

THE EFFECT OF MINING AND RELATED ACTIVITIES ON THE
SEDIMENT-TRACE ELEMENT GEOCHEMISTRY OF
LAKE COEUR D'ALENE, IDAHO
PART II: SUBSURFACE SEDIMENTS

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

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CONVERSION FACTORS

Length

<u>Multiply</u>	<u>by</u>	<u>to obtain</u>
centimeter (cm)	0.03937	inch
millimeter (mm)	39.37	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile

Area

kilometer ² (km ²)	0.3861	square mile
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Mass

metric ton	1.102311	ton
gram (g)	0.03527396	ounce

Temperature

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32)$$

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

by

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ABSTRACT

During the summer of 1990, 12 gravity cores were collected in Lake Coeur d'Alene, Idaho, at various depths and in a variety of depositional environments. All core subsamples were analyzed to determine bulk sediment chemistry; selected subsamples were analyzed for trace element partitioning and ¹³⁷Cs activity. The purpose of these analyses was to determine the trace element concentrations and distributions in the sediment column and to try to establish a trace element geochemical history of the lake in relation to mining and mining related discharge operations in the area.

Substantial portions of the near-surface sediments in Lake Coeur d'Alene are markedly enriched in Ag, As, Cd, Hg, Pb, Sb and Zn, and somewhat enriched in Cu, Fe and Mn. Variations in the thickness of the trace element-rich sediments, which range in thickness from more than 119cm to as little as 17cm, indicate that the source of much of this material is the Coeur d'Alene River. An estimated 75 million metric tons of trace element-rich sediments have been deposited on/in the lakebed. Estimated trace element masses in excess of those considered representative of background conditions, range from a high of 468,000 metric tons of Pb to a low of 260 metric tons of Hg.

The similarity between the trace element-rich surface and subsurface sediments with respect to: their location, their bulk chemistry, their interelement relations and their trace element partitioning indicate that the sources and/or concentrating mechanisms causing the trace element enrichment in the lake sediments, probably have been the same throughout their depositional history. Based on a Mt. St. Helens' ash layer from the 1980 eruption, ages estimated from ^{137}Cs activity, and the presence of 80 discernible and presumably annual layers in a core collected near the Coeur d'Alene River delta, indicate that deposition rates for the trace element-rich sediments have ranged from 2.1 to 1.3 cm/year. These data also indicate that the deposition of trace element-rich sediments began, at least in the Coeur d'Alene River delta, some time between 1895 and 1910, dates consistent with the onset of mining and ore-processing activities that began in the area in the 1880's.

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 body of the lake 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 miles downstream on the Spokane River) was completed, (Meckel Engineering, et al., 1983) (Fig. 1). The St. Joe and CDA Rivers annually account for 94% ($\sim 4.73 \text{ Gm}^3/\text{yr}$) 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 (Fig. 1).

The South Fork of the CDA River, which flows into the CDA River, and thence into Lake CDA, 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, Cu, Pb and Zn in the U.S. (e.g., Bender, 1991). Until 1968, when tailings ponds were established to trap/retain tailings and limit sediment transport, most of the mining and ore-processing wastes were discharged directly into the South Fork of the CDA River. These materials were highly enriched in Ag, As, Cd, Cu, Fe, Mn, Pb, Sb and Zn (Rabe and Bauer, 1977; Bender, 1991). It has been estimated that during the course of mining, processing and smelting operations in the area, about 115 million metric tons of mine tailings were produced and that 60% of this material probably entered the South Fork of the CDA and the CDA River system (Javorka, 1991). In 1983, as a result of the elevated trace element concentrations in the mining and processing wastes, the U.S. Environmental Protection Agency (EPA) established the Bunker Hill Superfund Site that encompasses 54 km^2 in the Kellogg and Smeltonville Flats area; some 50 km upstream of Lake CDA. (e.g., Bender, 1991; Fig. 1).

Over the years, several environmental studies have indicated that large amounts of mining, milling, and ore-processing wastes, enriched in a variety of trace elements, have been deposited throughout the lower CDA River and Lake CDA, and have had a substantial effect 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, 1974b; Norbeck, 1974; Funk, et al., 1975; Sheppard and Funk, 1975; Johnson, et al., 1976; Inoannou; 1979; Wai, et al., 1985; Savage, 1986; Neufeld, 1987; Woods, 1989; Krieger, 1990; Piske, 1990; Bender, 1991; Horowitz, et al., 1993).

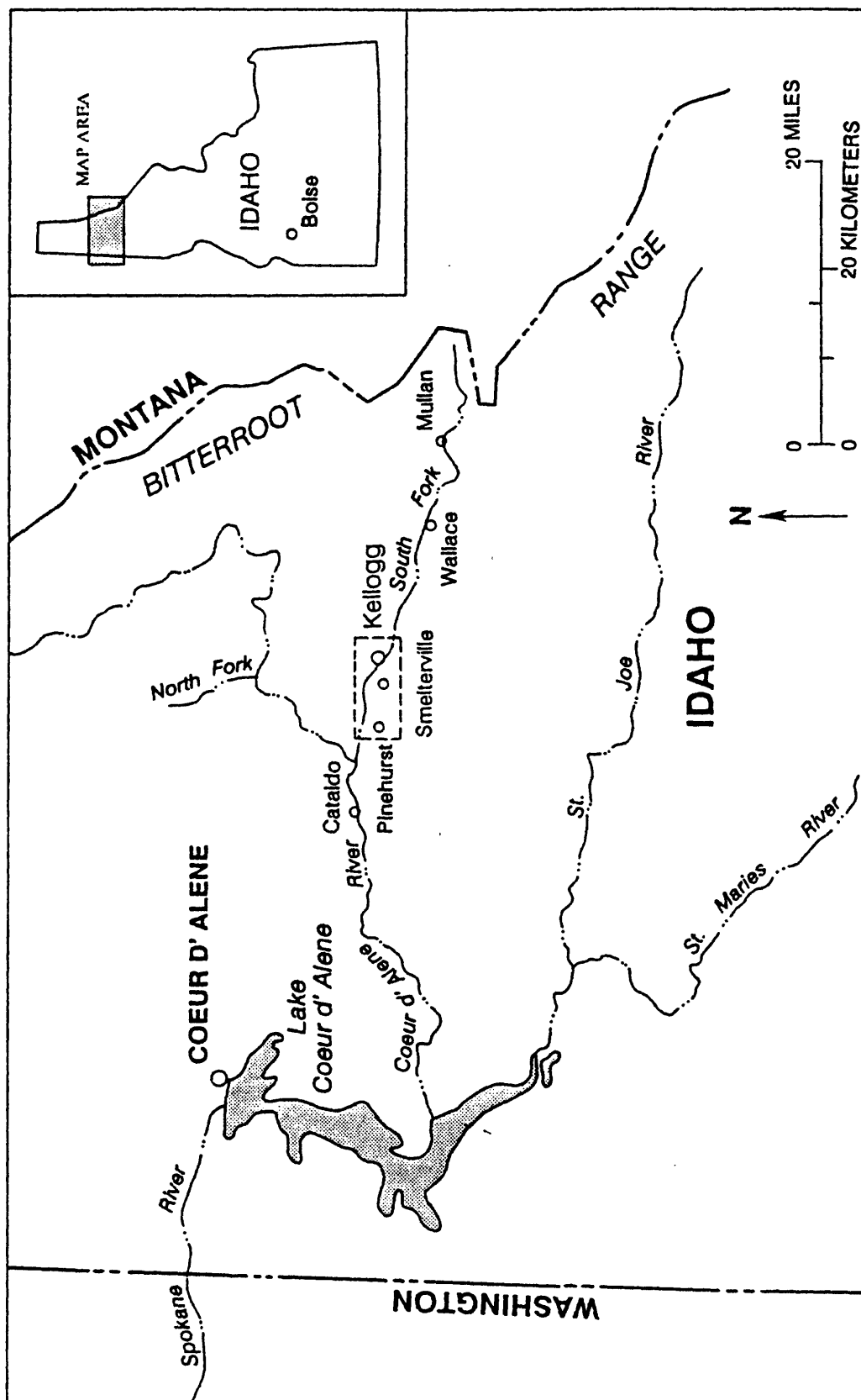


Figure 1. General location map of the South Fork of the Coeur d'Alene River, the St. Joe River, and Lake Coeur d'Alene. The dashed box outlines the location of the 54 km² U.S. EPA Bunker Hill Superfund Site (after Bender, 1991).

A detailed examination of the surficial sediments of Lake CDA were reported previously, and showed (Horowitz, et al., 1993):

- 1) Surface sediments in most of Lake CDA (~85%) are substantially enriched in Ag, As, Cu, Cd, Hg, Pb, Sb and Zn relative to sediments in the southern portion of the lake near the St. Joe River.
- 2) Trace element enriched sediments are typically very fine grained (mean grain sizes $\ll 63\mu\text{m}$) and are readily remobilized by currents within the lake.
- 3) Based on both the chemical analyses of separated heavy and light mineral fractions, and a two-step sequential extraction procedure, most of the enriched trace element concentrations are associated with an operationally defined (by partial chemical extraction) Fe oxide phase; much smaller percentages are associated with operationally defined (by partial chemical extraction) organics/sulfide or refractory phases. The sulfide/heavy mineral phases are almost certainly detrital, coming from the banks and floodplain of the South Fork of the CDA and the CDA Rivers. The Fe oxides seem to be both detrital and authigenic.
- 4) Within the lake, the presence, concentration, and distribution of the enriched trace elements indicate that the CDA River is acting as a source for this material.
- 5) Within the lake, the point source pattern is complicated by a combination of (a) the formation of trace element rich authigenic Fe oxides due to remobilization from anoxic bed sediments, and (b) physical remobilization by currents and wind-driven waves.

The goal of the present study was to examine the subsurface sediments to determine their bulk chemistry, the mass of trace element-rich sediments on/in the lakebed, and to establish a sediment-geochemical history for the lake. The results of this portion of the study are reported herein.

SAMPLE COLLECTION, TREATMENT, AND ANALYTICAL METHODS

Sample collection

Twelve gravity cores were collected in Lake CDA in June 1990. Preliminary sampling sites were identified, prior to collection, based on the results from the geochemical surface-sediment survey carried out in 1989 (Horowitz, et al., 1993). Site selection represented an attempt to obtain cores useful in evaluating the vertical and geochemical differences in sediment-associated trace elements from different depositional and geochemical environments within the lake (e.g., the CDA River delta, the main stem of the lake, the backs of several bays perpendicular to the main stem). During sampling operations, coring sites were located using a portable Global Positioning System (GPS).

Samples were collected using a stainless steel 2.44m (8 foot) Wildco* gravity core with a clear polycarbonate liner and a non-metallic core catcher. Upon recovery, the liner was removed from the core barrel, kept in a vertical position, and capped at both ends. Any water remaining in the liner at the sediment-water interface was removed through a small hole to prevent any additional disturbance of the surface and near-surface sediments. After draining, the liner was trimmed to remove excess material, recapped, and the caps taped in place. The cores were stored on ice at 4°C until they could be taken ashore and frozen. The cores remained frozen during storage, were shipped to a USGS laboratory in Atlanta in that state, and were kept frozen until they could be processed.

Sample pretreatment

Each core was split while frozen; one half was returned to the freezer for archiving whereas the other half was allowed to thaw. Before sampling, each half-core was described, measured, and photographed. Subsamples were then removed from the thawed half-core. Wherever feasible (e.g., when sufficient mass could be collected to permit subsequent analyses), individual subsamples were removed from obvious layers, or where significant color or textural changes could be visually identified. Wherever the core appeared to be homogeneous, aliquots from 5 cm intervals were removed. Aliquots were removed using a non-metallic spatula and stored in separately labeled polypropylene vials. The samples, in their vials, were returned to the freezer for storage, until they could be freeze-dried. In all, 442 subsamples were obtained from the 12 cores.

Analytical Techniques

All the core samples were analyzed for Fe, Mn, Al, Ti, As, Cu, Zn, Cd, Pb, As, Sb, Hg and TOC. Selected samples were subjected to heavy-mineral separations using bromoform ($\rho = 2.96 \text{ g/cm}^3$) followed by total chemical analyses of the light and heavy fractions. Selected heavy and light fractions also were examined and chemically analyzed using SEM/EDAX. These techniques were the same as those used on previously collected surface sediment samples from Lake CDA, and are described in detail elsewhere (Horowitz, et al., 1993). Precision and bias for the chemical analyses were monitored using a variety of standard reference materials and sample duplicates. Precision was better than $\pm 10\%$; no bias was detected.

¹³⁷Cs Determinations

The activity of ¹³⁷Cs was determined by manually pressing $4.00 \pm 0.01 \text{ g}$ of dry sediment to a fixed height ($4.00 \pm 0.05 \text{ cm}$) in standardized vials to achieve conditions of constant bulk sediment density and sample shape. Prepared samples were counted using a high resolution solid-state HpGe detector coupled to a multichannel analyzer. System calibration was achieved using sediments doped with NIST-traceable standard solutions of ¹³⁷Cs. Approximately 3 days of counting time per sample were required to achieve measurement precision between 7 - 20% in the vicinity of maximum activities because of the relatively small sample sizes and/or relatively low activities. For samples in which the ¹³⁷Cs activities were close to the detection limit, sample size and counting time limitations commonly produced errors as large as 50%.

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

RESULTS AND DISCUSSION

General observations

The locations and general descriptions of all 12 gravity cores are provided in Table 1 and Fig. 2. With the exception of cores 7 and 146 (to be discussed later), all the cores have similar physical features. Each contains an upper, heavily banded section, and a lower, homogeneous section. The banded upper sections tend to be tan to brown and are occasionally interspersed with thin, dark brown to black bands. Where the bands or layers are thick enough, it is possible to observe graded bedding (finer material at the top of each layer grading into coarser material toward the bottom). The banded sections of most of the cores also contain a single, distinctive gray/white layer located anywhere from 0.3 to 21.5cm from their tops (Table 1). This singular band is similar in color and texture to the Mt. St. Helens' ash layer identified in some of the surface grab samples collected during the previous year, which contained material from the May 1980 eruption (Horowitz, et al., 1993). The banded sections range in thickness from 17 to 119 cm (Table 1). In several cases, especially where the banded sections are thickest (e.g., cores 123 and 6, Table 1), it is possible to identify as many as 80 individual layers. Band thickness varies from as little as 1 or 2mm to as much as 20mm. If the bands represent annual runoff events, or periods of annual deposition, then substantial differences in local sedimentation rates occurred through time. The large differences in the thickness of the banded sections, combined with the differences in depth to the ash layer in the various cores, may indicate large variations in sedimentation/deposition rates in different areas of the lake. These differences could also indicate that the material settled, was physically remobilized by currents or wind-driven waves, and then settled again, prior to final deposition on the lake bed. The lower unbanded core sections tend to be dark olive in color and display no discernible changes in grain size.

Most of the cores contain several disconnected 3 to 5cm sections which display large numbers of small (<0.5mm) vesicles, probably due to former gas bubbles or gas production; however, there was no detectable odor. As the cores thawed prior to sampling, the interstitial water on the surface of the split cores, as well as along the edges near the core liners, developed obvious red tinges. This was inferred to be caused by the oxidation of reduced Fe in the interstitial water, and probably indicates that major sections of the sampled sediment column exist in a reducing environment.

In most of the cores, but most notably in cores near the CDA River delta (123, 8, and 9, Fig. 2, Table 1), the lower sections just below the banded zones contain structures that appear to have been formed by prior biological activity (e.g., infilled burrows and worm tubes, H. Markewich, pers. comm., 1993). The banded zones lacked such structures. Previous sampling indicated little or no benthic biological activity in surface sediments in this area (Horowitz, et al., 1993). Thus, the banding may reflect a lack of infauna and associated bioturbation.

Core 146 was collected at the extreme southern end of Lake CDA in Chatcolet Lake (Fig. 2). The core contains no banding and is dark olive throughout its length. This color is identical to that found below the banded sections in all the other cores. Despite the fact that the southern end of Lake CDA was blanketed by Mt. St. Helens' ash (Sarna-Wojcicki, et al., 1981a), core 146 contains no visible ash layer. This could indicate rapid sedimentation rates, high physical energy, and/or bioturbation.

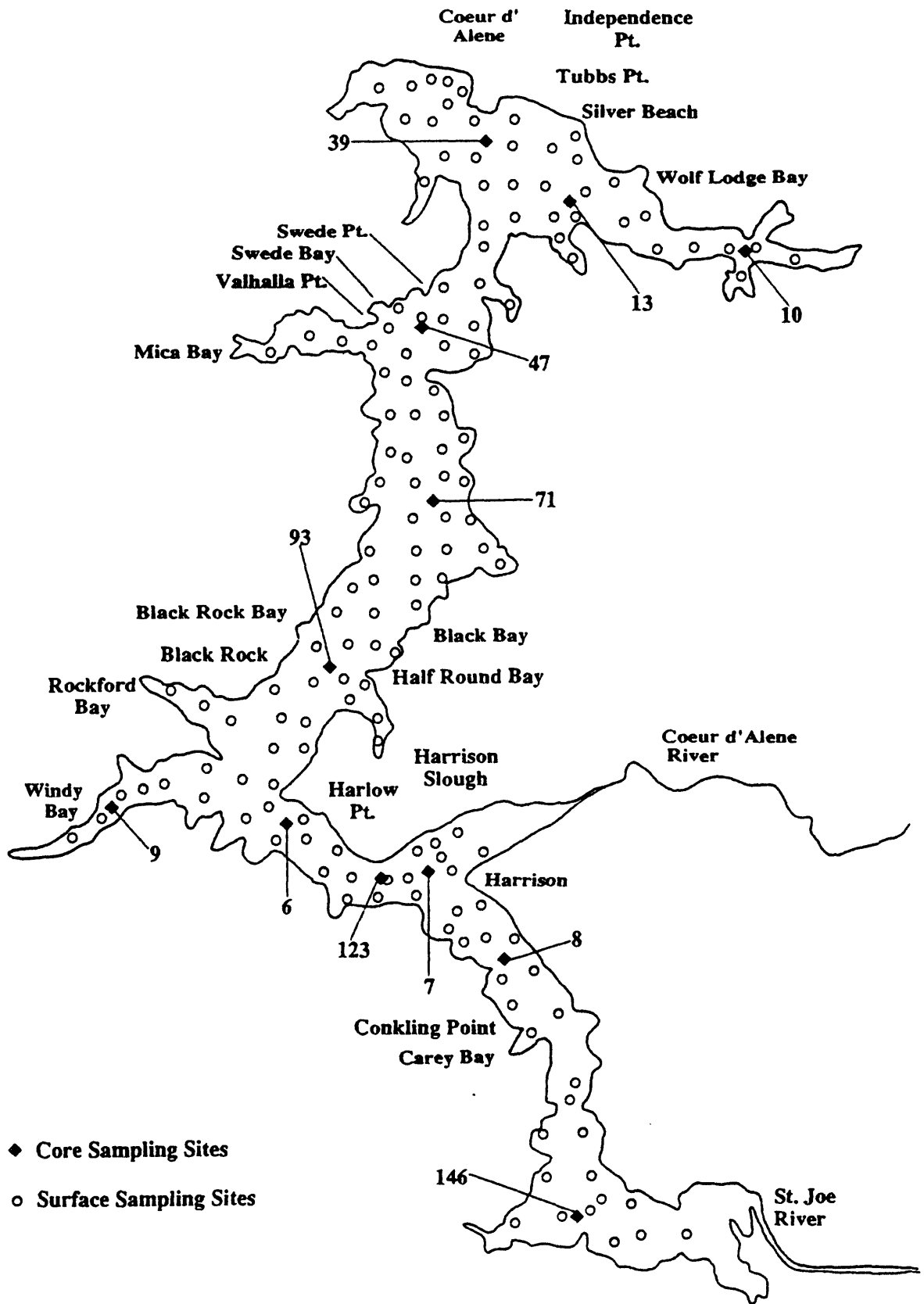


Figure 2. Lake Coeur d'Alene showing all sampling locations, cities and features cited in the text.

Table 1. Location and Description of the Gravity Cores Obtained from Lake Coeur d'Alene

Core Number	Location	Total Length (cm)	Depth/Thickness of Layered Zone(cm)	Depth/Thickness of Ash Layer (cm)	Depth/Thickness of Trace Element Maxima (cm)
Core 10	47°37'30"N, 116°40'43"W	130.0	25.0	2.3-2.5	18.0-20.0
Core 13	47°38'08"N, 116°44'27"W	128.5	17.0	N/D ¹	11.5-14.0
Core 39	47°39'10"N, 116°46'55"W	140.5	23.5	N/D ¹	7.5-13.5
Core 47	47°36'25"N, 116°48'17"W	128.0	26.0	0.3-0.4	19.0-21.0
Core 71	47°33'17"N, 116°48'00"W	129.0	30.0	0.5-0.7	19.0-21.0
Core 93	47°30'53"N, 116°49'51"W	124.0	31.0	0.5-0.8	23.0-25.5
Core 9	47°28'19"N, 116°55'08"W	122.0	34.0	3.5-3.7	27.0-29.0
Core 6	47°28'05"N, 116°51'08"W	114.5	41.0	5.0-6.5	N/D ¹
Core 123	47°27'16"N, 116°49'11"W	126.0	119.0	20.5-21.5	102.0-104.5
Core 7	47°27'27"N, 116°48'22"W	97.5	0 ²	N/D ¹	N/D ¹
Core 8	47°26'02"N, 116°46'43"W	105.0	35.0	9.6-9.8	21.0-24.0
Core 146	47°21'39"N, 116°45'06"W	105.0	0 ³	N/D ¹	N/D

N/D¹ - not detected, not present, not analyzed

0² - core does not contain layering, but does display evidence of slumping

0³ - core does not contain layering, basically a solid single color throughout its length

Core 7 was collected in relatively shallow water (<4m) in the CDA River delta within 0.3 km of the mouth of the river (Fig. 2). The sediments in this core are highly disturbed; numerous cross-bedded layers are evident in several discontinuous sections of the core. This cross-bedding, combined with other structures in the core, indicates that the CDA River delta is a high energy zone and/or an area where sediment slumping is taking place. Such sediment instability, along with active erosion, are most likely to occur during periods of high runoff and local turbulence when the inflowing water from the CDA River meets the northward flowing water from the St. Joe River (Fig. 1). The sediments in core 7 are the coarsest in the collection. The presence of large amounts of coarse-grained material in this part of Lake CDA is not surprising because coarse particles would have been deposited first, as a result of the decrease in energy associated with the transition from the river to lake (the CDA River delta). The grain size distribution in this core mirrors the results from the surface sediments collected in the same area (Horowitz, et al., 1993).

Bulk sediment chemistry and vertical trace element distribution patterns

The minimum, maximum, mean, and median bulk chemical data for all the core samples clearly show that the upper sediment column in Lake CDA is enriched in Ag, As, Cd, Hg, Pb, Sb and Zn. The cores are less enriched in Cu, Fe and Mn relative to both unenriched fluvial sediments throughout the U.S.A. and to unenriched surface and subsurface (e.g., Core 146) sediments from within the lake (e.g., Horowitz, 1991; Horowitz, et al., 1993, this study, Table 2). The highest trace element concentrations in Lake CDA sediments, typically by a factor of two or more, are associated with subsurface rather than surface material (Ag, Cu, Pb, Zn, Hg, As and Sb, the maximum column in Table 2); however, this pattern is reversed when the surface and subsurface median concentrations are considered (with the exception of Ag and Sb, the median column in Table 2). The highest median concentrations for Cu, Pb, Zn, Cd, Hg and As are found in the surface sediments, whereas the highest median concentration for Ag is found in the subsurface sediments. The median concentration for sediment-associated Sb is virtually the same for both. The generally higher median surface sediment concentrations may be the result of post-depositional remobilization, upward diffusion, and subsequent reprecipitation caused by reducing conditions in the sediment column which stripped some subsurface trace elements associated with Fe oxides from the sediments.

With the exception of core 7, the elevated trace element concentrations in the subsurface sediments occur only in the banded zones in the cores. As pointed out earlier, core 7 is highly disturbed, and lacks coherent banding; however, trace element concentrations are elevated throughout its length. The trace element-rich banded zones vary in thickness from a low of 17cm to a high of 119cm (cores 13 and 123 respectively, Table 1). The thickness of the banded zones in the cores increases with proximity to the mouth of the CDA River. This would indicate that, in the past, the CDA River has acted as a point source for the trace element-rich sediments deposited in Lake CDA. The recent geochemical survey of the surface sediments of Lake CDA also indicated that the CDA River currently is a point source for trace element-rich sediments entering and depositing in the lake (Horowitz, et al., 1993).

Individual trace element distribution and concentration patterns within the banded zones of each core display marked variability, in most instances covering at least two orders of magnitude (Table 2). Even so, all the concentrations are markedly enriched over background levels (Table 2). The downcore trace element distribution patterns for core 123 are fairly typical of all the cores containing both a banded and an unbanded zone (Fig. 3).

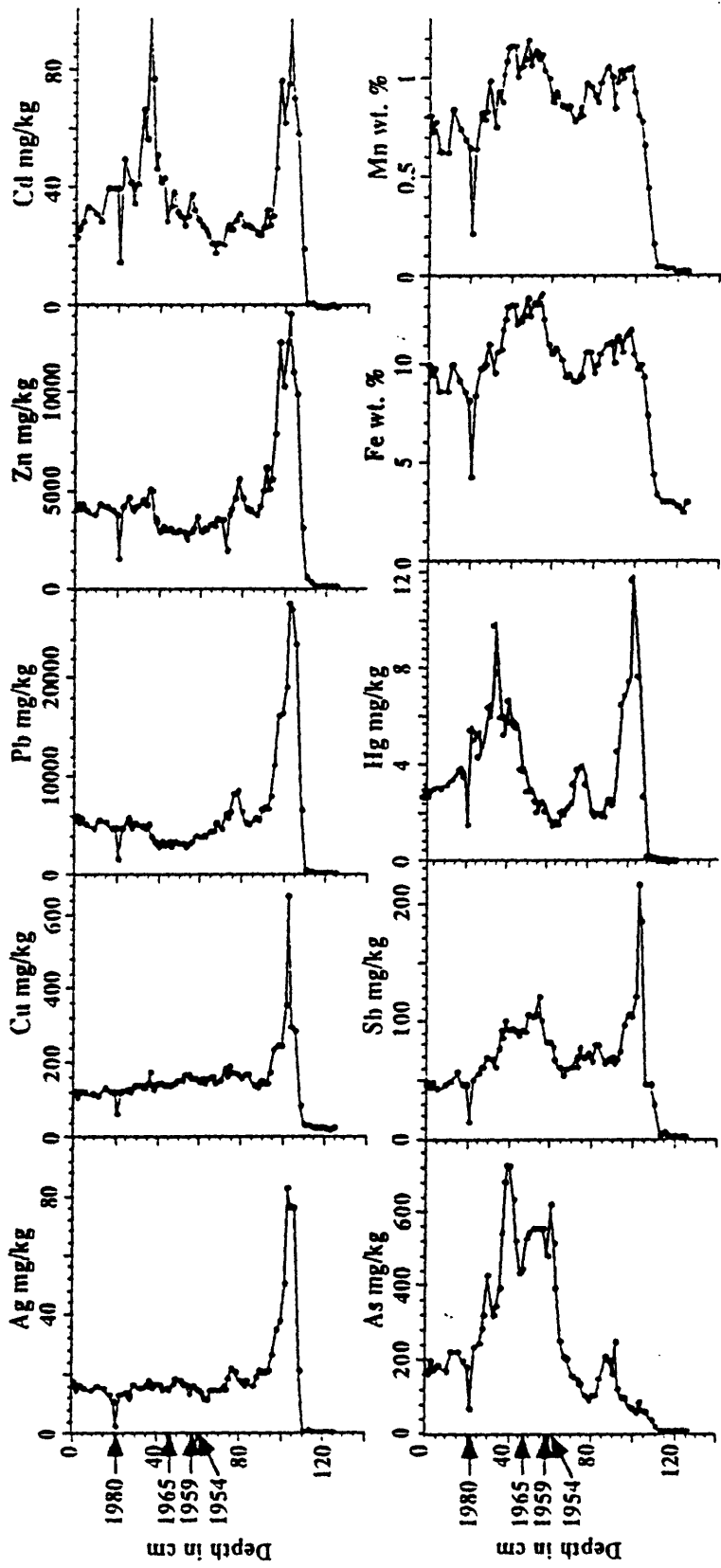


Figure 3. Plots of the vertical distribution patterns for selected trace and major elements in core 123.

Table 2. Minimum, maximum, mean and median concentrations for trace and major elements in surface and subsurface sediments from Lake Coeur d'Alene

<u>Elements (1)</u>	<u>Minimum</u>	<u>Maximum</u>	<u>Mean</u>	<u>Median</u>	<u>Unenriched Median (2)</u>
Ag ppm (S)	<0.5	21.0	6.0	4.0	<1
Ag ppm (C)	<0.1	82.5	15.0	15.0	0.5
Cu ppm (S)	9	215	72	70	25
Cu ppm (C)	20	650	91	60	30
Pb ppm (S)	14	7700	1900	1800	24
Pb ppm (C)	12	27500	3200	1250	33
Zn ppm (S)	63	9100	3600	3500	110
Zn ppm (C)	59	14000	2400	2100	118
Cd ppm (S)	<0.5	157	62	56	2.8
Cd ppm (C)	<0.1	137	25	26	0.3
Hg ppm (S)	0.02	4.90	1.80	1.60	0.05
Hg ppm (C)	<0.01	9.90	1.90	0.95	0.06
As ppm (S)	2.4	660	151	120	4.7
As ppm (C)	3.5	845	103	30	12
Sb ppm (S)	0.5	96	23	19	0.7
Sb ppm (C)	<0.1	215	34	18	1.2
Fe Wt. % (S)	1.9	16.4	5.1	4.9	3.0
Fe Wt. % (C)	2.6	13.7	6.7	5.7	4.7
Mn Wt. % (S)	0.01	2.46	0.67	0.65	0.05
Mn Wt. % (C)	0.01	6.90	0.45	0.26	0.09
Al Wt. % (S)	2.9	9.0	7.5	8.0	6.8
Al Wt. % (C)	3.5	11.0	7.6	8.1	8.0
Ti Wt. % (S)	0.13	0.64	0.34	0.34	0.40
Ti Wt. % (C)	0.10	0.65	0.32	0.31	0.33
TOC Wt. % (S)	0.3	15.6	2.5	2.2	2.5
TOC Wt. % (C)	<0.1	8.9	2.1	2.2	2.5

Elements (1) - (S) - surface samples; (C) - core samples

Unenriched Median (2) - (S) based on 17 samples from the southern part of Lake Coeur d'Alene and the St. Joe River, (C) based on 189 core sample aliquots.

Cores 8, 9, and 10 (Fig. 2) display similar patterns to core 123, but the trace element levels in the upper parts of their banded zones are lower than in the other cores. This probably is caused by the proximity of these sampling sites to inputs of sediments containing background-level trace element concentrations. These inputs dilute the trace element-rich sediments found elsewhere in the lake. Cores 9 and 10 were collected at the backs of Windy and Wolf Lodge Bays respectively (Fig. 2), areas subject to the transport and deposition of sediments from small, local streams that drain areas unaffected by mining and ore-processing activities. Trace element concentrations in the upper part of core 8 also are reduced, probably because of the transport and deposition of sediments that contain background-level trace element concentrations from the St. Joe River (Fig. 2). This pattern also could have been influenced by currents from the northward flowing St. Joe River, which either physically remobilized trace element-rich sediments deposited from the CDA River, or prevented substantial quantities of CDA River sediments from reaching this site.

Core 146 contains no banded zones nor elevated trace element concentrations. The trace element concentrations and distributions for this core mirror those from the surface sediment samples which indicate that there are no trace element-rich sediments south of Carey Bay and Conkling Point (Fig. 1, Horowitz, et al., 1993). The unbanded zones of all the other cores contain trace element concentrations roughly equivalent to those found in core 146. Therefore, the trace element concentrations for core 146, as well as those for the unbanded zones of all the other cores, probably represent background levels for the area (Table 2, 'unenriched median' column).

Surprisingly, despite evidence that reducing conditions exist in portions of the sediment column of Lake CDA (precipitation of Fe oxides when the cores were thawed prior to sampling, see *General observations*, above), the downcore trace element patterns (e.g., Mn and Fe) do not support this observation (Fig. 3). In other words, downcore trace element concentrations and distribution patterns indicate that the most of the subsurface sediment-associated trace elements are relatively inert and do not appear to have been substantially affected by post-depositional remobilization. For example, a typical Mn pattern under reducing conditions would show the highest concentrations at or near the surface, a sharp drop in concentration at the oxic-anoxic boundary, followed by a steady but very low concentration throughout the rest of the core. Such patterns do not appear in any of the Lake CDA cores. It is possible that reducing conditions do not exist in much of the sediment column; however, the precipitation of Fe oxides during thawing and core sampling, plus the high concentrations of trace elements in the surface and near-surface interstitial water and their concentration gradients (N. Simon, pers. comm., 1992), all point toward a reducing environment. The only apparent explanation for the lack of typical downcore trace element patterns indicative of reducing conditions appears to be the extremely high trace element concentrations in the sediments. That is, the losses in trace element concentrations that could be attributable to post-depositional solution and remobilization are relatively minor compared to the residual levels. Thus, the losses are masked by the very high trace element concentrations themselves. Although post-depositional remobilization does not appear to have a major impact on downcore concentrations and distribution patterns, the remobilized (solubilized) trace elements are more bioavailable than their sediment-associated counterparts, and could affect benthic infauna.

Most of the cores contain two very distinct trace element stratigraphic markers. The first is a pronounced trace element minima associated with the Mt. St. Helens' ash layer. In core 123, for example, this marker lies between 20.5 and 21.5cm (Fig. 3). When this same layer is present in the other cores, it is found at various depths ranging from 0.3 to 9.8cm (Table 1). The chemical data for this layer in core 123 indicate that it is by no means pure Mt. St. Helens' ash, but an admixture of trace element-rich sediment and ash.

Based on the chemistry of the ash layer in the core, the reported chemistry of Mt. St. Helens' ash (Sarna-Wojcicki, et al., 1981b), and the chemistry of the layers immediately above and below it, the ash layer appears to be composed of about 65-75% ash and 25-35% trace element-rich sediment.

The other significant stratigraphic marker found in most of the cores is a very distinct trace element maxima. These maxima always occur at, or near the base of the banded zones and at depths of 7.5 to 104.5cm in the sediment column (Table 1). In core 123, for example, the maximum occurs between 102 and 104.5cm (Fig. 3, Table 1). Based on the location of the maxima in the cores, and the extremely elevated trace element concentrations associated with them, they could represent the first substantial discharge of trace element-rich solids to Lake CDA from the drainage basin after the onset of sustained mining and ore-processing activities in the region. This is a possibility because the initial ore-processing procedures used in the area were inefficient, and did not improve until the introduction of flotation procedures to pre-concentrate the heavy ore minerals prior to further processing (e.g., Bender, 1991). A similar rationale was proposed by Bender (1991) to explain some trace element-rich bands in cores obtained in nearby Killarney Lake (a lateral lake adjacent to the CDA River). Alternatively, these maxima may represent a period of unusually high mining and ore-processing activity, or a period of unusually high discharge in the CDA drainage basin.

It should be noted that all the structures in the cores that appear to be caused by former biological activity (see *General observations*, above) are located in the unbanded zones. That is, the disappearance of the structures indicative of former benthic activity seems to coincide with the appearance of elevated trace element concentrations. Currently, it is impossible to determine if the absence of benthic infauna associated with the trace element-rich banded zones was the result of increased turbidity caused by rising concentrations of suspended sediments in Lake CDA, increased sedimentation rates associated with the increased turbidity, or to the elevated trace element concentrations themselves. All three factors were associated with the inception and continuation of mining and ore-processing activities in the CDA mining district. For example, the onset of mining and ore-processing in the area caused substantial increases in the turbidity of Lake CDA (e.g., Ellis, 1940; Rabe and Flaherty, 1974). Increased turbidity would almost certainly lead to increased sedimentation rates. Regardless of the specific cause, it would seem that the disappearance of at least some portion of the benthic invertebrate community, both in the past as well as in the present, was related to the onset and continuation of mining and ore-processing. Currently, turbidity, and presumably sedimentation rates, are low, and dissolved oxygen levels at the sediment-water interface do not fall below 30% of saturation (P. Woods, pers. comm., 1993). On the other hand, the interstitial water at the sediment-water interface contains substantial concentrations of Cu, Pb, and Zn (N. Simon, pers. comm., 1993). Therefore, although direct evidence is lacking, it would appear that a potential cause for at least the current lack of benthic invertebrate activity is related to the elevated trace element concentrations in the sediments.

Estimated Masses of Enriched Sediments and Associated Trace Elements

One of the reasons for collecting cores in the lake was to estimate the mass of trace element-rich sediments, as well as the mass of each enriched trace element, currently on/in the bed of Lake CDA. These estimates were calculated on the basis of the following assumptions and procedures (Table 3).

- 1) The lake was divided into 12 separate zones having a near-centrally located core in each zone.
- 2) The area of each zone was digitized from U.S. Geological Survey 7.5 minute topographic maps.
- 3) For purposes of this estimate, it was assumed that each core represented the thickness and chemical content (median concentration) of the entire zone within which it was located. The thickness of trace element-rich sediments in core 7 had to be estimated since the core never reached background levels. The estimated thickness was 150cm and was based on the gradient (change in trace element-rich thickness) between cores 6 and 123 and core 8 and 123. Core 6 was never chemically analyzed because the liner cracked and the sediment desiccated prior to sampling. The median chemical concentrations for core 6 were estimated as the average of the median values for cores 123 and 93.
- 4) The volume of enriched sediment for each zone was then determined by multiplying the area of each zone by the thickness of the trace element-rich section of the appropriate core.
- 5) The mass of enriched sediment for each zone was subsequently calculated by multiplying the volume of that zone by the density of the sediment [assumed to be 2.00g/cm^3 based on an average measured moisture content of 25% and an average dry density of 2.65g/cm^3 (the density of quartz)].
- 6) The mass of enriched sediment for the entire lake was determined by summing the results for each of the zones.
- 7) The mass of each enriched trace element, in each zone, was calculated by multiplying the mass of trace element-rich sediment in that zone by the median trace element concentration ($\mu\text{g/g}$), from the appropriate core.
- 8) The mass of each enriched sediment-associated trace element for the entire lake was determined by summing the results for each of the zones.
- 9) By substituting background median chemical concentration values obtained from core 146 and the unbanded zones of the other cores, in lieu of the enriched median concentrations used in step 7, normal (unenriched) trace element masses were estimated for the same volume of enriched sediments.
- 10) The excess mass of each sediment-associated trace element was estimated by subtracting the results from step 9 from those calculated from step 8.

Table 3. Calculated Estimates of the Masses of Trace Elements Associated With Enriched Sediments in Lake Coeur d'Alene

Element	Total Mass in Enriched Zone (tonnes)	Mass in Enriched Zone Per km ² (tonnes)	Mass if Sediment Contained Background Concentrations (tonnes)	Excess Due to Presence of Enriched Sediments (tonnes)
Ag	1,350	13	<38	>1312
Cu	10,000	99	2,600	7,400
Pb	470,000	4,350	1,700	468,000
Zn	240,000	2,900	9,600	230,000
Cd	3,300	31	16	3,284
Hg	265	2.4	5.3	260
As	12,000	111	495	11,500
Sb	4,650	43	53	4,600

Total Area of Lake (km²): 127.8

Area of Lake Containing Enriched Sediments (km²): 108.2

Percent of Lake Containing Enriched Sediments (%): 85

Weighted Average Thickness of Enriched Sediments in Enriched Zone Per km²:(cm): 35

Mass of Enriched Sediments (Gt): 75.2

The calculated estimates based on the foregoing steps and assumptions indicate that there are about 75 million metric tons of trace element-rich sediments currently blanketing about 85% of the bed of Lake CDA (Table 3). The masses of excess trace elements range from about 260 metric tons for Hg to more than 468,000 metric tons for Pb (Table 3). With the exception of Cu, the background masses of the other trace elements are essentially inconsequential relative to the enriched masses. The background trace element masses typically represent <2% of the estimated masses of enriched trace elements (Table 3). If the trace element-rich sediments were evenly distributed throughout the area of the lake which currently contains this type of material, they would represent a layer approximately 35cm thick.

The estimated mass of trace element-rich sediments, as well as the estimated masses of excess trace elements are a function of the assumptions used in calculating them. If the assumed sediment density was too low, then the calculated masses would increase (e.g., a density of 2.65g/cm³ would increase the estimate of trace element-rich sediments from 75 to 100 million metric tons). Alternatively, if the thicknesses of the trace element-rich sediments determined from each core were not representative of the entire zone within which it was located, then the estimates could increase or decrease. However, seismic reflection surveys indicate that sediment layering and thicknesses are quite uniform over the entire lakebed; thinning only appears to occur very close to the shoreline. Further, errors in the estimates for the median chemical concentrations in core 6, and the thickness of the trace element-rich section of core 7 could increase or decrease the calculated sediment and trace element masses. Regardless of these potential sources of error, alternative calculations indicate that the mass of trace element-rich sediments still is likely to be on the order of millions of metric tons.

Trace element interrelations

The enriched trace elements associated with the surface sediments display strong positive interrelations among themselves and with Fe and either a slightly negative or no correlation with Ti and TOC (Horowitz, et al., 1993). The strong correlations between and among the enriched trace elements, and the trace elements with Fe, most likely indicate a similar source {the major minerals found in the CDA mining district [galena (Pb), sphalerite (Zn, Fe), tetrahedrite (Cu, Sb, Ag, Hg), pyrite (Fe) and pyrrhotite (Fe)]} or a similar concentrating mechanism (association with Fe oxides).

Calculated correlation coefficients for the trace element-rich subsurface sediments strongly correspond to those found for the surface sediments. The similarity in the occurrence and strength of the various correlation coefficients for the surface and subsurface sediments is striking and would imply that the same sources and/or concentrating mechanisms were active throughout the period of deposition of the trace element-rich sediments in Lake CDA (Table 4). Two major differences in the calculated correlation coefficients for the trace element-rich surface and subsurface (banded zone) sediments are the much stronger correlations between the enriched trace elements and Mn, and between Mn and Fe, for the latter group (Table 4). This difference may be ascribed to reducing conditions in the sediment column that caused a certain amount of 'geochemical smearing' caused by post-depositional solution, remobilization, and reprecipitation (when the diffusing pore fluids reached an oxidized zone) of the Fe oxide-associated trace elements and accompanying Mn oxides. After remobilization, the Fe and Mn may have reprecipitated in the same physical phase (Fe/Mn oxyhydroxides), as separate phases in the same physical location, or the Mn on existing Fe sulfide minerals unaffected by the redox potential in the sediment column.

Table 4. Correlation coefficients* for the enriched elements (surface sediments/subsurface sediments), and some major elements, using log-transformed normalized (X/Ti/TOC) data (see Horowitz, et al, 1993)

	Ag	Cu	Pb	Zn	Cd	Hg	As	Sb	Fe	Mn	Al
Ag	1.00/1.00										
Cu	.94/.94	1.00/1.00									
Pb	.96/.94	.92/.89	1.00/1.00								
Zn	.85/.86	.96/.86	.86/.84	1.00/1.00							
Cd	.69/.68	.85/.72	.69/.65	.91/.86	1.00/1.00						
Hg	.95/.85	.93/.87	.92/.78	.88/.86	.77/.82	1.00/1.00					
As	.68/.46	.61/.54	.65/.33	.51/.52	.45/.59	.64/.72	1.00/1.00				
Sb	.95/.90	.92/.91	.96/.82	.88/.80	.72/.73	.96/.89	.60/.63	1.00/1.00			
Fe	.90/.78	.91/.84	.86/.68	.84/.75	.65/.63	.83/.84	.61/.81	.85/.79	1.00/1.00		
Mn	.60/.73	.56/.80	.56/.63	.48/.73	.43/.70	.57/.81	.76/.80	.53/.78	.64/.88	1.00/1.00	
Al	.68/.32	.87/.34	.68/.33	.90/.38	.89/.31	.69/.21	.44/.04	.68/.19	.72/.29	.39/.16	1.00/1.00

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

The strong trace element interrelations for all the enriched surface and subsurface sediments, treated as a group, differentiate them from the normal (background) surface and subsurface sediments, treated as a group (Fig. 4). In the vast majority of cases, the strong interelement correlations (>0.70) observed for the trace elements associated with the enriched sediments do not exist for the normal/background sediments (Fig. 4a). In the few cases when strong correlations appear for both groups (e.g., Pb and Zn, As and Mn), typically, the slopes are different (Fig. 4b). Further, although the enriched sediments all display very strong correlations with Fe, the background group either does not, or, when strong correlations do occur, the slopes differ from the enriched group (Fig. 4c). As with the surface sediments, this is probably indicative of a similar source (mining and ore-processing related discharges) or a similar concentrating mechanism (association with Fe oxides). One strong correlation (0.90) appears for the background group which did not appear for the enriched group, Fe with Al (Fig. 4d). This is probably the result of detrital, lattice-held Fe and Al, eroded from the local rocks and soil.

Trace element partitioning

Phase associations for the trace element-rich surface sediments were determined using heavy mineral separations and partial chemical extractions, with subsequent chemical analyses of the fractions or extracts. A limited number of heavy/light fractions also were examined by SEM/EDAX. These studies indicate that the majority of the enriched Pb, Cd, Zn, As, and Cu are associated with an operationally defined Fe oxide phase, the Ag could be associated with either Fe oxides or sulfides, whereas the Sb is predominantly associated with a refractory phase (Horowitz, et al., 1993). Heavy mineral concentrations and associated trace element contributions are limited. The highest concentration of heavy minerals (11%) is within the CDA River delta; this decreases rapidly to $<1\%$ within 2km of the delta. Heavy mineral-associated trace element contributions are equal to or less than the percentages of the heavy minerals themselves (Horowitz, et al., 1993).

Similar procedures were used to evaluate the phase associations for the trace element-rich subsurface sediments. However, partial chemical extractions were omitted because there were indications during core thawing and sampling (e.g., the precipitation of reduced Fe as Fe oxide), that at least some of the original sediment-trace element phase associations were altered. As data were already available on the surface sediments, emphasis was placed on evaluating the phase associations of the sediment-associated trace element maxima near the bases of the banded zones.

With the exception of the samples from core 123, the heavy mineral concentrations and associated trace element contributions in the subsurface samples were extremely limited, and similar to the results obtained for the surface sediment samples (generally $<1\%$, Table 5, Fig. 5, Horowitz, et al., 1993). Because these samples contain substantial quantities of sediment from the layers above and below the maxima, these results may not accurately reflect the phase associations of the specific layer(s) containing the trace element maxima.

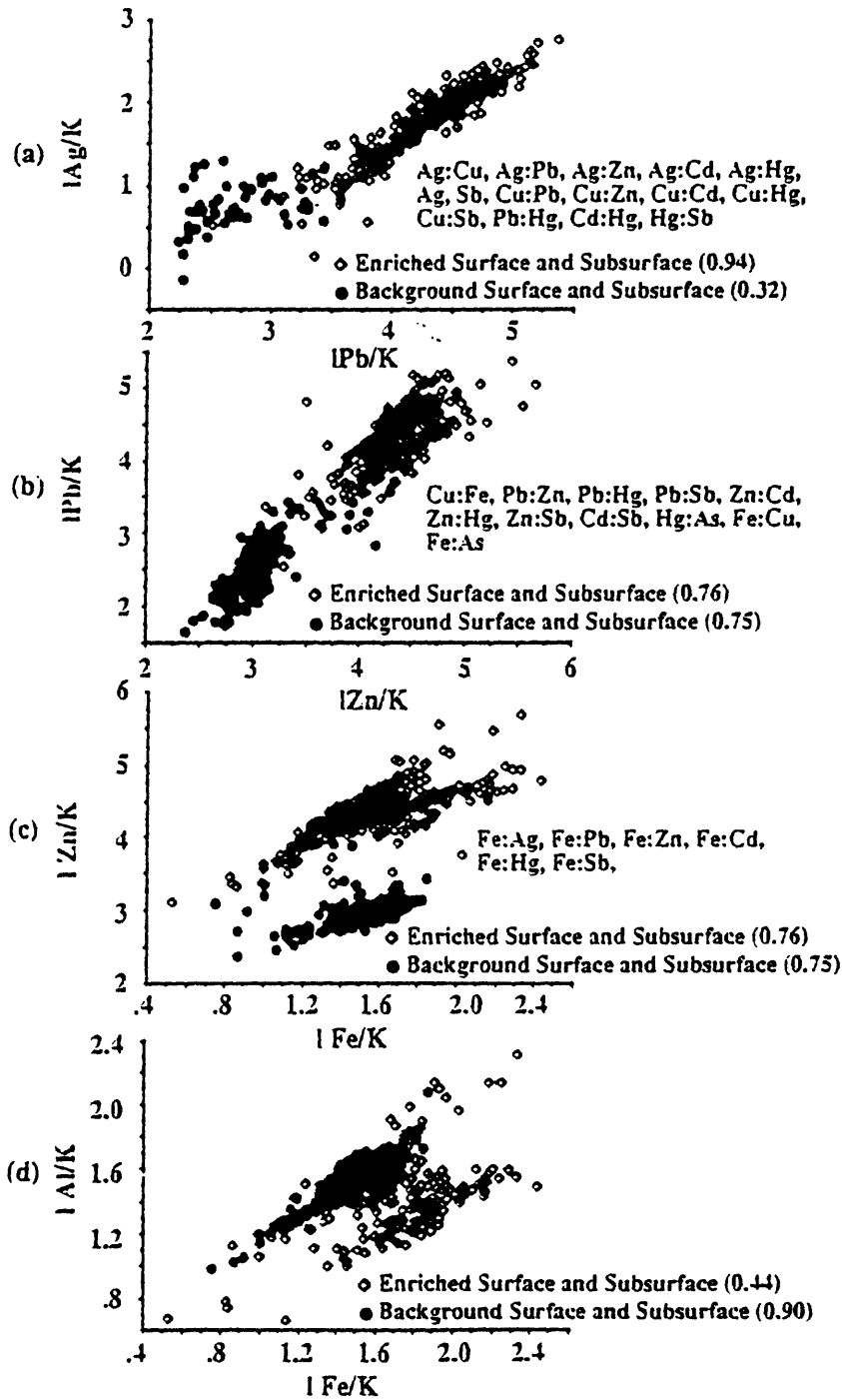


Figure 4. Selected plots of correlation coefficients comparing trace element-rich surface and subsurface samples with those for surface and subsurface background samples. The coefficients were calculated after normalization to Ti/TOC and log transformation (see Horowitz, et al., 1993). The element pairs listed adjacent to each graph display similar patterns to those shown in the graph: a) strong correlation coefficients for the enriched sediments which do not occur for background sediments, b) strong correlation coefficients for both enriched and background sediments where the slope for each set are different, c) strong correlation coefficients for the enriched sediment-associated trace elements and Fe which differentiate them from background sediments, and d) a graph of the correlation coefficients for Fe and Al which differentiate the trace element-rich surface and subsurface samples with those for surface and subsurface background samples.

The subsamples from core 123 are the only ones that contain large detectable quantities of heavy minerals (21-48%, Table 5, Fig. 5). The heavy mineral percentages for all three subsamples are markedly higher than for the other core samples, as are the heavy mineral-associated trace element contributions (Table 5, Fig. 5). The high percentage of heavy minerals could be caused by the proximity of the core 123 site (just outside the delta area) to the CDA River, which is a point source for this material. However, the heavy mineral and heavy mineral-associated trace element contribution percentages are all higher than the highest heavy mineral percentage (~11%) found in a surface sample from the CDA River delta (Horowitz, et al., 1993). The largest percentage (48%, Table 5, Fig. 5) of heavy minerals is associated with the layer containing the trace element maxima for this core. The trace element contributions attributable to the heavy fractions are all much higher than the fractions represent in the original samples. This is markedly different from the results from the other cores and from the surface sediments. These differences may be related to changes in the chemical or mineralogical composition of discharged mining and mining-related material over time.

Subsequent SEM/EDAX examination of some of the heavy fractions indicated the presence of a suite of heavy minerals, including sulfides, typical of the region and essentially the same as those found in the heavy fractions of the surface sediments (Horowitz, et al., 1993). Galena, sphalerite, Ti oxides, tetrahedrite, monazite, arsenopyrite, chalcopyrite and various Fe oxides were identified from the EDAX analyses. These results could indicate that the trace element maxima near the base of the banded zones are the result of the discharge of inefficiently processed ore material generated prior to the inception of more efficient milling procedures. The latter procedures retained higher percentages of the ore minerals entrained in the circuit feeding the flotation cells; thus, smaller quantities of heavy minerals were discharged as tailings. The similarity in the heavy fraction mineralogy in both the surface and subsurface samples imply that the sources or concentrating mechanisms for the trace element-rich sediments were the same throughout the course of their deposition in Lake CDA. Finally, as with the surface sediments, the mean grain sizes of the heavy minerals decreased with distance from the mouth of the CDA River. This further supports the view that the river is acting as a point source for the heavy minerals and that their current locations likely are the result of physical remobilization (by currents or wind-driven waves) within the lake.

Sediment-geochemical history of Lake CDA

One of the major reasons for obtaining cores in Lake CDA was to try to reconstruct the recent geochemical history of the lake from just before the inception of upstream mining and ore-processing activities through to the present (a period of about 110 years). This effort was concentrated on core 123 because of: a) the overall thickness of its banded trace element-rich section (~119cm), b) the thickness and number of its readily discernible individual layers (80), c) the presence of a datable (1980) Mt. St. Helens' ash layer (20.5-21.5cm) and d) the occurrence of background trace element levels at its base, below the banded zone (119-126cm). Three separate approaches were used to estimate the age of the base of the trace element-rich zone in the core.

An initial estimate of the age of the base of the trace element-rich zone was made by considering the 1990 date the core was obtained, the position and age of the 1980 Mt. St. Helens' ash layer, and the 10 layers between them. These factors may indicate that the layers are analogous to annual varves along river banks, and that each layer represents annual deposition. If that is the case, and there are 80 layers between the top of the core and the base of the trace element-rich zone, then deposition of trace element-rich sediments began around 1910.

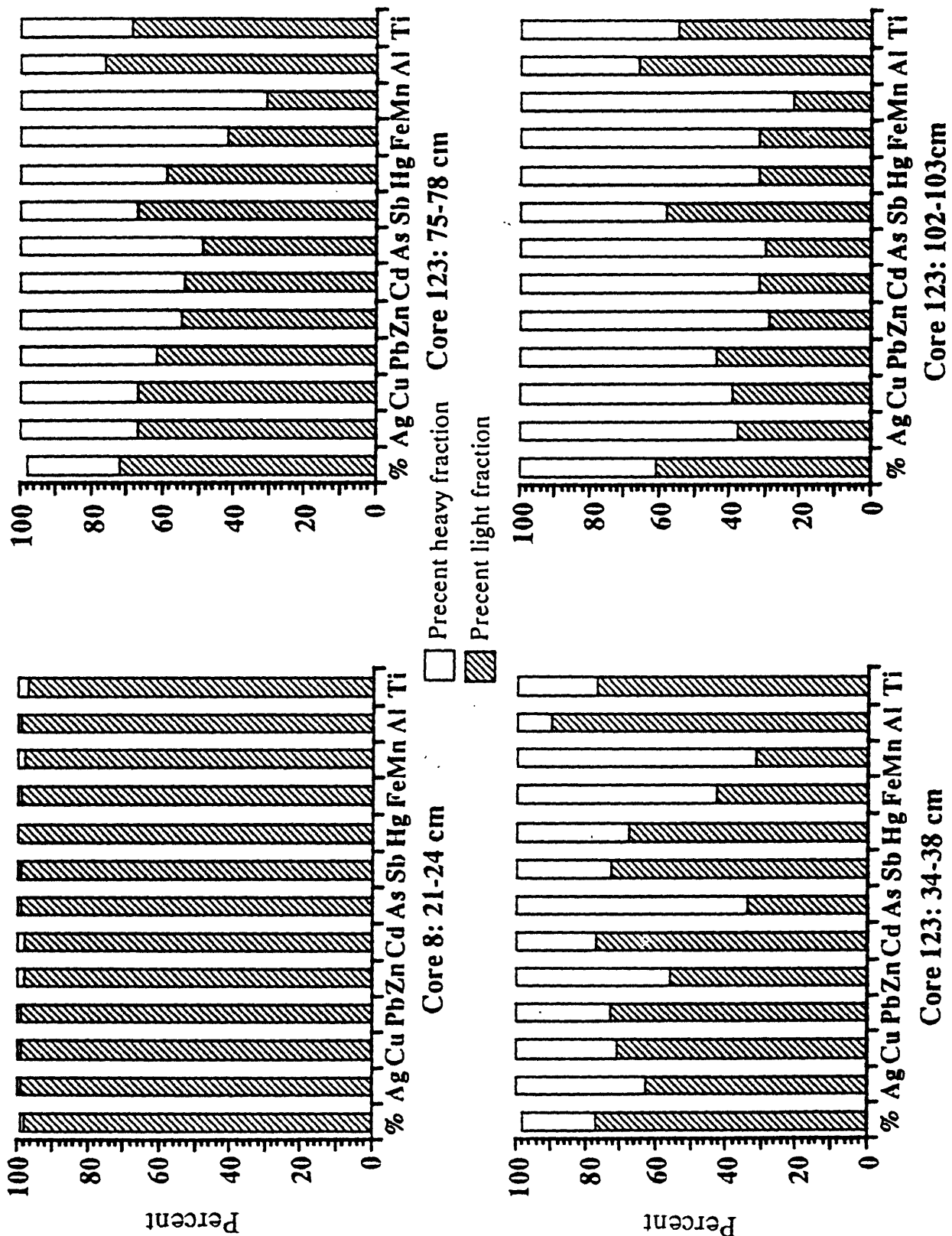


Figure 5. Graphical representation of the trace element contributions (in percent) from the heavy and light fractions from selected core samples from Lake Coeur d'Alene. The first column, labeled '%', indicates the percentage each fraction represents in the sample. The results for the core 8 sample are similar to those for samples from cores 9, 39, 47, and 93, as well as for similarly treated surface sediments (see Horowitz, et al., 1993).

Table 5. Heavy/light mineral fraction geochemistry of selected subsurface sediment samples from Lake Coeur d'Alene

Sample	% of Sample	Ag ppm	Cu ppm	Pb ppm	Zn ppm	Cd ppm	As ppm	Sb ppm	Hg ppm	Fe wt. %	Mn wt. %	Al wt. %	Ti wt. %
Core 8: 21-24cm+													
Bulk		29	220	12,000	5,800	36	41	63	3.8	7.2	0.50	8.5	0.32
Light Fraction	98	26	210	10,000	5,000	35	41	68	4.0	6.8	0.45	8.5	0.3
Heavy Fraction	1	37	300	14,000	8,000	64	60	90	N/D	14.1	0.95	6.5	1.2
Light Contribution		26	206	9,800	4,900	34	40	67	3.9	6.7	0.44	8.3	0.29
Heavy Contribution		0.4	3	140	80	0.6	0.6	0.9	N/D	0.1	0.01	0.1	0.01
Calculated Conc.		26	213	10,000	5,000	35	41	68	3.9	6.8	0.45	8.4	0.3
Core 9: 25-30cm+													
Bulk		23	179	7,900	3,200	29	37	67	2.9	7.5	0.43	8.8	0.45
Light Fraction	98	22	173	8,200	3,500	29	31	62	2.7	7.2	0.40	9.0	0.40
Heavy Fraction	2	14	153	9,900	3,300	30	36	55	2.1	8.6	0.50	8.6	1.7
Light Contribution		22	170	8,000	3,400	31	30	61	2.6	7.1	0.39	8.8	0.39
Heavy Contribution		0.3	4	220	75	0.7	1	1	0.05	0.3	0.01	0.2	0.04
Calculated Conc.		22	174	8,200	3,500	32	31	62	2.6	7.4	0.40	9.0	0.43
Core 47: 18-22cm+													
Bulk		35	220	15,000	5,600	47	35	81	4.5	8.1	0.60	9.4	0.36
Light Fraction	99	31	230	14,000	5,700	45	39	84	4.3	7.8	0.55	9.1	0.32
Heavy Fraction	1	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Light Contribution		31	228	14,000	5,600	45	39	83	4.2	7.7	0.54	9.0	0.32
Heavy Contribution		N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Calculated Conc.		31	228	14,000	5,600	45	39	83	4.2	7.7	0.54	9.0	0.32
Core 93: 20-27cm+													
Bulk		42	240	16,000	7,000	48	53	105	6.0	8.0	0.53	9.6	0.31
Light Fraction	99	42	230	15,000	6,100	48	55	120	6.0	7.5	0.48	9.6	0.28
Heavy Fraction	1	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Light Contribution		42	228	15,000	6,000	48	54	118	5.9	7.4	0.48	9.5	0.28
Heavy Contribution		N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Calculated Conc.		42	228	15,000	6,000	48	54	118	5.9	7.4	0.48	9.5	0.28
Core 123: 34-38cm													
Bulk		16	145	4,100	4,600	74	530	84	7.9	11.7	1.00	6.1	0.18
Light Fraction	77	13	125	3,800	2,900	75	210	80	7.0	6.4	0.37	5.9	0.17
Heavy Fraction	21	28	190	5,000	8,000	80	1,500	110	12.0	31	2.90	2.2	0.2
Light Contribution		10	96	2,900	2,200	58	162	62	5.4	4.9	0.29	4.5	0.13
Heavy Contribution		6	40	1,100	1,700	17	320	23	2.5	6.5	0.61	0.5	0.04
Calculated Conc.		16	136	4,000	3,900	75	482	85	7.9	11.4	0.90	5.0	0.17
Core 123: 75-78cm													
Bulk		16	145	8,000	5,000	30	95	70	3.9	10.5	0.97	5.7	0.15
Light Fraction	72	16	145	6,000	3,000	19	70	55	3.2	5.9	0.40	5.8	0.13
Heavy Fraction	26	24	195	10,000	7,000	46	200	95	6.0	22.7	2.50	5.0	0.18
Light Contribution		12	104	4,300	2,200	14	50	50	2.3	4.3	0.29	4.2	0.09
Heavy Contribution		6	51	2,600	1,800	12	52	25	1.6	5.9	0.65	1.3	0.05
Calculated Conc.		18	155	6,900	4,000	26	102	75	3.9	10.2	0.94	5.5	0.13
Core 123: 102-103cm													
Bulk		63	445	20,000	13,000	103	78	210	10.4	9.5	0.80	6.8	0.20
Light Fraction	52	41	270	15,000	6,200	46	40	170	6.0	5.5	0.31	7.3	0.18
Heavy Fraction	48	105	660	30,000	24,000	150	145	195	20.0	18.2	1.75	5.8	0.24
Light Contribution		25	165	9,200	3,800	28	24	104	3.7	3.4	0.19	4.5	0.11
Heavy Contribution		41	260	11,700	9,400	59	57	76	7.8	7.1	0.68	2.3	0.09
Calculated Conc.		66	425	20,900	13,200	87	81	180	11.5	10.5	0.87	6.8	0.2

N/D - not determined, insufficient sample

+ - Similar results also were obtained from cores 39: 7.0-13.5cm and from similarly treated surface sediments (see Horowitz, et al., 1993).

A trial to test the feasibility of obtaining absolute ages for the upper portion of the core entailed determining the ^{137}Cs activity in 4 samples. The samples were selected on the assumption that each layer represented annual deposition. Therefore, counting backward from the Mt. St. Helens' ash layer, samples representing deposition from 1979-80 (21.5-24.5cm), 1963-64 (48.0-50.0cm), 1957-58 (56.0-59.0), and 1945-46 (78.5-81.0) were evaluated for ^{137}Cs activity. The activities determined for these samples are consistent with the assigned ages and indicate that each layer could represent annual deposition.

After the trial, ^{137}Cs activity was determined for all the sampled layers in core 123. Often, the resolution of a ^{137}Cs profile is only sufficient to interpret a broad single activity maximum. However, the distribution of ^{137}Cs in core 123 (Fig. 6, upper graph) has several features that were used to develop a sediment chronology. The graph shows a strong maximum at about 45cm and a secondary peak at 55cm. No ^{137}Cs was detected below 60cm, nor in the ash layer between 20.5-21.5cm. These features are consistent with the assignment of dates of 1963-1964 for the maximum, and 1958-1959 for the earlier secondary peak. The onset of measurable fallout and sedimentary ^{137}Cs activity occurs around 1954. The assignment of these dates [plus the dated ash layer (1980)], leads to an age-depth model that follows the following equation:

$$z = (w_0/B) [1 - e^{-Bt}]$$

where w_0 is the linear rate at the surface (cm yr^{-1}) and B describes the degree of nonlinearity which is principally due to compaction effects. Weighted least-squares values of w_0 and B are $2.06 \pm 0.02 \text{ cm yr}^{-1}$ and $0.0133 \pm 0.006 \text{ yr}^{-1}$ respectively. Assignment of ages to each depth interval using this equation permits replotting the ^{137}Cs activity (dashed line) against model year, along with the annually averaged atmospheric fallout rate (solid line) which is arbitrarily normalized to the peak value (Fig. 6, lower graph). The plotted atmospheric fallout rate is a representation of the well-developed loading function for the Great Lakes region, Lake Superior in particular (Robbins, 1985). Model application produces a predicted age of 1895 for the base of the banded (trace element-rich) zone, albeit the confidence limits for this date are large.

A notable difference between the core 123 profile and the idealized loading function is the higher ^{137}Cs activity during the 1958-1959 period. This variance could be caused by local differences in atmospheric loading, or in-lake transport and deposition processes. Alternatively, the markedly higher ^{137}Cs activities in post-1970 sediments are probably not due to regional differences, and may have resulted from a combination of postdepositional redistribution processes and contributions from long-term ^{137}Cs transport within the lake (e.g., focusing), as well as from ^{137}Cs stored in the catchment. The post-1970 ^{137}Cs activity follows an exponential decay curve with about a 10 year time constant.

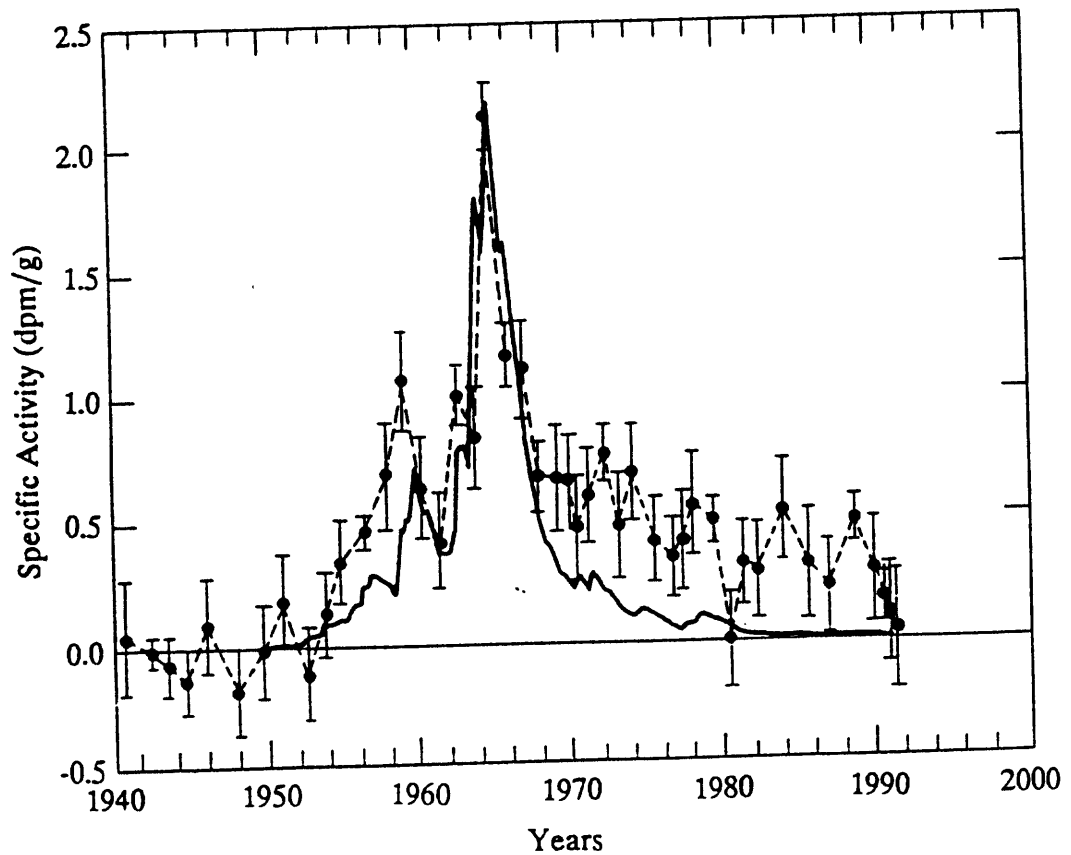
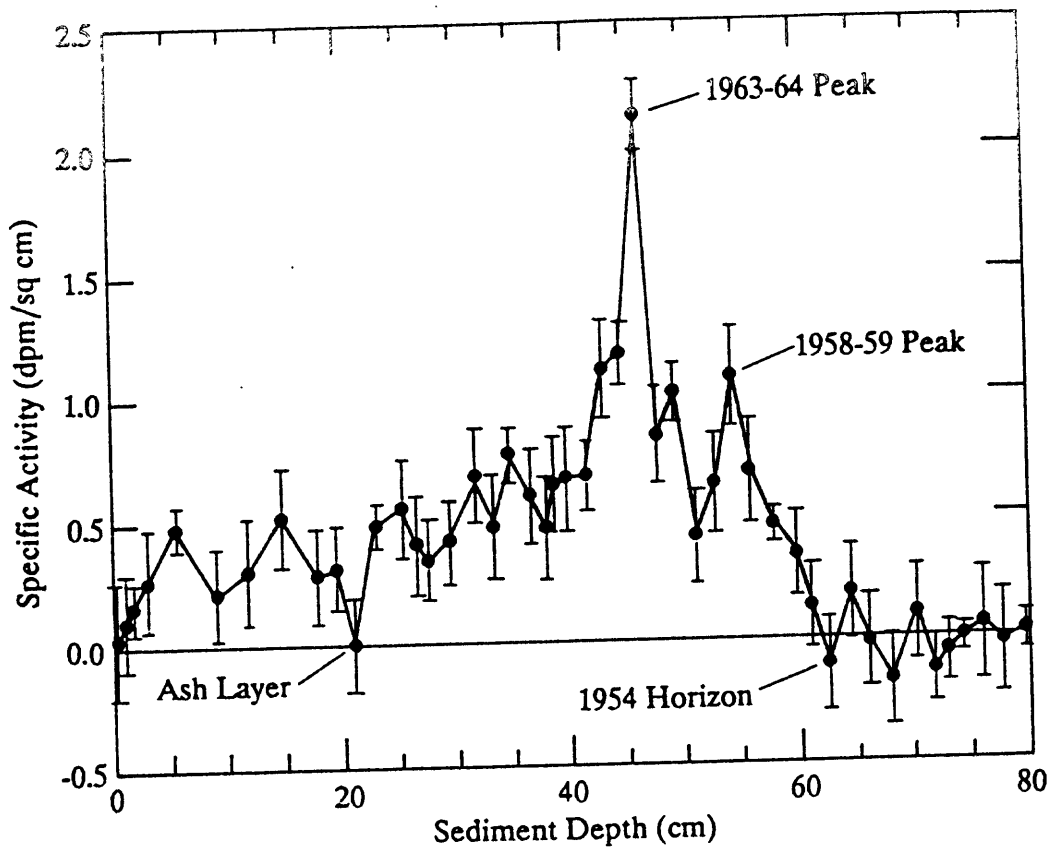


Figure 6. The upper graph is a plot of ^{137}Cs activity (dpm cm^{-2}) against sediment depth (cm). The lower graph is a recast of the upper plot and displays ^{137}Cs activity (dpm g^{-1}) against age (dashed line). The solid line is a plot of the well-developed loading function for the Great Lakes region (Robbins, 1985).

By combining a) the date of collection for the core (1990), b) with the date for the ash layer (1980), and c) with the three dates estimated from the ^{137}Cs activity (1965, 1959, and 1954) it is possible to estimate average sedimentation rates for the core site. Without considering the effects of compaction, and assuming constant deposition between the dated points, the average annual rates are as follows: 2.1cm/ year (1980-1990), 1.7cm/ year (1965-1980), 1.3cm/year (1959-1965) and 1.4cm/year (1954-1959). These results indicate that sedimentation reached a constant of 1.3-1.4cm/year for material deposited prior to 1965. The general decrease in sedimentation rates with increasing depth in the core could be the result of compaction, rather than actual changes in sedimentation rates over time; a view supported by the general decrease in moisture content with increasing depth. The depth of the 1954 layer is 61.0cm, the depth of the base of the trace element-rich zone is 119.0cm; thus, the thickness of the undated portion of the trace element-rich zone is 58 cm. If the sedimentation rate for this section of the core is assumed to be 1.35 cm/year, then the undated section represents a period of 43 years and the age for the start of trace element-rich sediment deposition is 1911.

The relative consistency of the three estimated dates (1910, 1895, and 1911) for the base of the trace element-rich banded zone in core 123, using three somewhat different, albeit not completely independent approaches, is encouraging. Certainly, the three estimated dates are consistent with the 1880-1890 period assigned for the onset of mining and ore-processing activities in the CDA mining district (e.g., Bender, 1991). However, final confirmation of the age of the base of the trace element-rich zone requires the use of another radioisotope, probably ^{210}Pb .

CONCLUSIONS

Substantial portions of the subsurface sediments blanketing 85% of the bed of Lake CDA are enriched in Ag, As, Cd, Cu, Hg, Pb, Sb and Zn. The thickness of the enriched sediments ranges from 17cm to more than 119cm; the thickness of these deposits increase with proximity to the mouth of the CDA River. The CDA River seems to be the source for the majority of the trace element-rich sediments in the lake. The similarity in the locations of the trace element-rich surface and subsurface sediments, the trace element concentrations, the correlations between and among the trace elements, and the trace element partitioning, suggest that the sources and concentrating mechanisms causing the trace element enrichment in the lake probably have been much the same throughout the last 100-110 years. An estimated 75 million metric tons of trace element-rich bed sediments have been deposited in Lake CDA. Estimates of enriched trace element masses (masses above calculated background levels) range from 468,000 metric tons for Pb to 260 metric tons for Hg. Core sections containing elevated sediment-associated trace element concentrations do not contain any structures indicative of benthic invertebrate activity, whereas such structures were identified in core sections containing background trace element concentrations. Most of the subsurface enriched trace elements are not associated with sulfide minerals; they probably are associated, like their surface sediment counterparts, with an operationally defined Fe oxide phase. Based on the presence of a Mt. St. Helens' ash layer, three dates based on ^{137}Cs activity, the presence of 80 discernible layers, and calculated sedimentation rates for a core from the CDA River delta, the age of the onset of trace element enrichment in the lake probably falls between 1895 and 1910. These dates are consistent with the onset of mining and ore-processing in the CDA mining district, and these activities probably represent the major source for the extreme trace element enrichments in the sediments of Lake CDA.

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