

# **Effect of Mining-Related Activities on the Sediment-Trace Element Geochemistry of Lake Coeur d'Alene, Idaho, USA--Part 1: Surface Sediments**

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# **The Effect of Mining and Related Activities on the Sediment-Trace Element Geochemistry of Lake Coeur d'Alene, Idaho, U.S.A.--Part 1: Surface Sediments**

*By Arthur J. Horowitz, Kent A. Elrick, and Robert B. Cook*

## **ABSTRACT**

During the summer of 1989, 172 surface sediment sample sites were occupied in Lake Coeur d'Alene, the Coeur d'Alene River, and the St. Joe River, Idaho, at a density of approximately 1/km<sup>2</sup>. Additional samples were collected from the banks of the South Fork of the Coeur d'Alene and the Coeur d'Alene Rivers in 1991. All the samples were collected to determine trace element concentrations and distribution patterns and to relate them to mining, mining-related, and discharge operations that have occurred in the Coeur d'Alene district since the 1880's, some of which are ongoing.

The majority of the surface sediments in Lake Coeur d'Alene north of Conkling Point and Carey Bay are substantially enriched in Ag, Cu, Pb, Zn, Cd, Hg, As, and Sb relative to unimpacted sediments in the southern portion of the lake near the St. Joe River. All the trace element-enriched sediments are extremely fine grained (mean grain sizes <63  $\mu$ m). The majority of the enriched trace elements, based on both the chemical analyses of separated heavy and light mineral fractions and a two-step sequential extraction procedure, are associated with an operationally defined Fe oxide phase; much smaller percentages are associated either with operationally defined organics/sulfides or refractory phases. The presence, concentration, and distribution of the Fe oxides and heavy minerals indicates that a major portion of the enriched trace elements probably are coming from the Coeur d'Alene River, which is serving as a point source. Within the lake, this relatively simple pattern is complicated by a combination of (1) formation of trace element-rich authigenic Fe oxides that appear to have reprecipitated from material solubilized from anoxic bed sediments and (2) physical remobilization by currents and wind-driven waves. The majority of the enriched trace elements associated with "Fe oxides" may become environmentally available upon burial in the anoxic lake bottom sediments. Fewer trace elements are associated with sulfide minerals; these trace elements may become environmentally available only if they are exhumed and exposed to an oxic environment. The processes that have caused the trace element enrichment in the surface sediments of Lake Coeur d'Alene are likely to continue for the foreseeable future.

## **INTRODUCTION**

Lake Coeur d'Alene (CDA) is a natural (submerged river bed) lake in the northern panhandle of Idaho (Fig. 1). The lake lies between the Selkirk and the CDA Mountains and extends northward from the St. Joe River to the headwaters of the Spokane River near the city of CDA (Meckel Engineering et al., 1983; Bender, 1991). The main

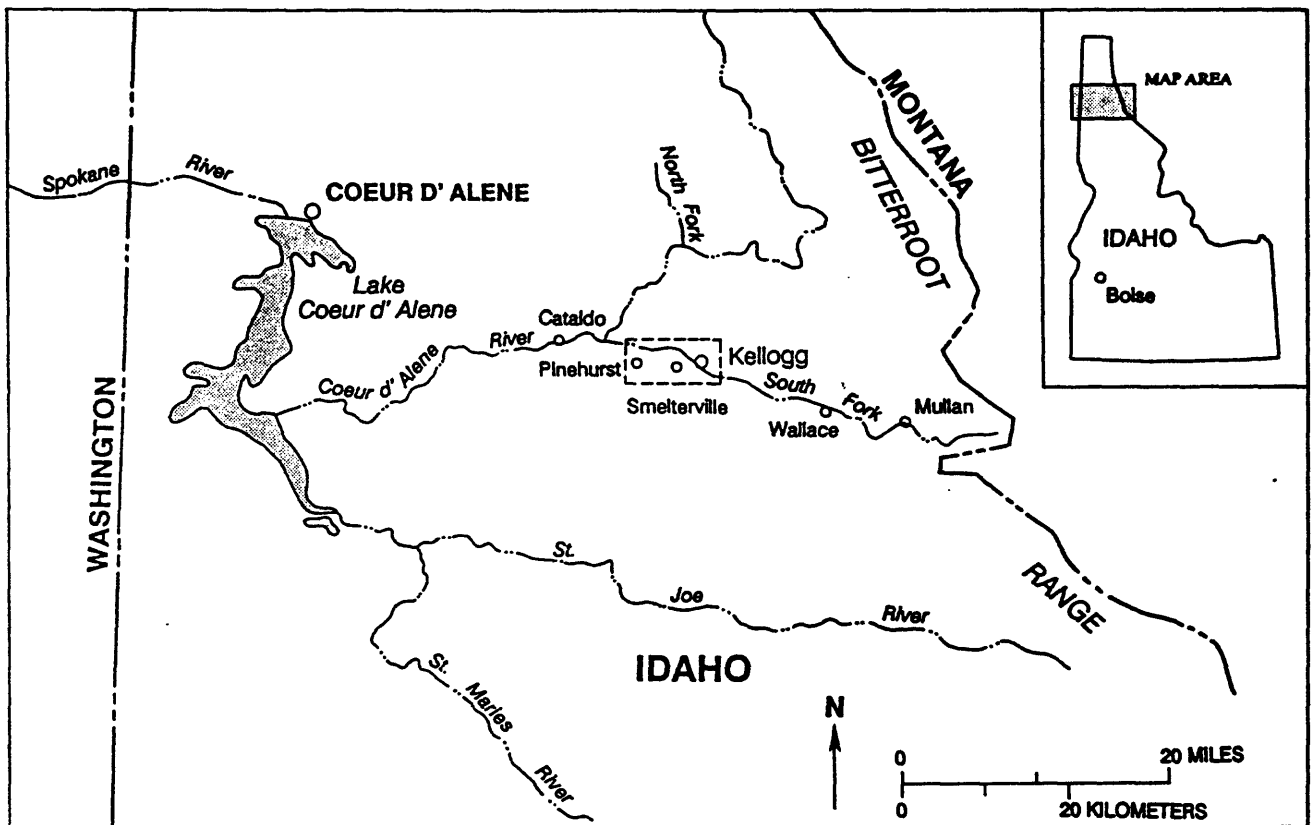


Figure 1. General location map of the South Fork of the Coeur d'Alene River, the St. Joe River, and Lake Coeur d'Alene. The dashed box outlines the location of the 54 km<sup>2</sup> U.S. EPA Bunker Hill Superfund Site.

body of Lake CDA is about 3.2 km wide by 40 km long; however, the southern part is composed of four smaller interconnected lakes that were formed in 1906 when the Post Falls Dam (10 mi downstream on the Spokane River) was completed (Meckel Engineering et al., 1983) (Fig. 1). The St. Joe and CDA Rivers account for 94% (~4.73 billion m<sup>3</sup>/yr) of the inflow to Lake CDA (Meckel Engineering et al., 1983; Javorka, 1991). Major outflow from the lake occurs at the northern end through the Spokane River. Urban development has increased around Lake CDA and centers on the cities of CDA and Harrison. Much of the shoreline, especially along the bays of the northern part of the lake, supports a substantial year-round residential population. Finally, Lake CDA is a major recreational area for swimming, boating, and fishing (Meckel Engineering et al., 1983; Javorka, 1991).

The South Fork of the CDA River begins in the Bitterroot Mountain Range near the Idaho/Montana border and flows slightly north of west through the CDA mining district and the cities of Mullan, Wallace, Kellogg, Smelterville, and Pinehurst and joins the main stem of the CDA River some 4.8 km above Cataldo at Enaville (Fig. 1). Between Wallace and Enaville, the South Fork flows rapidly, with a gradient of 5.7m/km, and little sediment is deposited in the river bed or along its banks and flood plain (Mink, 1971; Norbeck, 1974; Bender, 1991). Below Enaville, the gradient of the CDA River decreases to 0.19m/km due to backwater from the Post Falls Dam, and substantial quantities of sediment are deposited in the main channel and along the banks and flood plain (Bender, 1991). Annually, during high flow (e.g., spring snowmelt and runoff), these sediments are resuspended, transported, and redeposited both in the river and in the lake (Bender, 1991).

The South Fork drains a substantial part of the CDA mining district and the so-called Silver Valley. The mining district has been in operation since the 1880's and was one of the major sources of Ag, Pb, and Zn in the United States (e.g., Bender, 1991). Until 1968, when tailings ponds were established to limit sediment transport, most of the mining and ore-processing wastes were discharged directly into the South Fork of the CDA River. As late as 1964, additional estimates indicated that some 2200 t/d of mining and processing wastes still were entering the South Fork (Reece et al., 1978). It has been estimated that during the course of mining, processing, and smelting operations in the area, some 115 million t of mine tailings were produced and that over 60% of this material probably entered the South Fork of the CDA and the CDA River system (Javorka, 1991). These materials were highly enriched in Ag, As, Cd, Cu, Fe, Mn, Pb, Sb, and Zn (Rabe and Bauer, 1977; Bender, 1991). In 1983, as a result of the elevated trace element concentrations of the mining and processing wastes, the U.S. Environmental Protection Agency established the Bunker Hill Superfund Site that encompasses 54 km<sup>2</sup> in the Kellogg and Smelterville Flats area (e.g., Bender, 1991; Fig. 1).

The St. Joe River is south of, and roughly parallels, the South Fork of the CDA and the CDA Rivers (Fig. 1). The St. Joe River has an average annual discharge slightly higher than that of the CDA River (2.45 billion m<sup>3</sup>/yr compared to 2.28 billion m<sup>3</sup>/yr). The river has been used primarily by the logging industry, has supported no major mining activities, and has been reported to be relatively uncontaminated with trace elements (Mink, 1971; Rabe and Flaherty, 1974; Bender, 1991).

Between the 1880's (onset of mining operations) and the 1930's, jig tailings containing elevated trace element concentrations were left in massive piles along the valley of the South Fork of the CDA River, especially in the Kellogg-Smelterville Flats area (Inoannou, 1979). In the 1930's, a dam was constructed downstream from Smelterville to retain the tailings in settling ponds as an aid to secondary ore recovery and to reduce the remobilization and transport of mining and milling wastes (Johnson et al., 1976; Bender, 1991). In 1968, more than 25 yr after Ellis (1940) first recommended it, tailings ponds were constructed to reduce the quantity of mining, milling, and smelting wastes entering the South Fork of the CDA River. Based on decreases in turbidity, the ponds appeared to reduce the suspended sediment load in the river and lake (Mink, 1971; Ellsworth, 1972). Mining wastes are still actively discharged to the South Fork of the CDA River under a U.S. EPA NPDES permit that allows up to 5 t/yr of Pb (Neufeld, 1987).

Over the years, numerous environmental studies carried out in the CDA region have indicated that large amounts of mining, milling, and ore-processing wastes enriched in As, Cu, Cd, Fe, Mn, Pb, Sb, and Zn have been deposited throughout the lower CDA River and Lake CDA and have had a substantial impact on the sediment geochemistry, the water quality, and the biota of the South Fork of the CDA River, the main stem of the CDA River, Lake CDA, and the Spokane River (Ellis, 1940; Galbraith, 1971; Ellsworth, 1972; Funk et al., 1973; Bauer, 1974; Maxfield et al. 1974a, b; Norbeck, 1974; Funk et al., 1975; Sheppard and Funk, 1975; Johnson et al., 1976; Inoannou, 1979; Wai et al., 1985; Savage, 1986; Neufeld, 1987; Krieger, 1990; Piske, 1990; Bender, 1991). Although natural processes may contribute some trace elements to the drainage basin, the majority appear to originate from mining and ore processing in the CDA mining district. As early as 1923, it was noted that the silt load of the CDA River had increased commensurately with mining operations and that a substantial sediment plume could be detected far into Lake CDA (Kemmerer et al., 1923, as cited in Bender, 1991). Maxfield et al. (1974a, b) reported highly variable, but elevated, trace element concentrations in sediments from the CDA River delta; variations were related to sediment grain size, with the highest concentrations being associated with the finer silt and clay fractions. On the basis of a limited number of core samples, Funk et al. (1975) detected elevated trace element levels in the CDA River delta near Harrison. The elevated levels could be detected in sediments as far as the northern end of Lake CDA at the headwaters of the Spokane River; however, the thickness of these deposits decreased with proximity to the outlet of the lake (80 cm reducing down to about 5 cm). Finally, substantially elevated trace element concentrations have been reported from a variety of U.S. EPA collected sediment samples from Lake CDA and various sections of the CDA River (Hornig et al., 1988).

## **SAMPLE COLLECTION, TREATMENT, AND ANALYTICAL METHODS**

### **Sample collection**

About 172 surface bed sediment sample sites were occupied in Lake Coeur d'Alene, the Coeur d'Alene River, and the St. Joe River, Idaho, at a density of approximately  $1/\text{km}^2$  during one week in August 1989 (Fig. 2). Preliminary sampling sites were located prior to collection by using 1980 U.S. Geological Survey 7.5-min Topo-



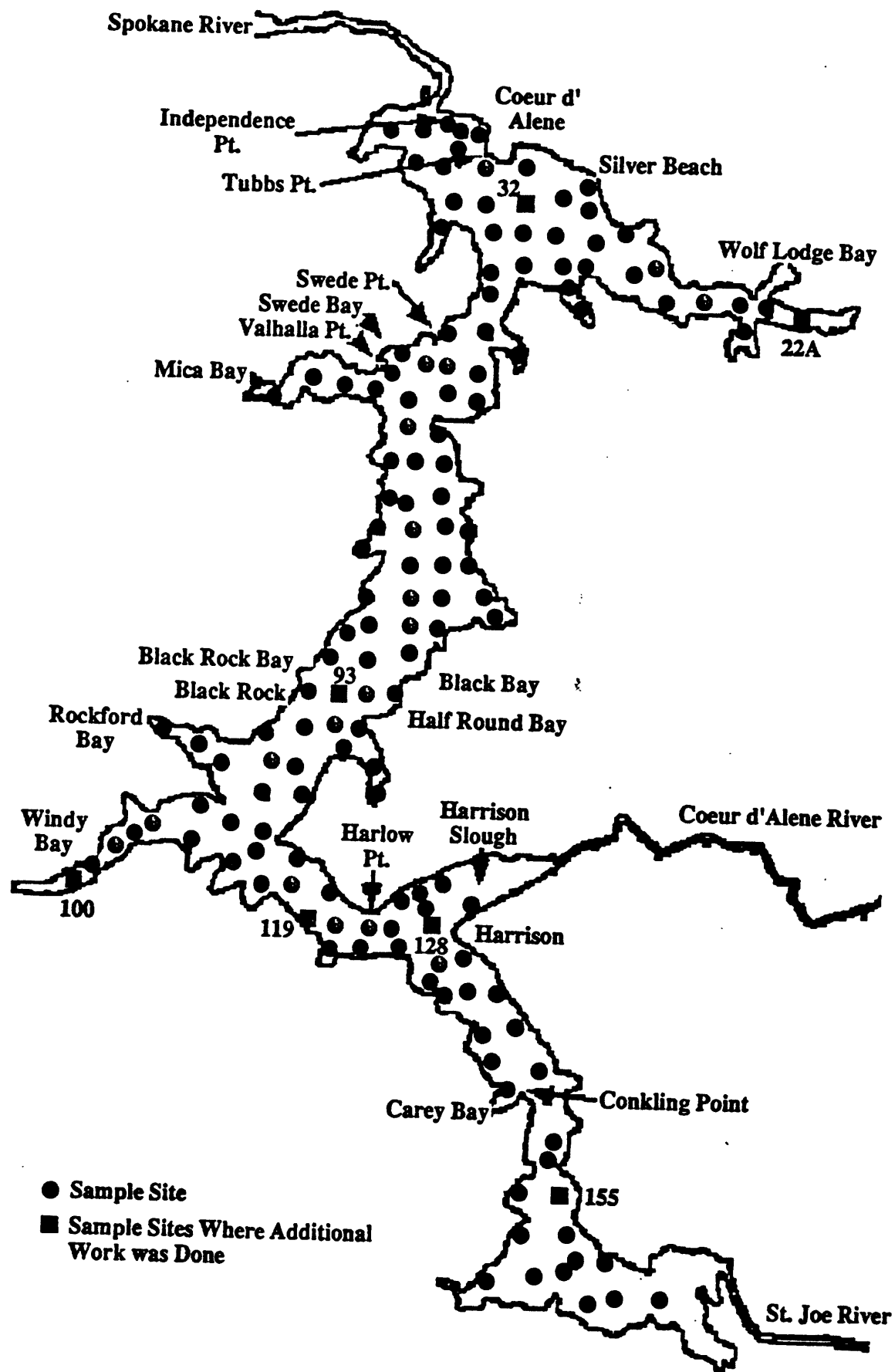


Figure 2. Detailed map of Lake Coeur d'Alene including all sampling locations and cities and features cited in the text.

graphic Series maps. During the sampling operation, actual sites were located and mapped by taking manual cross-bearings using prominent natural physical and/or manmade structures. Attempts to sample the upper Spokane River failed because the river bottom appeared to be armored.

Samples were collected using a stainless steel Ekman grab sampler. Subsamples were removed from the grab by using polypropylene sample containers. The subsamples were removed from the upper 2 cm of sediment in each grab; care was exercised to ensure that no material was removed from near the metal walls of the sampler. As soon as the subsamples were removed, the containers were capped, labeled, and stored on ice at 4°C. The samples were maintained at that temperature during storage, shipped to Atlanta, and kept chilled until they could be processed. Also, a limited group of samples from the river bank were collected by hand by using a plastic trowel along the lower part of the CDA River. These samples were stored and preserved in the same way as the grab samples. Additional bank samples were collected along the South Fork of the CDA and the CDA Rivers during 1991. These samples were collected and preserved in the same way as those collected during 1989.

## **Sample pretreatment**

Each sample was homogenized by using an acid-rinsed glass rod and sieved through a 2000- $\mu$ m polyester screen to remove overly large material (wood chips, leaf litter, etc.). The samples were then freeze dried. Appropriate-sized aliquots were removed for specific procedures using an acrylic riffle splitter. Where necessary, aliquots for bulk chemical analyses were ground to <100 mesh by using a sealed ceramic ball mill.

## **Bulk chemical analysis**

Chemical analyses for Fe, Mn, Al, Ti, Cu, Zn, Cd, Pb, Ni, Co, Cr, As, Sb, Se, and Hg were made following a slight modification of the procedures of Horowitz et al. (1989). For all chemical elements other than As, Sb, Se, and Hg, 500-mg aliquots were digested with a combination of HF/HClO<sub>4</sub>/aqua regia in Teflon<sup>1</sup> beakers at 200°C; the resulting salts were solubilized by using 50 mL of 2% HCl. Determination was by flame atomic absorption spectrophotometry (AAS) using mixed salt standards. The same digestion procedure was used for As, Sb, and Se, but final solutions were made up in 50% HCl. Selenium was determined on the digestate; As and Sb were determined after addition of urea and an oxalic acid/hydroxylamine solution and reduction by using KI. Determination of all three was by hydride generation AAS. Mercury was determined by using 500-mg aliquots digested with LeFort aqua regia at 100°C and a cold vapor technique. Precision and bias (usually better than  $\pm 10\%$ ) were monitored by replicate analyses of selected samples and by the concomitant digestion and analysis of NIST sediment and U.S. Geological Survey rock and soil standards and are similar to those reported in Horowitz and Elrick (1985) and Elrick and Horowitz

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1. The use of brand names is for identification purposes only, and does not constitute an endorsement by the U.S. Geological Survey.

(1985; 1987). Total organic carbon (TOC) was determined on aliquots pretreated with 10% HCl to remove inorganic carbonates by the evolution of CO<sub>2</sub> using a Leco CR-12 carbon analyzer. Precision was better than  $\pm 10\%$ ; no bias was detected.

## Grain-size separations

Grain-size separations were made on selected samples for subsequent chemical analyses following the procedures of Horowitz and Elrick (1986, 1988) that consisted of sieving and air elutriation. Unground, freeze-dried sample aliquots were placed on an acrylic sieve frame fitted with a 63- $\mu\text{m}$  polyester mesh and wet sieved with deionized water. Material passing through the sieve, and that retained by it, was freeze dried. Material  $>63\ \mu\text{m}$  was sized by using a stack of acrylic sieves fitted with polyester screens on a shaker table ( $>1000$ , 500-1000, 250-500, 125-250, and 63-125  $\mu\text{m}$ ). The material from the pan was added to that which had passed through the 63- $\mu\text{m}$  mesh during the wet sieving, and additional size fractions were separated using air elutriation (32-63, 16-32, 8-16, 4-8, 2-4, and  $<2\ \mu\text{m}$ ).

## Heavy-mineral separations

Heavy-mineral separations were made on selected samples for subsequent chemical analyses to help partition (determine the phase associations) the trace elements in the Lake CDA samples. Initial attempts entailed the use of either methylene iodide (density = 3.00 mg/L) or sodium polytungstate (density = 3.30 mg/L). Neither heavy liquid proved successful because the former caused the sediment to flocculate and the latter partially or completely dissolved the iron oxides present. The actual separations were made using a combination of bromoform ( $r = 2.96\ \text{mg/L}$ ), and 100  $\mu\text{L}$  of a surfactant to prevent flocculation. A 10-g sample was floated on 50 mL of the heavy liquid in a 50-mL polypropylene centrifuge tube. The tube was spun at 2000 rpm (RCF = 400  $\times g$ ) for 30 min. The heavy mineral fraction that accumulated at the bottom of the centrifuge tube was frozen with liquid nitrogen, and the supernate and light fraction were decanted. The light fraction was washed three separate times with acetone followed by a single deionized water rinse to remove the bromoform and oven dried at 105°C before chemical analysis. The frozen heavy-mineral fraction was thawed at room temperature and washed and dried in the same manner as the light fraction before chemical analysis.

## Geochemical phase determinations

Operationally defined geochemical phase determinations were carried out on dried, unground aliquots by using selected procedures from methods developed by Tessier et al. (1979) and Chao and Zhou (1983) to partition the trace elements into an Fe oxide phase and an organic/sulfide phase. The Fe oxide procedure used 0.25M hydroxylamine hydrochloride in 0.25M HCl heated at 50°C for 30 min in a shaking water bath, and the organics/sulfide procedure used 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 3.2M ammonium acetate in 20% V/V HNO<sub>3</sub> shaken at room temperature for 30 min. Two 1-g aliquots were sequentially

extracted, first for Fe oxide, and then for organics/sulfides, in 50-mL centrifuge tubes. Between extractions, the samples were centrifuged at 3000 rpm (RCF = 895 x g), the supernate decanted and discarded, and the residue washed with deionized water. One residue was retained for subsequent chemical analysis to determine Fe oxide-associated trace elements, whereas the other was subjected to the remaining extraction. The second extract was treated in the same way as the first two, and the residue was subsequently analyzed to determine the organics/sulfide-associated trace elements. Chemical analyses of the residues were performed following the same procedures used for the bulk analyses (see above). Precision and bias were monitored by carrying out replicate determinations and by using U.S. Geological Survey MAG-1 and one or two of the GXR-1 through GXR-6 standards. Precision and bias were similar to those for the bulk determinations.

### **Scanning electron microscopy**

Some of the heavy/light-mineral separates also were subjected to scanning electron microscopy (SEM) linked to an energy dispersive X-ray (EDAX) system to obtain selected chemical data that were used to infer mineralogy. The heavy-mineral separates were mounted on glass slides with an epoxy resin and polished. Before SEM/EDAX analysis, the slides were mounted on metal stubs and coated with a carbon film. The treated slides were examined in a backscattering mode at 30 KeV to select likely candidates for subsequent EDAX analysis.

## **RESULTS AND DISCUSSION**

### **General observations**

The August 1989 surface sediment sampling program took place after an extended period of low flow from both the CDA and St. Joe Rivers. Therefore, Lake CDA contained little suspended sediment, and the bottom could be observed to depths of 4 to 5 m. In the shallow areas around the CDA River delta near Harrison (Fig. 2), macrophyte beds were extensive. Substantive streams of bubbles emanating from irregular sediment mounds indicated active gas production. On the basis of the 1980 U.S. Geological Survey 7.5-min Topographic Series maps used for navigation and locating sample sites, the increase in the size and extent of the macrophyte beds in the shallow areas of Lake CDA has been substantive. Macrophytes are abundant in areas around the CDA River delta and in and near the mouth of the St. Joe River. Although the sampling program was not designed or intended to assess the benthic invertebrate population, it appeared that the grab samples from the bed of Lake CDA outside the areas of the macrophyte beds contained little or no benthic infauna.

The vast majority of the surface sediment samples collected from the main body of Lake CDA and from many of the bays (e.g., Wolf Lodge, Mica, Rockford, and Windy) north of the CDA River delta were tan to brown in color and visually appeared to be fine to very fine grained (<63  $\mu\text{m}$ ). Many of the samples obtained from the main body of Lake CDA had very thin (on the order of a few millimeters) surface veneers of reddish, fine-grained material containing numerous black flecks. Based on an examination of the bank deposits along the CDA River below the

area of mining and ore-processing operations, this reddish material might be fine-grained mining and ore-processing waste eroded from the river banks or flood plain of the CDA River. It also might be 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.

Many of the sediment samples collected in the main body of Lake CDA south of Rockford Bay, to the mouth of the St. Joe River, contained an extremely cohesive, light-gray, silty-clay, grain-sized layer from 1.5 to 3 cm below the surface. On the basis of color and texture, these layers probably represent Mount St. Helen's ash, which blanketed the southern part of Lake CDA after the 1981 eruption. The average depth of this cohesive layer would imply a recent sedimentation rate on the order of 0.3 to 0.5 cm/yr.

All attempts to collect surface sediments from the upper 6 km of the Spokane River failed. The only material recovered was an occasional rounded cobble indicating that this section of the river bottom is armored. Surface sediments were collected along the lower 6 km and the lower 14 km of the St. Joe and the CDA Rivers, respectively. Sediments from the St. Joe River were dark olive and substantially coarser (fine to medium sand with some silt) than those found in Lake CDA. The sediments from the CDA River appeared to be coarser grained than the material collected from the CDA River delta and the main body of Lake CDA. Most of the CDA River samples contained substantial quantities of reddish-black material similar in color, but finer sized, than that in exposed varves along both banks of the river.

## **Bulk chemistry**

The minimum, maximum, mean, and median bulk chemical data for all the Lake CDA surface sediments clearly show that most of the surface sediments are markedly enriched in Ag, As, Cd, Hg, Pb, Sb, and Zn and somewhat enriched in Cu, Fe, and Mn (Table 1) relative to unimpacted fluvial sediments throughout the U.S. (e.g., Horowitz et al, 1989; Horowitz, 1991). The samples containing elevated trace element levels also display marked chemical variability over a wide concentration range, in some cases up to 3 orders of magnitude (e.g., Hg, Pb, Zn; Table 1). All enriched samples were collected from the main body of Lake CDA, and all the major and many of the minor bays north of Conkling Point and Carey Bay (near the southern end of Lake CDA, but north of the mouth of the St. Joe River; Fig. 2). Samples collected from the lake south of Carey Bay and Conkling Point and from the very back of several of the northern bays (Wolf Lodge, Rockford, and Windy Bays) display trace element concentrations similar to unimpacted fluvial sediments throughout the United States. (e.g., Horowitz et al, 1989; Horowitz, 1991; Table 1).

Initial correlation coefficients were calculated by using the data from the trace element enriched samples. The coefficients show strong interrelations among the enriched trace elements. The enriched trace elements also show positive correlations with Fe and either a slightly negative or no correlation with Ti and TOC. Through a combination of data normalization to Ti/TOC and log transformations, many of the original interrelations were enhanced and/or clarified (Horowitz et al., 1988; Horowitz, 1991; Table 2). The strong correlations between and among the

**Table 1. Minimum, maximum, mean, and median concentrations for trace and major elements in surface sediments from Lake Coeur d'Alene.**

| <b><u>Elements</u></b> | <b><u>Minimun</u></b> | <b><u>Maximum</u></b> | <b><u>Mean</u></b> | <b><u>Median</u></b> | <b><u>Uncontam-<br/>inated<br/>Median (1)</u></b> |
|------------------------|-----------------------|-----------------------|--------------------|----------------------|---|
| <b>Ag ppm</b>          | <b>&lt;0.5</b>        | <b>21.0</b>           | <b>6.0</b>         | <b>4.0</b>           | <b>&lt;1</b>                                      |
| <b>Cu ppm</b>          | <b>9</b>              | <b>215</b>            | <b>72</b>          | <b>70</b>            | <b>25</b>   |
| <b>Pb ppm</b>          | <b>14</b>             | <b>7700</b>           | <b>1900</b>        | <b>1800</b>          | <b>24</b>   |
| <b>Zn ppm</b>          | <b>63</b>             | <b>9100</b>           | <b>3600</b>        | <b>3500</b>          | <b>110</b>  |
| <b>Ni ppm</b>          | <b>4</b>              | <b>104</b>            | <b>21</b>          | <b>21</b>            | <b>16</b>   |
| <b>Co ppm</b>          | <b>5</b>              | <b>43</b>             | <b>23</b>          | <b>26</b>            | <b>12</b>   |
| <b>Cd ppm</b>          | <b>&lt;0.5</b>        | <b>157</b>            | <b>62</b>          | <b>56</b>            | <b>3</b>  |
| <b>Cr ppm</b>          | <b>&lt;1</b>          | <b>102</b>            | <b>41</b>          | <b>41</b>            | <b>41</b>   |
| <b>Hg ppm</b>          | <b>0.02</b>           | <b>4.90</b>           | <b>1.80</b>        | <b>1.60</b>          | <b>0.05</b>                                       |
| <b>As ppm</b>          | <b>2.4</b>            | <b>660</b>            | <b>151</b>         | <b>120</b>           | <b>5</b>  |
| <b>Sb ppm</b>          | <b>0.5</b>            | <b>96</b>             | <b>23</b>          | <b>19</b>            | <b>1</b>  |
| <b>Se ppm</b>          | <b>0.1</b>            | <b>0.6</b>            | <b>0.3</b>         | <b>0.2</b>           | <b>0.2</b>  |
| <b>Fe Wt. %</b>        | <b>1.9</b>            | <b>16.4</b>           | <b>5.1</b>         | <b>4.9</b>           | <b>3.0</b>  |
| <b>Mn Wt. %</b>        | <b>0.01</b>           | <b>2.46</b>           | <b>0.67</b>        | <b>0.65</b>          | <b>0.05</b>                                       |
| <b>Al Wt. %</b>        | <b>2.9</b>            | <b>9.0</b>            | <b>7.5</b>         | <b>8.0</b>           | <b>6.8</b>  |
| <b>Ti Wt. %</b>        | <b>0.13</b>           | <b>0.64</b>           | <b>0.34</b>        | <b>0.34</b>          | <b>0.40</b>                                       |
| <b>TOC Wt. %</b>       | <b>0.3</b>            | <b>15.6</b>           | <b>2.5</b>         | <b>2.2</b>           | <b>2.5</b>  |

Uncontaminated Median (1) - based on 17 samples from the southern part of Lake Coeur d'Alene and the St. Joe River.

Table 2. Correlation coefficients\* for the enriched elements, and some major elements, using log-transformed normalized (X/Ti/TOC) data

|    | Ag   | Cu   | Pb   | Zn   | Cd   | Hg   | As   | Sb   | Fe   | Mn   | Al   |
|----|------|------|------|------|------|------|------|------|------|------|------|
| Ag | 1.00 |      |      |      |      |      |      |      |      |      |      |
| Cu | .94  | 1.00 |      |      |      |      |      |      |      |      |      |
| Pb | .96  | .92  | 1.00 |      |      |      |      |      |      |      |      |
| Zn | .85  | .96  | .86  | 1.00 |      |      |      |      |      |      |      |
| Cd | .69  | .85  | .69  | .91  | 1.00 |      |      |      |      |      |      |
| Hg | .95  | .93  | .92  | .88  | .77  | 1.00 |      |      |      |      |      |
| As | .68  | .61  | .65  | .51  | .45  | .64  | 1.00 |      |      |      |      |
| Sb | .95  | .92  | .96  | .88  | .72  | .96  | .60  | 1.00 |      |      |      |
| Fe | .90  | .91  | .86  | .84  | .65  | .83  | .61  | .85  | 1.00 |      |      |
| Mn | .60  | .56  | .56  | .48  | .43  | .57  | .76  | .53  | .64  | 1.00 |      |
| Al | .68  | .87  | .68  | .90  | .89  | .69  | .44  | .68  | .72  | .39  | 1.00 |

\* All correlations are significant at the 99% confidence level.

enriched trace elements could imply a similar source and/or a similar concentrating mechanism. The same could also be said for the correlations between the enriched trace elements and Fe and Al (Table 2). Galena (PbS), sphalerite (ZnFeS), and tetrahedrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>) are the most common ore minerals in the CDA mining district; also, the sphalerite contains substantial quantities of Cd, whereas the tetrahedrite is a major source of Ag and contains substantial quantities of Hg (e.g., Fryklund, 1964; Chan, 1966). The positive correlations among Ag, Cu, Hg, Pb, Sb, and Zn in the Lake CDA surface sediments may indicate that the ores and/or the ore-processing waste from the CDA mining district are a major source for the enriched trace elements. The positive correlations between these elements and Fe also could indicate the same thing because the ores contain substantial quantities of Fe sulfides (e.g., pyrite, pyrrhotite); it may also indicate that the enriched trace elements are associated with or concentrated by Fe oxides.

The surficial distribution patterns for all the samples enriched in trace elements are fairly consistent (e.g., Fig. 3 for Pb). 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 after it enters Lake CDA). Secondary highs were found south of Harlow Point (As, Hg, Pb, Zn); in a deep section of the center of the main stem of the lake in an area bounded by Black Rock and Black Rock Bay to the west and Half Round and Black Bays to the east (As, Cd, Hg, Zn); in the area of Valhalla Point, Swede Bay, and Swede Point near the mouth of Mica Bay (Ag, Cu, Hg, Pb, Sb); near the mouth of Wolf Lodge Bay (Ag, Cu, Cd, Hg, Pb, Zn); and finally, near Independence Point, Tubbs Point, and Silver Beach (Cu, Cd, Hg, Pb, Zn) in and around the corporate limits of the city of CDA (Fig. 3). This is not to say that the sediments from other parts of Lake CDA contain normal or near-normal concentrations, only that these areas have especially elevated concentrations.

Not unexpectedly, the chemical distribution patterns in Lake CDA surficial sediments appear to be consistent with the CDA River (suspended material from the banks and flood plain, plus ongoing discharges) acting as a major point source for the enriched trace elements. Additionally, the patterns also appear to reflect the velocity and direction of water movement through the system (generally from south to north). For example, some of the highest trace element concentrations in the lake are found just adjacent to the CDA River delta (Harrison Slough). This would be consistent with the expected reduction in water velocity when the CDA River enters the lake, causing a concomitant loss in sediment-transporting capacity. Further, most of the sites where secondary trace element enrichment maxima occur coincide with locations where the geomorphology of the lake causes a distinct change in current direction/velocity and where a loss in sediment-transporting capacity is likely to occur (e.g., Harlow, Valhalla, Swede, Independence, Tubbs Points; Fig. 2). These observations are in general agreement with several previous findings (e.g., Funk et al., 1973, 1975). They also would be consistent with the enriched trace elements being transported into the lake by the CDA River.

However, the surficial trace element patterns also appear to indicate that this explanation of the source, movement, and redistribution of trace element-rich material in Lake CDA is probably an oversimplification. This is because it does not account for the enriched sediment-trace element concentrations that occur in surficial sediments



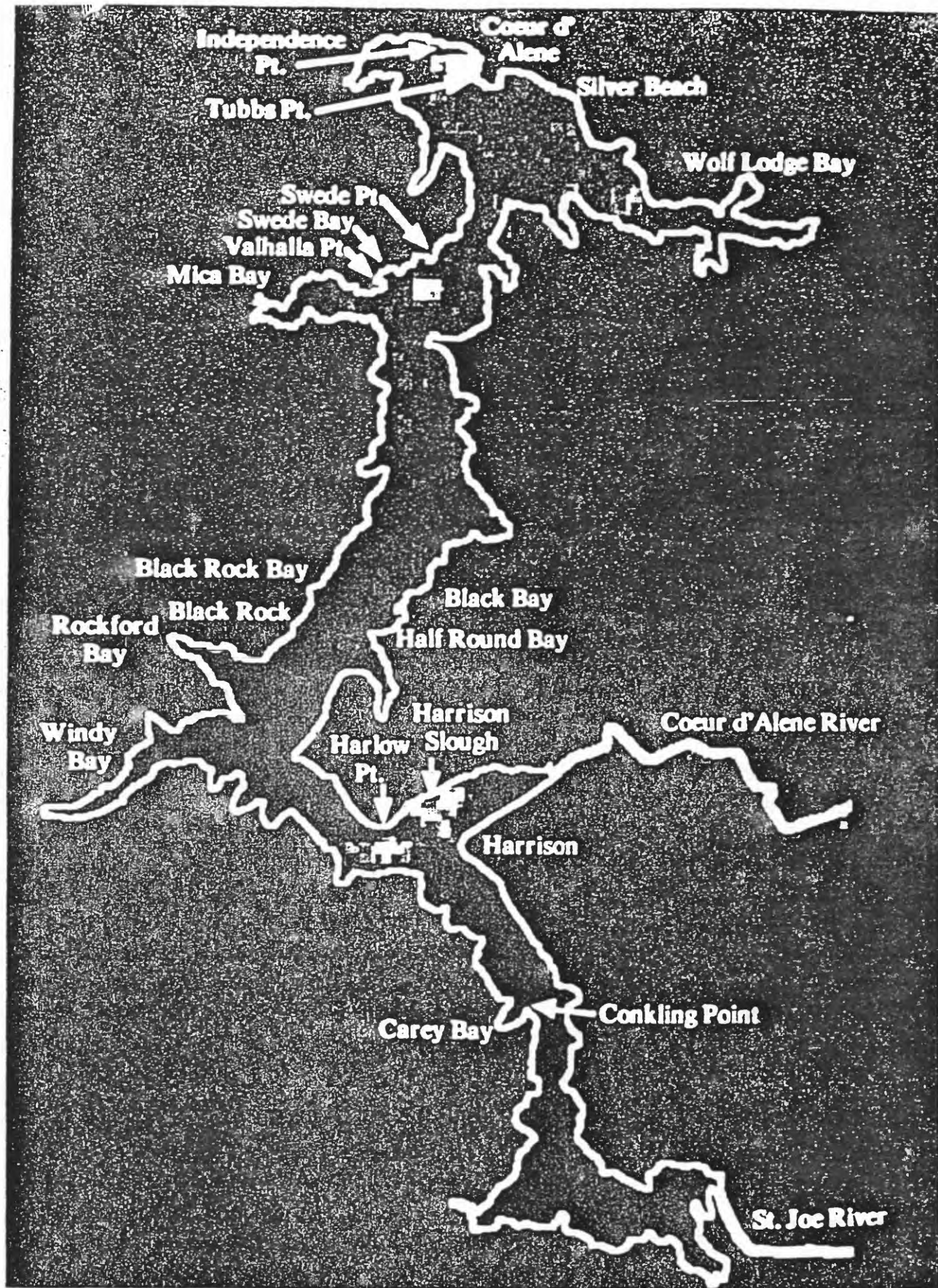


Figure 3. Map of the distribution of Pb in the surface sediments of Lake Couer d'Alene. Concentration increases from dark to light; therefore, the areas of highest concentration appear as white blobs (e.g., near Harrison Slough, Harlow Point, Swede Bay, and Tubbs and Independence Points).

collected as far south of the CDA River delta as Conkling Point (notwithstanding the strong northward current flow due to the influence of the St. Joe River; Fig. 2). It also does not explain the elevated trace element concentrations found well back from the mouths of Windy, Rockford, Mica, and Wolf Lodge Bays that are perpendicular to the major current flow in the lake. Further, the trace element-distribution patterns do not support the view that the major source of the enriched trace elements in Lake CDA sediments are caused by heavy minerals and/or coarse-grained sediment carried by the CDA River, because a consistent decrease in enriched trace element levels does not occur from south to north. In fact, some of the most elevated trace element levels occur well away from the mouth of the CDA River (Ag, Cu, Cd, Hg). Therefore, although the trace element patterns in Lake CDA do not preclude the CDA River or heavy minerals from being an important source of the enriched trace elements in the surface sediments, it appears that there may be a secondary source(s) for at least some of the enriched trace elements and/or physical factors other than just the predominant current direction and velocity (e.g., wind-generated wave/current action leading to the physical postdepositional remobilization of the fine-grained trace element-rich surface sediments) can affect the surficial trace element distribution patterns.

### **Chemical variations with sediment grain size**

A limited number of samples (seven) from selected sites within Lake CDA that have both high- and low-bulk trace element concentrations were separated into standard grain-size fractions for subsequent chemical analyses both as an aid to understanding the trace element distribution patterns and as an aid to understanding trace element partitioning in the surficial sediments (Fig. 2 for locations; Table 3). Each of the four trace element-enriched samples are extremely fine grained with mean grain sizes well below the sand-silt break ( $<20\ \mu\text{m}$ ). Even the "coarsest" trace element-enriched sample (CDA 128 with a mean grain size of  $20\ \mu\text{m}$ ), which was collected in the CDA River delta near Harrison, is composed of  $\pm 85\%$   $<63\text{-}\mu\text{m}$  particles (Table 3).

The trace element-enriched samples contain elevated concentrations of Ag, As, Cu, Cd, Hg, Pb, Sb, and Zn (Table 3). The highest concentrations of these elements are in the size fractions finer than  $16\ \mu\text{m}$  (Table 3). The two samples nearest the mouth of the CDA River (CDA 119 and 128) have the highest trace element concentrations in the  $<2\text{-}\mu\text{m}$  fraction, whereas the two samples farthest from the mouth of the river generally have the highest concentrations in the 4- to 8- or the 8- to  $16\text{-}\mu\text{m}$  fractions. This is the reverse of the expected pattern if the CDA River was acting as the single major source of the enriched trace elements and/or if the major cause of the enriched elements was the presence of sulfide (heavy) minerals. In either case, the highest concentrations would be expected closest to the mouth of the CDA River, and the size fraction(s) associated with the highest concentrations should decrease as distance from the river increases.

When the relative contributions of the various size fractions are considered (determined by multiplying the chemical concentration by the percent the size fraction represents in the sample) rather than just concentration, a slightly different pattern emerges (Table 4). This change is a function of the relative proportions of the various size

**Table 3. Size fraction geochemistry of selected Lake Coeur d'Alene surface sediment samples**

| Sample       | % of<br>Sample | TOC<br>wt. % | Ag<br>ppm | Cu<br>ppm | Pb<br>ppm | Zn<br>ppm | Ni<br>ppm | Co<br>ppm | Cd<br>ppm | Cr<br>ppm | Hg<br>ppm | As<br>ppm | Sb<br>ppm | Se<br>ppm | Fe<br>wt. % | Mn<br>wt. % | Al<br>wt. % | Ti<br>wt. % |
|--------------|----------------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|-------------|-------------|-------------|
| CDA 32 Bulk  |                | 2.6          | 8.0       | 112       | 2700      | 6300      | 25        | 30        | 126       | 50        | 2.9       | 126       | 39        | 0.4       | 5.1         | 0.28        | 8.3         | 0.3         |
| >63 µm       | 7              | 4.3          | 7.0       | 106       | 2500      | 6200      | 26        | 32        | 161       | 45        | 3.6       | 120       | 35        | 0.3       | 4.8         | 0.24        | 8.8         | 0.3         |
| <63 µm       | 93             | 2.7          | 9.0       | 108       | 2600      | 6100      | 27        | 29        | 119       | 52        | 3.0       | 125       | 40        | 0.4       | 5.2         | 0.30        | 8.5         | 0.3         |
| Cal. Bulk    |                | 2.9          | 8.5       | 108       | 2600      | 6100      | 27        | 29        | 122       | 51        | 3.0       | 125       | 40        | 0.4       | 5.1         | 0.30        | 8.5         | 0.3         |
| >63 µm %Cont |                | 12           | 7         | 7         | 7         | 7         | 8         | 8         | 10        | 7         | 9         | 7         | 7         | 6         | 7           | 6           | 8           | 7           |
| <63 µm %Cont |                | 97           | 99        | 89        | 90        | 90        | 100       | 90        | 88        | 96        | 95        | 92        | 95        | 93        | 94          | 99          | 94          | 93          |
| <2 µm        | 23             | 2.8          | 9.4       | 149       | 2700      | 6400      | 29        | 26        | 119       | 52        | 3.0       | 130       | 43        | 0.4       | 5.0         | 0.31        | 7.8         | 0.3         |
| 2-4 µm       | 14             | 2.9          | 9.4       | 122       | 2700      | 6500      | 29        | 28        | 119       | 53        | 3.0       | 125       | 45        | 0.4       | 5.2         | 0.31        | 8.1         | 0.3         |
| 4-8 µm       | 16             | 3.3          | 9.4       | 128       | 2900      | 6800      | 30        | 30        | 134       | 55        | 3.5       | 135       | 46        | 0.4       | 5.5         | 0.34        | 8.4         | 0.3         |
| 8-16 µm      | 24             | 2.9          | 8.6       | 123       | 2800      | 6700      | 30        | 30        | 134       | 54        | 3.3       | 130       | 43        | 0.4       | 5.4         | 0.32        | 8.6         | 0.4         |
| 16-32 µm     | 8              | 2.1          | 6.3       | 100       | 2000      | 4900      | 27        | 28        | 99        | 47        | 2.5       | 95        | 31        | 0.3       | 4.7         | 0.28        | 8.5         | 0.4         |
| 32-63 µm     | 7              | 1.5          | 5.7       | 102       | 1700      | 3900      | 26        | 27        | 76        | 46        | 1.7       | 80        | 26        | 0.2       | 4.8         | 0.24        | 8.7         | 0.4         |
| CDA 93 Bulk  |                | 1.8          | 9.0       | 104       | 2600      | 4800      | 27        | 39        | 87        | 54        | 4.8       | 400       | 43        | 0.5       | 5.7         | 0.65        | 8.4         | 0.3         |
| >63 µm       | 3              | 2.6          | 4.0       | 70        | 1500      | 2700      | 21        | 33        | 62        | 35        | 9.9       | 175       | 39        | 0.2       | 4.6         | 0.50        | 9.3         | 0.4         |
| <63 µm       | 97             | 2.2          | 9.0       | 99        | 2700      | 5000      | 22        | 35        | 86        | 53        | 4.4       | 380       | 42        | 0.3       | 5.7         | 0.68        | 8.3         | 0.3         |
| Cal. Bulk    |                | 2.2          | 8.3       | 97        | 2600      | 4800      | 22        | 35        | 84        | 52        | 5.0       | 370       | 42        | 0.3       | 5.6         | 0.66        | 8.4         | 0.3         |
| >63 µm %Cont |                | 4            | 1         | 2         | 1         | 1         | 2         | 3         | 2         | 2         | 5         | 1         | 2         | 1         | 2           | 2           | 3           | 3           |
| <63 µm %Cont |                | 122          | 93        | 93        | 100       | 101       | 80        | 88        | 96        | 96        | 89        | 93        | 95        | 58        | 98          | 101         | 97          | 92          |
| <2 µm        | 29             | 2.2          | 10        | 121       | 3100      | 5100      | 32        | 35        | 90        | 66        | 4.4       | 360       | 42        | 0.4       | 5.5         | 0.62        | 9.2         | 0.4         |
| 2-4 µm       | 23             | 1.9          | 9.0       | 106       | 2800      | 4900      | 26        | 33        | 83        | 62        | 4.1       | 330       | 38        | 0.3       | 5.4         | 0.61        | 8.9         | 0.3         |
| 4-8 µm       | 21             | 1.9          | 8.0       | 99        | 2500      | 5300      | 26        | 35        | 94        | 53        | 4.4       | 415       | 38        | 0.3       | 5.9         | 0.70        | 8.0         | 0.3         |
| 8-16 µm      | 15             | 2.2          | 8.0       | 102       | 3000      | 6200      | 28        | 43        | 119       | 51        | 4.8       | 420       | 39        | 0.4       | 6.1         | 0.88        | 7.8         | 0.3         |
| 16-32 µm     | 5              | 2.1          | 6.0       | 93        | 2500      | 4400      | 28        | 39        | 80        | 52        | 3.8       | 355       | 32        | 0.3       | 5.6         | 0.92        | 8.4         | 0.4         |
| 32-63 µm     | 3              | 1.8          | 7.0       | 105       | 2400      | 3400      | 30        | 37        | 63        | 57        | 0.7       | 260       | 29        | 0.3       | 5.5         | 1.02        | 9.1         | 0.4         |

|              |              |     |      |     |      |      |     |    |    |    |     |     |     |      |      |      |     |     |
|--------------|--------------|-----|------|-----|------|------|-----|----|----|----|-----|-----|-----|------|------|------|-----|-----|
| CDA 119 Bulk |              | 1.9 | 8.0  | 85  | 2900 | 2900 | 19  | 23 | 33 | 41 | 2.1 | 660 | 25  | 0.2  | 6.5  | 1.00 | 7.6 | 0.3 |
|              | 4            | 3.7 | 7.0  | 100 | 3500 | 3700 | 23  | 31 | 73 | 42 | 2.2 | 990 | 26  | 0.2  | 6.0  | 1.40 | 7.1 | 0.3 |
|              | 96           | 2.0 | 8.0  | 80  | 3100 | 3000 | 18  | 22 | 33 | 41 | 2.0 | 660 | 24  | 0.1  | 6.3  | 1.00 | 7.3 | 0.3 |
|              | Cal. Bulk    | 2.1 | 8.0  | 81  | 3100 | 3100 | 18  | 23 | 35 | 41 | 2.0 | 680 | 24  | 0.1  | 6.3  | 1.00 | 7.3 | 0.3 |
| >63 µm %Cont |              | 8   | 4    | 5   | 5    | 5    | 5   | 6  | 9  | 4  | 4   | 6   | 4   | 4    | 4    | 6    | 4   | 4   |
|              | <63 µm %Cont | 101 | 101  | 90  | 100  | 100  | 91  | 92 | 94 | 96 | 92  | 96  | 92  | 48   | 93   | 96   | 92  | 93  |
|              | <2 µm        | 2.7 | 12   | 122 | 4300 | 3900 | 29  | 28 | 45 | 56 | 2.6 | 810 | 33  | 0.3  | 5.8  | 1.00 | 8.4 | 0.3 |
|              | 2-4 µm       | 2.5 | 10   | 103 | 3700 | 3600 | 24  | 25 | 38 | 55 | 2.3 | 710 | 29  | 0.2  | 5.7  | 0.95 | 8.4 | 0.3 |
| 8-16 µm      |              | 2.3 | 9.0  | 84  | 3200 | 3100 | 22  | 22 | 32 | 47 | 2.1 | 680 | 25  | 0.2  | 5.9  | 0.99 | 7.7 | 0.3 |
|              | 8-16 µm      | 1.9 | 7.0  | 71  | 2600 | 2700 | 19  | 20 | 27 | 38 | 1.8 | 600 | 22  | 0.1  | 6.6  | 1.10 | 6.5 | 0.3 |
|              | 16-32 µm     | 1.4 | 5.0  | 54  | 1800 | 2100 | 17  | 15 | 19 | 34 | 1.4 | 380 | 17  | <0.1 | 6.9  | 1.00 | 5.7 | 0.3 |
|              | 32-63 µm     | 1.1 | 4.0  | 43  | 1300 | 1500 | 14  | 12 | 14 | 31 | 1.1 | 220 | 14  | <0.1 | 7.9  | 0.88 | 5.0 | 0.3 |
| CDA 128 Bulk |              | 1.9 | 11   | 97  | 3900 | 3200 | 13  | 18 | 27 | 35 | 3.6 | 480 | 31  | 0.1  | 8.7  | 0.80 | 5.8 | 0.3 |
|              | >63 µm       | 2.1 | 7.0  | 61  | 2200 | 2000 | 9   | 9  | 32 | 20 | 4.2 | 260 | 24  | <0.1 | 7.3  | 0.7  | 4.1 | 0.2 |
|              | <63 µm       | 2.1 | 12.0 | 99  | 4100 | 3500 | 17  | 15 | 27 | 37 | 3.6 | 650 | 37  | 0.2  | 9.0  | 0.79 | 6.1 | 0.3 |
|              | Cal. Bulk    | 2.1 | 12   | 96  | 4000 | 3400 | 16  | 15 | 27 | 36 | 4.0 | 620 | 36  |      | 8.9  | 0.78 | 6.0 | 0.2 |
| >63 µm %Cont |              | 16  | 10   | 9   | 8    | 9    | 10  | 7  | 17 | 8  | 17  | 8   | 11  | 12   | 12   | 13   | 11  | 10  |
|              | <63 µm %Cont | 91  | 95   | 87  | 90   | 93   | 111 | 71 | 86 | 90 | 85  | 116 | 102 | 88   | 84   | 90   | 85  | 85  |
|              | <2 µm        | 3.3 | 17   | 164 | 7200 | 4700 | 28  | 27 | 45 | 56 | 4.8 | 970 | 52  | 0.4  | 7.3  | 0.59 | 8.1 | 0.3 |
|              | 2-4 µm       | 3.2 | 16   | 150 | 6500 | 4600 | 26  | 25 | 41 | 55 | 4.7 | 910 | 49  | 0.3  | 7.0  | 0.58 | 8.2 | 0.3 |
| 8-16 µm      |              | 2.9 | 15   | 127 | 5700 | 4100 | 22  | 22 | 35 | 50 | 4.6 | 790 | 45  | 0.3  | 7.2  | 0.63 | 7.6 | 0.3 |
|              | 8-16 µm      | 2.1 | 14   | 108 | 4800 | 3600 | 18  | 20 | 30 | 42 | 4.4 | 700 | 42  | 0.2  | 8.1  | 0.75 | 6.4 | 0.3 |
|              | 16-32 µm     | 1.3 | 8.0  | 64  | 2300 | 2300 | 13  | 12 | 16 | 29 | 2.5 | 320 | 25  | <0.1 | 10.0 | 0.86 | 5.0 | 0.2 |
|              | 32-63 µm     | 1.7 | 6.0  | 49  | 980  | 1500 | 10  | 8  | 10 | 19 | 1.4 | 180 | 19  | <0.1 | 12.0 | 1.00 | 3.8 | 0.2 |

|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|--------------|-----------|-----|------|----|-----|------|----|----|-----|----|------|-----|-----|------|-----|------|------|-----|
| CDA 22A Bulk | 68        | 1.1 | <1   | 9  | 50  | 420  | 14 | 7  | 6.0 | 28 | 0.3  | 9.0 | 1.0 | <0.1 | 1.9 | 0.05 | 5.1  | 0.4 |
|              |           | 0.7 | 0.3  | 5  | 27  | 210  | 9  | 5  | 2.8 | 23 | 0.05 | 2.0 | 0.9 | <0.1 | 1.4 | 0.03 | 4.1  | 0.4 |
|              | 32        | 2.4 | 0.4  | 19 | 91  | 800  | 18 | 10 | 9.7 | 47 | 0.11 | 16  | 2.0 | 0.1  | 2.7 | 0.06 | 7.6  | 0.4 |
|              | Cal. Bulk | 1.2 | 0.3  | 9  | 47  | 399  | 12 | 7  | 5.0 | 31 | 0.1  | 6.5 | 1.3 |      | 1.8 | 0.04 | 5.2  | 0.4 |
| >63 µm %Cont | 43        | 43  |      | 38 | 37  | 34   | 44 | 49 | 32  | 56 | 11   | 15  | 61  |      | 50  | 41   | 55   | 68  |
|              | 70        | 70  |      | 68 | 58  | 61   | 41 | 46 | 52  | 54 | 89   | 57  | 64  |      | 45  | 38   | 48   | 32  |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
| <63 µm %Cont | 2         | 4.8 | 0.4  | 52 | 233 | 1490 | 29 | 13 | 22  | 62 | 0.55 | 34  | 4.0 | 0.2  | 3.6 | 0.09 | 8.5  | 0.3 |
|              | 3         | 4.2 | 0.1  | 38 | 153 | 1300 | 29 | 12 | 18  | 68 | 0.28 | 26  | 2.7 | 0.2  | 3.4 | 0.08 | 10.3 | 0.3 |
|              | 6         | 3.7 | <0.1 | 31 | 125 | 1140 | 25 | 12 | 15  | 63 | 0.18 | 21  | 2.2 | 0.2  | 3.2 | 0.07 | 9.2  | 0.3 |
|              | 10        | 2.7 | <0.1 | 26 | 100 | 890  | 21 | 10 | 11  | 51 | 0.13 | 17  | 1.8 | 0.1  | 2.8 | 0.07 | 8.0  | 0.4 |
| 16-32 µm     | 5         | 1.3 | <0.1 | 21 | 66  | 530  | 17 | 7  | 5.6 | 42 | 0.04 | 10  | 1.4 | <0.1 | 2.2 | 0.05 | 6.7  | 0.4 |
|              | 6         | 0.6 | <0.1 | 11 | 43  | 320  | 16 | 6  | 3.4 | 39 | 0.11 | 5.0 | 1.2 | <0.1 | 1.8 | 0.04 | 5.6  | 0.5 |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
| CDA 100 Bulk | 15        | 1.5 | <1   | 18 | 45  | 230  | 14 | 12 | 1.3 | 42 | 0.01 | 2.4 | 2.2 | 0.1  | 3.1 | 0.07 | 7.1  | 0.6 |
|              |           | 2.6 | 0.2  | 18 | 41  | 233  | 14 | 14 | 2.1 | 35 | 0.02 | 3.2 | 0.5 | 0.1  | 3.3 | 0.07 | 7.8  | 0.6 |
|              | 85        | 1.4 | 0.1  | 16 | 42  | 218  | 15 | 12 | 1.4 | 43 | 0.05 | 3.9 | 0.7 | <0.1 | 3.1 | 0.06 | 7.5  | 0.6 |
|              | Cal. Bulk | 1.6 | 0.1  | 16 | 42  | 220  | 15 | 12 | 1.5 | 42 | 0.10 | 3.8 | 0.7 | 0    | 3.1 | 0.06 | 7.5  | 0.6 |
| >63 µm %Cont | 26        | 26  |      | 15 | 14  | 15   | 15 | 18 | 24  | 13 | 8    | 20  | 3   | 15   | 16  | 15   | 16   | 15  |
|              | 79        | 79  |      | 76 | 79  | 81   | 91 | 85 | 92  | 87 | 106  | 138 | 27  |      | 85  | 73   | 90   | 85  |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
| <63 µm %Cont | 3         | 3.9 | 2.4  | 66 | 128 | 300  | 36 | 20 | 7.6 | 72 | 0.40 | 14  | 2.0 | 0.2  | 5.3 | 0.12 | 9.6  | 0.7 |
|              | 4         | 3.6 | 1.8  | 54 | 104 | 265  | 30 | 18 | 4.2 | 66 | 0.22 | 11  | 1.8 | <0.1 | 5.0 | 0.11 | 9.3  | 0.7 |
|              | 8         | 3.0 | 0.8  | 39 | 81  | 431  | 25 | 17 | 3.2 | 60 | 0.13 | 7.7 | 1.4 | <0.1 | 4.1 | 0.09 | 8.4  | 0.6 |
|              | 25        | 1.9 | 0.5  | 25 | 53  | 277  | 18 | 12 | 2.1 | 47 | 0.10 | 5.5 | 1.0 | <0.1 | 3.3 | 0.07 | 7.7  | 0.6 |
| 16-32 µm     | 20        | 0.9 | 0.5  | 15 | 25  | 133  | 12 | 9  | 0.9 | 37 | 0.07 | 3.1 | 0.5 | <0.1 | 2.6 | 0.05 | 6.9  | 0.5 |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
| 32-63 µm     | 24        | 0.4 | 0.3  | 9  | 16  | 84   | 10 | 8  | 0.5 | 33 | 0.03 | 1.8 | 0.3 | <0.1 | 2.5 | 0.04 | 6.4  | 0.6 |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |
|              |           |     |      |    |     |      |    |    |     |    |      |     |     |      |     |      |      |     |

|              |              |      |    |    |    |     |    |    |      |    |      |     |     |      |     |      |     |     |
|--------------|--------------|------|----|----|----|-----|----|----|------|----|------|-----|-----|------|-----|------|-----|-----|
| CDA 155 Bulk |              | 3.5  | <1 | 31 | 28 | 133 | 18 | 13 | <0.5 | 46 | 0.10 | 4.0 | 0.7 | 0.2  | 3.4 | 0.05 | 7.8 | 0.4 |
|              | 6            | 10.0 | <1 | 40 | 29 | 150 | 18 | 11 | 0.4  | 42 | 0.11 | 5.5 | 1.1 | 0.5  | 3.6 | 0.06 | 7.3 | 0.3 |
|              | 94           | 3.0  | <1 | 29 | 26 | 130 | 19 | 9  | <0.5 | 35 | 0.05 | 4.1 | 0.9 | 0.1  | 3.5 | 0.05 | 8.0 | 0.4 |
|              | Cal Bulk     | 3.4  |    | 30 | 26 | 131 | 19 | 9  |      | 35 | 0.10 | 4.2 | 0.9 | 0.1  | 3.5 | 0.05 | 8.0 | 0.4 |
| >63 µm %Cont |              | 17   |    | 8  | 6  | 7   | 6  | 5  |      | 5  | 13   | 8   | 9   | 15   | 6   | 7    | 6   | 5   |
|              | <63 µm %Cont | 81   |    | 88 | 87 | 92  | 99 | 65 |      | 72 | 94   | 96  | 121 | 47   | 97  | 94   | 96  | 94  |
| <2 µm        |              | 4.6  | <1 | 52 | 47 | 172 | 37 | 11 | 2.4  | 51 | 0.10 | 3.1 | 1.6 | 0.1  | 3.7 | 0.05 | 8.4 | 0.4 |
|              | 2-4 µm       | 4.7  | <1 | 46 | 35 | 155 | 25 | 11 | <0.5 | 54 | 0.16 | 7.1 | 1.3 | 0.4  | 3.6 | 0.05 | 8.7 | 0.4 |
|              | 4-8 µm       | 4.6  | <1 | 41 | 29 | 148 | 22 | 11 | <0.5 | 53 | 0.10 | 6.5 | 1.1 | 0.4  | 3.6 | 0.05 | 8.6 | 0.4 |
|              | 8-16 µm      | 4.1  | <1 | 35 | 27 | 140 | 19 | 12 | <0.5 | 46 | 0.09 | 5.6 | 0.9 | 0.3  | 3.5 | 0.05 | 8.3 | 0.4 |
|              | 16-32 µm     | 1.6  | <1 | 28 | 18 | 102 | 15 | 10 | <0.5 | 32 | 0.08 | 3.5 | 0.7 | 0.1  | 2.9 | 0.04 | 7.4 | 0.4 |
|              | 32-63 µm     | 0.5  | <1 | 19 | 16 | 69  | 11 | 7  | <0.5 | 24 | 0.04 | 1.9 | 0.6 | <0.1 | 2.2 | 0.03 | 6.4 | 0.4 |

**Table 4. Chemical contributions (ppm) for the <63- $\mu$ m size fractions of selected surface sediment samples from Lake Coeur d'Alene**

| <b>Sample</b>  | <b>% of Sample</b> | <b>Ag ppm</b> | <b>Cu ppm</b> | <b>Pb ppm</b> | <b>Zn ppm</b> | <b>Cd ppm</b> | <b>Hg ppm</b> | <b>As ppm</b> | <b>Sb ppm</b> |
|----------------|--------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| <b>CDA 32</b>  |                    |               |               |               |               |               |               |               |               |
| <2 $\mu$ m     | 23                 | 2.2           | 34            | 620           | 1470          | 27            | 0.7           | 30            | 10            |
| 2-4 $\mu$ m    | 14                 | 1.3           | 17            | 380           | 910           | 17            | 0.4           | 18            | 6             |
| 4-8 $\mu$ m    | 16                 | 1.5           | 21            | 460           | 1090          | 21            | 0.6           | 22            | 7             |
| 8-16 $\mu$ m   | 24                 | 2.1           | 30            | 670           | 1610          | 32            | 0.8           | 31            | 10            |
| 16-32 $\mu$ m  | 8                  | 0.5           | 8             | 160           | 390           | 8             | 0.2           | 8             | 3             |
| 32-63 $\mu$ m  | 7                  | 0.4           | 7             | 120           | 270           | 5             | 0.1           | 6             | 2             |
| <b>CDA 93</b>  |                    |               |               |               |               |               |               |               |               |
| <2 $\mu$ m     | 29                 | 2.9           | 35            | 900           | 1480          | 26            | 1.3           | 104           | 12            |
| 2-4 $\mu$ m    | 23                 | 2.1           | 24            | 640           | 1130          | 19            | 0.9           | 76            | 9             |
| 4-8 $\mu$ m    | 21                 | 1.7           | 21            | 530           | 1110          | 20            | 0.9           | 87            | 8             |
| 8-16 $\mu$ m   | 15                 | 1.2           | 15            | 450           | 930           | 18            | 0.7           | 63            | 6             |
| 16-32 $\mu$ m  | 5                  | 0.3           | 5             | 130           | 220           | 4             | 0.2           | 18            | 2             |
| 32-63 $\mu$ m  | 3                  | 0.2           | 3             | 70            | 100           | 2             | 0.0           | 8             | 1             |
| <b>CDA 119</b> |                    |               |               |               |               |               |               |               |               |
| <2 $\mu$ m     | 19                 | 2.3           | 23            | 820           | 740           | 9             | 0.5           | 154           | 6             |
| 2-4 $\mu$ m    | 15                 | 1.5           | 15            | 560           | 540           | 6             | 0.3           | 107           | 4             |
| 4-8 $\mu$ m    | 22                 | 2.0           | 19            | 700           | 680           | 7             | 0.5           | 150           | 6             |
| 8-16 $\mu$ m   | 29                 | 2.0           | 21            | 750           | 780           | 8             | 0.5           | 174           | 6             |
| 16-32 $\mu$ m  | 9                  | 0.5           | 5             | 160           | 190           | 2             | 0.1           | 34            | 2             |
| 32-63 $\mu$ m  | 5                  | 0.2           | 2             | 70            | 80            | 1             | 0.1           | 11            | 1             |
| <b>CDA 128</b> |                    |               |               |               |               |               |               |               |               |
| <2 $\mu$ m     | 8                  | 1.4           | 13            | 580           | 380           | 4             | 0.4           | 78            | 4             |
| 2-4 $\mu$ m    | 9                  | 1.4           | 14            | 590           | 410           | 4             | 0.4           | 82            | 4             |
| 4-8 $\mu$ m    | 15                 | 2.3           | 19            | 860           | 620           | 5             | 0.7           | 119           | 7             |
| 8-16 $\mu$ m   | 25                 | 3.5           | 27            | 1200          | 900           | 8             | 1.1           | 175           | 11            |
| 16-32 $\mu$ m  | 12                 | 1.0           | 8             | 280           | 280           | 2             | 0.3           | 38            | 3             |
| 32-63 $\mu$ m  | 17                 | 1.0           | 8             | 170           | 260           | 2             | 0.2           | 31            | 3             |

fractions in conjunction with their respective trace element concentrations. The <2- $\mu\text{m}$  fractions contribute (occasionally the 8- to 16- $\mu\text{m}$  fraction) the highest concentration of trace elements to the three samples furthest from the mouth (CDA 32, 93, and 119), whereas the 8- to 16- $\mu\text{m}$  fraction contributes the highest concentration in the sample closest to the mouth (CDA 128) of the CDA River. Secondary highs occur either in the 2- to 4- $\mu\text{m}$  fraction (CDA 93), the 4- to 8- $\mu\text{m}$  fraction (CDA 128), or in the 8- to 16- $\mu\text{m}$  fractions (CDA 32 and 119).

In general, the trace element concentration patterns for the three samples furthest from the mouth of the CDA River tend to be unimodal, whereas the trace element contribution patterns tend to be bimodal for the various size fractions (Tables 3, 4). In essence, the differences in trace element concentration between the various size fractions are not sufficiently large to overcome the dominant effect of the relative proportions of the various size fractions (e.g., regardless of the concentration differences between the various fractions, the greatest contributions come from the largest fraction). The bimodal nature of the patterns for these three samples may be indicative of more than a single source for the enriched trace elements. However, the sample closest to the mouth of the CDA River has a unimodal concentration and contribution pattern with the highest values for both occurring in different fractions. The <2- $\mu\text{m}$  fraction has the highest concentrations whereas the 8- to 16- $\mu\text{m}$  fraction has the highest contributions (Tables 3, 4). The patterns for the sample closest to the mouth of the CDA River appear more indicative of a single rather than a multiple source for the enriched trace elements. These results both support and contradict some previous findings reported by Maxfield et al. (1974a, b) and Funk et al. (1975) which indicated that the highest concentrations were associated with the finest size fractions and that the effect of the CDA River-transported trace elements in Lake CDA (based on the decreasing thickness of the enriched layers) decreased from the mouth of the CDA River to the head of the Spokane River (from south to north).

The three samples having normal bulk trace element concentrations that were separated into various grain size ranges and chemically analyzed come from the back of Wolf Lodge Bay (CDA 22A), the back of Windy Bay (CDA 100), and the southern end of Lake CDA off the right bank of the St. Joe River at the boundary between Lake CDA and Round Lake (CDA 155) (Fig. 2). Generally, all three samples display classic unimodal grain size-trace element patterns of increasing concentration with decreasing grain size (Table 3). Contributions for these samples also are unimodal and reflect the relative proportions of the various size fractions (e.g., the largest fraction contributes the most trace elements to the sample).

### **Chemical variations with sediment density**

To further clarify trace element partitioning and distribution patterns in the lake, the fine fractions (<63  $\mu\text{m}$ ) of the same four trace element-rich samples used in the grain-size studies were separated into heavy ( $r = >2.96 \text{ mg/L}$ ) and light ( $r = <2.96 \text{ mg/L}$ ) fractions. All four samples had relatively small amounts of heavy minerals, which ranged from as little as 0.4% to 11%, with the heavy fraction increasing in percentage with proximity to the mouth of the



**Table 5. Heavy/light mineral fraction geochemistry of the <63- $\mu$ m fraction of selected Lake Coeur d'Alene surface sediment samples**

| <b>Sample</b>         | <b>% of Sample</b> | <b>Ag ppm</b> | <b>Cu ppm</b> | <b>Pb ppm</b> | <b>Zn ppm</b> | <b>Cd ppm</b> | <b>As ppm</b> | <b>Sb ppm</b> | <b>Fe wt. %</b> | <b>Mn wt. %</b> | <b>Ti wt. %</b> |
|-----------------------|--------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|-----------------|-----------------|-----------------|
| <b>CDA 32</b>         |                    |               |               |               |               |               |               |               |                 |                 |                 |
| CDA <63- $\mu$ m Bulk | 93                 | 8.6           | 108           | 2600          | 6100          | 119           | 125           | 40            | 5.2             | 0.30            | 0.34            |
| <63 $\mu$ m Heavy     | 0.4                | <5.5          | 110           | 825           | 1800          | 28            | <500          | <100          | 24.8            | 0.55            | 3.3             |
| <63 $\mu$ m Light     | 99.6               | 8.3           | 109           | 2700          | 6700          | 125           | 120           | 52            | 5.1             | 0.30            | 0.33            |
| <63 Heavy % Cont      |                    | <1            | <1            | <1            | <1            | <1            | <4            | <1            | 2               | <1              | 4               |
| <63 Light % Cont      |                    | 96            | 101           | 105           | 109           | 105           | 96            | 129           | 98              | 100             | 97              |
| Cal. Total            |                    | 8.3           | 109           | 2700          | 6700          | 125           | 120           | 52            | 5.1             | 0.30            | 0.34            |
| <b>CDA 93</b>         |                    |               |               |               |               |               |               |               |                 |                 |                 |
| CDA <63- $\mu$ m Bulk | 97                 | 8.6           | 99            | 2700          | 5000          | 86            | 380           | 42            | 5.7             | 0.68            | 0.32            |
| <63 $\mu$ m Heavy     | 0.6                | 1.8           | 161           | 985           | 3600          | 32            | 357           | <100          | 25.4            | 0.72            | 1.79            |
| <63 $\mu$ m Light     | 99.4               | 8.6           | 101           | 2800          | 5500          | 92            | 350           | 52            | 5.6             | 0.66            | 0.35            |
| <63 Heavy % Cont      |                    | <1            | 1             | <1            | <1            | <1            | 1             | <1            | 3               | 1               | 3               |
| <63 Light % Cont      |                    | 99            | 101           | 104           | 110           | 107           | 92            | 123           | 97              | 97              | 108             |
| Cal. Total            |                    | 8.6           | 101           | 2800          | 5500          | 92            | 350           | 52            | 5.7             | 0.66            | 0.36            |
| <b>CDA 119</b>        |                    |               |               |               |               |               |               |               |                 |                 |                 |
| CDA <63- $\mu$ m Bulk | 96                 | 8.4           | 80            | 3000          | 3000          | 33            | 660           | 24            | 6.3             | 1.00            | 0.31            |
| <63 $\mu$ m Heavy     | 3                  | 15.6          | 117           | 2100          | 3700          | 28            | 330           | <100          | 40.5            | 1.21            | 0.69            |
| <63 $\mu$ m Light     | 97                 | 8.4           | 79            | 3100          | 3200          | 32            | 560           | 30            | 5.5             | 0.96            | 0.3             |
| <63 Heavy % Cont      |                    | 6             | 5             | 2             | 4             | 3             | 2             | <1            | 21              | 4               | 7               |
| <63 Light % Cont      |                    | 97            | 96            | 98            | 103           | 95            | 82            | 121           | 84              | 93              | 94              |
| Cal. Total            |                    | 8.6           | 80            | 3000          | 3200          | 32            | 560           | 29            | 6.6             | 0.97            | 0.31            |
| <b>CDA 128</b>        |                    |               |               |               |               |               |               |               |                 |                 |                 |
| CDA <63- $\mu$ m Bulk | 85                 | 12.2          | 99            | 4100          | 3500          | 27            | 650           | 37            | 9               | 0.79            | 0.25            |
| <63 $\mu$ m Heavy     | 11                 | 18            | 116           | 2300          | 3800          | 27            | 410           | 31            | 38.2            | 3.40            | 0.36            |
| <63 $\mu$ m Light     | 89                 | 10.2          | 89            | 4000          | 3300          | 24            | 550           | 36            | 5.4             | 0.46            | 0.25            |
| <63 Heavy % Cont      |                    | 17            | 13            | 6             | 12            | 11            | 7             | 10            | 48              | 49              | 16              |
| <63 Light % Cont      |                    | 74            | 80            | 87            | 84            | 79            | 75            | 86            | 53              | 52              | 89              |
| Cal. Total            |                    | 11.1          | 92            | 3900          | 3400          | 24            | 535           | 35            | 9.1             | 0.80            | 0.26            |

**Table 6. Percentages of trace elements associated with oxide and organic/sulfide fractions in selected Lake Coeur d' Alene sediment samples.**

| Sample                           | Ag<br>ppm | Cu<br>ppm | Pb<br>ppm | Zn<br>ppm | Ni<br>ppm | Co<br>ppm | Cd<br>ppm | Cr<br>ppm | As<br>ppm | Sb<br>ppm | Fe<br>wt. % | Mn<br>wt. % | Al<br>wt. % | Ti<br>wt. % |
|----------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|-------------|-------------|-------------|
| CDA 32 Bulk                      | 8         | 112       | 2700      | 6300      | 25        | 30        | 126       | 50        | 126       | 39        | 5.1         | 0.28        | 8.3         | 0.34        |
| % Removed by Oxide<br>Extraction | 0         | 56        | 95        | 89        | 20        | 67        | 95        | 22        | 71        | 13        | 37          | 82          | 10          | 0           |
| % Removed by<br>Organic/Sulfide  | 100       | 29        | 4         | 8         | 20        | 13        | 5         | 22        | 4         | 0         | 14          | 9           | 4           | 9           |
| CDA 93 Bulk                      | 9         | 104       | 2600      | 4800      | 27        | 39        | 87        | 54        | 400       | 43        | 5.7         | 0.65        | 8.4         | 0.34        |
| % Removed by Oxide<br>Extraction | 0         | 51        | 94        | 79        | 26        | 74        | 89        | 15        | 65        | 19        | 33          | 82          | 1           | 0           |
| % Removed by<br>Organic/Sulfide  | 36        | 36        | 2         | 16        | 15        | 5         | 10        | 15        | 13        | 5         | 21          | 14          | 12          | 6           |
| CDA 119 Bulk                     | 8         | 85        | 2900      | 2900      | 19        | 23        | 33        | 41        | 660       | 25        | 6.5         | 1           | 7.6         | 0.32        |
| % Removed by Oxide<br>Extraction | 40        | 61        | 94        | 79        | 32        | 70        | 90        | 12        | 82        | 20        | 35          | 80          | 13          | 6           |
| % Removed by<br>Organic/Sulfide  | 36        | 21        | 4         | 12        | 0         | 9         | 7         | 10        | 5         | 0         | 25          | 17          | 5           | 0           |
| CDA 128 Bulk                     | 11        | 97        | 3900      | 3200      | 13        | 18        | 27        | 35        | 480       | 31        | 8.7         | 0.8         | 5.8         | 0.25        |
| % Removed by Oxide<br>Extraction | 58        | 64        | 95        | 76        | 23        | 61        | 85        | 17        | 77        | 3         | 39          | 59          | 16          | 0           |
| % Removed by<br>Organic/Sulfide  | 9         | 12        | 3         | 7         | 0         | 17        | 4         | 0         | 2         | 13        | 25          | 28          | 0           | 0           |

CDA River (Table 5). This distribution pattern would be indicative of the CDA River acting as a point source for the heavy fraction.

The chemical analyses of both fractions provide additional insights into trace element phase associations and dispersion patterns (Table 5). The highest trace element concentrations for Ag, Cu, Cd, Sb, and Zn shift from the light fraction to the heavy fraction as sample proximity approaches the mouth of the CDA River. However, Pb is always highest in the light fraction, whereas Fe is always highest in the heavy fraction (Table 5). Note that the Fe concentration in the heavy fraction increases by over 60% with proximity to the mouth of the CDA River, whereas the Fe concentration in the light fraction remains remarkably consistent (~5%). The Fe contributions also increase with proximity to the CDA River, but these changes are a direct reflection of the relative percentages of the heavy and light fractions. However, in all cases, the light fractions dominate as the source for the majority of the enriched trace elements because these fractions constitute the majority of each of the four samples (Table 5). In fact, with the exception of Fe and Mn in CDA 128, and, regardless of the higher trace element concentrations associated with the heavy fractions in the southernmost samples, the heavy fractions rarely contribute more than their percentages in the samples. The relatively small percentage of the heavy fractions in the samples, as well as the relatively small percentage contributions from the heavy fraction to the overall trace element concentrations in the samples, were unexpected because the cause and provenance for the enriched metals in the lake sediments had always been presumed to be sulfide (heavy) minerals from the CDA mining district (e.g., Bender, 1991; Javorka, 1991).

Subsequent reflected light microscopy and SEM/EDAX examination of the separated heavy fractions indicated the presence of a relatively standard suite of heavy minerals, including sulfides, typical of the region. The presence of such minerals as galena, sphalerite, Ti oxides, tetrahedrite, monazite, arsenopyrite, chalcopyrite, and various Fe sulfides was confirmed from the EDAX analyses. Many of the heavy minerals were coated by Fe oxide rinds. Of particular interest were the changes in the mean grain sizes of the trace element bearing-minerals (e.g., galena, sphalerite, tetrahedrite) with increasing distance from the mouth of the CDA River. It was empirically determined that the mean grain sizes of the heavy mineral suites from each of the four samples decreased with increasing distance from the mouth of the CDA River; those minerals from the sample closest to the river had mean grain sizes on the order of 30 to 40  $\mu\text{m}$ , whereas those from the sample farthest from the river were on the order of some 5 to 15  $\mu\text{m}$ . This pattern would be consistent with the CDA River acting as a point source for the heavy minerals.

### **Chemical variations with geochemical phases**

A final evaluation of the phase association(s) of the various enriched trace elements was made by using a two-step sequential extraction procedure designed to segregate elements associated with Fe oxides, organics/sulfides, and those in a more resistant (refractory) matrix (Table 6). These extractions were made on whole unground samples. On the basis of the physical and chemical results from the grain size, heavy-mineral, and SEM/EDAX evaluations, the results from the extractions confirmed many of the conclusions already cited above. The majority of the Pb

(~95%), Cd (~90%), Zn (~80%), As (~75%), and Cu (~55%) appears to be associated with an operationally defined Fe oxide phase, whereas the remaining percentages appear to be associated with either an operationally defined organics/sulfides-phase or are tightly bound in mineral lattices (Table 6). Silver displays the widest variability with all of it being associated with organics/sulfides in one case (100%, CDA 32), to another where the majority of the Ag is associated with Fe oxides (~58%, CDA 128). Antimony appears to be associated predominantly with a refractory (lattice-held) phase. There do not appear to be any consistent phase association patterns with proximity to the mouth of the CDA River, except for Ag, Cu, and Zn. The Fe oxide-associated Ag and Cu appear to increase, whereas the Fe oxide-associated Zn appears to decrease with proximity to the CDA River; however, these conclusions should be viewed with caution due to the limitations associated with using sequential extractions to determine trace element phase associations (e.g., Horowitz, 1991).

On the basis of the results from the chemical extractions, as well as the subsequent chemical analyses and SEM/EDAX and optical examinations of the heavy- and light-mineral separates, there is little doubt that the vast majority of the elevated trace elements (As, Cu, Cd, Pb, Zn) in the surface sediments from Lake CDA are associated with Fe oxides either in the form of coatings or separate grains; very limited percentages, with the possible exception of Ag, appear to be associated with sulfide (heavy-mineral) phases. Antimony displays the only major exception to this pattern, appearing to be concentrated predominantly in a refractory phase.

The CDA River appears to be the source of the heavy minerals found in the trace element enriched surface sediments of Lake CDA. There also appears to be two sources for the Fe oxides, and the enriched trace elements associated with them, in the same Lake CDA surface sediments: (1) their formation and/or precipitation during smelting operations or in the settling ponds near Wallace and Smelterville or along the channel and banks of the South Fork of the CDA River and the CDA River proper, with subsequent transport into Lake CDA, and/or (2) formation of authigenic Fe oxides within Lake CDA itself. Examination of selected bank deposits from the CDA River reveals substantial quantities of trace elements associated with both heavy minerals and Fe oxides (Table 7). The Ag levels in the bulk and heavy mineral fractions of the bank deposits in the Smelterville area are high enough to be considered ore grade. Note that the percentage of heavy minerals in the bank deposits decreases markedly between Smelterville (~80%) and the confluence of the North and South Forks of the CDA River and Cataldo Flats (~20%); this percentage decreases even further at the CDA River delta (~11%) and in the main stem of the lake (<3%). The decrease in the percentage of heavy minerals appears to be indicative of a steady winnowing process whereby the heavy and light fractions making up the bank and deltaic deposits are physically separated, with the latter being preferentially transported downstream relative to the former.

Active Fe oxide formation was directly observed in isolated pools (possibly natural seeps or rain puddles) in the Cataldo Flats area during the summer of 1991. The contents of several of these pools were discharging directly into the CDA River. Thus, the CDA River certainly can be viewed as a source for at least some of the Fe oxides. In addition, the thin veneer of fine-grained Fe oxides found in many of the surface grab samples from the lake either

Table 7. Chemical concentrations for the bulk, heavy, and light fractions of selected bank samples from the South Fork of the Coeur d'Alene River

| Sample  | Percent of Sample | Ag   | Cu  | Pb     | Zn     | Cd   | Hg   | As  | Sb  | Fe   | Mn   | Al  | Ti   |
|---|-------------------|------|-----|--------|--------|------|------|-----|-----|------|------|-----|------|
| <u>South Fork at Smelterville, Right Bank</u>                               |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 150  | 590 | 63,000 | 12,000 | 43.5 | 18.1 | 90  | 240 | 17.1 | 0.62 | 3.4 | 0.13 |
| Light   | 41                | 36   | 150 | 8,100  | 3,700  | 16.1 | 3.30 | 30  | 130 | 4.9  | 0.14 | 4.2 | 0.11 |
| Heavy   | 58                | 140  | 730 | 80,000 | 16,000 | 51.0 | 18.4 | 120 | 160 | 24.3 | 0.83 | 3.0 | 0.14 |
| <u>South Fork at Smelterville I. Left Bank</u>                              |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 173  | 650 | 55,000 | 8,800  | 20.1 | 21.0 | 100 | 340 | 15.4 | 0.58 | 3.9 | 0.15 |
| Light   | 40                | 73   | 265 | 21,000 | 3,600  | 12.8 | 7.00 | 40  | 220 | 5.4  | 0.13 | 4.4 | 0.11 |
| Heavy   | 60                | 178  | 920 | 58,000 | 12,000 | 24.0 | 28.6 | 140 | 320 | 24.2 | 0.90 | 3.3 | 0.15 |
| <u>South Fork at Smelterville II. Left Bank</u>                             |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 185  | 670 | 71,000 | 9,000  | 18.9 | 17.9 | 96  | 395 | 15.1 | 0.51 | 4.0 | 0.15 |
| Light   | 42                | 67   | 240 | 16,000 | 3,200  | 7.5  | 10.0 | 40  | 200 | 5.1  | 0.13 | 4.5 | 0.11 |
| Heavy   | 58                | 230  | 930 | 76,000 | 13,000 | 23.0 | 27.8 | 140 | 300 | 23.7 | 0.77 | 3.4 | 0.15 |
| <u>Just Below Confluence with the North Fork of the Coeur d'Alene River</u> |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 15.5 | 240 | 5,600  | 4,500  | 64.0 | 3.40 | 170 | 85  | 9.2  | 0.56 | 4.9 | 0.24 |
| Light   | 81                | 9.7  | 160 | 4,900  | 3,300  | 49.4 | 4.30 | 100 | 50  | 4.1  | 0.15 | 5.2 | 0.17 |
| Heavy   | 17                | 42.2 | 425 | 7,300  | 7,300  | 56.0 | 5.70 | 330 | 160 | 38.6 | 2.60 | 2.0 | 0.38 |
| <u>Cataldo Flats, Bottom of Drop</u>  |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 10.3 | 76  | 2,800  | 7,700  | 14.0 | 0.67 | 150 | 48  | 8.7  | 0.90 | 3.2 | 0.13 |
| Light   | 78                | 15.0 | 47  | 1,400  | 5,100  | 6.4  | 0.45 | 80  | 35  | 2.8  | 0.33 | 3.6 | 0.11 |
| Heavy   | 21                | 20.4 | 185 | 7,000  | 15,000 | 27.4 | 1.47 | 330 | 70  | 33.4 | 3.00 | 1.9 | 0.14 |
| <u>Cataldo Flats, Mid Seep at Bottom</u>                                    |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 11.8 | 84  | 2,500  | 6,500  | 8.4  | 0.72 | 140 | 49  | 7.6  | 0.85 | 3.3 | 0.13 |
| Light   | 78                | 5.8  | 38  | 1,400  | 3,700  | 3.1  | 0.33 | 75  | 26  | 2.7  | 0.30 | 3.7 | 0.12 |
| Heavy   | 21                | 26.6 | 220 | 8,600  | 16,000 | 34.6 | 1.38 | 500 | 70  | 38.0 | 3.25 | 1.6 | 0.14 |
| <u>Cataldo Flats, Seep Solids at River Edge</u>                             |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 11.6 | 100 | 3,800  | 7,800  | 12.9 | 1.88 | 160 | 52  | 8.8  | 0.89 | 3.9 | 0.17 |
| Light   | 78                | 7.4  | 62  | 2,600  | 5,400  | 8.1  | 1.23 | 80  | 33  | 3.8  | 0.33 | 4.4 | 0.15 |
| Heavy   | 20                | 25.4 | 250 | 8,600  | 14,000 | 28.8 | 2.80 | 420 | 60  | 36.8 | 3.00 | 1.8 | 0.16 |
| <u>Cataldo Flats, Surface Flocc of Seep</u>                                 |                   |      |     |        |        |      |      |     |     |      |      |     |      |
| Bulk  |                   | 11.3 | 89  | 2,000  | 19,000 | 9.4  | 1.57 | 170 | 48  | 14.9 | 0.85 | 3.4 | 0.14 |
| Light   | 75                | 9.0  | 54  | 2,800  | 17,000 | 6.1  | 1.18 | 100 | 29  | 8.4  | 0.31 | 3.7 | 0.11 |
| Heavy   | 23                | 20.2 | 175 | 6,800  | 27,000 | 20.4 | 2.42 | 430 | 70  | 37.2 | 2.57 | 1.9 | 0.16 |

could have been transported from the CDA River or could be authigenic. The presence of authigenic Fe oxides in Lake CDA could be due to deposition and burial of detrital Fe oxides in the lake, subsequent remobilization under reducing conditions, upward diffusion in the pore waters, and reprecipitation once the fluids have passed through the anoxic/oxic boundary. The presence of reducing conditions in the sediment column is supported by some of the trace element patterns (especially for Mn) in analyzed core samples reported by Funk et al. (1975) and possibly by the direct observation of sediment degassing in shallow portions of the lake (see "General observations" at the beginning of this section). Finally, initial chemical analyses of several cores collected during the summer of 1991 clearly indicate the presence of an oxic/anoxic boundary around 10 to 15 cm into the sediment column (Horowitz et al., 1992). Trace element remobilization from within the sediment column is likely to continue for the foreseeable future and may be exacerbated by the increased nutrient-induced eutrophication that has been reported in the lake (e.g., Meckel Engineering et al., 1983; Javorka, 1991; this study, on the basis of the increased expansion of macrophyte beds).

It appears that there are at least two source areas for the majority of the enriched trace elements found in the surface sediments of Lake CDA: (1) heavy minerals (especially sulfides) and Fe oxides which have been transported from and by the CDA River and (2) the bed sediments in the lake due to postdepositional dissolution, upward migration, and subsequent reprecipitation. The heavy mineral dispersion patterns in the surface sediments indicate that the CDA River is acting as a point source for these materials (presumably for at least some of the Fe oxides as well), with decreasing concentrations and grain sizes occurring as the distance from the river increases northward in Lake CDA. This pattern is overlain and complicated by the physical remobilization of fine-grained sediments by currents and wind-driven waves and by the presence of authigenic Fe oxides coming from the bed sediments, within the lake.

The major amounts of trace element-rich bank and flood-plain deposits in conjunction with postdepositional remobilization and reprecipitation from the sediment column in Lake CDA itself, are likely to ensure continued elevated trace element concentrations in the surface sediments of the lake for the foreseeable future, unless active intervention is undertaken. 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 sulfides, when these surface sediments are buried and subjected to anoxic conditions, the Fe oxides and associated trace elements may be solubilized and made environmentally available and as such, are in a more environmentally available form than originally postulated. More detailed evaluations of the ongoing processes in the sediment column will be carried out on a series of gravity cores collected during the summer of 1991 (Horowitz et al., 1992), through detailed studies of pore water dispersion through the upper sediment column, and at the sediment-water interface, scheduled for the summer of 1992.

## CONCLUSIONS

The overwhelming majority of the surface sediments in Lake CDA north of Carey Bay and Conkling Point are substantially enriched in a variety of trace elements including Ag, As, Cu, Cd, Hg, Pb, Sb, and Zn. All the enriched sediments are extremely fine grained and thus, are subject to physical remobilization during periods of high

discharge from the CDA or the St. Joe Rivers and/or by wind-driven waves and currents. The majority of the enriched trace elements are associated with an operationally defined Fe oxide phase; markedly smaller percentages are associated either with operationally defined organics/sulfides or refractory phases. The source of the enriched Fe oxides appears to be a combination of detrital material transported by the CDA River and authigenic deposits reprecipitated from solubilized material within anoxic sediments in the bed of Lake CDA. The association of the majority of the enriched trace elements with "Fe oxides" makes them substantially more environmentally available than if they were associated with sulfide minerals. Ultimately, the source for the enriched trace elements almost certainly can be ascribed to the mining, ore-processing, and smelting operations that have occurred since the 1880's in the CDA mining district.

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