HEAVY METAL DYNAMICS IN THE ATHABASCA RIVER: SEDIMENT CONCENTRATIONS PRIOR TO MAJOR ALBERTA OIL SANDS DEVELOPMENT

by

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TABLE OF CONTENTS

List of Tables
List of Figures
Abstract

1. INTRODUCTION
1.1 Heavy Metal Pollution of River Sediments
1.2 Geologic Heavy Metal Sources
1.3 Anthropogenic Heavy Metal Sources

2. METHODOLOGY
2.1 Sampling Sites and Methods
2.2 Analytical Methods

3. RESULTS AND DISCUSSION
3.1 Particle Size
3.2 Total Metal Concentrations
3.2.1 Major Elements
3.2.2 Minor Elements
3.3 Partial Metal Concentrations
3.4 Organic Analyses
3.5 Element Forms
3.5.1 Metal-Organic Relations
3.5.2 Metal-Metal Relations

4. CONCLUSIONS

5. RECOMMENDATIONS

6. ACKNOWLEDGEMENTS

7. COSTS

8. LIST OF REFERENCES

9. APPENDICES
9.1 Locations of All Samples
9.2 Visual Estimates of Texture-All Samples
9.3 Total Element Concentrations-Blind Duplicates
9.4 Total Element Concentrations-Selected
9.5 Partial Element and Organic Concentrations
9.6 Heavy Metals in Sediments of AOSERP Area-
Other Reports

Abstract

Exploitation of the bituminous sands may elevate heavy metal levels in the sediments of drainage systems of the AOSERP area via waterborne or airborne emissions.

One hundred and six dredged sediments and twenty-four sediment cores were collected from the Athabasca River system from just above Fort McMurray to the confluence of Riviere des Rochers with the Slave River. A preliminary sample suite representing all of the drainage units and textural variations was selected for detailed analyses by several total and partial extraction techniques. The objective was to document the natural heavy metal geochemistry of the sediment and to assess cultural influences if any on concentrations.

These preliminary analyses indicate that absolute concentrations are low when compared to data for polluted sediments or even for sediments from different natural geological terrains elsewhere. Concentration variations appear to be functions of natural sedimentological, mineralogical and geochemical controls. Highest heavy metal concentrations occurred in the finest grained sediments from Lake Athabasca. Vanadium, the heavy metal most commonly associated with the oil sands appeared to be present in the drainage sediments in a stable organic compound, which was unextractable by hydrochloric acid, sodium hydroxide, or benzene/methanol. Its occurrence in the drainage sediment may be in the same general form as in the original bituminous oil sands. If so, it appears to

..-/ii

be unaffected by chemical or bacterial degradation in the bottom sediment.

Recommendations for further work, which will require additional funding, are in decreasing order of priority: x-ray diffraction of selected sediments; organic extraction and fractionation of selected sediments; analyses of selected sediment cores; determination of sedimentation rates for selected cores; completion of analyses of the dredged sample suite; analyses of lake sediments from lakes off the mainstem system; detailed grid sediment sampling immediately downstream from extraction plant effluents; collection of a suspended sediment sample suite; and analyses of oil slicks (air-water interface).

1. INTRODUCTION

Heavy metals are among the most dangerous pollutants of water systems (Forstner and Muller, 1976). Unlike many organic wastes, they are not degraded. They can become strongly enriched in the aquatic food chain and ultimately cause human disease (Hopps and Cannon, 1972).

Bottom river sediments play a key role in defining the degree and extent of heavy metal pollution of aquatic sediments. The main reason is because heavy metals and heavy metal compounds are usually incorporated in the suspended load and finally in the bottom sediment of rivers and lakes (Allan and Timperley, 1975; Forstner, 1976). Sediment heavy metal concentrations are considered more reliable indicators of pollution than concentrations in river waters. Fluctuations of several orders of magnitude can be found when determining pollutant values for German rivers (Forstner and Muller, 1976). The reasons are related to changes in water discharge, changes in relative significance of different source areas, and irregular local emissions.

An investigation of the dynamics of heavy metals in the Athabasca River system (Figure 1) necessitates in depth studies of transport in solution or in particulate form. A key item of any such investigation is a knowledge of the concentrations of heavy metals in the bottom sediments of the mainstem river and lakes.

The present study involved analyses of a limited sample suite to provide information on the historic concentrations of heavy metals in bottom sediments.

.../2

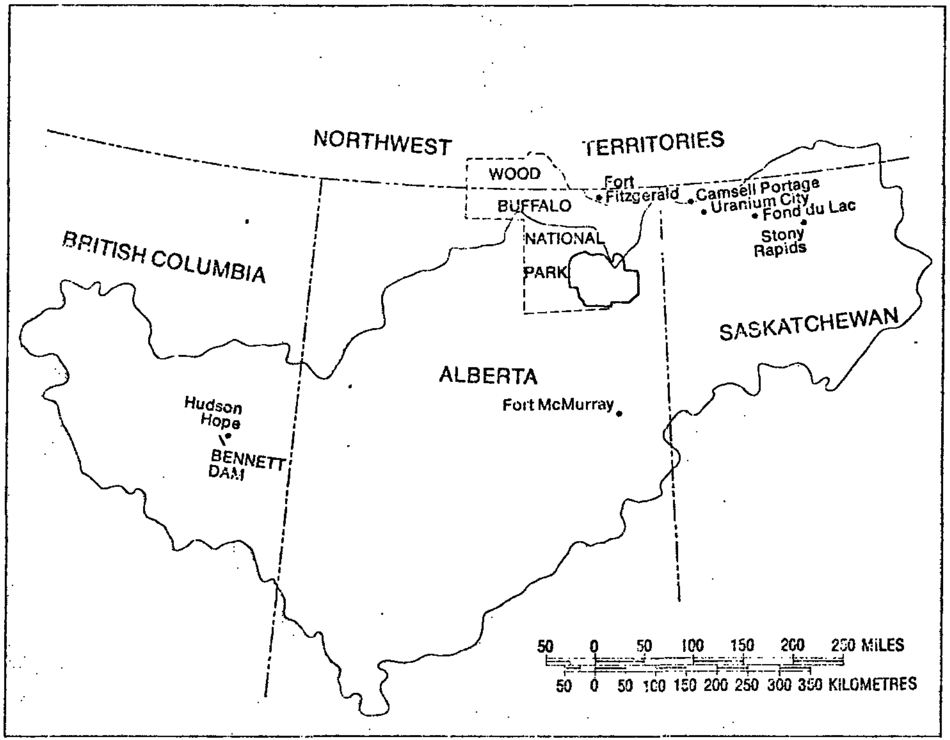

Figure 1. The Peace-Athabasca Drainage Basin, showing the location of Fort McMurray.

This will allow a future assessment of changes with respect to background levels resulting from airborne or waterborne release of heavy metals to the drainage system. An advantage of sediment analyses is that each sample represents an integration of the geochemical fingerprint of the system. Frequent sampling and analyses, as required when water is the sample media, are not needed.

The results are general in nature and relevant to several AOSERP concerns pertiment to the Hydrology Research Committee, namely

1. What effect will extraction of the tar sands have on water quality of the river and Lake Athabasca?
2. What might be the effect of a tailings dike failure?
3. What affect will the addition of particles have on the chemistry of the Athabasca River delta?

The objectives of the study were:

1. To determine the distribution and concentration of various heavy metals in the bottom sediments of the Athabasca River drainage system beneath Fort MacMurray and above the Slave River confluence;
2. To review the results in terms of historic input of metals to the drainage system and to assess present bottom sediment contamination;
3. To investigate by selective dissolution analyses (SDA) possible modes of occurrence of metals in the sediment.
4. To recommend a bottom sediment collection and analysis program to monitor the toxic metal impact of Tar Sands extraction.

1.1 Heavy Metal Pollution of River Sediments

Heavy metal contamination of rivers, lakes, deltas, estuaries, bays, coastal zones and oceans is

.../3

being increasingly reported in the literature. Because of their normally non-degradable character, the cleaning-up of heavy metal contamination of a river often simply means a transfer of the problem, albeit at a less toxic level, down the drainage system. Accordingly the best protection is early detection and prevention.

A detailed global review of river sediment contamination (Forstner and Muller, 1976) reveals the problem of heavy metal contamination of river sediments to be extensive and common. The reader is referred to this excellent review as the best presently available on the subject. Meanwhile we have compiled from our files, the following references on heavy metal contamination of rivers. The total list is more than enough to justify concern for our waterways on a global scale and every effort to avoid adding the Athabasca-Slave-MacKenzie river system to the rapidly expanding number of documented cases.

Rivers of the world recently examined from the standpoint of heavy metal contamination include: the Nile in Egypt (Ashry, 1973); the Vesdre in Belgium (Boelen and De Boeck, 1976); the Back in Maryland, U.S.A. (Bricker et al., 1976); the Hudson in New York, U.S.A. (Helsinger, 1975; Catanzaro, 1976); the Ta-Tu in Taiwan (Chung and Jeng, 1974); the Yarra in Australia (Dale et al., 1974); the Danube in Austria (Draskovic et al., 1972; Ebner and Gams, 1973; Heyn et al., 1974; Rehwoldt et al., 1974 and 1975); the Salzach in Austria (Ebner and Gams, 1975); the Columbia in Washington U.S.A. (Fix, 1975; Haushild et al., 1975); the Amazon in Brazil (Irion and Forstner, 1975); the Quishon in Israel (Kronfeld and Navrot, 1974); the Guyahoga in New York, U.S.A. (Lo and Shong, 1976);

.../4

the Moscow in the U.S.S.R. (Liperovskaya and Drozhbina, 1972); the Illinois in Illinois, U.S.A. (Mathis and Cummings, 1973); the Quae Yai in Thailand (McGarry et al., 1975); the Ottawa in Canada (Merritt, 1975; Rust and Waslenchuk, 1974; Oliver and Agemian, 1974); the Rhone in Switzerland (Vernet and Johnston, 1974); the Elbe in Germany (Mueller and Forstner, 1976); the Altrhein in Germany (Laskowski, et al., 1976); the Jintsu in Japan (Nitta, 1972); the Volga in the U.S.S.R. (Neklyudov, 1973); the Nida in Poland (Pasternak, 1973); the Fork in Oklahoma, U.S.A. (Pigg et al., 1975); the James in Missouri, U.S.A. (Proctor and Lance, 1973); the Waikato in New Zealand (Reay, 1973); the Rhine in Germany (Schleichert, 1975); and in the Netherlands (De Groot et al., 1971); the Po in Italy (Smedile and Tibaldi, 1974): the Buffalo in Arkansas, U.S.A. (Steele and Wagner, 1975); the Tama in Japan (Susuki et al., 1975 1976a, 1976b); Tanizaki and Nagatsuka, 1974); and the Glan and Gurk in Austria (Ebner and Gams, 1975).

Besides these specific river studies, there have been several investigations of heavy metal contamination of drainage areas: rivers in eastern Kansas, U.S.A. (Angino and Schneider, 1975); rivers near Himeji City in Japan (Azuni and Yoneda, 1975); the Salmon River area of B.C., Canada (Bhoojedhur, 1975) and Idaho, U.S.A. (Emmett, 1975); rivers in Delaware, U.S.A. (Biggs and Miller, 1973); rivers of the Issyk-Kul basin in the U.S.S.R. (Kadyrov et al., 1971); the Juntsu river area of Japan (Kano, 1973); rivers of the Cayuga Lake basin of New York, U.S.A. (Kubota et al., 1974); rivers in the upper Neckar region of Germany (Lodeman and Bukenberger, 1973); the rivers of western Puerto Rico (Montgomery and

.../5

Echevarria, 1975); rivers in Kazakhstan in the U.S.S.R. (Mun and Boyarinova, 1973); and in streams of the northwestern U.S.A. (Wood, 1975).

Several recent publications deal with more general aspects of heavy metal contamination and transport in river systems. Some focus on sediments (Cooper and Harris, 1974; Drachev and Kalinina, 1974; Forstner and Mueller, 1976; Forstner and Patchimeelam, 1976; Hem, 1976; Perhac, 1974; Steele et al., 1975; Van Drill and DeGroot, 1974; and Whitney, 1975). References dealing with the extraction of heavy metals from interstitial waters in sediments of polluted river systems are rare (Krasintseva et al., 1973; Hart, 1976, DeGroot, 1977).

Sediments are normally a net sink for toxic metals. Interest in Hg contaminated sediments at Minimata, Japan and the English-Wabigoon River system of north western Ontario, Canada, (Armstrong and Hamilton, 1973; Parks, 1974) arose because of the realisation that for Hg this sink is not permanent. The metal is slowly released and passes up the food chain. Other examples of drainage systems in Canada with Hg contaminated sediments are the LacQuevillon-LacMatagami system (Thomas et al., 1975), the Ottawa River at Ottawa (Rust and Waslenchuk, 1974), and the Laurentian Great Lakes (Thomas, 1972, 1973; Thomas et al., 1974). The Alberta Oil Sands area is different from the above in that the sands are natural sources of heavy metals.

.../6

In the cases described above, industrial sources could usually be clearly identified. In the Oil Sands area this may be problematical and necessitates an early characterisation of natural sediment concentrations prior to major oil sand extraction operations.

The references above and those in Forstner and Muller (1976) deal mainly with the heavy metals which have todate received most attention: Hg>Cd>Pb>Zn>Cu and not with the predominant heavy metals found in the bituminous Oil Sands: V and Ni. Data on Ni concentrations in drainage system sediments is largely confined to lakes (Allan, 1974; Allan and Brunskill, 1976; Forstner, 1976, 1977). Measurements of V concentrations of sediment from freshwater lakes and rivers are very scarce. The only extensive values known to us are those for Lake Winnipeg sediments (Allan and Brunskill, 1976). For the Oil Sands Area there is some data for sediment collected during Peace-Athabasca Delta Study (Water Quality Branch, 1972) and as part of the OSERP program on water quality of the Athabasca River (Korchinski, 1977).

1.2 Geologic Heavy Metal Sources

The main source of heavy metals in the Oil Sands Area is bitumen. As for most oils, this is enriched in V, Ni and Fe. The first has possibly replaced Mg as the central metal ion in the chlorophyll-a of the plankton from which the oil was derived (Hodgson, 1954). The V/Ni ratio (2.4:1) of the bitumen is characteristic of cretaceous oils (Hodgson, 1954).

The sand fraction of the Oil Sands contains a significant proportion of heavy minerals, in particular zircon, rutile and anatase, and is a source of Zr and Ti

.../7

(Kramers and Brown, 1976). Other sources of metals, particularily Zn and Pb might be the underlying cretaceous bedrock and/or groundwater. Deposits of Pb and Zn have been associated with similar bedrock north of the Oil Sands area at Pine Point.

1.3 Anthropogenic Heavy Metal Sources

During the extraction and processing for the Oil Sands, heavy metals can be released to the environment via airborne and waterborne pathways.

Airborne Emissions: By 1985, five plants may be operating in the Oil Sands area and total particulate emissions have been estimated at 89.3 tonnes/day or 32,594 tonnes/year (Table 1).

Table 1. Emission Rates from Oil Sands Plants in 1985 (Anon. 1976)

Plant	SO_2	Particulates
	tonnes/day	
GCOS	354	40.6
Syncrude	292	12.7
Shell	118	12
Petrofina	171	12
Home	109	12
Total	1044	89.3

The particulate emissions from Fort McMurray have also been predicted at approximately 125 tonnes per year, assuming a growth in the town corresponding to the establishment of the five extraction plants.

The fly ash is known to contain high concentrations

.../8

of V (1.4 to 1.48%) and Ni (0.54 to 0.66%) (Stemerowicz et al., 1976). Although this could be an economical source for these elements it is unlikely that they will be removed as present V resources will exceed world demand for many years (Brown et al., 1974). Jacks (1976) studied V from automobile emissions and deposited in snow near Stockholm. He stated that V in this form is at present considered to be particularily dangerous. Alternatively, Greenhill (1976) notes that V concentrates in fish livers, that workers in V mines have low cholestrol levels, and that V can decrease dental caries in children. The dangers of V in the porphyrin form are not yet clear.

Fly ash and gaseous emissions will be spread over a wide area, draining to the Athabasca River. The impact of the airborne fallout of heavy metals will not be confined simply to direct fallout on the river, delta, Lake Athabasca and other lakes in the area but will include a component leached from the much larger area affected by fallout. At a predicted rate of 64,000 to 106,000 tonnes/year SO_2 from the Syncrude Plant alone, this area would involve a blanket coverage of up to 450 sq. miles with extension up to 3,800 sq. miles depending on meteorological conditions (Murray and Kurtz, 1976). When all five plants are operating, an area of several thousand square miles could be affected. GCOS (Great Canadian Oil Sands) emission rates for various heavy metals as particulates are given in Table 2.

Table 2. Emission Rates for Some Heavy Metals in Particulates Collected in GCOS Plant Precipitators.

Element	Wt. %	Emission Rate kg/day
V_2O_5	4.70	1,900
TiO_2	3.33	1,330
NiO	1.36	545
MnO_3	0.18	72

.../9

Leaching and transport of heavy metals deposited as particulates could have a greater impact on the Athabasca River than might be anticipated because of the synergistic effects of acid precipitation produced by concurrent SO_2 release to the atmosphere. A study of the pH of snow around the GCOS Plant revealed that snows in the immediate vicinity of the plant were alkaline (Barrie and Whelpdale, 1976) rather than acidic. This is most likely due to rlease of Ca, Mg and Na oxides and hydroxides from combustion of coke. The dissolution of these particulates in snow samples could compensate for the acidity that would be expected from the SO_2 emissions.

Analyses of fly ash deposited on test precipitators at GCOS are given in Table 3 (Tottrup Services, 1976).

Table 3. Element Concentrations in Test Precipitator Fly-Ash

Element	Concentration
	ppm
V	25,467
Ti	17,060
Ni	9,980
Mo	2,350
Mn	897
Cu	383
Cr	180
Cd	<10
Zn	397
Be	<10
Hg	0.007
As	7

These values provide an approximation of the minimum metal concentrations which could be reached in the

.../10

finest particulates picked up by the precipitators. Finer particles, released to the atmosphere as particulate emissions, may be even more enriched in some of these heavy metals. The low concentrations of Hg, and, to a lesser degree, As in the scrubbed particulates may reflect the almost complete release of these metals in gaseous form following combustion of coke.

Waterborne Emissions

Heavy metal pollution of the Athabasca River could be catastrophic should the Tar Island tailings dyke fail. Present dyke seepage, which flows along the west bank of the river, is diluted to 1/400 in 1 mile and 1/3000 and 1/6000 in 20 miles during winter and summer flows respectively (Bouthillier, 1976). Seepage water contains 1,000 mg/l total solids of which only 15 mg/l is suspended solids. There has been dyke seepage for many years, perhaps since 1965 when it was first used. Generally, seepage is on the order of 182-347 gallons/day (Atkinson et al., 1976). Much of this evaporates. However, raising the dyke to its ultimate projected height could increase the seepage 2 to 3 times. The seepage water is high in Cd, Cr and Pb. It can also be high in Zn. As, Hg, Ni have not been detected at above normal concentrations (Gallup, 1976). Very few samples have been analysed, but the present total heavy metal release is estimated at 0.5 lbs/day (Gallup, 1976).

There have also been periodic deliberate discharges of ponded surface water related to compaction of tailings and increasing the height of the dyke. Such random discharges can often be missed by water sampling programmes.

.../11

In the tailings pond, "clear" water extends to a depth of about 15' above a mineral sludge (Morgenstern, 1976). In 1968, 110 million cubic ft. of this water were discharged to the river in conjunction with increasing the height of the dyke.

2. METHODOLOGY

2.1 Sampling Sites and Methods

River sediments were collected from the Athabasca River from Fort McMurray to the Peace-Athabasca Delta. Sediments were also collected from the delta lakes and sloughs, from Lake Athabasca and Riviere des Rochers. The length of the river system sampled was over 200 km from above Fort McMurray to the junction of Riviere des Rochers and the Slave River (Figure 2). Suspended sediments were collected by the Water Survey of Canada at three sediment sampling stations; Athabasca River-Fort McMurray; Clearwater River-Draper; and Athabasca River-Embarras Airport. The bottom sediment sampling was carried out by the C.C.I.W.-W.N.R. technical staff.

The sediment samples were collected during late August-early September, 1976. Sample sites in the Athabasca River Delta and on Lake Athabasca were reached by Bell G-47 helicopter. Sample sites on the Athabasca River from Bitumount to Embarras Portage were reached by Cessna 185. Sample sites in other parts of the drainage system were reached by boat. Dredged sediments were collected using a 2-liter Eckman or a stainless steel mini-Shipek dredge. Sediment cores were obtained using a Phleger Corer.

.../12

A common difficulty in collection of clay rich sediment was its impenetrability. All samples were shipped to Winnipeg at as early a date as possible. In Winnipeg all samples were frozen until they could be freeze-dried. Freeze drying of the samples was a continuous operation from September, 1976 to April, 1977. Although two freeze dryers were in operation, this process proved to be a predicted bottleneck in the operation.

2.2 Analytical Methods

Twenty-one samples (Figure 2) were selected for analyses. The remainder of the sample suite was freeze dried and stored for future use. These twenty-one samples and five blind duplicates were submitted to four laboratories for a variety of analyses.

All four laboratories were asked to perform total chemical analyses for specific elements. The method of total analyses was to be the one normally employed by each laboratory.

The analytical methodologies for total element concentration were as follows:

Laboratory 1: The sediment was refluxed with HF and HNO_3-$HClO_4$. After evaporation to dryness, the residue was taken up in 4% HNO_3. Metal concentrations in this solution were determined by Radio Frequency Plasma Emission Spectroscopy (RFPES).

Laboratory 2: 100mg of sediment was placed in a Teflon cup and 4.0 ml HNO_3, 1.0 ml $HClO_4$ and 6.0 ml HF added. The bomb was sealed and heated for 3.5 hr. at 140°C. On cooling, the contents are placed in a 124 ml bottle containing 4.8 g H_3BO_3 and about 30 ml of deionised water. The solutions were analysed for V, Ni, Cu, Co, Zn, Mn,

.../13

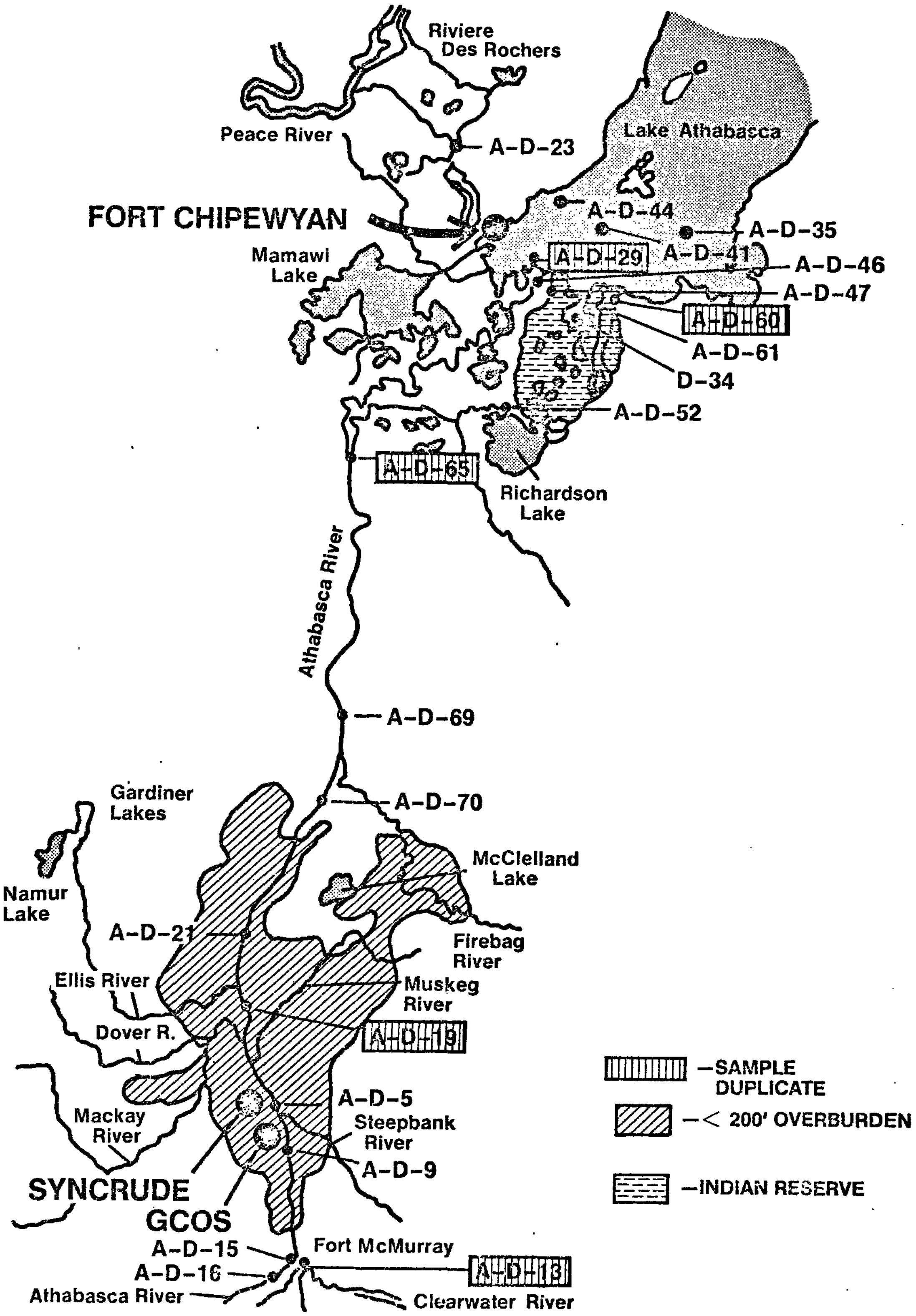

Figure 2. Locations of Analysed Samples, Alberta Oil Sands Study Area.

and Fe by atomic absorption spectroscopy, using a Perkin Elmer 403.

Total Hg in the sediments was determined by the cold vapour atomic absorption technique by extracting the samples with a 2:1 H_2SO_4-HNO_3 solution. On cooling, 2 ml of HCl were added. The solutions were shaken in a water bath at 50-60°C for 2 hrs. After cooling, 15 ml of $KMnO_4$ were added. After 0.5 hr., 5 ml of $K_2S_2O_8$ were added. Additional persulphate was added until the colour persists for 15 mins. Then, 10 ml of hydroxylamine sulphate-sodium chloride solution were added. A clear, centrifuged aliquot was analysed by flameless atomic absorption on a Perkin Elmer 403.

Laboratory 3: For all metals, except Hg, 0.5 g of dry sediment was weighed into a platinum crucible, wetted with a few drops of 20% (V/V) sulphuric acid, 1 ml of hydrofluoric acid added, and heated on a hot plate to dryness. The hydrofluoric acid treatment was repeated twice more. To the cooled crucibles one-half gram of potassium persulphate ($K_2S_2O_8$) was added and the sample was fused over a Meker burner. The fused sample was dissolved in hot hydrochloric acid (1:1) and made up to 25 ml volume. Standards and blanks were similarily treated. Aliquots (or diluted aliquots) of these digests were analysed for Cr, Cu, Fe, Mn, Ni, and Zn, using an air-acetylene flame on a Varian AA5 Atomic Absorption Spectrophotometer equipped with a Model BC-6 simultaneous background corrector. Vanadium was analysed using a nitrous oxide-acetylene flame on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. No background absorption was evident on checking these samples. Hg was extracted with 10 ml aqua regia per 1.0 g sediment. Standards and blanks were carried

.../14

through the procedure. An aliquot of the digest was analysed for Hg by the semi-automated method of Armstrong and Uthe (1971).

Laboratory 4: Ten ml of aqua regia were added to 2 g of the sediment sample. The solution was allowed to sit overnight. Samples were then heated on a hot plate for 45 mins., filtered through a No. 42 Whatman paper, and made up to 25 ml volume with deionised water. The solutions were analysed directly by atomic absorption spectroscopy. V and Ni were analysed using a nitrous oxide-acetylene flame. Only laboratory 1 provided major element data and this is used in the discussion.

Laboratory 2 carried out an additional series of selective dissolution analyses, carbon and nitrogen analyses, and determinations of fulvic and humic acid concentrations. Analytical methods were as follows:

1. Carbon and nitrogen were determined by CHN analyser using the standard techniques.

2. The partial metal extraction using 0.5N HCl used ten grams of sediment, extracted with 100 ml of 0.5N HCl. The solution was filtered and analysed directly by atomic absorption spectroscopy on a Perkin Elmer 403.

3. Another extraction used 1:1 benzene-methanol. The supernatant was removed by centrifugation and placed in a Teflon Bomb. The procedure for analyses of metals then follows that given above for total metals by laboratory 2. The residue from the benzene-methanol extraction was evaporated to dryness and weighed. The residue was then extracted with 0.1N NaOH. The supernatant was again removed by centrifugation and placed in a Teflon Bomb. The procedure was again the same as for total metals.

.../15

3. RESULTS AND DISCUSSION

Without exception, the heavy metal concentrations in all of the sediment samples are such that it is extremely unlikely that any of them have been affected by cultural inputs. The metal concentrations are very low when compared to sediments from contaminated drainage systems elsewhere in the world (Allan, 1975; Forstner and Muller, 1976). The concentrations are also commonly lower than found naturally in other geological terrains (Allan 1975; Forstner, 1976). The distribution of concentrations is such as to preclude evidence for any point source inputs of cultural origin and variations from site to site are largely controlled by variations in textural, amorphous oxide-hydroxide, or organic concentrations. The mean concentrations reveal geological background values that can be used for comparison with future data obtained during expansion of oils sands extraction facilities.

3.1 Particle Size

Grain size was estimated by inspection in the field (Appendix 2; Tables 1 and 2). It may be determined more exactly if a more detailed study is done. Many of the river samples may be described as coarse sand, whereas the delta and lake sediments were predominantly clay-sized. Obviously the finer textured material is carried further from the oil sands area. Although much of the fine sediment is apparently deposited in the delta and in the shallow western end of Lake Athabasca, a proportion probably finds its way via the Riviere des Rochers to the Slave River and perhaps even Great Slave Lake.

.../16

Earth satellite imagery might be used to determine the degree of flow through of Athabasca River water to Riviere des Rochers. Some physical limnological studies of mixing of Athabasca River water with Lake Athabasca water will be necessary to tie this transfer down quantitatively.

3.2 Total Metal Analyses

These were performed by a variety of techniques by four different laboratories. The laboratories were free to use whatever method they normally used for total metal analyses. No specific detection limits were requested. Five blind duplicates were included in the sample suites. The results for these blind duplicates (Appendix 3; Tables 1 to 4) and the results for the sample suite (Appendix 4; Tables 1 to 4) were examined to assess precision and accuracy of the analytical methods employed.

In all cases, the precision was satisfactory to excellent for most elements. One exception appeared to be the Ni results provided by laboratory 2. The reason may eventually be traced to contamination from the bombs used in this technique. However, this would require further extensive analyses of more samples, before a firm conclusion could be drawn. A comparison of the element concentrations from the four laboratories indicates that the technique used by laboratory 1 may overestimate Zn. It also appears that the technique used by laboratory 4 did not extract all of the V present. On the basis of comparing the concentrations obtained by each laboratory for the blind duplicates, plus a comparison of the values for individual elements obtained by each laboratory for the sample suite, we

.../17

we concluded that the results for V, Ni, Cu, Zn, Mn, Fe and Hg provided by laboratory 3 appeared to be the most reliable and are used in the discussion along with the total major element data provided by laboratory 1.

River bottom sediments are normally dominated by quartz, feldspars, carbonates, layer silicates, and small amounts of heavy minerals. These mineral particles are coated with amorphous inorganic oxides, hydroxides and organic material of humic or fulvic acid affinities. Downstream from the Oil Sands area, the organic fraction may involve derivatives of bitumen and be associated with higher Fe, V, and Ni as in the case for Cretaceous heavy oils in Alberta (Hodgson, 1954).

The sediment geochemistry at a site will depend on the availability of source material and the energy regime at the site. At sites of high-energy current action the sediment may be coarse grained and dominated by silica, feldspar, and heavy mineral components and have a lower organic content. The heavy minerals found in economically extractable quantities in the Oil Sands are rutile, anatase and zircon (Kramers and Brown, 1976). The elements associated with these are Ti and Zr. At sites of lower-energy current action the sediment will be fine grained and made up largely of layer silicates and have a higher organic content. Via sorbtion and exchange processes, the latter should have higher concentrations of trace metals not associated with heavy minerals.

Given that the above is a reasonable analogy of sediment composition in the area, the results of the total element analyses reveal no unexpected perturbations. The finer grained sediments usually have

.../18

the higher Al and Fe concentrations probably present in layer silicates, organic, and inorganic amorphous coatings. The higher Fe concentrations are associated with higher V and Ni concentrations indicating a possible common source, the bitumen of the Oil Sands, and/or a common fraction e.g. the organic phase of the sediment.

3.2.1 Major Elements: Limited data is available on element concentrations in river sediments from the glaciated, forested, interior lowlands of western Canada. Comparison of this data with that for Lake Winnipeg sediments (Allan and Brunskill, 1976) may be applicable because both are derived largely from sedimentary bedrock and the method of major element analysis was the same.

Aluminum: Concentrations in Lake Winnipeg sediments are on the order of 5 to 8%. This is generally higher than for the sediments of the Athabasca River (3 to 5%) but similar to those for the Athabasca River Delta and Lake Athabasca sediments (5 to 6%). This probably is a reflection of variation in concentration of layered aluminosilicates in the various sediments.

Iron and Titanium: Concentrations in the various Athabasca River system sediments are generally 1 to 3%. In Lake Winnipeg sediments they are also 1 to 3%. The coarser sediments do not have the highest Fe and Ti concentrations, although they probably have the highest concentrations of heavy minerals containing these elements. Heavy liquid fractionations followed by x-ray diffraction could resolve this question. The finer grained sediments, with their greater surface areas and organic concentrations, have the higher Fe

.../19

and Ti concentrations. This could be due partly to the amorphous Fe coatings, and partly to Fe and Ti rich clay sized, accessary minerals or Fe and Ti rich clay sized layer silicates. The Ti concentrations of the Lake Winnipeg samples appear slightly higher than in the Athabasca River and Delta sediments but similar (0.4%) to the Lake Athabasca sediments.

Phosphorus concentrations in the surface sediments of the Athabasca system appear unusually high (1300 to 1800 ppm). This is 2 to 2.5 times the Lake Winnipeg sediment values. These concentration differences would require substantiation by another analytical technique before speculation on their meaning.

Sodium: This element can be present as sand and silt sized feldspars, in layer silicates, in organic materials, and as an exchangeable ion. There appears to be little variation with location or texture in the Athabasca sediments. Values of 0.7 to 0.8% are higher than many found in sediments from the south basin of Lake Winnipeg (0.4%) but similar to those in the north basin (0.8 to 1.0%).

Calcium and Magnesium: In view of the abundance of Devonian limestone and dolomite in the study area, the calcium and magnesium are most likely present as dolomite among the finer particles. Selective leaching with weak acids and subsequent x-ray diffraction of selected samples we could detect such minerals. Concentrations are similar in sediments from the north basin of Lake Winnipeg for both Ca and Mg. Only Mg is similar to the south basin sediments of Lake Winnipeg.

.../20

3.2.2 Trace Elements: We consider the results from laboratory 3 to be the best in terms of absolute values. However, our main site for comparative purposes is Lake Winnipeg and these samples were analysed by the RFPES technique of laboratory 1. Thus, comparisons of concentrations are made on the basis of the laboratory 1 analyses. The total concentrations are considered to reflect natural conditions and are of a magnitude that the use of the results from any of the laboratories would not change the conclusions.

Vanadium and Nickel: Again, the finer textured sediments have the higher concentrations. In general, in sediments of similar texture, there is an increase in concentration of these elements from river sediment, to delta, to lake. Since the finest particle sizes are carried to the delta then to the lake, the increase in concentration is as expected. In addition to decreasing particle size, increasing organic content down-drainage may be a factor causing concentration increases. The absolute concentrations do not appear to reflect a cultural point source input such as industrial effluents in the Alberta Oil Sands Area, but rather a natural progression of geological sorting processes downstream. The concentrations of V are similar to those (about 150 ppm) found in off-shore sediments of an oil rich area of southern California (Table 4). Some sediments from Lake Winnipeg have higher V concentrations than the Athabasca drainage system. This could be related to the vanadium content of oil rich clays in the Red River basin. The Ni concentrations (Table 5) are low when compared to many lake sediments elsewhere (Allan and Brunskill, 1976, Forstner, 1977). None of the sediments analysed appear to be culturally contaminated.

.../21

Table 4. COMPARISON OF MEAN VANADIUM CONCENTRATIONS IN SEDIMENTS OF DRAINAGE SYSTEMS IN NORTH AMERICA

Area	Number Samples	Vanadium Concentration Mean	Vanadium Concentration Range
		- - - ppm	- - - - - -
Athabasca River (Ft. McMurray to Delta)	10	62	15-100
Athabasca River Delta	6	90	22-127
Lake Athabasca	4	115	76-148
Riviere Des Roches	1	136	136
Athabasca River System (Ft. McMurray to Slave River)	21	84	15-148
South Basin Lake Winnipeg	21	191	63-232
North Basin Lake Winnipeg	21	158	53-214
Lake Winnipeg	50	169	53-232
Santa Barbara[1] Basin, California	13	150	148-152
Santa Monica[1] Basin, California	12	150	125-175
Soledad Basin,[1] California	16	120	90-175
San Pedro Basin,[1] California	16	125	100-130

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1. Based on analyses of 1 sediment core from each basin. Each core was divided into the number of samples noted. Ref. Bruland et al., 1974.

2. Six sediment cores from Lake Erie (Kemp et al., 1976) showed no surface enrichment. Average total concentrations were 55 ppm but these values were considered low because of doubt with the analytical method.

Table 5. MEAN CONCENTRATIONS AND RATIOS OF VANADIUM[1] AND NICKEL IN BOTTOM SEDIMENTS OF THE ATHABASCA RIVER SYSTEM

Area	Texture[2]	Number Samples	Mean Concentrations V	Mean Concentrations Ni	Mean Ratio[3] V/Ni
			- - -ppm- - - - - -		
Athabasca River	S	3	29	7	4
	Sc	2	69	11	6
	St	1	27	7	6
	CS	3	109	18	7
	C	1	112	15	6
	ALL4	10	69	12	
Athabasca River Delta	S	1	25	4	6
	CS	2	139	24	6
	C	3	121	18	7
	ALL	6	111	18	6
Lake Athabasca	Sc	1	89	16	6
	C	3	183	27	7
	ALL	4	160	24	7
Riviere Des Roches	C	1	156	26	6
All Areas	ALL	21	103	17	6

1. Analyses by laboratory 3.
2. Visual estimate only.
3. The ratio in heavy oils is 3:1 (V/Ni).
3. All sample textures.

The ratio of V/Ni in Cretaceous heavy oils is 2.4:1. The ratio of V/Ni in the Athabasca drainage sediment was normally 6 to 7:1 (Table 5) indicating a relative enrichment of V via terrestrial geochemical processes.

Zinc, Copper, Cobalt, Chromium and Lead: Similar arguments apply here as for the other elements. The higher concentrations are in the finer textured sediments and present in amorphous inorganic-organic coatings. Concentrations are normal or even low in comparison with polluted river (Forstner, 1976; Forstner and Müller, 1976) and lake (Allan, 1975) sediments elsewhere.

Mercury: This element has received most attention of all the heavy metal contaminants of drainage systems (see Proc. 1st. Internat. Mercury Congress, Barcelona, 1974; Transport of Persistent Chemicals in Aquatic Ecosystems, Ottawa, 1974; Internat. Conf. on Heavy Metals in the Environment, Toronto, 1975, etc.).

Hg analyses of material collected on precipitators in the GCOS plant revealed very low concentrations. It is a well known fact that Hg from coal or coke combustion is almost completely released to the atmosphere by thermal power stations and can accumulate in nearby drainage sediments (Pezzetta and Iskandar, 1975). This may also be the case for oil sands plants.

The Hg concentrations in all sediments were very low. Mercury contaminated sediments can have anything from 1,000 ppb to 684 ppm Hg (Forstner and Müller, 1976). None of the sediments from the Athabasca drainage system come close to such high concentrations (Table 6; Appendix 4, Tables 2 and 3). Mean values ranged from only 30 to 63 ppb and are taken as reflecting normal geological concentrations for the area. There was the

.../22

Table 6.

MEAN CONCENTRATIONS OF MERCURY AND ARSENIC IN THE BOTTOM SEDIMENTS OF THE ATHABASCA RIVER SYSTEM

Area	Texture[1]	Number Samples	Mean Concentrations	
			Hg[2]	As[3]
			ppb	ppm
Athabasca River	S	3	10	2
	Sc	2	24	4
	St	1	25	2
	CS	3	51	4
	C	1	39	5
	ALL[2]	10	30	4
Athabasca River Delta	S	1	7	2
	CS	2	54	5
	C	3	45	4
	ALL	6	42	4
Lake Athabasca	Sc	1	31	3
	C	3	74	6
	ALL	4	63	5
Riviere Des Roches	C	1	61	6
All Areas	ALL	21	41	4

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1. Visual estimate only.
2. Mean of analytical values from laboratories.

usual increase from river to delta to lake corresponding to a change to finer texture with greater organic content. Lake Athabasca sediment had a mean concentration of 63 ppb. This is less than the surface sediment from many other Canadian lakes (Allan et al., 1974) and from Lake Winnipeg (about 150 ppb) (Allan and Brunskill, 1976). Although there is no evidence of cultural Hg contamination, the down stream increase in Hg concentrations shows that additions of Hg to the atmosphere would probably have the greatest impact on the delta and lake as these are the foci of deposition of finest textured suspended sediment.

Arsenic: As for Hg, this element is not found in appreciable concentration in the precipitator fly ash (Table 3). If found in the coke, this could mean that it will be released in quantity to the atmosphere.

The bottom sediment concentrations were again low and similar to those found in the surface sediments of many Canadian lakes (Allan et al., 1974). There is no apparent cultural source of arsenic.

All Other Elements: In general, the elements not discussed above appear to reflect geological, geochemical, mineralogical or sedimentological controls. There does not seem to be any cultural control for the elements analysed. There are no concentration levels for any of the elements that would cause suspicion of contamination of surface sediments. However, analyses of sediment cores would be required to firmly establish this hypothesis.

3.3 Partial Metal Concentrations

All of the partial element or selective dissolution

.../23

analyses (SDA) were carried out by laboratory 2. The results for the five blind duplicates (Appendix 5) showed that the precision was adequate in spite of the low concentrations extracted. Many of the results were beneath detection limits but this was not considered significant because of the relatively low concentrations recorded.

As opposed to the total analyses (which should not be affected by sample composition because the entire sample should be dissolved), the partial extractions remove operationally defined fractions. However, each technique should still remove the same fraction every time. Precision by the HCl extraction was good to very good. The NaOH results, where they exceed detection, were also good, with the possible exception of Fe. The benzene-methanol extractions are hard to comment on because most results are below detection limits.

In general, the organic analyses were precise with the exception of A-D-65. This may be related to its sandy composition.

Hydrochloric Acid Extraction: HCl (0.1N was used to extract the sediment by the method described earlier. This reagent, at this concentration, is expected to remove exchangeable and chemisorbed elements; amorphous inorganic coatings with their associated trace metal content; low molecular weight fulvic acid; certain polar organic compounds such as amino acid; and carbonates (Jackson, 1975a). Silicate mineral particles should not be significantly attacked. The extractant as expected removed lower concentrations (Table 7) than the total extraction procedures. In general, less than 10% of the total vanadium was extracted. Alternatively several

.../24

Table 7.

PARTIAL EXTRACTION OF ELEMENTS - LABORATORY 2

(0.1N HCl; Atomic Absorption)

Area	Sample Number	Texture[1]	Elements						
			V	Ni	Cu	Co	Zn	Mn	Fe
			ppm	ppm	ppm	ppm	ppm	ppm	%
Athabasca River	A-D-13	cs	11.0	17.0	8.0	5.0	24.0	250	0.70
	A-D-16	cs	9.0	24.0	9.0	< 5.0	34.0	240	0.66
(From above Fort McMurray to the Athabasca River Delta)	A-D-15	s	< 8.0	9.0	2.0	< 5.0	8.0	190	0.33
	A-D- 9	cs	< 8.0	24.0	12.0	8.0	37.0	330	0.74
	A-D- 5	st	< 8.0	< 5.0	2.0	< 5.0	6.0	160	0.25
	A-D-19	sc	< 8.0	21.0	8.0	< 5.0	24.0	240	0.65
	A-D-21	sc	< 8.0	11.0	3.4	5.0	13.0	160	0.39
	A-D-70	c	< 8.0	24.0	8.0	9.0	28.0	280	0.70
	A-D-69	s	< 8.0	11.0	2.2	6.0	12.0	150	0.38
	A-D-65	s	< 8.0	< 5.0	< 1.0	< 5.0	6.0	70	0.19
Athabasca River Delta	A-D-52	c	12.0	27.0	11.0	9.0	40.0	340	0.85
	D-34	c	13.0	28.0	14.0	8.0	45.0	480	1.20
	A-D-61	cs	14.0	29.0	14.0	13.0	44.0	580	1.00
	A-D-60	cs	14.0	27.0	12.0	11.0	40.0	430	0.87
	A-D-46	s	< 8.0	7.0	1.0	5.0	7.0	60	0.22
	A-D-47	c	9.0	20.0	9.0	10.0	27.0	310	0.75
Lake Athabasca	A-D-29	sc	< 8.0	19.0	8.0	< 5.0	28.0	250	0.73
	A-D-35	c	15.0	33.0	15.0	10.0	47.0	360	1.10
	A-D-41	c	10.0	35.0	16.0	6.0	52.0	600	1.20
	A-D-44	c	12.0	35.0	17.0	9.0	54.0	480	0.94
Riviere des Rochers	A-D-23	c	13.0	33.0	13.0	8.0	47.0	390	0.93

1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

of the nickel results are higher than the total analyses of laboratory 3 (Appendix 2), Table 3). As for the total Ni analyses by laboratory 2, it is usspected that Ni contamination is responsible.

About 75% of the Mn was also extracted and about 40% of the Fe, indicating their presence probably sorbed on/in amorphous inorganic or low molecular weight organic coatings.

Significant quantities of Cu and Zn were extracted In some cases the indication is that all of the Cu and about 50% of the Zn is extractable by 0.1N HCl.

Benzene-Methanol/NaOH Sequential Extractions: The 1:1 benzene/methanol reagent is expected to remove lipids; low molecular weight hydrocarbons; some bituminous material; chlorophyll-a degradation products; and other soluble organics, but not humic material ~~or humin~~ (Jackson, 1975b). The subsequent 0.1N NaOH extractant is expected to remove the humic material but not to significantly attack the mineral particles or amorphous inorganic coatings on these particles. All of the vanadium concentrations (Tables 8 and 9) were beneath detection in both extractions. Some 90% of the total V (Appendix 6, Table 3) is thus present in a form that is not extractable by any of the three partial extraction reagents employed.

Most of the other elements (Tables 8 and 9) were also extracted in amounts beneath detection limits. Exceptions were Zn and Cu. The low concentrations removed by the benzene/methanol and NaOH indicate that these elements are held primarily in the 0.1N HCl extractable fraction. Most likely they are present in inorganic amorphous iron coatings on mineral grains.

.../25

Table 8. PARTIAL EXTRACTION OF ELEMENTS - LABORATORY 2

(1:1 by volume benzene-methanol; Atomic Absorption)

Area	Sample Number	Texture[1]	Elements						
			V	Ni	Cu	Co	Zn	Mn	Fe
			-ppm-						
Athabasca River	A-D-13	cs	< 5	< 5	< 1	< 5	12	< 1	< 4
	A-D-16	cs	< 5	< 5	< 1	< 5	< 1	< 1	< 4
	A-D-15	s	< 5	< 5	1	< 5	8	< 1	< 4
	A-D- 9	cs	< 5	< 5	< 1	< 5	12	< 1	< 4
	A-D- 5	st	< 5	< 5	< 1	< 5	< 1	< 1	4
	A-D-19	sc	< 5	< 5	< 1	< 5	2	< 1	< 4
	A-D-21	sc	< 5	< 5	< 1	< 5	1	< 1	< 4
	A-D-70	c	< 5	< 5	< 1	< 5	< 1	< 1	6
	A-D-69	s	< 5	< 5	< 1	< 5	< 1	< 1	9
	A-D-65	s	< 5	< 5	< 1	< 5	< 1	< 1	< 4
Athabasca River Delta	A-D-52	c	< 5	< 5	2	< 5	3	< 1	< 4
	D-34	c	< 5	< 5	< 1	< 5	12	< 1	5
	A-D-61	cs	< 5	< 5	< 1	< 5	3	< 1	4
	A-D-60	cs	< 5	< 5	< 1	< 5	2	< 1	< 4
	A-D-46	s	< 5	< 5	< 1	< 5	< 1	< 1	6
	A-D-47	c	< 5	< 5	< 1	< 5	4	< 1	< 4
Lake Athabasca	A-D-29	sc	< 5	< 5	< 1	< 5	2	< 1	< 4
	A-D-35	c	< 5	< 5	< 1	< 5	5	< 1	5
	A-D-41	c	< 5	< 5	< 1	< 5	5	< 1	< 4
	A-D-44	c	< 5	< 5	< 1	< 5	< 1	< 1	< 4
Riviere des Rochers	A-D-23	c	< 5	< 5	< 1	< 5	1	< 1	4

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1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

Table 9. PARTIAL EXTRACTION OF ELEMENTS - LABORATORY 2

(0.1$\underline{N}$ NaOH; Atomic Absorption)

Area	Sample Number	Texture[1]	Elements						
			V	Ni	Cu	Co	Zn	Mn	Fe
			ppm						
Athabasca River (From above Fort McMurray to the Athabasca River Delta)	A-D-13	cs	< 10	< 5	4	< 5	1	6	255
	A-D-16	cs	< 10	< 5	8	< 5	1	2	173
	A-D-15	s	< 10	< 5	< 1	< 5	1	< 1	18
	A-D- 9	cs	< 10	< 5	7	< 5	2	9	380
	A-D- 5	st	< 10	< 5	< 1	< 5	1	2	93
	A-D-19	sc	< 10	< 5	4	< 5	2	8	391
	A-D-21	sc	< 10	< 5	1	< 5	1	1	81
	A-D-70	c	< 10	< 5	5	< 5	1	6	312
	A-D-69	s	< 10	< 5	< 1	< 5	1	< 1	40
	A-D-65	s	< 10	< 5	< 1	< 5	1	< 1	26
Athabasca River Delta	A-D-52	c	< 10	< 5	7	< 5	1	9	363
	D-34	c	< 10	< 5	12	< 5	1	8	242
	A-D-61	cs	< 10	< 5	11	< 5	1	17	373
	A-D-60	cs	< 10	< 5	9	< 5	1	11	322
	A-D-46	s	< 10	< 5	< 1	< 5	1	< 1	35
	A-D-47	c	< 10	< 5	6	< 5	1	12	413
Lake Athabasca	A-D-29	sc	< 10	< 5	6	< 5	1	5	202
	A-D-35	c	< 10	< 5	11	< 5	1	5	283
	A-D-41	c	< 10	< 5	12	< 5	2	7	252
	A-D-44	c	< 10	< 5	11	< 5	2	6	293
Riviere des Rochers	A-D-23	c	< 10	< 5	9	< 5	1	6	283

[1] Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

The benzene/methanol removed little Mn and Fe. The NaOH removed some 10% to 30% of the Fe removed by the HCl, and about 1% of the total iron. Iron present in extractable organics does not appear to be a major component of the sediment.

The comparison of the fractions of Zn and V removed by the total and partial extractants shows that some 50% of the former but only 10% or less of the latter is removed by the partial extractants. From this we conclude that much of the Zn may be present as exchangeable or chemisorbed ions or coatings on mineral grains. Alternatively most of the V is not in this form but is also not expected to be present in mineral particles. The obvious conclusion is that the V is present in a very high molecular weight organic compound. This may mean that the sediment organic fraction is close to its original composition in the oil sands in that it has not undergone chemical or bacteriological decomposition to a form which can be extracted by the caustic reagents used here. Because of this, it is unlikely that this V would enter the food chain and would probably be retained indefinitely in the sediments. This is the present natural geological situation. What may occur if V is introduced to the river in a different form following oil sands processing is open to speculation.

3.4 Organic Analyses

The visual estimates of texture provide little information on organic content. Inorganic and organic carbon analyses were performed by laboratory 2. Analyses of the blind duplicates showed precision to be satisfactory. An exception was A-D-65 and may be attributed to its sandy texture and an associated sub-sampling problem.

For the coarser grained and sandy samples the inorganic carbon, as expected, equals or exceeds the organic carbon content (Table 10). In the finer textured, clayey sediments the organic to inorganic carbon ratio appears to be about 3:1. The higher C/N ratios indicate that the organic material has not undergone a great deal of alteration and if extracted and studied in detail, probably has affinities with the relatively fulvic rich and relatively poorly mineralized organic material in the soils of the oil sands area. Fulvic and humic acid contents were determined. Fulvic acids are known to predominate in northern forest soils. They also appear to be the dominant fraction in the sediments.

3.5 Element Forms

Throughout this discussion, it has been implied that many of the easily extractable metals are probably present on or in organic-inorganic amorphous coatings on fine particle size minerals. Often with such relatively simple SDA techniques as employed here, it is problematical as to whether the sorbed metals are associated with inorganic (Fe, Al, Mn) coatings or with organic matter. The sorbtion capacity may vary with different layer silicate lattices or changes in organic composition. Generally the cation exchange capacity (CEC) and/or sorbtion due to organic material is far higher by weight than the capacity of even clays with maximum CEC e.g. vermiculite, a common mineral in sub-Arctic surficial sediments (Allan *et al.*, 1969). These materials are usually present in the finest particle

Table 10. ORGANIC ANALYSES - LABORATORY 2

(CHN Analyser)

Area	Sample Number	Texture[1]	Organic Carbon	Inorganic Carbon	Nitrogen	C/N	Fulvic Acid	Humic Acid
			- - - - %	- - - - - -	ppm		- - - g/kgC-	- -
Athabasca River	A-D-13	cs	1.40	0.42	830	22	2.1	1.6
	A-D-16	cs	1.16	0.69	755	25	1.8	1.1
(From above Fort	A-D-15	s	0.19	0.25	110	40	0.5	<0.1
McMurray to the	A-D- 9	cs	1.74	0.84	975	26	3.0	2.3
Athabasca River	A-D- 5	st	0.20	0.21	110	37	0.7	0.2
Delta)	A-D-19	sc	1.63	0.60	745	30	2.8	2.3
	A-D-21	sc	0.33	0.46	205	39	1.0	<0.1
	A-D-70	c	1.45	0.69	760	28	2.2	2.0
	A-D-69	s	0.18	0.35	530	10	0.5	<0.1
	A-D-65	s	0.16	0.08	400	6	0.4	<0.1
Athabasca River Delta	A-D-52	c	1.63	0.86	970	26	2.8	2.4
	A-D-34	c	1.87	1.25	1,620	25	3.2	1.9
	A-D-61	cs	1.95	1.24	1,310	24	3.6	1.8
	A-D-60	cs	1.89	0.92	1,070	26	3.1	2.0
	A-D-46	s	0.03	0.24	220	12	0.5	<0.1
	A-D-47	c	1.09	0.86	870	22	2.5	1.7
Lake Athabasca	A-D-29	sc	0.99	0.64	660	25	1.7	0.8
	A-D-35	c	2.00	0.78	1,345	21	2.8	2.1
	A-D-41	c	1,84	0.62	1,380	18	2.5	1.5
	A-D-44	c	1.57	0.56	1,210	18	2.1	1.0
Riviere des Rochers	A-D-23	c	1.27	0.69	1,050	19	1.7	1.0

1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

size fractions (≤5μ). Thus there is often a correlation in non-contaminated sediments between "clay" content and element concentration. This has been alluded to be the control for most of the element concentration variations in sediment from the Athabasca drainage system. The "clay" fraction is a complex mixture of fine particle size silicate minerals (dominated usually by layer silicates) and organic material often coated with organic-inorganic (Fe, Al, Mn) coatings. All of these parameters (element concentration, particle size distribution, cation exchange capacity, sorbtion capacity, organic content, amorphous Fe, Al and Mn) are likely to correlate to varying degrees with each other. To prove categorically whether one or the other is the true control would require far more complex extractions than used here and may be of little real value because of the close interaction of all of the parameters in natural sediments.

The significance of the above preamble is that as long as element concentrations correlate with one of the above parameters, then there is a reasonable chance variations are natural, providing that the absolute concentrations are geologically possible and show no obvious culturally controlled distribution pattern.

3.5.1 Metal-Organic Relations

The parameter used to represent organic content was organic carbon. V and Ni are the two heavy elements most commonly associated with the bitumen of the Alberta Oil Sands. Plots of V and Ni against organic carbon (Figures 3 and 4, respectively) show good correlation for all of the samples from the Athabasca River and

.../28

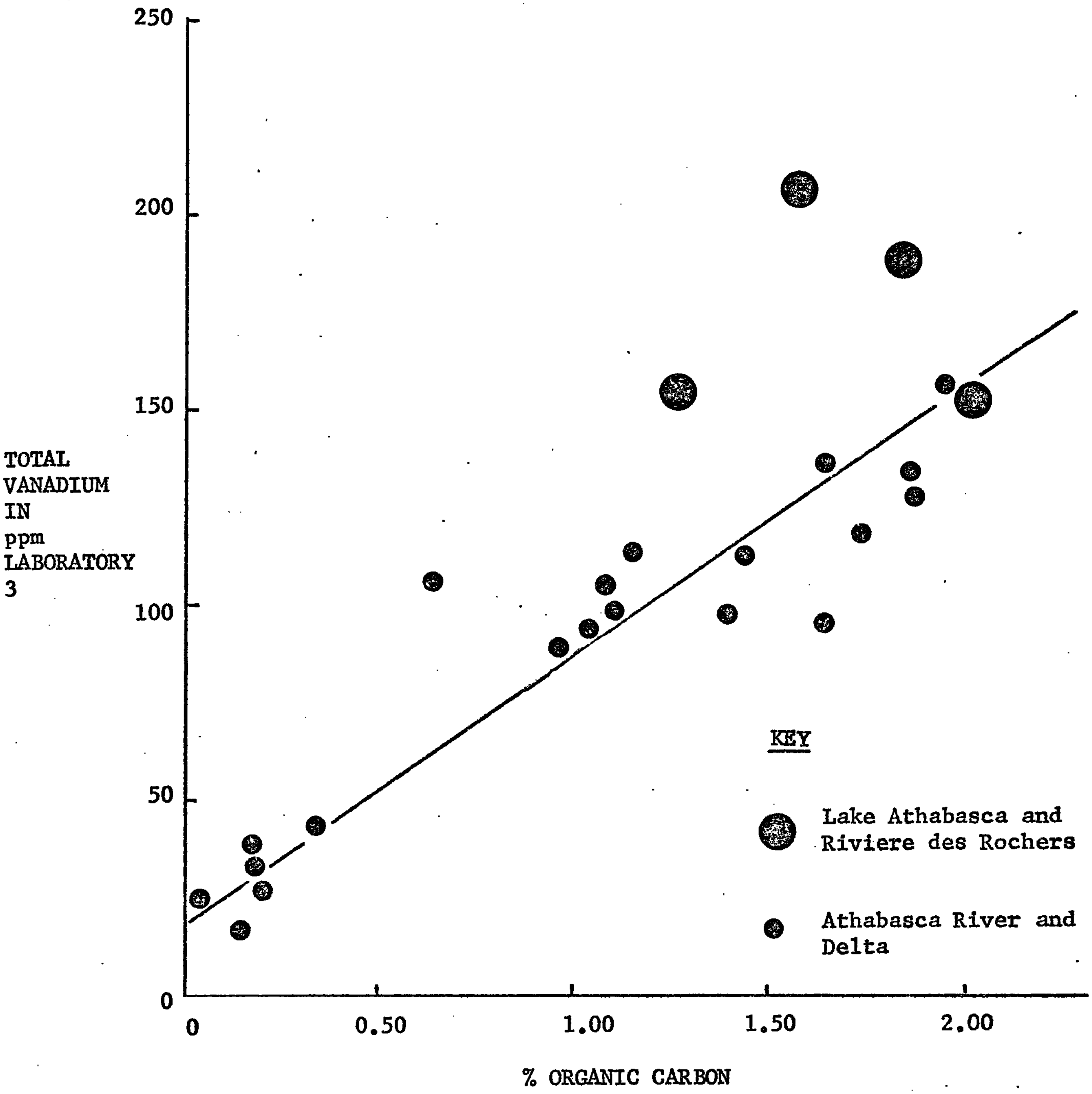

Figure 3. Total Vanadium VS Organic Carbon

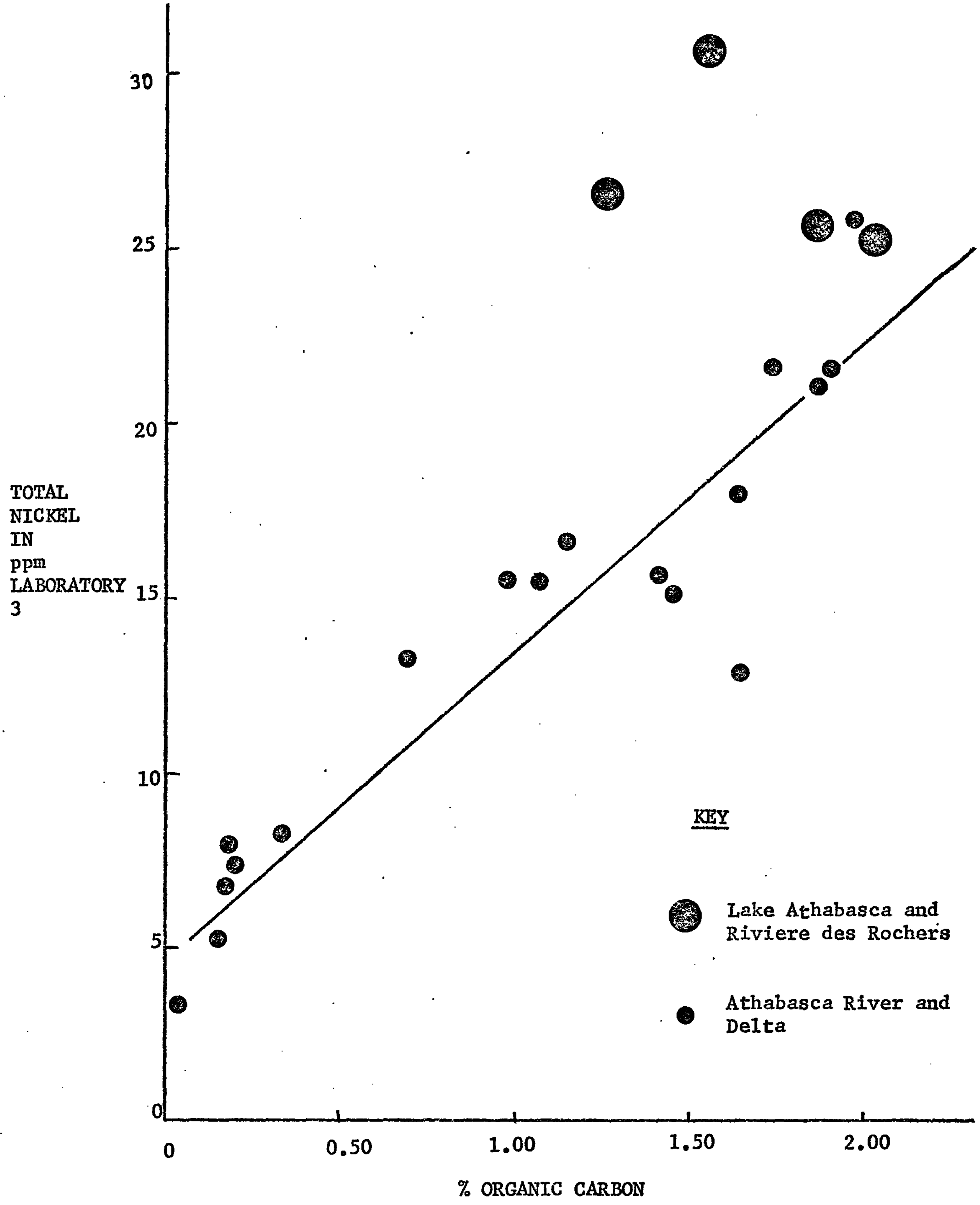

Figure 4. Total Nickel VS Organic Carbon

from its channels in the delta. The samples from Lake Athabasca and Riviere des Rochers are very fine textured and plot as expected at the upper end of the correlation. Four samples are not sufficient to draw conclusions on. However, the V and Ni content of these four samples does not appear to be so closely related to organic content, perhaps indicating a change in form due to diagenetic processes.

Another aspect of the plots is that the correlation between organic carbon and total V and Ni is good in spite of the fact that the partial extractions removed such a small proportion of the total vanadium. If the V were present in silicates, the correlation would have been poor. Thus, our argument for V in the form of a resistent organic compound in the sediments appears substantiated.

3.5.2 Metal-Metal Relations

Unlike V and Ni, we hypothesised earlier that most of the other heavy metals (Zn, Cu, Co, etc.,) are probably present in or on amorphous inorganic coatings.

To test this hypothesis we plotted zinc versus iron as extracted by the 0.1N HCl (Figure 5). The correlation using all samples was excellent indicating that the Zn extracted by this technique is probably in the form hypothesised.

Similar plots for many of the other elements versus Fe, organic content, particle size and the other parameters mentioned above is possible. They would serve little purpose here, because of our main interest in V and Ni and in the detection of cultural inputs. As mentioned above, these plots would simply confirm the natural geological, mineralogical, geochemical controls on all of the element variations.

.../29

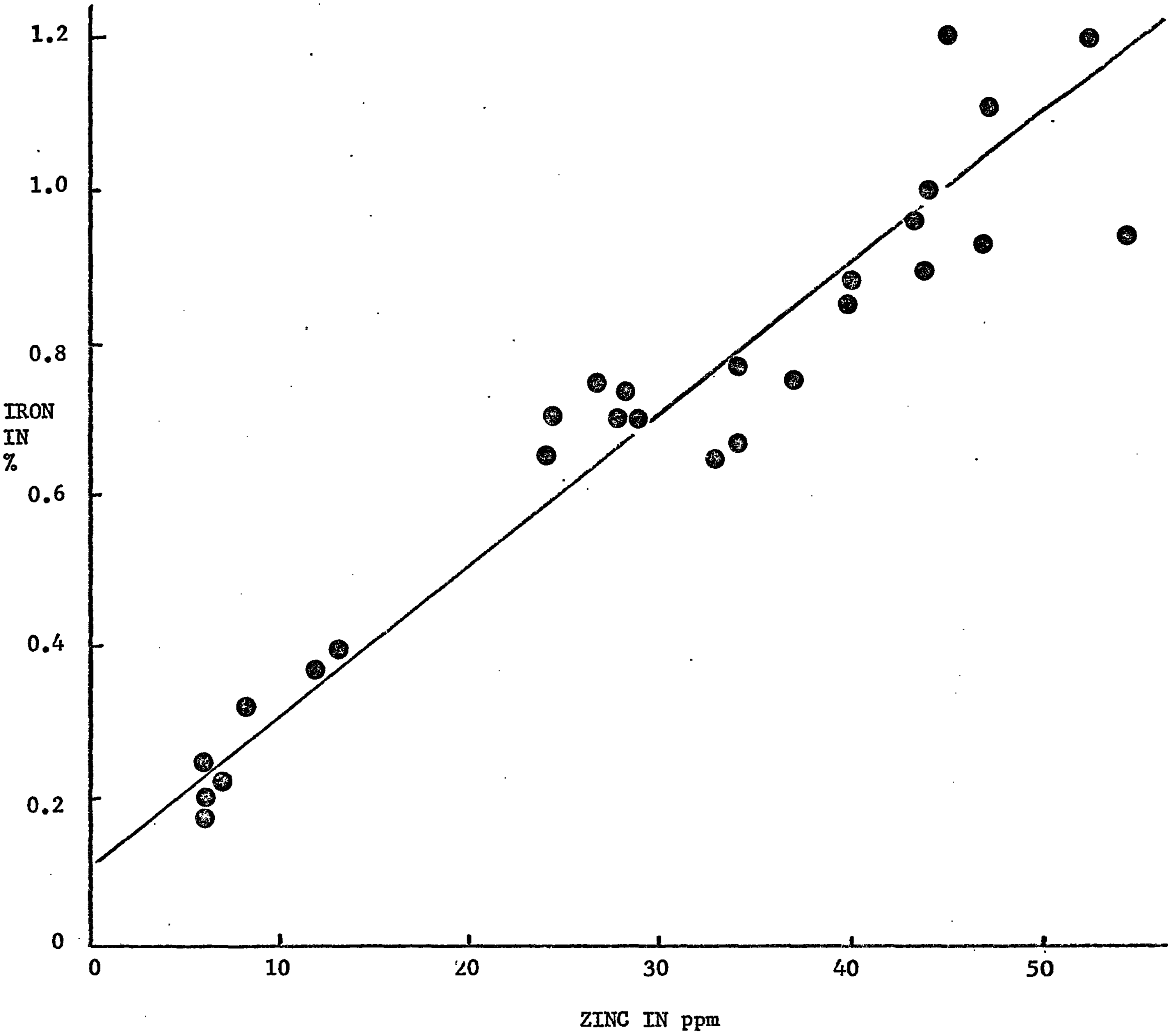

Figure 5. Iron VS Zinc in Partial Extract Using 0.1N HCl

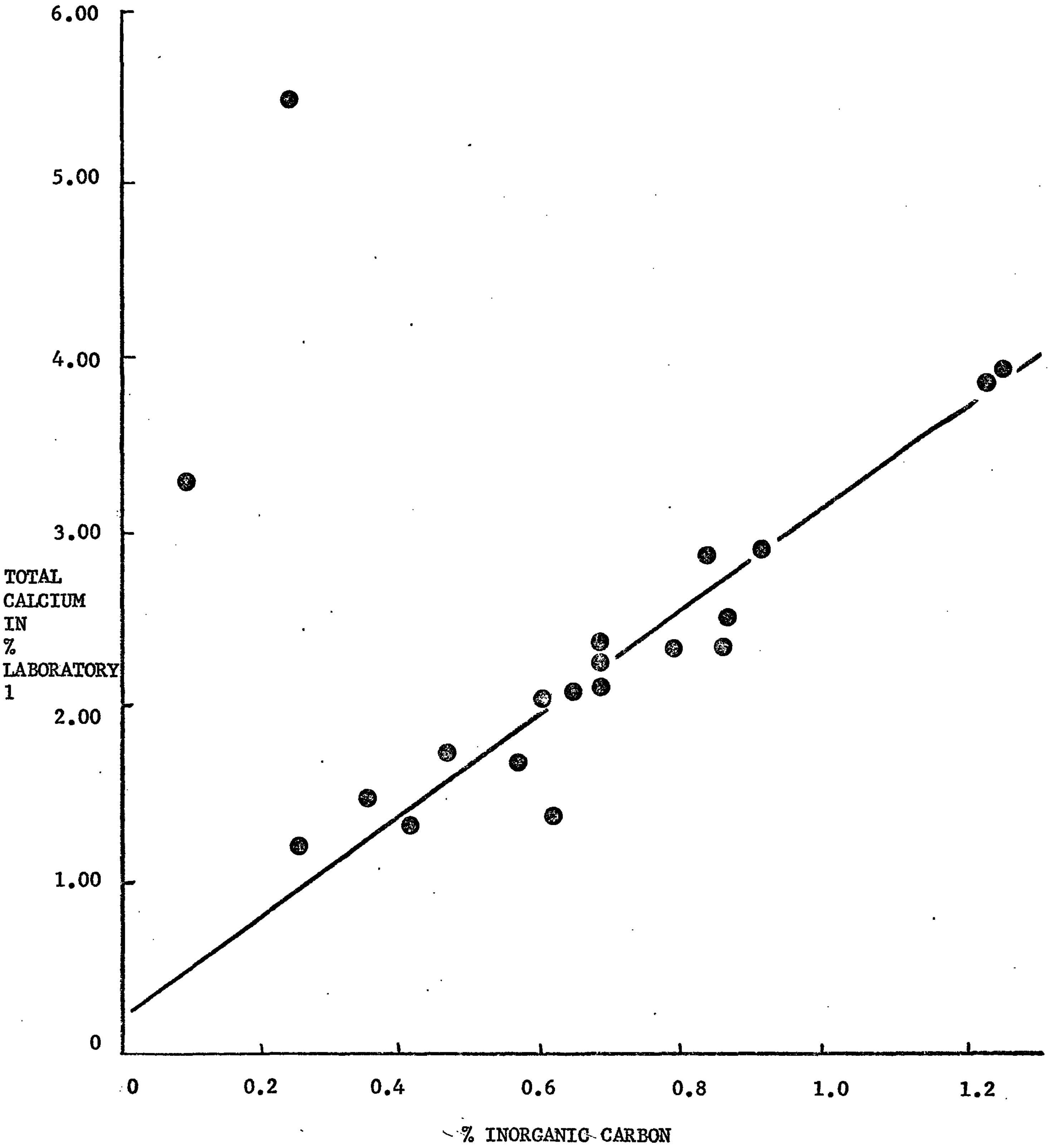

Figure 6. Total Calcium VS Inorganic Carbon

A final example, from a slightly different concept, is the correlation between inorganic carbon (carbonate) and total Ca (Figure 6). The correlation for all but two samples was excellent, suggesting that most of the Ca is present as dolomite particles, probably of clay size. The two samples which did not fit the correlation had very low inorganic carbon content but very high Ca. Both were sands. The high Ca and low carbon could be due to plagioclase feldspars in the coarse silt and sand fractions. X-ray diffraction would be needed to confirm these tentative interpretations. This example is merely intended to show that correlations of total elements with each other are probably dominated by mineralogy, especially in the coarser, sandier sediments.

4. CONCLUSIONS

The main conclusions drawn from this study are as follows:

(1) There is presently no evidence of cultural contamination of drainage sediments by heavy metals at least as far as can be determined from the analyses performed so far on the relatively few samples used.

(2) Variations in all element concentrations reflect geological, geochemical, mineralogical and sedimentological controls only. The most obvious of these is the association of slightly higher element concentrations with finer textured sediments which in turn is related to increases in several parameters including surface area, amorphous inorganic-organic coatings, layer silicates, and organic content.

.../30

(3) Lake Athabasca sediments have the highest concentrations of several elements because of these natural controls.

(4) V, the heavy element most commonly associated with the Alberta Oil Sands, is present in the bottom sediments in the same or lower concentrations than in drainage sediments elsewhere. Caustic reagents removed only a small fraction of the total V. Total V correlates well with organic carbon. The implication is that the V in the sediments is probably in a form similar to that in which it occurs in the Oil Sands proper and has thus undergone little chemical or bacteriological alteration. It would appear to have little chance of entering the food chain should geochemical controls in the drainage system remain the same.

5. RECOMMENDATIONS

This study was not costly (see below). The text above contains many hypotheses and tenuous correlations on element forms. To more clearly define these would require further detailed analyses of selected samples. Also, the statement on the lack of any cultural impact only apply to the specific samples analysed. A greater density of analysed dredged samples along with analyses of finely divided sediment cores could lend greater strength to this conclusion. Appendix 1 shows the samples presently freeze dried and stored by C.C.I.W. at the Freshwater Institute. It is our opinion that the conclusions arrived at on the basis of the limited costs are adequate for a baseline study. However,

.../31

if further use of these samples were made we would recommend the following (decreasing priority):

(1) Carry out selective dissolution analyses (carbonates) and saturation procedures (clays) followed by XRD of selected samples, to more clearly document the minerology of the sediment;

(2) Select a small number of samples and extract with various reagents, including pyridene (B. Afghan, C.C.I.W. Pers. Comm.), and followed by sephadex column fractionation and metal analyses, to try and more completely define the sediment metal-organic complexes;

(3) Analyse the lake sediment cores (see Appendix 1) for key elements and determine sedimentation rates on selected cores by radiometric methods, to determine historical changes in element loadings;

(4) Complete the analyses of the total dredged sediment sample suite (see Appendix 1) using three techniques,

  a: total analyses by laboratory 3 method;
  b: 0.1N HCl extraction by laboratory 2 method;
  c: pyridene extraction according to J.F. Ryan (C.C.I.W. Pers. Comm.);

(5) Analyse suite of lake sediments from OSERP Area including Mildred Lake, Kearl Lake, Namur Lake, etc., (samples already collected and prepared) for comparison with river and Lake Athabasca sediments and in anticipation of future regional airborne heavy metal fallout;

(6) Carry out detailed cross-section and grid pattern sampling and metal analyses of river sediments

.../32

for 3 to 5 miles downstream of all proposed extraction plants;

(7) In cooperation with other I.W.D. groups, collect and analyse suspended sediment samples from the mainstem of the drainage system;

(8) Sample and analyse oil slicks (water-air interface) for heavy metals.

6. ACKNOWLEDGEMENTS

Our interest in the AOSERP Area was greatly increased after discussions with Mr. M. Kochinski, Water Quality Laboratories, Calgary, who has been studying the water and suspended sediment phases of the drainage system. We appreciate his bringing to our attention, the possibility of our involvement.

We wish to thank all four laboratories for the analyses performed. Considering the low concentrations for all elements, the results from any of them would have served our study. The acceptance of blind duplicates in the sample suite was appreciated. As expected with complex analyses, a few of the results imply that some elements in these sediments may be difficult to determine.

The sampling was carried out by Messrs. M. Roy and R. Woychuk of C.C.I.W.-W.N.R. For a two-man operation in a remote area, their sample coverage was no mean feat. Mr. Roy was also responsible for sample preparation, analytical contracts and related logistical items. Mr. Woychuk has and will be more involved with sephadex column studies of selected sediments.

.../33

The sampling crew greatly appreciated the assistance of Mr. J. Anderson, Alberta D.O.E. and other AOSERP field staff. We wish to thank Mr. R. Froelich of AOSERP for his continued interest in our project and the Hydrology Committee of AOSERP for financial support.

We also wish to thank Mr. E. F. Durrant, Former Director, I.W.D.-W.N.R. for allowing us to become involved in this external project.

7. COSTS

With any operation of this kind, cost effectiveness is considered by us to be of significance. The funding of this project by AOSERP was as follows:

	$K
Sampling	4.4
Analyses	
Total	1.6
Partial/Organic	3.2
Other	
Total	9.2

We feel that the return for this expenditure is satisfactory. Also, a large sample suite is now on hand for future analyses. The return for further expenditures on sample analyses is likely to be lower in that the main conclusions are unlikely to change. The only hidden costs were salaries for the people involved and the office space, etc., at the Freshwater Institute. Typing of the manuscript was also covered by our own budget.

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9. APPENDICES

9.1 Locations of all Sample Sites.

9.2 Visual Estimates of Texture-All Samples.

9.3 Total Element Concentrations-Blind Duplicates.

9.4 Total Element Concentrations-Selected Sample Suite.

9.5 Partial Element and Organic Concentrations-Blind Duplicates.

9.6 Heavy Metals in Sediments of AOSERP Area-Other Reports.

APPENDIX 1.

Locations of All Sample Sites

Figure 1:	McClelland Lake to Richardson Lake.
Figure 2:	Lake Athabasca and Riviere des Rochers.
Figure 3:	Athabasca River Delta.
Figure 4:	Fort McMurray to Bitumont.

KEY

All samples prefixed D are dredged
All samples prefixed C are cores

In texture tables samples are A-D and A-C. The A has been dropped here for drafting purposes.

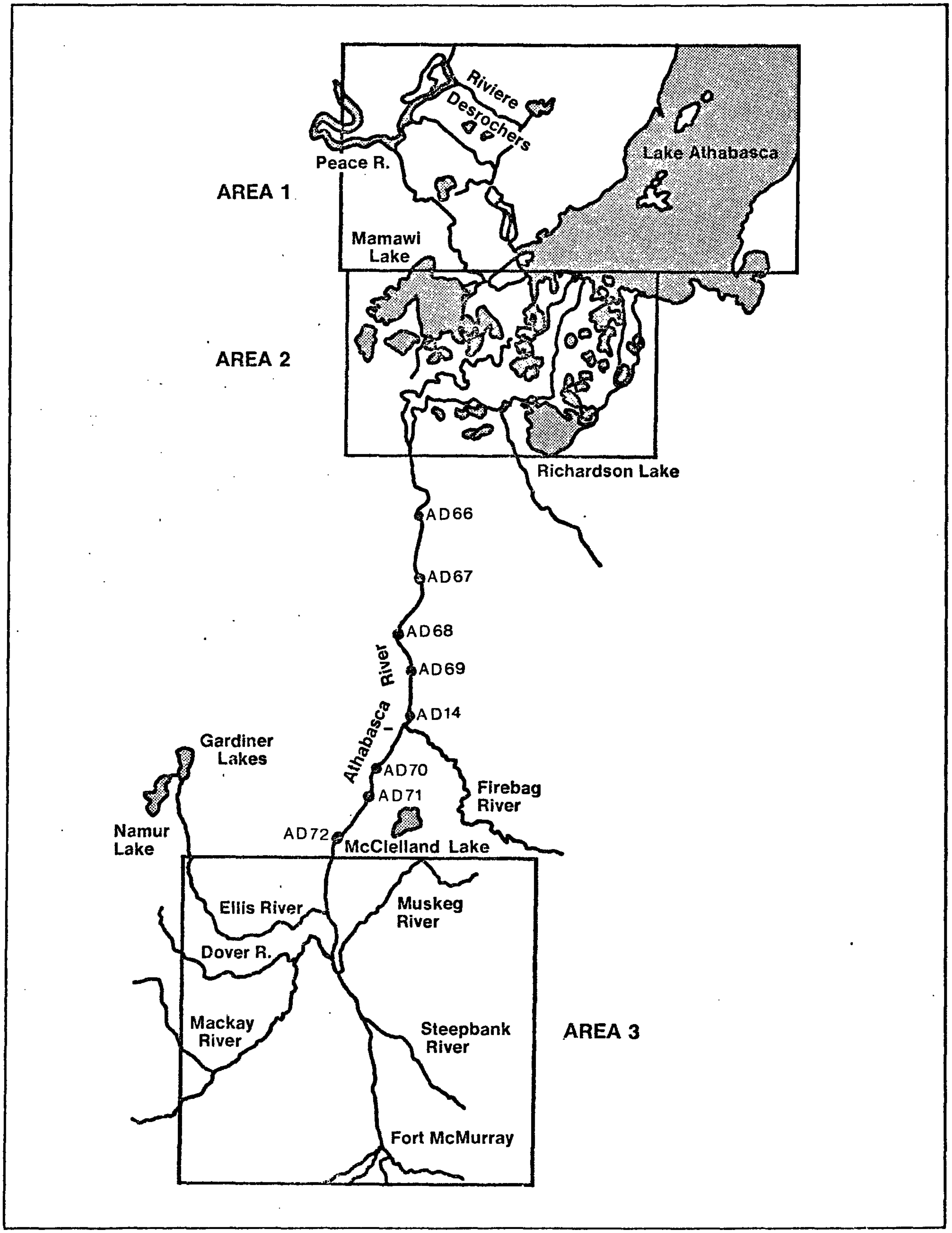

Figure 1: McClelland Lake to Richardson Lake.

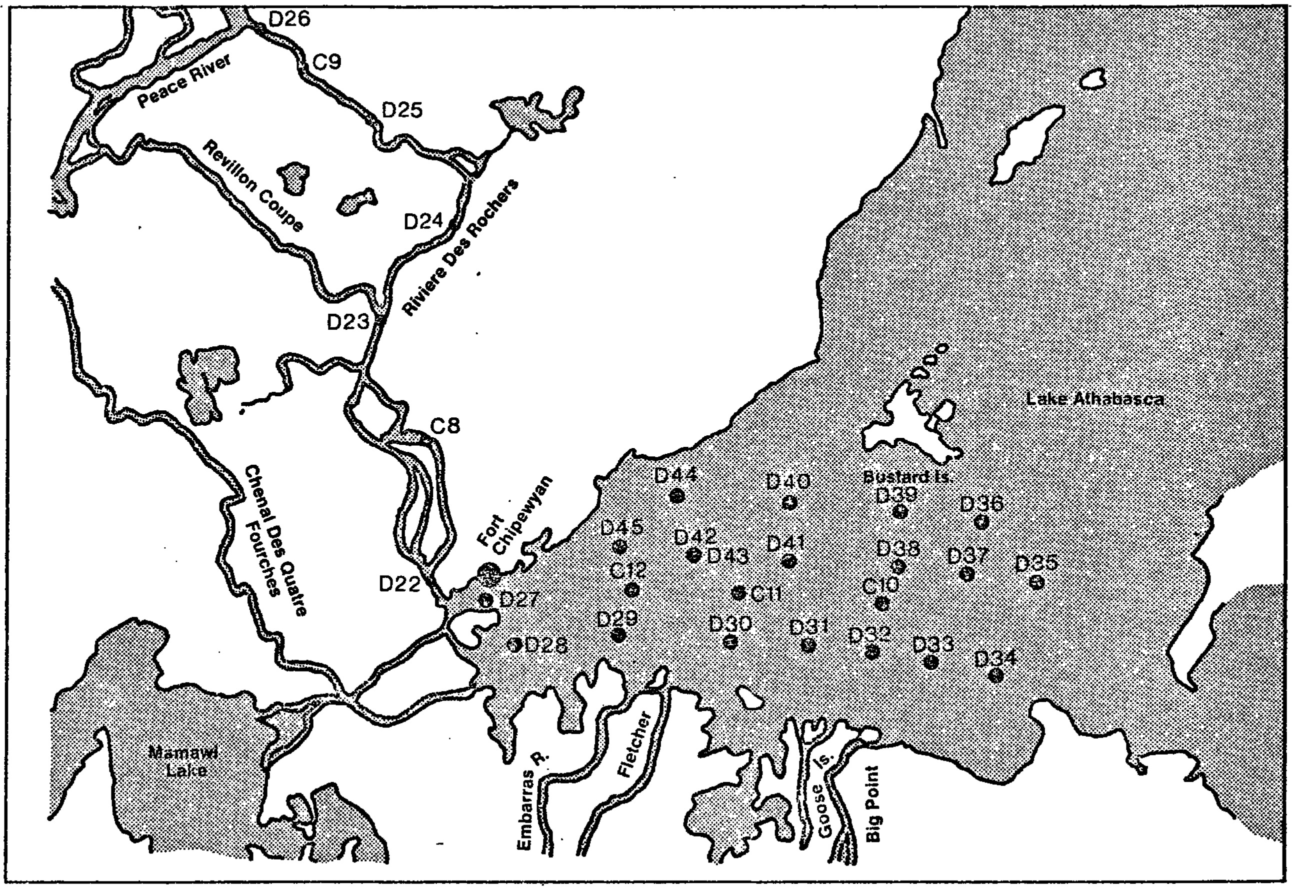

Figure 2: Lake Athabasca and Riviere des Rochers.

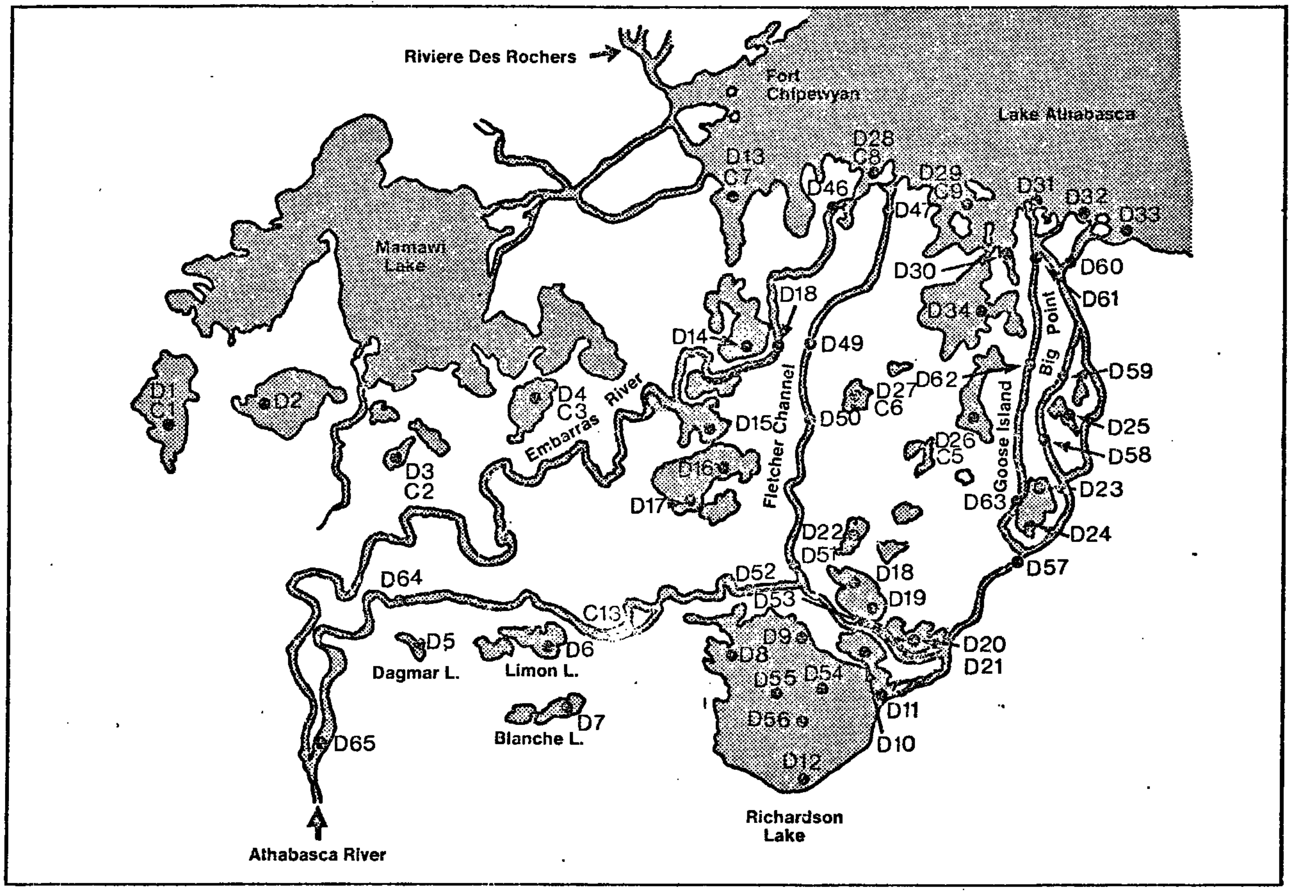

Figure 3: Athabasca River Delta.

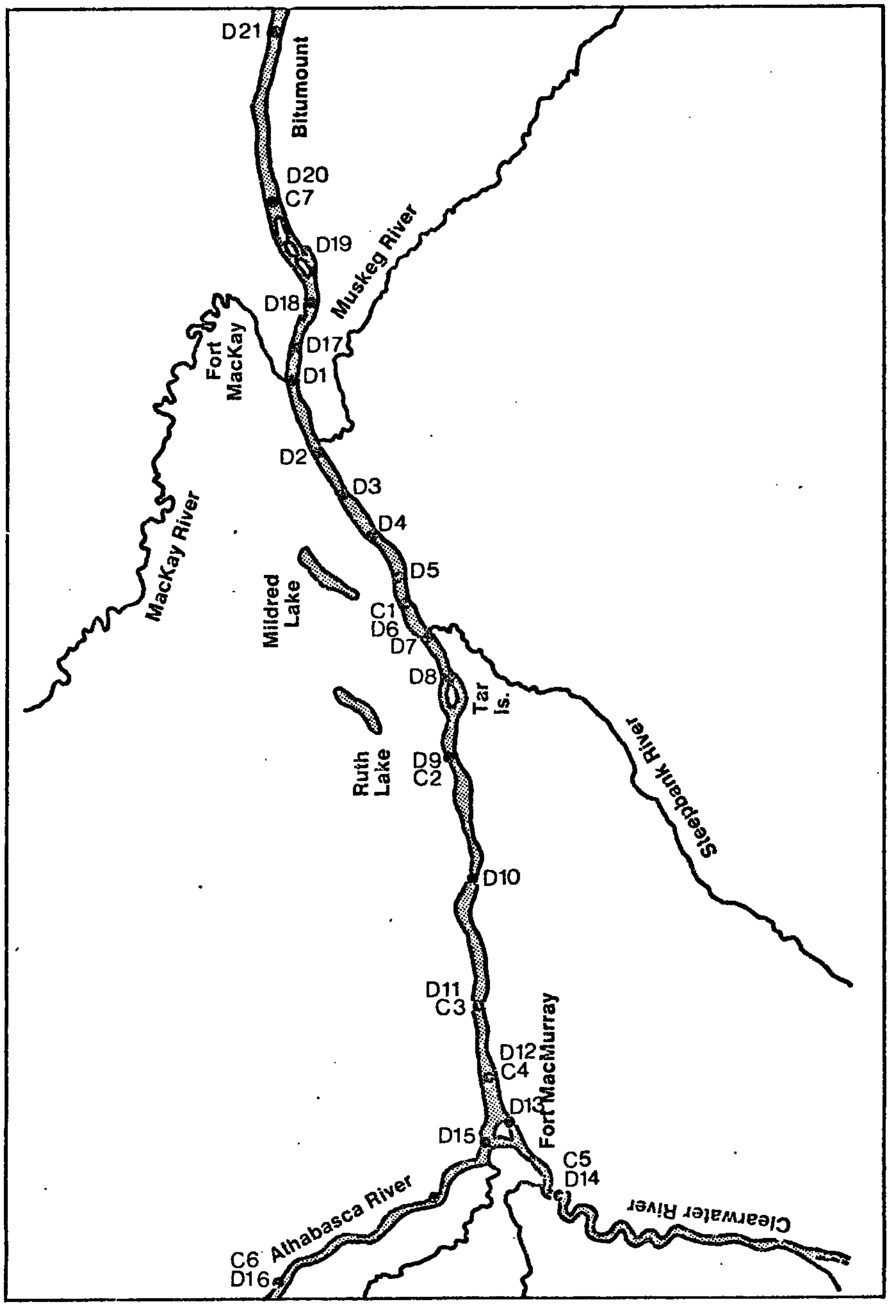

Figure 4. Fort McMurray to Bitumont.

APPENDIX 2.

Visual Estimates of Texture-All Samples.

Table 1: River and Lake Sediments.

Table 2: Delta Sediments.

Table 1. SAMPLE NUMBERS AND TEXTURE ESTIMATED VISUALLY OF BOTTOM SEDIMENTS FROM THE ATHABASCA RIVER SYSTEM AND LAKE ATHABASCA

A-D-1 - sand
" 2 - sand and clay
" 3 - sand and clay
" 4 - sand and tar fragments
" 5 - sand and tar fragments
" 6 - clay and sand
" 7 - sand
" 8 - sand and clay
" 9 - clay and sand
" 10 - sand
" 11 - clay and sand
" 12 - sand and clay
" 13 - clay and sand
" 14 - sand and clay
" 15 - sand
" 16 - clay and sand
" 17 - clay and sand
" 18 - clay and sand
" 19 - sand and clay
" 20 - clay and sand
" 21 - sand and clay
" 22 - clay
" 23 - clay
" 24 - clay
" 25 - clay
" 26 - clay and sand
" 27 - clay and sand
" 28 - clay
" 29 - sand and clay
" 30 - sand and clay
" 31 - clay and sand
" 32 - sand
" 33 - sand and clay
" 34 - sand
" 35 - clay
" 36 - sand and clay
" 37 - clay
" 38 - sand and clay
" 39 - clay
" 40 - clay
" 41 - clay
" 42 - clay
" 43 - clay
" 44 - clay
" 45 - clay
" 46 - sand
" 47 - clay
" 48 - sand
" 49 - sand
" 50 - sand
" 51 - clay and sand
" 52 - clay
" 53 - sand and clay
" 54 - clay
" 55 - clay
" 56 - clay
" 57 - sand
" 58 - clay
" 59 - clay
" 60 - clay and sand
" 61 - clay and sand
" 62 - clay and sand
" 63 - sand and clay
" 64 - clay
" 65 - sand
" 66 - sand and clay
" 67 - sand
" 68 - sand and clay
" 69 - sand
" 70 - clay
" 71 - sand and clay
" 72 - sand and clay

Table 2. SAMPLE NUMBERS AND TEXTURE ESTIMATED VISUALLY OF BOTTOM SEDIMENTS FROM THE ATHABASCA RIVER DELTA

D- 1 - organic marsh decay
D- 2 - organic marsh decay
D- 3 - organic marsh decay
D- 4 - organic marsh decay
D- 5 - clay and organic
D- 6 - clay and organic
D- 7 - clay and organic
D- 8 - clay
D- 9 - sand and clay
D-10 - clay
D-11 - clay
D-12 - sand and clay
D-13 - clay and organic
D-14 - clay and organic
D-15 - clay and organic
D-16 - clay and organic
D-17 - clay and organic
D-18 - organic marsh decay
D-19 - organic marsh decay
D-20 - organic marsh decay
D-21 - organic marsh decay
D-22 - clay and sand
D-23 - clay and organic
D-24 - organic marsh decay
D-25 - organic marsh decay
D-26 - clay and sand
D-27 - clay and sand
D-28 - clay and sand
D-29 - clay and sand
D-30 - clay
D-31 - clay
D-32 - clay
D-33 - clay
D-34 - clay and sand

APPENDIX 3.

Total Element Concentrations-Blind Duplicates.

Table 1: Laboratory 1.

Table 2: Laboratory 2.

Table 3: Laboratory 3.

Table 4: Laboratory 4.

Table 1: DUPLICATE TOTAL ANALYSES - LABORATORY 1

(Reflux HF, HNO_3-$HCIO_4$; Radio Frequency Plasma Emission Spectroscopy)

Sample Number	Elements							
	V	Ni	Cu	Zn	Mn	Fe	Na	Ca
	ppm					%		
A-D-13	93	29	18	79	393	2.51	0.74	1.31
	94	32	18	81	403	2.53	0.74	1.30
A-D-19	74	28	15	68	355	2.08	0.81	2.04
	71	29	14	72	358	2.04	0.96	1.99
A-D-29	76	29	15	77	362	2.06	0.89	2.07
	78	31	15	76	360	2.04	0.82	2.04
A-D-60	111	38	21	100	570	2.92	0.74	2.85
	113	40	25	108	577	3.12	0.67	2.92
A-D-65	15	11	1	21	93	0.58	0.45	0.33
	17	11	4	22	101	0.64	0.46	0.38

Table 2: DUPLICATE TOTAL ANALYSES - LABORATORY 2.

($HF-HNO_3-HCIO_4$ Extraction; Sealed Teflon Bomb; Atomic Absorption)

(Hg by $H_2SO_4-HNO_3-HCIO_4-KMnO_4-K_2S_2O_8$ digestion;
Cold Vapour Atomic Absorption)

Sample Number	Elements						
	V	Ni	Cu	Zn	Mn	Hg	Fe
	- - - - - - - - - ppm - - - - - - - - -					ppb	%
A-D-13	<80	110	27	60	340	34	2.20
	<80	50	21	49	320	36	1.70
A-D-19	<80	110	31	50	350	38	2.00
	100	60	15	49	310	40	2.00
A-D-29	100	130	28	50	320	34	2.00
	89	40	11	59	320	54	1.86
A-D-60	110	170	28	90	550	54	2.80
	130	60	35	80	520	58	2.60
A-D-65	<80	89	<10	30	79	6	0.51
	<80	10	<10	30	89	6	0.59

Table 3: DUPLICATE TOTAL ANALYSES - LABORATORY 3.

(V by HF; $K_2S_2O_8$ fusion; Atomic Absorption)

(Other elements by Aqua Regia (3:1 Conc. HCl:Conc.HNO_3); Atomic Absorption)

Sample Number	Elements						
	V	Ni	Cu	Zn	Mn	Hg	Fe
	ppm					ppb	%
A-D-13	97	15	12	48	324	46	1.74
	106	13	11	45	325	39	1.72
A-D-19	95	12	10	44	318	35	1.48
	89	16	9	42	313	32	1.46
A-D-29	89	16	10	45	312	28	1.43
	88	16	9	43	318	29	1.41
A-D-60	128	21	17	65	531	51	2.11
	130	21	17	64	546	56	2.05
A-D-65	18	5	<1	10	82	9	0.46
	24	5	<1	10	86	6	0.46

Table 4: DUPLICATE TOTAL ANALYSES - LABORATORY 4.

(Aqua Regia Extraction (3:1 Conc.HCl:Conc.HNO_3); Atomic Absorption)

Sample Number	Elements					
	V	Ni	Cu	Zn	Mg	Fe
	- - - - - ppm - - - - - -				- - - % - - - -	
A-D-13	23	18	13	44	0.08	1.61
	26	16	12	38	0.60	1.48
A-D-19	15	16	10	38	0.08	1.34
	23	16	11	36	0.48	1.30
A-D-29	20	15	11	40	0.17	1.33
	23	14	10	36	0.53	1.14
A-D-60	33	23	17	51	1.17	1.77
	28	26	16	50	0.73	1.63
A-D-65	<3		1	14	0.09	0.41
	<3	8	1	15	0.11	0.46

APPENDIX 4.

Total Element Concentrations-Selected Sample Suite.

Table 1: Laboratory 1

Table 2: Laboratory 2.

Table 3: Laboratory 3.

Table 4: Laboratory 4.

Table 1. TOTAL MAJOR ELEMENTS IN DREDGED BOTTOM SEDIMENTS - LABORATORY 1

(Reflux HF, HNO_3-$HClO_4$; Radio Frequency Plasma Emission Spectroscopy)

Area	Sample Number	Texture[1]	Elements						
			Al	Fe	Na	Ca	Mg	P	Ti
						%			
Athabasca River	A-D-13	cs	5.13	2.51	0.74	1.32	1.01	0.13	0.33
	A-D-16	cs	5.66	2.45	0.89	2.34	1.09	0.13	0.32
(From above Fort McMurray to the Athabasca River Delta)	A-D-15	s	2.78	1.09	0.74	1.20	0.32	nd[2]	0.11
	A-D-9	cs	5.66	2.58	0.81	2.89	1.16	0.13	0.33
	A-D-5	st	2.22	1.09	0.52	0.89	0.27	nd	0.12
	A-D-19	sc	4.68	2.08	0.81	2.04	0.83	0.13	0.27
	A-D-21	sc	3.19	1.39	0.67	1.72	0.63	nd	0.22
	A-D-70	c	5.11	2.36	0.89	2.30	1.03	0.13	0.29
	A-D-69	s	3.39	1.39	0.96	1.49	0.57	nd	0.27
	A-D-65	s	1.59	0.58	0.45	0.33	0.18	nd	0.05
Athabasca River Delta	A-D-52	c	5.56	2.64	0.82	2.35	1.08	0.13	0.34
	D-34	c	6.35	2.95	0.74	3.88	1.35	0.13	0.38
	A-D-61	cs	6.77	3.27	0.74	3.83	1.45	0.18	0.39
	A-D-60	cs	6.09	2.92	0.74	2.85	1.28	0.13	0.35
	A-D-46	s	1.94	0.71	0.52	0.55	0.26	nd	0.14
	A-D-47	c	4.51	2.01	0.74	2.45	0.94	0.13	0.28
Lake Athabasca	A-D-29	sc	4.81	2.06	0.89	2.07	0.91	0.13	0.28
	A-D-35	c	6.62	3.20	0.82	2.26	1.35	0.18	0.39
	A-D-41	c	5.82	2.89	0.59	1.38	1.10	0.13	0.36
	A-D-44	c	6.72	3.29	0.82	1.63	1.18	0.18	0.44
Riviere des Rochers	A-D-23	c	6.19	3.03	0.74	2.19	1.16	0.18	0.37

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1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.
2. nd=not detected.

Table 1 (cont.) TOTAL TRACE ELEMENTS IN DREDGED BOTTOM SEDIMENTS - LABORATORY 1

(Reflux HF, HNO_3-$HClO_4$; Radio Frequency Plasma Emission Spectroscopy)

Area	Sample Number	Texture[1]	Elements										
			Be	Ba	Sr	V	Ni	Cu	Co	Cr	Zn	Pb	Mn
			ppm										
Athabasca River	A-D-13	cs	1.7	610	137	93	29	18	14	88	79	nd[2]	393
	A-D-16	cs	2.2	730	204	100	33	19	13	93	96	nd	356
(From above Fort McMurray to the Athabasca River Delta)	A-D-15	s	1.0	470	155	31	13	4	4	33	36	nd	283
	A-D- 9	cs	2.4	780	205	98	34	21	13	96	94	nd	442
	A-D- 5	st	1.1	540	128	27	12	5	2	36	31	nd	231
	A-D-19	sc	1.9	680	190	74	28	15	13	72	69	nd	355
	A-D-21	sc	1.3	560	153	46	20	6	12	52	48	nd	283
	A-D-70	c	2.0	890	189	90	32	6	21	85	88	nd	381
	A-D-69	s	1.3	1,250	182	47	17	6	12	54	45	nd	283
	A-D-65	s	0.5	360	94	15	11	1	6	24	21	nd	93
Athabasca River Delta	A-D-52	c	2.2	770	185	96	34	20	17	100	93	nd	458
	D-34	c	2.8	770	197	113	38	23	19	109	101	nd	623
	A-D-61	cs	3.0	1,130	190	127	42	24	29	120	113	nd	733
	A-D-60	cs	2.5	710	179	111	38	21	20	104	100	nd	570
	A-D-46	s	0.7	390	118	22	8	1	7	27	32	nd	122
	A-D-47	c	1.9	650	172	73	29	14	14	73	70	10	377
Lake Athabasca	A-D-29	sc	1.9	710	187	76	29	15	19	78	77	nd	362
	A-D-35	c	2.5	920	170	122	40	25	23	114	111	nd	486
	A-D-41	c	2.2	660	130	113	38	21	21	102	103	nd	629
	A-D-44	c	2.6	1,160	152	148	46	28	23	127	129	nd	630
Riviere des Rochers	A-D-23	c	2.5	870	161	136	41	23	21	119	121	nd	533

1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.
2. nd=not detected.

Table 2. TOTAL ELEMENTS IN DREDGED BOTTOM SEDIMENTS - LABORATORY 2

($HF-HNO_3-HClO_4$ Extraction; Sealed Teflon Bomb; Atomic Absorption)

(Hg by $H_2SO_4-HNO_3-HClO_4-KMnO_4-K_2S_2O_8$ digestion; Cold Vapour Atomic Absorption)

Area	Sample Number	Texture[1]	Elements							
			V	Ni	Cu	Co	Zn	Mn	Hg	Fe
			ppm	ppm	ppm	ppm	ppm	ppm	ppb	%
Athabasca River (From above Fort McMurray to the Athabasca River Delta)	A-D-13	cs	<80	110	27	<50	60	340	34	2.20
	A-D-16	cs	30	120	30	70	60	330	46	2.30
	A-D-15	s	<80	120	19	69	30	270	10	0.92
	A-D- 9	cs	90	110	38	80	80	420	76	2.50
	A-D- 5	st	<80	120	11	50	20	110	20	0.66
	A-D-19	sc	<80	110	31	<50	50	350	38	2.00
	A-D-21	sc	<80	100	15	<50	30	200	10	1.20
	A-D-70	c	<80	49	12	50	69	340	42	2.10
	A-D-69	s	<80	130	<10	<50	30	180	12	0.95
	A-D-65	s	<80	89	<10	<50	30	79	6	0.51
Athabasca River	A-D-52	c	100	150	28	<50	70	430	56	2.60
	D-34	c	150	150	31	70	80	570	55	2.95
	A-D-61	cs	110	190	29	60	90	680	63	3.30
	A-D-60	cs	110	170	28	80	90	550	54	2.80
	A-D-46	s	<80	100	<10	70	10	67	8	0.50
	A-D-47	c	<80	140	19	60	60	360	43	2.10
Lake Athabasca	A-D-29	sc	100	130	28	<50	50	320	34	2.00
	A-D-35	c	180	160	39	80	100	710	78	3.40
	A-D-41	c	140	120	32	90	90	450	79	3.00
	A-D-44	c	130	160	39	80	100	560	86	3.10
Riviere des Rochers	A-D-23	c	140	140	33	80	100	510	64	2.90

1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

Table 3. TOTAL ELEMENTS IN DREDGED BOTTOM SEDIMENTS - LABORATORY 3

(V by HF; $K_2S_2O_8$ fusion; atomic absorption) (Other elements by Aqua Regia extraction 3:1 Conc.HCl:Conc.HNO_3; Atomic Absorption) (Hg by cold vapour atomic absorption)

Area	Sample Number	Texture[1]	Elements							
			V	Ni	Cu	Zn	Mn	As	Hg	Fe
			ppm	ppm	ppm	ppm	ppm	ppm	ppb	%
Athabasca River (From above Fort McMurray to the Athabasca River Delta)	A-D-13	cs	97	15.3	11.6	48.0	324	4.2	46	1.74
	A-D-16	cs	113	16.6	13.4	56.4	313	4.6	36	1.70
	A-D-15	s	32	6.8	1.9	16.0	248	2.7	10	0.74
	A-D- 9	cs	118	21.3	16.4	60.2	406	5.2	70	1.81
	A-D- 5	st	27	7.1	2.6	16.8	189	1.6	29	0.79
	A-D-19	sc	95	12.9	9.8	44.3	318	4.3	35	1.48
	A-D-21	sc	43	8.1	3.5	22.9	201	2.7	11	0.93
	A-D-70	c	112	15.0	11.4	49.8	346	4.8	36	1.67
	A-D-69	s	38	8.8	1.8	20.7	179	2.1	9	0.83
	A-D-65	s	18	5.1	0.30	9.6	82	2.0	9	0.46
Athabasca River Delta	A-D-52	c	137	17.9	14.8	57.2	418	5.1	48	1.82
	D-34	c	133	20.8	16.7	64.0	603	4.4	45	2.07
	A-D-61	cs	156	25.8	19.8	71.0	722	5.7	46	2.23
	A-D-60	cs	128	21.1	17.2	64.8	531	4.4	51	2.11
	A-D-46	s	25	4.2	0.45	18.8	71	1.9	5	0.44
	A-D-47	c	105	15.7	10.2	44.1	350	4.2	25	1.49
Lake Athabasca	A-D-29	sc	89	15.7	9.6	44.9	312	3.4	28	1.43
	A-D-35	c	152	25.3	19.9	73.4	450	5.4	66	2.32
	A-D-41	c	189	25.4	20.4	79.1	728	6.3	62	2.51
	A-D-44	c	207	30.7	24.9	92.7	620	6.6	69	2.50
Riviere des Rochers	A-D-23	c	156	26.3	19.5	81.0	484	6.2	57	2.27

[1] Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

Table 4. TOTAL ELEMENTS IN DREDGED BOTTOM SEDIMENTS - LABORATORY 4

(Aqua Regia Extraction (3:1 Conc.HCl:Conc.HNO_3); Atomic Absorption)

Area	Sample Number	Texture[1]	Elements						
			V	Ni	Cu	Zn	Pb	Fe	Mg
			ppm					%	
Athabasca River (From above Fort McMurray to the Athabasca River Delta)	A-D-13	cs	22.5	17.5	12.5	43.8	5.0	1.61	0.08
	A-D-16	cs	21.3	20.0	13.8	47.5	6.3	1.25	0.08
	A-D-15	s	8.8	8.8	2.5	21.3	<1.0	0.68	0.16
	A-D- 9	cs	25.0	22.5	17.0	53.8	7.5	1.66	0.07
	A-D- 5	st	5.0	6.3	2.0	18.8	<1.0	0.54	0.12
	A-D-19	sc	15.0	16.3	10.1	37.5	5.0	1.34	0.08
	A-D-21	sc	8.8	8.8	4.5	26.5	2.5	0.79	0.61
	A-D-70	c	27.5	18.8	12.8	43.8	5.0	1.42	0.58
	A-D-69	s	10.0	8.8	2.5	23.5	1.3	0.69	0.27
	A-D-65	s	<2.5	7.5	1.1	13.8	<1.0	0.41	0.10
Athabasca River Delta	A-D-52	c	30.0	20.0	14.8	47.5	7.5	1.52	0.90
	D-34	c	27.5	23.8	17.0	56.3	7.5	1.58	0.16
	A-D-61	cs	32.5	25.0	18.8	56.3	8.8	1.84	1.24
	A-D-60	cs	32.5	22.5	16.8	51.3	8.8	1.77	1.17
	A-D-46	s	5.0	2.5	1.5	13.8	1.3	0.33	0.09
	A-D-47	c	23.8	16.3	10.8	37.5	5.0	1.23	0.97
Lake Athabasca	A-D-29	sc	20.0	15.0	10.5	40.0	5.0	1.33	0.17
	A-D-35	c	28.8	25.0	20.3	62.5	8.8	1.91	1.16
	A-D-41	c	35.0	30.0	20.8	71.3	8.8	2.13	1.02
	A-D-44	c	27.5	30.0	22.5	77.5	8.8	2.06	1.02
Riviere des Rochers	A-D-23	c	33.8	28.9	20.6	77.5	8.8	2.10	0.17

1. Visual inspection prior to chemical analysis; s=sand, sc=sand with some clay, st=sand with some tar fragments, cs=clay with some sand, c=clay.

APPENDIX 5.

Partial Element and Organic Concentrations-Blind Duplicates.

Table 1: 0.1N HCl Extraction.

Table 2: 0.1N NaOH Extraction.

Table 3: Benzene/Methanol Extraction.

Table 4: Organic Analyses.

Table 1: DUPLICATE PARTIAL ELEMENTS - LABORATORY 2.

(0.1N HCl Extraction)

Sample	Elements						
Number	V	Ni	Zn	Cu	Co	Mn	Fe
	ppm						%
A-D-13	11	17	24	8	5	250	0.70
	<8	15	28	9	9	270	0.70
A-D-19	<8	21	24	8	<5	240	0.65
	8	20	33	9	12	260	0.64
A-D-29	<8	19	28	8	<5	250	0.73
	14	24	34	9	8	260	0.76
A-D-60	14	27	40	12	11	430	0.87
	10	31	44	12	12	440	0.89
A-D-65	<8	<5	6	<1	<5	70	0.19
	8	<5	6	1	5	66	0.19

Table 2: DUPLICATE PARTIAL ELEMENTS - LABORATORY 2.

(0.1N NaOH Extraction)

Sample	Elements						
Number	V	Ni	Zn	Cu	Co	Fe	Mn
	ppm						
A-D-13	< 10	< 5	1	4	< 5	255	6
	< 10	< 5	2	5	< 5	333	7
A-D-19	< 10	< 5	2	4	< 5	391	8
	< 10	< 5	1	5	< 5	333	4
A-D-29	< 10	< 5	1	6	< 5	202	5
	< 10	< 5	1	6	< 5	253	7
A-D-60	< 10	< 5	1	9	< 5	322	11
	< 10	< 5	1	9	< 5	313	11
A-D-65	< 10	< 5	1	< 1	< 5	26	< 1
	< 10	< 5	1	< 1	< 5	47	< 1

Table 3: DUPLICATE PARTIAL ELEMENTS - LABORATORY 2.

(1:1 by volume; benzene/methanol extraction)

Sample Number	Elements V	Ni	Zn	Cu	Co	Fe	Mn
	- - - -	- - - -	- - - -	-ppm-	- - - -	- - - -	- - - -
A-D-13	<5	<5	12	<1	<5	<4	<1
	<5	<5	5	<1	<5	29	<1
A-D-19	<5	<5	2	<1	<5	<4	<1
	<5	<5	6	<1	<5	12	<1
A-D-29	<5	<5	2	<1	<5	<4	<1
	<5	<5	<1	<1	<5	<4	<1
A-D-60	<5	<5	2	<1	<5	<4	<1
	<5	<5	4	<1	<5	<4	<1
A-D-65	<5	<5	<1	<1	<5	<4	<1
	<5	<5	<1	<1	<5	<4	<1

Table 4: DUPLICATE NUTRIENT-ORGANIC ANALYSES - LABORATORY 2.

(C and N by CN analyser; Fulvic and Humic acid by 0.1N NaOH, acidification with HCl (humic ppt. weighed), desaltation of extract, drying and weighing)

Sample Number	Inorganic C	Organic C	Total N	Fulvic Acid	Humic Acid
	- - - - - -%-	- - - - - -	ppm	- - -g/kg	C- - -
A-D-13	0.42	1.40	830	2.1	1.6
	0.44	1.72	945	2.4	2.0
A-D-19	0.60	1.63	745	2.8	2.3
	0.61	1.24	920	2.4	2.0
A-D-29	0.64	0.99	660	1.7	0.8
	0.68	1.04	710	1.7	1.3
A-D-60	0.92	1.89	1070	3.1	2.0
	0.96	1.92	1380	3.1	2.4
A-D-65	0.08	0.16	400	0.4	<0.1
	0.12	1.10	120	0.5	0.1

APPENDIX 6.

Heavy Metal Data on Sediments in other Reports.

Table 1: Data from Korchinski (1976).

Table 2: Data from Peace-Athabasca Delta Report, Water Quality Branch (1971-72).

Table 3: Data from Lutz and Hendzel (1977).

Table 1: HEAVY METALS IN BOTTOM SEDIMENTS FROM THE ATHABASCA RIVER DRAINAGE SYSTEM

(from Korchinski, 1976)

Location	Sand	TOC	V	Ni	Zn	Pb	Cu	Cd	Co	Mn	Hg	Fe
	%	%	ppm								ppb	%
Athabasca River at Ft. McMurray	75	1.8	<80	140	50	<80	17	<10	<50	300	29	1.8
Poplar Creek at WSC Gauge	72	1.5	<80	50	30	<80	17	<10	50	160	30	1.0
MacKay River near mouth	97	---	<80	20	10	<80	<10	<10	60	130	16	1.2
Calumet River near mouth	53	3.8	<80	80	30	<80	31	<10	<50	170	33	1.3
Eymundson River near mouth	96	0.2	<80	<50	40	<80	<10	<10	<50	160	14	1.1
Firebag River near mouth	57	1.8	<80	70	40	<80	<10	<10	70	130	18	1.0

Table 2: HEAVY METALS IN BOTTOM SEDIMENTS FROM THE ATHABASCA RIVER DELTA AREA (from Water Quality Branch, 1971-72).

Element	Extraction	Lake[1]								
		Athabasca			Clair			Mamauri		Baril
		West	Centre	East	West	East	South	West	East	Centre
		conc. in ppm								
Hg	Exch. (ppb)	3	--	--	1	3	<1	<1	<1	8
	Sol. (ppb)	150	170	160	150	160	30	130	100	170
Zn	Exch.	3	--	--	3	3	1	2	2	2
	Sol.	88	130	106	94	83	20	73	68	124
Pb	Exch.	<1	--	--	<1	<1	<1	<1	<1	<1
	Sol.	15	18	18	15	14	35	12	12	19
Cu	Exch.	<1	--	--	<1	<1	<1	<1	<1	<1
	Sol.	23	28	26	23	24	3	18	16	33
Mn	Exch.	425	--	--	743	352	132	475	431	631
	Sol.	7650	5900	6000	4500	6750	4100	5400	5650	6650
Fe	Exch.	4	--	--	5	1	2	1	1	3
	Sol. (%)	1.9	2.7	2.6	2.5	1.6	0.5	1.9	1.7	3.0

[1] All sample clay except south Claire which was fine clay.

Table 3. HEAVY METALS IN SEDIMENTS (ppm) DRY WEIGHT

(from Lutz and Hendzel, 1977)

Sample Site	As	Cd	Cr	Cu	Fe	Mn	Pb	Ni	V	Zn	Hg	Loss on Ignition
					%						ppb	
Slave River	7	0.6	100	59	2.2	306	30	28	92	76	50	5.2
Lake Athabasca	4	0.2	116	17	1.6	307	9	47	66	53	40	5.2
Richardson Lake	4	0.1	103	58	1.8	330	14	88	102	72	50	9.7
Athabasca River	4	0.1	116	34	1.7	275	10	48	56	46	50	5.4
Steepbank River	<1	<0.1	52	2	0.6	111	2	19	12	10	10	0.4
Athabasca River (at Clarke River)	3	0.1	75	12	1.2	232	4	34	39	32	20	2.8
Athabasca River (at McLean Creek)	3	0.1	91	15	1.5	262	5	38	53	44	20	4.5
Clearwater River	3	0.1	100	11	1.7	314	5	28	58	42	20	4.7
Athabasca River	4	0.1	92	18	1.7	249	4	34	65	49	30	5.7
Muskeg River	3	0.1	59	26	2.2	327	10	20	86	57	40	6.4
MacKay River	3	0.1	71	19	1.6	205	6	37	62	47	40	2.5
Ells River	3	<0.1	40	8	1.1	101	3	23	33	24	20	2.4
Steepbank River	1	<0.1	34	5	0.7	104	2	9	16	15	10	1.4
Firebag River	1	<0.1	41	12	0.7	102	2	9	15	16	20	1.6
Mean	3	0.1	78	21	1.4	230	8	33	54	42	30	4.1