtained from locations south of Harlow Point. Two cores were extracted from site V in Figure 2.2. Eh and pH data were taken from one core immediately upon sampling while a second core was preserved ( $N_{2(g)}$  at  $4^{\circ}C$ ) for experimentation. Eh measurements were taken at 0 (top of core), 5.1, 10.2, 15.2, 20.3, 25.4, and 30.5 cm depths, whereas pH values were taken at depths of 0, 15.2, and 25.4 cm.

### 2.2.2 Dredging Equipment

The apparatus used to simulate dredging operations was a Biostat M Fermentor (B. Braun). The Biostat M was equipped with a 2 L glass culture vessel with ports for pH and Eh electrodes machined in the cover. Mechanical mixing of the sediments in the reaction vessel was achieved with a double-impeller mixer operating at 300 rpm.

Dredging simulations were carried out on two portions of the core, one from the 30 to 55 cm depth (core-bottom; trial 1) and the second from the top 30 cm (0-30 cm, core-top; trial 2) of the core. The water content of the core was determined by drying 10 g of wet sediment at  $105^{\circ}C$ . To initiate the experiments, an amount of wet sediment equal to 31.5 g of dry-equivalent was placed into the reaction cell with 1 L of 0.1 M NaCl. The suspension was then oxygenated by flowing atmospheric air ( $P_{O_2} \hat{A} 0.2 \text{ atm}$ ) at a rate of  $1 \text{ L min}^{-1}$  into the cell through a gas diffuser. The oxygenated suspension was then sampled periodically over an 800 h reaction period by removing 20 mL of the suspension and filtering it through a  $0.45 \mu\text{m}$  membrane filter. Dissolved concentrations of As, Fe, Mn, Pb, and Zn were measured in the filtered solutions. Additionally, the pH and Eh of the suspension were recorded at each sampling interval.

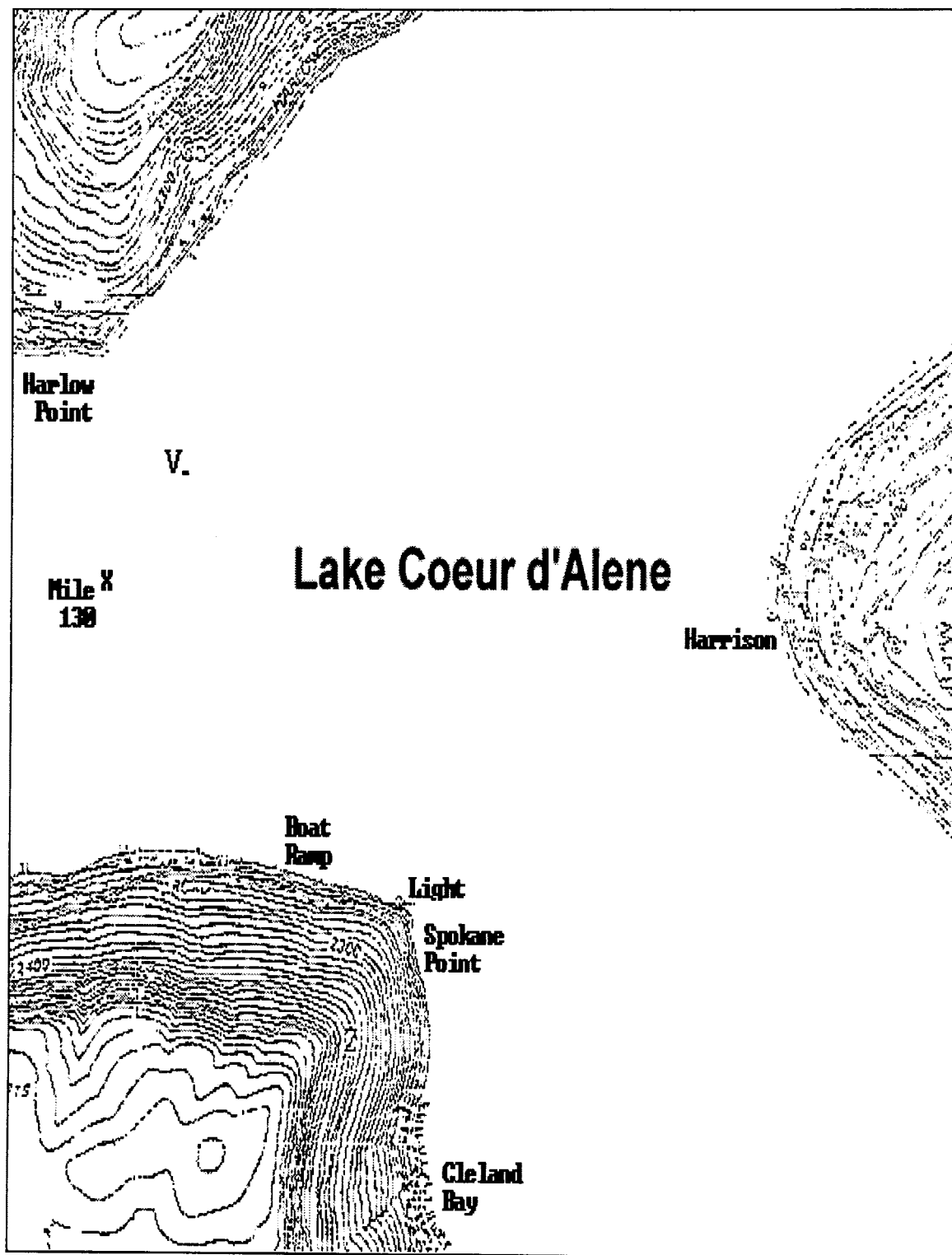


Figure 2.2 Location of site where gravity cores were taken; note site V. is the location of extraction for the gravity cores.

### 2.2.3 Analytical Procedures

Direct electrode potentials (Eh, relative to the standard hydrogen electrode) were determined using a combination Pt electrode with a Ag/AgCl reference. The Pt electrode was placed in the sediment solutions, and the potential (mV) was recorded after a stable reading was obtained. Dissolved ion concentrations of As, Fe, Mn, Pb, and Zn were measured by inductively coupled plasma (ICP) optical emission spectrophotometry (Thermo Jarrell Ash IRIS ICP-OES).

Both pore water and selective dissolution analysis (SDA) were performed on the cores. Pore water extractions were done using a pressure plate at 1 atm. The core was sectioned into 10 cm segments; pore waters were extracted and then 1 g of sediment was dried and crushed for selective dissolution analysis (SDA). The SDA was used to operationally define the partitioning of the elements in the organic, amorphous, crystalline, and sulfide fractions. They were initiated in duplicate with a 0.875 g sample from the core (pre-dredged) and a 0.5 g sample from the sediment remains of the two dredging trials (post-dredged). Discrepancies in total metal abundance (Tables 2.2, 2.3, 2.4) of the pre- and post-dredged sediment are attributed to the fact that pre-dredged sediments are expressed as the averages of 10 cm core intervals, whereas the post-dredged sediments are a homogenous mixture of the core and vary in density from the pre-dredged sediment.

The first extraction was a 0.1 M sodium pyrophosphate solution, which was used to extract ions associated with the organic-phase of the sediments (Alexsandrova, 1960; McKeague, 1967; Bascomb, 1968; McKeague et al., 1971; Stevenson, 1982; Soil Survey Staff, 1992; Dahlgren, 1994). Unfortunately the sodium pyrophosphate may displace anionic sorbates, such as arsenate or arsenite, and has trace amounts of arsenic making these values somewhat tenuous. For the next extraction, 0.0125 g of sediment was reacted with 0.2 M ammonium oxalate in the dark (AOD) to remove the noncrystalline materials (McKeague and Day, 1966; McKeague et al., 1971; Schwertmann, 1973; Fey and LeRoux, 1977; Hodges and Zelazny, 1980). The remaining solids (0.485 g) were then reacted with a 0.3 M sodium citrate, 1 M sodium bicarbonate, and 0.5 g sodium dithionite (CBD) solution to remove the crystalline and noncrystalline iron and manganese (hydr)oxides of the

sediment solids (Aguilera and Jackson, 1953; Mehra and Jackson, 1960; Arshad et al., 1972; Jackson, 1979; Jackson et al. 1986; Dahlgren, 1994). Then a  $\text{KClO}_3/\text{HCL}$  treatment followed by 4 N boiling  $\text{HNO}_3$  was performed to remove the sulfide fractions (Chao and Sanzolone, 1977). Organic matter content was analyzed using loss on ignition at  $400^\circ\text{C}$  (Soil Survey Staff, 1992).

A digestion of the solids was performed using 0.50 g of sample digested with 3 mL 3-1-2  $\text{HCl-HNO}_3\text{-H}_2\text{O}$  at  $95^\circ\text{C}$  for 1 h. The digestion was done on the initial core along with the sediments remaining after the two (core bottom and core top) dredging trials.

### 2.2.4 Equilibrium Modeling Predictions

The MINTEQA2 speciation program (Allison et al., 1990) was used to help predict reaction trends, including redox transformations and precipitation reactions. On the basis of measured pH, Eh, and concentrations of As, Fe, Mn, Pb, and Zn, predicted ratios of  $\text{Fe}^{+2}/\text{Fe}^{+3}$  and  $\text{AsO}_3^{-3}/\text{AsO}_4^{-3}$ , and saturation indices were estimated for samples taken at times 0, 427, and 811 h for the core-bottom, and at times 0, 407, and 861 h for the core-top. These times represent the beginning, middle, and end of the two core dredging trials.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Initial Sediment Characteristics

Upon removing the sediment cores, Eh and pH values of the sediments were taken and the cores were visually inspected; organic matter content was also determined on these cores. The core contained mainly silt with high density organic matter located at the bottom. A mustard brown rind from 10 cm below the surface of the core was noted and was determined to be siderite ( $\text{FeCO}_3$ ) based on X-ray diffraction patterns. There was approximately 1.5 to 1.6 % organic matter throughout the core (Table 2.1).



**Table 2.1: Carbon content of sediment prior to dredging.**

Core depth (cm)	Weight before ignition	Weight after ignition	Mineral content	Carbon Content
	----- g -----	----- g -----	----- % -----	
T1 (30-55)	13	12.784	98.338	1.662
T2 (0-30)	13	12.7956	98.427	1.573

The Eh values at the top of the core were -40 mV and dropped to -150 mV, 5.1 cm below core surface (Fig. 2.3).

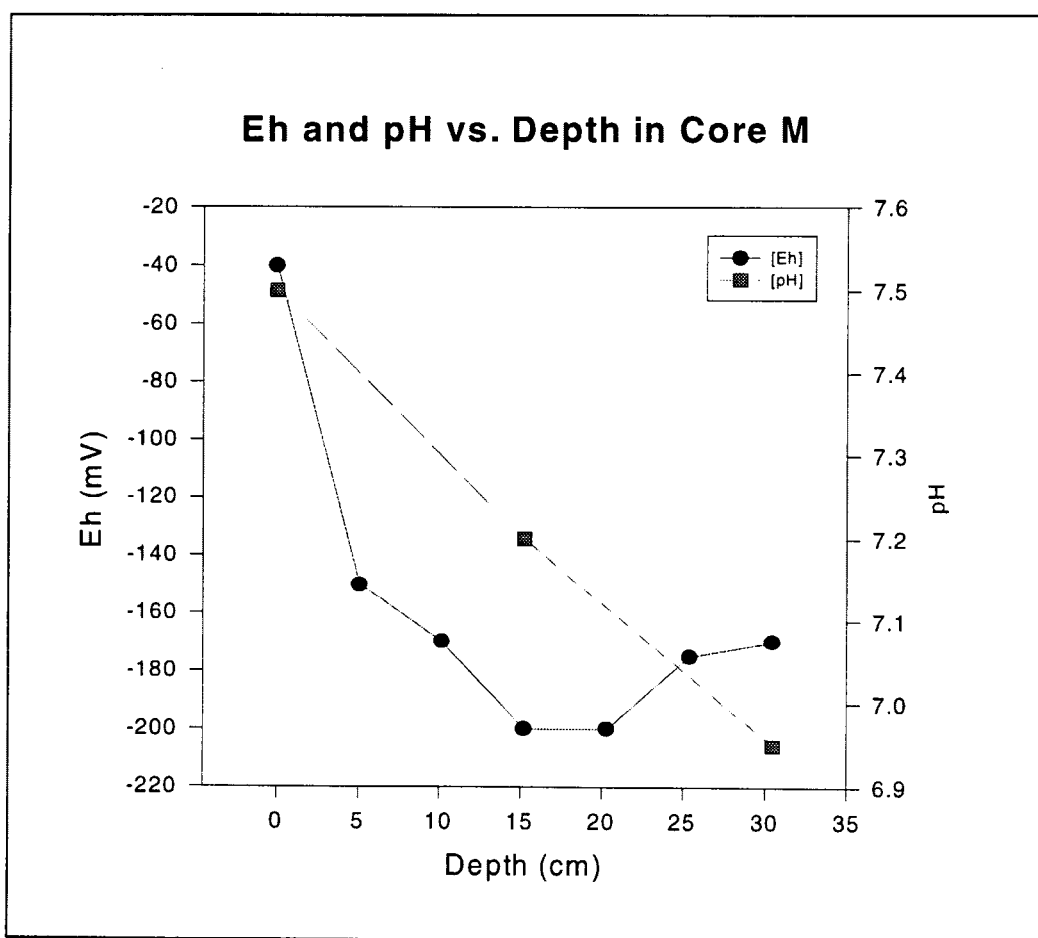


Figure 2.3 Redox potential and pH of sediment upon sampling.

The values declined to -200 mV at 15.2 - 20.3 cm but increased to -175 mV at 25.4 cm below the sediment-water interface. Redox potentials are referred to as oxic at  $E_h > 400$  mV, suboxic between 100 and 400 mV, and anoxic at  $E_h < 100$  mV (Sposito, 1981). These values indicate that at the time of extraction the core was in an anoxic state. At the sediment-water interface, the pH was 7.5 which decreased to 7.2 at 15.2 cm and 6.95 at 30.5 cm.

Pore water extractions were performed to determine the aqueous metal concentrations in the core (Fig. 2.4).

### Pore Water Concentrations

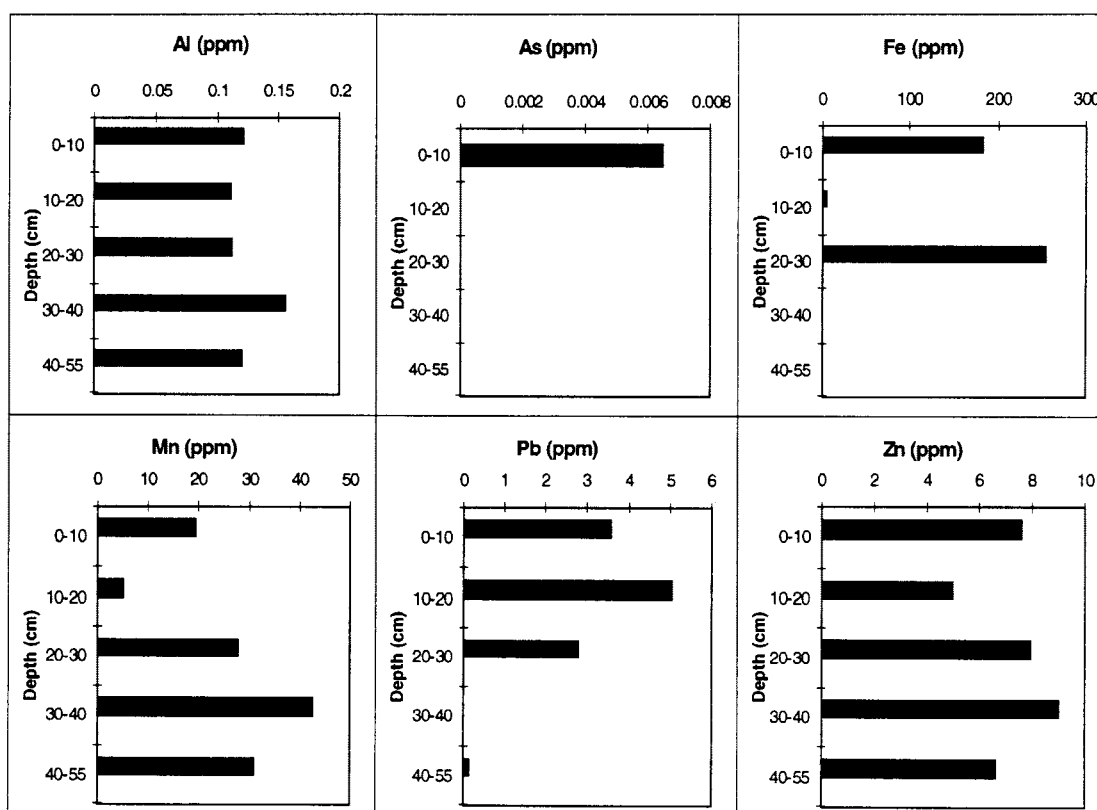


Figure 2.4 Pore water concentrations of Al, As, Fe, Mn, Pb, and Zn with depth.

Arsenic (0.0065 ppm) is found in solution only in the upper 10 cm of the core. Likewise, pore water concentrations for Fe at core depths 0-10 cm, 10-20 cm, and 20-30 cm are 183, 5, and 255 ppm, respectively. These values are observed only in the upper region of the core. The concentrations for Fe are higher than values found after oxygenation of the sediment.

Lead concentration in pore water range from 3 to 5 ppm at 0-30 cm and 0.02 to 0.1 ppm at 30-55 cm, whereas zinc values are between 5 and 7 ppm at 0-30 cm and 6.6-9.0 ppm at 30-55 cm. Manganese concentrations ranged from 5 to 27.7 ppm between 0-30 cm and 30.8 to 42.5 ppm between 30-55 cm. These concentrations were substantial throughout the entire core, and correlate closely with the maximum contaminant released upon agitation and oxygenation (*vida infra*).

Total metal and As concentrations for the solids are shown in Table 2.2.

**Table 2.2: Digestion of 0.5 g of pre- and post-dredged sediments.**

Core depth (cm)	As	Fe	Mn	Pb	Zn
Pre-dredged ----- mg/L -----					
0-1	172	8150	6571	4373	3341
0-10	247	8530	7193	3832	3276
10-20	343	10980	9269	3409	2587
20-30	196	10250	8984	6091	3524
30-40	111	10100	9207	7088	3863
40-54	163	11870	10964	6603	4076
54-55	134	13220	12491	8369	5731
Post-dredged					
T1 (30-55)	479	13360	10391	3963	2493
T2 (0-30)	211	8190	5270	5035	2113

Pre- and post-dredged sediments contain high levels of contaminants, therefore precaution must be taken in their disposal. Further characterization of constituents in the cores helps to delineate amounts of crystalline and noncrystalline materials. Selective dissolution methods have been used to operationally define the partitioning of various inorganic soil constituents (e.g., Jackson et al., 1986). Accordingly, selective dissolution of the sediments were done and the results presented in Table 2.3. High metal values in the organic fraction (Table 2.3) differ from previously reported results (Maxfield et al., 1974; Horowitz et al., 1992; Horowitz et al.; 1993). Therefore, metal partitioning in the core may not be representative of heavy metal distribution found throughout the entire lakebed.

**Table 2.3: Metal content of sediments used for the two dredging trials.**

Core depth (cm)	As	Fe	Mn	Pb	Zn
----- g/kg -----					
<u>Sodium Pyrophosphate-extractable*</u>					
0-1	0.38 ± 0.09	53.49 ± 5.06	11.15 ± 0.64	21.09 ± 1.00	8.80 ± 0.63
0-10	0.44 ± 0.01	50.16 ± 5.13	10.50 ± 1.55	21.23 ± 1.04	8.56 ± 0.48
10-20	0.41 ± 0.04	46.77 ± 0.41	8.05 ± 0.01	22.13 ± 0.33	7.50 ± 0.06
20-30	0.19 ± 0.10	29.73 ± 3.34	3.74 ± 0.28	29.17 ± 1.85	6.52 ± 0.37
30-40	0.16 ± 0.01	31.08 ± 3.42	3.78 ± 0.38	34.94 ± 2.35	7.29 ± 0.57
40-54	0.12 ± 0.07	25.65 ± 3.20	2.79 ± 0.36	28.14 ± 0.13	5.84 ± 0.34
54-55	0.11 ± 0.01	25.42 ± 0.94	3.31 ± 0.01	29.29 ± 0.11	5.78 ± 0.04
<u>AOD-extractable*</u>					
0-1	0.00 ± 0.00	15.96 ± 1.45	1.12 ± 0.08	0.52 ± 0.30	0.71 ± 0.13
0-10	0.00 ± 0.01	12.67 ± 2.41	0.82 ± 0.40	0.39 ± 0.06	0.58 ± 0.09
10-20	0.00 ± 0.00	8.74 ± 0.33	0.58 ± 0.02	0.13 ± 0.01	0.23 ± 0.04
20-30	0.00 ± 0.04	19.43 ± 15.57	1.90 ± 1.89	0.31 ± 0.06	0.60 ± 0.48
30-40	0.00 ± 0.02	19.39 ± 7.62	2.14 ± 0.90	0.20 ± 0.09	0.46 ± 0.24
40-54	0.00 ± 0.02	14.31 ± 7.32	1.37 ± 0.93	0.23 ± 0.05	0.33 ± 0.13
54-55	0.00 ± 0.02	24.99 ± 4.57	2.75 ± 0.68	0.24 ± 0.10	0.40 ± 0.10
<u>CBD-extractable*</u>					
0-1	0.01 ± 0.00	7.17 ± 1.81	0.21 ± 0.02	0.08 ± 0.02	0.19 ± 0.01
0-10	0.00 ± 0.00	7.29 ± 1.13	0.24 ± 0.07	0.08 ± 0.00	0.25 ± 0.01
10-20	0.00 ± 0.00	5.62 ± 0.09	0.27 ± 0.02	0.10 ± 0.08	0.19 ± 0.02
20-30	0.00 ± 0.00	4.66 ± 0.04	0.22 ± 0.02	0.06 ± 0.02	0.17 ± 0.00
30-40	0.00 ± 0.00	4.55 ± 0.06	0.27 ± 0.02	0.06 ± 0.01	0.22 ± 0.05
40-54	0.00 ± 0.00	3.90 ± 0.50	0.19 ± 0.03	0.05 ± 0.02	0.39 ± 0.28
54-55	0.00 ± 0.00	4.45 ± .085	0.21 ± 0.07	0.07 ± 0.00	0.19 ± 0.04
<u>Potassium Chlorate-extractable*</u>					
0-1	0.00 ± 0.01	18.26 ± 0.85	1.82 ± 0.08	0.37 ± 0.19	0.84 ± 0.06
0-10	0.00 ± 0.01	18.47 ± 3.94	1.83 ± 0.42	0.33 ± 0.06	0.80 ± 0.10
10-20	0.01 ± 0.00	30.32 ± 0.95	3.28 ± 0.10	0.24 ± 0.03	0.83 ± 0.05
20-30	0.00 ± 0.00	26.75 ± 0.20	3.10 ± 0.01	0.56 ± 0.00	1.06 ± 0.01
30-40	0.00 ± 0.02	26.31 ± 1.42	3.03 ± 0.24	0.42 ± 0.08	1.04 ± 0.13
40-54	0.00 ± 0.01	29.6 ± 2.00	3.60 ± 0.35	0.58 ± 0.02	1.21 ± 0.08
54-55	0.00 ± 0.02	33.11 ± 1.12	4.16 ± 0.21	0.82 ± 0.16	1.56 ± 0.24

\*-values done in duplicate with standard deviations.

The most significant quantities of As were observed in the pyrophosphate extractions, 0.36 g As/Kg sediment for 0-30 cm depth and 0.12 g As/Kg sediment for 30-60 cm depth, indicating that this element was dominantly partitioned into the organic phase of the sediments (Table 2.3). One should note, however, that pyrophosphate may displace anionic sorbates, such as arsenate or arsenite, thus making these values somewhat tenuous. Similarly, Pb and Zn were also dominantly associated with the organic fraction of the sediments based on SDA. In contrast, Fe was partitioned in the organic, amorphous, and sulfide fractions -- very little crystalline Fe (hydr)oxides were observed. Manganese was dominantly associated with the organic and sulfide fractions of the sediment.

### 2.3.2 Dredging Simulations

The solution pH and Eh and concentration levels of As, Fe, Mn, Pb, Zn were analyzed as a function of time after the sediments were exposed to  $O_{2(g)}$  and agitation; they were then compared to drinking water standards (U.S. EPA, 1994) to address water quality within Lake CDA as dredging occurs. In both dredging trials, pH fluctuates with respect to time (Fig. 2.5).

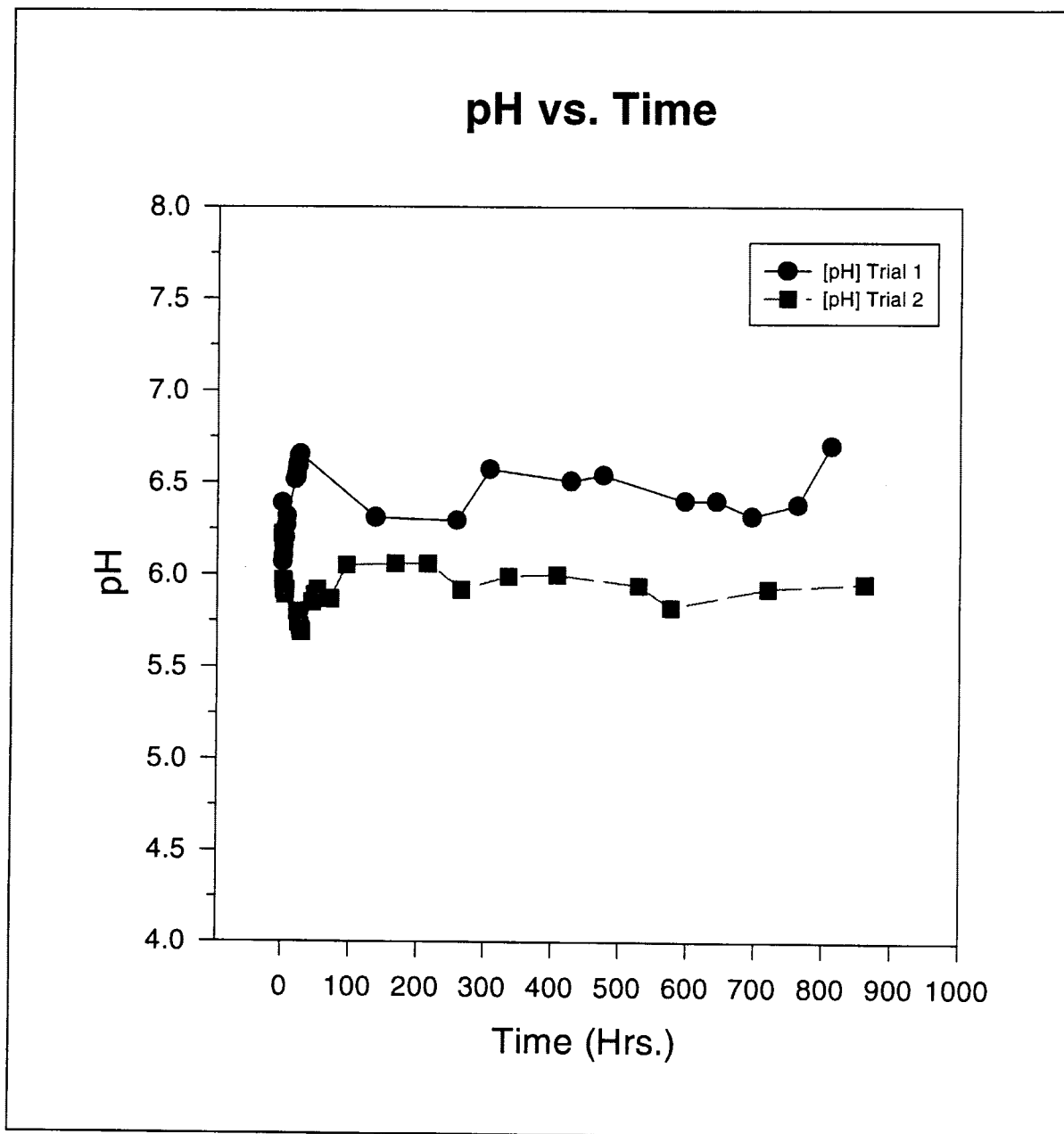


Figure 2.5 Changes of pH upon oxygenation.

The pH for the core-bottom ranged from 6.06 to 6.7, whereas in core-top the pH values range from 5.7 to 6.22.

The Eh (Fig. 2.6) of solution at the start of both trials was less than 300 mV indicating that the sediment suspension were at or below the suboxic/oxic boundary.

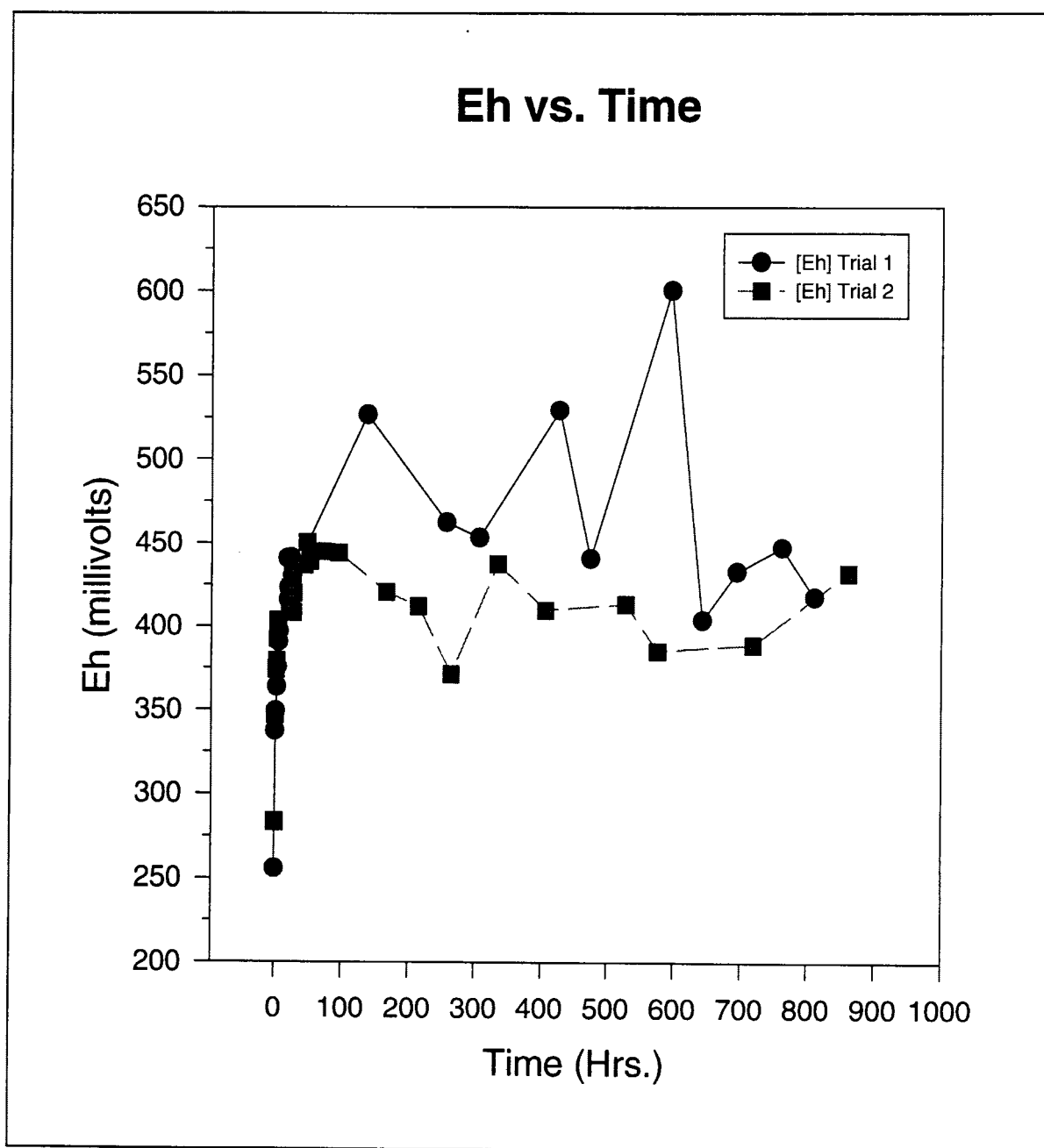


Figure 2.6 Eh values with respect to time.

During both trials, redox conditions changed from suboxic to oxic as time progressed.

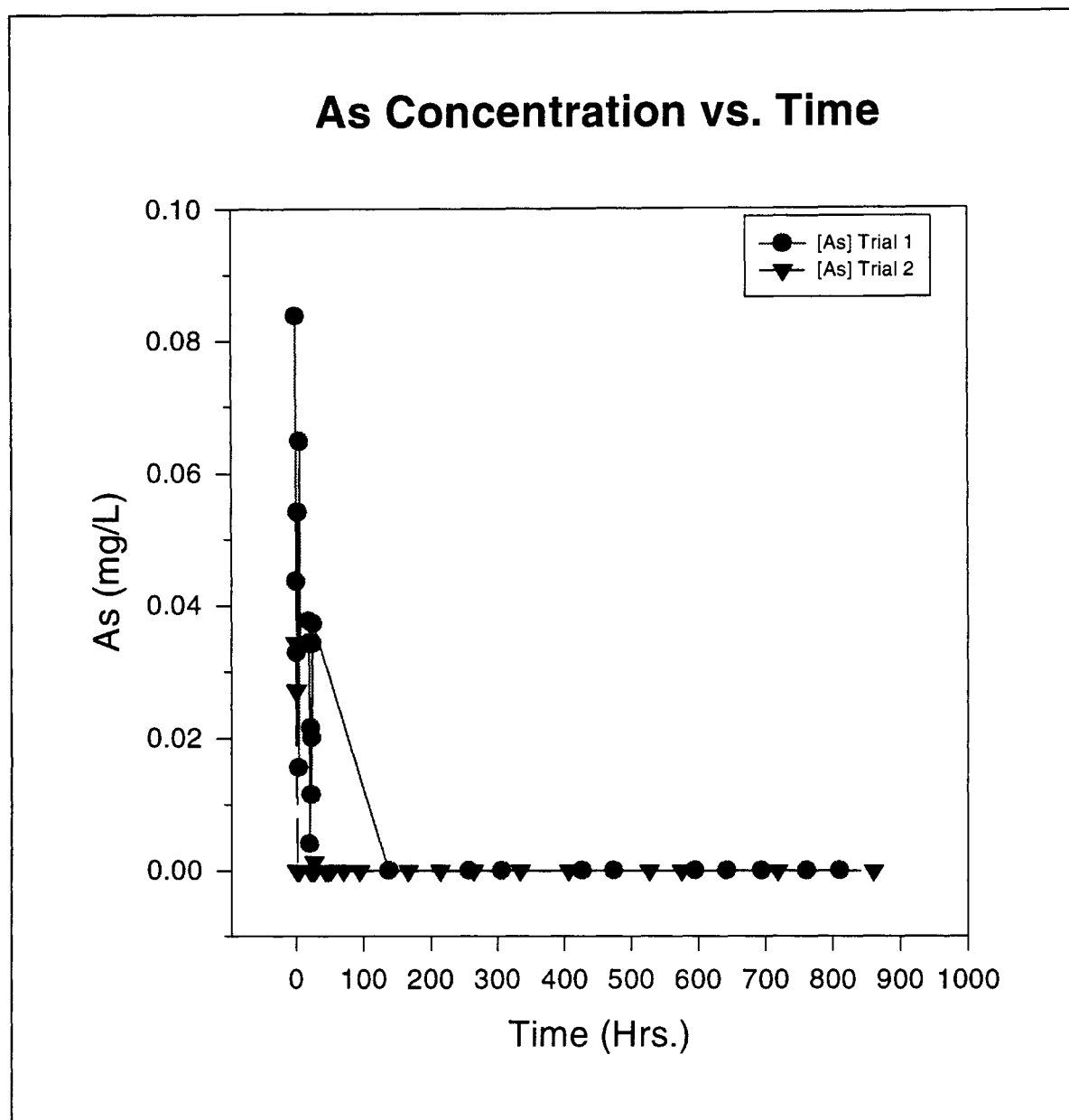


Figure 2.7 As concentration as a function of time.

Arsenic concentrations for the two dredging trials are shown in Fig. 2.7. In the core-bottom trial, the sample taken at the initiation of the experiment contained 0.0838 ppm As, whereas in the core-top dredging-simulation the As value was 0.0343 ppm. For both trials, the highest As values were encountered within the first 100 h and declined to below our detection limits thereafter. The maximum drinking water standard for As (the maximum permissible level of a contaminant in water which is delivered to any user of a public water system) is 0.05 mg/L (U.S. EPA, 1994). This indicates that only the core bottom simulations



had As concentrations at high enough levels to be detrimental to water quality within the lake, for short, transient periods after oxygenation.

For both trials, the Fe concentrations were highest in the first hour (5 and 4.7 ppm) and declined during the first 50 h to below detection limits (Fig. 2.8).

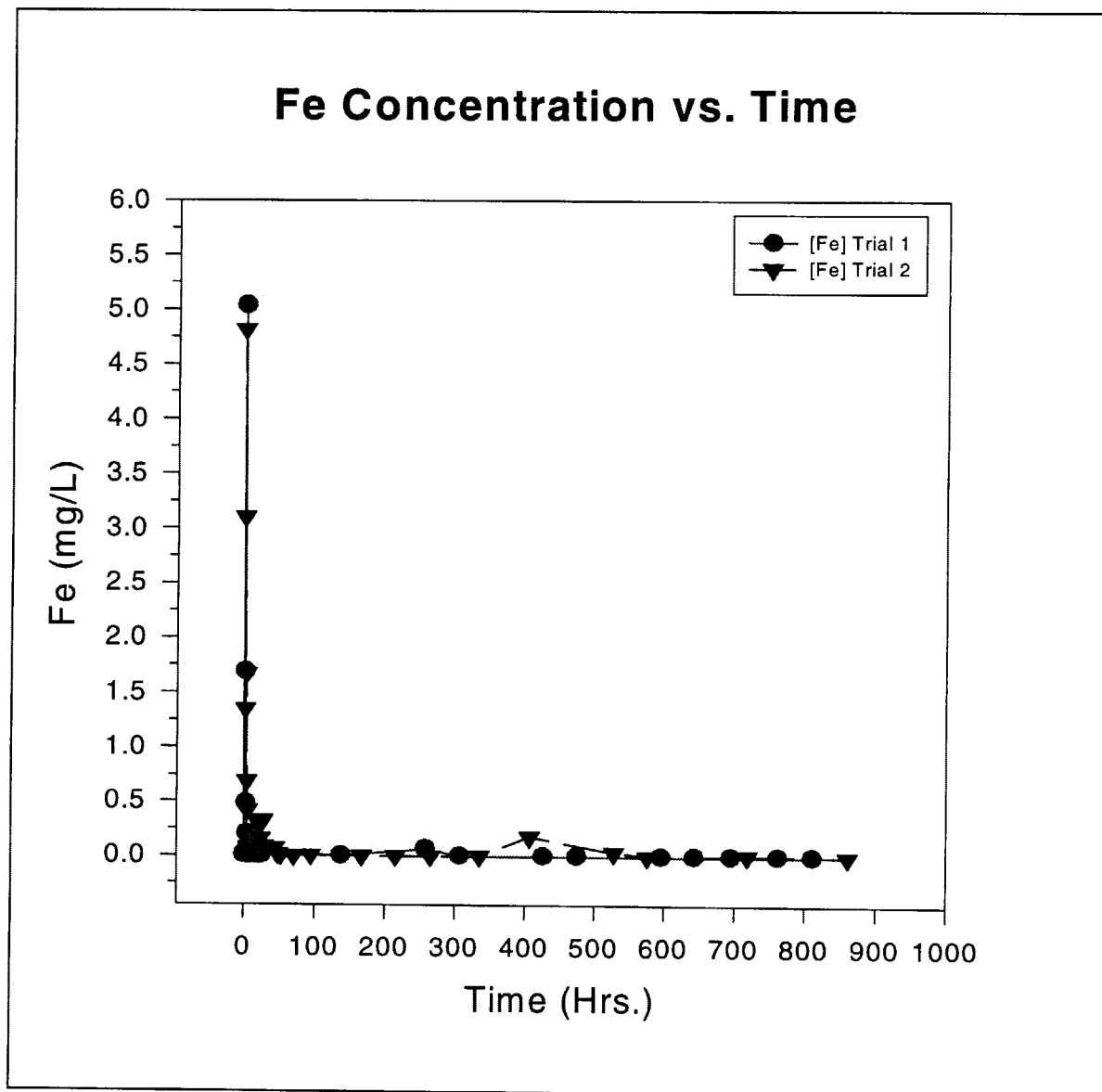


Figure 2.8 Iron concentrations upon oxygenation.

By allowing oxygen into the system, Fe(II) oxidized to Fe(III) which subsequently precipitated as  $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ . Amorphous iron has a high surface area which allows for the adsorption of many metal ions found in solution (Wyman, 1994) and may have been a principle sorbent of metals released upon oxygenation.

In dredging-simulations using the core-bottom, the Mn levels increased to 6 ppm over the first 150 h and remained throughout the 800 h of experimentation (Fig. 2.9).

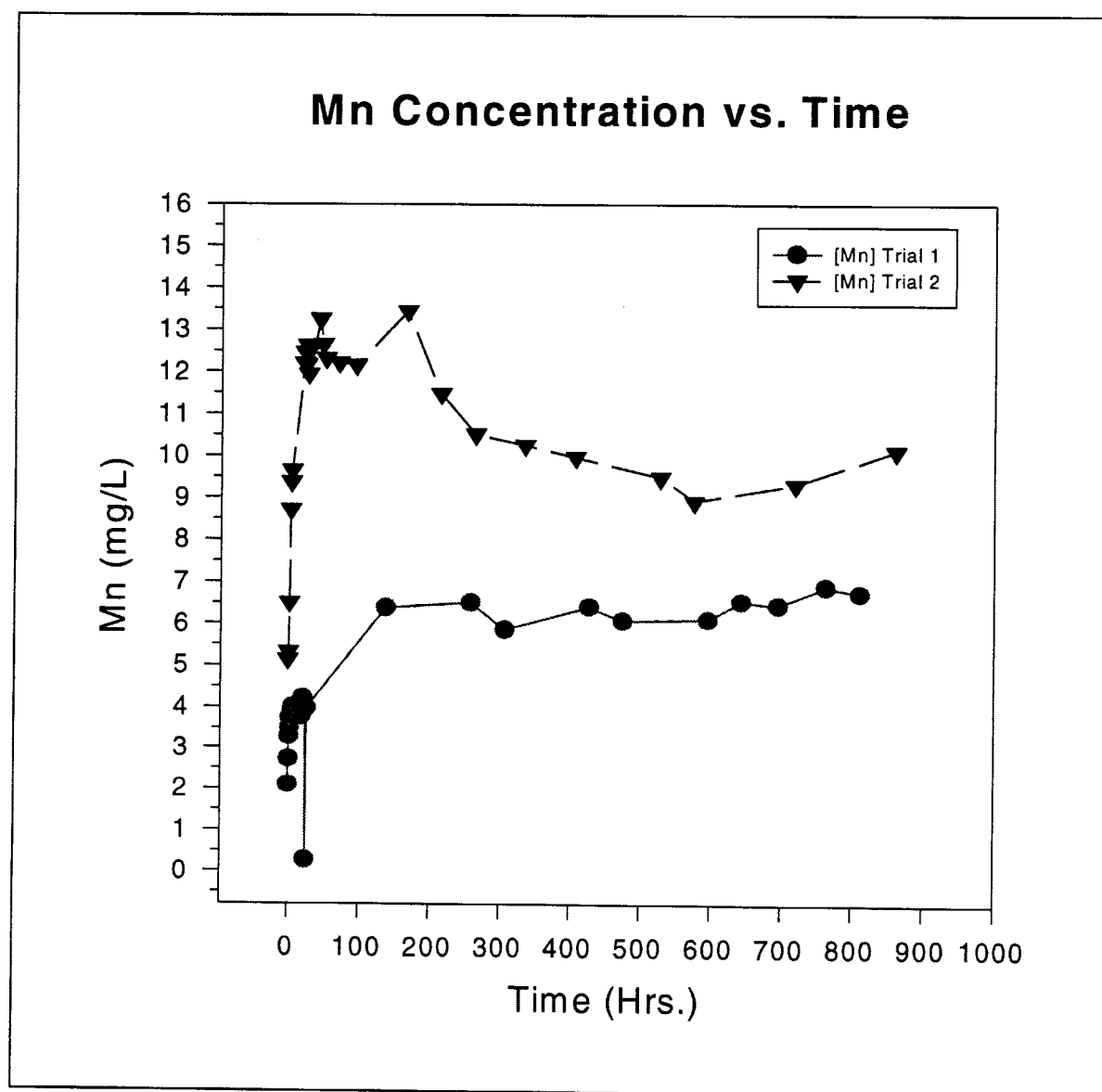


Figure 2.9 Mn concentration of the two solutions from the two dredging trials.

In the core-top dredging-simulation, Mn values increased to 13 ppm within 175 h and gradually decreased to 10 ppm over the next 700 h. Manganese (IV) and (III) are highly insoluble; therefore, the Mn ion in solution is most likely  $Mn^{+2}$ , which upon oxidation precipitated as Mn(III)/Mn(IV)-oxides. The formation of manganese oxides in our system is relevant because they also have a high affinity for many metal ions. Unfortunately, on the basis of the solution data it does not appear that Mn precipitated extensively ( $\Delta Mn_{sol} = 3$  ppm) from solution during the initial 800 h of oxidation.

Lead concentrations (Fig. 2.10) in trial 1 increased to above 0.10 ppm in the first 24 h and dropped to 0.02 ppm after 24 h.

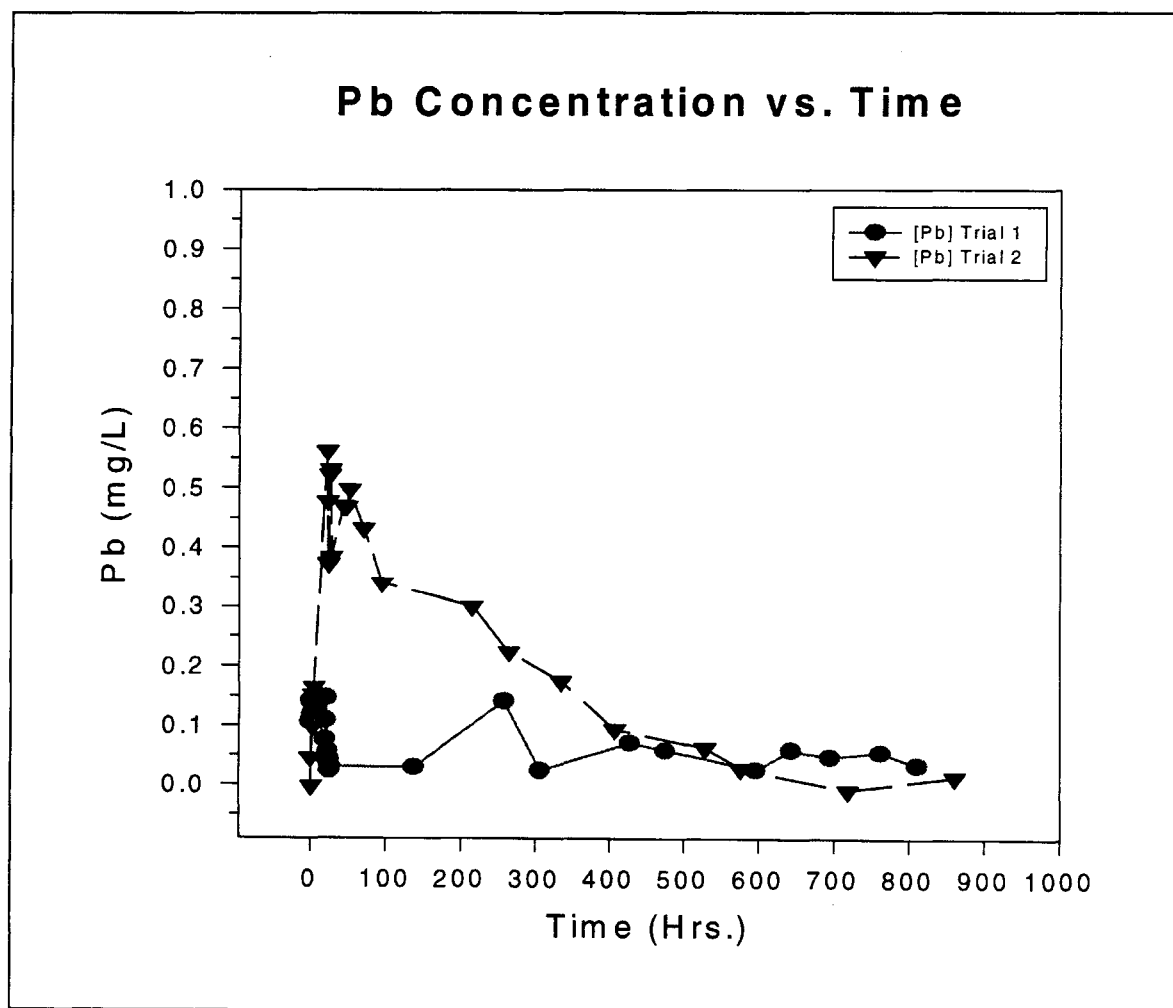


Figure 2.10 Pb concentration with respect to time.

Lead concentrations in trial 2 (core-top) were 0.57 ppm in the first 24 h. After 200 h, the concentrations gradually decline but still remain above 0.015 ppm, the maximum permissible level (U.S. EPA, 1994). The release of Pb for both trials was higher than the U.S. EPA allowable concentration, indicating that the release of Pb from dredging in Lake CDA will have a major short term impact on water quality.

Zinc concentrations (Fig. 2.11) fluctuated between 0.6 and 3.4 ppm in the core-bottom dredging experiment.

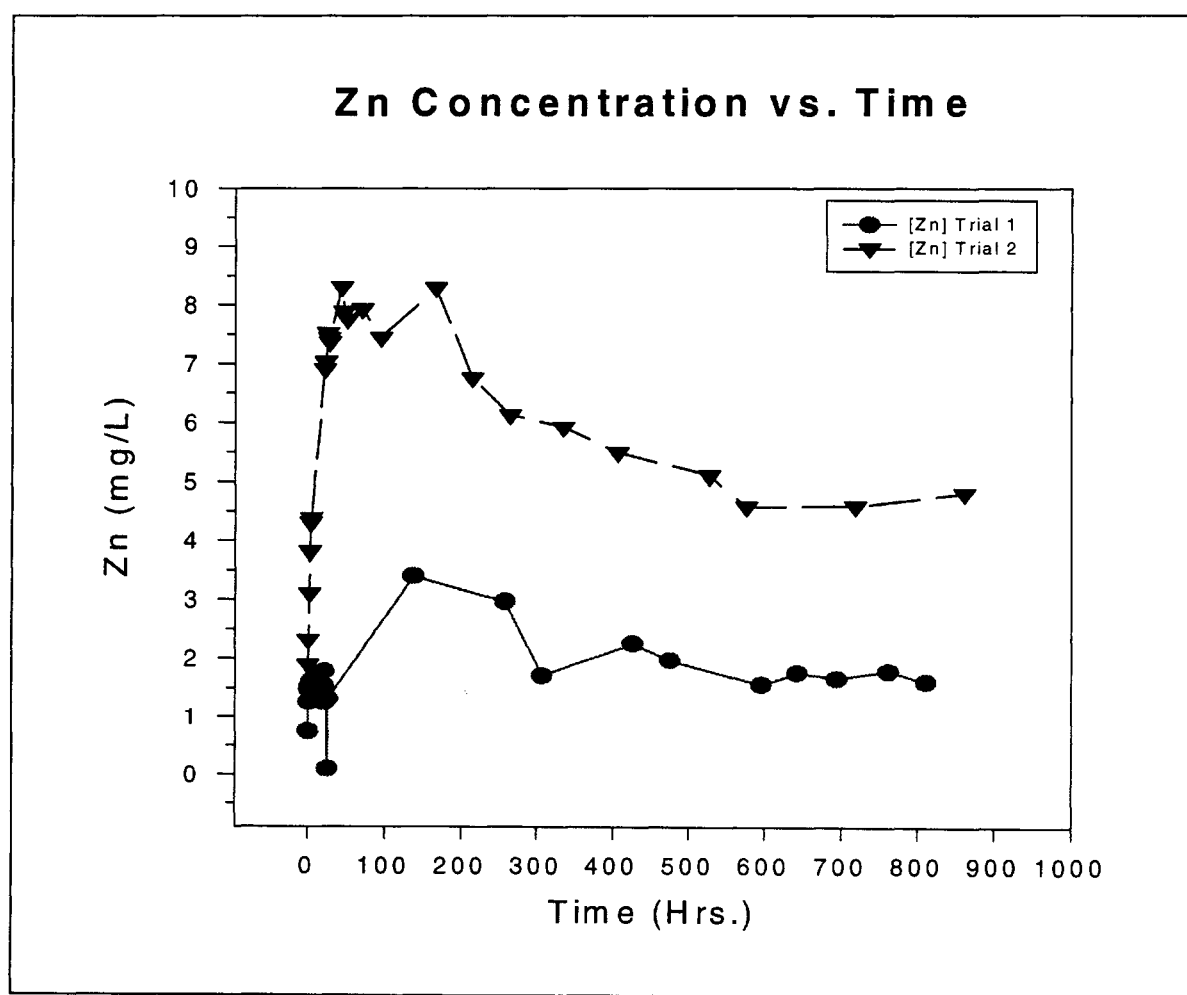


Figure 2.11 Zn concentration as a function of time.

In the core-top dredging experiment Zn increased from 2 to 8.3 ppm in the first 100 h and

gradually declined to about 5 ppm at 600 h. It is evident from the two trials that the release of Zn occurs over extended periods of time and therefore may affect water quality throughout a dredging operation. Furthermore, the release of Zn at these concentrations is extremely detrimental to rainbow trout, *Salmo gairdneri* in the region. The acute toxicity TL<sub>50</sub> 96 hour (toxic limit for 50 percent within 96 hours), is from 0.10 mg/L - 0.91 mg/L depending on the physical parameters of the fish and the chemical characteristics of the river water (Norton, 1980).

The SDA's were also done on the sediment remains from the two dredging trials (Table 2.4).

**Table 2.4: Mineralogical properties of pre- and post-dredged sediments from Lake Coeur d' Alene.**

Core depth (cm)	As	Fe	Mn	Pb	Zn
Pre-Dredged	----- g/kg -----				
	<u>Sodium Pyrophosphate-extractable*</u>				
T1 (30-55)	0.13 ± 0.03	27.38 ± 2.52	3.29 ± 0.25	30.80 ± 0.86	6.30 ± 0.32
T2 (0-30)	0.35 ± 0.06	45.04 ± 3.49	8.36 ± 0.62	23.41 ± 1.10	7.85 ± 0.39
	<u>AOD-extractable*</u>				
T1 (30-55)	0.00 ± 0.00	19.56 ± 6.50	2.09 ± 0.84	0.22 ± 0.08	0.40 ± 0.16
T2 (0-30)	0.00 ± 0.00	14.20 ± 4.94	1.11 ± 0.60	0.34 ± 0.11	0.53 ± 0.19
	<u>CBD-extractable*</u>				
T1 (30-55)	0.00 ± 0.00	4.30 ± 0.47	0.22 ± 0.04	0.06 ± 0.01	0.27 ± 0.12
T2 (0-30)	0.00 ± 0.00	6.19 ± 0.77	0.24 ± .033	0.08 ± 0.03	0.20 ± 0.01
	<u>Potassium Chlorate-extractable*</u>				
T1 (30-55)	0.00 ± 0.00	29.67 ± 1.51	3.60 ± 0.27	0.61 ± 0.09	1.27 ± 0.15
T2 (0-30)	0.00 ± 0.00	23.45 ± 1.49	2.51 ± 0.15	0.38 ± 0.09	0.88 ± 0.06
Post-Dredged	<u>Sodium Pyrophosphate-extractable*</u>				
T1 (30-55)	0.23 ± 0.00	4.43 ± 0.22	0.38 ± 0.02	1.43 ± 0.05	1.20 ± 0.02
T2 (0-30)	0.11 ± 0.03	6.63 ± 0.90	0.21 ± 0.01	2.65 ± 0.48	0.97 ± 0.08
	<u>AOD-extractable*</u>				
T1 (30-55)	0.71 ± 0.15	49.89 ± 6.73	3.24 ± 0.50	0.67 ± 0.01	0.85 ± 0.34
T2 (0-30)	0.54 ± 0.00	41.39 ± 3.64	2.43 ± 0.08	1.18 ± 0.43	0.96 ± 0.22
	<u>CBD-extractable*</u>				
T1 (30-55)	0.80 ± 0.80	39.81 ± 8.78	4.87 ± 0.68	0.02 ± 0.00	0.48 ± 0.14
T2 (0-30)	0.41 ± 0.14	16.43 ± 4.48	2.08 ± 0.63	0.02 ± 0.01	0.31 ± 0.06
	<u>Potassium Chlorate-extractable*</u>				
T1 (30-55)	0.12 ± 0.00	9.46 ± 1.93	0.63 ± 0.21	0.28 ± 0.00	0.74 ± 0.11
T2 (0-30)	0.12 ± 0.03	6.89 ± 1.33	0.47 ± 0.18	0.31 ± 0.12	0.95 ± 0.40

\*values done in duplicate with standard deviations.

The metal values decreased after the pyrophosphate extraction, indicating that during dredging contaminants were released from the organic fraction. The contaminant levels increased in the AOD and CBD extracts. An increase of Fe in the AOD and CBD further supports the precipitation of iron (hydr)oxides during dredging. Furthermore, As, Mn, and

Zn concentrations also increased in CBD extractions after dredging. This indicates that the contaminants sorbed to amorphous and crystalline metal oxides during the dredging process. In the potassium chlorate extracts, Fe and Mn decreased, Pb and Zn remained the same, and the As slightly increased after the dredging simulations. The decrease in Mn and Fe indicates that with oxygenation these contaminants are released from the sulfide bound fractions of the core, in addition to being released from the organic-fraction.

### 2.3.3 Thermodynamic Predictions

The MINTEQA2 speciation program was used to predict  $\text{AsO}_3^{-3}/\text{AsO}_4^{-3}$ ,  $\text{Fe}^{+2}/\text{Fe}^{+3}$ , and various saturation indices. Based on the pH readings, without consideration of carbonate complexes, all of the reduced species are undersaturated with respect to potential minerals at the initiation of the dredging simulations. MINTEQA2 predicted that for the measured pH, Eh, As, Fe, and Mn concentrations the oxidized species of As, Fe and Mn would be favored. This prediction indicates that As(V), the less toxic less soluble species of As, and Fe(III), the less soluble species of Fe, should form. Under oxic conditions, Fe(hydr)oxides, e.g., ferrihydrite, are over-saturated. Therefore, under stable idealized conditions, oxidized species of As, Fe and Mn are predicted to form, with subsequent precipitation of Fe(hydr)oxides and Mn-oxides.

## 2.4 CONCLUSIONS/SUMMARY

High levels of mining wastes in Lake Coeur d'Alene need to be addressed with a remediation plan, which may include dredging. There exists a need to better understand the effects of dredging on inorganic contaminants within lake CDA. The environmental conditions leading to contaminant release from sediments can be better understood by a systematic analysis of cores taken from contaminated lakes.

In pore water extracts, Fe and As were found in the upper part of the core (0-30 cm) whereas Mn, Pb, and Zn were found in amounts well above detection limits throughout the entire core. Arsenic and Pb concentrations were high after the sodium pyrophosphate

extraction procedure indicating that the majority of these contaminants were bound in the organic fraction. Iron was in the organic, sulfidic, and noncrystalline fractions. Manganese and Zn were bound with organic and sulfide fractions. The SDA's of the oxidized sediments of two dredging trials attest that contaminants bound to the organic fraction before dredging were released by dredging, and subsequently were incorporated into the amorphous and crystalline fractions, and Fe and Mn are released from the organic and sulfidic fraction of the core.

The Eh readings taken at the time of sampling indicate that the core was reduced prior to dredging. Arsenic, Fe, Mn, Pb, and Zn contaminant concentrations were analyzed for release into solution with respect to time. Arsenic and Pb concentrations were above maximum contaminant levels for drinking water, indicating that dredging would have an adverse effect on water quality. Furthermore, Zn concentrations were also at levels toxic to freshwater biota.



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## **STUDY TWO: MOBILITY OF TRACE-ELEMENT CONTAMINANTS UPON FLOODING OF SEDIMENTS IN THE COEUR D'ALENE RIVER, IDAHO.**

### **3.0 SUMMARY**

The Main Stem (MSCDR) and South Fork (SFCDR) of the Coeur d'Alene River, ID are contaminated with heavy metals from numerous years of mining. Accordingly, an environmental remediation plan is necessary to control the release of heavy metals as flooding occurs in this region. In order to address the environmental ramifications of flooding, water quality in the river system was assessed, contaminants in the riverbank sediments were geochemically phase partitioned, and their release were measured under simulated laboratory flooding experiments. To simulate flooding experiments, 18 columns were constructed allowing the sediment-water interface to be monitored for pH, Eh and dissolved concentrations of As, Fe, Mn, Pb, and Zn. These columns were subjected to two flooding events. The first event involved the addition of  $N_{2(g)}$  or  $O_{2(g)}$  purged river water to the columns and the second event had purged river water amended with a nutrient source (D-glucose). During the first event, Zn was released at an average concentration of 10.41 mg/L into solution from sediment taken along the MSCDR at Cataldo, ID. For the second event, nutrient loading stimulated microbial activity which in turn increased aqueous contaminant levels drastically from sediments at all three sites; mean values of trace element contaminants from the three sites are As = 1.54, Pb = 7.57, and Zn = 79.29 mg/L. The release of contaminants due to flooding is degrading water quality in the river system and may be detrimental to the aquatic biota. Our results indicate that sediments currently situated in the riverbanks are releasing contaminants into the river system as flooding occurs and a remediation plan is necessary to eliminate this problem. In particular, extreme precaution must be used in the region to limit nutrient additions into the river system.

### 3.1 INTRODUCTION

The Coeur d'Alene mining district in northern Idaho has been active for over 100 years. Between the years 1884 to 1991, mines in the region produced 1 billion troy ounces of silver, 187,815 tons of copper, 8,014,041 tons of lead, 3,243,269 tons of zinc, and 518,552 troy ounces of gold (Springer 1993; Hoffman, 1995). With the production of large quantities of ore came the onset of extensive mine and milling wastes. Waste removal practices in the early years of mining entailed storing wastes on site or disposal of them into adjacent waterways. The distribution, quantification, and environmental ramifications of these wastes has been examined extensively (Ellis, 1932; Galbraith, 1972; Maxfield et al., 1974; Ioannou, 1979; Rabe and Bauer, 1977; Keeley, 1979; Wai et al., 1985; Wai and Mok, 1985; Mok and Wai, 1990; Bender, 1991; Horowitz et al., 1992; Horowitz et al., 1993; Hoffman, 1995; Horowitz et al., 1995). According to Ellis, in 1932, there were no fish fauna, bottom fauna, or plankton living in the Main Stem or South Fork of the Coeur d'Alene River (SFCDR), or in Lake Coeur d'Alene near the inlet of the MSCDR. In the summer of 1973, Rainbow trout placed in live boxes at several locations in the Coeur d'Alene River died within 48 hours (Funk et al., 1975). Today, fish and other aquatic life are returning to the MSCDR.

Recent flooding that has occurred in the region is spreading mine wastes from riverbanks and tailing deposits into nearby agricultural areas. The redistribution of mine wastes and flooding caused temporary evacuation in the region during the spring of 1996. As reclamation processes attempt to remediate the area it is imperative to understand the damage that preexisting mine wastes situated in the riverbanks are having on the aquatic biota.

Arsenic in aquatic environments has been studied extensively (Brannon and Patrick, 1987; Moore et al. 1988; Seyler and Martin, 1989; Belzile and Tessier, 1990; Mok and Wai, 1990; Anderson and Bruland 1991; Cornett et al., 1992; Driehaus et al., 1995). Seyler and Martin (1989) state that based on thermodynamic calculations As(V) is mainly found in oxic waters, whereas in anoxic systems As(III) should be the stable form. According to Mok and Wai (1990), samples collected from January to June 1987 in the Coeur d'Alene river system

contained predominantly As(III) in the Main Stem and the South Fork, while As(V) was observed in the North Fork. Both Pb and Zn are present as divalent cations in aquatic systems; Pb has a tendency to form compounds of low solubility with major anions of natural waters, while Zn is usually more soluble (Hem, 1976; Vymazal, 1985; McKee, 1989; Tessier et al., 1989; Marani et al., 1995). From April to August 1969, Pb was found in solution at values less than 0.1 mg/L (Mink, 1971). However, from January to June 1987, Zn values in the Coeur d'Alene system were as high as 2.73 mg/L in the South Fork, whereas in the Main Stem they were lower at 0.47 mg/L (Mok and Wai, 1990). Manganese and iron are redox active, with reduced divalent species being soluble and higher oxidation states, Fe(III), Mn(III), and Mn(IV), being comparatively insoluble in natural waters (Murray, 1975; McKenzie, 1979; Wilson, 1980; Tessier et al., 1985; Sigg, 1987; Matsunga et al. 1993).

To recommend remediation actions, the objectives of this study include: assessing water quality in the river system; categorizing contaminant phase partitioning in the sediment; measuring the release of metals under simulated minor and major flooding events; and measuring the release of contaminants when a supplemental nutrient source (e.g., septic tanks and sewage) leaches into the Coeur d'Alene River system during a flooding event. To meet the objectives of the study, three sampling sites were studied: (i) The MSCDR near the inlet of lake CDA, (ii) The MSCDR at Cataldo just below the confluence of the North and South Fork of the Coeur d'Alene, and (iii) SFCDR near the Shoshone county airport in Smelterville, ID, which drains the mining district and has sediments classified as ore quality (Swanson, 1992) (Figure 3.1). Site (i) was chosen to address water quality entering Lake CDA, site (ii) was chosen to determine how metals are released into the larger Main Stem River system, and site (iii) was chosen to determine how metals are released in the smaller South Fork River system.

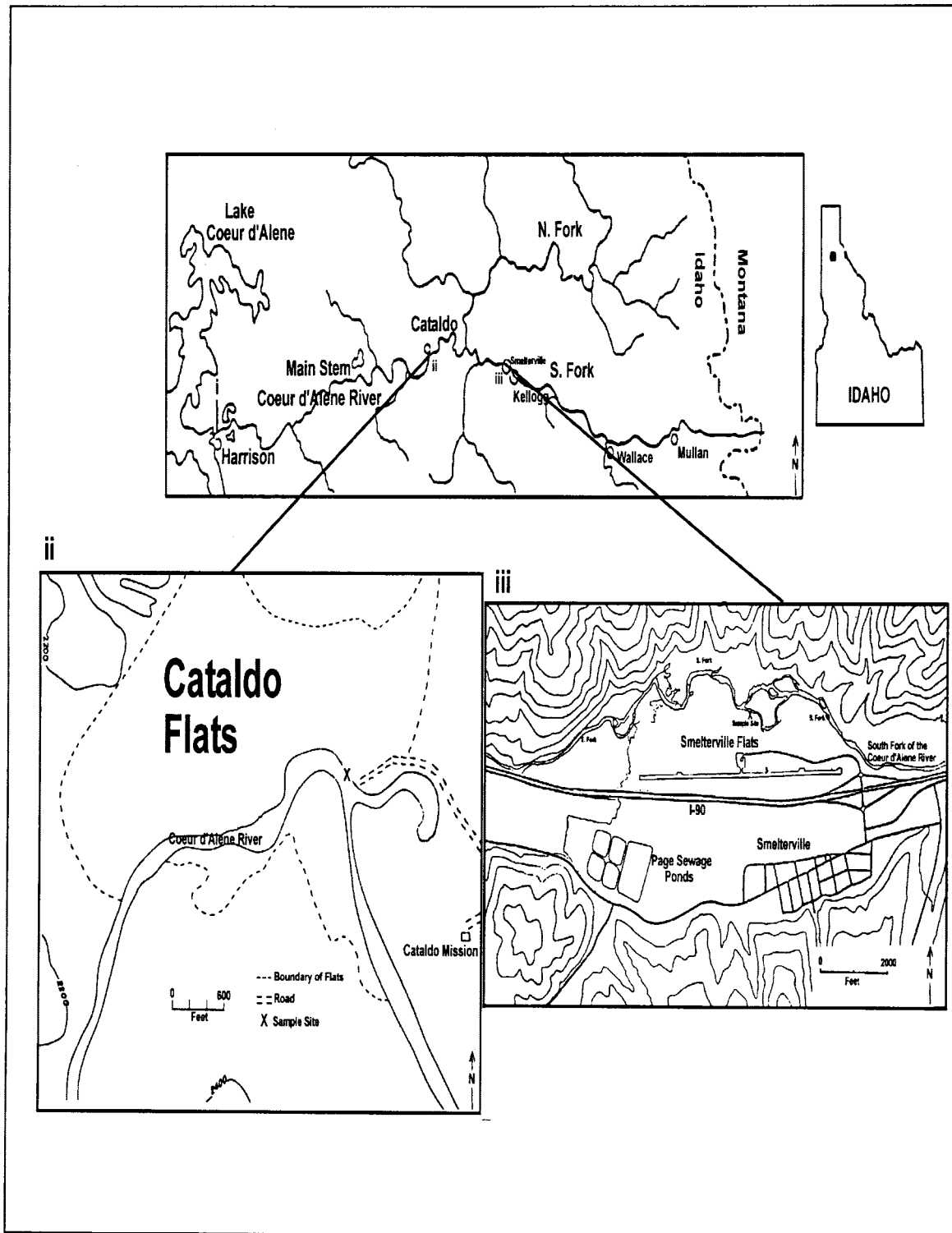


Figure 3.1 Location map of the Coeur d'Alene River system and sampling locations used in this experiment. (Galbraith et al., 1972; Mok and Wai, 1990; Swanson, 1992).



## 3.2 MATERIALS AND METHODS

### 3.2.1 River Characteristics

The SFCDR flows from its headwaters in the Bitterroot Mountains to where it meets the North Fork of the Coeur d'Alene River 4.8 km above Cataldo at Enaville, ID., and then it continues as the MSCDR for 48.2 km to Lake CDA (Bender, 1991). The SFCDR drains the CDA mining district and has a drainage of 434.5 km<sup>2</sup>, whereas the MSCDR has a drainage area of about 257.5 km<sup>2</sup> (Mink, 1971). The SFCDR is a relatively shallow and swift-moving stream with a gradient of about 14.7 m/km, whereas the MSCDR is relatively deep and slow moving (Norbeck, 1974). The area of the entire basin that both rivers flow through is roughly 2221 km<sup>2</sup> (Mink, 1971). The SFCDR and MSCDR are polluted with 1.22 m and 3.05 m of wastes from jig tailings (an early mining technique) and finer grained wastes from selective flotation (Norton, 1970; Norbeck, 1974; Bennett, 1994).

### 3.2.2 Column Construction

Eighteen columns (45.72 cm lengths of 3.81 cm inside diameter GENOVA PVC Piping) were used for this experiment. In the columns, three ports were located at: (a) the sediment-water interface, (b) 7.62 cm below the interface, and (c) at the bottom of the column. After sampling, Tygon<sup>®</sup> tubing containing glass wool was inserted into each port and sealed with epoxy. The tubing allowed for insertion of pH and Eh electrodes directly into the columns. The top caps of the columns contained 2 ports, a gas inlet and outlet, which permitted gas purging of each column (Fig. 3.2). The outlet port was submerged in a water trap to prevent oxygen from diffusing into the N<sub>2(g)</sub> purged columns.

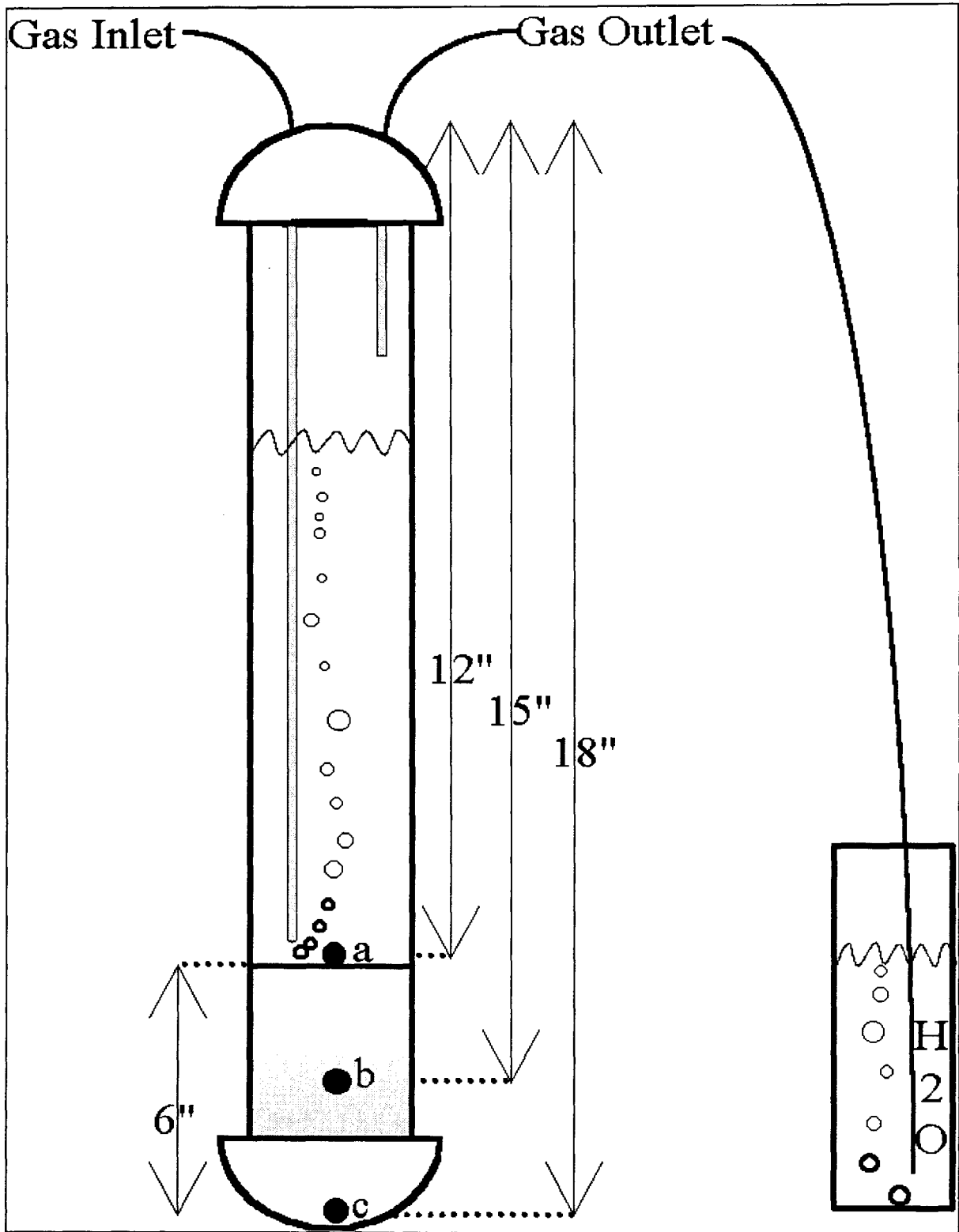


Figure 3.2 Column used for the simulated laboratory flooding trials.

### 3.2.3 Sampling Procedure

Cores were extracted perpendicular to the riverbank sediment to depths of 15.2 cm. After sediment collection, the bottom of each column was capped and the columns were brought back to our laboratory; 30.5 cm of the column was left above the sediment allowing for the addition of 250 mL of river water. Upon extraction, river level was 30.5 cm below the cores and land surface was 40.6 cm above the cores. Six cores were extracted from three sites (cores 1-6 were taken from MSCDR near the inlet to Lake CDA, cores 7-12 from MSCDR at Cataldo, and cores 13-18 from SFCDR at Smeltonville) for a total of 18 cores on March 15, 1996. Prior to each flooding event, 18, 1 L Nalgene bottles of water were collected (6 from each of the three sites) while measuring pH, Eh (mV), and dissolved oxygen (DO), the water was brought back to the laboratory, filtered through a 0.45  $\mu\text{m}$  membrane filter, and analyzed for dissolved Al, As, Fe, Mn, Pb, and Zn. The water from the bottles was used to flood the corresponding columns (i.e., bottle 1 flooded column 1, bottle 2 flooded column 2, etc.). The data presented in this study are from the port located at the sediment-water interface. All materials used in this experiment were acid rinsed (0.5 M HCl) prior to use.

### 3.2.4 Chemical Extractions

Two sets of SDA's (selective dissolution analysis) were done on the sediment from the columns. The first set was initiated to operationally define the partitioning of elements in the organic, amorphous, crystalline, sulfide, and the remaining crystalline fractions from the riverbank sediment. The second set was done to determine the operationally defined exchangeable, carbonate, iron and manganese oxides, organic, and remaining crystalline fractions. Both sets were initiated in duplicate with a 0.5 g sample (with controls and blanks) from the columns and rinsed with 5 mL distilled, deionized (DI) water after each extraction procedure.

The first extraction was a 0.1 M sodium pyrophosphate solution, which was used to extract ions associated with the organic-phase of the sediments (Alexandrova, 1960;

McKeague, 1967; Bascomb, 1968; McKeague et al., 1971; Stevenson, 1982; Soil Survey Staff, 1992; Dahlgren, 1994). Unfortunately the sodium pyrophosphate may displace anionic sorbates, such as arsenate or arsenite, and has trace amounts of arsenic making these values somewhat tenuous. For the next extraction, 0.0125 g of sediment was reacted with 0.2 M ammonium oxalate in the dark (AOD) to remove the noncrystalline materials (McKeague and Day, 1966; McKeague et al., 1971; Schwertmann, 1973; Fey and LeRoux, 1977; Hodges and Zelazny, 1980). The remaining solids (0.485 g) were then reacted with a 0.3 M sodium citrate, 1 M sodium bicarbonate, and 0.5 g sodium dithionite (CBD) solution to remove the crystalline and noncrystalline iron and manganese (hydr)oxides of the sediment solids (Aguilera and Jackson, 1953; Mehra and Jackson, 1960; Arshad et al., 1972; Jackson, 1979; Jackson et al. 1986; Dahlgren, 1994). Then a  $\text{KClO}_3/\text{HCl}$  treatment followed by 4 N boiling  $\text{HNO}_3$  was performed to remove the sulfide fractions (Chao and Sanzolone, 1977). Finally, an aqua regia/hydrofluoric digestion of the remaining solids was done by 3 mL 3-1-2  $\text{HCl-HNO}_3\text{-H}_2\text{O}$  at  $95^\circ\text{C}$  for 1 h, then cooled and followed by 5 mL of  $\text{HF}$ , shaken, and then neutralized with 20 mL saturated boric acid and 0.5 g of  $\text{HBO}_{3(s)}$  (Jackson, 1979; Sridhar and Jackson, 1974).

The second set of chemical extractions was initiated by adding 4 mL of 1 M  $\text{MgCl}_2$  at pH 7 for 1 h to remove the exchangeable metals from the contaminated riverbank sediments (Gupta and Chen, 1978; Tessier et al., 1979; Tessier et al., 1989). The sediment was then leached with 4 mL of 1 M Na-acetate/acetic acid at pH 5 to remove the carbonate fraction (Gupta and Chen, 1978; Tessier et al., 1979; Tessier et al.; 1985). Next, the Fe and Mn oxides were removed via the addition of 10 mL of 0.3 M  $\text{Na}_2\text{S}_2\text{O}_4$  + 0.175 M Na-citrate + 0.025 M H-citrate (Anderson and Jenne, 1970; Tessier et al., 1979; Brannon and Patrick, 1987; Moore et al., 1988). Then the organic fraction was analyzed after 1.5 mL of 0.02 M  $\text{HNO}_3$  was heated to  $85^\circ\text{C}$  for 2 h, followed by 2.5 mL 30%  $\text{H}_2\text{O}_2$  (adjusted to pH 2 with  $\text{HNO}_3$ ) heated to  $85^\circ\text{C}$  for 3 h, and then a second addition of 2.5 mL 30%  $\text{H}_2\text{O}_2$  (adjusted to pH 2 with  $\text{HNO}_3$ ). Upon cooling, 5 mL of 3.2 M  $\text{NH}_4\text{OAc}$  in 20% (v/v)  $\text{HNO}_3$  was added and the whole solution was diluted with 10 mL DI water (Gupta and Chen, 1978; Tessier et al., 1979). Finally, the residual was subjected to a complete digestion as described above

(Jackson, 1979; Sridhar and Jackson, 1974). Both sets of extractions were filtered through a 0.45  $\mu\text{m}$  membrane filter prior to ICP analysis.

### 3.2.5 Flooding Simulations

Eighteen cores from the three sites were subjected to 4, 14 day flooding events (trials *a*, *b*, *c*, and *d*, respectively). Water samples for the 4 trials were collected on 4/20/96 for trial *a*, 6/13/96 for trial *b*, 7/20/96 for trial *c*, and 8/31/96 for trial *d*. In the first two events, sampling was taken in 8 mL aliquots, refrigerated, filtered through a 0.45  $\mu\text{m}$  membrane filter, whereas for the third and fourth trials, samples were immediately filtered and acidified with 2 drops concentrated HCL prior to ICP analysis. The *a*, *b*, and *c* trials were all done similarly, whereas trial *d* involved adding 1.25 g D-glucose and 0.625 g ammonium sulfate to the water simulating an added nutrient source leaching into the river system.

Six cores from each site were flooded with 250 mL of water, while 3 cores were purged with  $\text{N}_{2(\text{g})}$  and 3 cores were purged with air. Cores 1-3, 7-9, 13-15 were purged with  $\text{N}_{2(\text{g})}$  and cores 4-6, 10-12, 16-18 were purged with air (Fig. 3.3). The cores purged with  $\text{N}_{2(\text{g})}$  are simulating a deep flooding event, whereas the cores purged with air are simulating a minor flooding event. The  $\text{N}_{2(\text{g})}$  purged columns simulate high flood stages (deep water environments) which are limited in dissolved oxygen content, whereas the air purged columns are simulating a minor rise in water levels where surface waters are higher in dissolved oxygen. In all four flooding events, the port at the sediment-water interface of each column was monitored for pH, Eh, and dissolved concentrations of Al, As, Fe, Mn, Pb, and Zn.

### 3.2.6 Analytical Procedures

Direct electrode potentials (Eh, relative to the standard hydrogen electrode) were determined using a MI-800-411B Redox electrode (Microelectrodes<sup>®</sup>). The electrode was placed at the sediment-water interface, and the potential (mV) was recorded after a stable reading was obtained. Likewise, pH was determined at the sediment-water interface using a

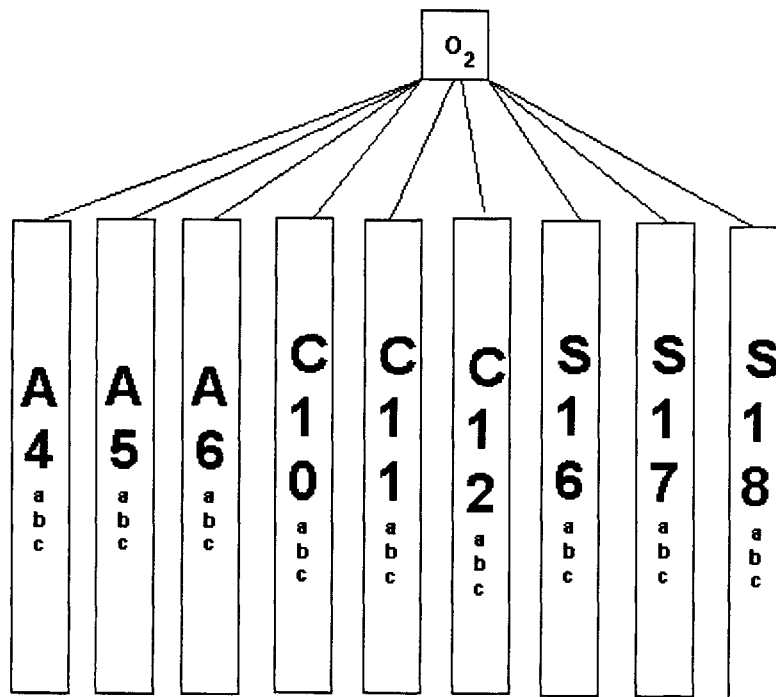
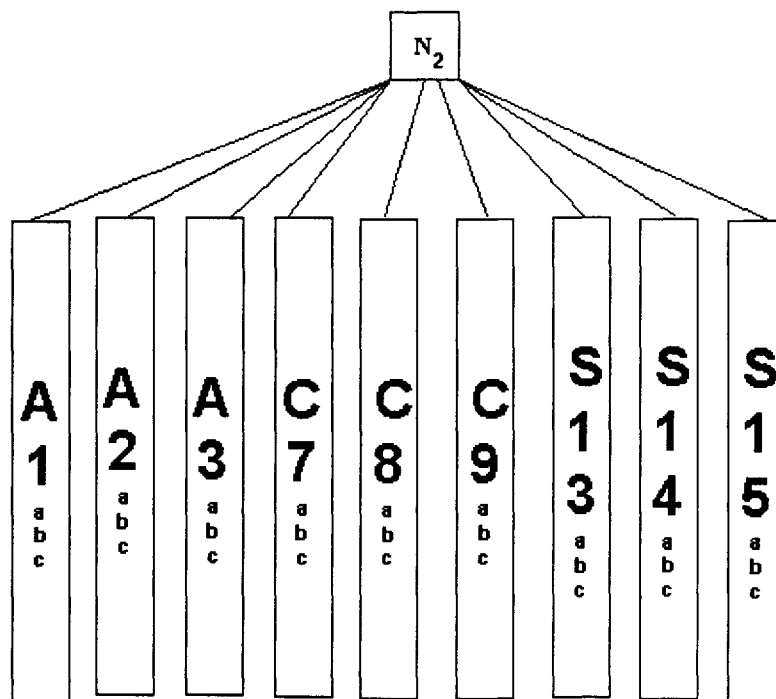


Figure 3.3 Columns purged with  $N_{2(g)}$  and air ( $O_{2(g)}$ ), (A= site i, C=site ii, S=site iii).

MI-411B Micro-combination pH probe (Microelectrode®). Dissolved ion concentrations of Al, As, Fe, Mn, Pb, and Zn were measured by inductively coupled plasma (ICP) optical emission spectrophotometry (Thermo Jarrell Ash IRIS ICP-OES).

Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), selective dissolution analysis (SDA) were done on the sediment from the three sites. The SEM was performed on a Amray 1600; XRD was performed using a Siemens D5000 Diffraktometer; and the SDA's were done following procedures by Tessier et al. (1979), and Jackson et al. (1986). Scanning Electron Microscopy was done to look at the composition of sediment for the experiment while EDS was done to quantify contamination on grains from the three sites. X-ray diffraction was utilized to determine the crystalline constituents in the homogenized riverbank sediment.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Solid-Phase Characterization

X-ray diffraction was used to determine the crystalline components of sediments from the three sites. The sediment from the MSCDR near the inlet to lake CDA contained quartz, muscovite, and siderite. The samples from Cataldo and Smeltonville contained crystalline quartz and muscovite.

The results from EDS of materials from the three sites are shown in Table 3.1.

**Table 3.1: EDS of sediment from the three sites.**

Site	%	Al	As	Fe	Mn	Pb	Zn
		----- % -----					
i	Atomic	10.93	0.62	23.27	1.10	0.36	0.41
	Wt.	8.14	1.29	35.91	0.16	2.08	0.74
ii	Atomic	13.13	0.55	23.46	0.52	0.21	0.45
	Wt.	9.87	1.16	36.53	0.80	1.22	0.82
iii	Atomic	13.97	0.83	21.18	1.91	0.41	0.51
	Wt.	10.44	1.72	32.76	2.90	2.34	0.93

At the three sites, Fe is the most abundant elemental constituent of the wastes followed by Al. All the solids from the three sites have elevated concentrations of As, Pb and Zn associated with mine and milling wastes (Ellis, 1932; Bennett, 1994). The sediment from site i (which is situated farthest from the CDA mining district) is a result of selective floatation which created fine grained wastes that were transported farther downstream reaching Lake CDA (Bennett, 1994). The sediment from site ii came from the riverbank situated at Cataldo Mission Flats. The flats formed as a result of dredging of preexisting mine wastes from the river. The wastes in the region are mainly from jig tailings which are larger size and from early mining operations. Finally, the solids from Smeltonville (site iii) contained the highest amounts of As, Mn, Pb, and Zn. This material is from the SFCDR which directly drains the CDA mining district and is situated in the Bunker Hill Superfund Site.

### 3.3.2 Phase Partitioning of Contaminants

The results from the geochemical analysis of twelve sediment samples from each site are shown in Tables 3.2 and 3.3. Phase partitioning of metals in sediments provide an assessment of their reactivity and bioavailability. Contaminants bound in the organic fraction are available for release by microbial oxidation. Two extractions (sodium pyrophosphate and hydrogen peroxide) were used to quantify contaminants in this fraction of the sediments. Metals are retained via electrostatic forces on some solids and to quantify these amounts an exchangeable extraction was used. In the Coeur d'Alene region a common constituent of the gangue material is siderite, calcite, dolomite and other carbonates. Changes in pH can release contaminants that are bound to carbonates; therefore, an extraction procedure was used to determine contamination associated with this sediment fraction. Heavy metal mobility in aquatic systems is affected by redox cycling of iron and manganese. Extractions used to reduce Fe(III) and Mn(IV) can quantify contamination associated with these elements and give information on contaminant release upon reductive dissolution of such solids. Finally, mine tailings in the region come from mined sulfide ores.



Therefore, a potassium chlorate extraction was used to determine how ions bound with sulfides could become available as oxidative dissolution occurs in the sediments.

Based on the sodium pyrophosphate extraction (Table 3.2), Fe, Mn, and Pb are the most abundant elements in the organic fractions of the sediment. Aluminum concentrations at the MSCDR near the inlet to Lake CDA are lower than at Cataldo or Smeltonville. Arsenic values are low, ranging from 10.95 at Cataldo to 31.95 mg/kg As at MSCDR near the inlet to Lake CDA. Zinc concentrations are high in the organic fraction from sediments at Cataldo and Smeltonville, which are in close proximity to the old smelter located at Bunker Hill.

The (AOD) extraction and the (CBD) extraction (Table 3.2) indicate that Fe and Mn are abundant in the noncrystalline and total oxide fractions. Therefore, contaminants bound to these materials may be released upon reductive dissolution. In general, As is associated with noncrystalline solids (66.26 to 140.17 mg/kg), whereas the total in the CBD extractable crystalline and noncrystalline material is 60.51 to 230.09 mg/kg. Lead is abundant in both the AOD and CBD extractions of the sediment. Lead in the noncrystalline (AOD) fraction may feasibly be dissolved from the grain coatings during flooding and is of environmental concern in the region. There is abundant Zn associated with Fe and Mn oxides in the sediment from the three sites. Zinc is likely associated with manganese oxides (Zasoski and Bureau, 1988) which are a common constituent of the mine wastes in the area.

The potassium chlorate extraction (Table 3.2) shows that substantial amounts of Al, Fe, Mn, Pb, and Zn are bound as sulfides. However, As is found in similar concentrations (51.96 to 143.58 mg/kg) as the preceding extractions. Arsenopyrite ( $\text{FeAsS}$ ), pyrite ( $\text{FeS}_2$ ), galena ( $\text{PbS}$ ), and sphalerite ( $\text{ZnS}$ ) were mined throughout the district (Hobbs et al., 1965; Bennett et al., 1989; Horowitz et al., 1992;). Therefore, it is not surprising that Al, Fe, Mn, Pb, and Zn associated with mine wastes would be bound as sulfides in the sediment and contaminants would be available as oxidative dissolution occurs. The aqua regia/hydrofluoric extractions (Table 3.2) attest that there is not a lot of As, Mn, Pb, and Zn strongly bound in the remaining solids. However, there are still relevant amounts of Al and Fe within the solid fractions.

In the exchangeable fractions (Table 3.3), only Mn, Pb, and Zn were detected. All the elements studied were present in the carbonate extractions (Table 3.3), with Pb, Zn, and Mn being the most abundant. Based on x-ray diffraction, siderite ( $\text{FeCO}_3$ ) is found in sediment from the Smeltonville site. Consequently, Fe values should be much higher than noted by this extraction.

Metals removed from the organic fraction (Table 3.3) via hydrogen peroxide have substantially higher values for Al, Fe, Mn, Pb, and Zn than those removed with the sodium pyrophosphate extraction (Table 3.2). Hydrogen peroxide used in extraction of organic matter is much more aggressive than sodium pyrophosphate; thus, the higher results are expected and procedurally dependent (Lavkulich and Weins, 1970).

In the second set of extractions, a citrate dithionite (C-D) extraction was used to remove total iron and manganese oxides from the sediment without differentiating between crystalline and noncrystalline fractions, i.e., AOD was not performed prior to the C-D extraction. As mentioned previously, metals bound to iron and manganese oxides (Table 3.3) may be released during redox cycling of Fe and Mn. Arsenic values (53.19 to 154.73 mg/kg) are extremely high compared to the results from the prior two extractions (exchangeable, and carbonate) indicating it may be released during reductive dissolution of Fe or Mn oxides. In the C-D extracts aluminum concentrations are high (243.92 to 786.78 mg/kg) along with Zn (375.10 to 696.9 mg/kg), while Pb is fairly consistent (158.43 to 199.92 mg/kg) at the three sites.

Based on the second set of aqua regia/hydrofluoric extractions (Table 3.3), Al is less prevalent than the first set of extractions; however, there is generally more Fe, Pb and Zn bound in the remaining crystalline fraction than are shown in the first set of extractions (Table 3.2). Since there was not a potassium chlorate extraction prior to the aqua regia/hydrofluoric extraction, these slightly elevated values are possibly a result of the sulfide fraction remaining in the final digest.

**Table 3.2: Results from the first set of chemical extractions.**

Site	Al	As	Fe	Mn	Pb	Zn
mg/kg						
Sodium Pyrophosphate*						
i	196.53±191.18	31.95±15.68	1577.95±1026.63	589.80±248.31	933.42±819.63	222.13±182.97
ii	452.85±158.68	10.95±2.27	3146.98±742.30	425.05±235.81	2173.96±1014.80	543.05±424.36
iii	515.20±101.55	29.65±4.95	2641.10±256.65	800.03±315.30	815.13±528.21	524.27±204.30
Ammonium Oxalate (AOD)*						
i	415.94±190.27	140.17±68.70	10716.82±6614.21	1189.54±844.02	872.84±498.83	307.33±150.76
ii	576.80±238.13	66.26±17.41	13280.17±10172.11	894.79±774.86	1540.21±846.67	589.73±538.85
iii	689.01±278.58	122.78±53.65	10622.83±6491.97	1554.25±634.55	1238.16±910.90	410.55±138.96
Citrate Bicarbonate Dithionite (CBD)*						
i	462.83±149.43	230.09±75.28	27588.43±9802.26	2058.80±1495.77	550.73±200.68	661.67±217.03
ii	714.55±261.58	60.51±9.30	28122.62±7697.69	1785.94±1946.73	534.34±111.25	917.97±373.30
iii	830.92±89.07	172.84±34.62	29615.36±3073.05	2983.07±1028.51	758.99±144.96	957.95±152.73
Potassium Chlorate*						
i	2133.79±813.63	143.58±70.33	70793.09±20663.98	6156.92±2903.74	2072.22±961.95	856.51±156.28
ii	3583.42±528.80	51.96±5.32	36120.13±14559.94	2970.48±4639.51	3158.97±853.26	1167.83±347.80
iii	2585.13±334.65	143.31±31.30	37335.01±9260.78	2902.08±1306.33	3538.46±398.09	1118.03±169.67
Hydrofluoric*						
i	37859.27±8671.93	60.05±33.90	4460.35±1045.30	309.56±118.03	29.54±4.58	343.19±309.96
ii	48467.07±16097.96	22.20±6.74	4854.92±979.71	213.48±63.40	40.20±10.48	60.82±28.20
iii	52719.33±5566.70	8.93±2.11	5807.53±589.75	254.53±41.07	35.45±5.38	52.07±5.73

\*-Values presented as averages and standard deviations of 12 samples collected at each site.

**Table 3.3: Results from the second set of chemical extractions.**

Site	Al	As	Fe	Mn	Pb	Zn
mg/kg						
Exchangeable*						
i	0.00±0.00	0.00±0.00	0.00±0.00	28.39±16.70	34.13±64.72	682.58±1294.44
ii	0.00±0.00	0.00±0.00	0.00±0.00	61.95±24.24	672.44±642.73	13448.72±12854.54
iii	0.00±0.00	0.00±0.00	0.07±0.25	36.11±18.66	15.14±14.39	302.78±287.81
Carbonates*						
i	2.05±4.57	0.13±0.03	23.12±37.86	105.57±30.29	570.20±667.76	85.51±38.82
ii	9.58±7.18	0.10±0.02	19.73±16.54	45.96±15.55	747.18±387.63	107.32±91.45
iii	6.74±2.50	0.09±0.02	14.49±3.96	121.76±21.01	227.12±95.79	193.23±67.79
Bound to Iron and Manganese Oxides*						
i	243.92±59.41	136.03±36.82	18369.17±3884.43	2169.25±1595.84	158.43±79.49	375.10±106.31
ii	755.00±171.97	53.19±31.57	34151.50±18632.25	3626.87±3407.72	165.99±50.90	958.45±596.08
iii	786.78±165.88	154.73±42.57	22363.50±8690.70	6670.67±4504.17	199.92±105.18	696.90±350.67
Organic Matter*						
i	398.23±84.55	18.59±2.47	9403.45±3037.34	3133.48±342.16	1750.89±556.58	438.76±108.46
ii	1117.75±210.90	18.64±3.57	3194.10±1276.39	1893.05±2476.73	4370.98±1092.04	563.40±159.39
iii	899.02±151.97	23.11±3.87	5277.58±1237.22	1063.74±549.96	3984.67±822.64	417.43±73.28
Hydrofluoric*						
i	5097.18±471.85	33.50±11.38	10126.05±2366.82	352.56±174.21	71.15±17.39	152.22±32.70
ii	7203.74±763.10	10.83±5.20	5998.58±2657.38	85.54±20.68	50.19±19.26	102.00±35.50
iii	6035.48±784.48	23.75±6.25	5457.60±983.78	83.42±23.30	49.21±11.05	115.33±25.29

\*-Values presented as averages and standard deviations of 12 samples collected at each site.

### 3.3.3 Water Quality in the River System

For this study, water samples were collected 4 times, during high- (April), moderate- (June and July), and low-flow (August) from the three sites and analyzed for dissolved ion concentrations. The results of these data (average of six samples per site) are presented in Table 3.4.

**Table 3.4: Water quality data for the Coeur d'Alene River.**

Site	Al	As	Fe	Mn	Pb	Zn
----- mg/L -----						
trial a (4/20/96)*						
i	0.07±0.02	0.00±0.01	0.14±0.03	0.12±0.03	0.06±0.03	0.20±0.05
ii	0.03±0.01	0.00±0.01	0.12±0.01	0.18±0.03	0.07±0.01	0.26±0.05
iii	0.14±0.07	0.02±0.01	0.25±0.01	1.09±0.09	0.05±0.04	1.39±0.11
trial b (6/13/96)*						
i	0.00±0.00	0.01±0.01	0.05±0.03	0.08±0.09	0.00±0.00	0.31±0.06
ii	0.00±0.01	0.01±0.01	0.12±0.07	0.35±0.21	0.00±0.01	0.45±0.27
iii	0.02±0.00	0.01±0.01	0.02±0.01	0.57±0.02	0.00±0.00	1.00±0.02
trial c (7/20/96)*						
i	0.09±0.02	0.00±0.00	0.05±0.07	0.33±0.09	0.02±0.01	0.55±0.10
ii	0.07±0.05	0.00±0.00	0.10±0.03	0.65±1.08	0.02±0.01	0.75±0.80
iii	0.13±0.01	0.00±0.00	0.04±0.07	3.30±0.05	0.01±0.01	2.68±0.04
trial d (8/31/96)*						
i	0.11±0.01	0.07±0.08	0.03±0.02	0.20±0.04	0.01±0.01	0.58±0.03
ii	0.12±0.01	0.03±0.02	0.04±0.01	0.71±0.02	0.01±0.01	1.08±0.03
iii	0.19±0.01	0.14±0.21	0.05±0.08	5.09±0.12	0.01±0.01	4.24±0.21

\*-Values presented as averages and standard deviations of 6 samples from each site. Water was used for simulated flooding events.

This water was then used to initiate the flooding trials. Results from previous studies (Mink, 1971; Rabe and Brauer, 1977; and Mok and Wai, 1990) indicate that due to dilution, metal concentrations are lower in the high-flow of spring, and higher in the low-flow of summer. In April, after a very high flow period, Mn and Zn concentrations are low (< 1.4 mg/L) and Pb concentrations are at their highest (0.05 to 0.07 mg/L) (Table 3.4). In June, metal values decreased, whereas in July, Mn and Zn increased in the SFCDR. Finally, during the lowest flow period there are the highest values of Mn and Zn (5.09 and 4.24 mg/L). In general, our results are in agreement (with the exception of Pb) with previous investigations. This indicates that water quality in the CDA river basin has not improved in the last 25 years.

### 3.3.4 Simulated Flooding Events

The simulated minor and extreme flooding events for trials *a*, *b*, *c*, and *d* for the three sites are shown in Figures 3.4 - 3.9. For each site, three cores were subjected to a simulated extreme flooding event ( $N_{2(g)}$  purged) and 3 cores were subjected to a simulated minor (aerated) flooding event while dissolved aqueous metal concentrations were measured with respect to time.

The following discussion is for the *a*, *b*, and *c* flooding trials (April, June, July) at the three sites. The minor flooding (Fig. 3.4) and the extreme flooding event (Fig. 3.5) for the MSCDR near the inlet to Lake CDA (trials *a*, *b*, *c*) produce Mn concentrations < 2.0 mg/L. During the minor flooding event for the MSCDR at Cataldo (Fig. 3.6), Zn is released in the aqueous environment (10.41 mg/L) and remains throughout the period studied; Mn is found at lower concentrations (< 3.8 mg/L) in the three trials. On the other hand, the extreme flooding event at Cataldo (Fig. 3.7) produced < 6.70 mg/L Zn and only 2.18 mg/L Pb after 288 h. The SFCDR at Smeltonville simulated flooding events (Fig. 3.8 and 3.9) resulted in low dissolved concentrations of Zn and Mn. The values for the flooding events from the MSCDR near the inlet to Lake CDA, and the SFCDR at Smeltonville, have similar metal concentrations in the river water (Table 7) used to flood the columns. Based on Eh readings, the columns at these two sites did not get significantly reduced, and Fe and Mn remained as insoluble oxyhydroxides. It appears that conditions were unfavorable for microbial activity which resulted in little reductive dissolution of Fe and Mn (hydr)oxides. At Cataldo, the release of Zn at these concentrations is extremely detrimental to rainbow trout, *Salmo gairdneri* in the region. The acute toxicity,  $TL_{50}$  96 hour (toxic limit for 50 percent within 96 hours), is from 0.10 mg/L - 0.91 mg/L, depending on the physical parameters of the fish and the chemical characteristics of the river water (Norton, 1980). Therefore, when oxygenated river water contacts contaminated bank sediment in the MSCDR at Cataldo, Zn is dissolved and directly released into the aqueous environment at levels potentially harmful to fish.

### Simulated Minor Flooding Event MSCDR Near the Inlet to Lake CDA

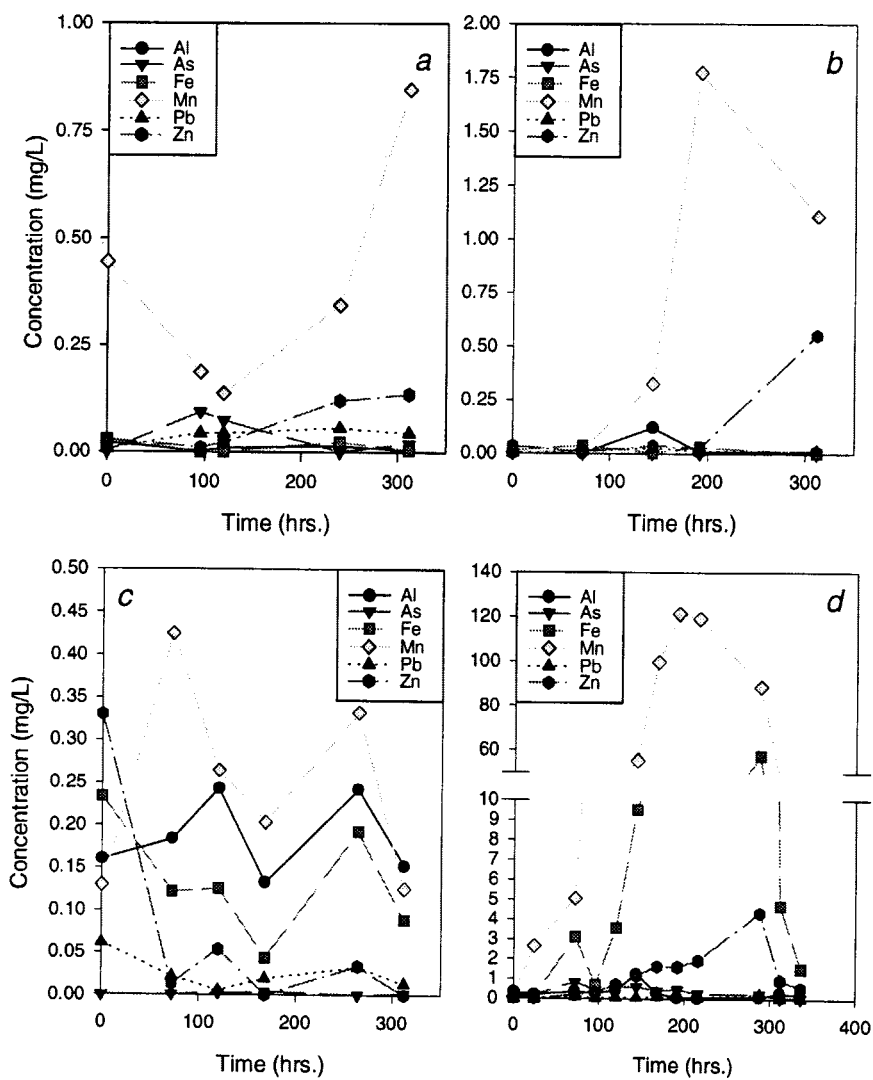


Figure 3.4 Simulated minor flooding event MSCDR near the inlet to Lake Coeur d'Alene (site i).

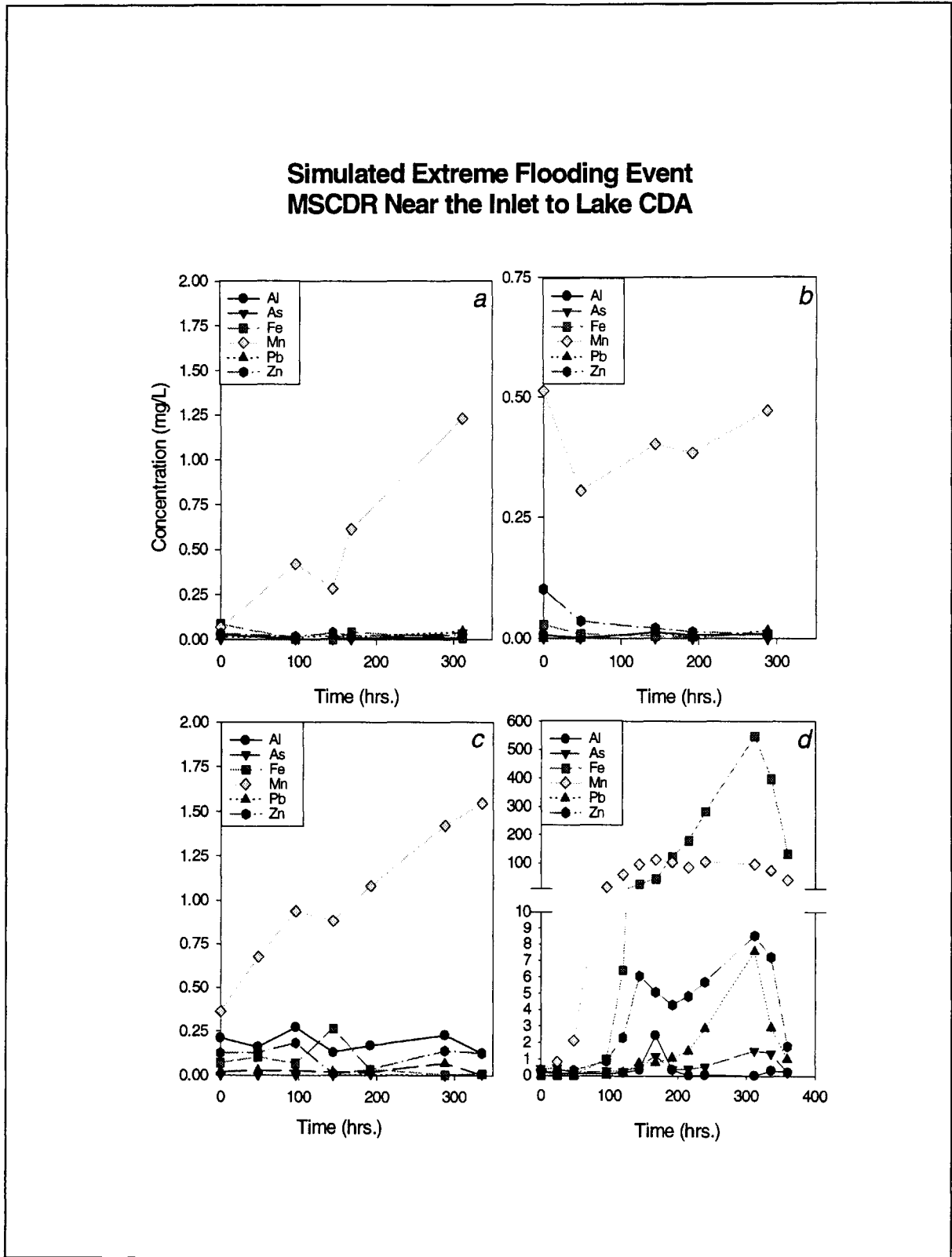


Figure 3.5 Simulated extreme flooding event MSCDR near the inlet to Lake Coeur d'Alene (site i).

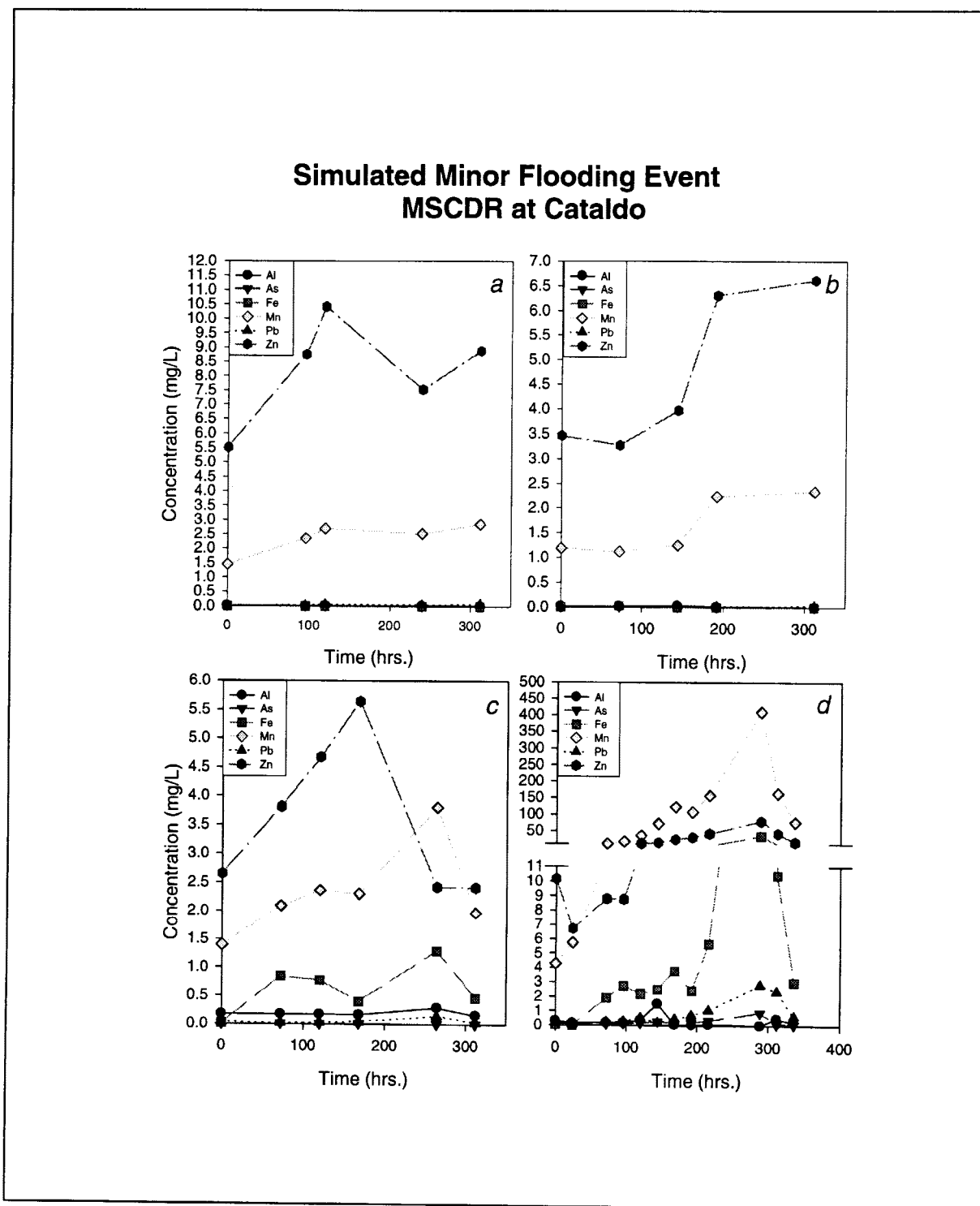


Figure 3.6 Simulated minor flooding event MSCDR at Cataldo (site ii).



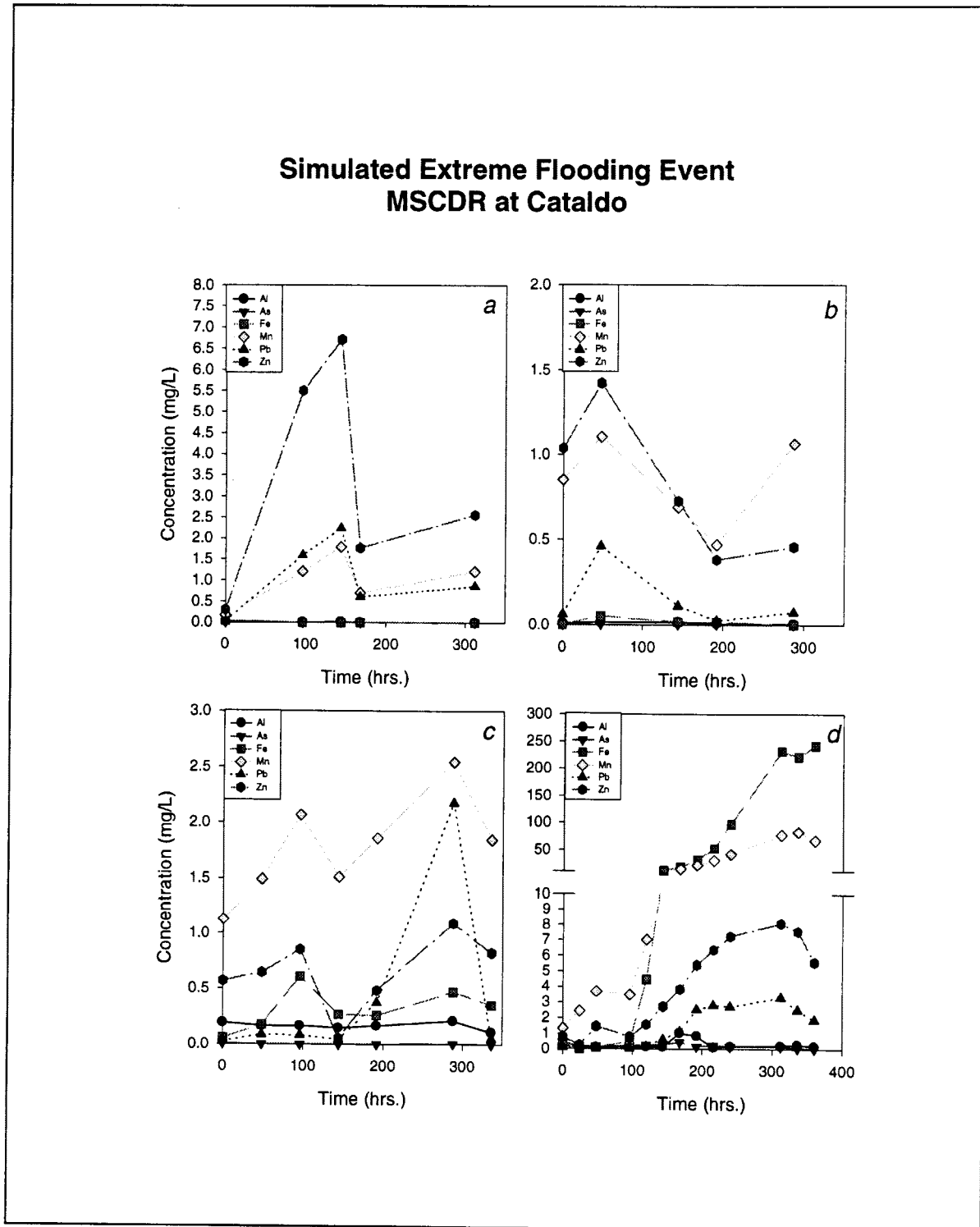


Figure 3.7 Simulated extreme flooding event MSCDR at Cataldo (site ii).

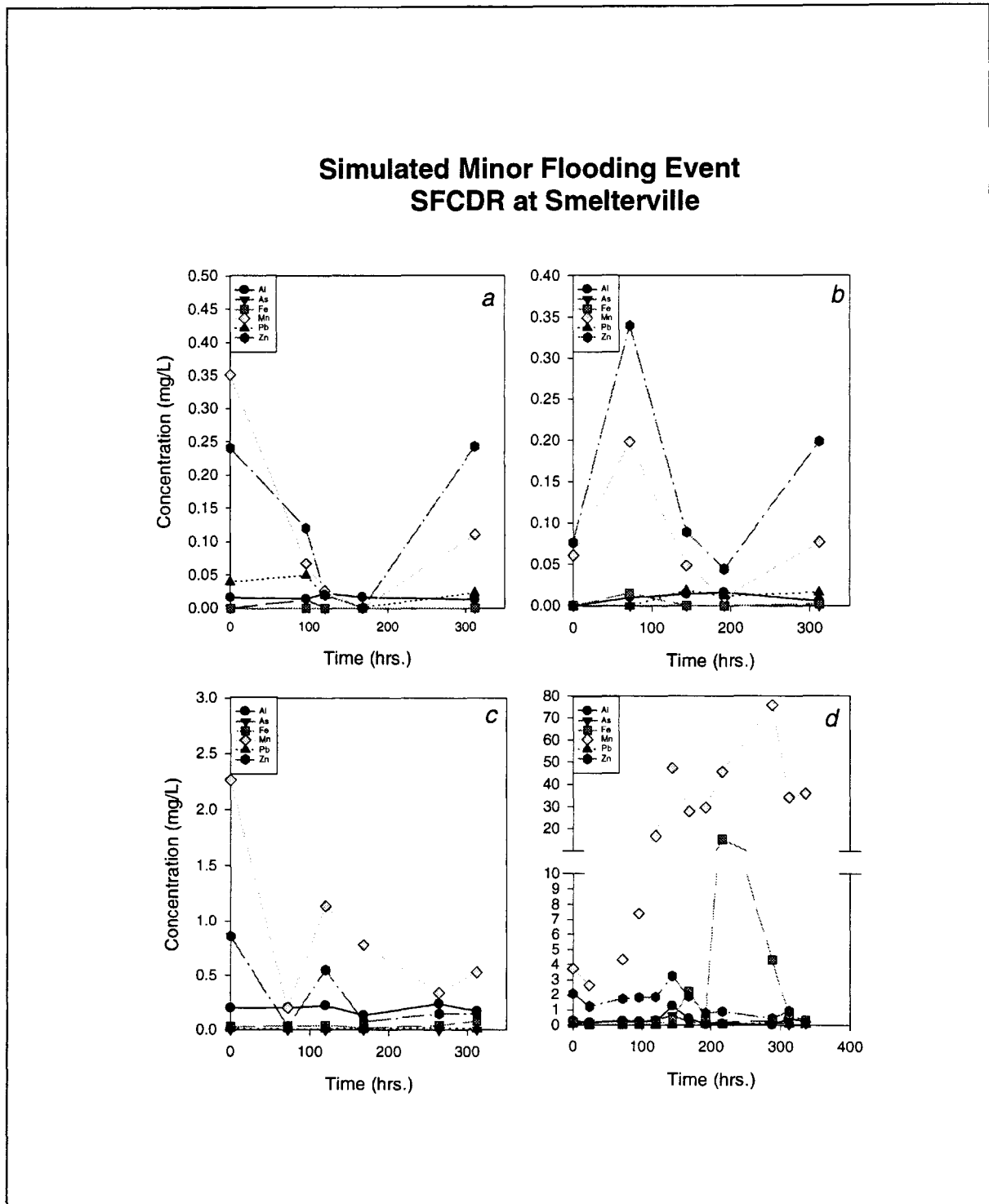


Figure 3.8 Simulated minor flooding event SFCDR at Smelterville (site iii).

### Simulated Extreme Flooding Event SFCDR at Smelerville

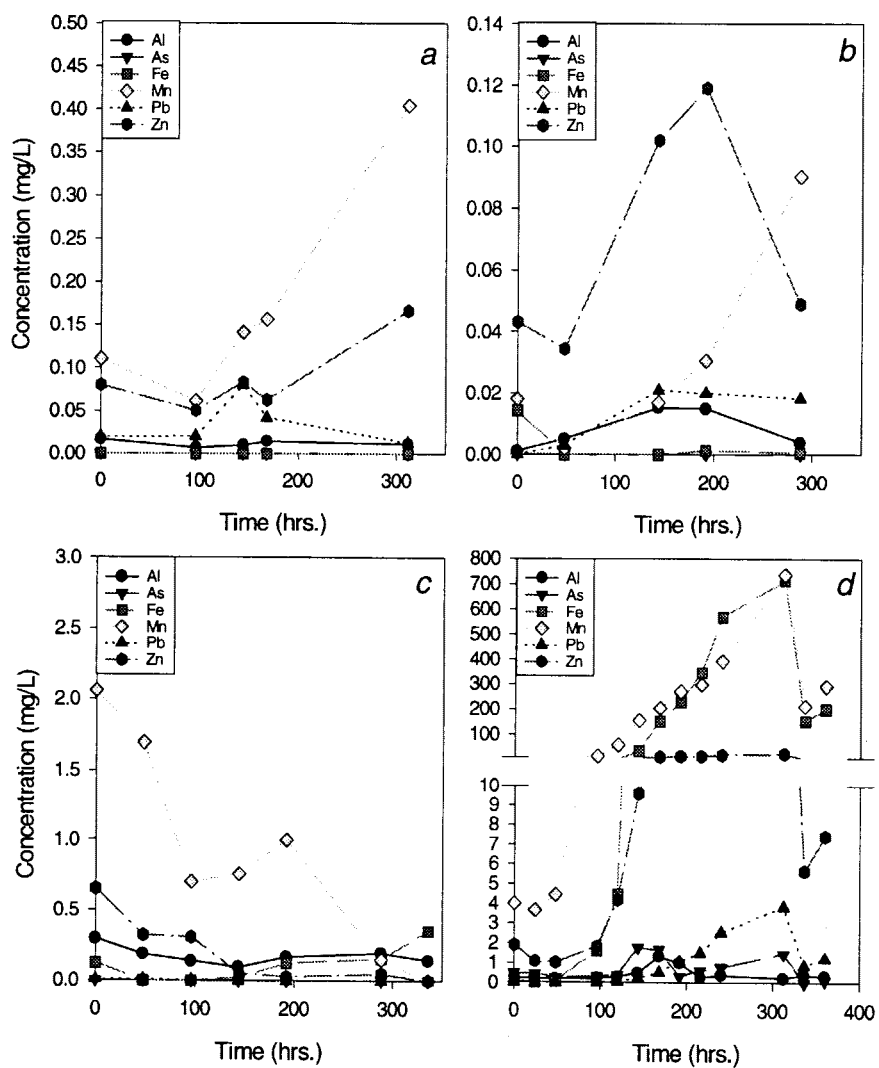


Figure 3.9 Simulated extreme flooding event SFCDR at Smelerville (site iii).

The simulated minor and extreme flooding events with an added nutrient source (trial *d*) resulted in much higher dissolved metal concentrations than the three previous flooding events. For the minor flooding event at the MSCDR near the inlet to Lake CDA (Fig. 3.4), there were peak concentrations of 0.82 mg/L As after 72 h, 57.65 mg/L Fe after 288 h, 121.26 mg/L Mn after 168 h, and 4.33 mg/L Zn after 288 h. During the extreme flooding event (Fig. 3.5), As increased 38.5 %, Fe increased over 2,027 %, Mn 72 %, Pb 108 %, and Zn 85 % relative to trials *a*, *b*, and *c*. The minor flooding event at Cataldo (Fig. 3.6) produced peaks for all metal solution concentrations at 288 h (As = 0.91 mg/L, Fe = 35.21 mg/L, Mn = 410.03 mg/L, Pb = 2.80 mg/L, and Zn = 79.29 mg/L). The extreme flooding event at Cataldo (Fig. 3.7) produced rising aqueous metal concentrations with time (As increased 45 %, Fe 391 %, Mn 32 %, Pb and Zn 1 %). The minor flooding event at Smeltonville (Fig. 3.8) produced As = 0.63 mg/L after 144 hr, Fe = 15.31 mg/L after 216hr, Mn = 75.76 mg/L after 288 hr, Pb = 0.16 mg/L after 288 hr and Zn = 3.25 mg/L after 144hr. On the other hand, the extreme flooding event (Fig. 3.9) produced rising concentrations which generally peaked at 312 hr (As = 1.47 mg/L, Fe = 735 mg/L, Mn = 714.80 mg/L, Pb = 2.5 mg/L, and Zn = 24.45 mg/L).

In general, the highest concentrations from the amended purged river water with D-glucose and ammonium sulfate appeared later in the flooding events due to enhanced microbial activity. The addition of a nutrient source to the water stimulated extensive microbial activity that resulted in the reduction of Fe and Mn and the release of As, Pb, and Zn into solution. In the final flooding event (trial *d*) contaminant release was greater from the  $N_{2(g)}$  purged amended sediments; however, significant amounts of contaminants were released from the air ( $P_{O_2(g)} = 0.2$  atm) purged amended columns. Therefore, if an added nutrient source (e.g., septic tank sewage) leaches into the river system while flooding occurs, there will be a release of contaminants which will degrade water quality and effect the aquatic biota.

### 3.4 CONCLUSIONS/SUMMARY

High levels of mining wastes in the Coeur d'Alene river system need to be addressed with a remediation plan. There exists a need to better understand the effects of flooding on inorganic constituents located in the riverbanks of the MSCDR and SFCDR. The environmental conditions leading to contaminant release from sediments in the Coeur d'Alene river system can be better understood by phase partitioning contaminants in the sediment and monitoring their release into the river system as flooding occurs in the region.

Scanning Electron Microscopy, EDS, and XRD were all done to quantify heavy metal contamination in the region. Energy Dispersive Spectroscopy confirmed that heavy metal contamination existed at the three sites. The diversity of contamination in the region is attributed to mining techniques such as jigging and selective flotation. The contamination in riverbanks from the SCFCDR at Smelterville is expected since it directly drains the mining district. In early mining operations, Zn could not be extracted from ores; therefore, tailings discharged into the river basin were highly contaminated with Zn, making this metal a concern in the region.

Chemical extraction of the riverbank sediment indicates that each contaminant is present in the organic fraction. Iron and Mn oxides are also present, and reductive dissolution can result in the release of contaminants bound to them. Arsenic is partitioned fairly evenly in the noncrystalline and crystalline oxide fractions, while Pb is more abundant in the noncrystalline fraction at the three sites. Amorphous Pb and As can feasibly be dissolved from the grain coatings during flooding and are of environmental concern. The potassium chlorate extraction shows that substantial amounts of Al, Fe, Mn, Pb, and Zn are bound as sulfides and are available for release as oxidative dissolution occurs.

Water quality data indicates that Zn and Mn concentrations in the river water are high during the low-flow of summer and low in the high-flow of spring. However, Pb concentrations were highest during the high-flow of spring. The release of contaminants during a nutrient influx to the system coupled with preexisting metal concentrations in the river water may be extremely detrimental to aquatic biota in the river system.

Flooding events for the MSCDR near the inlet to Lake CDA and the SFCDR at Smeltonville produced low values of Zn and Mn in solution. However, flooding at Cataldo released Zn into the aqueous environment which can adversely affect the biota. In the nutrient added (D-glycerol and ammonium sulfate) flooding simulation, contaminant concentrations increased drastically at all three sites. Microbial activity caused the reduction of Fe and Mn which in turn released excessive amounts of As, Pb, and Zn into solution. Therefore, extreme precaution must be used in the region to limit nutrient additions into the river system.

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## 4.0 CONCLUSIONS

### 4.1 CONCLUSIONS STUDY ONE:

#### RELEASE OF CONTAMINANTS FROM OXYGENATED SEDIMENT OF LAKE CDA (SIMULATED DREDGING EXPERIMENT).

In order for an environmental management plan to be initiated in the CDA basin there exists a need to better understand possible remediation alternatives. Two studies were initiated to quantify the release of contaminants in the CDA basin. The first study attempted to quantify the release of As, Fe, Mn, Pb, and Zn as dredging occurs in Lake CDA. The second study was conducted to quantify the release of these same contaminants as flooding occurs in the MSCDR and SFCDR.

One possible environmental management plan for Lake CDA may include dredging. A systematic study on the dredging of heavy metals from lakes sediments was conducted. The procedure used in this study is as follows: 1) pore water total metal concentration, 2) total metal abundance in the organic, amorphous, crystalline and sulfidic fractions of the solid phase, 3) simulated dredging while measuring pH, Eh, and contaminant release over time, and 4) comparison of experimental data with results predicted from the MINTEQA2 speciation program. To simulate dredging operations, cores taken by gravity drilling were placed into a reaction vessel and mixed while being oxygenated for 800 hours. Conclusions from this study are:

1. In pore water extracts, Fe and As are present dominantly in the upper 30 cm of the core, whereas Mn, Pb, and Zn are in amounts well above detection limits throughout the entire core. Therefore, trace element contaminants in the sediments may be released to solution as agitation occurs (i.e. dredging).
2. Arsenic and Pb concentrations are primarily associated with the organic fraction of the sediments. Iron was in the organic, sulfidic, and noncrystalline fractions. Manganese and Zn were bound within organic and sulfide fractions.

3. The SDA's of the oxidized sediments of two dredging trials attest that contaminants in the organic fraction before dredging were released upon agitation, and subsequently were incorporated into the amorphous and crystalline fractions.
4. In the dredging simulations, As and Pb concentrations were above maximum contaminant levels for drinking water, indicating that dredging would have an adverse effect on water quality. Furthermore, Zn was released at levels toxic to Rainbow Trout whose  $TD_{c 50}$  is (0.1 mg/L to 0.91 mg/L) (Norton, 1980).
5. Dredging Lake CDA would be detrimental to water quality of the lake, having an adverse effect on the biota.

#### 4.1.1 CONCLUSIONS STUDY TWO:

##### MOBILITY OF TRACE-ELEMENT CONTAMINANTS UPON FLOODING IN THE COEUR D'ALENE RIVER SYSTEM (SIMULATED FLOODING EXPERIMENT).

In order to address the environmental ramifications of flooding, water quality in the river system was assessed, contaminants in the riverbank sediments were geochemically phase partitioned, and their release were measured under simulated laboratory flooding experiments. To simulate flooding experiments, 18 columns were constructed allowing the sediment-water interface to be monitored for pH, Eh and dissolved concentrations of As, Fe, Mn, Pb, and Zn. These columns were subjected to two flooding events. The first event involved the addition of  $N_{2(g)}$  or  $O_{2(g)}$  purged river water to the columns and the second event had purged river water amended with a nutrient source (D-glucose). Conclusions from this study are:

1. Energy Dispersive Spectroscopy confirmed that heavy metal contamination existed in the MSCDR and the SFCDR. The diversity of contamination in the region is attributed to varying mining techniques such as jigging and selective flotation.
2. Selective chemical extractions of riverbank sediment indicates that each contaminant is present in the organic fraction. Iron and Mn are also bound as crystalline materials, while As is partitioned fairly evenly in the noncrystalline and crystalline fraction. Lead is more abundant in the noncrystalline fraction at the three sites. Amorphous Pb and As

can feasibly be dissolved from the grain coatings during flooding and are of environmental concern. The potassium chlorate extraction shows that substantial amounts of Al, Fe, Mn, Pb, and Zn are contained as sulfides. Oxidative dissolution can cause the release of contaminants from the sulfide fractions.

3. Water quality data indicates that Zn and Mn concentrations in the river water are high during the low-flow of summer and low in the high-flow of spring. However, Pb concentrations were highest during the high-flow of spring. Therefore, water quality in the river has not improved in the last 25 years.
4. Flooding events for the MSCDR near the inlet to Lake CDA and the SFCDR at Smeltonville resulted in low concentrations of Zn and Mn in solution. However, flooding at Cataldo released Zn into the aqueous environment which can adversely affect the biota.
5. When a nutrient source was added (D-glycerol and ammonium sulfate), flooding stimulated contaminant dissolution drastically at all three sites. Microbial activity caused the reduction of Fe and Mn which in turn released extensive amounts of As, Pb, and Zn into solution. Therefore, extreme caution must be used in the region to limit nutrient additions into the river system.

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**APPENDIX I**



Metal digestion of 0.5 g sample with 3-1-2 HCl-HNO<sub>3</sub>-H<sub>2</sub>O All values in ppm or expressed otherwise

Core	Mo	Cu	Pb	Zn	Ag	Ni	Co	Mn	Fe (%)	As	U	Au	Th	Sr	Cd
Core L (0-10cm)	3	129	3832	3276	12	18	23	7193	8.53	247	<5	<2	15	12	65.2
Core L (10-20cm)	4	161	3409	2587	14.1	20	25	9269	10.98	343	<5	<2	20	10	38.1
Core L (20-30cm)	3	169	6091	3524	14.8	18	19	8984	10.25	196	<5	<2	18	14	28.7
Core L (30-40cm)	3	185	7088	3863	15.5	15	16	9207	10.1	111	<5	<2	20	14	32
Core L (45-50cm)	4	146	6603	4076	17	20	21	10964	11.87	163	<5	<2	23	15	32.1
Core L Top	2	122	4373	3341	11.5	19	22	6571	8.15	172	<5	<2	16	14	50.7
Core L Bottom 55 cm	4	156	8369	5731	19.6	19	19	12491	13.22	134	<5	<2	29	15	35.9
Core M (0-10cm)	3	137	4974	3976	12.9	18	19	7877	10.09	247	<5	<2	18	14	54.1
Core M (10-20cm)	3	157	4858	4420	15.4	19	22	9761	11.69	381	<5	<2	22	12	89.8
Core M (20-30cm)	5	162	3295	2875	15.6	20	26	10925	12.92	473	<5	<2	22	11	47.1
RE Core M (20-30cm)	4	167	3276	2997	16.1	19	28	11118	13.16	471	<5	<2	25	11	50.9
Leftovers Trial 1	7	219	3963	2493	21.3	33	20	10391	13.36	479	<5	<2	24	7	29.2
Leftovers Trial 2	10	139	5035	2113	8.4	107	13	5270	8.19	211	<5	<2	13	9	13.3

RE= rerun

Core	Sb	Bi	V	Ca (%)	P (%)	La	Cr	Mg (%)	Ba	Ti (%)	B	Al (%)	Na (%)	K (%)	W
Core L (0-10cm)	41	4	24	0.27	0.087	19	19	0.48	161	0.05	<3	1.16	0.02	0.1	<2
Core L (10-20cm)	73	8	16	0.29	0.046	17	21	0.51	160	0.03	<3	0.93	0.01	0.11	<2
Core L (20-30cm)	43	5	12	0.42	0.03	16	16	0.48	158	0.02	<3	0.75	0.01	0.13	<2
Core L (30-40cm)	44	5	10	0.4	0.027	16	15	0.47	166	0.02	<3	0.64	<0.01	0.12	<2
Core L (45-50cm)	42	9	13	0.42	0.033	16	19	0.58	158	0.02	<3	0.76	0.01	0.12	<2
Core L Top	34	<2	26	0.29	0.08	21	19	0.49	199	0.05	<3	1.36	0.03	0.12	<2
Core L Bottom 55 cm	44	9	12	0.5	0.03	15	17	0.64	153	0.02	<3	0.68	0.01	0.12	<2
Core M (0-10cm)	39	5	19	0.32	0.077	20	18	0.51	161	0.04	<3	1.07	0.02	0.09	<2
Core M (10-20cm)	61	6	14	0.33	0.084	16	19	0.51	124	0.02	<3	0.77	0.01	0.07	<2
Core M (20-30cm)	76	8	14	0.33	0.075	15	21	0.54	152	0.02	<3	0.71	0.01	0.09	<2
RE Core M (20-30cm)	80	12	15	0.33	0.085	16	23	0.56	153	0.03	<3	0.82	0.01	0.1	<2
Leftovers Trial 1	121	11	16	0.2	0.036	16	51	0.55	126	0.03	<3	0.93	0.15	0.11	<2
Leftovers Trial 2	36	4	22	0.16	0.088	22	94	0.46	167	0.01	<3	1.2	0.15	0.1	<2

RE= rerun

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**Sample times for study one (dredging experiment).**


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Sample #	Time	Time into exp.	Ph	Eh (mV)	Date
Reagent Blank	2:00 PM	0	5.153	442.7	6/29/95
1	3:30 PM	0	6.386	255.8	6/29/95
2	4:30 PM	1	6.066	337.4	6/29/95
3	5:30 PM	2	6.105	349.2	6/29/95
4	6:30 PM	3	6.155	363.7	6/29/95
5	7:30 PM	4	6.2	375.4	6/29/95
6	9:30 PM	6	6.265	390.6	6/29/95
7	10:30 PM	7	6.314	396.9	6/29/95
8	10:30 AM	19	6.512	440.4	6/30/95
9	11:30 AM	20	6.524	415.7	6/30/95
10	12:30 AM	21	6.55	423.4	6/30/95
11	1:30 PM	22	6.574	431.4	6/30/95
12	2:30 PM	23	6.597	423.5	6/30/95
13	3:30 PM	24	6.59	440.8	6/30/95
14	4:30 PM	25	6.641	420.8	6/30/95
15	5:30 PM	26	6.65	430.1	6/30/95
16	10:30 AM	138	6.31	526.3	7/5/95
17	10:30 AM	258	6.293	462.2	7/10/95
18	11:30 AM	307	6.569	453.1	7/12/95
19	11:30 AM	427	6.508	529.1	7/17/95
20	11:30 AM	475	6.538	440.4	7/19/95
21	12:30 AM	596	6.4	600.1	7/24/95
22	11:30 AM	643	6.4	403.6	7/26/95
23	3:30 PM	695	6.32	432.8	7/28/95
24	10:30 AM	762	6.38	447.5	7/31/95
25	11:30 AM	811	6.7	417.5	8/2/95

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**Sample times for study one (dredging experiment).**

Sample #	Time	Time into exp.	Ph	Eh (mV)	Date
Reagent Blank	10:30 AM	0	5.35	229.3	8/3/95
1	10:30 AM	0	5.57	84.5	8/3/95
2	11:30 AM	1	6.08	40.5	8/3/95
3	12:30 AM	2	6.04	52.1	8/3/95
4	1:30 PM	3	5.97	74.7	8/3/95
5	2:30 PM	4	6.17	79.7	8/3/95
6	3:30 PM	5	5.97	92.7	8/3/95
7	4:30 PM	6	5.9	99.6	8/3/95
8	5:30 PM	7	5.92	116.5	8/3/95
9	11:30 AM	97	5.6	253.1	8/7/95
10	10:30 AM	120	5.69	285.1	8/8/95
11	8:30 AM	142	5.73	240.9	8/9/95
12	12:30 AM	146	5.65	245.9	8/9/95
13	2:30 AM	172	6.2	277.6	8/10/95
14	11:30 AM	193	6.27	235.5	8/11/95
15	11:30 AM	265	6.09	205.5	8/14/95
16	11:30 AM	312	6.07	218.4	8/16/95
17	4:30 AM	317	6	194.6	8/16/95
18	12:30 AM	434	5.78	261.2	8/21/95
19	11:30 AM	504	5.89	208.3	8/24/95
20	12:30 AM	626	6.12	160.2	8/29/1995*
21	12:30 AM	674	6.068	196.2	8/31/1995*
22	8:30 AM	958	6.438	223.1	9/12/1995*

\*-3 samples collected. pH and Eh shown as averages of three samples.

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**Sample times for study one (dredging experiment).**


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Sample #	Time	Time into exp.	Ph	Eh (mV)	Date
Reagent Blank	12:30 AM	0	6.03	293	8/7/95
1	12:30 AM	0	6.22	283.4	8/7/95
2	1:30 PM	1	5.97	347	8/7/95
3	2:30 PM	2	5.96	374.3	8/7/95
4	3:30 PM	3	5.92	379.2	8/7/95
5	4:30 PM	4	5.89	392.7	8/7/95
6	5:30 PM	5	5.92	403.5	8/7/95
7	10:30 AM	22	5.8	412.7	8/8/95
8	11:30 AM	23	5.8	422.7	8/8/95
9	12:30 AM	24	5.74	416.1	8/8/95
10	2:30 PM	26	5.72	430.9	8/8/95
11	3:30 PM	27	5.7	408.2	8/8/95
12	4:30 PM	28	5.69	419.7	8/8/95
13	8:30 AM	44	5.85	436.7	8/9/95
14	12:30 AM	48	5.89	450.2	8/9/95
15	4:30 AM	52	5.92	439.1	8/9/95
16	11:30 AM	71	5.87	444.7	8/10/95
17	11:30 AM	95	6.05	444.2	8/11/95
18	11:30 AM	167	6.06	420.3	8/14/95
19	11:30 AM	215	6.06	412	8/16/95
20	1:30 AM	265	5.92	371.3	8/18/1995*
21	11:30 AM	335	5.99	437.2	8/21/1995*
22	11:30 AM	407	6	409.7	8/24/1995*
23	12:30 AM	528	5.94	413.16	8/29/1995*
24	11:30 AM	576	5.822	385.3	8/31/1995*
25	11:30 AM	719	5.926	388.9	9/6/1995*
26	9:30 AM	861	5.953	432.1	9/12/1995*

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\*-3 samples collected. pH and Eh shown as averages of three samples.

**APPENDIX II**

**EDS percentages of sediment from the MSCDR near the inlet to Lake Coeur d'Alene.**

MSCDR	Na	Al	Si	K	Ca	Mn	Fe	Pb	Zn	P	As
Atomic %	1.49	10.93	57.47	3.18	0.29	1.1	23.27	0.36	0.41	0.59	0.62
Wt. %	0.95	8.14	44.6	3.44	0.32	0.16	35.91	2.08	0.74	0.51	1.29

**EDS percentages of sediment from the SFCDR at Cataldo.**

	Na	Al	Si	K	Ca	Mn	Fe	Pb	Zn	P	As	S	Ti
Atomic %	1.8	13.13	53.93	3.81	0.15	0.52	23.46	0.21	0.45	0.46	0.55	1.19	0.33
Wt. %	1.15	9.87	42.23	4.16	0.17	0.8	36.53	1.22	0.82	0.4	1.16	1.06	0.44

**EDS percentages of sediment from the SFCDR at Smelterville.**

	Na	Al	Si	K	Ca	Mn	Fe	Pb	Zn	As	Ti	Na
Atomic %	1.87	13.97	54.52	3.81	0.59	1.91	21.18	0.41	0.51	0.83	0.41	1.87
Wt. %	1.19	10.44	42.4	4.12	0.65	2.9	32.76	2.34	0.93	1.72	0.54	1.19

**EDS percentages from the sediment remains of T1.**

T1	Ca	Na	K	Mg	Fe	Mn	Pb	Zn	S	Al	Si	O
Atomic %	0.19	2.6	1.31	1.23	3.73	0.26	0.14	0.65	0.95	6.68	20.41	61.85
Wt. %	0.34	2.7	2.31	1.35	9.41	0.64	1.32	1.91	1.38	8.13	25.86	44.65

**EDS percentages from the sediment remains of T1.**

T1	CaO	Na2O	K2O	MgO	FeO	MnO	PbO	ZnO	SO3	Al2O3	SiO2
Compound %	0.48	3.64	2.78	2.24	12.11	0.82	1.42	2.38	3.44	15.37	55.32

**EDS percentages of the sediment remains of T2.**

T2	Na	Al	Si	S	K	Ca	Mn	Fe	Pb	Zn	P	As	O
Atomic %	1.88	3.71	8.94	10.78	0.67	0.07	0.07	0.65	0.22	0.1	0.19	0.71	65.33
Wt. %	1.85	4.28	10.74	14.78	1.12	0.13	0.16	1.91	1.94	0.27	0.26	2.26	44.7

**EDS percentages of the sediment remains of T2.**

T2	Na2O	Al2O3	SiO2	SO3	K2O	CaO	MnO	FeO	PbO	ZnO	P2O5	As
Compound %	2.5	8.08	22.98	36.91	1.35	0.18	0.21	22.53	2.09	0.34	0.59	2.26

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**Field data for water in the CDR and locations of cores.**


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**MSCDR Near Inlet to Lake CDA.** 3/15/96


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Eh (mV)	pH	DO (mg/L)	Temp
422	6.48	10.5	41°F

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Core No. 1 - 16" below bank, 12" above water

Core No. 2 - 16" below bank, 12" above water, 1" to right of core 1.

Core No. 3 - 16" below bank, 12" above water, 1" to right of #2

Core No. 4 - 20" below bank, 8" above water, 1" to right of #2, 1" below #2

Core No. 5 - 16" below bank, 12" above water, 1" above #2 &amp; #3

Core No. 6 - 16" below bank, 12" above water, 1" to Rt. of #4.

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**MSCDR Cataldo** 3/15/96


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Eh (mV)	pH	DO (mg/L)	Temp
417	6.3	11.3	40°F

---

Core No. 7 - 22" below bank, 16" above water

Core No. 8 - 22" below bank, 16" above water, 1.7" to right of core 7.

Core No. 9 - 24" below bank, 14" above water, 1.7" to right of core 8.

Core No. 10 - 22" below bank, 16" above water, 2" to right of core 9.

Core No. 11 - 22" below bank, 16" above water, 2" to right of core 10.

Core No. 12 - 25" below bank, 13" above water, 3" to right of core 9.

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**SFCDR Smelterville** 3/15/96


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Eh (mV)	pH	DO (mg/L)	Temp
425.1	6.3	11.5	11.5°F

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Core No. 13 - 12" below bank, 5" above water

Core No. 14 - 12" below bank, 5" above water, 1.5" to left of #13.

Core No. 15 - 12" below bank, 5" above water, 2" to Rt. of #13.

Core No. 16 - 12" below bank, 5" above water, 2" to Rt. of #15.

Core No. 17 - 12" below bank, 5" above water, 2" to Rt. of #16.

Core No. 18 - 11.5" below bank, 5" above water, 0.5" above # 15.



<b>Field data for water in the SFCDR.</b>			
<b>SFCDR Smelterville</b>			3/15/96
Eh (mV)	pH	DO (mg/L)	Temp
426.00	6.30	11.50	42° F
<b>SFCDR Smelterville<sup>a</sup></b>			4/20/96
Eh	pH	DO	Temp
425.10	6.62	10.19	10.9° C
<b>SFCDR Smelterville<sup>b</sup></b>			6/13/96
Eh	pH	DO	Temp
505.40	6.77	9.37	15° C
<b>SFCDR Smelterville<sup>c</sup></b>			7/20/96
Eh (mV)	pH	DO (mg/L)	Temp
242.50	7.07	9.81	-----
<b>SFCDR Smelterville<sup>d</sup></b>			8/30/96
Eh (mV)	pH	DO (mg/L)	Temp
417.40	7.03	11.15	-----

<b>Field data for water in the MSCDR.</b>			
<b>MSCDR Near Inlet to Lake CDA.</b>			3/15/96
Eh (mV)	pH	DO (mg/L)	Temp
426	6.3	11.5	42°F
<b>MSCDR Near Inlet to Lake CDA.<sup>a</sup></b>			4/20/96
Eh (mV)	pH	DO (mg/L)	Temp
497.3	6.68	10.2	12°C
<b>MSCDR Near Inlet to Lake CDA.<sup>b</sup></b>			6/13/96
Eh (mV)	pH	DO (mg/L)	Temp
512.9	6.81	8.72	17°C
<b>MSCDR Near Inlet to Lake CDA.<sup>c</sup></b>			7/20/96
Eh (mV)	pH	DO (mg/L)	Temp
326.4	6.87	9.74	-----
<b>MSCDR Near Inlet to Lake CDA.<sup>d</sup></b>			8/30/96
Eh (mV)	pH	DO (mg/L)	Temp
457.6	7.02	9.95	-----
<b>MSCDR Cataldo</b>			3/15/96
Eh (mV)	pH	DO (mg/L)	Temp
417	6.3	11.3	40°F
<b>MSCDR Cataldo<sup>a</sup></b>			4/20/96
Eh (mV)	pH	DO (mg/L)	Temp
438.7	6.57	10.98	10°C
<b>MSCDR Cataldo<sup>b</sup></b>			6/13/96
Eh (mV)	pH	DO (mg/L)	Temp
512.09	6.19	8.62	18°C
<b>MSCDR Cataldo<sup>c</sup></b>			7/20/96
Eh (mV)	pH	DO (mg/L)	Temp
326.4	6.86	9.74	-----
<b>MSCDR Cataldo<sup>d</sup></b>			8/30/96
Eh (mV)	pH	DO (mg/L)	Temp
463.4	6.54	11.1	-----

**Simulated Extreme Flooding Event  
MSCDR Near Inlet to Lake CDA<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.03	0.00	0.09	0.07	0.01	0.03	6.82	420.86
96.00	0.00	0.00	0.00	0.42	0.01	0.02	7.28	508.13
144.00	0.00	0.00	0.00	0.28	0.02	0.04	7.93	
168.00	0.01	0.00	0.04	0.61	0.02	0.02	7.06	
312.00	0.01	0.04	0.01	1.23	0.04	0.03	7.88	438.07

**Simulated Minor Flooding Event  
MSCDR Near Inlet to Lake CDA<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.02	0.00	0.03	0.45	0.01	0.03	7.00	539.23
96.00	0.00	0.09	0.00	0.19	0.04	0.01	7.56	
120.00	0.01	0.07	0.00	0.14	0.04	0.02		
240.00	0.01	0.00	0.02	0.34	0.06	0.12		
312.00	0.00	0.02	0.00	0.85	0.04	0.14	7.05	566.00

**Simulated Extreme Flooding Event  
MSCDR Near Inlet to Lake CDA<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.01	0.00	0.03	0.51	0.00	0.10	9.17	348.13
48.00	0.00	0.00	0.01	0.31	0.00	0.04	8.10	345.90
144.00	0.01	0.00	0.01	0.40	0.01	0.02	7.27	340.57
192.00	0.01	0.00	0.00	0.38	0.00	0.01	6.78	362.70
288.00	0.01	0.00	0.01	0.47	0.02	0.01	7.57	396.73

**Simulated Minor Flooding Event  
MSCDR Near Inlet to Lake CDA<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.00	0.00	0.01	0.00	0.00	0.03	8.98	439.00
72.00	0.00	0.00	0.04	0.02	0.01	0.01	7.02	474.50
144.00	0.12	0.00	0.00	0.32	0.03	0.03	6.19	399.00
192.00	0.00	0.00	0.03	1.77	0.01	0.02	6.62	475.10
312.00	0.01	0.00	0.00	1.11	0.01	0.55	7.09	446.89

**Simulated Extreme Flooding Event  
MSCDR at Cataldo<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.02	0.00	0.04	0.17	0.03	0.30	6.79	482.00
96.00	0.01	0.00	0.00	1.20	1.59	5.50	6.39	516.40
144.00	0.02	0.01	0.00	1.78	2.24	6.70	5.77	
168.00	0.01	0.00	0.00	0.70	0.61	1.76	5.37	
312.00	0.00	0.01	0.00	1.20	0.86	2.56	6.28	510.33

**Simulated Minor Flooding Event  
MSCDR at Cataldo<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.01	0.01	0.00	1.45	0.01	5.51	6.60	551.00
96.00	0.00	0.01	0.00	2.35	0.03	8.75	6.43	
120.00	0.01	0.01	0.00	2.69	0.06	10.41		
240.00	0.00	0.00	0.00	2.52	0.04	7.52		
312.00	0.01	0.00	0.00	2.86	0.07	8.88	6.12	603.43

**Simulated Extreme Flooding Event  
MSCDR at Cataldo<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.01	0.00	0.00	0.85	0.06	1.04	8.00	405.00
48.00	0.01	0.00	0.05	1.10	0.46	1.42	7.51	395.30
144.00	0.01	0.00	0.02	0.69	0.11	0.73	6.44	461.50
192.00	0.00	0.00	0.02	0.47	0.02	0.38	6.63	428.30
288.00	0.00	0.00	0.00	1.06	0.07	0.46	7.10	422.13

**Simulated Minor Flooding Event  
MSCDR at Cataldo<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.01	0.00	0.00	1.18	0.00	3.46	8.75	507.30
72.00	0.02	0.00	0.02	1.12	0.01	3.27	7.04	446.00
144.00	0.02	0.00	0.00	1.25	0.03	3.97	5.96	471.57
192.00	0.00	0.00	0.00	2.24	0.01	6.30	6.34	515.33
312.00	0.00	0.00	0.00	2.34	0.03	6.61	7.03	464.57

**Simulated Extreme Flooding Event  
SFCDR at Smelterville<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.02	0.00	0.00	0.11	0.02	0.08	7.11	538.00
96.00	0.01	0.00	0.00	0.06	0.02	0.05	7.10	507.30
144.00	0.01	0.00	0.00	0.14	0.08	0.08	7.71	
168.00	0.01	0.00	0.00	0.16	0.04	0.06	6.90	
312.00	0.01	0.00	0.00	0.40	0.01	0.17	7.37	422.13

**Simulated Minor Flooding Event  
SFCDR at Smelterville<sup>a</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.02	0.00	0.00	0.35	0.04	0.24	7.01	536.63
96.00	0.01	0.01	0.00	0.07	0.05	0.12	8.31	
120.00	0.02	0.00	0.00	0.03	0.02	0.02		
168.00	0.02	0.00	0.00	0.00	0.00	0.00		
312.00	0.01	0.00	0.00	0.11	0.02	0.24	8.53	551.66

**Simulated Extreme Flooding Event  
SFCDR at Smelterville<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.00	0.00	0.01	0.02	0.00	0.04	8.70	472.66
48.00	0.01	0.00	0.00	0.00	0.00	0.03	7.71	381.90
144.00	0.02	0.00	0.00	0.02	0.02	0.10	7.04	434.56
192.00	0.02	0.00	0.00	0.03	0.02	0.12	6.90	408.17
288.00	0.00	0.00	0.00	0.09	0.02	0.05	6.97	436.77

**Simulated Minor Flooding Event  
SFCDR at Smelterville<sup>b</sup>**

Time (hrs.)	Al	As	Fe	Mn	Pb	Zn	pH	Eh
	----- mg/L -----							
0.00	0.00	0.00	0.00	0.06	0.00	0.08	9.17	422.33
72.00	0.01	0.00	0.02	0.20	0.00	0.34	7.31	433.87
144.00	0.01	0.00	0.00	0.05	0.02	0.09	5.03	425.70
192.00	0.02	0.00	0.00	0.01	0.01	0.04	7.10	489.57
312.00	0.01	0.00	0.00	0.08	0.02	0.20	7.13	453.87

**Table 1A. Metals bound to organic matter (sodium pyrophosphate).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>	----- mg/kg -----					
1 MSCDR (i)	55.59±45.65	20.61±16.42	733.95±547.51	641.85±402.41	443.34±410.77	124.02±112.22
2 MSCDR (i)	139.67±8.17	58.80±0.25	1217.55±48.15	186.57±17.82	2598.45±78.70	167.48±4.60
3 MSCDR (i)	115.98±2.46	38.43±1.32	1286.70±12.73	738.00±36.91	944.55±15.49	152.42±3.84
4 MSCDR (i)	599.70±3.82	14.56±0.28	3702.00±29.70	810.45±15.06	307.35±4.03	605.85±10.82
5 MSCDR (i)	136.82±2.48	31.92±1.57	1321.95±67.67	680.40±37.76	503.10±25.88	137.73±4.12
6 MSCDR (i)	131.45±2.82	27.38±0.57	1205.55±11.67	481.50±34.37	803.70±26.73	145.26±1.10
7 MSCDR (ii)	484.20±11.03	11.19±0.09	2974.35±57.49	289.88±7.70	2428.35±93.97	111.18±1.95
8 MSCDR (ii)	534.30±0.85	10.68±0.16	2753.70±70.85	312.90±5.09	2416.05±30.76	160.56±1.40
9 MSCDR (ii)	356.40±20.36	9.15±0.06	2209.80±48.37	255.38±21.62	2543.25±47.73	198.51±14.21
10 MSCDR (ii)	708.3±9.33	14.90±2.53	4518.00±144.25	914.70±17.82	267.48±4.03	344.46±6.15
11 MSCDR (ii)	414.15±7.00	11.28±0.24	3138.00±59.40	349.05±20.58	3469.50±99.70	985.95±14.21
12 MSCDR (ii)	219.74±16.06	8.53±0.71	32.88.00±318.20	428.40±3.82	1919.10±174.37	1102.05±104.16
13 SFCDR (iii)	626.10±56.00	32.76±2.38	2787.15±189.01	683.10±15.27	907.35±63.43	436.95±14.64
14 SFCDR (iii)	613.35±1.48	28.07±0.07	2722.20±3.82	737.10±14.42	961.05±28.64	388.80±7.64
15 SFCDR (iii)	489.15±15.91	20.21±1.18	2832.00±122.19	594.75±23.55	1608.75±50.70	307.62±15.95
16 SFCDR (iii)	570.75±7.85	32.97±0.93	2849.40±11.03	544.50±0.42	1057.20±11.88	428.10±8.49
17 SFCDR (iii)	384.00±21.21	31.28±0.45	2395.95±105.01	794.10±33.52	202.68±1.70	810.15±23.55
18 SFCDR (iii)	407.85±25.67	32.62±3.76	2259.90±190.92	1446.60±71.70	153.75±7.38	774.00±73.82

**Table 1B. Metals bound to organic matter in control soils (sodium pyrophosphate).**

Controls	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Palouse Soil	587.40±40.31	3.10±0.08	1080.15±93.13	226.82±19.41	8.40±0.41	9.51±0.58
Santa Soil	728.10±17.39	2.45±0.50	565.35±20.15	281.55±10.18	6.98±1.15	4.84±0.84

**Table 1C. Metals bound to organic matter in Lake CDA sediment (sodium pyrophosphate).**

Study One	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Core L (0-10 cm)	505.05±10.39	46.86±1.27	4230.00±123.04	822.15±13.36	2045.85±3.18	856.35±7.00
Leftovers from T2	285.24±74.76	57.59±12.96	2763.60±639.79	79.53±9.72	1249.80±285.65	263.12±47.71

**Table 2A. Noncrystalline metals in the riverbank sediments (AOD).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>						
	----- mg/kg -----					
1 MSCDR (i)	346.50±175.65	153.80±44.55	12105.00±4886.11	1903.50±232.64	970.45±242.61	375.30±144.25
2 MSCDR (i)	617.90±289.35	199.55±27.65	11587.50±3496.64	562.35±40.94	1048.20±203.36	333.15±151.53
3 MSCDR (i)	344.45±286.59	160.15±149.27	12535.40±17429.62	655.70±915.42	863.65±1179.95	362.90±377.45
4 MSCDR (ii)	534.60±5.23	60.00±2.83	6401.50±661.14	2069.50±243.95	809.35±125.79	282.15±27.08
5 MSCDR (ii)	353.35±191.13	137.25±73.47	11814.00±8974.60	1447.10±1367.40	981.10±960.11	218.80±132.37
6 MSCDR (ii)	298.85±9.26	130.25±13.79	9857.50±2690.54	499.10±44.69	564.30±66.19	271.70±96.45
7 MSCDR (ii)	536.85±436.07	54.65±21.43	8155.50±7614.83	378.00±269.69	1282.80±1243.38	173.35±70.36
8 MSCDR (ii)	487.10±35.36	56.35±5.87	7008.00±668.92	421.30±5.23	1156.50±51.62	157.40±16.83
9 MSCDR (ii)	469.70±102.95	62.80±6.22	7121.50±84.15	414.50±150.90	1314.00±224.86	273.35±81.81
10 MSCDR (ii)	562.80±24.75	76.60±4.67	6331.00±2580.94	2312.00±770.75	752.45±401.00	438.80±204.50
11 MSCDR (ii)	924.95±289.98	82.70±38.47	29690.00±8584.28	725.40±194.03	2633.00±773.57	1463.00±438.41
12 MSCDR (ii)	479.40±181.73	64.45±7.00	21375.00±5112.38	1117.55±509.75	2102.50±857.72	1032.50±253.85
13 SFCDR (iii)	803.60±266.15	128.50±65.20	10072.50±4776.51	1291.95±414.44	1207.80±657.89	393.90±228.11
14 SFCDR (iii)	582.05±121.55	118.85±0.49	9136.00±1533.01	1317.50±170.41	1112.10±195.02	360.25±2.19
15 SFCDR (iii)	704.25±180.95	96.05±28.64	8977.50±5914.95	1447.00±190.92	1163.00±1148.34	397.80±15.41
16 SFCDR (iii)	1096.00±397.39	204.60±74.67	22125.00±7643.82	2435.00±940.45	2747.50±1020.36	616.35±211.50
17 SFCDR (iii)	432.25±16.19	101.95±17.32	6701.50±260.92	1409.00±76.37	544.30±20.36	349.25±10.68
18 SFCDR (iii)	515.90±66.61	86.70±48.22	6724.50±2960.66	1425.65±1184.19	654.25±223.94	345.75±93.41

**Table 2B. Noncrystalline metals (AOD) bound to control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Palouse Soil	1411.50±34.65	50.25±10.39	3184.50±238.29	228.65±32.88	36.10±7.78	83.25±45.18
Santa Soil	561.40±23.48	30.40±6.51	1098.65±180.10	90.50±4.81	22.85±7.14	77.00±46.24

**Table 2C. Noncrystalline metals (AOD) bound to Lake CDA sediments.**

Study One	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Core L (0-10 cm)	1474.00±285.67	92.00±22.49	24800.00±919.24	2140.50±19.09	825.85±87.33	1195.50±161.93
Leftovers from T2	732.85±404.68	87.35±10.25	17591.50±14041.02	1421.25±1070.21	566.50±464.29	532.75±262.12

**Table 3A. Crystalline and noncrystalline metals in the riverbank sediments (CBD).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>				mg/kg		
1 MSCDR (i)	303.97±54.21	242.26±35.25	28102.54±3372.35	2935.89±134.17	633.97±80.32	860.38±101.71
2 MSCDR (i)	248.92±17.12	197.72±4.68	11078.19±375.31	110.87±20.23	202.23±20.74	234.24±10.03
3 MSCDR (i)	466.67±11.97	305.13±14.87	33884.58±2411.41	1337.56±138.34	487.95±176.23	686.02±65.82
4 MSCDR (i)	602.44±13.60	89.82±3.30	20516.65±462.34	4424.35±734.30	685.90±184.94	645.64±4.35
5 MSCDR (i)	613.97±33.90	277.95±10.15	38230.73±2429.54	2534.74±114.04	651.15±164.45	793.72±44.06
6 MSCDR (i)	540.13±47.68	267.69±18.13	33717.92±2610.85	1009.36±74.88	643.20±73.07	750.00±69.62
7 MSCDR (ii)	803.72±99.54	60.69±7.00	27755.10±3754.91	697.56±48.41	495.51±126.74	535.51±75.97
8 MSCDR (ii)	1120.13±35.72	76.23±1.09	31769.20±979.07	1234.74±58.93	430.38±6.71	861.15±0.18
9 MSCDR (ii)	889.49±67.45	65.24±3.35	32858.94±2810.29	1054.23±202.52	467.44±23.21	1064.23±90.11
10 MSCDR (ii)	586.28±61.46	54.36±2.28	14891.01±1717.00	5903.84±317.29	650.38±55.30	523.85±28.28
11 MSCDR (ii)	458.59±12.51	55.14±6.18	24141.00±917.42	558.08±72.34	543.97±165.90	950.13±0.91
12 MSCDR (ii)	429.10±3.08	51.41±2.76	37320.48±1504.87	1267.18±138.88	618.33±118.76	1572.95±75.61
13 SFCDR (iii)	889.23±45.69	178.00±18.67	29205.10±2357.02	2385.13±282.12	717.05±159.01	863.97±95.19
14 SFCDR (iii)	837.82±62.91	156.91±3.21	27423.05±1903.75	2961.54±300.97	984.61±101.53	832.95±72.34
15 SFCDR (iii)	897.95±19.58	119.83±0.96	32884.58±634.58	1911.28±133.44	776.15±156.29	1046.28±52.76
16 SFCDR (iii)	827.56±81.77	166.62±5.69	29743.56±2284.50	2432.82±28.65	703.72±52.76	888.97±58.38
17 SFCDR (iii)	716.02±16.14	199.68±5.17	26948.69±507.67	3503.84±146.86	668.08±3.81	932.05±20.67
18 SFCDR (iii)	816.92±176.60	216.00±36.66	31487.15±6019.47	4703.84±1158.57	704.36±183.85	1183.46±242.05

**Table 3B. Crystalline and noncrystalline metals (CBD) bound to control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
				mg/kg		
Palouse Soil	794.10±7.25	28.31±1.27	6891.02±114.22	192.88±6.15	4.87±0.62	10.53±0.34
Santa Soil	617.44±101.90	21.85±1.56	4028.20±641.83	118.54±19.65	4.32±0.85	6.22±2.05

**Table 3C. Total crystalline and noncrystalline material (CBD) in sediment from Lake CDA.**

Study One	Al	As	Fe	Mn	Pb	Zn
				mg/kg		
Core L (0-10 cm)	471.92±76.69	33.90±5.08	6653.84±1189.39	314.69±86.92	68.53±3.97	288.91±68.63
Leftovers from T2	310.00±78.69	37.82±1.56	5453.84±848.53	138.26±12.44	137.15±50.26	213.28±49.42



**Table 4A. Contaminants bound in the sulfide fraction of the riverbank sediments (potassium perchlorate).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
Study Two	mg/kg					
1 MSCDR (i)	1459.49±244.84	147.26±30.02	74553.77±5207.20	5216.41±156.65	1861.54±311.85	874.05±70.49
2 MSCDR (i)	1644.51±17.12	41.88±2.51	95066.57±1290.92	10550.76±126.19	1020.61±50.33	885.64±60.19
3 MSCDR (i)	1779.69±47.58	162.47±21.34	72933.26±4946.12	4442.05±13.05	1812.10±134.89	750.26±232.80
4 MSCDR (i)	3791.79±245.13	81.28±14.32	30174.33±1595.52	8974.35±3092.41	3971.28±269.79	1107.38±63.68
5 MSCDR (i)	2078.97±21.76	242.26±18.28	76810.18±1435.97	3637.95±129.09	2087.90±142.58	811.69±39.74
6 MSCDR (i)	2048.31±36.12	186.33±13.62	75220.44±3452.13	4120.00±42.06	1679.90±104.00	710.05±50.62
7 MSCDR (ii)	3692.30±211.77	53.68±5.77	30358.94±1740.57	882.87±168.55	2162.05±89.93	786.36±48.30
8 MSCDR (ii)	3994.87±30.46	50.39±1.00	25487.15±1174.88	837.13±116.33	2808.20±287.19	941.54±33.94
9 MSCDR (ii)	3548.71±75.42	60.32±2.16	43005.09±2161.21	838.15±43.51	2953.84±116.04	1239.90±48.88
10 MSCDR (ii)	4052.30±485.91	46.58±3.60	20464.59±3462.28	12895.37±163.90	4632.82±7.25	890.97±108.06
11 MSCDR (ii)	3578.46±190.01	50.81±6.21	36061.50±8064.64	1186.46±139.25	2831.79±155.20	1470.56±45.25
12 MSCDR (ii)	2633.84±380.02	49.95±1.39	61343.53±9790.70	1182.87±99.94	3565.12±820.97	1677.64±225.26
13 SFCDR (iii)	2784.61±364.07	143.25±15.59	44430.72±17985.88	2242.05±278.49	3940.51±800.66	1316.31±306.63
14 SFCDR (iii)	2467.69±52.22	123.03±11.44	36892.27±9587.63	2412.82±625.88	3350.77±320.55	1150.46±67.16
15 SFCDR (iii)	3168.20±21.76	117.06±2.60	36892.27±8456.26	2125.33±446.46	3866.66±365.52	1152.00±41.77
16 SFCDR (iii)	2379.48±98.63	112.68±11.26	26102.54±1552.01	1900.00±144.90	3370.25±66.72	869.95±35.68
17 SFCDR (iii)	2356.92±49.32	182.10±14.95	42215.34±1276.42	3263.59±194.36	3233.84±4.35	1131.28±82.39
18 SFCDR (iii)	2353.84±33.36	181.77±1.12	37476.89±7136.33	5468.71±205.97	3468.71±17.41	1088.20±8.12

**Table 4B. Contaminants bound in the sulfide fraction (potassium perchlorate) of the control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Palouse Soil	4674.87±40.61	14.75±2.76	8898.45±110.24	97.12±5.56	0.73±1.03	29.56±0.15
Santa Soil	4333.33±1008.08	20.08±2.20	8100.50±1961.04	85.62±25.09	0.11±0.16	18.97±4.96

**Table 4C. Contaminants in the sulfide fraction (potassium perchlorate) of sediment from Lake CDA.**

Study One	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Core L (0-10 cm)	3029.74±34.81	75.84±5.83	54287.13±1000.83	4111.79±71.07	695.59±56.28	1329.13±30.61
Leftovers from T2	1716.31±375.38	25.72±1.97	62451.22±14.50	5005.12±113.14	377.44±55.70	728.72±50.04

**Table 5A. Metals strongly bound to the remaining crystalline fraction (HNO<sub>3</sub>/HCL/HF/Boric Acid).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
Study Two	mg/kg					
1 MSCDR (i)	4798.20±322.02	44.89±2.15	11823.90±3411.51	265.58±14.37	71.13±8.52	197.04±16.57
2 MSCDR (i)	4581.06±375.22	13.53±2.76	8438.10±742.04	697.62±44.80	96.53±7.89	174.11±16.15
3 MSCDR (i)	5290.89±56.47	27.78±1.05	10203.60±2678.80	357.75±40.56	78.12±23.56	127.97±7.09
4 MSCDR (i)	5527.83±192.74	36.95±3.92	10992.30±2795.48	289.54±7.37	57.35±2.81	168.66±5.93
5 MSCDR (i)	5295.18±934.31	42.41±8.92	10470.90±4186.21	170.97±31.97	60.34±20.60	125.70±29.17
6 MSCDR (i)	5089.92±235.21	35.45±2.00	8827.50±574.03	333.86±31.41	63.46±9.29	119.86±9.71
7 MSCDR (ii)	8514.00±9.33	7.59±0.48	4393.62±722.44	70.35±14.85	33.88±2.37	60.45±21.30
8 MSCDR (ii)	7175.52±819.51	7.08±0.60	4235.22±425.62	73.56±6.39	28.22±1.64	75.54±7.33
9 MSCDR (ii)	6561.39±0.47	14.33±1.74	6399.03±526.89	119.53±29.49	67.04±34.94	153.32±17.27
10 MSCDR (ii)	6771.60±168.01	20.23±0.96	5819.22±188.54	91.91±7.33	62.69±8.04	128.70±4.01
11 MSCDR (ii)	7530.60±93.34	6.47±0.36	3996.96±175.48	85.60±4.95	52.01±3.89	78.67±5.69
12 MSCDR (ii)	6669.30±527.36	9.27±0.18	11147.40±1960.10	72.30±2.19	57.27±17.02	115.30±4.29
13 SFCDR (iii)	6306.30±172.68	23.13±0.75	6143.28±7.47	120.15±3.13	62.55±0.80	129.95±1.31
14 SFCDR (iii)	6450.51±454.09	20.24±1.02	6011.94±133.47	94.38±4.48	61.77±3.04	134.05±0.19
15 SFCDR (iii)	5180.67±2007.24	21.84±11.65	4302.21±2071.64	58.59±27.84	39.82±15.66	86.89±48.49
16 SFCDR (iii)	5882.25±452.22	17.06±0.32	4731.54±70.94	88.08±2.94	43.61±5.39	91.11±1.17
17 SFCDR (iii)	6077.94±52.27	28.83±0.49	5466.12±128.81	62.95±0.99	44.69±4.45	118.07±5.04
18 SFCDR (iii)	6315.21±371.02	31.37±1.44	6090.48±484.42	76.40±2.19	42.82±2.43	131.90±13.21

**Table 5B. Digestion of metals in control soils (HNO<sub>3</sub>/HCL/HF/Boric Acid).**

Controls	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Palouse Soil	10791.00±3602.85	2.14±0.43	3140.61±179.68	38.73±1.80	8.64±0.36	7.44±0.06
Santa Soil	9240.00±261.35	3.69±0.70	3456.42±91.47	35.81±0.45	8.79±1.06	4.86±0.07

**Table 5C. Digestion of metals strongly bound in Lake CDA sediment (HNO<sub>3</sub>/HCL/HF/Boric Acid).**

Study One	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Core L (0-10 cm)	7857.30±490.02	17.37±1.22	5995.11±443.82	382.54±35.38	105.47±29.96	104.58±12.83
Leftovers from T2	5292.86±1516.74	6.52±2.03	5829.12±1640.88	407.65±123.16	80.24±58.74	71.06±21.79

**Table 6A. Exchangeable metals.**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>	----- mg/kg -----					
1 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	18.07±1.13	2.62±0.32	52.48±6.39
2 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	63.21±0.86	172.25±14.07	3445.00±281.43
3 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	28.75±3.66	8.41±1.33	168.14±26.67
4 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	19.67±0.02	5.48±0.18	109.60±3.51
5 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	19.75±1.38	4.67±0.07	93.48±1.30
6 MSCDR (i)	0.00±0.00	0.00±0.00	0.00±0.00	20.89±0.49	11.34±0.35	226.80±7.07
7 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	66.44±2.09	1902±115.82	38056±2302.34
8 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	56.16±4.89	902.80±17.82	18056±356.38
9 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	88.31±39.92	517.70±26.73	10354±534.57
10 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	24.69±2.43	25.42±10.56	508.32±211.11
11 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	58.85±4.23	480.10±35.78	9602.0±715.59
12 MSCDR (ii)	0.00±0.00	0.00±0.00	0.00±0.00	77.27±1.97	205.80±6.22	4116±124.45
13 SFCDR (iii)	0.00±0.00	0.00±0.00	0.00±0.00	41.59±2.39	29.80±2.66	596.0±53.17
14 SFCDR (iii)	0.00±0.00	0.00±0.00	0.00±0.00	20.49±0.84	6.56±0.69	131.14±13.72
15 SFCDR (iii)	0.00±0.00	0.00±0.00	0.00±0.00	28.02±0.28	10.03±0.36	200.64±7.30
16 SFCDR (iii)	0.00±0.00	0.00±0.00	0.00±0.00	72.21±8.08	38.03±3.86	760.60±77.22
17 SFCDR (iii)	0.00±0.00	0.00±0.00	0.00±0.00	33.27±2.62	4.55±1.15	91.06±22.94
18 SFCDR (iii)	0.00±0.00	0.00±0.00	0.43±0.60	21.08±0.42	1.86±0.32	37.26±6.48

**Table 6B. Exchangeable metals in control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Palouse Soil	0.00±0.00	0.00±0.00	0.00±0.00	62.40±5.77	0.00±0.00	0.00±0.00
Santa Soil	0.00±0.00	0.00±0.00	0.00±0.00	28.58±1.44	0.45±0.28	8.90±5.63

**Table 6C. Exchangeable metals in sediment from Lake CDA.**

Study One	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Core L (0-10 cm)	0.00±0.00	0.00±0.00	0.34±0.10	371.30±6.65	254.70±6.65	5094±132.94
Leftovers from T2	0.00±0.00	0.00±0.00	0.00±0.00	37.93±3.04	281.20±26.02	5624±520.43

**Table 7A. Metals bound to the carbonate fraction of the sediment.**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>	----- mg/kg -----					
1 MSCDR (i)	0.08±0.11	0.12±0.01	6.55±0.47	156.38±5.37	240.90±15.98	99.71±3.61
2 MSCDR (i)	11.82±0.94	0.17±0.01	104.02±0.20	88.43±5.33	1983±199	152.53±13.87
3 MSCDR (i)	0.08±0.11	0.11±0.04	6.91±1.23	84.83±14.92	298±44.12	49.74±11.12
4 MSCDR (i)	0.03±0.04	0.12±0.00	9.87±0.04	89.60±0.65	295.70±3.54	101.13±2.42
5 MSCDR (i)	0.00±0.00	0.10±0.03	2.83±0.19	132.68±7.18	174.12±28.91	59.49±0.10
6 MSCDR (i)	0.32±0.18	0.13±0.01	8.51±1.18	81.49±2.87	429.50±31.54	50.45±0.33
7 MSCDR (ii)	18.62±0.24	0.09±0.03	16.01±4.09	43.94±26.56	832.60±41.86	16.04±0.47
8 MSCDR (ii)	17.83±0.24	0.11±0.01	14.33±2.25	28.20±5.74	710.60±24.32	20.29±2.25
9 MSCDR (ii)	6.73±2.59	0.11±0.03	8.48±1.82	36.84±9.90	745.90±79.05	33.63±0.07
10 MSCDR (ii)	9.70±3.04	0.10±0.02	18.10±6.34	65.88±9.76	218.20±20.93	156.58±19.69
11 MSCDR (ii)	4.60±1.41	0.12±0.02	53.17±10.03	49.54±4.84	1435.20±185.83	233.0±24.32
12 MSCDR (ii)	0.00±0.00	0.09±0.02	8.27±1.18	51.38±4.53	540.60±15.84	184.37±4.29
13 SFCDR (iii)	9.82±1.35	0.09±0.00	19.08±1.11	103.29±6.15	327.20±2.55	147.16±7.18
14 SFCDR (iii)	8.94±2.35	0.12±0.01	17.58±3.90	115.82±1.62	267.60±22.91	159.86±4.67
15 SFCDR (iii)	7.13±0.10	0.09±0.02	16.64±0.38	93.24±2.83	237.30±0.71	134.02±2.55
16 SFCDR (iii)	4.84±0.90	0.08±0.01	8.89±1.03	127.64±10.32	317.30±4.38	151.14±9.11
17 SFCDR (iii)	3.43±0.01	0.09±0.00	12.12±1.02	142.30±1.16	129.68±20.45	295.10±1.84
18 SFCDR (iii)	6.28±1.55	0.11±0.01	12.65±1.72	148.25±1.74	83.64±3.54	272.10±12.59

**Table 7B. Metals bound to carbonates in control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Palouse Soil	2.72±3.85	0.08±0.05	1.75±0.21	25.47±2.67	1.33±1.17	0.78±0.13
Santa Soil	5.77±5.88	0.06±0.04	7.62±0.80	25.53±0.92	9.24±1.06	6.68±0.21

**Table 7C. Metals bound to carbonates in Lake CDA sediment.**

Study One	Al	As	Fe	Mn	Pb	Zn
	----- mg/kg -----					
Core L (0-10 cm)	18.14±0.01	0.22±0.01	640.30±24.47	218.0±6.22	863.60±52.89	333.30±14.00
Leftovers from T2	8.69±2.71	0.25±0.02	355.50±25.60	18.77±1.33	598.90±25.31	102.07±8.44

**Table 8A. Contaminants bound to Iron and Manganese Oxides.**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
<b>Study Two</b>				mg/kg		
1 MSCDR (i)	185.29±1.65	122.48±2.49	18404.00±274.36	4016.00±107.48	213.2±3.39	463.90±0.14
2 MSCDR (i)	172.60±10.30	209.35±18.17	10371.00±352.14	190.78±22.66	37.56±1.41	199.79±7.65
3 MSCDR (i)	236.50±2.97	110.85±2.93	18970.00±220.62	1662.50±195.59	132.75±4.99	335.20±8.49
4 MSCDR (i)	238.20±2.26	107.90±1.95	21160.00±282.84	1491.40±61.94	159.60±8.68	517.10±11.46
5 MSCDR (i)	329.90±10.32	121.36±0.62	20900.00±311.13	4409.00±371.94	282.20±2.83	393.70±5.80
6 MSCDR (i)	301.00±8.77	144.24±5.69	20410.00±410.12	1245.80±23.48	125.25±2.84	340.90±15.41
7 MSCDR (ii)	939.00±101.26	38.20±1.47	25970.00±5303.30	6563.00±7024.40	170.61±45.52	494.30±150.33
8 MSCDR (ii)	919.00±1.98	38.31±1.00	22220.00±113.14	1905.50±832.26	126.47±1.68	503.20±2.83
9 MSCDR (ii)	594.10±18.24	38.75±0.21	23320.00±311.13	1408.50±298.54	112.80±0.82	602.00±16.12
10 MSCDR (iii)	836.00±56.29	116.34±2.83	18999.00±1053.59	7544.00±1994.04	242.30±3.82	713.60±30.55
11 MSCDR (ii)	660.70±141.85	59.32±17.54	49940.00±9644.94	1687.20±293.59	145.25±12.40	1721.60±340.54
12 MSCDR (iii)	581.20±163.77	28.20±6.11	64460.00±15754.34	2653.00±657.61	198.53±52.99	1716.00±486.49
13 SFCDR (iii)	724.50±4.10	139.16±0.28	18341.00±12.73	4261.00±222.03	146.67±1.00	505.50±12.30
14 SFCDR (iii)	644.10±42.85	107.00±6.48	18195.00±878.23	4607.00±114.55	134.52±10.97	532.20±6.51
15 SFCDR (iii)	877.50±3.82	179.34±0.28	21200.00±28.28	3622.00±107.48	167.69±10.37	502.30±7.50
16 SFCDR (iii)	804.40±59.40	139.38±6.51	19192.00±506.29	4237.00±179.61	121.06±2.88	492.30±29.56
17 SFCDR (iii)	879.60±373.07	199.74±78.15	34125.00±20074.76	8123.00±4863.48	243.96±78.97	1053.60±521.56
18 SFCDR (iii)	790.60±274.36	163.73±52.99	23128.00±7682.01	15174.00±82.02	385.60±116.81	1095.50±498.38

**Table 8B. Contaminants bound to Iron and Manganese Oxides in c**

Controls	Al	As	Fe	Mn	Pb	Zn
				mg/kg		
Palouse Soil	475.40±26.30	8.80±0.16	2951.00±176.78	261.40±2.26	3.84±0.43	1.04±1.48
Santa Soil	483.60±41.30	8.17±0.46	3448.00±910.75	260.50±8.06	5.84±0.26	3.73±1.71

**Table 8C. Contaminants bound to Iron and Manganese Oxides in Lake CDA sediment**

Study One	Al	As	Fe	Mn	Pb	Zn
				mg/kg		
Core L (0-10 cm)	439.80±4.24	63.51±1.26	8219.00±148.49	310.40±13.29	46.64±1.64	443.50±12.30
Leftovers from T2	369.90±10.04	145.48±1.05	8053.00±114.55	143.50±0.68	46.21±2.56	322.20±4.53

**Table 9A. Contaminants bound in the organic fraction of the sediment (hydrogen peroxide).**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
Study Two	mg/kg					
1 MSCDR (i)	366.28±61.48	17.97±1.61	9395.54±1503.46	3169.28±270.08	2330.45±98.32	469.45±51.27
2 MSCDR (i)	276.80±1.35	23.59±1.65	15508.92±299.97	3192.67±95.71	801.50±189.54	567.48±1.18
3 MSCDR (i)	335.45±21.79	17.41±0.01	8212.54±1746.61	2739.71±286.21	1509.90±300.74	380.54±37.74
4 MSCDR (i)	470.98±6.80	17.47±0.33	7886.55±211.32	3583.80±61.77	1622.08±14.81	546.42±1.90
5 MSCDR (i)	486.59±9.58	18.10±0.22	6918.85±165.15	2756.70±10.49	2272.31±90.53	271.41±7.26
6 MSCDR (i)	453.30±50.55	17.02±0.39	8498.27±173.13	3358.75±95.88	1969.12±16.46	397.25±29.02
7 MSCDR (ii)	813.17±17.01	16.62±0.38	1819.00±35.39	7019.59±884.90	6489.93±77.31	324.87±5.97
8 MSCDR (ii)	1447.54±123.46	16.69±0.49	2340.51±275.94	1135.75±1367.75	3439.55±743.26	506.70±21.42
9 MSCDR (ii)	1237.26±1.02	16.01±0.15	2602.42±207.62	440.07±360.07	3853.20±524.10	601.05±42.98
10 MSCDR (ii)	1110.32±90.26	25.14±3.89	4008.78±229.85	1484.02±195.61	4576.92±313.98	462.99±19.35
11 MSCDR (ii)	1101.78±52.34	20.18±0.78	5198.22±1564.52	799.12±20.72	3791.96±55.46	711.37±23.10
12 MSCDR (ii)	996.44±34.56	17.20±0.98	3195.68±10.35	479.73±27.66	4074.34±28.76	773.40±31.48
13 SFCDR (iii)	881.31±1.02	23.55±0.32	6332.15±176.0	1369.62±21.80	4314.44±153.91	408.81±2.15
14 SFCDR (iii)	959.49±3.26	24.33±0.40	4000.65±123.24	774.00±13.16	4874.14±304.35	484.60±8.58
15 SFCDR (iii)	1009.52±3.03	24.65±0.00	5045.40±1072.84	813.70±0.80	3861.82±92.35	407.79±7.55
16 SFCDR (iii)	781.56±436.42	17.07±8.26	5061.19±2690.97	583.75±276.78	3672.32±2132.65	329.94±176.76
17 SFCDR (iii)	904.70±6.15	24.65±0.08	5078.48±1055.02	750.22±3.61	3591.40±328.59	455.91±6.98
18 SFCDR (iii)	857.53±8.61	24.41±2.60	6147.59±80.21	2091.13±34.83	3593.89±152.43	417.51±3.43

**Table 9B. Contaminants bound to organic matter in control soils (hydrogen peroxide).**

Controls	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Palouse Soil	2560.06±2.92	16.77±0.41	936.83±62.56	34.98±5.63	12.02±1.28	6.66±0.54
Santa Soil	2247.66±234.34	15.92±0.55	1292.10±68.12	48.01±12.59	16.05±4.11	13.44±1.51

**Table 9C. Metals bound to organic matter (hydrogen peroxide) in Lake CDA sediment.**

Study One	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Core L (0-10 cm)	753.91±99.49	58.40±6.91	14114.47±1956.13	2529.75±307.23	450.38±183.80	696.35±50.88
Leftovers from T2	656.86±16.03	21.18±2.45	14502.39±818.79	3019.03±230.59	804.03±168.50	392.95±13.20

**Table 10A. Digestion of metals strongly bound to the remaining crystalline fraction.**

Column/Loc/Site	Al	As	Fe	Mn	Pb	Zn
Study Two	mg/kg					
1 MSCDR (i)	37730.0±15518.45	68.80±21.33	5249.72±946.79	440.78±60.98	29.55±7.56	425.07±132.93
2 MSCDR (i)	46552.80±9820.30	119.00±35.32	5920.04±1416.42	435.06±109.53	35.69±5.84	938.28±100.97
3 MSCDR (i)	38267.60±3092.60	63.73±4.59	3983.56±504.87	316.46±32.31	28.98±1.24	276.67±119.15
4 MSCDR (i)	33157.60±8109.67	43.87±4.42	3886.68±69.30	146.41±4.16	26.85±2.30	67.93±13.23
5 MSCDR (i)	32488.40±8683.84	37.69±2.57	3569.44±517.15	224.70±33.38	25.60±2.67	106.32±14.53
6 MSCDR (i)	38959.20±9131.29	27.22±9.06	4152.68±438.35	293.97±34.41	30.56±1.44	244.86±28.00
7 MSCDR (ii)	67480.00±237.59	21.57±2.09	6302.80±154.43	274.48±20.16	49.30±0.57	78.43±11.36
8 MSCDR (ii)	44881.20±8644.24	20.20±2.40	4611.32±532.59	198.94±20.55	38.85±4.51	43.43±4.44
9 MSCDR (ii)	47454.40±22459.97	28.14±0.36	4142.04±888.18	238.84±68.82	34.17±4.69	34.72±4.82
10 MSCDR (ii)	41888.00±11982.35	26.28±13.11	4816.84±90.68	117.80±0.44	34.28±1.47	37.95±3.05
11 MSCDR (ii)	27946.80±10584.54	18.96±10.42	3810.80±1079.44	181.13±47.40	45.18±27.97	65.15±30.86
12 MSCDR (ii)	61152.00±3801.41	18.05±6.40	5445.72±281.54	269.70±23.05	39.43±4.30	105.22±1.11
13 SFCDR (iii)	45861.20±10434.07	11.07±0.31	5386.92±895.31	245.08±46.13	33.67±2.97	55.84±4.98
14 SFCDR (iii)	51170.00±2910.45	6.33±3.35	5775.00±346.48	264.01±28.23	37.32±1.33	52.08±1.71
15 SFCDR (iii)	60256.00±1663.12	7.98±0.54	6554.80±296.98	313.10±4.28	43.79±0.34	45.71±4.41
16 SFCDR (iii)	53530.40±1639.36	10.71±2.10	5961.20±91.08	277.56±2.18	36.31±6.64	51.64±1.73
17 SFCDR (iii)	51735.60±336.58	8.27±0.46	5692.40±1017.67	214.00±25.54	31.31±4.73	49.72±11.49
18 SFCDR (iii)	53762.80±249.47	9.25±0.91	5474.84±65.34	213.42±2.85	30.30±0.16	57.40±0.95

**Table 10B. Digestion of metals strongly bound to the remaining crystal fraction in control soils.**

Controls	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Palouse Soil	78876±28154.16	41.64±32.11	11362.40±3753.89	51.60±34.65	17.28±6.09	23.69±3.52
Santa Soil	65128.00±9503.52	8.94±3.63	9713.20±518.73	158.93±15.76	35.92±10.15	47.52±12.39

**Table 10C. Digestion of metals strongly bound to the remaining crystal fraction in Lake CDA sediment.**

Study One	Al	As	Fe	Mn	Pb	Zn
	mg/kg					
Core L (0-10 cm)	57898.40±5789.22	78.85±7.84	7470.40±776.12	237.38±19.40	42.78±1.22	323.09±39.56
Leftovers from T2	50369.20±5523.92	25.07±2.83	7672.00±657.33	408.49±2.73	38.34±4.93	199.50±19.76

**Table 11A. Water quality for first flooding simulation (4/20/96).**

Column/Loc.	Al	As	Fe	Mn	Pb	Zn
	-----mg/L-----					
1 MSCDR	0.11	0.00	0.19	0.16	0.04	0.30
2 MSCDR	0.08	0.00	0.15	0.15	0.05	0.23
3 MSCDR	0.07	0.00	0.13	0.13	0.08	0.20
4 MSCDR	0.05	0.02	0.13	0.11	0.12	0.17
5 MSCDR	0.04	0.00	0.11	0.09	0.05	0.14
6 MSCDR	0.08	0.00	0.14	0.14	0.04	0.21
7 MSCDR	0.02	0.00	0.12	0.20	0.07	0.29
8 MSCDR	0.03	0.00	0.12	0.19	0.07	0.27
9 MSCDR	0.03	0.00	0.12	0.19	0.07	0.29
10 MSCDR	0.02	0.00	0.11	0.18	0.09	0.28
11 MSCDR	0.02	0.00	0.13	0.14	0.07	0.19
12 MSCDR	0.04	0.02	0.14	0.23	0.06	0.34
13 SFCDR	0.06	0.04	0.22	0.94	0.06	1.21
14 SFCDR	0.21	0.01	0.25	1.13	0.03	1.48
15 SFCDR	0.06	0.00	0.25	1.01	0.00	1.28
16 SFCDR	0.21	0.01	0.24	1.15	0.08	1.50
17 SFCDR	0.16	0.02	0.26	1.12	0.04	1.41
18 SFCDR	0.15	0.01	0.26	1.16	0.06	1.44

**Table 11B. Water quality for second flooding simulation (6/13/96).**

Column/Loc.	Al	As	Fe	Mn	Pb	Zn
	-----mg/L-----					
1 MSCDR	0.00	0.02	0.05	0.18	0.00	0.32
2 MSCDR	0.00	0.01	0.05	0.07	0.00	0.32
3 MSCDR	0.00	0.02	0.04	0.02	0.00	0.28
4 MSCDR	0.00	0.00	0.04	0.03	0.00	0.28
5 MSCDR	0.00	0.04	0.06	0.08	0.00	0.33
6 MSCDR	0.00	0.00	0.05	0.08	0.00	0.31
7 MSCDR	0.01	0.02	0.12	0.26	0.00	0.44
8 MSCDR	0.00	0.01	0.08	0.25	0.00	0.42
9 MSCDR	0.01	0.02	0.23	0.74	0.00	0.53
10 MSCDR	0.00	0.01	0.10	0.31	0.01	0.44
11 MSCDR	0.00	0.02	0.11	0.33	0.00	0.43
12 MSCDR	0.00	0.00	0.08	0.21	0.00	0.42
13 SFCDR	0.02	0.03	0.02	0.59	0.00	1.09
14 SFCDR	0.02	0.00	0.01	0.59	0.00	1.01
15 SFCDR	0.02	0.01	0.01	0.57	0.00	0.96
16 SFCDR	0.02	0.02	0.03	0.56	0.00	0.96
17 SFCDR	0.02	0.00	0.01	0.55	0.00	0.99
18 SFCDR	0.02	0.01	0.02	0.59	0.00	0.99



**Table 11C. Water quality for third flooding simulation (7/20/96).**

Column/Loc.	Al	As	Fe	Mn	Pb	Zn
	----- mg/L -----					
1 MSCDR	0.07	0.00	0.02	0.25	0.02	0.50
2 MSCDR	0.08	0.00	0.04	0.31	0.03	0.53
3 MSCDR	0.11	0.00	0.09	0.40	0.04	0.60
4 MSCDR	0.10	0.00	0.07	0.35	0.02	0.62
5 MSCDR	0.07	0.00	0.04	0.32	0.01	0.53
6 MSCDR	0.11	0.00	0.06	0.33	0.02	0.52
7 MSCDR	0.06	0.00	0.21	0.55	0.02	0.78
8 MSCDR	0.03	0.00	0.08	0.60	0.01	0.73
9 MSCDR	0.02	0.00	0.10	0.70	0.03	0.71
10 MSCDR	0.08	0.00	0.04	0.68	0.02	0.76
11 MSCDR	0.11	0.00	0.11	0.66	0.01	0.77
12 MSCDR	0.09	0.00	0.04	0.74	0.02	0.76
13 SFCDR	0.14	0.00	0.03	3.33	0.01	2.70
14 SFCDR	0.13	0.00	0.02	3.22	0.01	2.62
15 SFCDR	0.14	0.00	0.17	3.28	0.01	2.67
16 SFCDR	0.13	0.00	0.02	3.35	0.03	2.74
17 SFCDR	0.12	0.01	0.01	3.29	0.02	2.67
18 SFCDR	0.13	0.00	0.01	3.34	0.00	2.68

**Table 11D. Water quality for fourth flooding simulation (8/31/96).**

Column/Loc.	Al	As	Fe	Mn	Pb	Zn
	----- mg/L -----					
1 MSCDR	0.11	0.06	0.02	0.18	0.01	0.59
2 MSCDR	0.11	0.05	0.01	0.17	0.01	0.57
3 MSCDR	0.12	0.04	0.08	0.28	0.02	0.62
4 MSCDR	0.11	0.03	0.04	0.18	0.01	0.54
5 MSCDR	0.10	0.03	0.02	0.19	0.01	0.59
6 MSCDR	0.13	0.23	0.04	0.18	0.00	0.54
7 MSCDR	0.13	0.04	0.04	0.73	0.01	1.08
8 MSCDR	0.12	0.06	0.06	0.73	0.01	1.07
9 MSCDR	0.11	0.02	0.05	0.72	0.02	1.10
10 MSCDR	0.12	0.03	0.04	0.70	0.01	1.09
11 MSCDR	0.12	0.03	0.03	0.68	0.01	1.03
12 MSCDR	0.11	0.00	0.03	0.69	0.01	1.10
13 SFCDR	0.22	0.03	0.01	4.98	0.01	4.15
14 SFCDR	0.22	0.03	0.01	5.05	0.01	4.14
15 SFCDR	0.25	0.08	0.01	5.24	0.00	4.61
16 SFCDR	0.21	0.56	0.01	5.17	0.00	4.09
17 SFCDR	0.21	0.11	0.02	4.93	0.00	4.07
18 SFCDR	0.22	0.03	0.21	5.15	0.02	4.37