THE NATURE OF HEAVY METAL CONTAMINATION IN ORGANIC LAKE SEDIMENTS NEAR THE BUCHANS MASSIVE SULPHIDE BASE METAL MINES, CENTRAL NEWFOUNDLAND

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The Nature of Heavy Metal Contamination
in Organic Lake Sediments Near the
Buchans Massive Sulphide
Base Metal Mines,
Central Newfoundland

By

Peter G. Haring

A Thesis
Submitted in Partial Fulfilment of the Requirements
for the Degree of
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April, 2002

Dedicated to my father, Ludwig

"Until we meet again,

you will always be

close in my heart"

Abstract

The Buchans mine closed in 1984 after 57 years of operation. Several orebodies, including Lucky Strike, Oriental, Old Buchans, Rothermere and MacLean, produced 16,196,876 tonnes of ore with an average grade of 14.51% Zn, 7.56% Pb, 1.33% Cu, 126 grams/tonne Ag and 1.37 grams/tonne Au. Copper (chalcopyrite), lead (galena) and Zinc (sphalerite) concentrates were shipped from the port of Botwood. The baritic, polymetallic orebodies were Canada's highest grade volcanogenic massive sulphide deposits.

To determine the impact that mining activities in and around the Buchans community had on the watersheds of the area, six lake sediment cores were collected. Four of these were taken in Red Indian Lake and two were taken in Buchans Lake, also named Sandy Lake. All cores were extracted with a K.B. Gravity Lake Sediment Corer and due to the water depth in Red Indian Lake, a Deep Water Operating Kit had to be used as an attachment.

To determine the availability of the heavy metals to the environment that might be caused by subtle changes of pH or Eh, this study utilized a four step sequential extraction procedure. The four discrete operationally defined fractions that were measured were as follows: (I) Exchangeable/Carbonate, (II) Fe/Mn

Oxide, (III) Organic/Sulphide, and (IV) Silicate.

Each core was sectioned into two centimetre intervals and total concentrations were measured on 29 elements, including Cu, Pb and Zn, on all dry sediment intervals by inductively coupled plasma - optical emission spectroscopy (ICP-OES) using HCl/HF/HClO$_4$ digestion. Furthermore, select base metals (Cu, Pb and Zn) were analysed on the 'wet' and 'dry' samples extracted from lake sediment core RIL2B using the four step sequential extraction procedure to determine the degree to which the various metals reported to the different phase fractions.

The total element analysis on all cores showed significant enhancement in base metals in the upper sediment intervals, particularly in Red Indian Lake, where the concentrations of copper, lead and zinc were reported as high as 4270 ppm, 2993 ppm and 12,576 ppm, (dry weight) respectively. The results for all duplicate samples showed excellent correlation demonstrating a high degree of reproducibility. The agreement between the results obtained from the standard reference materials (LKSD 1-4) and the 'certified' published results also demonstrated a high degree of reliability.

The sequential extraction analyses on the 'wet' and 'dry' sediment intervals from lake sediment core RIL2B showed that a significant amount of copper, lead and zinc reported to the Exchangeable/Carbonate phase with the highest values measured as 715 ppm, 2070 ppm and 2675 ppm respectively. It was also demonstrated that sediment drying appears to have a significant redistribution effect on the amount of metal reporting to the different phases. Drying of the sediment appears to increase the amount of Cu and slightly decreases the amount of Pb and Zn reporting to the Exchangeable/Carbonate phase. The reproducibility and reliability of the sequential extraction procedure was demonstrated from the analyses of the standard reference ore MP-1A.

In conclusion, the upper lake sediments in Red Indian Lake and Buchans Lake are heavily contaminated with base metals, with the most pronounced effects occurring in Red Indian Lake. Furthermore, as demonstrated from the high concentrations of Cu, Pb and Zn that report to the first phase of the four step sequential extraction procedure, a significant amount of the metals in the lake sediments of Red Indian Lake are potentially available for release to the environment with moderate increases in acidity. The sediments have incorporated a considerable burden of pollutants and a significant portion of the lake sediments from Red Indian Lake could be considered as hazardous waste. However, since the mine closure, the lake sediments appear to be showing reduced levels of pollutants. Proper site remediation is essential for lake sediment recovery.

Acknowledgements

The writer is grateful and indebted to many people without whose help this study would not be possible.

The writer is especially grateful to Dr. Peter Davenport who suggested the project and provided supervision and guidance along the way. Furthermore, special thanks are extended to the Department of Mines and Energy for providing financial support to this project from start to finish. This financial support included supplying necessary equipment such as corers, absorbing the cost of all field work including accommodations, as well as the use of their laboratory facilities on Higgins's Line for sample preparation and analysis.

Furthermore, special thanks are extended to the Department of Environment for the use of their coring equipment as well as the use of staff personnel in helping with coring of the lakes. Craig Cummings and Al Thompson of the Department of Environment were especially helpful during the lake sediment coring process.

All sample coring, sample preparation and sample analyses were conducted by the writer.

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Chapter 1

1.1 Introduction

The study area (Fig 1.1) is located near the town of Buchans deep in the interior of the island portion of Newfoundland near a river first called Sandy River and later renamed Buchans River. Buchans Lake discharges into Red Indian Lake via Buchans River. Red Indian Lake is a large, deep lake that discharges to the sea via the Exploits River. It is accessible by paved road (Route 370) which connects to the Trans-Canada Highway near the community of Badger.

The Buchans area is characterized by gently rolling boggy lowlands, low rounded peaks and ridges, and numerous ponds. Vegetation varies from near tundra at higher levels to heavy spruce forest in protected areas. Outcrop is generally limited to topographic highs and to river channels.

1.2 History of Mining

Base metal sulphides had first been discovered on the shores of Buchans River in 1905 by a Micmac Indian named Matty Mitchell. Matty carried out seasonal prospecting for the Anglo-Newfoundland Development Company Limited between the years 1904-1906. It is said that at the end of the 1906 season, he was paid a bonus of $2.50, the equivalent of a barrel of flour, for

Figure 1.1 Map of Newfoundland indicating the 'Study Area'

his discovery of the Buchans River deposit in 1905 (Neary, 1981).

The original discovery was made on Anglo-Newfoundland Development Company Limited leasehold land. The A.N.D. Company (now Price Nfld. Pulp and Paper Limited, a subsidiary of Abitibi- Price Inc.) explored the prospect and developed a small deposit of copper, lead and zinc sulphides. However, metallurgical constraints with the fine grained sulphide aggregate made early attempts at creating a producing mine difficult and the prospect was closed down in 1911.

The American Smelting and Refining Company (ASARCO) first became involved with the deposit in 1916 and by 1925 had developed a successful selective flotation process to treat the lead and zinc ores. It wasn't until 1935 that a process was developed to treat the copper ore. In 1926 ASARCO entered into a 50 year agreement with the A.N.D. Company to put the property into production. Production began in 1928 at a rate of 500 tonnes per day and in 1930 the milling capacity was increased to a rate of 1250 tonnes per day.

The Oriental No. 1 and Lucky Strike Orebodies were discovered by resistivity surveys carried out in 1926 under the supervision of Hans Lundberg which represented the first successful application of geophysics in North America. The Rothermere and MacLean (formerly Rothermere #4) Orebodies were discovered between 1947 and 1950 as a result of intensive drilling under the supervision of H.J. MacLean. E.A. Swanson became chief geologist in 1951 and was credited with the discovery of the Oriental #2 Orebody in 1953. Since then the sub-economic Clementine and Sandfill prospects have been discovered but available tonnages did not warrant production (Neary, 1981). The locations of the major ore deposits that were mined are shown in Figure 1.2. The annual mine production from the individual Buchans mines is shown in Table 1.1.

1.3 Geology

1.3.1 Regional Geology

The Buchans deposits occur in central Newfoundland at the northern extension of the North American Appalachian orogenic belt. The Buchans Group, which contains the Buchans ore deposits, forms part of the Dunnage Zone of central Newfoundland, a deformed volcano-sedimentary terrane which records the opening and subsequent closure of the lower Paleozoic Iapetus Ocean (Williams, 1978; 1979).

The available stratigraphic and geochemical data suggest that the Central Volcanic Belt of Newfoundland is an Ordovician-Silurian island arc complex built upon Cambro-Ordovician oceanic crust. Island arc volcanism occurred in two distinct phases: 1) a Lower to Middle Ordovician (pre-

Figure 1.2 Ore deposits of the Buchans area

Table 1.1 Annual Mine Production - Total and Individual Buchans Mines (Tons), (Neary, 1981, updated by G. Neary)

Year	Total (All Mines)	Lucky Strike	Oriental	Old Buchans	Rothermere	MacLean
1928	33.974	33.974				
1929	163.114	163.114				
1930	188.299	188.299				
1931	311.299	311.299				
1932	438.225	438.225				
1933	439.450	439.450				
1934	442.670	442.670				
1935	448.600	413.905	34.695			
1936	433.000	305.294	127.706			
1937	453.700	305.478	148.222			
1938	459.000	300.358	158.642			
1939	468.669	316.413	152.256			
1940	489.000	330.143	158.857			
1941	451.000	307.066	143.934			
1942	372.000	250.028	121.972			
1943	408.000	259.664	143.291	5.045		
1944	405.500	259.530	143.307	2.663		
1945	391.000	218.744	165.414	6.842		
1946	384.500	198.137	175.557	10.806		
1947	341.000	170.691	152.669	17.640		
1948	319.000	163.206	137.009	18.785		
1949	334.000	187.467	127.006	19.527		
1950	328.000	167.351	135.202	21.568	3.879	
1951	324.000	165.785	113.592	15.627	28.996	
1952	334.000	148.912	99.897	25.092	60.099	
1953	346.000	127.949	81.013	38.644	98.394	
1954	340.000	70.118	76.932	31.173	161.777	
1955	291.000	38.229	67.818	141	184.812	
1956	366.000	17.994	101.433		246.573	
1957	371.000	16.095	115.516		239.389	
1958	389.000	1.945	102.966		284.089	
1959	359.000		106.111		252.006	883
1960	386.000		105.721		279.958	321
1961	387.000		101.703		275.435	9.862
1962	378.000		79.544		200.528	97.928
1963	376.000		17.503		111.346	247.151
1964	383.000		40.875		89.992	252.133
1965	366.000		65.674		83.109	217.217
1966	355.000		49.387		106.630	198.983
1967	378.000		44.198		134.111	199.691

Table 1.1 Annual Mine Production (cont'd) - Total and Individual Buchans Mines (Tons), (Neary, 1981, updated by G. Neary)

Year	Total (All Mines)	Lucky Strike	Oriental	Old Buchans	Rothermere	MacLean
1968	378.000		31.168		137.954	208.878
1969	371.000		36.807		109.898	224.295
1970	359.000				102.271	256.729
1971	173.000				45.012	127.988
1972	291.000	6.752			78.360	205.888
1973	124.000	3.583			27.880	92.537
1974	264.000	20.792			59.123	184.085
1975	232.000	19.772			44.404	167.824
1976	208.000	22.440			35.199	150.361
1977	192.000	20.471		2.716	21.133	147.680
1978	202.000	31.254		866	5.869	164.011
1979	125.000	10.889				114.111
1980	83.000		15.460			64.620
1981	76.000		27.872			48.128
1982						
1983	42.000		4.648			37.352
1984	102.000		5.667			96.333
Tons	17.854.000	6.893.486	3.717.244	217.135	3.508.226	3.514.989
Tonnes	16.196.863	6.253.660	3.372.224	196.981	3.182.607	3.188.742

Caradocian) phase of extensive submarine volcanism recognizable throughout the whole Central Volcanic Belt; and 2) an Upper Ordovician-Silurian (post Caradocian) phase which is characterized by contrasting volcanic regimes in three distinct belts (Kean et al., 1981).

The Buchans Group lies on the western edge of the mixed volcanic-sedimentary terrane of central Newfoundland. Whalen and Currie (1987) include it in the Topsails igneous terrane, based on general similarities to the Glover Formation to the west and intrusions in the Topsail igneous terrane which could have been the source of granitoid clasts in the Buchans Group. The thrust fault between the Hungry Mountain Complex and the Buchans Group which is a major zone of dislocation is also a logical boundary between the dominantly granitic, crystalline terrane of the Topsails to the west and the dominantly volcanic and sedimentary terranes of central Newfoundland to the east.

To the south, the Buchans Group is either in fault contact with, or sits conformably on, the Skidder Basalt. The Skidder Basalt was previously thought to be a part of the Buchans Group (Thurlow and Swanson, 1981) but studies by Pickett and Barbour (1984) and Pickett (1987) indicate that the Skidder Basalt has Ophiolitic affinities and, therefore, should not be classified in the Buchans Group.

To the east, the Buchans Group structurally overlies the Lower to Middle Ordovician Victoria Lake Group in the south and Middle to Upper Ordovician black shale and greywacke in the north, along a presumed high-angle reverse fault (Kean *et al.*, 1981; Thurlow, 1984; Kean and Evans, 1986). This fault brings the Buchans Group in contact with progressively younger rocks to the north (Kean *et al.*, 1981). The generalized geology of the area is illustrated in Figure 1.3.

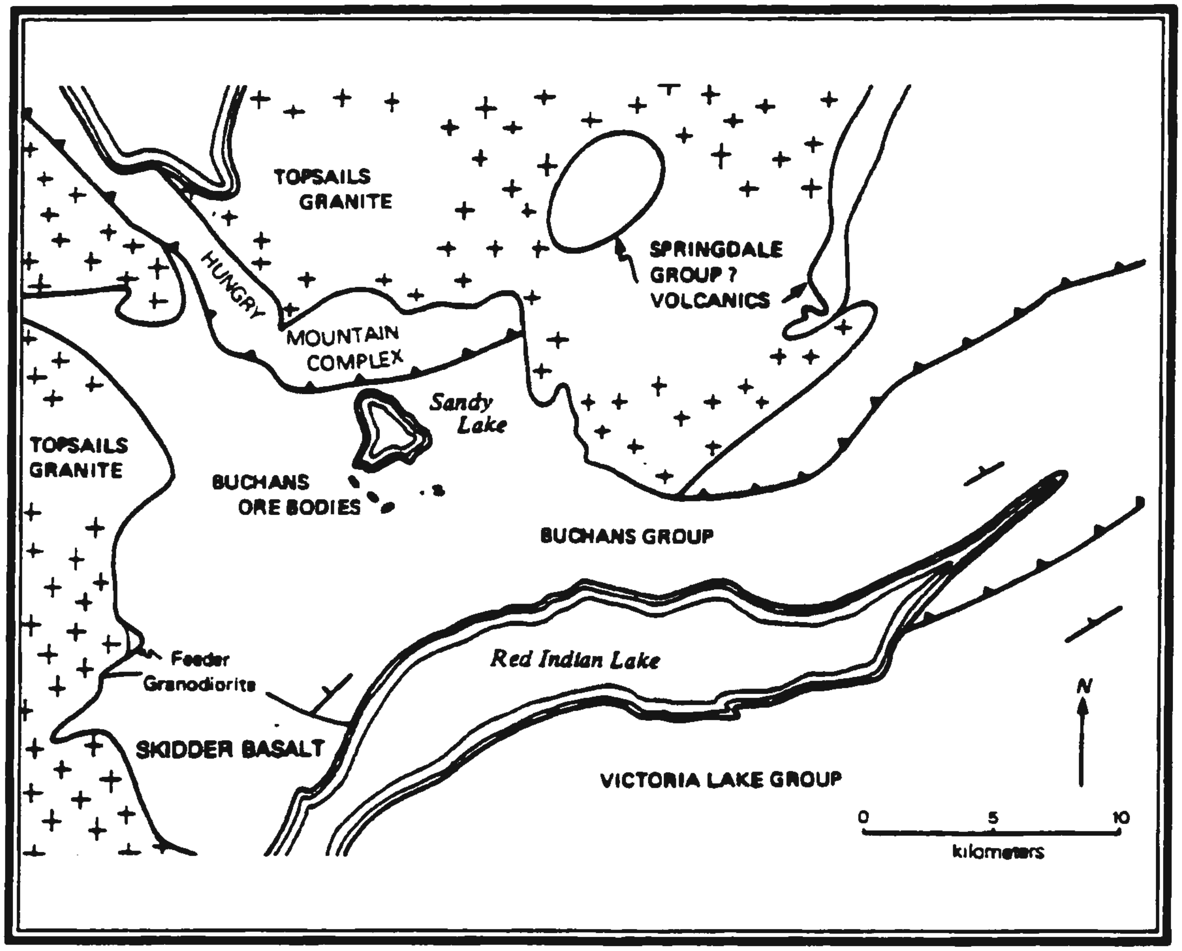

Figure 1.3 General geology of the Buchans area (Thurlow and Swanson, 1987)

1.3.2 The Buchans Group

The Buchans Group can be envisaged as a thrust belt composed of a series of sheets separated by significant thrust faults (Thurlow and Swanson, 1987). A simplified structural-stratigraphic map of the Buchans area is illustrated in Figure 1.4. The stratigraphic sequences of the Buchans group consist of four formations: Sandy Lake Formation; Buchans River Formation; Ski Hill Formation; and, Lundberg Hill Formation. The Buchans orebodies occur as part of the Buchans River Formation within two thrust sheets; the Lucky Strike sheet which hosts the Lucky Strike, Rothermere and MacLean orebodies, and the structurally higher Oriental sheet, which hosts the Oriental orebodies. The Buchans Group lies structurally above the Victoria Lake Group (Kean, 1977) and the ophiolitic Skidder Basalt (Pickett and Barbour, 1984; Pickett, 1987). The upper contact of the Buchans Group is both an intrusive contact against granites of the Silurian Topsails Granite, or a fault contact against structurally overlying plutonic rocks of the Hungry Mountain Complex (Thurlow, 1981; Whelan and Currie, 1987).

The Lundberg Hill Formation occupies a known surface and subsurface area of more than 200 square kilometres and may reach a maximum thickness of approximately 1 km. Within the Oriental block, the dominant lithologies are rhyolitic

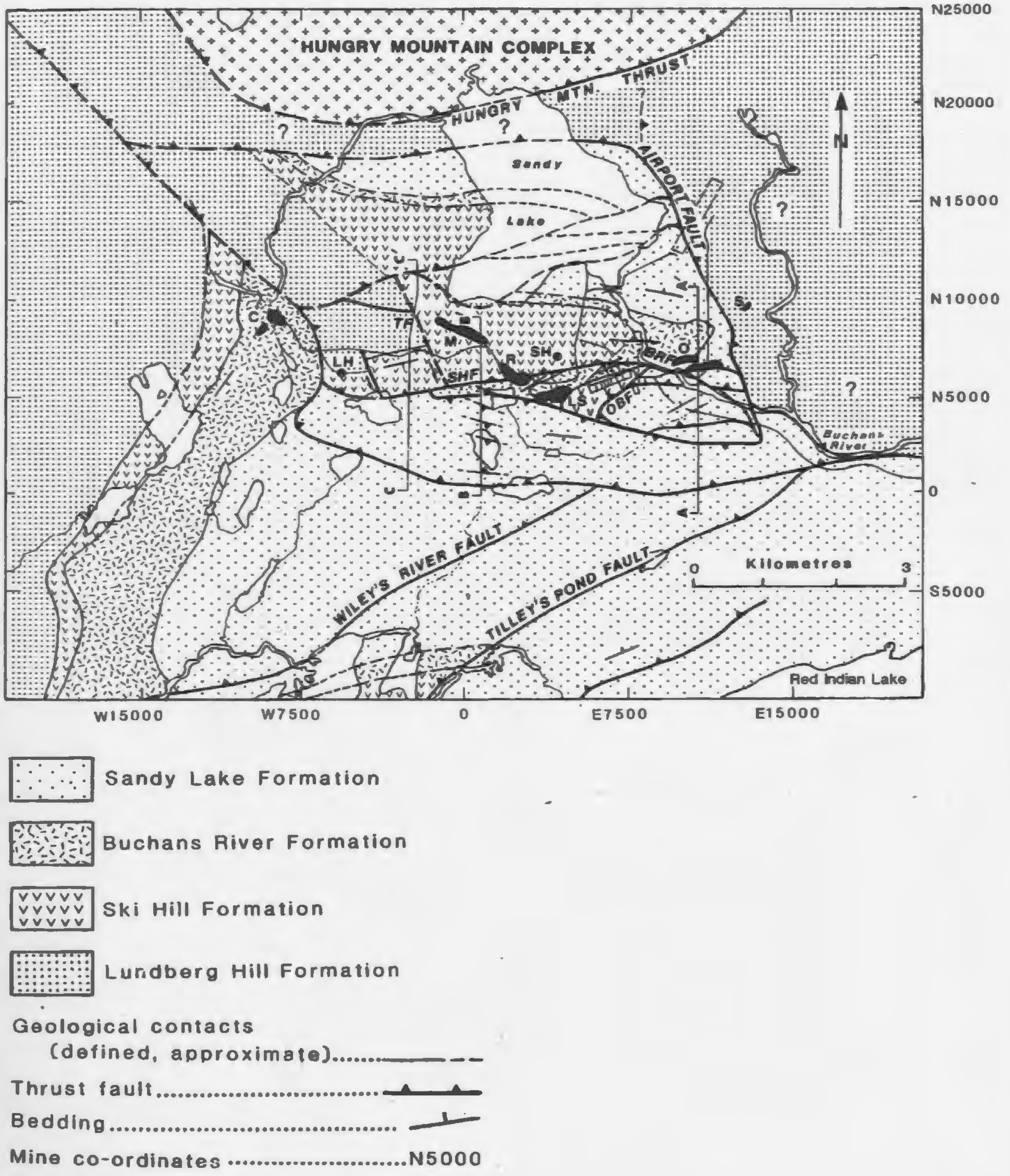

Figure 1.4 Simplified structural-stratigraphic map of the Buchans Group (Thurlow and Swanson, 1987)

pyroclastic rocks which are characterized by prominent 5-10 mm quartz phenocrysts and smaller zoned plagioclase crystals. In other thrust blocks, these felsic pyroclastic rocks are interbedded with subaqueous, dominantly epiclastic, pyroclastic flows which grade upward from a base of polylithic breccia through pumiceous pyroclastic rock into tuffaceous wacke, siltstone and cherty mudstone. Rhyolite bodies containing either large or small quartz phenocrysts, bedded tuffaceous sedimentary rocks with multicoloured mudstone-chert and basaltic pillow lava units locally form important units within the formation.

The Ski Hill Formation consists of a thick pile of black to dark green breccia, pyroclastic rocks and pillow lava of basaltic to andesitic composition. It conformably overlies pyroclastic and tuffaceous sedimentary rocks of the Lundberg Hill Formation. Most flows and fragments in breccias are amygdular and porphyritic with plagioclase and augite phenocrysts. Amygules filled with combinations of calcite, chlorite, prehnite and pumpellyite are typical throughout the Buchans Group but the Ski Hill Formation also contains abundant zones with distinctive elongate quartz-filled amygdules. Hematite is not abundant except near the stratigraphic top of the unit. In the vicinity of the Lucky Strike and Oriental in situ orebodies, a zone of significant hydrothermal alteration obscures the contact between the Ski Hill and Buchans River formations.

The Buchans River Formation hosts all of the major volcanogenic sulphide orebodies of the Buchans Group. In the vicinity of the orebodies, the maximum thickness is in the range of 200 to 400 m. In general, the formation consists of lowermost quartz-poor pumiceous pyroclastic rocks, rhyolite and pyritic siltstone, overlain by quarty-rich rhyolite and crystal-vitric tuff and the transported ore breccias. These are in turn overlain by a thick sequence of felsic tuff with local quartz and feldspar phyric rhyolite. In the vicinity of Lucky Strike and Oriental orebodies, all units below the ore have been silicified, chloritized and sericitized extensively.

The felsic tuff of the Buchans River Formation in the Oriental block is overlain conformably by both hematitic basaltic pillow lava - pillow breccia and by arkosic volcaniclastic conglomerate which form the base of the lithologically complex Sandy Lake Formation. The arkosic conglomerate is matrix supported and mainly contains rounded rhyolite cobbles with 5 to 10 mm quartz phenocrysts identical to those in the Lundberg Hill Formation. Some interbedding near the contact between the two formations is present as one lens of arkose occurs within tuffs of the Buchans River Formation. This lens of arkose, and that of the overlying Sandy Lake Formation evidently were derived from a different source than the volcanic units of the underlying Buchans River Formation (Thurlow and Swanson, 1987).

1.3.3 Ore Deposits

The Buchans ores are high grade polymetallic massive sulphide deposits within the Buchans River Formation (Thurlow and Swanson, 1981). The Lucky Strike Ore Horizon hosts the Lucky Strike, Rothermere and MacLean deposits. The Oriental Ore Horizon hosts the Oriental and Old Buchans deposits.

Within the Buchans orebodies, three genetically related ore types occur; stockwork ore, in situ ore and mechanically transported fragmental ore. Stockwork mineralization consists of sub-economic to low grade networks of veinlet and disseminated base metal sulphides within highly silicified and locally chloritized host rocks. In situ ore lies stratigraphically above stockwork mineralization and consists of thick high grade lenses conformable within the host pyroclastics and breccias. Transported ore consists of low to high grade accumulations of sulphide and barite fragments which were derived from in situ ore, transported by density flows and deposited in paleotopographic depressions. In terms of economic importance, in situ and transported ore are of approximately equal significance and together have accounted for 98% of production. Large tonnages of sub-economic stockwork mineralization are present but only local zones attain ore grade. The distribution of the various ores is shown below in Figure 1.5.

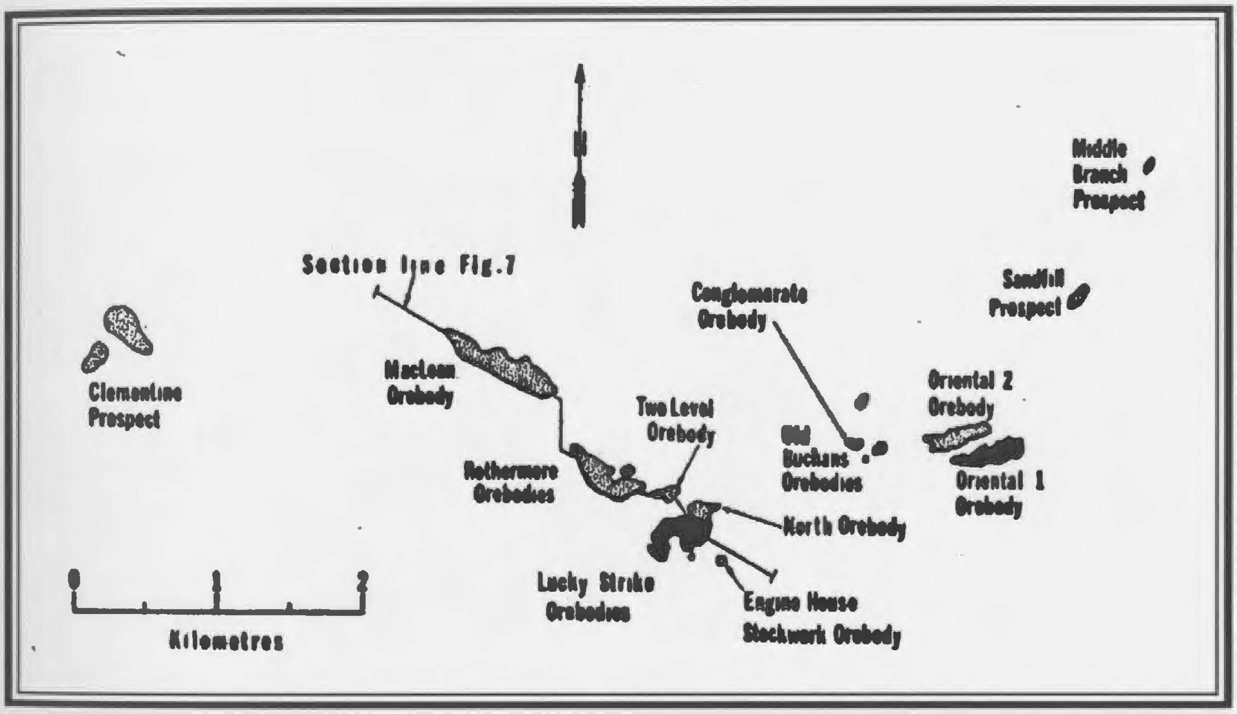

Figure 1.5 Distribution of orebodies at Buchans. In situ ore, solid black; transported ore, stippled

Tonnages, grades and mineral composition percentages of the Buchans ore deposits are listed in Table 1.2. Within the Lucky Strike Ore Horizon, the in situ Lucky Strike orebody was the highest grade and largest unit orebody of the Buchans deposits, with 5,555,485 tonnes mined at an average grade of 1.63% Cu, 8.61% Pb and 18.42% Zn. The transported Lucky Strike-North orebody contained 620,510 tonnes grading 0.46% Cu, 4.54%

Table 1.2 Tonnages, Grades and Mineral Percentages of the Buchans Ore Deposits (Thurlow and Swanson, 1981)

Orebody	Gross Tonnage	Cu[1]	Pb[1]	Zn[1]	Cp[2]	Gn[2]	Sl[2]	Py[2]	Ba[2]
Lucky Strike Ore Horizon									
In Situ Ores									
Lucky Strike Main	4.752.373	1.67	8.42	18.36	4.8	9.7	27.4	14.0	26
Lucky Strike - New Year	803.112	1.40	9.75	18.76	4.0	11.3	28.0	7.4	26
Transported Ores									
Lucky Strike - North	620.510	0.46	4.54	8.20	1.3	5.2	12.2	2.4	55
Two Level	328.596	0.50	4.56	8.02	1.4	5.3	12.0	3.8	55
Rothermere #1	3.402.000	1.15	7.73	12.68	3.3	8.9	18.9	6.0	31
Rothermere #2	195.615	1.44	7.65	13.73	4.2	8.8	20.5	9.5	30
[3]MacLean	3.653.000	1.13	7.46	13.50	3.3	8.6	20.1	6.0	24
Oriental Ore Horizon									
In Situ Ores									
Oriental #1	2.738.664	1.71	8.47	15.80	4.9	9.8	23.6	7.7	24
Old Buchans East	133.353	1.65	7.57	14.27	4.8	8.7	21.2	15.1	24
Old Buchans West	19.907	1.70	10.40	16.80	4.9	12.0	25.0	7.7	24
Transported Ores									
Oriental #2	928.863	0.76	6.20	9.41	2.2	7.2	14.0	4.6	30
Old Buchans Conglomerate	72.763	0.76	5.88	9.47	2.2	6.8	14.1	3.5	31
Total In Situ Ores	**8,447,409**	**1.66**	**8.55**	**17.50**	**4.8**	**9.8**	**26.0**	**14.4**	**25**
Total Transported Ores	**9,201,346**	**1.04**	**7.12**	**12.20**	**3.0**	**8.3**	**18.2**	**7.5**	**30**
Total Gross Tonnage[3]	**17,648,756**	**1.33**	**7.81**	**14.74**	**3.8**	**9.0**	**22.0**	**8.2**	**28**

[1] Percentage grade (Mill Heads)

[2] Percentages of major ore-bearing minerals (Cp-chalcopyrite, Gn-galena, Sl-sphalerite, Py-pyrite and Ba-barite)

[3] Total milled to December 31, 1979 (updated values to mine closure not available)

Pb and 8.20% Zn. The transported Rothermere and MacLean orebodies contained 3,597,615 and 3,653,000 tonnes grading 1.16% Cu, 7.72% Pb and 12.74% Zn and 1.13% Cu, 7.46% Pb and 13.50% Zn, respectively.

Within the Oriental Ore Horizon, the in situ Oriental #1 orebody contained 2,738,664 tonnes grading 1.71% Cu, 8.47% Pb and 15.80% Zn. The in situ Old Buchans orebody contained 153,260 tonnes grading 1.65% Cu, 7.57% Pb and 14.27% Zn. The transported Oriental #2 orebody contained 928,863 tonnes grading 0.76% Cu, 6.2% Pb and 9.41% Zn. The transported Old Buchans orebody contained 72,763 tonnes grading 0.76% Cu, 5.88% Pb and 9.47% Zn (Thurlow and Swanson, 1981).

1.4 Present Study

During March, 1995 a study was carried out in the Buchans area to determine the trace element speciation of lake sediment cores in an area that had been affected by tailings disposal from previous mining. A map locating Tailings Pond #1 and Tailings Pond #2 is shown in Figure 1.6. Both tailings ponds discharge into Simms Brook which flows into Buchans Brook approximately halfway between Buchans Lake and Red Indian Lake.

Two cores were obtained in Buchans Lake (BL1A, BL1B) to serve as useful background data as this lake is 'upstream'

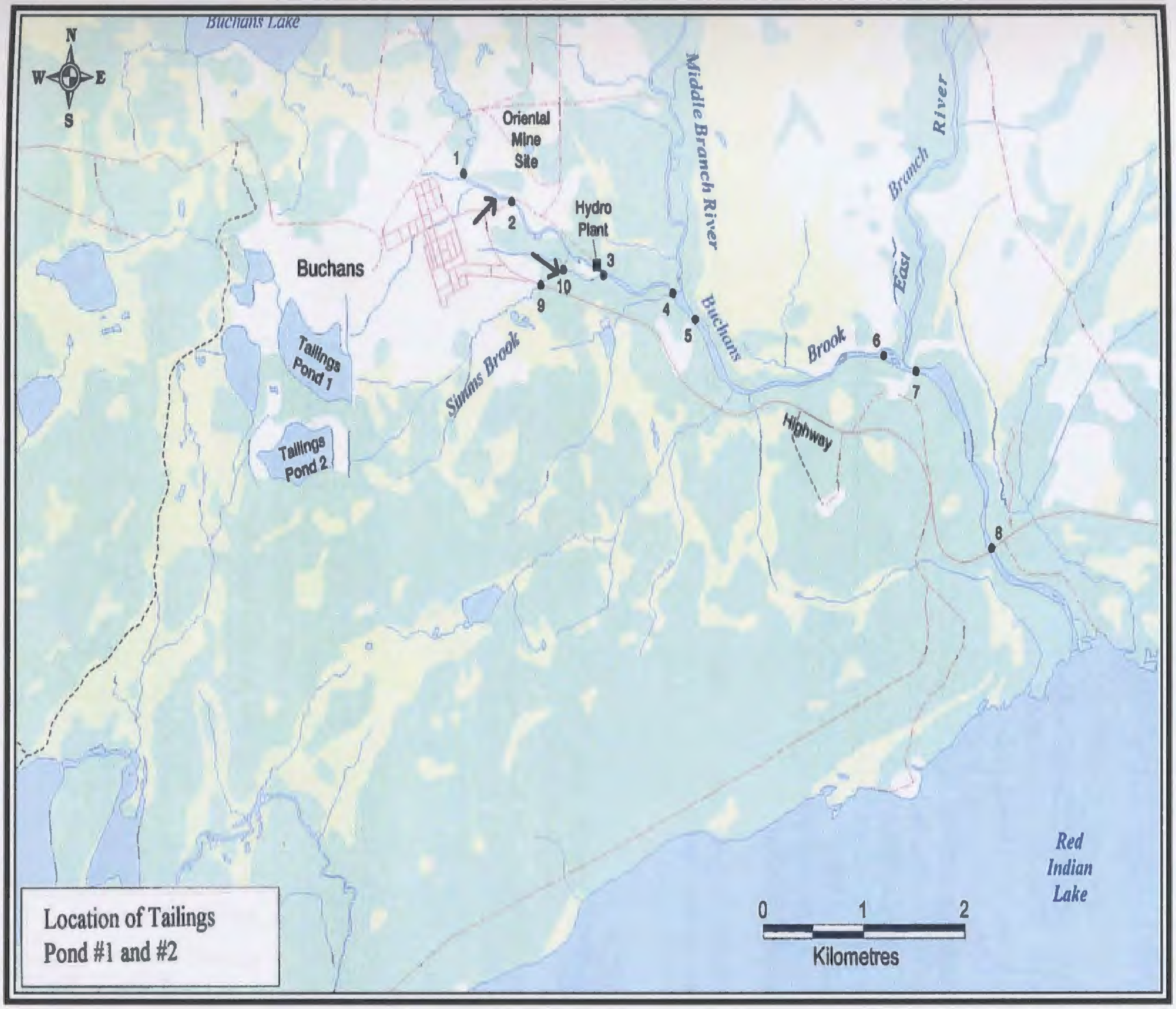

Figure 1.6 Location of Tailings Pond #1 and Tailings Pond #2

from the area affected by tailings discharge. However, airborne contamination from dust particles associated with overburden stripping, crushing procedures at the mill, and general mining activities in the immediate vicinity may result in slightly elevated base metal concentrations in the upper sections of the cores. Therefore, it is important that each core should span both the 'mining period' and the 'pre-mining period' in order to give a measure of local 'natural' background.

Two duplicate lake sediment cores were obtained in the deep basin of Red Indian Lake (RIL1A, RIL1B) approximately midway between where Buchans River flows into Red Indian Lake and where Red Indian Lake discharges into the Exploits River. This site was chosen to determine the extent tailings discharge into the lake had on contamination of the lake sediments.

Furthermore, two duplicate lake sediment cores were obtained in the deep basin of Red Indian Lake (RIL2A, RIL2B) approximately 30 kilometres from where the first two cores were sampled towards where Lloyds River flows into Red Indian Lake. This site was selected to determine the extent of contamination in Red Indian Lake. The sampling locations of the six lake sediment cores are shown in Figure 1.7. The coring sites, their UTM coordinates, water depth and core lengths are given in Appendix A.

All lake sediment cores were sectioned into two

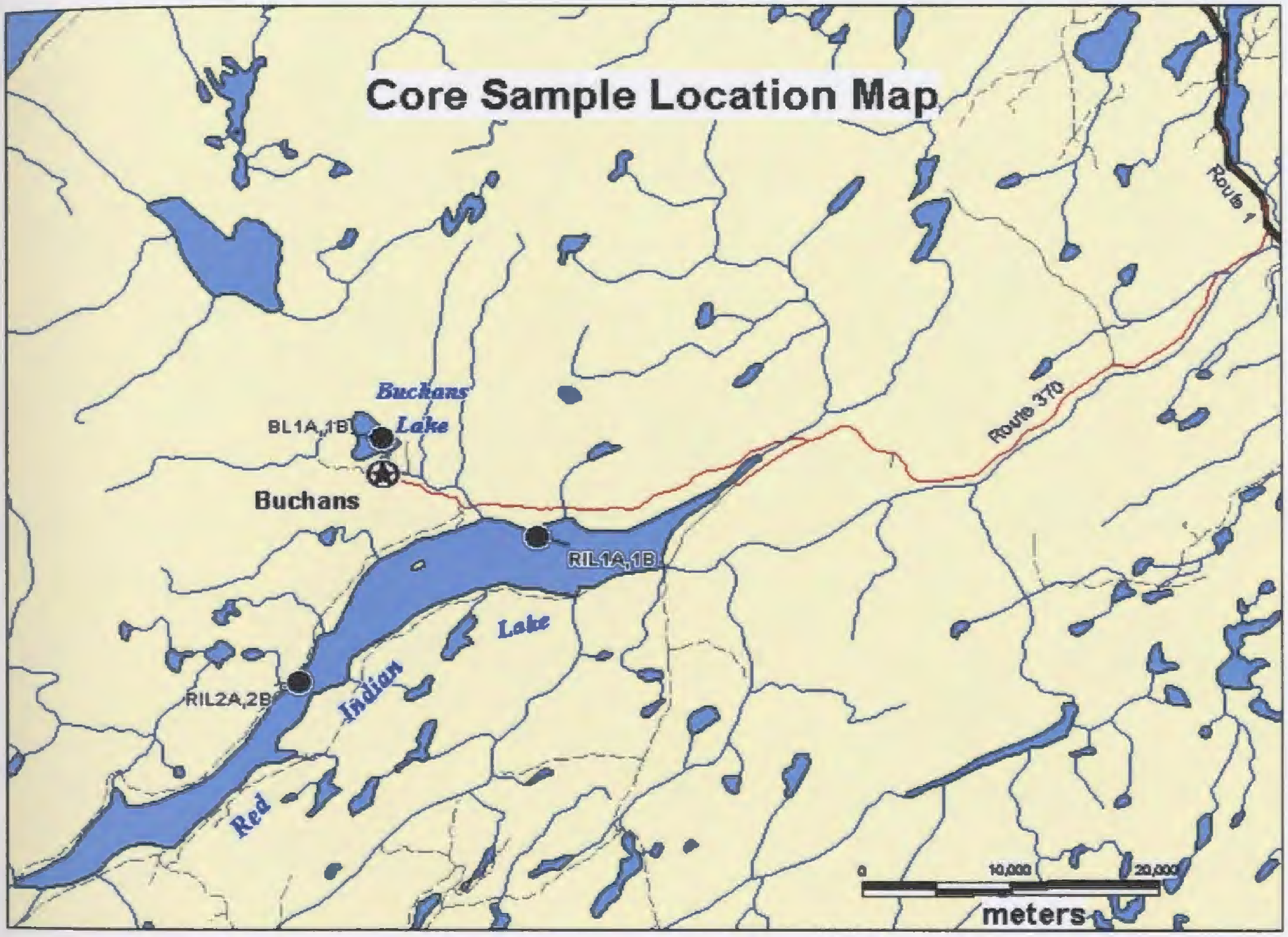

Figure 1.7 Map of Buchans Lake and Red Indian Lake indicating core sample site locations

centimetre intervals. Total metal analyses were conducted on all intervals of the six lake sediment cores. Furthermore the four-step sequential extraction procedure "*Speciation of Heavy Metals in Soils and Sediments: An Account of the Improvement and Harmonization of Extraction Techniques Undertaken under the Auspices of the BCR of the Commission of the European Communities*" (Quevauviller et *al.*, 1993) was carried out on one of the lake sediment cores in Red Indian Lake (RIL2B). This procedure was carried out on the lake sediment intervals as soon as they were extruded (wet), as well as after they were dried.

All analysis were conducted by the writer using a Fisons Instruments Maxim III Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). The operating conditions and detection limits for the various elements are listed in Appendix B.

Chapter 2: Trace Metal Speciation

2.1 Definition

When assessing the environmental implications of contaminated lake sediments, the total concentration of the constituent of interest is not the most important factor. The amount of the total that is easily released to the environment with moderate changes to the acidity or oxidation potential of the aquatic system becomes the most important consideration for current and future environmental impact on the ecosystem.

The labile fraction refers to the portion of the total that is easily mobilized to the environment by simple processes such as ion exchange, slight acidification or changes in redox conditions. If most of a toxic element of interest is tightly held within the crystalline lattice structure, moderate changes to pH or Eh will not release it and environmental damage will be minimal. Simply put, if there are two distinct systems and one system has twice the total concentration of a heavy metal as the other system but only half of the total in 'labile' fractions, the systems will produce similar environmental impacts.

Therefore, the use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment. Such as assumption is clearly incorrect.

One of the first tasks is the clarification of the term 'speciation'. The use of the term speciation has become widespread with several different meanings. Chemical speciation, in the context of sediments has been defined as: The process of identifying and quantifying the different defined species, forms or phases present in a material. The 'species' are further defined:

a) functionally,

b) operationally or

c) as specific compounds or oxidation states of an element.

Speciation can also be defined in a similar way as the description of the amounts and kinds of species, forms and phases present. The 'species' can be defined, as above,

a) functionally, as for example as 'plant-available species' as 'mobile forms' or as 'exchangeable cations', or defined,

b) operationally, by the procedures, reagents or extractants used to isolate them: examples include the physical isolation of a sediment solution or a particle fraction, or the use of acid ammonium oxalate to extract metals associated with 'moderately reducible' sediment components.

Recently, the term 'speciation' has been defined as the determination of a specific form (monatomic or molecular) or configuration in which an element can occur or to a distinct group of atoms consistently present in different matrices. In this thesis, the term speciation will be used in the former, more traditional usage, in an operationally defined context. The limitation of this usage is that the amount of metal reporting to a particular fraction is strictly dependent upon the procedures and reagents used.

2.2 Previous Work

In the past, most studies dealing with particulate metals in natural water systems (i.e. metals associated with suspended matter or bottom sediments) were based on total metal concentrations. Until the method developed by Tessier *et al.* (1979), relatively few attempts were made to evaluate the speciation of particulate metals.

A sequential extraction scheme consists of a series of successive chemical treatments of a sample, each being more drastic in action or of a different nature than the previous one. The order in which the extractants are used is critical and may well depend on sample type and overall composition.

The water soluble fraction of a soil or sediment is the first phase to be brought into solution in any sequential scheme. Unless dealing with evaporites, this fraction is usually negligible. The easily exchangeable metals which are bound by electrostatic attraction on exchange surface sites are the next to be brought into solution usually by neutral salts. Metals co-precipitated with carbonates are released next with dilute acid. Some schemes next liberate the Fe-Mn oxide phase with reducing agents whereas other researchers would release species from the sulphides and organics. Finally the residual, or metals that are bound to the crystal lattice, are released with strong acid.

Several early experimental procedures, varying in manipulative complexity, were proposed for determining the speciation of particulate trace metals. These procedures were grouped into (i) methods designed to effect the separation between residual and non residual metals only (Loring, 1976; Agemian and Chau, 1977; Malo, 1977), and (ii) more elaborate methods of metal fractionation making use of sequential extractions (Nissenbaum, 1972; Gupta and Chen, 1975; Luoma and Jenne, 1976; Gibbs, 1977; Salomons and De Groot, 1977).

The widely used method developed by Tessier *et al.* (1979), adopted a five-step process as follows:

1) *Exchangeable*: The sediment (1 gm) was extracted at room temperature for 1 hour with 8 mL of 1M $MgCl_2$, pH 7 or sodium acetate solution (1M NaOAc, pH 8.2).

2) *Bound to Carbonates*: The residue from 1) was leached at room temperature with 8 mL of 1M NaOAc adjusted to pH 5 with

acetic acid.

3) *Bound to Fe-Mn Oxides*: The residue from 2) was extracted with 20 mL of either 0.3M $Na_2S_2O_4$ + 0.175M Na-citrate + 0.025M H-citrate, as prescribed by Anderson and Jenne (1970), or 0.04M $NH_2OH.HCl$ in 25% (v/v) HOAc.

4) *Bound to Organics and Sulphides*: The method adopted by Gupta and Chen (1975) was used. To the residue from 3) were added 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture heated to 85 °C for 2 hours. A second 3 mL aliquot of 30% H_2O_2 was added and the sample heated again to 85 °C for 3 hours. After cooling, 5 mL of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated for 30 minutes. The NH_4OAc inhibits adsorption of extracted metals onto the oxidized sediment.

5) *Residual*: The residue from 4) was digested with a HF-$HClO_4$ mixture.

In the choice of reagents for sequential extraction, particular emphasis is placed on the potential selectivity of each leaching solution. Many reagents, including the salts ammonium acetate, sodium acetate, and magnesium chloride have been employed to liberate exchangeable metals. NH_4OAc (pH 7) was the method of choice, although workers (Chapman, 1965; Wagemann *et al.*, 1977) have shown that partial attack of the carbonates also takes place.

Reagents recommended for dissolving the carbonate fraction generally make use of sodium acetate and/or acetic acid under acidic conditions (Nissenbaum, 1972; Gupta and Chen, 1975; Chester and Hughes, 1967; Kunze, 1965; McLaren and Crawford, 1973). Grossman and Millet (1961) reported that organic carbon and free iron concentrations in non calcareous soil samples were unchanged after contact with 1M NaOAc for nine weeks. Others studies (Nissenbaum, 1972; Gupta and Chen, 1975; McLaren and Crawford, 1973) have demonstrated that as the acidity increases (pH < 5) partial attack of Fe and Mn oxides occur.

The most successful methods for leaching iron and manganese oxides involved the combined action of reagents reducing these metals to their ferrous and manganous forms and agents capable of keeping in solution the relatively large amounts of metals liberated. The two couples that were most often used were hydroxylamine hydrochloride - acetic acid and sodium dithionite - citrate. Examination of the results of Gupta and Chen (1975), who employed both combinations in parallel experiments, reveals that trace metal concentrations were consistently lower in the leachates obtained with dithionite - citrate. The differences were greatest for lead (approximately 100 times lower) and similar for copper and zinc (approximately 5-10 times lower). The lower amounts of trace metals extracted in the dithionite - citrate extract could be attributed to the higher pH value (around 7) in the extractant. The attack of the combined acid reducing agents on the lattice structure of the minerals had been ruled out. Chester and Hughes (1967) indicated that the structure of the minerals would remain intact.

Hydrogen peroxide in an acidic medium is generally used to oxidize organic matter in soil and sediment, even though oxidation of all forms of organic matter may not be complete. More efficient methods for destroying organic matter do exist using concentrated nitric acid separately or in combination with hydrochloric or perchloric acids. However, concentrated acids also attack the silicate lattices.

Forstner (1993) attempted to separate the Fe - Mn oxide phase into the easily reducible and moderately reducible. Despite the advantages of sequential extractions compared to total metal concentration analysis for environmental implications of long-term adverse effects from contaminated sediments, Forstner stresses the limitations and uncertainties of the procedure. First and foremost, the reactions are not selective and are influenced by the duration of the experiment and by the ratio of solid matter to volume of extractants. Secondly, labile phases could be transformed during sample preparation, which can occur especially for samples from reducing sites. Consequently, it becomes important not to forget changes of the sample matrix during recovery and processing of the sample material.

Work by Hall *et al.* (1996) utilized a five-step process that groups adsorbed/exchangeable/carbonate into the first step and uses 1M CH_3COONa as the extractant. The next step targets the amorphous Fe oxyhydroxide which are extracted with 0.25M $NH_2OH.HCl$ in 0.25M HCl. The third step addresses the crystalline Fe oxide which are extracted with 1M $NH_2OH.HCl$ in 25% CH_3COOH. In the fourth step, metals held in sulphides and organics are extracted with $KClO_3/HCl$ followed by HNO_3. In the final step, residual metals are extracted with $HF-HClO_4-HNO_3-HCl$.

Hall (1998) has found that the high concentration of HCl at 0.25M used in the extraction of the amorphous Fe oxide phase lead to significant dissolution of sphalerite and galena. Less than 1% of these sulphides are dissolved if the acid concentration is reduced to 0.05M HCl. Although tests based on synthetic amorphous Fe oxyhydroxide indicated that their extraction was complete in 0.25M $NH_2OH.HCl$/0.05M HCl, application of the entire sequential scheme revealed that reducing the acid strength from 0.25M HCl to 0.05M HCl can lead to significant increase in the concentration of an element reporting to the "crystalline Fe oxide" phase as well as that in the sulphide phase.

2.3 Method Used in This Study

This study utilizes a four-step process as follows: 1) Exchangeable and Carbonate-held metals extracted with 0.11M acetic acid; 2) Fe-Mn oxide phase extracted with 0.1M hydroxylamine hydrochloride adjusted to pH 2; 3) Organic and Sulphide phases attacked with 30% H_2O_2 and extracted with 1M ammonium acetate; and 4) Residual/Silicate extracted with $HF/HCl/HClO_4$.

The protocol for the sequential extraction scheme for sediment analysis used in this study was as follows:

APPARATUS

All laboratory-ware was borosilicate glass, polyethylene, polypropylene or Teflon. All vessels in contact with samples or reagents were cleaned by immersing in 4M HNO_3 overnight and rinsing with distilled water. Blanks were inserted throughout each step by using two empty vessels, taken through the cleaning procedure, and only adding the various reagents used in each step. These blank solutions were analysed along with the sample solutions from each step described below. A mechanical shaker, with a horizontal rotary was used at a speed of 30 RPM. The centrifugation was carried out at 2500 RPM. The temperature of the room was maintained at 20 $^{+}/_{-}$ 2 °C throughout the extraction procedure.

REAGENTS

Water

Glass-distilled water was used throughout the procedure (simple deionized water may contain organically complexed metals and should not be used). A sample of distilled water was analysed with each batch of step 1 extracts to determine metal content.

Solution A (acetic acid, 0.11M)

In a fume hood, 25 +/- 0.2 mL of redistilled glacial acetic acid (Fisher Scientific) was added to about 0.5 L of distilled water in a 1 L polyethylene bottle and made up to 1 L with distilled water (0.43M acetic acid). Distilled water was added to 250 mL of this solution and made up to a final volume of 1 L to obtain an acetic acid solution of 0.11M. A sample of each batch of solution A was analysed to determine blank metal content.

Solution B (hydroxylamine hydrochloride, 0.1M)

6.95 g of hydroxylamine hydrochloride (J.T. Baker) was dissolved in 900 mL of distilled water and adjusted to pH 2 with HNO_3 and made up to 1 L with distilled water. This solution was prepared on the same day as the extraction was carried out. A sample of each batch of solution B was analysed to determine blank metal content.

Solution C (hydrogen peroxide solution, 300 mg/g or 8.8M)

The H_2O_2, as supplied by the manufacturer (Fisher Scientific), was used. A sample of solution C was analysed to determine blank metal content.

Solution D (ammonium acetate 1M)

77.08 g of ammonium acetate (Fisher Scientific) was dissolved in 900 mL of distilled water and adjusted to pH 2 with HNO_3 and made up to 1 L with distilled water. A sample of each batch of solution D was analysed to determine blank metal content.

SEQUENTIAL EXTRACTION PROCEDURE

The extractable contents of the following metals; Cu, Pb, Zn, Fe, Mn and Ca were determined using the procedure below.

The four-step sequential extraction procedure was carried out on the fresh 'wet' lake sediment 2 cm intervals from core RIL2B immediately upon sub-sectioning, as well as the same lake sediment intervals after they had been dried. The purpose of the 'wet' extraction was to attempt to determine if there were differences in the fractions of base metals that reported to the various phases that could be attributed to the drying process. The dried sub-samples were obtained by extracting 2 cm intervals of core, drying at 110 °C and grinding to ensure that all sediment passed through 80 mesh (<180 um).

Before sub-sampling the dried sediment, the content of the sample bottle was shaken for one minute to ensure a homogenous sample.

The extraction procedure was carried out on 0.5 g of dry sample. For the 'wet' samples, 1 cc of sample was taken and accurately weighed immediately due to the rapid loss of moisture. Another 1 cc sub-sample was accurately weighed and oven dried at 110 °C overnight. From this a correction 'to dry mass' was obtained and applied to all analytical values reported (quantity per g dry sediment).

The sequential extraction procedure was carried out as follows:

Step 1a Add 40 mL of solution A to 0.5000 +/- 0.0002 g of dry sediment (for 'wet' sediment go to step 1b) in a 100 mL stoppered polypropylene centrifuge tube and extract by shaking for 16 hours at ambient temperature. No delay should occur between the addition of the extractant solution and the beginning of shaking. Separate the extract from the solid residue by centrifuging at 2500 RPM for 20 minutes and decanting the supernatant liquid into a polyethylene container. Stopper the container and analyse the extract immediately or store the solution at 4 °C. Wash the residue by adding 20 mL of distilled water, shaking for 15 minutes and centrifuging. Decant the supernatant and discard, taking care not to discard any solid residue.

Break the "cake" obtained upon centrifugation by using a vibrating rod prior to the next step. This must be done prior to the start of each step.

Step 1b Add 40 mL of solution A to approximately 1 cc of 'wet' sediment that has been accurately weighed in a 100 mL stoppered polypropylene centrifuge tube and proceed as per step 1a.

Step 2 Add 40 mL of solution B to the residue from step 1 in the centrifuge tube and extract immediately by shaking for 16 hours at ambient temperature. Centrifuge and decant the supernatant liquid and retain the extractant for analysis. Wash the residue and retain for step 3.

Step 3 Add carefully in a fume hood, small aliquots to avoid losses due to violent reaction, 10 mL of solution C to the residue in the centrifuge tube. Cover the vessel with a watch glass and digest at room temperature for 1 hour with occasional manual shaking. Continue the digestion for 1 hour at 85 °C and reduce the volume to near dryness by further heating of the uncovered vessel in a steam bath or equivalent.

Add a further aliquot of 10 mL of solution C. Heat the covered vessel again to 85 C and digest for 1 hour. Remove the cover and reduce the volume of the liquid to near dryness.

Add 40 mL of extracting solution D to the cool moist residue and shake for 16 hours at ambient temperature. Centrifuge and decant the supernatant liquid and retain the extractant for analysis. Wash the residue and retain for step 4.

Step 4 Transfer the residue in the centrifuge to a 100 mL Teflon beaker with 5 mL of distilled water. Add 15 mL HF, 5 mL HCl and 5 mL 1:1 $HClO_4$ and let stand overnight. Evaporate to dryness at 200 °C. Add approximately 50 mL of 20% (v/v) HCl and digest at 100 °C until dissolved. Transfer to a 50 mL volumetric flask. Add 1 mL of a 5% boric acid (Fisher Scientific) solution to complex any remaining HF and make up to volume with 20% (v/v) HCl. Transfer to a stoppered polyethylene storage bottle and retain for analysis.

With each batch of extractions two blank samples (i.e. vessels with no sediment) shall be carried through the complete procedure for background correction.

Chapter 3: Field and Laboratory Methods

3.1 Sample Collection and Storage

3.1.1 Coring Equipment

Lake sediment cores were collected from Buchans Lake and Red Indian Lake during the winter of 1995 using a K.B. Gravity Corer. Due to the water depth of Red Indian Lake, the coring assembly had to be equipped with a Deep Water Operating Kit. Photo 1 shows a photograph of the sample collection system. This system provides an effective water-sediment interface collection in deep water, and at the same time provides adequate sediment for an effective depth profile of the sediment cores.

The coring assembly consisted of three main parts; coring tube, core head, and plunger release mechanism that was attached to a metal weight by a 10 metre section of rope. This metal weight was attachable to the Deep Water Operating Kit when required. The coring tubes were of high strength Lexan with an outside diameter of 70mm and inside diameter of 64 mm. The coring tubes ranged in length from 70 cm to 90 cm. The tubes were securely fastened to the main core head which allowed the free flow of water through the tube during descent through the water. The plunger release mechanism was activated after the coring tube entered the sediment by the release of the metal

Photo 1. K.B. Gravity Corer equipped with a Deep Water Operating Kit. The Lexan tube is attached to the core head which contains the plunger mechanism. The core head is attached to the Deep Water Operating Kit via the metal weight. The Deep Water Operating Kit is attached to the large coil of ½ inch nylon rope. Photograph is of Al Thompson (left) and myself on Red Indian Lake.

weight on the upper portion of the rope. This metal weight was either manually released, as was the case in Buchans Lake, or released automatically by the Deep Water Operating Kit, as was the case in Red Indian Lake. The metal weight would descend the 10 metres of rope and impact the core head and release the plunger mechanism. The time that it takes the metal weight to descend the rope and activate the plunger mechanism allowed sufficient time for adequate core retrieval. The release of the plunger provided a vacuum seal on the top of the coring tube and ensured sediment retention during its retrieval up through the water column.

3.1.2 Sample Collection and Preservation

The sampling locations of the deep basins within the lakes were identified using bathymetry maps provided by ASARCO. Once the sampling sites were selected, holes were drilled in the ice with a 25 cm gas powered ice auger (Photo 2), and the exact depth of the lake at the sampling location was determined with a Honeywell Depth Finder.

On Buchans Lake, in 7.9 metres of water, the coring assembly was slowly lowered in the water until the coring tube was approximately three metres from the sediment-water interface. The rope was then manually released and the coring assembly descended to the bottom of the lake and into the sediment. As soon as the coring assembly started to enter the

Photo 2. Drilling through the ice with a 10" gas powered ice auger on Red Indian Lake.

sediment, the metal weight attached to the top of the rope was released and lake sediment core BL1A was collected. Before the coring assembly was retrieved from the lake surface (water-air interface), a rubber bung was inserted into the bottom of the coring tube and secured with duct tape. Next the upper portion of the sediment tube was released from the core head. Only enough water was removed from the top of the coring tube to allow another rubber bung to be inserted and secured with duct tape. Care was taken to minimize disturbance of the lake sediment core during transportation. The procedure was repeated 10 metres to the south to allow the collection of lake sediment core BL1B in 8.5 metres of water.

For sediment retrieval in Red Indian Lake, 150 metres of 12.5 mm nylon rope was attached to the Deep Water Operating Kit. The metal weight of the coring assembly was then attached to the Deep Water Operating Kit. The entire coring assembly was slowly lowered to approximately three metres from the sediment-water interface, at which time the entire coring assembly was released. As soon as the coring tube started to enter the sediment, the Deep Water Operating Kit automatically released the metal weight which enabled the collection of the lake sediment cores.

Sampling was attempted in the deep basin of Red Indian Lake between Buchans River and the Exploits in approximately 100 metres of water. Upon retrieving the coring assembly, no sediment core was recovered and coarse sand particles were observed on the coring tube. The first sampling site on Red Indian Lake was then moved approximately 150 metres towards the shore and core RIL1A was retrieved in 58.5 metres of water. RIL1B was retrieved 10 metres to the west in 57.6 metres of water. The second site on Red Indian Lake was approximately 30 kilometres to the southwest. RIL2A was retrieved in 88.8 metres of water and RIL2B was retrieved in 89.4 metres of water, 10 metres to the east of RIL2A. An example of a lake sediment core from Red Indian Lake is shown in Photo 3.

Once the sediment cores were collected, they were kept in an upright position at approximately 4 °C until they could be transported to the Department of Earth Sciences, Memorial University of Newfoundland, and placed in their cold storage room at 4 °C until core processing. All cores were transported and stored in a vertical position.

3.1.3 Core Processing

BL1A, RIL1A, RIL2A, BL1B and RIL1B were removed from the cold storage room at the Department of Earth Sciences and taken to the Department of Mines and Energy's Geochemical Laboratory at the Howley Building on Higgins Line, St. John's, for processing and total trace element analysis. Each core was processed before the next core was removed from cold storage.

Photo 3. Extruded lake sediment core from Red Indian Lake

Care was taken to ensure that the cores remained in an upright position during transportation.

Once at the laboratory, extrusion of the lake sediment core in 2 cm intervals was aided by a sediment core extrusion assembly. The coring tube containing the lake sediment core was secured to the assembly. The rubber bung was removed from the bottom of the coring tube and another bung for use with the plunger assembly was snugly inserted. The water that was present on the top of the sediment column in the coring tube was carefully siphoned off to avoid disturbance of the upper sediment.

The piston on the core extrusion assembly was moved upwards until it was brought into contact with the rubber bung inside the coring tube and then forced upward, moving the entire sediment column with it, until the top of the lake sediment core was flush with the top of the coring tube. The piston assembly could be adjusted to move the entire sediment column upwards in 2 cm intervals by adjusting two aluminum spacers on the core extrusion assembly.

A 2 cm length of Lexan tube with the same inside and outside diameter as the coring tube containing the lake sediment was then placed on top of the coring tube containing the sediment to be extruded. With the lake sediment core now flush with the top of the coring tube, the two aluminum spacers were moved all the way upwards until they both made contact with the piston. The bottom spacer was now tightened into place and the upper spacer was moved upwards 2 cm and tightened into place. The lower spacer was now loosened and the piston assembly forced upwards until the two spacers came into contact again. The bottom spacer was again tightened and secured into place. This procedure resulted in the 2 cm section of lake sediment core moving upwards into the 2 cm piece of Lexan tubing.

A thin plastic cutter was then inserted between the coring tube containing the 2 cm extruded sediment and the other coring tube containing the rest of the lake sediment core. This procedure was repeated until the entire lake sediment core was sectioned into 2 cm intervals. The bottom sediment that was in contact with the rubber bung was discarded. Also, the outer 2-3 mm of the extruded core sections that were next to the coring tube were discarded due to the possibility of cross-contamination as the sediment core moved upwards through the coring tube.

The lake sediment intervals were placed into sediment paper bags and labelled. The sediments were then dried in an oven at 110 C for 24 hours. Once dried, the samples were digested and analysed for total element analysis.

Before RIL2B was processed a decision was made to perform the sequential extraction procedure on both the 'wet' and 'dry' sediment intervals from the same core. Since all other cores were processed and in a dried form at this time, RIL2B was selected for sequential extraction analysis. From the total element analysis of the duplicate lake sediment core RIL2A, it was determined that significant elevation in Cu, Pb and Zn existed in the upper 14 centimetres of the core to warrant further investigation by the sequential extraction procedure.

During processing of lake sediment core RIL2B, two separate 1 cc sub-samples were collected with a cut-off syringe from each 2 cm sediment interval as soon as it was extruded from the core. The first 1 cc sub-sample was immediately placed into a clean, pre-weighed, numbered ceramic crucible for determination of free water content. The second 1 cc sub-sample was then placed into a pre-weighed 100 mL polypropylene tube and immediately re-weighed for a sample wet weight determination. From the free water analysis of the first 1 cc sub-sample, a calculated equivalent-to-dry weight could be determined for the 'wet' sub-sample used in the sequential extraction procedure.

An assumption that is made here is that both 1 cc sub-samples taken within the same 2 cm sediment interval are identical. With the significant variation within the upper lake sediment, as demonstrated by the chemical profiles generated from RIL2A, this is not an entirely accurate assumption. Care was taken to extrude both 1 cc sub-samples from approximately the same level within the 2 cm interval in an attempt to collect as similar samples as possible. Sample variation will also be present between the 'wet' and 'dry' sub-samples from the same sediment interval within lake sediment core RIL2B. The dry sub-sample was taken from a homogenous 2 cm interval, whereas the 'wet' sub-sample was from a discrete 1 cc section extruded from within the 2 cm interval. This variation will limit our ability to compare the results between the 'wet' and 'dry' sequential analyses. Consequently, this will hinder our ability to assess the effects of drying on the amount of a particular element that reports to the different phase fractions.

The four-step sequential extraction procedure was performed immediately after the 'wet' sub-samples were weighed. The remaining lake sediments from the 2 cm intervals were placed into labelled sediment paper bags and dried in an oven at 110 °C for 24 hours to be used for total element and 'dry' sequential base metal analysis.

3.2 Sample Preparation and Geochemical Analysis

3.2.1 Sample Preparation

After the lake sediment samples were dried in an oven at 110 C, they were grinded to ensure all sediment passed through 80 mesh (<180 um) stainless steel sieves and placed in numbered plastic vials. At this stage blind duplicates and standard reference materials (SRMs) were inserted for quality control in the analysis array. Blind duplicates were inserted with one pair for every twenty samples at position 10, 30, 50 etc., while various SRMs were inserted prior to sample digestion at a frequency of one in twenty at position 20, 40, 60 etc.. The SRMs used for total element analysis were LKSD 1-4 and the SRM used for the sequential base metal analysis was the certified ore MP-1A.

3.2.2 Free Water Analysis

For Free Water determinations, 1 cc sub-samples from the 2 cm intervals of lake sediment core RIL2B were placed in clean, numbered, pre-weighed ceramic crucibles. The crucibles containing the 1 cc sub-samples were immediately re-weighed to obtain a wet sample + crucible weight (T_{20}). After all sub-samples were determined for T_{20} weight, the crucibles were placed in a drying oven at 110 °C overnight. The samples were removed from the drying oven and placed in a desiccator for approximately 25 minutes to cool. They were then re-weighed at room temperature to obtain a dry sample + crucible weight (T_{110}). The % Free Water was calculated as follows:

$$\textbf{\% Free Water} = ((T_{20} - T_{110}) \ / \ \textbf{Wet Sample Weight}) * 100$$

where, **Wet Sample Weight =** T_{20} **- Empty Crucible Weight.**

3.2.3 Trace Element Analysis - Total

Total element analysis of all lake sediment samples were carried out at the Geochemical Laboratory of the Newfoundland Department of Mines and Energy by a Fisons Instruments Maxim III Inductively Coupled Plasma - Optical Emission Spectroscope (ICP-OES). The following elements were analysed: Mo, Cr, P, Zn, Pb, Co, Ni, Fe, Mg, Ga, Ti, V, Be, Ca, Nb, Cu, Na, Zr, Dy, Sc, Y, Al, Mn, Sr, La, Ce, Ba, Li, and K. The HF/HCl/$HClO_4$ digestion is incomplete for barite yielding low Ba results. Due to the high barite content of the orebodies, a digestion using a lithium metaborate fusion followed by an acid digestion would have been used if Ba results were required.

Sample dissolution for total element analysis was conducted by accurately weighing 1.0000 $^{+}/_{-}$ 0.0005 gm of dried sediment into a small glass beaker. The sample was then ashed at 500 °C for four hours, and transferred to a 125 mL Teflon beaker. A 15 mL aliquot of concentrated HF, 5 mL of concentrated HCl and 5 mL of a 1:1 mixture of $HClO_4$ were added. The samples were swirled, placed on a hotplate and left to digest overnight at room temperature. The samples were then heated to 200 °C and brought to dryness. Approximately 50 ml of a 20% (v/v) HCl solution was added and the samples were heated again at 100 °C until the solid residue dissolved. The solution was transferred to 50 mL volumetric flasks, cooled, and made up to volume with the 20% (v/v) HCl solution. The volumetric flasks contained 1 mL of a 5% boric acid solution to complex any remaining HF. All samples were then transferred to clean polyethylene storage bottles prior to analysis.

3.2.4 Sequential Base Metal Analysis

Sequential element analyses for selected base metals were performed on the 'wet' and 'dry' sediment intervals from lake sediment core RIL2B. All analyses were determined at the Geochemical Laboratory of the Newfoundland Department of Mines and Energy by ICP-OES. The following elements were analysed: Cu, Pb, Zn, Ca, Mn and Fe. The working range of the standards used was approximated from the results of the total element analysis of lake sediment core RIL2A.

The four-step sequential extraction procedure was explained in detail in Section 2.3.

For the 'dry' sediment extraction, 0.5000 +/- 0.0005 gm sample was used. The final volume for steps 1-3 was 40 mL (dilution factor of 80) whereas the final volume for step 4 was 50 mL (dilution factor of 100). For the 'wet' sediments from RIL2B, the 1 cc sub-samples, when calculated to an equivalent dry weight, yielded samples ranging in weight from 0.1273 gm to 0.4994 gm producing dilution factors ranging from 80.1 to 314.2 for the first three steps and 100.0 to 392.8 for the fourth step.

For Red Indian Lake, the sediment interval with the lowest % Free Water coincided with the highest base metal concentrations. Therefore, the middle calibration standards for all four steps were made up to roughly equal the highest concentration of the element within the sediment column, as determined from lake sediment core RIL2A. The dilution factors for all 'wet' sediment sub-samples were calculated and factored into the final results.

Chapter 4: Results

4.1 Elemental Analysis - Total

4.1.1 Buchans Lake Core BL1A

Analysis of core BL1A showed significant Cu, Pb and Zn enrichment in the upper 20-22 cm of sediment. No major differences were observed in the other elements analyzed. Chemical data for total trace element analysis of all cores are reported in Appendix C.

Although radiometric dating was not performed on the sediment samples, a subtle color change at approximately 21 cm as well as significant changes in the chemical composition of base metals at the same interval suggests the commencement of mining occurred sometime during the 20-22 cm interval. From surface to a depth of approximately 21 cm the sediment color was determined to be 5YR2.5/1 according to the Munsell Soil Color Chart (Munsell, 1975). The lower sediment core from approximately 21 cm to 46.2 cm was determined to be 5YR2.5/2 in color. From these results, the study suggests that the concentration of elements in the sediment below 22 cm can be considered background levels. With the possibility of sediment mixing or elemental migration within the sediment column since deposition, concentrations below 24 cm were chosen as background.

For core BL1A, the background levels for Cu, Pb and Zn were determined to be between 15-26 ppm, 14-25 ppm, and 87-138 ppm, respectively. The upper 20 cm of sediment demonstrated significant enrichment with respect to base metals. The elevated copper values ranged from 44 ppm (6-8 cm) to 143 ppm (16-18 cm); the lead values ranged from 109 ppm (6-8 cm) to 594 ppm (18-20 cm); and, the zinc values ranged from 318 ppm (8-10 cm) to 745 ppm (18-20 cm) as shown in Figure 4.1.

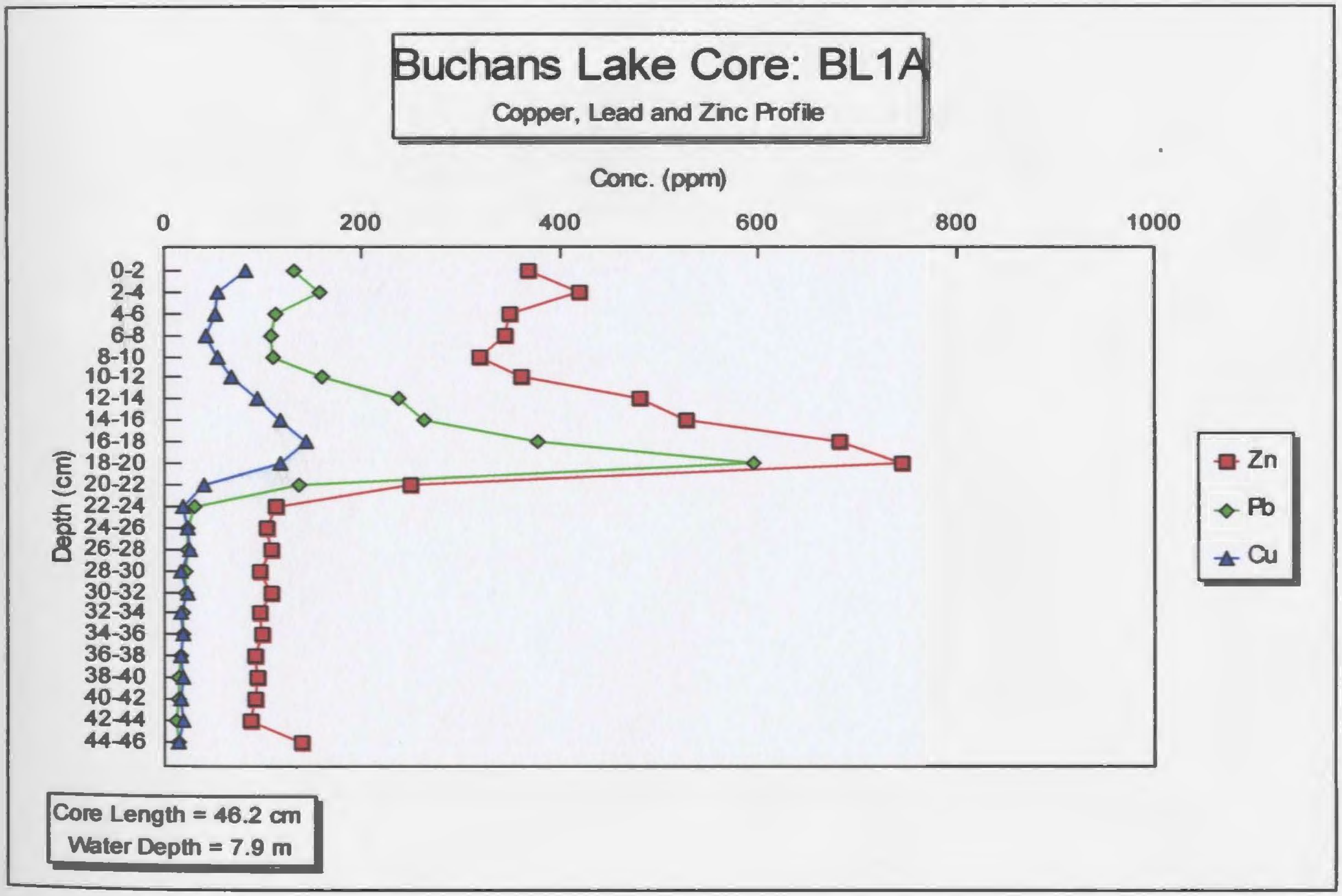

Figure 4.1 Cu, Pb and Zn profile of lake sediment core BL1A

4.1.2 Buchans Lake Core BL1B

Analysis of core BL1B again showed similar background concentrations as well as the same color change at approximately 21 cm as core BL1A. Figure 4.2 showed that the upper 20 cm of sediment were similarly enriched in Cu, Pb and Zn as core BL1A. The elevated copper values ranged from 47 ppm (6-8 cm) to 148 ppm (16-18 cm); the lead values ranged from 110 ppm (8-10 cm) to 604 ppm (18-20 cm); and, the zinc values ranged from 315 ppm (8-10 cm) to 761 ppm (18-20 cm).

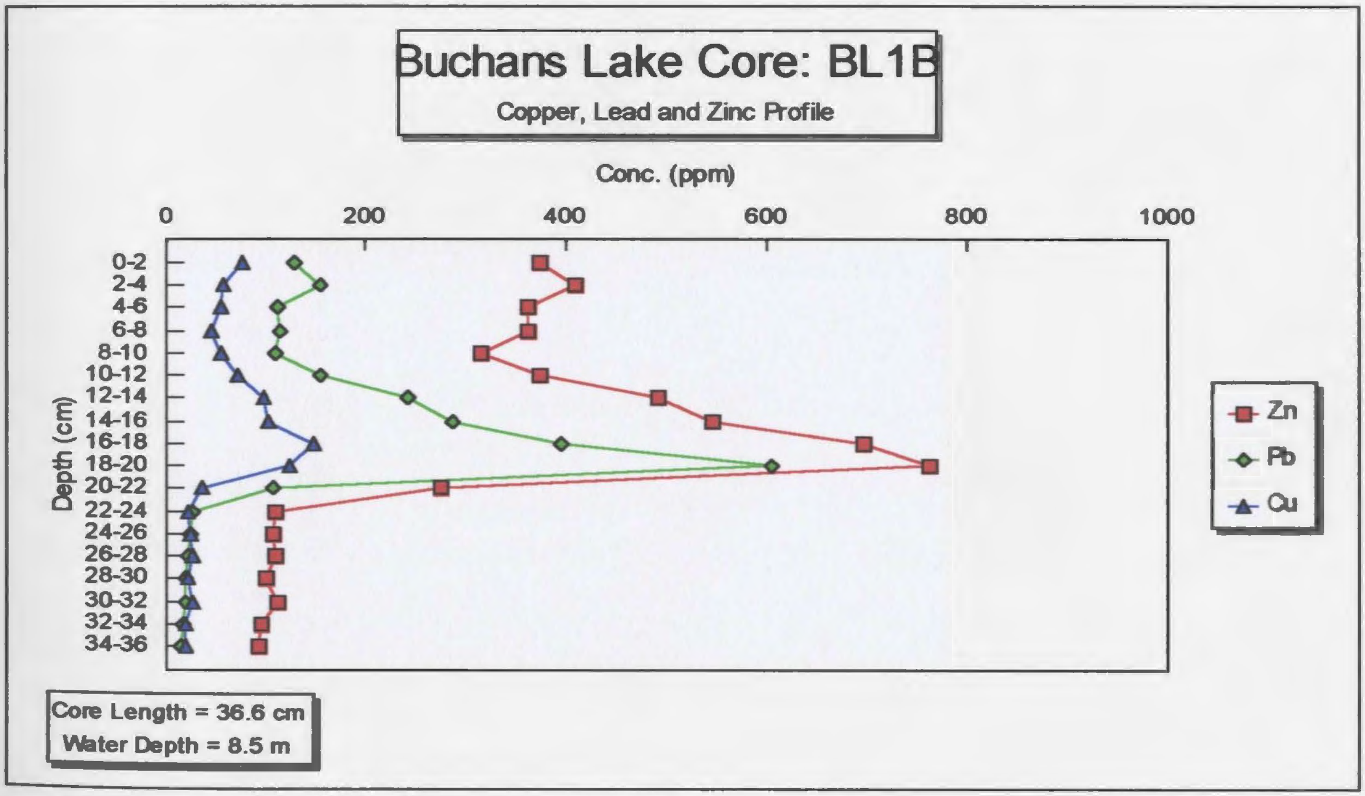

Figure 4.2 Cu, Pb and Zn profile of lake sediment core BL1B

4.1.3 Red Indian Lake Core RIL1A

Analysis of core RIL1A showed significant Cu, Pb and Zn enrichment in the upper 22-24 cm of sediment and values which are 10-200 times higher than found in Buchans Lake. This is expected as tailings from mining operations were deposited directly into Buchans River until 1966 and subsequently into various tailings ponds that discharged into Simms Brook which flowed directly into Buchans River and eventually into Red Indian Lake (Fig. 1.6). No significant differences were observed in the other elements analyzed with the exception of Ba and Mo. Ba results were expected to be high in the upper sediment due to the presence of barite minerals within the sulfide ore. However, the trace element digestion used for total element analysis was incomplete for barite and the Ba results were invalid.

A distinct color change at approximately 23 cm as well as a significant change in the chemical composition of base metals in the sediment from the 22-24 cm interval to the 24-26 cm interval (background) suggests the commencement of mining occurred within the 22-24 cm interval. Based on the color change of the sediment as well as the chemical profiles of the metals, it appears that the transition between pre-mining and mining occurred between the 22-24 cm sediment interval and therefore the concentration of elements in the sediment below 24 cm can be considered background levels. Since the concentration of base metals were slightly elevated in the 24-26 cm interval as well, the concentrations of metals below 26 cm were chosen as background.

As opposed to cores BL1A and BL1B in which there was only one color change within the sediment column, core RIL1A demonstrated numerous subtle color changes. The first 4 cm of the sediment had a color measurement of 5YR3/2 and from 4 cm to approximately 23 cm predominately 7.5YR4/0 with some 7.5YR3/0 observed between 8-9 cm and 22-23 cm and small bands at about 13 cm and 18 cm. A distinct color change was observed from 23 to 38.4 cm with the predominant color determined to be 10YR3/1. A sharp black band (7.5YR3/0) was observed at approximately 33 cm. A fine yellow-green band (5Y5/2) was observed at approximately 37 cm. A thorough examination of the color changes observed was beyond the scope of this study but a brief explanation will be provided in the discussion section.

For core RIL1A, the background levels for Cu, Pb and Zn were determined to be between 22-41 ppm, 17-44 ppm, and 127-160 ppm, respectively. The upper 24 cm of sediment demonstrated significant enrichment with respect to base metals. The elevated copper values ranged from 502 ppm (0-2 cm) to 4270 ppm (20-22 cm); the lead values ranged from 1697 ppm (10-12 cm) to 2993 ppm (20-22 cm); and, the zinc values ranged from 1961 ppm

(0-2 cm) to 12,502 ppm (20-22 cm) as shown in Figure 4.3.

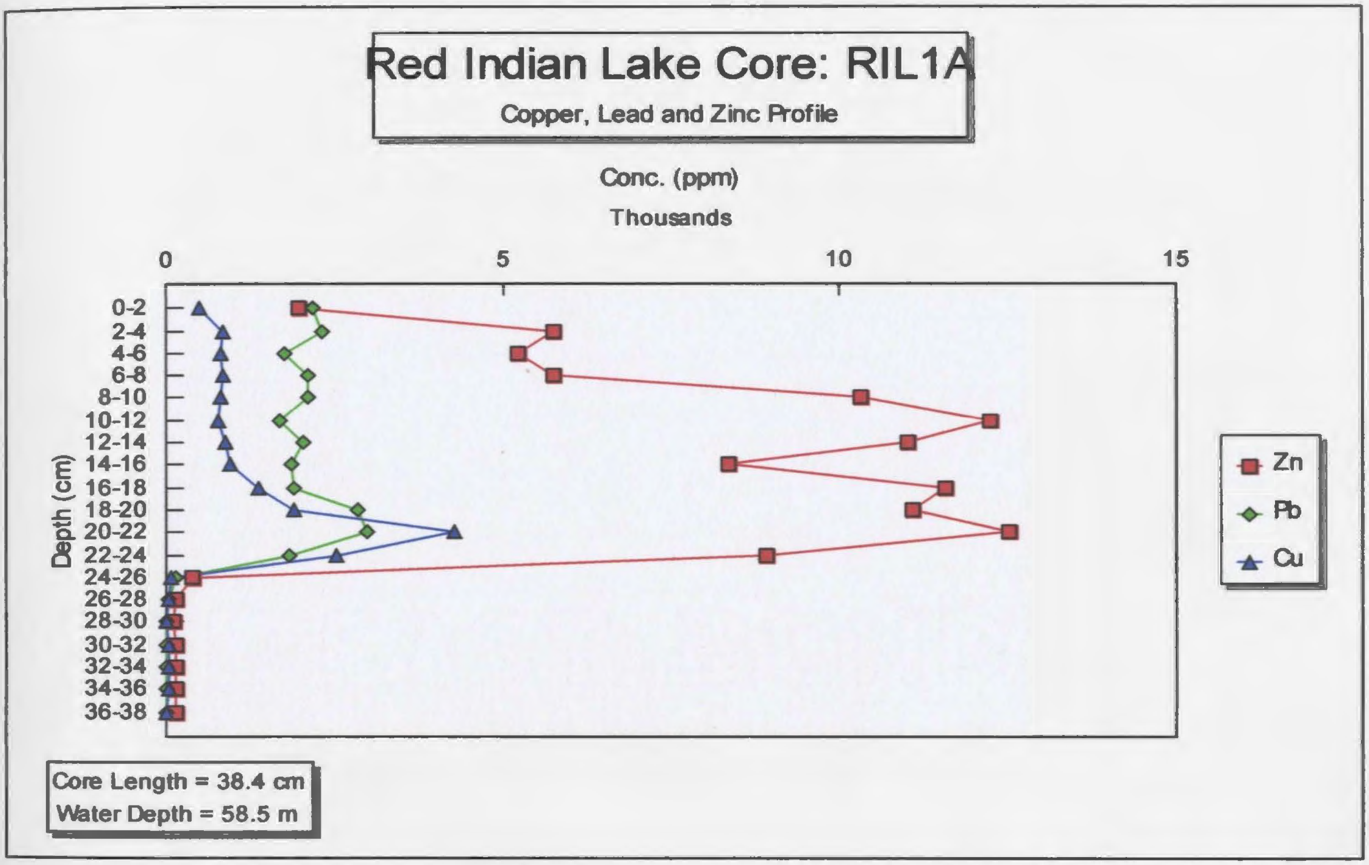

Figure 4.3 Cu, Pb and Zn profile of lake sediment core RIL1A

4.1.4 Red Indian Lake Core RIL1B

Analysis of core RIL1B also showed similar background concentrations as well as similar color changes within the entire sediment column as in core RIL1A. Figure 4.4 showed that the upper 24 cm of sediment were similarly enriched in Cu, Pb and Zn as core RIL1A. The elevated copper values ranged from 487 ppm (0-2 cm) to 4183 ppm (20-22 cm); the lead values ranged from 1722 ppm (10-12 cm) to 2985 ppm (20-22 cm); and the zinc values ranged from 1894 ppm (0-2 cm) to 12,576 ppm (20-22 cm).

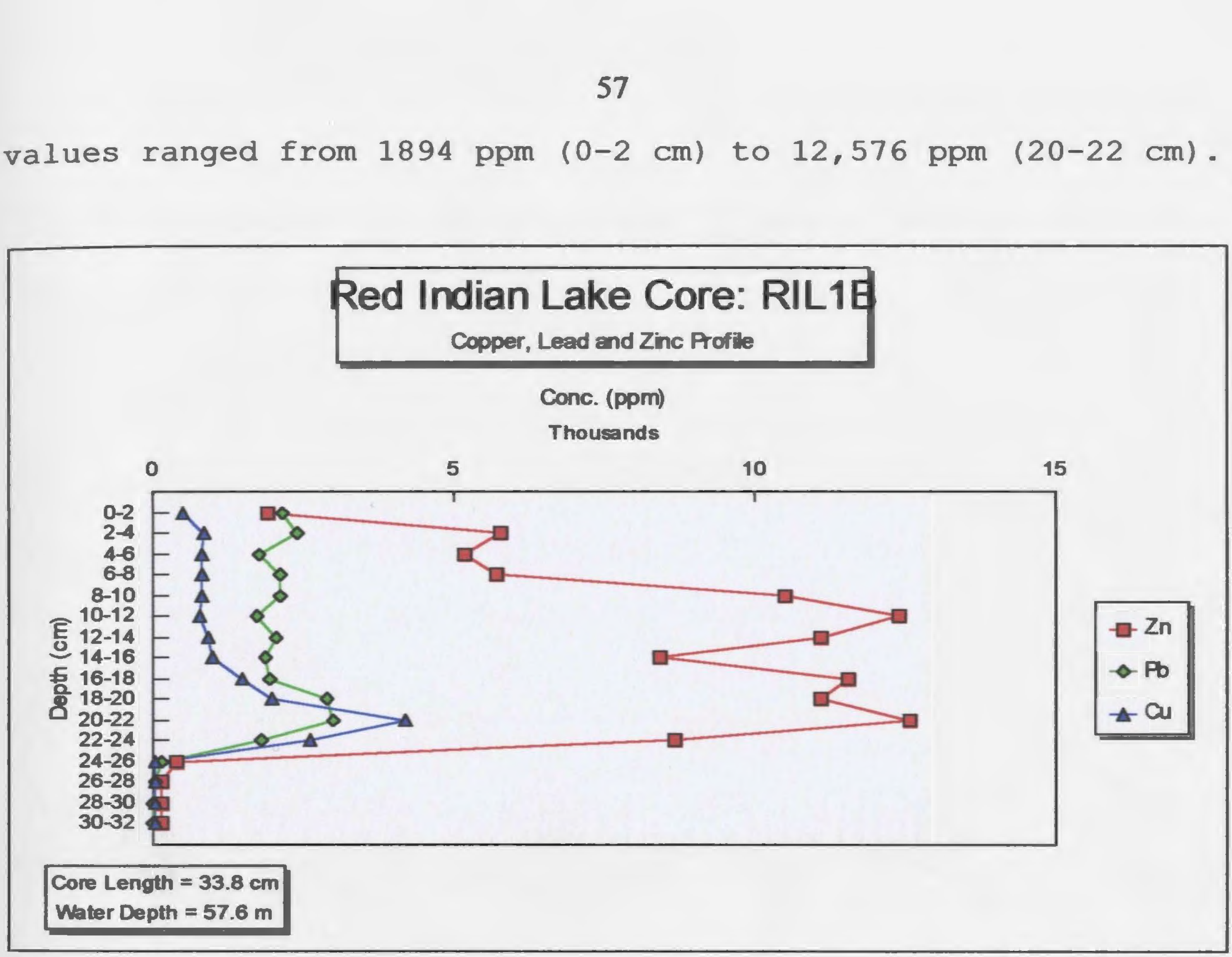

Figure 4.4 Cu, Pb and Zn profile of lake sediment core RIL1B

4.1.5 Red Indian Lake Core RIL2A

Analysis of core RIL2A showed significant Cu, Pb and Zn enrichment in the upper 14-16 cm of sediment with slightly elevated values up to 20-22 cm. The smaller interval of enrichment at this site was attributed to the site location, as discussed earlier. The largest volume of tailings were deposited between Buchans River and the Exploits in the direction of drainage (RIL1A and RIL1B). Again, no significant variations were observed in the other elements analyzed with the exception of Ba and Mo. Distinct color changes were observed at approximately 15 cm and 21 cm. Significant changes in the chemical composition of base metals from 14-16 cm to 16-18 cm as well as subtle changes in the chemical composition from 20-22 cm to 22-24 cm made it difficult to determine which sediment interval (14-16 cm or 22-24 cm) corresponded to the commencement of mining. Since the concentration of base metals below 24 cm were more consistent, the values below 24 cm were chosen as background.

Similar to cores RIL1A and RIL1B, core RIL2A demonstrated numerous subtle color changes with distinct color changes occurring at approximately 15 cm and 21 cm. The first 3 cm of the sediment had a color measurement of 10YR4/6 and from 3 cm to approximately 7.5 cm the color was determined to be 10YR4/2. From 7.5 cm to approximately 11 cm there was another color change to 10YR6/3. From 11 cm to 15 cm the color was determined to be 10YR5/2. From 15 cm to 21 cm the color was 10YR4/1. From 21 cm to the end of the core (34.2 cm) the color was 10YR3/3.

For core RIL2A, the background levels for Cu, Pb and Zn were determined to be between 34-47 ppm, 19-21 ppm, and 154-169 ppm, respectively. The upper 16 cm of sediment demonstrated significant enrichment with respect to base metals. The elevated copper values ranged from 225 ppm (0-2 cm) to 2112 ppm

(12-14 cm); the lead values ranged from 2050 ppm (0-2 cm) to 4457 ppm (10-12 cm); and, the zinc values ranged from 839 ppm (0-2 cm) to 9732 ppm (10-12 cm) as shown in Figure 4.5.

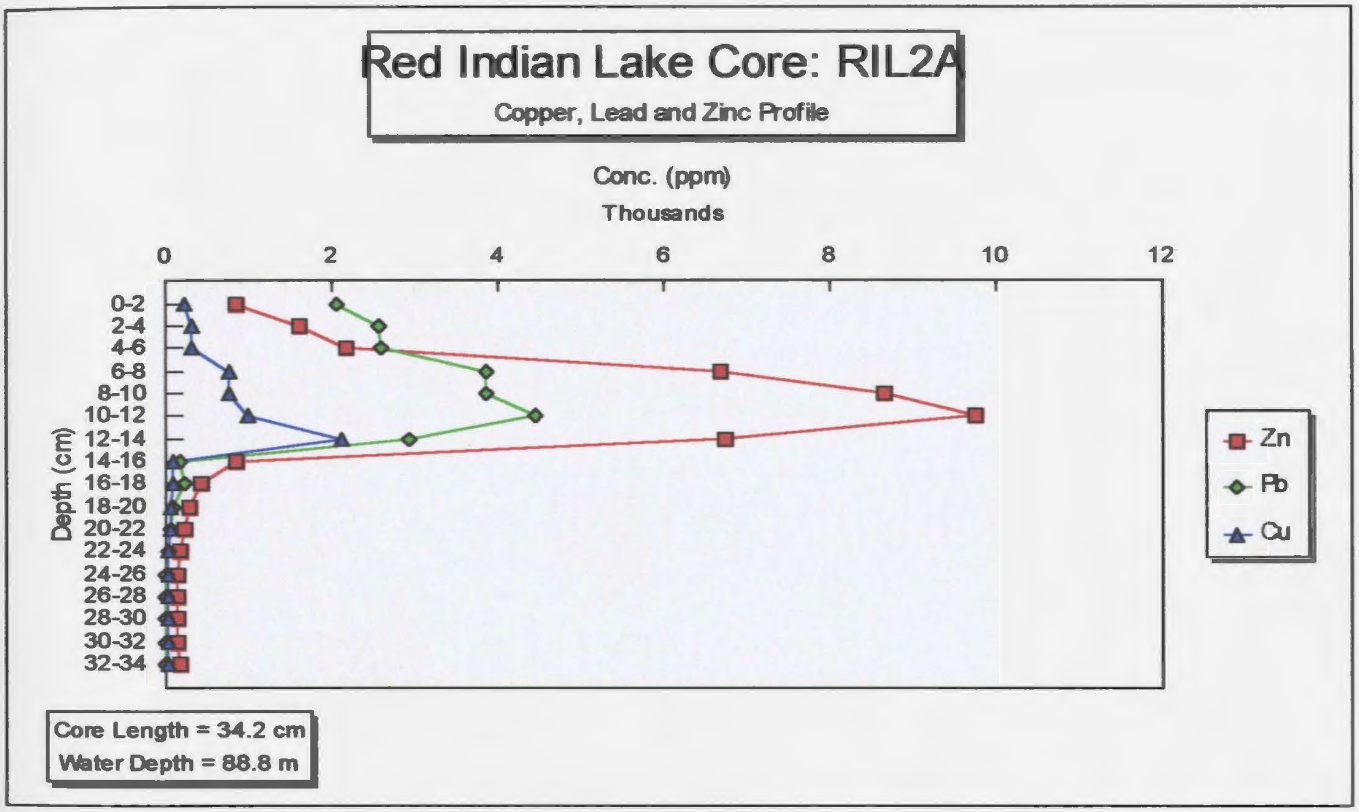

Figure 4.5 Cu, Pb and Zn profile of lake sediment core RIL2A

4.1.6 Red Indian Lake Core RIL2B

Analysis of core RIL2B showed similar background concentrations as well as similar color changes within the entire sediment column as in core RIL2A. Figure 4.6 showed that the upper 16 cm of sediment were similarly enriched in Cu, Pb and Zn as core RIL2A. The elevated copper values ranged from 236 ppm (0-2 cm) to 2205 ppm (12-14 cm); the lead values ranged from 2102 ppm (0-2 cm) to 4527 ppm (10-12 cm); and, the zinc values ranged from 802 ppm (0-2 cm) to 9575 ppm (10-12 cm).

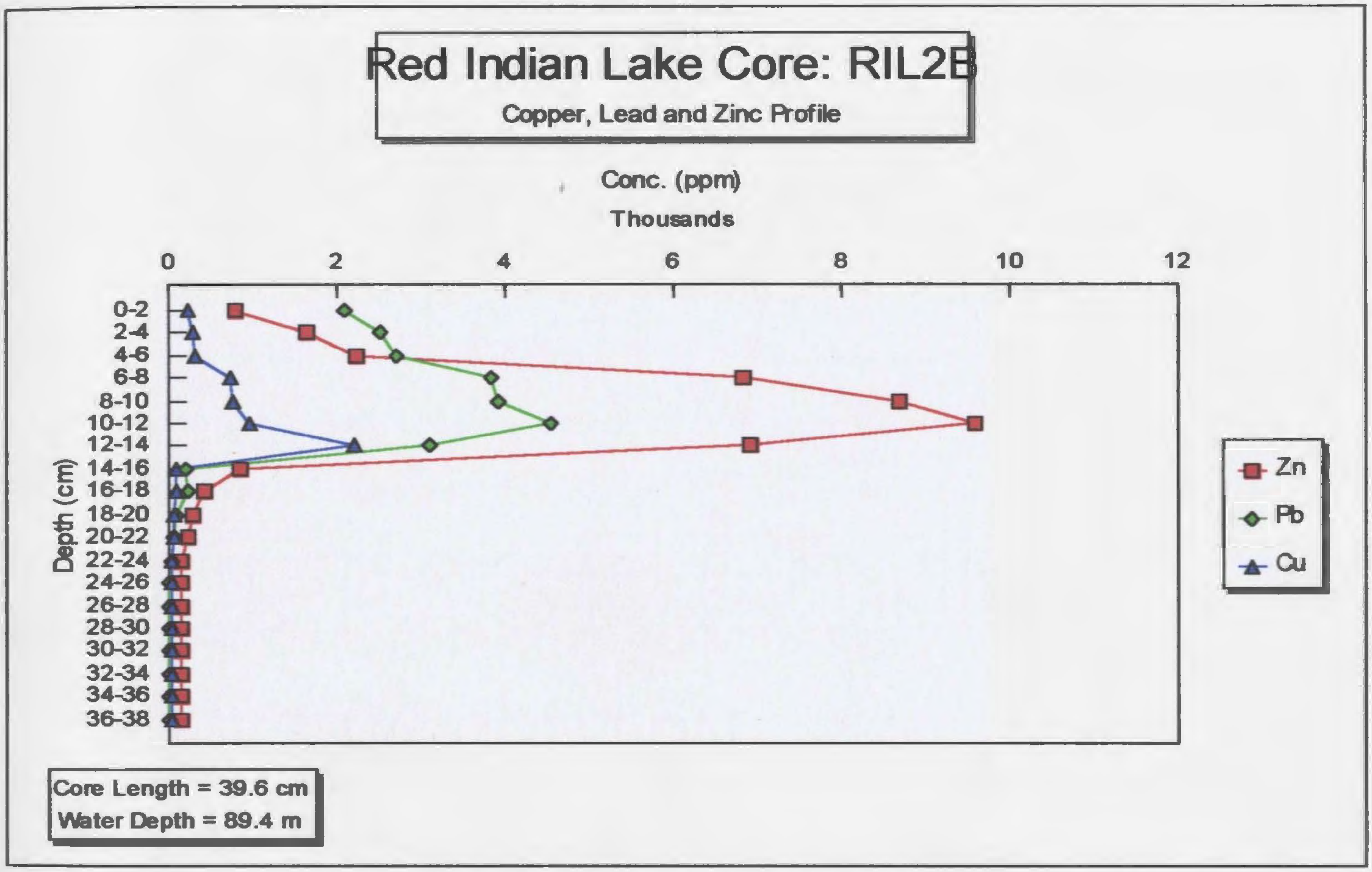

Figure 4.6 Cu, Pb and Zn profile of lake sediment core RIL2B

4.2 Elemental Analysis - Sequential Extraction

4.2.1 Red Indian Lake Core RIL2B (Dry)

Chemical data for the sequential element analysis of Cu, Pb, Zn, Fe, Mn and Ca on both the 'dry' and 'wet' lake sediment core RIL2B are reported in Appendix D. Due to the relatively low concentration of base metals in the lower section of the core (background levels) compared to the contaminated upper section of the core, the discussion of results were primarily limited to the elevated upper segments. In terms of accuracy, the higher concentrations of base metals in the upper sections of the core were within the optimum working range of the prepared standards for ICP-OES, whereas the results of the lower sections of the core were closer to the detection limits.

Analysis of 'dry' core RIL2B showed significant concentrations of Cu, Pb and Zn reported to the environmentally sensitive phases (exchangeable/carbonate and Fe/Mn oxides) of the sequential extraction in the upper sediment intervals. Discussion of the base metal distribution among the different phases will focus on the top sediment interval (0-2 cm) as well as the interval with the highest metal concentration,. For Cu and Pb, the sediment with the highest total concentration (12-14 cm and 10-12 cm, respectively) also had the highest concentration of that metal reporting to the first phase. However, for Zn the highest concentration of metal was reported in the 10-12 cm interval whereas the 8-10 cm interval had the highest concentration of zinc reporting to the first phase.

The sequential element analysis indicated significant amount of Cu reported to the first three phases for the contaminated upper sections of the core (Figs. 4.7 and 4.8). For the uppermost sediment (0-2 cm), 26.4% of the Cu (68 ppm) reported to Phase 1, 54.6% of the Cu (142 ppm) reported to Phase

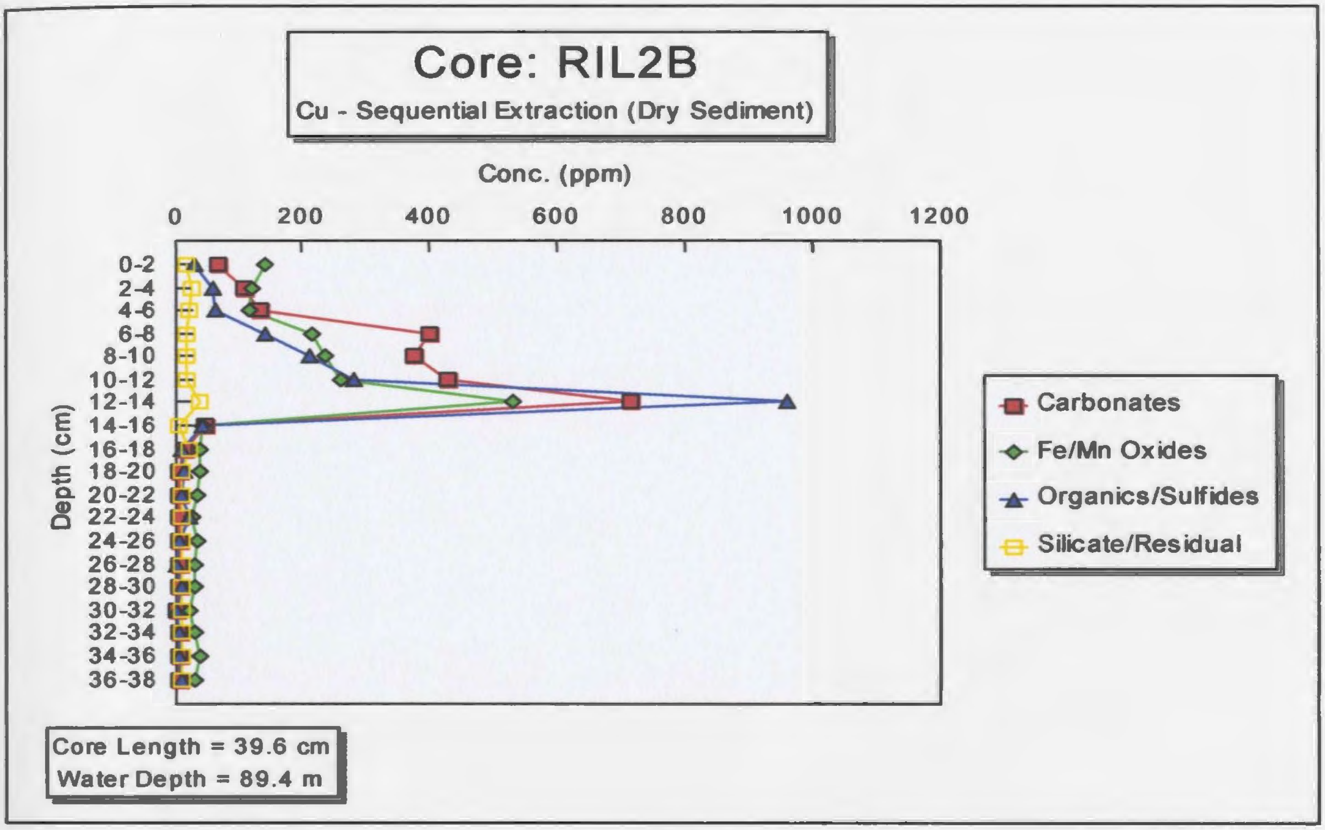

Figure 4.7 Sequential Extraction of Cu on core RIL2B (Dry)

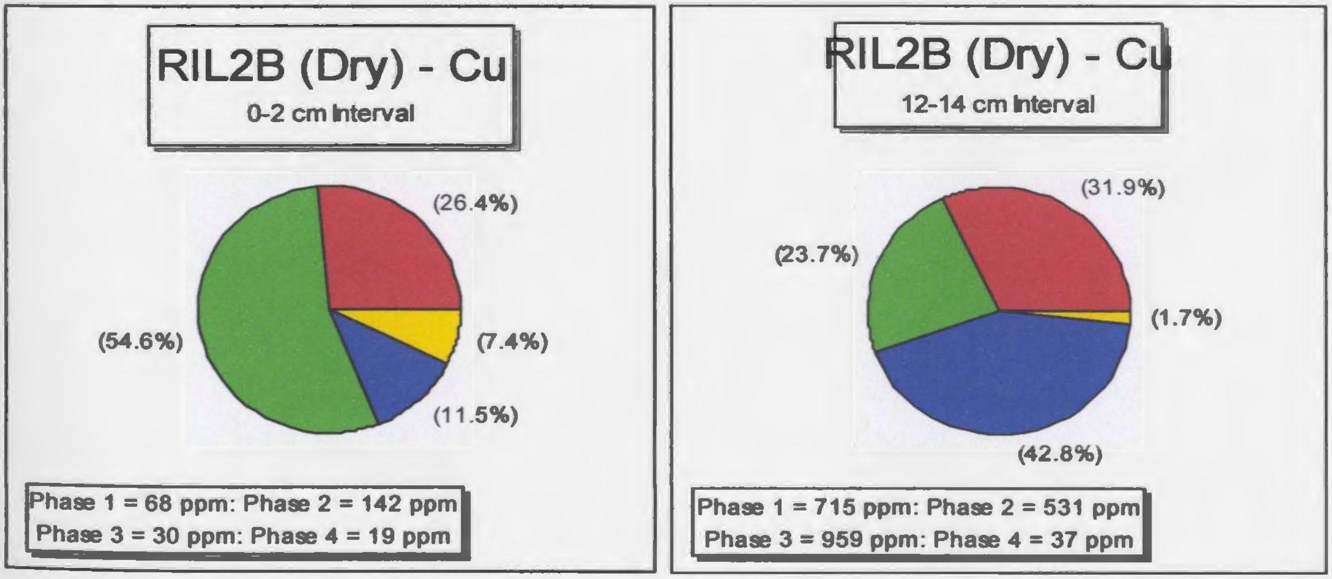

Figure 4.8 Sequential extraction of Cu on selected intervals (0-2 cm, 12-14 cm) of lake sediment core RIL2B (Dry)

2, 11.5% of the Cu (30 ppm) reported to Phase 3, and only 7.4% of the Cu (19 ppm) reported to Phase 4. For the section with the highest copper concentration (12-14 cm), 31.9% of the Cu (715 ppm) reported to Phase 1, 23.7% of the Cu (531 ppm) reported to Phase 2, 42.8% of the Cu (959 ppm) reported to Phase 3, and only 1.7% of the Cu (37 ppm) reported to Phase 4. From the 4-6 cm interval to the top of the sediment core (0-2 cm), the amount of Cu that reported to the exchangeable/carbonate phase decreased from 134 ppm to 68 ppm whereas the amount of Cu that reported to the Fe/Mn oxide phase increased from 116 ppm to 142 ppm. Sediment below 24 cm (background) had 2-6 ppm Cu reporting to phase 1 and 23-37 ppm Cu reporting to phase 2.

The sequential element analysis indicated significant amount of Pb reported to the first two phases for the contaminated upper sections of the core (Figs. 4.9 and 4.10). For the 0-2 cm interval, 17.3% of the Pb (366 ppm) reported to Phase 1, 79.9% of the Pb (1688 ppm) reported to Phase 2, 1.7% of the Pb (36 ppm) reported to Phase 3, and 1.1% of the Pb (24 ppm) reported to Phase 4. For the section with the highest lead concentration (10-12 cm), 44.5% of the Pb (2070 ppm) reported to Phase 1, 53.0% of the Pb (2468 ppm) reported to Phase 2, 1.0% of the Pb (45 ppm) reported to Phase 3, and 1.6% of the Pb (74 ppm) reported to Phase 4. Similar trends were observed with the amount of Pb reporting to the first two phases in the upper six

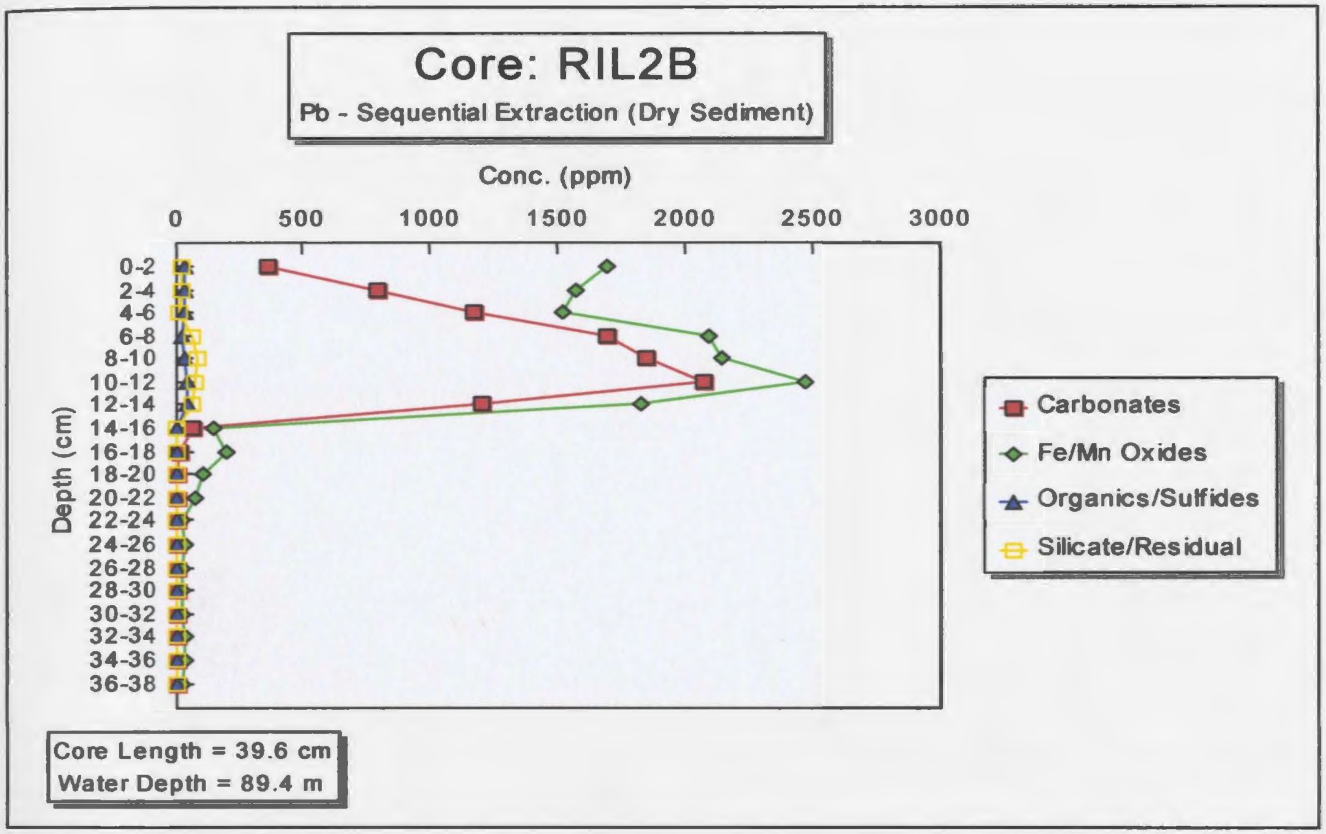

Figure 4.9 Sequential extraction of Pb on core RIL2B (Dry)

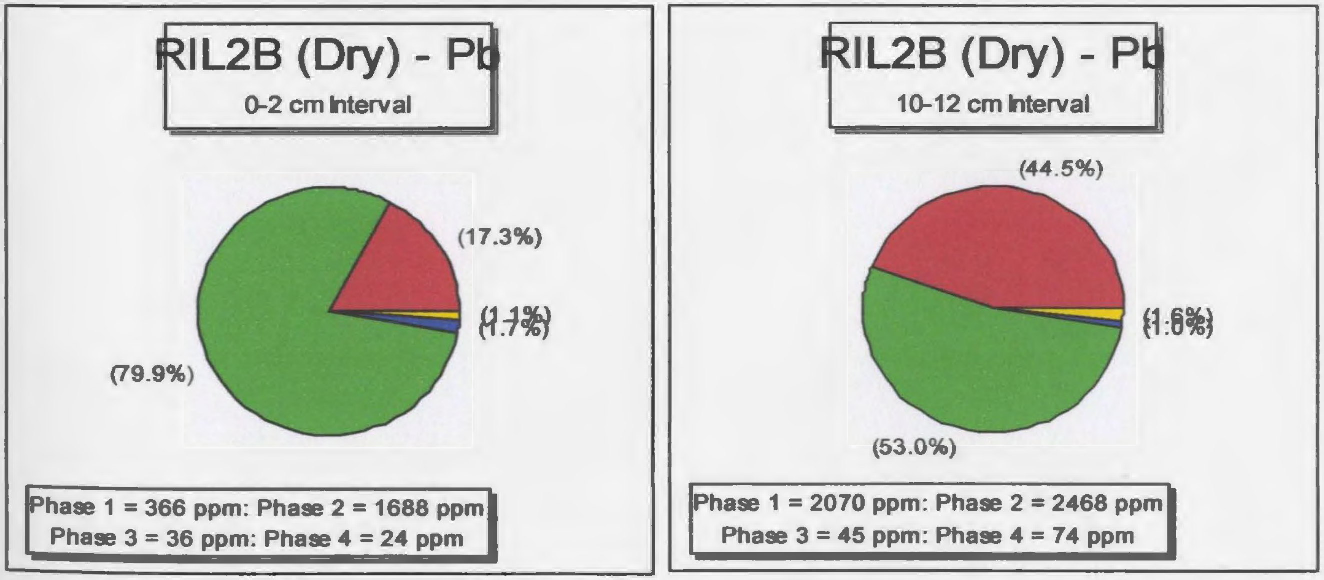

Figure 4.10 Sequential extraction of Pb on selected intervals (0-2 cm, 10-12 cm) of lake sediment core RIL2B (Dry)

centimeters of sediment as was observed with Cu. The difference was that the amount of Pb that reported to the exchangeable/carbonate phase decreased significantly from 1169 ppm to 366 ppm whereas the amount of Pb that reported to the Fe/Mn phase increased slightly from 1519 ppm to 1688 ppm. Sediment below 24 cm had 0-2 ppm Pb reporting to phase 1 and 22-32 ppm Pb reporting to phase 2.

The sequential element analysis indicated significant amount of Zn reported to the first three phases for the contaminated upper sections of the core (Figs. 4.11 and 4.12). For the 0-2 cm interval, 37.2% of the Zn (317 ppm) reported to Phase 1, 20.3% of the Zn (173 ppm) reported to Phase 2, 32.2% of the Zn (275 ppm) reported to Phase 3, and 10.3% of the Zn (88 ppm) reported to Phase 4. For the section with the highest zinc concentration (10-12 cm), 12.1% of the Zn (1189 ppm) reported to Phase 1, 6.1% of the Zn (597 ppm) reported to Phase 2, 80.0% of the Zn (7832 ppm) reported to Phase 3, and only 1.8% of the Zn (172 ppm) reported to Phase 4. For the section with the highest concentration of zinc reporting to the exchangeable/carbonate phase (8-10 cm), 23.3% of the Zn (2160 ppm) reported to Phase 1, 7.4% of the Zn (691 ppm) reported to Phase 2, 67.5% of the Zn (6275 ppm) reported to Phase 3, and only 1.8% of the Zn (166 ppm) reported to Phase 4. From the 4-6 cm interval to the top of the sediment core (0-2 cm), the amount of Zn that reported to

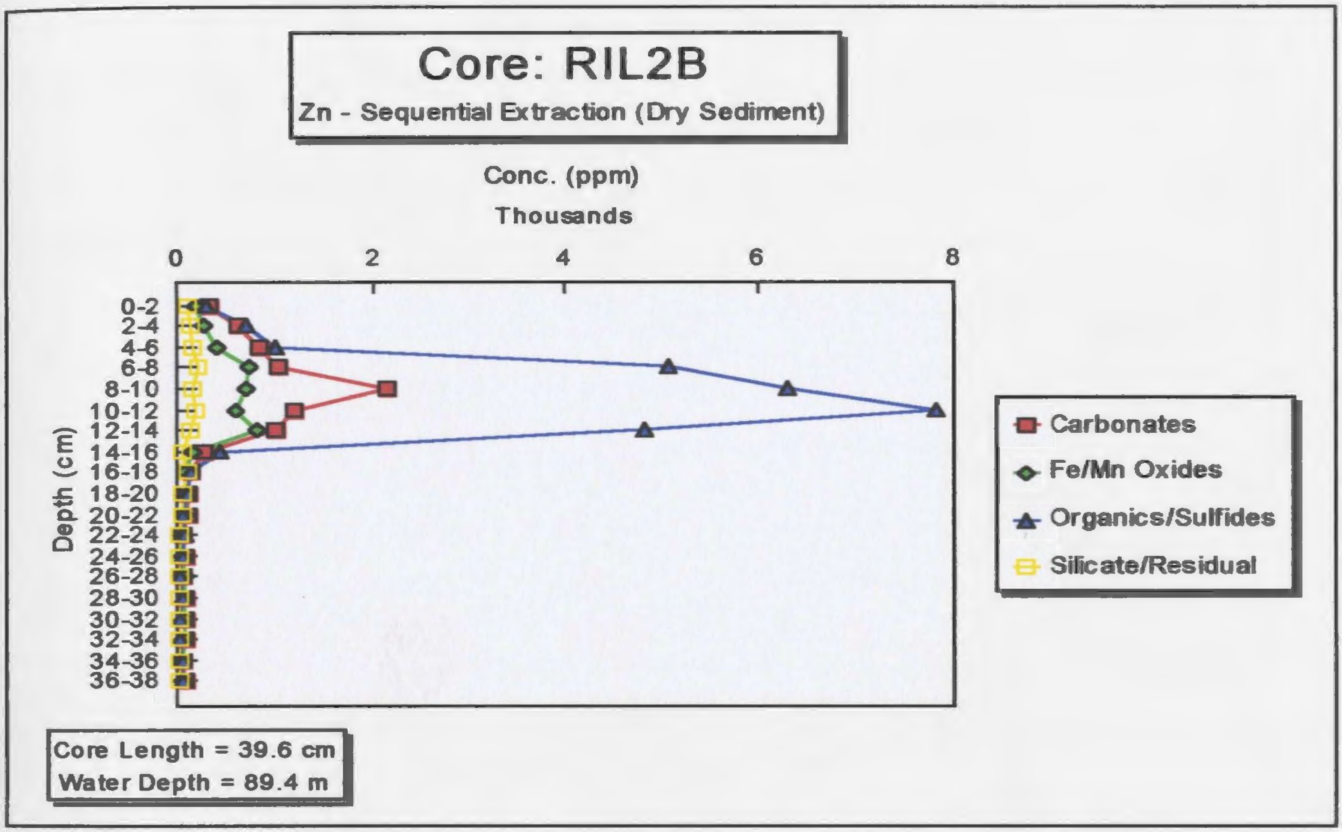

Figure 4.11 Sequential extraction of Zn on core RIL2B (Dry)

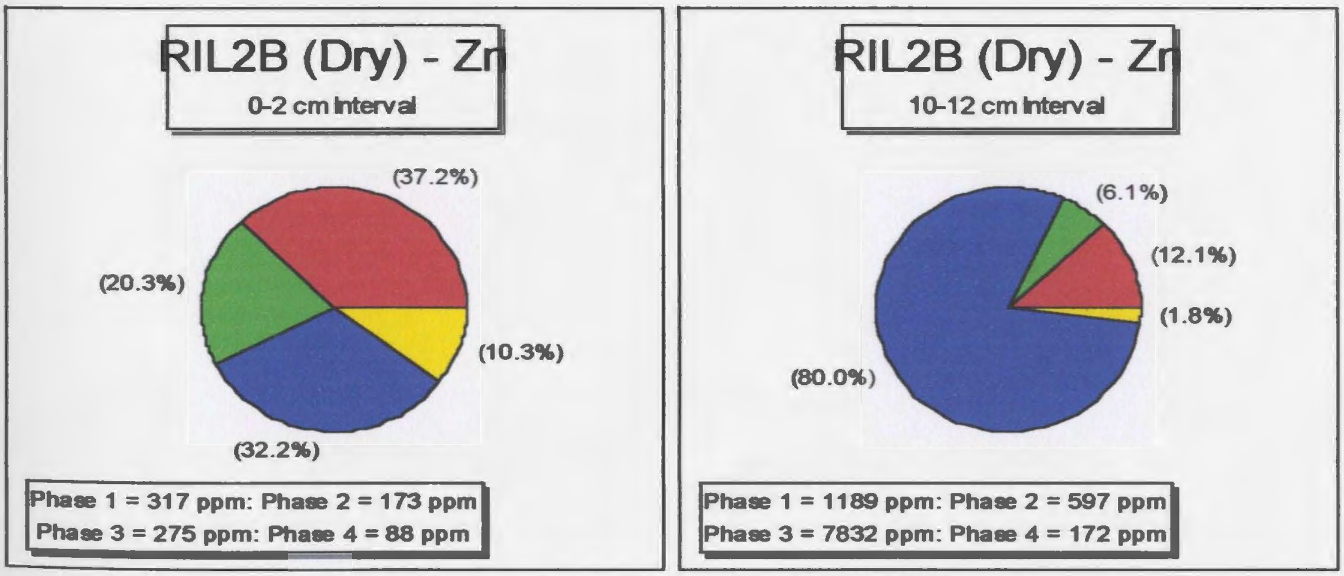

Figure 4.12 Sequential extraction of Zn on selected intervals (0-2 cm, 10-12 cm) of lake sediment core RIL2B (Dry)

the first two phases decreased. The Zn decreased from 836 ppm to 317 ppm and from 391 ppm to 173 ppm in phases 1 and 2, respectively. Sediment below 24 cm had 50-67 ppm Zn reporting to phase 1 and 38-65 ppm Zn reporting to phase 2.

The upper sediment intervals down to approximately 20 cm showed excellent correlation for base metals Cu, Pb and Zn between the results of the sum of the four sequential extraction phases and the results of the total element analysis, as reported in Appendix C (Figure 4.13). In the upper 20 cm, the largest variation from the total element analysis was 9.7% for Cu (0-2 cm), 9.9% for Pb (18-20 cm) and 9.3% for Zn (16-18 cm).

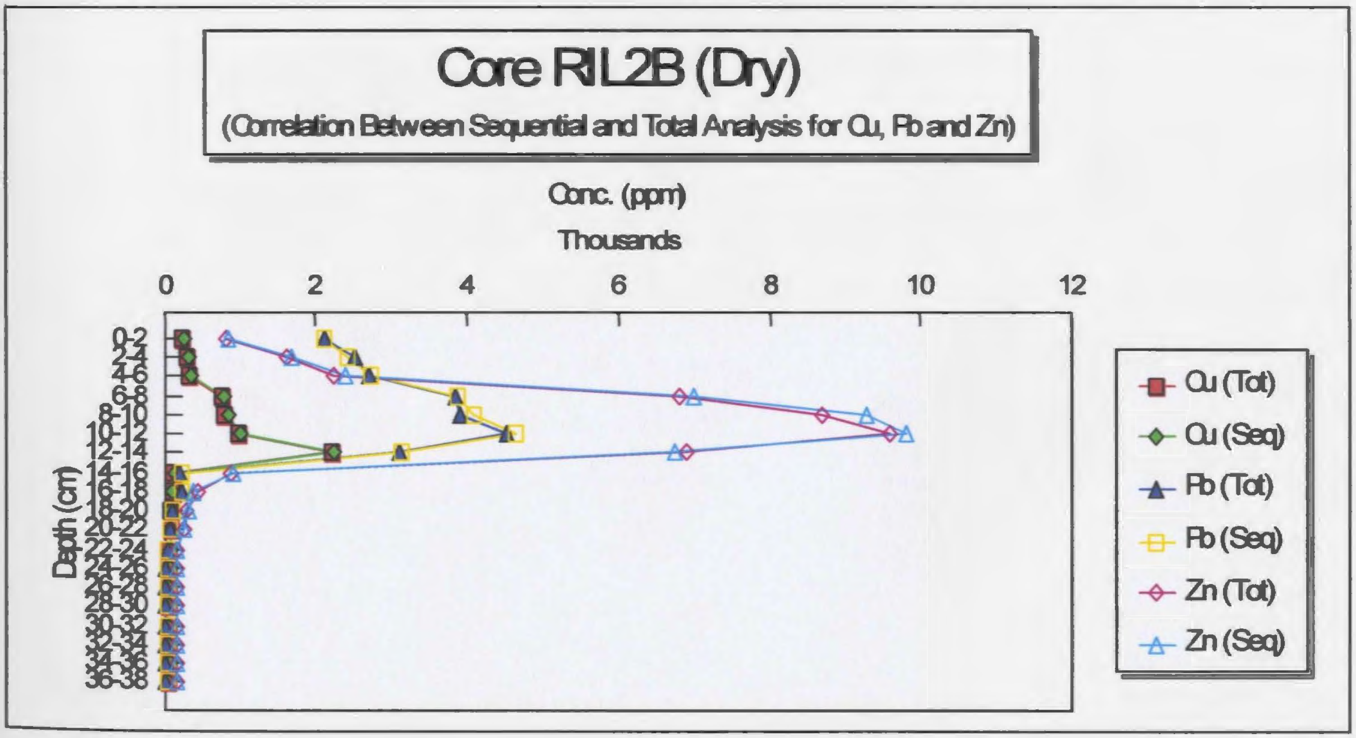

Figure 4.13 Comparison of the total element analysis of Cu, Pb and Zn with the sum of the four sequential extraction phases of lake sediment core RIL2B (Dry)

4.2.2 Red Indian Lake Core RIL2B (Wet)

For reasons previously mentioned on core RIL2B (Dry), the discussion of results were primarily limited to the elevated upper segments.

Analysis for the upper 'wet' sediment intervals down to approximately 20 cm did not correlate as well as the results for the 'dry' core for the base metals Cu, Pb and Zn between the results of the sum of the four sequential extraction phases and the results of the total element analysis, as reported in Appendix C (Figure 4.14).

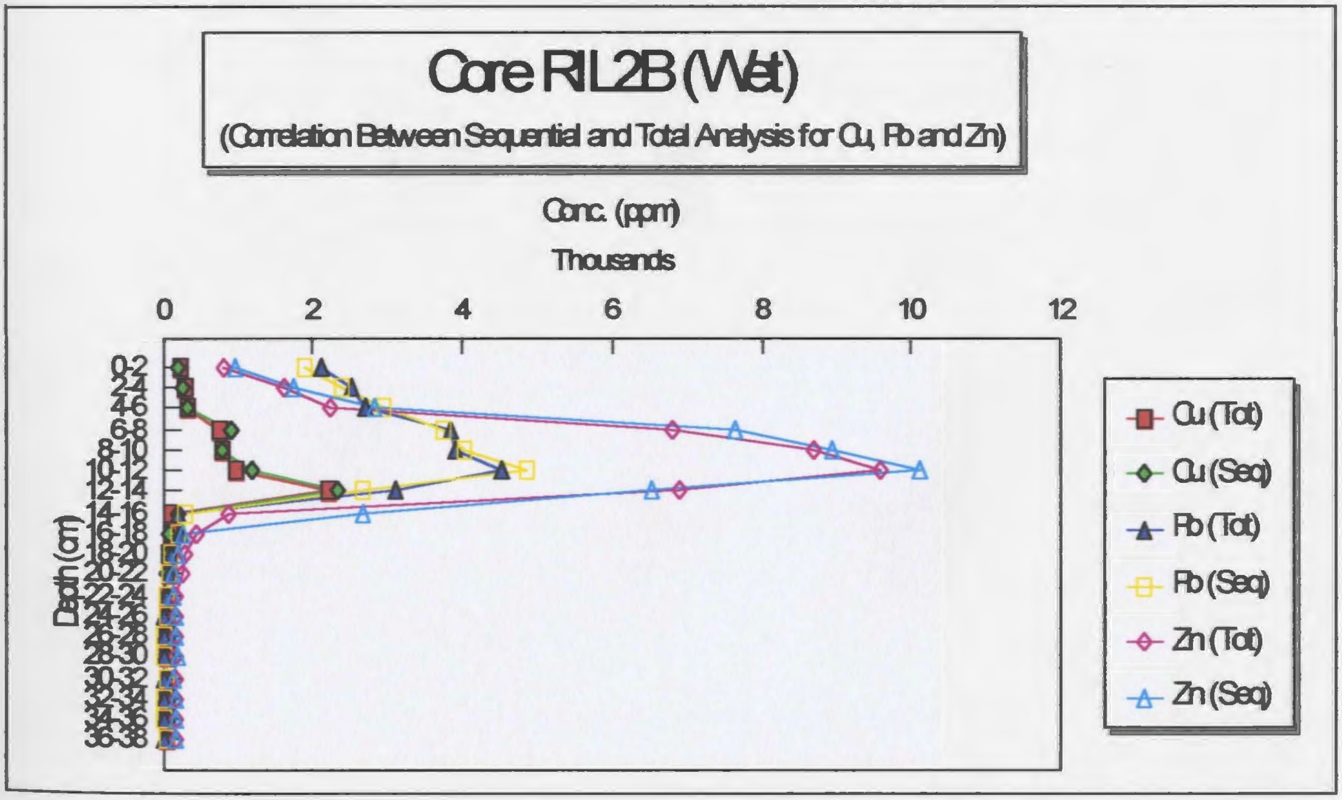

Figure 4.14 Comparison of the total element analysis of Cu, Pb and Zn with the sum of the four sequential extraction phases of lake sediment core RIL2B (Wet)

The variation between the sequential element analysis for the 'wet' intervals and the total element analysis of the same interval for Cu, Pb and Zn was generally below 20-25%, with some sections showing significantly higher variations. The total metal concentrations for Cu, Pb and Zn on the 14-16 cm interval were 107 ppm, 203 ppm and 862 ppm. For the 'wet' sediment extraction on the 14-16 cm interval the sum of the four phases for Cu, Pb and Zn were 194 ppm, 270 ppm and 2677 ppm, respectively, resulting in a variation from the total element analysis of 81 for Cu, 33% for Pb and 210% for Zn.

From the chemical profile of this core, it appeared that mining began sometime during the deposition of the 14-16 cm interval. The dramatic differences observed between the Cu, Pb and Zn concentrations in the 'wet' sediment extraction and the total element analysis in the 14-16 cm interval was likely a result of the two sub-samples of the same interval not being identical. The reason for this was that although the total element and sequential element analysis for core RIL2B (Dry) were performed on the same dried, homogenous samples, the sequential element analysis for core RIL2B (Wet) was performed on discrete 1 cc subsections within the 2 cm intervals.

The sequential element analysis indicated significant amount of Cu reported to the first three phases for the contaminated upper sections of the core (Figs. 4.15 and 4.16).

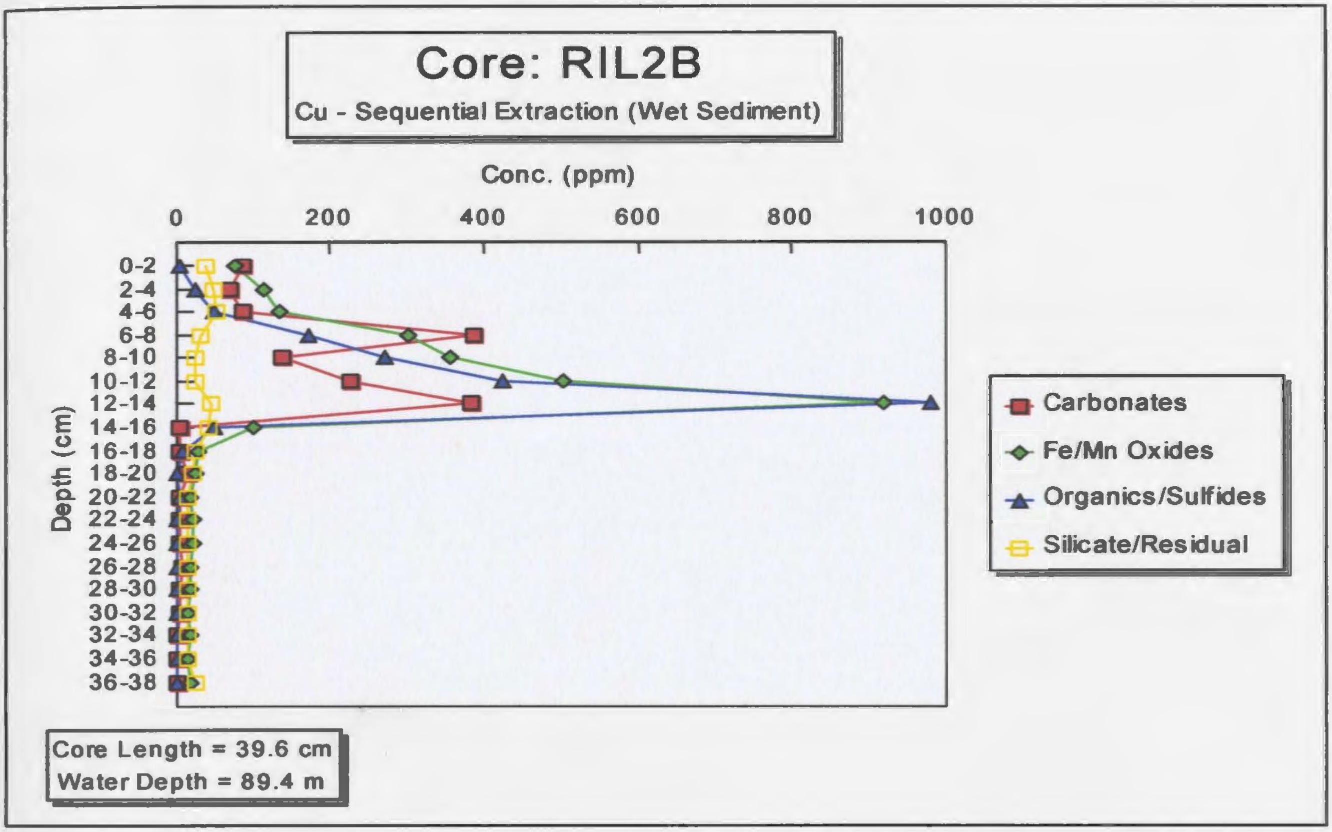

Figure 4.15 Sequential extraction of Cu on core RIL2B (Wet)

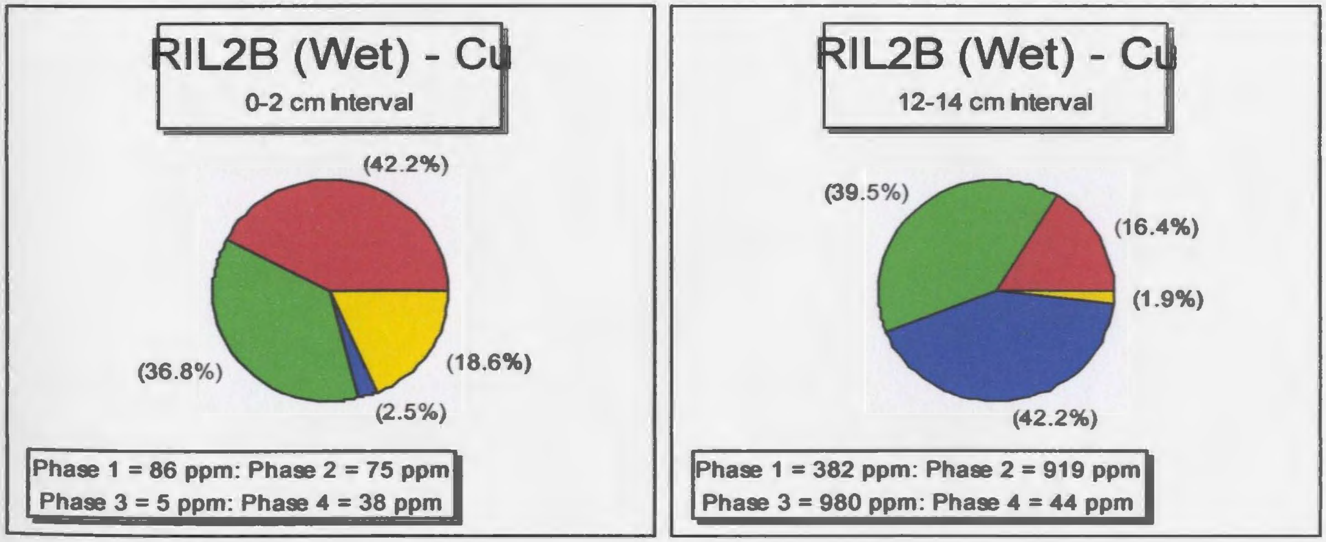

Figure 4.16 Sequential extraction of Cu on selected intervals (0-2 cm, 12-14 cm) of lake sediment core RIL2B (Wet)

For the 0-2 cm interval, 42.2% of the Cu (86 ppm) reported to Phase 1, 36.8% of the Cu (75 ppm) reported to Phase 2, 2.5% of the Cu (5 ppm) reported to Phase 3, and 18.6% of the Cu (38 ppm) reported to Phase 4. For the section with the highest copper concentration (12-14 cm), 16.4% of the Cu (382 ppm) reported to Phase 1, 39.5% of the Cu (919 ppm) reported to Phase 2, 42.2% of the Cu (980 ppm) reported to Phase 3, and only 1.9% of the Cu (44 ppm) reported to Phase 4. From the 4-6 cm interval to the top of the sediment core (0-2 cm), the amount of Cu that reported to the exchangeable/carbonate phase remained fairly constant (86-88 ppm) whereas the amount of Cu that reported to the Fe/Mn oxide phase decreased from 135 ppm to 75 ppm.

The sequential element analysis indicated significant amount of Pb reported to the first two phases for the contaminated upper sections of the core (Figs. 4.17 and 4.18). For the 0-2 cm interval, 36.6% of the Pb (697 ppm) reported to Phase 1, 61.5% of the Pb (1172 ppm) reported to Phase 2, 0.9% of the Pb (17 ppm) reported to Phase 3, and 1.0% of the Pb (19 ppm) reported to Phase 4. For the section with the highest lead concentration (10-12 cm), 42.3% of the Pb (2057 ppm) reported to Phase 1, 55.4% of the Pb (2698 ppm) reported to Phase 2, 0.9% of the Pb (45 ppm) reported to Phase 3, and 1.4% of the Pb (67 ppm) reported to Phase 4. From the 4-6 cm interval to the top of the

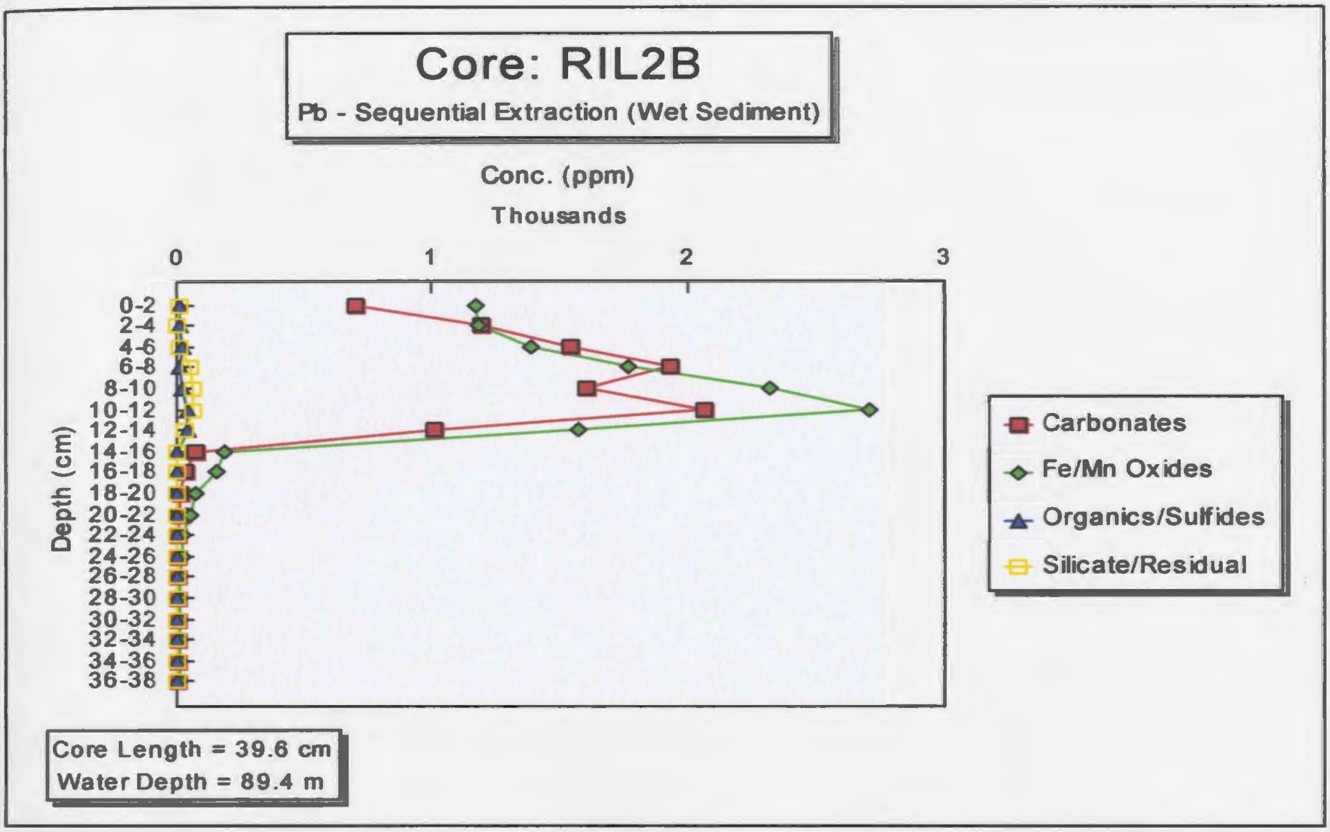

Figure 4.17 Sequential extraction of Pb on core RIL2B (Wet)

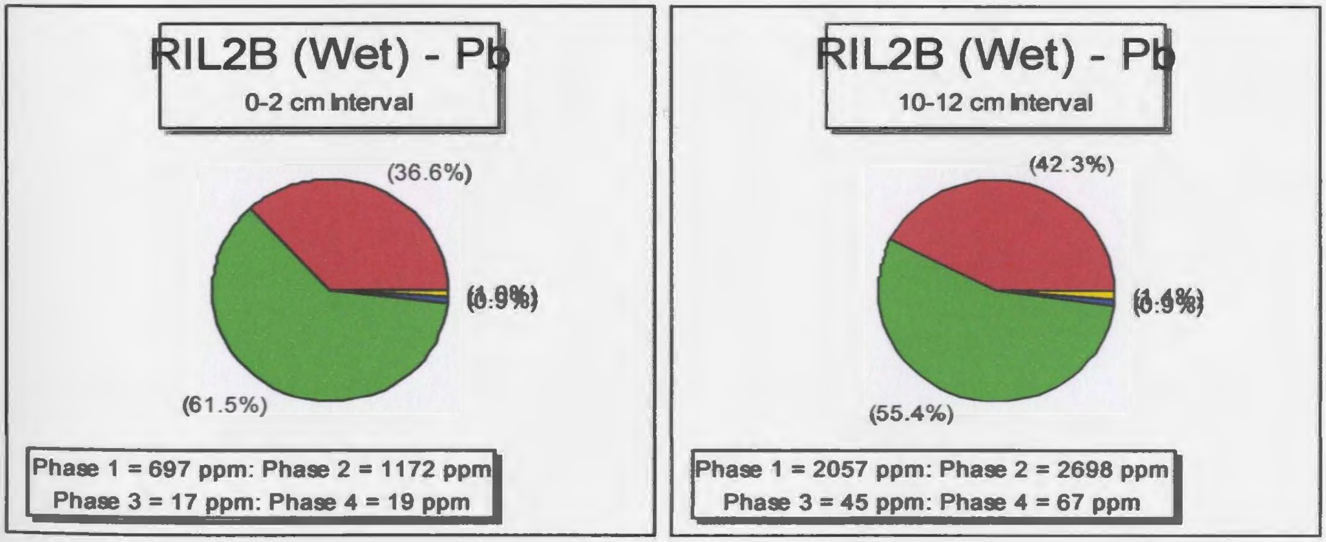

Figure 4.18 Sequential extraction of Pb on selected intervals (0-2 cm, 10-12 cm) of lake sediment core RIL2B (Wet)

sediment core (0-2 cm), the amount of Pb that reported to the first two phases decreased. For the first phase, the Pb decreased from 1537 ppm to 697 ppm. For the second phase, the Pb decreased from 1382 ppm to 1172 ppm.

The sequential element analysis indicated significant amount of Zn reported to the first three phases for the contaminated upper sections of the core (Figs 4.19 and 4.20), with the majority of the Zn reporting to Phases 1 and 3 for the heavily contaminated mid-sections. For the 0-2 cm interval, 54.4% of the Zn (524 ppm) reported to Phase 1, 19.1% of the Zn (184 ppm) reported to Phase 2, 5.2% of the Zn (50 ppm) reported to Phase 3, and 21.4% of the Zn (206 ppm) reported to Phase 4. For the section with the highest zinc concentration (10-12 cm), 9.5% of the Zn (967 ppm) reported to Phase 1, 3.9% of the Zn (394 ppm) reported to Phase 2, 82.9% of the Zn (8399 ppm) reported to Phase 3, and 3.6% of the Zn (368 ppm) reported to Phase 4. For the section with the highest concentration of zinc reporting to the exchangeable/carbonate phase (8-10 cm), 30.0% of the Zn (2675 ppm) reported to Phase 1, 4.3% of the Zn (381 ppm) reported to Phase 2, 63.7% of the Zn (5685 ppm) reported to Phase 3, and only 2.1% of the Zn (185 ppm) reported to Phase 4. From the 4-6 cm interval to the top of the sediment core (0-2 cm), the amount of Zn that reported to the first two phases decreased. For the first phase the Zn decreased from 1534 ppm

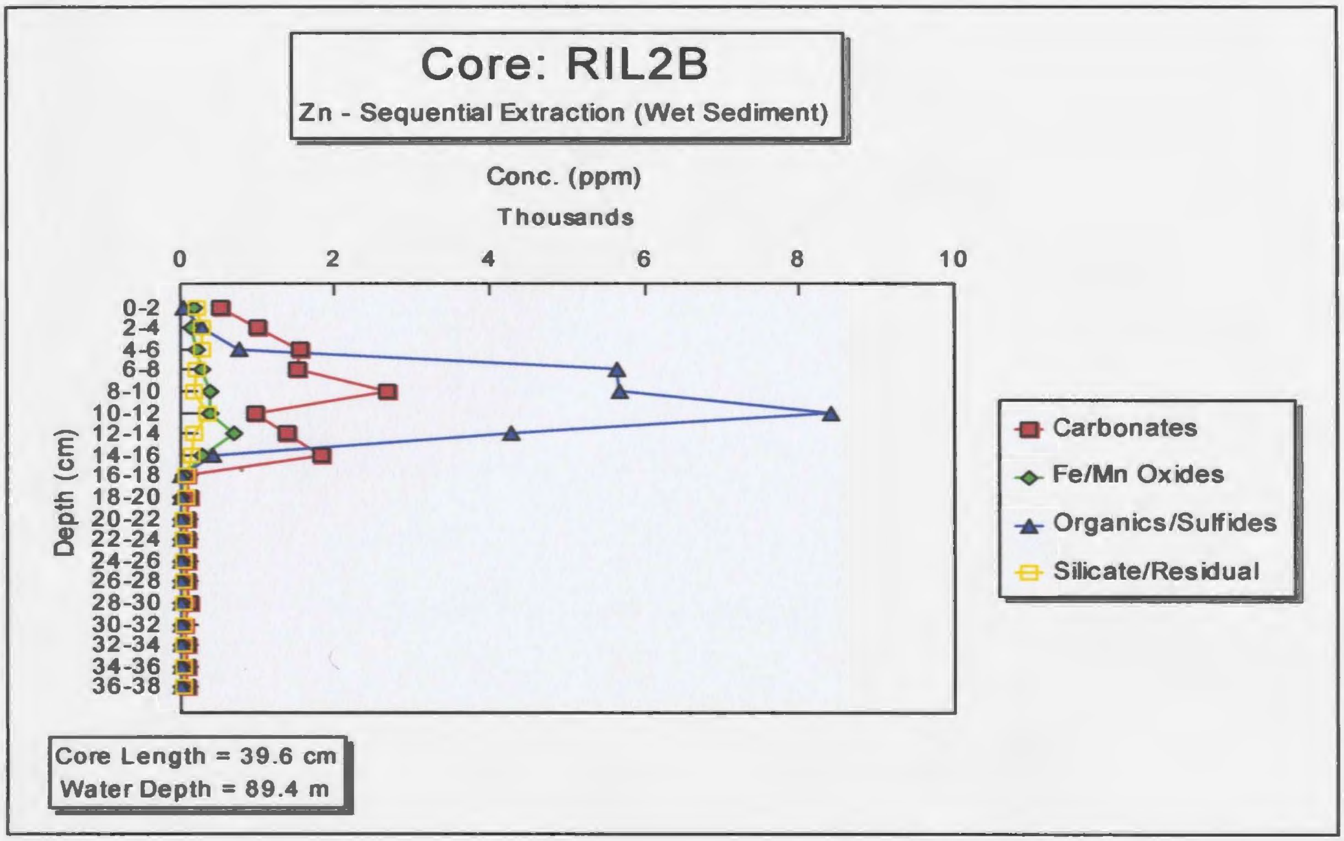

Figure 4.19 Sequential extraction of Zn on core RIL2B (Wet)

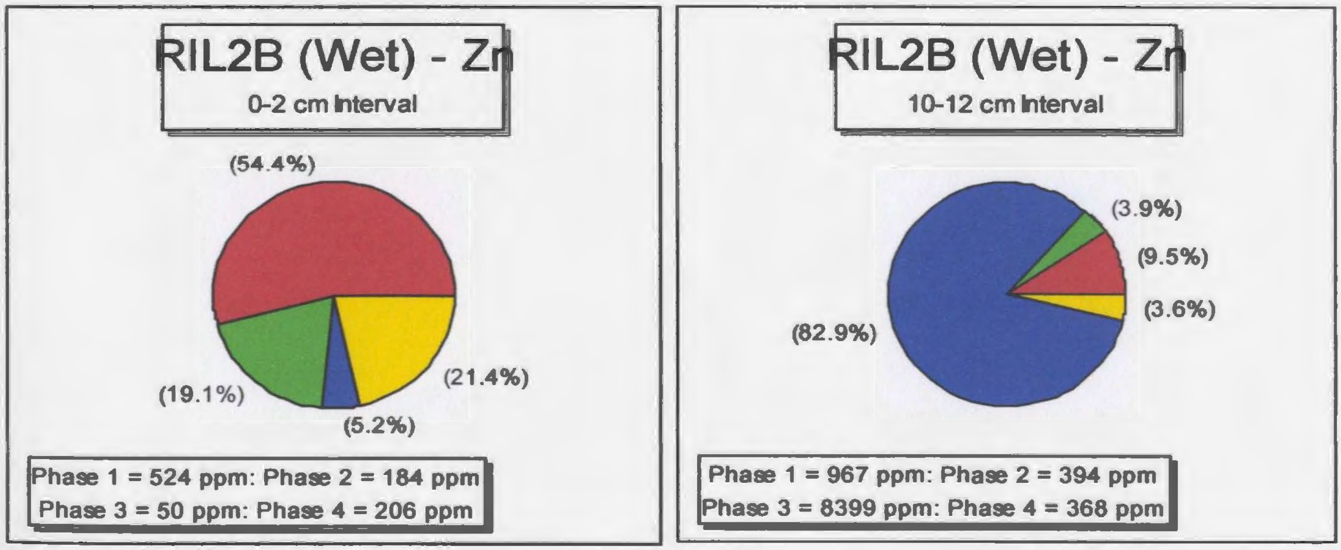

Figure 4.20 Sequential extraction of Zn on selected intervals (0-2 cm, 10-12 cm) of lake sediment core RIL2B (Wet)

to 524 ppm. For the second phase the Zn decreased from 220 ppm to 184 ppm.

The Cu, Pb and Zn values below 24 cm (background) for the first and second phases were 10-100 times lower than the upper elevated intervals.

4.3 Quality Control and Quality Assurance

For total trace element analysis, QA/QC procedures employed by the Geochemical Laboratory, NF Department of Mines and Energy, were strictly adhered to. This involved the random inclusion of blind duplicates among all cores at sample positions 10, 30, 50, ..., various standard reference materials inserted at the digestion stage (LKSD 1-4 and MP-1A) at sample positions 20, 40, 60, ..., blanks and reference standards. The reference standards used were the middle calibration standards of the ICP-OES. The results of the duplicate samples and standard reference materials (LKSD 1-4) for total trace element analysis are given in Appendix E. At concentrations at least a decade above the detection limits, relative standard deviations (RSDs) are generally below 5%.

Each pair of cores sampled at the same sites were very similar in all the element profiles (Figs. 4.1 and 4.2, Figs. 4.3 and 4.4, and Figs. 4.5 and 4.6 illustrated the Cu, Pb and Zn similarities). This confirmed the sampling approach and the chemical analysis by ICP-OES as being highly reproducible.

Four 0.5 gm samples of SRM MP-1A (CANMET Report 82-14E) were also included with the 'dry' and 'wet' sequential extraction procedures for quality control. The mean and standard deviation, accompanied by the certified total concentrations for Cu, Pb and Zn were given in Tables 4.1 - 4.3, respectively. Perhaps the most striking feature of the results was the excellent precision evident throughout, regardless of the significant number of manipulations involved in the sequential extraction procedure. For Cu, Pb and Zn, most values for precision were in the 1-5 % RSD range.

Accuracy was difficult to assess in the absence of SRMs 'certified' for their phase-selective elemental concentrations. However, comparison of the summed results of the four phases with the certified values for the total concentrations provided some estimate of overall accuracy. It was shown from Tables 4.1 - 4.3 that these two values agree within their respective standard deviations in the vast majority of cases, with less than 10% variation from the recommended values for Cu, Pb and Zn.

Table 4.1 Results (Mean, Std. Dev. and RSD) for Cu: Application of Sequential Leach Procedure to SRM MP-1A

Copper (Cu)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Sum (ppm)	Recomm. Value
MP-1A	806	1285	9404	2584	14079	14400
MP-1A	796	1284	9504	2575	14159	14400
MP-1A	805	1246	9179	2695	13925	14400
MP-1A	826	1233	9399	2656	14114	14400
Mean	**808**	**1262**	**9372**	**2628**	**14069***	**14400**
Std Dev	**12.7**	**26.5**	**137**	**57.8**	**102**	
RSD	**1.57**	**2.10**	**1.46**	**2.20**	**0.72**	

* 2.30 below the recommended value.

Table 4.2 Results (Mean, Std. Dev. and RSD) for Pb: Application of Sequential Leach Procedure to SRM MP-1A

Lead (Pb)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Sum (ppm)	Recomm. Value
MP-1A	1471	30377	9084	4348	45280	43300
MP-1A	1451	31147	8790	4241	45629	43300
MP-1A	1486	29345	9916	4827	45574	43300
MP-1A	1474	28204	9901	4679	44258	43300
Mean	**1471**	**29768**	**9423**	**4524**	**45185***	**43300**
Std Dev	**14.5**	**1278**	**574**	**275**	**637**	
RSD	**0.99**	**4.29**	**6.08**	**6.08**	**1.41**	

* 4.35% above the recommended value.

Table 4.3 Results (Mean, Std. Dev. and RSD) for Zn: Application of Sequential Leach Procedure to SRM MP-1A

Zinc (Zn)	**Phase 1 (ppm)**	**Phase 2 (ppm)**	**Phase 3 (ppm)**	**Phase 4 (ppm)**	**Sum (ppm)**	**Recomm. Value**
MP-1A	22064	3992	149540	31087	206683	190200
MP-1A	24764	4001	147997	29654	206416	190200
MP-1A	24070	3681	146771	31397	205919	190200
MP-1A	23161	3419	146028	31276	203884	190200
Mean	**23515**	**3773**	**147584**	**30854**	**205726***	**190200**
Std Dev	**1169**	**279**	**1536**	**810**	**1268**	
RSD	**4.97**	**7.40**	**1.04**	**2.62**	**0.62**	

* 8.16% above the recommended value.

Chapter 5: Discussion and Conclusion

5.1 Summary - Total Base Metal Analysis

Measurement of chemical changes in lake sediment cores from the Buchans area has been effective for discerning anthropogenic effects associated with a major base metal mining operation that produced high grade ore from 1928 to 1984. In Buchans Lake, total element analysis of Cu, Pb and Zn showed elevated levels in the upper sediment intervals approximately an order of magnitude higher than in the lower, 'background' sediment intervals. For both lake sediment cores in Buchans Lake, the only subtle color change at approximately 21 cm can be inferred as the commencement of mining in the area. The observed change in sediment color was a result of the town development and mining operations including land clearing and overburden stripping which resulted in increased erosion and runoff as well as airborne dust from general mining operations.

For Red Indian Lake, the site where lake sediment cores RIL1A and RIL1B were collected showed that the elevated Cu, Pb and Zn concentrations in the upper contaminated sediment intervals of the cores were significantly enhanced, with the highest values of Cu (4270 ppm) and Pb (2993 ppm) reported in the 20-22 cm interval of lake sediment core RIL1A and the highest value of Zn (12,576 ppm) reported in the 20-22 cm interval of lake sediment core RIL1B. For the other site sampled on Red Indian Lake, the highest concentration of Cu (2205 ppm) was reported in the 12-14 cm interval of lake sediment core RIL2B. The highest concentration of Pb (4527 ppm) was reported in the 10-12 cm interval of lake sediment core RIL2B. The highest concentration of Zn (9732 ppm) was reported in the 10-12 cm interval of lake sediment core RIL2A. The elevated Cu, Pb and Zn concentrations in the lake sediments are a result of tailings from the mining operation being discharged directly into Buchans Brook and subsequently into Red Indian Lake. This was the practice of tailings disposal since the commencement of mining operations in 1928 until 1966. Since 1966, tailings were contained within a series of on-site tailings ponds. However, during its operation and since its closure, this mine has discharged effluents which exceed the limits of the *Metal Mining Liquid Effluent Regulations, 1977* (MMLER).

Whitford (2001) has conducted an aquatic habitat survey of Buchans Brook and has found that liquid effluents were discharged to Buchans Brook from several locations during the mine operation. Presently, releases from the tailings ponds continue to flow to Buchans Brook via drainage known locally as Simms Brook. Also, mine effluent from the Oriental mine site and metal contaminated surface drainage flow into Buchans Brook.

Over time, monitoring has been conducted at various sites in Simms Brook and Buchans Brook to determine pH and levels of dissolved copper, lead and zinc. The levels of dissolved metals have decreased since the mine closure but those for zinc still exceed the provincial criteria of 0.5 ppm as set out in the *Environmental Control Water and Sewer Regulations*, NEWFOUNDLAND REGULATION 1078/96. Recent data indicate that the highest zinc value reported in Buchans Brook (7.7 ppm) was at the Oriental Bridge sampling site during October, 2000.

Both lake sediment cores RIL1A and RIL1B had a distinct color change at approximately 23 cm and both lake sediment cores RIL2A and RIL2B had a distinct color change at approximately 15 cm. These color changes in the sediment core can be inferred as the commencement of mining operations in the area. The numerous subtle color changes observed above the distinct color change in all four cores are a result of numerous factors. Primarily it is a result of the different tailings from the various orebodies being deposited into Buchans Brook during the various production phases of the mining operation, as well as increased erosion and runoff due to land clearing and airborne dust from general mining operations. At various times throughout the mine life multiple orebodies were mined simultaneously generating variable tailings which were deposited in Buchans Brook, resulting in the subtle color changes that were observed throughout the upper sections of the cores.

The first deposit to be mined was the highest grade Lucky Strike deposit which was mined from 1928 until 1958. This deposit was mined again from 1972 to 1979 but only in small tonnages. The largest tonnages mined from the Lucky Strike deposit were in the early 1930s. Consequently, as a result of early constraints on process extraction, poor tailings management until 1966, and the fact that the highest grade deposits were mined first, the highest values of Cu, Pb and Zn reported in the lake sediment cores from Red Indian Lake were observed in the intervals just above the lower 'background' levels (pre-mining).

The 0-2 cm sediment intervals of all lake sediment cores in Red Indian Lake contain some sediment deposited since mine closure. From cores RIL1A and RIL1B it appears that the levels of Cu (502 ppm and 487 ppm, respectively) and Zn (1961 ppm and 1894 ppm, respectively) are declining but the level of Pb (2194 ppm and 2147 ppm, respectively) is remaining relatively constant (Figures 4.3 and 4.4). From cores RIL2A and RIL2B it appears that the levels of Cu (225 ppm and 236 ppm, respectively), Pb (2050 ppm and 2102 ppm, respectively) and Zn (839 ppm and 802 ppm, respectively) are all declining (Figures 4.5 and 4.6). However, all values for Cu, Pb and Zn in the 0-2 cm interval of the four lake sediment cores in Red Indian Lake exceed the Canadian Council of Ministers of the Environment (CCME) Canadian Soil Quality Guidelines. For Industrial use, the maximum recommended Soil Quality Guidelines for Cu, Pb and Zn are 100 ppm, 400 ppm and 380 ppm respectively. Until the sediment that has been (and is currently being) deposited since mine closure can be isolated and analyzed, it remains very difficult to determine the extent to which the levels of Cu, Pb and Zn are actually decreasing.

In 1992 Environment Canada started a process to revise the MMLER and they decided that the impacts of metal mining effluent on the aquatic environment needed to be assessed. As a result, the Assessment of the Aquatic Effects of Mining in Canada (AQUAMIN) was initiated on the basis of that recommendation. To conduct AQUAMIN it was necessary to obtain as much information as possible. Various groups, including mining companies, the Mining Association of Canada, Provincial agencies and Federal Government agencies across Canada were asked to submit relevant documents. In total, 18 case studies and numerous non-case studies of various mining operations across Canada were prepared to assess the effects on the receiving environments. The final report was prepared in April, 1996 and it was determined that changes to sediment quality were reported in most case studies where adequate sediment surveys were undertaken. The main conclusion from this review of aquatic effects is that a variety of conditions (e.g. nature of mining operations and the receiving environment) affected the magnitude and extent of effects observed.

For example, the *AQUAMIN Supporting Document II: Regional Syntheses* showed that Newfoundland Zinc operated a mine from 1975 until 1989 in western Newfoundland and produced nearly 7 million tonnes of zinc ore from both open pit and underground mines. As a result of the low levels of pyrite in the ore and the buffering capacity of the carbonate host rock, acid mine drainage and resulting metal contamination of the receiving waters were never a problem at this site. Conversely, Lac Matagami mine site located in central Quebec included many base metal mines. Sediment analysis showed that the mining activities had an impact in terms of contaminating the beds of watercourses over a distance of several kilometers downstream from the discharge sites. The data demonstrated that there were high accumulations of zinc (up to 6000 ppm) and, to a lesser extent, copper in the sediments near the mine sites.

Furthermore, the Flin Flon deposits which straddle the Manitoba-Saskatchewan border have produced 62 million tonnes of Cu and Zn ore from 1930 to 1992. Conversations with Wayne Fraser, Director of Environmental Services, Hudson Bay Mining and Smelting Company Limited, who have mined the deposits, have indicated that proper dam installations in their tailings ponds since commencement of mining in 1930 have resulted in effective tailings disposal. As a result, only slightly elevated levels of base metals were detected in lake sediments of the downstream receiving water bodies.

AQUAMIN reviewers noted that there were major difficulties in obtaining representative sediment samples and concluded that quantitative estimates of the magnitude and extent of effects on sediments were not possible for most mine sites. Difficulties encountered included sediment particle size, a lack of appropriate reference stations, sampling problems, and the influence of geochemical properties of individual metals (e.g. tailings, different orebodies, ore treatment technologies and the receiving environment).

5.2 Summary - Sequential Base Metal Analysis

Sequential extraction schemes have been developed in the past 25 years to determine how trace metals are bound in sediments. However, the lack of uniformity in these various schemes does not allow for adequate comparison of results nor for the procedures to be validated. Indeed, the results obtained by sequential extraction are operationally defined. That is, the 'forms' of the metals are defined by the method and the distinctive procedure employed.

In this study, the most 'labile' fraction contains the metals associated with the Exchangeable/Carbonate phase. For the sequential extraction performed on both the 'wet' and 'dry' sediment intervals of lake sediment core RIL2B, a significant amount of Cu, Pb and Zn was associated with this fraction.

For lake sediment core RIL2B, the largest Cu enrichment occurred in the 12-14 cm interval. For the enriched sediment, significant amount of Cu reported to the first three phases with only a small fraction reporting to the fourth phase. For the 'dry' sediment, 715 ppm (31.9%) reported to the Exchangeable/Carbonate phase, 531 ppm (23.7%) reported to the Fe/Mn oxide phase, 959 ppm (42.8%) reported to the Organic/Sulphide phase, and only 37 ppm (1.7%) reported to the Silicate phase in the 12-14 cm interval. For the same interval of the 'wet' sediment, 382 ppm (16.4%) reported to the Exchangeable/Carbonate phase, 919 ppm (39.5%) reported to the Fe/Mn oxide phase, 980 ppm (42.2%) reported to the Organic/Sulphide phase, and only 44 ppm (1.9%) reported to the Silicate phase. Bearing in mind the inherent limitations in drawing comparisons between the 'wet' and 'dry' sediments, it appears that the drying process has very little effect on the amount of Cu reporting to the Organic/Sulphide or Silicate phases in this sediment interval. However, drying appears to significantly increase the amount of Cu reporting to the Exchangeable/Carbonate phase and significantly decreases the amount of Cu reporting to the Fe/Mn oxide phase in this sediment interval. This trend of increasing the amount of Cu reporting to the first phase as a result of drying the sediments is observed throughout most of the enriched upper sections of the core as shown in Figure 5.1.

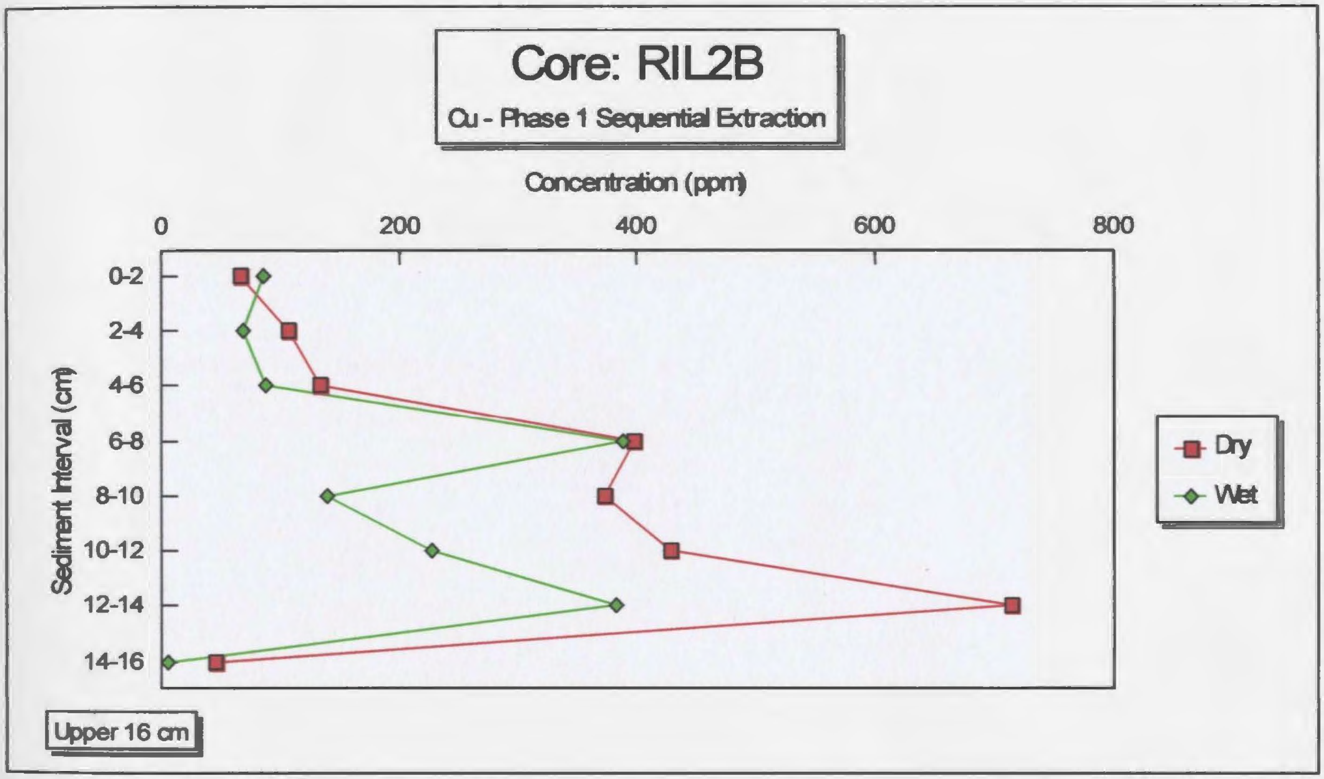

Figure 5.1 Cu associated with the Exchangeable/Carbonate phase in the upper 16 cm of lake sediment core RIL2B (wet and dry)

For lake sediment core RIL2B, the largest Pb enrichment occurred in the 10-12 cm interval. For the enriched sediment, significant amount of Pb reported to the first two phases with only a small fraction reporting to the last two phases. For the 'dry' sediment, 2070 ppm (44.5%) reported to the Exchangeable/Carbonate phase, 2468 ppm (53.0%) reported to the Fe/Mn oxide phase, and only 45 ppm (1.0%) reported to the Organic/Sulphide phase and 74 ppm (1.6%) reported to the Silicate phase in the 10-12 cm interval. For the same interval of the 'wet' sediment, 2057 ppm (42.3%) reported to the Exchangeable/Carbonate phase, 2698 ppm (55.4%) reported to the Fe/Mn oxide phase, and only 45 ppm (0.9%) reported to the Organic/Sulphide phase and 67 ppm (1.4%) reported to the Silicate phase. For this sediment interval, it appears that drying the sediment has virtually no effect on the redistribution of Pb in the various phases.

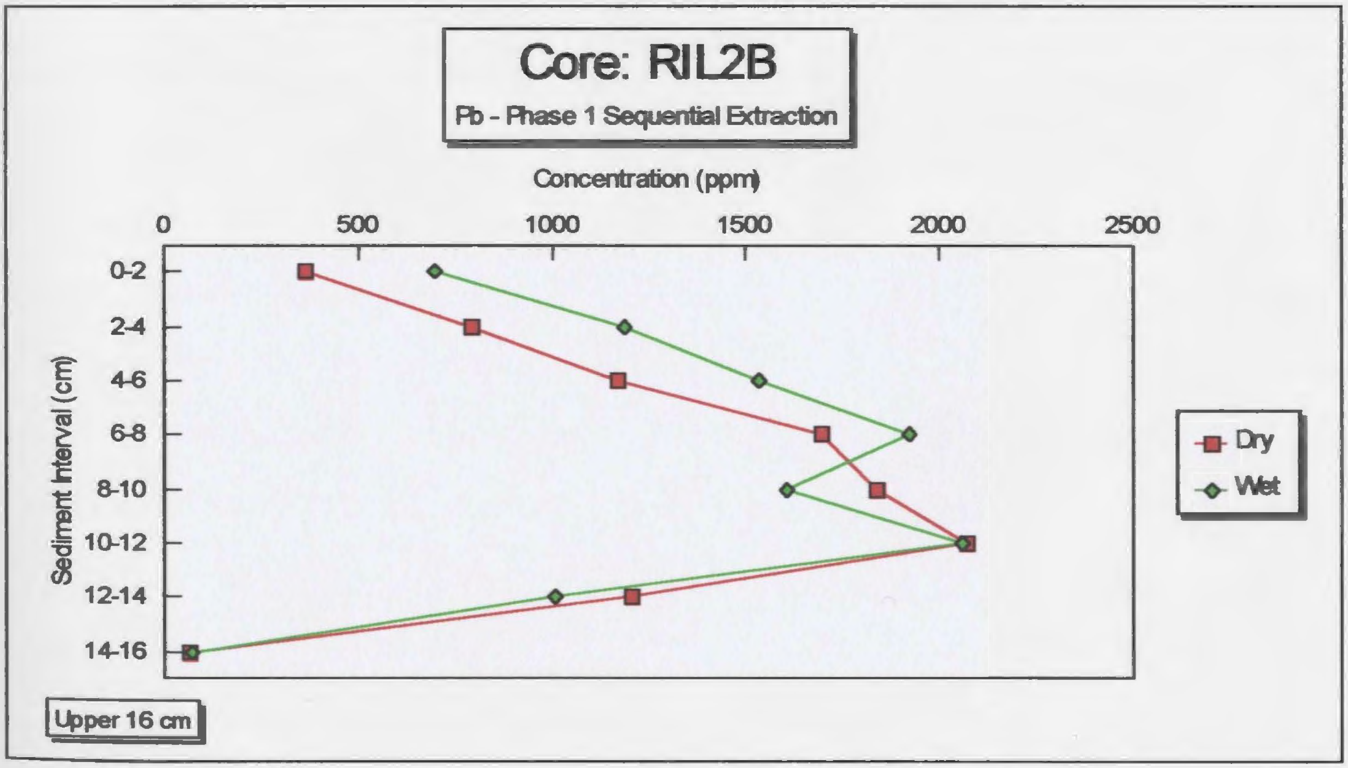

Figure 5.2 Pb associated with the Exchangeable/Carbonate phase in the upper 16 cm of lake sediment core RIL2B (wet and dry)

However, as shown in Figure 5.2, most of the sediment intervals in the upper enriched sections of the core indicate that drying of the sediment appears to slightly decrease the amount of Pb that reports to the first phase.

For lake sediment core RIL2B, the largest Zn enrichment occurred in the 10-12 cm interval. For the enriched sediment, significant amount of Zn reported to the first three phases with the largest amount of Zn associated with the Organic/Sulphide phase. For the 'dry' sediment, 1189 ppm (12.1%) reported to the Exchangeable/Carbonate phase, 597 ppm (6.1%) reported to the Fe/Mn oxide phase, 7832 ppm (80.0%) reported to the Organic/Sulphide phase, and 172 ppm (1.8%) reported to the Silicate phase in the 10-12 cm interval. For the same interval of the 'wet' sediment, 967 ppm (9.5%) reported to the Exchangeable/Carbonate phase, 394 ppm (3.9%) reported to the Fe/Mn oxide phase, 8399 ppm (82.9%) reported to the Organic/Sulphide phase, and 368 ppm (3.6%) reported to the Silicate phase. It appears that drying slightly increases the amount of Zn reporting to the first two phases for this sediment interval.

However, as shown in Figure 5.3, it appears that drying the sediment appears to slightly decrease the amount of Zn reporting to the first phase for all the other upper enriched sediment intervals (0-10 cm and 12-16 cm).

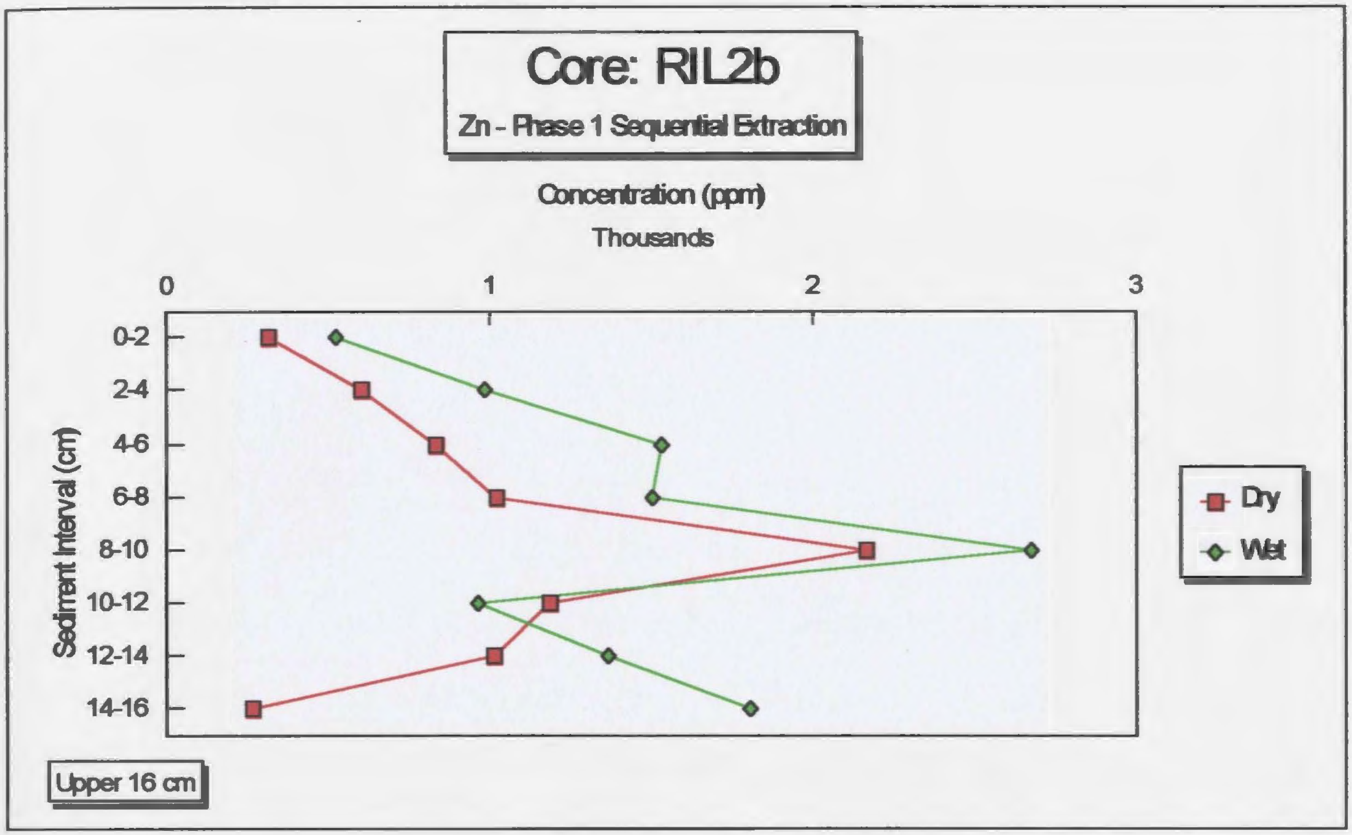

Figure 5.3 Zn associated with the Exchangeable/Carbonate phase in the upper 16 cm of lake sediment core RIL2B (wet and dry)

As mentioned previously, caution must be exercised in drawing conclusions regarding comparisons between the 'wet' and 'dry' sediment samples. Both samples are not identical as the 'dry' sediment is from a dried homogenous 2 cm interval whereas the 'wet' sample is from a unique 1 cc sub-sample extruded within the heterogeneous 2 cm interval immediately upon core processing. Furthermore, there are distinct differences throughout the enriched sediment column of the lake sediment core as a result of different orebodies being mined, and hence different tailings being deposited, at various times throughout the mine life. As well, improvements in ore treatment throughout the mine life resulted in changes to the chemical composition of the tailings that were ultimately deposited into Red Indian Lake. Finally, the use of settling and tailings ponds after 1966 resulted in changes to the metal loadings to Buchans Brook and Red Indian Lake since that time.

Previous studies have shown that drying oxic samples at elevated temperatures (50-100 C) does have a significant redistribution effect on element associations. Oven drying causes instant and major changes in overall sediment equilibrium by converting fractions relevant to trace element binding into highly unstable and reactive forms (Bartlett and James, 1980). Drying of sediments caused changes in the extractability of trace metals which were found to be mostly consistent with their partitioning between Fe- and Mn-oxides, and organic matter (Thomson *et al.*, 1980). The extractability of copper was found to be enhanced to more than twice that of the control by sediment drying.

During sampling, storage, and analysis of an environmental sample, typically characterized by a pronounced disequilibrium, species transformation occurs. In polluted ('stressed') systems entropy increases, and their is an accompanying increase in instability. The greater the stress in the environment, the more difficult is sample handling and storage prior to analysis. Reliable and generally applicable methods for the preservation of the original distribution of the species in natural sediment samples do not yet exist. Thus, it is important to be aware of the kinds and degrees of changes taking place in the sediments while they are actually being studied. Wet chemical extractions have been shown to provide a convenient means to determine the metals associated with the principal accumulative phases in the sediments (Kersten and Forstner, 1989).

In practice, it is usually impossible to retroactively correct data that have been obtained from dried sediments to those which exist originally in the field. Such data may even be of limited value for comparing the bioavailable concentrations of trace metals in samples collected within the same environment (Bartlett and James, 1980).

It is also imperative to be aware of the different time scales involved with sediment deposition and metabolic processes, the latter being typically of the same order as sample handling times. Consequently, sampling variance, as well as artifacts introduced during sample processing, can be more than an order of magnitude greater than analytical technique variances in trace element speciation.

Two sequential schemes (a modified Tessier procedure with five steps and a three step protocol designed by BCR) were applied to heavy metal contaminated sediments (Lopez-Sanchez et al., 1993). The difference between the three step protocol designed by BCR and the protocol used in this thesis is that this thesis adds a forth step to determine the Silicate phase whereas the Silicate phase is calculated by subtraction from total metal analysis in the three step protocol. The study showed that the metal partitioning obtained with both procedures are quite different.

With the three step protocol, significant amounts of heavy metals are extracted in the Organic/Sulphide fraction. The modified Tessier procedure indicated that non residual metals are distributed among the second, third and forth fractions, which are related with carbonates, Fe/Mn oxides and Organic/Sulphide fractions, respectively. Copper showed similar behavior with both procedures. Significant amounts of lead were extracted in the second and third fractions of the modified Tessier procedure whereas with the three step BCR protocol, the hydrogen peroxide reagent extracted the higher amount of the metal. For zinc, the amounts extracted with the modified Tessier procedure in the second and third fractions are higher than the amount released with the oxidizing reagent. On the contrary, with the three step protocol the amount of Zn extracted in the Organic/Sulphide step is similar to the amount extracted in the previous two steps combined. The residual fraction obtained in the BCR protocol is in general higher than that obtained using the modified Tessier procedure.

5.3 Environmental Implications

For the Red Indian Lake watershed, there has been a significant burden of pollutants deposited to the lake sediments in the area since mining began in 1928. In Red Indian Lake, it has been shown that there is a significant enrichment in the concentration of Cu, Pb and Zn in the upper sections of the lake sediment cores. The fraction of metals reporting to the Exchangeable/Carbonate phase are the most labile in that increases in acidity will remove these metals first. Therefore, if this fraction only is considered as the environmentally sensitive fraction, a considerable amount (ppm) of Cu, Pb and Zn was associated with the Exchangeable/Carbonate phase and is potentially available for release in acidic conditions. As well, a significant amount of base metals were found to be associated with the Fe/Mn oxide phase. However, this study failed to distinguish between the easily reduced substrates and the moderately reduced substrates associated with the Fe/ Mn oxide phase. Therefore, it is difficult to assess the amount of metal that will be released to the environment with changes to the redox potential of the system. Furthermore, depending on the pH and redox conditions at the time of sediment deposition up to the time of sediment retrieval, a significant portion of base metals may already have been leached from the lake sediments.

Significant redistribution of base metals between the different phases of the sequential extraction procedure occurs as a result of sediment drying. The drying process appears to affect the base metals to varying degrees. In the contaminated upper section of the lake sediments from Red Indian Lake, drying tends to significantly increase the amount of Cu reporting to the first phase but slightly decreases the amount of Pb and Zn reporting to the first phase. Since the 'wet' sediments more closely resemble their state in the natural environment, the results of the 'wet' sequential extraction procedure were used in the assessment of the bio-availability of the metals.

Returning the lakes to their original condition is neither feasible or logical. The sediments have incorporated a considerable burden of pollutants and a significant portion of the lake sediments from Red Indian Lake could potentially be considered as hazardous waste. The sediment currently being deposited into the lake appears to have reduced levels of pollutants. This was difficult to assess in this study because the upper 2 cm of sediment most likely contains sediment deposited during the mining operation as well as sediment deposited since mine closure. Consequently, this can only be verified by isolating the sediment that has been deposited since the mine closure. Further work that would assess the current sediment deposition to Red Indian Lake would aid in the understanding of the watershed recovery. As well, a study to assess the water chemistry would be beneficial in the evaluation of the effect of sediment dissolution on water quality.

With proper site remediation, the contaminated upper layer of lake sediment will eventually be covered with new sediment that more closely resembles background levels. This site remediation must involve proper tailings management including re-vegetation of exposed tailings and possibly liming the existing tailings ponds to neutralize them and effectively precipitate out the metals in solution. As well, surface runoff from remaining exposed ore deposits must be curtailed. Currently, the Lucky Strike 'Glory Hole' which was produced as a result of open pit mining of the Lucky Strike deposit is being filled with water. If in the future the water level exceeds the capacity of the 'Glory Hole', the overflow will have to be properly treated. In summary, all effluent and runoff from the mine site with metal concentrations exceeding the MMLER must be contained in polishing or settling ponds and properly treated to reduce the metal levels. This can only be achieved with an effective monitoring regime that adequately assesses all effluents that potentially end up in Red Indian Lake.

Finally, even with proper site remediation, the process of lake sediment recovery will take several years. In today's mining environment, the principle of pollution prevention at the source is proving to be much more effective than dealing with pollution at the 'end of pipe'. In essence, it is much easier to prevent pollution than to clean it up.

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Appendix A

Lake Sediment Coring Site UTM Coordinates

Lake Sediment	Zone	Easting	Northing	NTS
RIL1A	21	520700	5403000	12A15
RIL1B	21	520690	5403000	12A15
RIL2A	21	504600	5392300	12A10
RIL2B	21	504610	5392300	12A10
BL1A	21	510200	5410300	12A15
BL1B	21	510200	5410290	12A15

Lake Sediment Core Length and Water Depth

Lake Sediment	Water Depth (ft)	Core Length (cm)
RIL1A	193	38.4
RIL1B	190	33.8
RIL2A	293	34.2
RIL2B	295	39.6
BL1A	26	46.2
BL1B	28	36.6

Appendix B

Reporting Name, Wavelength and Method Detection Limit for Trace Elements by Fison Instruments Maxim III ICP-OES (Finch, 1998)

Reporting Name	Wavelength (nm)	Method Detection Limit
Al	396.152	0.01%
Ba	455.397	1 ppm
Be	313.077	0.1 ppm
Ca	422.673	0.01%
Ce	418.673	1 ppm
Co	228.617	1 ppm
Cr	205.561	1 ppm
Cu	324.574	1 ppm
Dy	353.170	0.1 ppm
Fe	271.441	0.01%
Ga	294.364	1 ppm
K	766.488	0.01%
La	408.670	1 ppm
Li	670.784	0.1 ppm
Mg	279.077	0.01%
Mn	403.447	1 ppm
Mo	202.031	1 ppm
Na	588.995	0.01%
Nb	319.497	1 ppm
Ni	231.605	1 ppm
P	213.617	1 ppm
Pb	220.355	1 ppm
Sc	361.383	0.1 ppm
Sr	407.771	1 ppm
Ti	307.864	1 ppm
V	310.231	1 ppm
Y	371.027	1 ppm
Zn	213.857	1 ppm
Zr	343.822	1 ppm

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1A

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	4	21	592	368	131	6	10	3.34	0.18	13
2-4	3	18	565	419	158	6	7	3.09	0.18	15
4-6	4	16	471	350	113	5	5	2.44	0.16	12
6-8	4	18	476	344	109	5	6	2.44	0.18	15
8-10	4	17	564	318	111	5	6	2.49	0.16	16
10-12	4	17	627	360	160	5	6	2.48	0.14	13
12-14	4	20	648	480	237	5	9	2.47	0.16	13
14-16	4	20	679	528	263	5	9	2.54	0.16	13
16-18	4	20	666	680	377	5	8	2.66	0.15	12
18-20	4	16	585	745	594	5	7	2.61	0.14	13
20-22	4	27	789	248	136	8	8	3.77	0.36	15
22-24	5	27	762	113	31	9	6	4.08	0.40	16
24-26	5	34	752	104	25	9	13	3.90	0.37	15
26-28	5	38	750	109	24	8	14	3.83	0.37	15
28-30	4	27	707	97	21	8	8	3.88	0.38	15
30-32	5	31	765	108	21	9	10	4.28	0.36	15
32-34	4	27	680	96	19	9	7	4.08	0.39	16
34-36	5	28	722	99	19	10	8	4.46	0.38	16
36-38	5	28	718	93	16	11	7	4.46	0.39	15
38-40	5	28	728	94	15	11	8	4.38	0.38	14
40-42	5	29	773	91	14	10	8	4.23	0.38	14
42-44	4	27	716	87	13	9	8	3.94	0.40	16
44-46	5	28	771	138	14	9	8	4.25	0.39	15

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1A

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	2087	55	1.5	0.58	6	82	0.70	78	4.4	5.3
2-4	2560	60	1.6	0.60	7	54	0.80	101	4.4	5.5
4-6	2503	52	1.4	0.62	7	53	0.81	103	3.7	4.9
6-8	2824	51	1.4	0.62	8	44	0.99	112	3.6	5.2
8-10	2840	54	1.3	0.60	8	55	0.82	100	3.5	5.1
10-12	2545	48	1.2	0.57	7	69	0.63	86	3.4	4.8
12-14	2490	48	1.3	0.61	6	95	0.65	86	3.6	5.0
14-16	2407	50	1.4	0.58	6	117	0.64	81	3.7	5.0
16-18	2253	48	1.3	0.59	6	143	0.62	76	3.3	4.8
18-20	2128	49	1.3	0.55	5	118	0.55	74	3.3	4.5
20-22	3112	78	2.0	0.74	7	41	1.25	109	4.3	7.9
22-24	3289	85	2.1	0.80	8	20	1.45	116	4.6	9.0
24-26	3101	85	2.0	0.76	7	25	1.31	104	4.4	8.6
26-28	3105	86	2.0	0.77	7	26	1.30	103	4.5	8.6
28-30	3105	82	2.0	0.86	8	18	1.49	110	4.4	8.5
30-32	3045	86	2.1	0.83	7	25	1.34	106	4.6	8.6
32-34	3196	86	2.1	0.89	7	18	1.53	113	4.6	8.8
34-36	3180	89	2.1	0.87	7	19	1.43	111	4.8	8.9
36-38	3231	89	2.0	0.85	7	17	1.45	112	4.7	8.9
38-40	3209	86	2.0	0.83	7	20	1.42	113	4.5	8.7
40-42	3153	86	2.0	0.84	7	17	1.37	109	4.5	8.7
42-44	3206	84	2.0	0.85	7	19	1.50	115	4.4	8.7
44-46	3214	88	2.1	0.85	7	15	1.37	109	4.7	9.0

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1A

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	28	2.97	2229	48	27	77	329	3.9	0.68
2-4	28	3.22	2228	52	26	77	352	4.2	0.82
4-6	23	2.91	2261	51	20	61	327	3.7	0.80
6-8	24	3.54	1923	56	20	60	343	4.5	1.05
8-10	23	3.23	1919	53	21	66	297	4.3	0.85
10-12	23	2.72	1987	47	21	58	259	3.9	0.65
12-14	22	2.78	1944	50	21	61	266	3.9	0.68
14-16	23	2.78	1882	48	23	58	256	3.8	0.67
16-18	22	2.73	1892	48	21	54	251	3.7	0.65
18-20	21	2.55	1794	45	20	59	229	3.1	0.58
20-22	27	4.24	1188	82	26	72	306	7.5	1.11
22-24	28	4.71	1058	91	27	80	318	7.3	1.20
24-26	27	4.55	1061	85	26	79	297	7.2	1.08
26-28	28	4.49	1077	85	26	77	298	6.6	1.08
28-30	27	4.75	1017	90	26	71	329	6.8	1.23
30-32	28	4.54	1136	84	27	80	293	6.8	1.05
32-34	28	4.84	1050	91	26	77	323	7.0	1.23
34-36	29	4.77	1114	88	28	85	311	7.2	1.16
36-38	29	4.69	1103	91	28	81	325	6.9	1.18
38-40	28	4.67	1098	88	26	75	325	6.6	1.15
40-42	28	4.68	1084	87	26	76	315	6.8	1.13
42-44	28	4.77	1020	90	25	79	323	7.0	1.23
44-46	29	4.72	1106	88	27	83	309	7.1	1.13

*** HCl/HF/HClO4 digestion incomplete for barite**

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1B

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	4	20	601	374	127	6	9	3.42	0.17	15
2-4	4	19	557	409	155	5	6	3.16	0.18	16
4-6	3	17	462	362	113	5	6	2.42	0.17	12
6-8	4	18	480	361	114	6	6	2.39	0.18	16
8-10	4	17	561	315	110	5	7	2.50	0.17	16
10-12	4	18	613	374	155	5	6	2.48	0.15	14
12-14	4	19	657	490	242	6	8	2.48	0.15	13
14-16	5	21	690	545	287	5	9	2.55	0.16	12
16-18	4	20	674	697	395	5	7	2.72	0.16	12
18-20	4	17	602	761	604	6	8	2.69	0.15	14
20-22	5	28	798	274	108	6	8	3.57	0.38	14
22-24	4	29	763	109	27	9	9	4.21	0.39	16
24-26	5	35	747	107	25	9	12	4.00	0.38	14
26-28	5	37	736	109	21	8	14	3.87	0.36	15
28-30	4	29	713	101	19	9	9	3.93	0.36	16
30-32	5	32	747	112	20	11	10	4.19	0.40	16
32-34	5	27	682	95	18	10	8	4.24	0.39	16
34-36	5	27	711	93	16	11	7	4.50	0.38	15

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1B

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	2107	57	1.6	0.60	7	77	0.75	81	4.1	5.7
2-4	2560	59	1.6	0.61	7	58	0.82	97	4.5	5.4
4-6	2578	54	1.4	0.62	7	55	0.82	104	3.9	5.1
6-8	2813	52	1.5	0.62	7	47	1.01	116	3.5	5.2
8-10	2848	55	1.2	0.62	8	55	0.82	93	3.5	5.2
10-12	2622	50	1.2	0.58	7	72	0.67	85	3.6	4.9
12-14	2507	51	1.3	0.61	7	97	0.68	83	3.5	4.9
14-16	2441	48	1.4	0.60	6	102	0.65	83	3.1	5.0
16-18	2315	50	1.4	0.59	6	148	0.59	71	3.2	4.9
18-20	2087	49	1.4	0.55	6	123	0.55	69	3.4	4.7
20-22	3152	82	2.1	0.69	8	37	1.29	117	4.4	8.2
22-24	3274	87	2.0	0.79	8	22	1.50	112	4.6	8.8
24-26	3127	88	2.0	0.80	7	25	1.45	100	4.7	8.8
26-28	3098	86	2.1	0.81	7	27	1.31	102	4.6	8.6
28-30	3107	85	2.1	0.85	8	23	1.42	109	4.6	8.5
30-32	3087	89	2.2	0.85	7	26	1.30	111	4.7	8.7
32-34	3230	89	2.1	0.87	7	20	1.43	113	4.6	8.9
34-36	3217	91	2.0	0.87	7	19	1.48	113	4.6	8.8

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: BL1B

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	30	3.02	2209	50	30	73	347	4.1	0.70
2-4	29	3.17	2230	50	25	77	362	4.3	0.80
4-6	24	3.01	2251	52	22	64	347	3.9	0.82
6-8	22	3.47	2007	57	19	59	343	4.5	0.99
8-10	23	3.20	1908	57	20	62	321	4.5	0.92
10-12	23	2.68	1973	51	20	62	270	4.0	0.65
12-14	23	2.69	1950	52	22	61	272	3.9	0.69
14-16	23	2.74	1902	48	24	61	255	3.8	0.69
16-18	22	2.70	1907	49	20	57	230	3.8	0.64
18-20	22	2.62	1842	49	19	57	238	3.2	0.61
20-22	29	4.19	1145	85	28	75	287	7.4	1.14
22-24	29	4.64	1027	90	28	79	321	7.2	1.18
24-26	27	4.52	1046	85	27	79	312	7.2	1.12
26-28	29	4.55	1052	86	26	74	307	6.9	1.11
28-30	28	4.54	1021	86	26	75	301	6.7	1.27
30-32	29	4.69	1117	86	27	81	308	6.9	1.10
32-34	29	4.61	1083	90	26	82	337	7.2	1.23
34-36	28	4.80	1132	89	28	80	316	7.1	1.20

* HCl/HF/HClO4 digestion incomplete for barite

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1A

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	51	39	593	1961	2194	13	14	10.33	0.62	15
2-4	45	27	410	5740	2314	6	8	7.12	0.63	16
4-6	33	26	391	5230	1750	7	9	6.22	0.65	16
6-8	21	33	439	5745	2096	9	12	5.89	0.71	16
8-10	21	37	419	10301	2119	7	10	4.92	0.83	21
10-12	27	31	336	12247	1697	5	9	4.54	0.82	22
12-14	36	31	303	10991	2038	5	8	5.35	0.88	21
14-16	46	32	276	8334	1854	5	8	7.07	0.87	23
16-18	44	44	305	11556	1899	4	8	7.25	0.81	27
18-20	57	47	336	11068	2830	5	9	8.10	0.73	27
20-22	54	30	400	12502	2993	6	10	7.55	0.64	24
22-24	29	30	493	8890	1833	8	13	5.66	0.60	24
24-26	10	44	740	386	151	17	21	5.62	0.81	18
26-28	6	41	882	160	44	17	17	6.78	0.70	17
28-30	7	30	991	127	23	15	11	9.35	0.47	15
30-32	7	33	1043	136	18	17	14	8.31	0.53	17
32-34	6	33	1054	140	17	16	12	8.48	0.51	17
34-36	6	35	1109	142	17	15	14	7.12	0.53	16
36-38	8	27	1166	136	17	16	10	10.80	0.44	16

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1A

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	2218	80	1.3	0.48	4	502	0.78	67	3.4	9.9
2-4	1904	68	0.9	0.35	4	857	0.70	66	2.5	7.6
4-6	2143	68	1.0	0.42	4	820	0.87	75	2.6	8.0
6-8	2402	77	1.1	0.49	5	859	0.96	81	2.8	9.4
8-10	2240	80	0.9	0.40	4	826	0.78	69	2.3	9.4
10-12	1768	73	0.6	0.28	3	763	0.60	57	2.2	8.2
12-14	1470	67	0.5	0.20	2	891	0.39	46	1.6	6.9
14-16	1259	60	0.5	0.18	2	952	0.30	50	1.3	5.2
16-18	1342	65	0.5	0.19	2	1374	0.31	51	1.3	5.4
18-20	1452	77	0.6	0.22	2	1893	0.33	48	1.6	5.8
20-22	1650	81	0.6	0.30	3	4270	0.38	47	1.7	6.3
22-24	2230	87	0.9	0.34	4	2532	0.59	57	2.4	8.7
24-26	3734	105	1.8	0.61	7	73	1.24	100	4.3	13.6
26-28	3245	100	2.0	0.60	6	41	1.12	91	5.2	12.2
28-30	2588	82	2.1	0.63	6	27	1.13	87	6.5	8.9
30-32	2832	89	2.3	0.64	6	30	1.25	92	5.5	9.8
32-34	2851	89	2.4	0.64	6	29	1.25	96	5.5	9.6
34-36	2925	92	2.4	0.66	7	32	1.23	97	6.0	9.9
36-38	2565	81	2.3	0.60	5	22	1.14	89	6.1	8.5

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1A

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	21	4.22	4894	344	17	52	264	12.5	0.86
2-4	16	3.63	1693	507	9	32	128	10.2	0.91
4-6	16	4.00	1057	441	9	35	164	9.6	1.04
6-8	18	4.35	1015	371	12	36	179	10.7	1.11
8-10	15	4.12	878	440	10	29	150	11.1	1.14
10-12	13	3.80	823	482	7	27	136	11.1	1.08
12-14	11	3.47	902	605	6	15	136	10.5	0.93
14-16	10	3.69	952	643	5	22	185	12.0	0.98
16-18	10	4.06	1086	653	4	15	122	12.3	1.05
18-20	10	3.70	1473	491	5	28	107	12.3	0.88
20-22	11	3.21	2052	452	6	22	90	10.3	0.67
22-24	15	3.79	2895	455	8	37	156	11.9	0.75
24-26	25	6.13	4876	117	24	71	800	16.7	1.28
26-28	29	5.53	10701	73	27	77	1388	14.4	1.13
28-30	30	4.63	27990	64	26	89	880	9.6	0.98
30-32	32	5.11	6162	68	28	96	782	10.2	1.12
32-34	33	5.15	5906	67	29	97	716	10.4	1.11
34-36	35	5.19	6632	68	32	112	673	10.3	1.10
36-38	30	4.68	20691	61	28	99	632	8.9	1.02

*** HCl/HF/HClO4 digestion incomplete for barite**

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1B

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	54	42	612	1894	2147	15	14	9.97	0.60	16
2-4	49	27	420	5776	2402	8	9	7.40	0.62	16
4-6	29	25	401	5185	1782	7	9	6.22	0.64	17
6-8	20	31	447	5722	2104	9	11	5.71	0.69	16
8-10	21	39	422	10512	2117	8	12	5.01	0.73	19
10-12	25	33	351	12403	1722	5	9	4.72	0.81	23
12-14	35	31	297	11104	2056	4	7	5.25	0.83	22
14-16	42	33	282	8407	1871	5	8	7.25	0.89	23
16-18	44	45	311	11562	1946	5	8	7.29	0.87	26
18-20	53	46	348	11112	2903	4	9	7.99	0.75	27
20-22	55	30	427	12576	2985	5	8	7.33	0.62	26
22-24	32	32	506	8685	1817	5	11	5.67	0.63	26
24-26	9	39	770	412	137	8	19	5.55	0.79	20
26-28	7	44	875	151	42	16	15	7.00	0.71	18
28-30	6	39	1013	133	21	17	14	9.27	0.49	16
30-32	7	33	1062	139	17	17	12	8.54	0.52	17

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1B

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	2260	79	1.4	0.49	4	487	0.76	63	3.4	10.4
2-4	1934	71	1.0	0.36	5	862	0.71	63	2.6	8.0
4-6	2175	68	1.0	0.40	4	826	0.87	72	2.6	8.0
6-8	2383	75	1.1	0.47	4	832	0.94	79	2.6	9.2
8-10	2301	79	1.0	0.41	4	802	0.80	70	2.2	9.5
10-12	1774	72	0.7	0.30	3	778	0.60	57	2.0	8.2
12-14	1502	68	0.6	0.21	2	905	0.40	45	1.8	7.1
14-16	1277	62	0.5	0.19	2	1007	0.32	49	1.4	5.4
16-18	1337	67	0.6	0.20	2	1501	0.31	51	1.3	5.4
18-20	1456	76	0.5	0.22	2	1976	0.33	47	1.7	6.0
20-22	1705	79	0.6	0.30	4	4183	0.36	47	1.7	6.2
22-24	2226	87	1.0	0.36	4	2612	0.63	49	2.6	9.4
24-26	3668	102	2.0	0.60	7	57	1.20	95	4.7	13.1
26-28	3177	105	2.1	0.60	7	36	1.18	94	5.3	12.3
28-30	2674	87	2.4	0.64	6	32	1.13	91	6.2	9.4
30-32	2851	89	2.3	0.64	7	30	1.23	92	5.7	9.9

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL1B

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	23	4.32	5012	360	17	49	250	12.2	0.87
2-4	17	3.67	1715	487	10	34	141	10.5	0.90
4-6	17	3.89	1047	447	11	37	172	10.0	1.05
6-8	18	4.42	998	375	12	35	174	10.5	1.11
8-10	16	4.21	856	458	10	30	148	11.2	1.13
10-12	12	3.78	832	500	8	26	140	11.0	1.11
12-14	11	3.45	891	611	6	14	140	10.9	0.95
14-16	10	3.70	962	637	5	20	175	11.9	0.99
16-18	9	3.99	1057	656	5	16	127	12.4	1.02
18-20	10	3.74	1527	507	5	28	102	12.3	0.90
20-22	11	3.31	2111	471	5	24	101	10.7	0.71
22-24	14	3.97	2875	449	8	35	160	11.5	0.79
24-26	27	5.95	5019	108	25	74	702	16.2	1.24
26-28	30	5.57	11004	69	27	80	1256	13.9	1.15
28-30	30	4.60	27563	67	29	92	883	10.1	1.04
30-32	33	5.20	6405	68	31	96	756	10.5	1.12

*** HCl/HF/HClO4 digestion incomplete for barite**

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2A

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	54	57	676	839	2050	23	25	8.05	0.81	15
2-4	68	51	657	1598	2565	19	20	8.38	0.86	16
4-6	12	59	626	2161	2607	20	22	6.44	0.99	18
6-8	17	61	571	6686	3869	11	15	5.20	1.10	25
8-10	21	54	458	8630	3850	8	13	4.34	1.06	25
10-12	25	82	488	9732	4457	9	15	4.91	1.05	35
12-14	22	54	536	6743	2938	13	17	5.12	0.92	30
14-16	8	60	729	838	185	21	25	6.75	0.97	19
16-18	14	42	1310	440	232	18	15	11.49	0.56	17
18-20	8	37	1352	277	96	20	17	8.62	0.60	14
20-22	10	41	1518	229	65	20	17	9.24	0.62	15
22-24	7	36	1240	162	28	22	15	10.90	0.52	13
24-26	7	35	1479	160	21	21	16	8.86	0.59	14
26-28	7	39	1524	155	19	24	17	10.54	0.51	13
28-30	6	38	1614	156	19	21	16	9.69	0.53	13
30-32	7	44	1699	154	19	25	19	8.83	0.57	13
32-34	5	32	1405	169	19	24	17	9.17	0.55	14

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2A

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	2934	116	1.5	0.68	4	225	0.92	64	5.2	14.4
2-4	3057	115	1.5	0.66	4	314	1.02	69	4.0	14.0
4-6	3708	133	1.6	0.66	5	325	1.15	84	3.6	16.7
6-8	2834	119	1.2	0.51	4	761	0.90	77	3.2	13.7
8-10	2373	106	0.9	0.39	4	774	0.68	64	2.4	10.9
10-12	2566	117	0.9	0.40	4	986	0.64	69	2.5	10.8
12-14	3070	131	1.0	0.52	4	2112	0.85	66	2.7	13.1
14-16	3809	128	1.6	0.66	6	92	1.15	75	4.0	16.6
16-18	2283	97	2.2	0.55	3	92	0.71	50	5.6	10.1
18-20	2388	99	2.3	0.60	4	66	0.77	53	6.1	10.5
20-22	2451	102	2.3	0.60	4	60	0.78	53	5.9	10.9
22-24	2153	93	2.3	0.55	4	42	0.66	47	6.4	9.3
24-26	2415	100	2.4	0.61	4	44	0.76	52	5.9	10.5
26-28	2241	98	2.4	0.57	3	42	0.68	50	4.5	10.0
28-30	2356	100	2.6	0.58	4	34	0.68	53	5.0	10.4
30-32	2483	102	2.5	0.60	4	45	0.75	55	5.2	11.0
32-34	2421	99	2.5	0.60	4	47	0.74	54	5.0	10.7

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2A

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	23	5.39	29728	205	22	59	1220	15.0	0.92
2-4	23	5.38	6905	326	22	56	808	15.6	0.99
4-6	24	6.16	3875	315	23	59	732	16.7	1.21
6-8	20	5.67	2677	567	19	49	313	15.0	1.42
8-10	16	5.34	2237	691	15	42	213	14.5	1.29
10-12	15	5.83	2806	458	13	37	177	15.7	1.45
12-14	16	5.40	3364	441	14	38	240	16.6	1.08
14-16	23	6.19	7326	113	23	58	1240	19.3	1.07
16-18	31	4.48	13855	107	29	86	741	10.6	0.62
18-20	33	4.82	15494	77	32	97	1194	11.1	0.65
20-22	32	4.83	12758	70	32	92	1817	11.1	0.65
22-24	32	4.41	20688	51	32	93	799	9.3	0.53
24-26	33	4.86	10532	56	33	100	665	10.8	0.62
26-28	34	4.51	23888	52	35	100	555	9.5	0.57
28-30	36	4.63	16534	53	37	111	537	9.9	0.58
30-32	35	4.87	12203	56	37	108	490	10.3	0.63
32-34	35	4.81	15698	54	35	104	494	10.0	0.63

*** HCl/HF/HClO4 digestion incomplete for barite**

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2B

Depth (cm)	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %	Ga ppm
0-2	57	59	692	802	2102	21	25	8.32	0.79	15
2-4	70	54	660	1627	2497	20	22	8.61	0.85	17
4-6	14	60	637	2220	2701	21	22	6.32	1.00	19
6-8	19	60	567	6821	3840	12	14	5.03	1.07	23
8-10	21	55	449	8683	3912	7	15	4.51	1.05	26
10-12	24	83	498	9575	4527	8	16	5.01	1.06	34
12-14	23	57	555	6894	3101	14	18	5.37	0.90	31
14-16	10	59	741	862	203	20	23	7.01	0.94	20
16-18	15	39	1283	429	227	20	17	11.72	0.59	16
18-20	8	37	1359	287	101	21	17	8.95	0.60	14
20-22	11	40	1492	241	65	21	17	9.45	0.60	15
22-24	8	36	1287	157	24	23	17	10.67	0.53	14
24-26	7	36	1501	155	21	22	16	8.88	0.60	14
26-28	7	39	1525	154	19	21	15	10.21	0.52	14
28-30	7	40	1624	160	20	23	17	10.01	0.52	13
30-32	7	42	1668	157	20	23	18	9.12	0.55	13
32-34	6	34	1427	163	21	25	17	9.34	0.55	14
34-36	5	35	1482	154	19	24	18	8.86	0.57	13
36-38	6	32	1406	160	19	23	17	9.18	0.54	13

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2B

Depth (cm)	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm	Sc ppm
0-2	3002	112	1.6	0.68	4	236	0.97	65	5.5	14.0
2-4	3111	117	1.6	0.66	4	297	1.02	66	4.1	13.9
4-6	3657	132	1.6	0.65	4	322	1.16	81	3.7	16.2
6-8	2898	124	1.1	0.53	5	747	0.88	79	3.4	13.9
8-10	2403	106	1.0	0.40	4	780	0.65	62	2.5	11.0
10-12	2562	115	1.0	0.41	4	953	0.66	67	2.5	11.1
12-14	2995	125	1.0	0.49	5	2205	0.89	66	2.5	12.9
14-16	3687	130	1.5	0.65	4	107	1.12	72	3.9	16.3
16-18	2354	100	2.1	0.55	4	87	0.74	52	5.2	10.0
18-20	2368	96	2.4	0.59	4	65	0.78	54	6.2	10.6
20-22	2439	99	2.3	0.60	4	60	0.77	55	6.0	10.7
22-24	2140	95	2.4	0.57	4	45	0.69	49	6.6	9.5
24-26	2395	101	2.5	0.62	4	44	0.75	50	6.2	10.6
26-28	2227	100	2.5	0.57	5	41	0.70	52	4.7	10.5
28-30	2346	103	2.6	0.59	4	37	0.68	55	5.1	10.6
30-32	2457	104	2.5	0.60	4	45	0.74	56	5.2	10.9
32-34	2400	101	2.5	0.60	5	47	0.74	53	5.1	10.7
34-36	2437	99	2.4	0.59	4	45	0.70	54	4.9	10.5
36-38	2398	102	2.5	0.61	4	45	0.72	51	5.0	10.8

Appendix C

Lake Sediment Geochemical Core Data - Total Elemental Analysis

Core: RIL2B

Depth (cm)	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba* ppm	Li ppm	K %
0-2	24	5.45	29056	198	22	60	1247	15.5	0.90
2-4	24	5.41	7205	330	22	56	836	15.7	0.99
4-6	24	5.97	3797	327	22	60	694	16.3	1.19
6-8	22	5.58	2651	582	21	50	321	15.5	1.39
8-10	19	5.42	2198	673	16	41	232	14.9	1.31
10-12	15	5.67	2802	460	12	38	180	15.5	1.47
12-14	17	5.41	3331	441	14	42	272	16.2	1.05
14-16	23	6.07	7464	108	21	61	1175	18.7	1.04
16-18	29	4.58	13727	105	31	90	693	10.9	0.64
18-20	33	4.87	15604	76	33	99	1256	11.0	0.65
20-22	33	4.92	13018	67	33	91	1768	11.0	0.66
22-24	34	4.51	20883	53	32	94	825	9.5	0.56
24-26	33	4.95	12011	55	34	98	642	10.6	0.63
26-28	33	4.50	23400	52	34	100	535	9.6	0.57
28-30	36	4.60	16295	53	36	107	542	10.0	0.58
30-32	36	4.94	12272	55	37	111	507	10.2	0.61
32-34	35	4.78	16104	54	38	105	492	10.1	0.63
34-36	34	4.63	14087	54	36	108	512	9.7	0.63
36-38	36	4.81	15327	52	36	102	489	10.0	0.62

*** HCl/HF/HClO4 digestion incomplete for barite**

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Copper (Cu)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	68	142	30	19	259
2-4	107	122	61	25	315
4-6	134	116	61	24	336
6-8	398	214	142	19	774
8-10	373	234	211	17	835
10-12	428	261	281	17	988
12-14	715	531	959	37	2242
14-16	46	43	42	7	138
16-18	13	40	9	24	86
18-20	5	40	12	10	67
20-22	6	33	9	11	59
22-24	6	25	21	9	61
24-26	6	36	6	9	57
26-28	6	32	1	8	47
28-30	4	29	9	12	54
30-32	2	23	3	9	37
32-34	4	32	5	9	50
34-36	4	37	6	8	55
36-38	4	31	10	8	53

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Lead (Pb)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	366	1688	36	24	2114
2-4	793	1568	30	22	2413
4-6	1169	1519	34	18	2740
6-8	1695	2092	26	70	3883
8-10	1841	2142	30	82	4095
10-12	2070	2468	45	74	4657
12-14	1205	1819	46	69	3139
14-16	64	148	2	4	219
16-18	19	198	9	7	233
18-20	3	102	4	1	111
20-22	2	72	4	1	79
22-24	0	28	7	4	39
24-26	1	31	0	2	34
26-28	0	29	0	0	29
28-30	0	25	4	2	32
30-32	1	22	2	3	27
32-34	2	30	1	1	34
34-36	2	32	0	0	35
36-38	1	23	1	1	27

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Zinc (Zn)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	317	173	275	88	852
2-4	603	249	698	130	1680
4-6	836	391	999	154	2380
6-8	1019	722	5063	203	7007
8-10	2160	691	6275	166	9292
10-12	1189	597	7832	172	9791
12-14	1014	802	4799	131	6747
14-16	269	158	430	42	899
16-18	121	70	115	83	389
18-20	84	89	98	38	309
20-22	97	73	52	42	264
22-24	45	37	58	24	164
24-26	67	38	39	27	170
26-28	55	62	28	22	168
28-30	58	58	34	24	175
30-32	57	63	24	23	167
32-34	59	65	20	22	167
34-36	50	52	32	25	158
36-38	56	52	52	17	176

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Iron (Fe)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	653	45377	2311	32394	80736
2-4	3723	37216	1262	41056	83257
4-6	3424	24865	855	30716	59860
6-8	3718	23921	294	22664	50597
8-10	4419	19646	1232	19256	44553
10-12	4616	22679	2517	18573	48385
12-14	5685	19799	2973	23092	51549
14-16	4804	28516	1096	33862	68278
16-18	4907	51627	3374	49831	109738
18-20	3081	65201	3756	19701	91738
20-22	3176	47105	6310	35727	92317
22-24	3591	60128	4291	31402	99412
24-26	2948	40852	6696	34915	85412
26-28	3333	69474	4781	21872	99461
28-30	3189	61460	5076	28129	97854
30-32	3025	64670	3892	21558	93145
32-34	3168	57797	5464	27155	93585
34-36	2911	57980	4276	22144	87311
36-38	3373	58402	3953	23524	89252

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Manganese (Mn)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	22775	2439	313	1114	26641
2-4	5679	503	106	606	6894
4-6	2852	226	49	390	3517
6-8	2147	138	27	352	2664
8-10	1917	114	30	295	2356
10-12	2176	139	32	252	2599
12-14	2561	180	51	311	3103
14-16	5905	848	163	720	7636
16-18	10936	1498	283	870	13587
18-20	13011	2793	117	293	16213
20-22	10253	874	267	626	12020
22-24	14437	3999	212	551	19199
24-26	9663	955	222	460	11301
26-28	16617	4127	162	352	21259
28-30	12554	1657	230	540	14981
30-32	9643	1563	142	342	11690
32-34	13206	1856	201	455	15718
34-36	11657	2215	137	318	14327
36-38	12475	1764	154	405	14798

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (0.5 gm Dry Sediment)

Element: Calcium (Ca)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	1780	558	213	3858	6408
2-4	991	576	267	4445	6279
4-6	853	612	258	4490	6213
6-8	783	799	277	3351	5211
8-10	722	482	155	2446	3805
10-12	834	489	123	2471	3918
12-14	893	490	82	3273	4739
14-16	886	506	280	4594	6266
16-18	1108	428	237	3836	5609
18-20	1975	502	180	2999	5656
20-22	1860	472	196	3357	5885
22-24	1701	484	189	3262	5636
24-26	1968	496	194	3289	5947
26-28	1984	512	201	2839	5535
28-30	1820	453	228	3206	5707
30-32	1855	463	242	3234	5794
32-34	2095	484	178	3073	5830
34-36	2044	497	198	3100	5839
36-38	1902	494	229	3324	5950

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet Sediment)

Element: Copper (Cu)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	86	75	5	38	204
2-4	69	113	26	49	257
4-6	88	135	50	51	324
6-8	387	301	172	32	892
8-10	139	356	272	24	791
10-12	227	502	425	26	1180
12-14	382	919	980	44	2325
14-16	5	99	49	41	194
16-18	4	28	7	25	64
18-20	16	24	0	21	61
20-22	4	19	4	15	42
22-24	4	21	1	15	41
24-26	4	21	0	15	40
26-28	8	18	0	15	41
28-30	5	18	0	15	38
30-32	5	16	1	15	37
32-34	2	20	0	14	36
34-36	3	16	1	16	36
36-38	2	20	1	26	49

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet sediment)

Element: Lead (Pb)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	697	1172	17	19	1905
2-4	1187	1178	14	8	2387
4-6	1537	1382	21	16	2956
6-8	1924	1762	15	61	3762
8-10	1604	2314	29	68	4015
10-12	2057	2698	45	67	4867
12-14	1008	1570	41	37	2656
14-16	72	190	4	4	270
16-18	35	162	2	0	198
18-20	13	71	2	1	87
20-22	12	57	0	0	69
22-24	9	20	0	0	29
24-26	3	21	0	2	26
26-28	5	16	2	0	22
28-30	1	16	0	0	17
30-32	7	15	2	0	24
32-34	1	19	2	0	21
34-36	5	11	1	2	19
36-38	5	18	1	2	26

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet sediment)

Element: Zinc (Zn)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	524	184	50	206	964
2-4	989	162	300	301	1752
4-6	1534	220	756	300	2810
6-8	1499	284	5637	232	7652
8-10	2675	381	5685	185	8927
10-12	967	394	8399	368	10128
12-14	1365	699	4279	185	6528
14-16	1807	290	434	146	2677
16-18	94	33	24	96	247
18-20	108	23	2	66	199
20-22	76	14	4	47	141
22-24	69	19	1	53	142
24-26	83	25	5	60	173
26-28	89	23	2	50	164
28-30	99	23	5	57	184
30-32	61	18	5	43	127
32-34	84	18	2	45	149
34-36	92	24	0	48	164
36-38	90	23	4	44	161

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet sediment)

Element: Iron (Fe)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	12431	40075	0	37107	89613
2-4	22396	13174	37	38674	74281
4-6	22283	8480	85	35161	66009
6-8	16114	7525	152	22781	46572
8-10	18190	5351	1178	21652	46371
10-12	19738	7254	2036	21304	50332
12-14	16623	8508	1509	22651	49292
14-16	29246	6546	331	38275	74398
16-18	33708	15297	1185	49293	99483
18-20	60327	22713	97	19327	102465
20-22	31391	19448	1096	30337	82272
22-24	67613	25509	67	19201	112390
24-26	23544	17326	1071	36674	78615
26-28	31940	19849	1852	35443	89084
28-30	32782	20277	1166	37884	92109
30-32	58664	21970	836	26377	107848
32-34	45526	18366	465	27738	92095
34-36	47370	19027	712	28539	95648
36-38	41834	20062	339	33982	96217

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet sediment)

Element: Manganese (Mn)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	22960	939	154	1206	25260
2-4	4477	203	41	586	5307
4-6	3367	118	36	527	4048
6-8	1920	81	21	406	2428
8-10	2003	82	26	354	2465
10-12	2005	82	28	308	2423
12-14	2327	100	23	306	2756
14-16	4327	227	68	592	5214
16-18	7049	364	120	703	8236
18-20	27541	2187	28	228	29984
20-22	7306	328	104	434	8172
22-24	18634	2576	31	292	21533
24-26	9055	431	131	624	10240
26-28	16251	723	197	935	18106
28-30	13658	592	146	805	15200
30-32	10816	516	58	437	11826
32-34	13164	475	73	573	14285
34-36	11535	435	60	448	12478
36-38	13135	428	80	524	14167

Appendix D

Lake Sediment Geochemical Data - Sequential Elemental Analysis

Lake Sediment Core: RIL2B (1 cc Wet sediment)

Element: Calcium (Ca)

Sediment Interval (cm)	Phase 1 (ppm)	Phase 2 (ppm)	Phase 3 (ppm)	Phase 4 (ppm)	Total (ppm)
0-2	1754	514	443	4325	7036
2-4	847	531	432	5013	6823
4-6	770	554	414	4915	6653
6-8	747	854	313	3806	5720
8-10	659	480	143	2931	4213
10-12	688	469	115	3085	4356
12-14	831	495	85	3717	5128
14-16	753	483	400	4598	6234
16-18	991	384	376	3951	5702
18-20	2229	505	331	2886	5950
20-22	1748	396	371	3387	5902
22-24	1701	402	274	2850	5227
24-26	1876	446	394	3704	6419
26-28	1864	471	366	3558	6258
28-30	1765	456	370	3698	6289
30-32	1784	481	403	3696	6364
32-34	1932	448	358	3110	5848
34-36	1752	435	392	3846	6425
36-38	1834	468	318	3485	6105

Appendix E

Quality Control/Quality Assurance Data - Total Elemental Analysis

Lab Number	Field Number	Mo ppm	Cr ppm	P ppm	Zn ppm	Pb ppm	Co ppm	Ni ppm	Fe %	Mg %
2620062	BL1A1416	4	20	679	528	263	5	9	2.54	0.16
2620070	BL1A1416	4	18	652	511	247	5	8	2.45	0.15
2620085	RIL1A1012	27	31	336	12247	1697	5	9	4.54	0.82
2620090	RIL1A1012	26	31	329	12556	1666	5	8	4.57	0.80
2620106	RIL2A1012	25	82	488	9732	4457	9	15	4.91	1.05
2620110	RIL2A1012	24	80	489	9800	4698	9	14	4.78	1.04
2620129	BL1B1820	4	17	602	761	604	6	8	2.69	0.15
2620130	BL1B1820	4	18	611	768	611	6	8	2.65	0.15
2620156	RIL1B1416	42	33	282	8407	1871	5	8	7.25	0.89
2620170	RIL1B1416	40	32	276	8378	1884	5	8	7.09	0.87
2620189	RIL2B6-8	19	60	567	6821	3840	12	14	5.03	1.07
2620190	RIL2B6-8	20	58	575	6784	3872	11	15	4.93	1.05
*** LKSD-1**		**10**	**31**	**698**	**331**	**82**	**11**	**16**	**2.8**	**1.04**
2620060	LKSD-1	9	24	681	324	81	12	15	2.85	0.99
2620140	LKSD-1	10	25	692	328	83	11	15	2.82	1.01
*** LKSD-2**		**<5**	**57**	**1222**	**209**	**44**	**17**	**26**	**4.3**	**1.01**
2620080	LKSD-2	<1	47	1285	202	41	19	23	4.30	0.99
2620160	LKSD-2	<1	49	1268	205	43	19	24	4.32	1.00
*** LKSD-3**		**<5**	**87**	**1091**	**152**	**29**	**30**	**47**	**4.0**	**1.20**
2620100	LKSD-3	<1	72	1056	145	30	34	46	4.17	1.14
2620180	LKSD-3	<1	74	1052	147	29	32	46	4.14	1.17
*** LKSD-4**		**<5**	**33**	**1440**	**194**	**91**	**11**	**31**	**2.8**	**0.56**
2620120	LKSD-4	2	28	1423	191	94	13	31	3.05	0.50

*** (Certified Reference Material)**

Appendix E

Quality Control/Quality Assurance Data - Total Elemental Analysis

Lab Number	Ga ppm	Ti ppm	V ppm	Be ppm	Ca %	Nb ppm	Cu ppm	Na %	Zr ppm	Dy ppm
2620062	13	2407	50	1.4	0.58	6	117	0.64	81	3.7
2620070	14	2326	47	1.3	0.60	6	114	0.66	79	3.6
2620085	22	1768	73	0.6	0.28	3	763	0.60	57	2.2
2620090	23	1778	73	0.7	0.28	3	764	0.60	58	2.1
2620106	35	2566	117	0.9	0.40	4	986	0.64	69	2.5
2620110	33	2474	114	0.9	0.40	4	987	0.64	68	2.4
2620129	14	2087	49	1.4	0.55	6	123	0.55	69	3.4
2620130	14	2036	47	1.3	0.56	6	120	0.55	71	3.4
2620156	23	1277	62	0.5	0.19	2	1007	0.32	49	1.4
2620170	22	1259	60	0.6	0.19	2	1002	0.32	50	1.5
2620189	23	2898	124	1.1	0.53	5	747	0.88	79	3.4
2620190	23	2940	121	1.1	0.54	6	755	0.86	80	3.4
LKSD-1	**10**	**3010**	**50**	**1.1**	**7.7**	**7**	**44**	**1.48**	**134**	**3.4**
2620060	13	3003	52	0.8	7.87	6	45	1.47	40	3.1
2620140	12	3008	51	0.9	7.82	6	45	1.48	42	3.2
LKSD-2	**18**	**3460**	**77**	**2.5**	**1.6**	**8**	**37**	**1.43**	**254**	**7.3**
2620080	18	3301	78	1.7	1.43	9	40	1.37	99	5.9
2620160	18	3337	77	1.8	1.45	8	39	1.38	102	6.0
LKSD-3	**17**	**3330**	**82**	**1.9**	**1.6**	**8**	**35**	**1.72**	**178**	**4.9**
2620100	19	3245	83	1.6	1.53	9	37	1.61	94	4.2
2620180	18	3274	81	1.7	1.53	9	36	1.64	92	4.3
LKSD-4	**12**	**2270**	**49**	**1.0**	**1.3**	**9**	**31**	**0.54**	**105**	**3.7**
2620120	10	1994	49	0.8	1.15	4	34	0.53	36	3.3

*** (Certified Reference Material)**

Appendix E

Quality Control/Quality Assurance Data - Total Elemental Analysis

Lab Number	Sc ppm	Y ppm	Al %	Mn ppm	Sr ppm	La ppm	Ce ppm	Ba ppm	Li ppm	K %
2620062	5.0	23	2.78	1882	48	23	58	256	3.8	0.67
2620070	5.0	22	2.73	1883	47	21	59	251	3.9	0.65
2620085	8.2	13	3.80	823	482	7	27	136	11.1	1.08
2620090	8.3	13	3.76	822	508	7	25	137	11.0	1.07
2620106	10.8	15	5.83	2806	458	13	37	177	15.7	1.45
2620110	10.5	15	5.94	2638	421	14	32	185	16.3	1.38
2620129	4.7	22	2.62	1842	49	19	57	238	3.2	0.61
2620130	4.8	21	2.65	1837	47	20	58	243	3.2	0.63
2620156	5.4	10	3.70	962	637	5	20	175	11.9	0.99
2620170	5.5	10	3.72	949	618	5	20	186	11.8	1.01
2620189	13.9	22	5.58	2651	582	21	50	321	15.5	1.39
2620190	13.7	22	5.67	2719	601	22	48	307	15.8	1.43
LKSD-1	**9**	**19**	**4.1**	**700**	**250**	**16**	**27**	**430**	**7**	**0.95**
2620060	8.0	20	3.97	743	270	18	33	429	7.2	0.97
2620140	8.2	20	4.01	727	265	17	31	428	7.1	0.96
LKSD-2	**13**	**44**	**6.5**	**2020**	**220**	**68**	**108**	**780**	**20**	**2.19**
2620080	12.3	38	6.04	2200	236	66	117	769	21.5	2.22
2620160	12.5	39	6.10	2184	232	68	115	774	21.3	2.20
LKSD-3	**13**	**30**	**6.6**	**1440**	**240**	**52**	**90**	**680**	**25**	**1.84**
2620100	12.2	26	6.27	1593	252	51	93	686	28.0	1.89
2620180	12.3	27	6.31	1571	249	52	91	684	27.7	1.85
LKSD-4	**7**	**23**	**3.1**	**500**	**110**	**26**	**48**	**330**	**12**	**0.68**
2620120	7.5	22	2.92	618	133	28	52	353	12.7	0.64

*** (Certified Reference Material)**