HEAVY METALS IN BOTTOM SEDIMENTS OF THE MAINSTEM ATHABASCA RIVER SYSTEM IN THE AOSERP STUDY AREA

by

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ABSTRACT

Dredged sediments and sediment cores were collected from sites along the Athabasca River system from between Fort McMurray and the confluence of Riviere des Rochers with the Slave River. A selected sample suite representing all of the drainage units and textural variations was analysed by several total and partial element extraction techniques.

None of the metal concentrations detected were unusual. The results indicate that total concentrations are low when compared to data for natural and for polluted sediments elsewhere. Concentration variations are functions of natural fluvial, geochemical processes and are strongly affected by sedimentological parameters including sediment texture, Fe/Mn mineral coatings, organic and carbonate contents. There was a general progression to higher concentrations of heavy metals downstream from the Athabasca River to its delta to Lake Athabasca. The highest heavy metal concentrations were in the fine textured sediments from Lake Athabasca.

Vanadium and nickel were strongly correlated with each other and with organic carbon content. V and Ni appear to be present in the bottom sediment in an organic form, unextractable by benzene/methanol, sodium hydroxide, or dilute hydrochloric acid.

ACKNOWLEDGEMENTS

Our interest in the AOSERP Study Area was stimulated by discussions with M. Korchinski, Water Quality Branch, Calgary who was studying the water and suspended sediment phases in the area. We appreciate his bringing to our attention the possibility of our involvement. A. Lutz was very helpful in discussions of analytical variability and techniques required for analyses of these samples.

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, some of the results reveal the difficulty of analyses for some elements in these sediments.

Sampling was carried out by M. Roy and R. Woychuk, Canada Centre for Inland Waters, Inland Waters Directorate, Western and Northern Region. For a two-man operation in a remote area, their sample coverage was no mean feat. Mr. Roy was also responsible for freeze drying the samples, arranging analytical contracts, and data compilation. K. Hoeppner did a tremendous job in typing the manuscript in a camera ready form for photo off-set reproduction.

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 and Dr. R. Seidner of AOSERP for their interest in our project. We 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.

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1. INTRODUCTION

In the Alberta Oil Sands Environmental Research Program (AOSERP) Study Area (Fig. 1) heavy metals in rivers and lakes may be elevated by waterborne and airborne emissions resulting from extraction and processing of the Athabasca Oil Sands. Heavy metals are among the most dangerous pollutants of water systems (Forstner and Muller 1976) because they are not degraded like many organic wastes. They can become strongly enriched in the aquatic food chain and ultimately result in human disease (Hopps and Cannon 1972). AOSERP reports dealing primarily with heavy metals in water (Korchinski in prep.) and biota (Lutz and Hendzel 1977) are available for the study area. This report is on heavy metals and their forms in the bottom sediments of the mainstem Athabasca River system.

River bottom sediments play a key role in defining the degree and extent of heavy metal pollution of a fluvial system. The main reason is because heavy metals and heavy metal compounds are complexes that are often incorporated in the suspended sediment load and thus finally deposited as bottom sediments in rivers (Forstner and Muller 1976) and lakes (Allan and Timperley 1975; Forstner 1976). Forstner and Muller (1976) consider bottom sediment heavy metal concentrations more reliable indicators of pollution than river water concentrations which can fluctuate by several orders of magnitude over short periods. These short term fluctuations, related to changes in water discharge, changes in relative significance of different source areas, and irregular local emissions, can be missed even by frequent water sampling programs.

The present study involved collection of a large sample suite followed by analysis of a smaller selected sample suite. The first general objective was to provide baseline information on the historic concentrations of heavy metals in the bottom sediments of the different components (river, delta, lake) of the mainstem

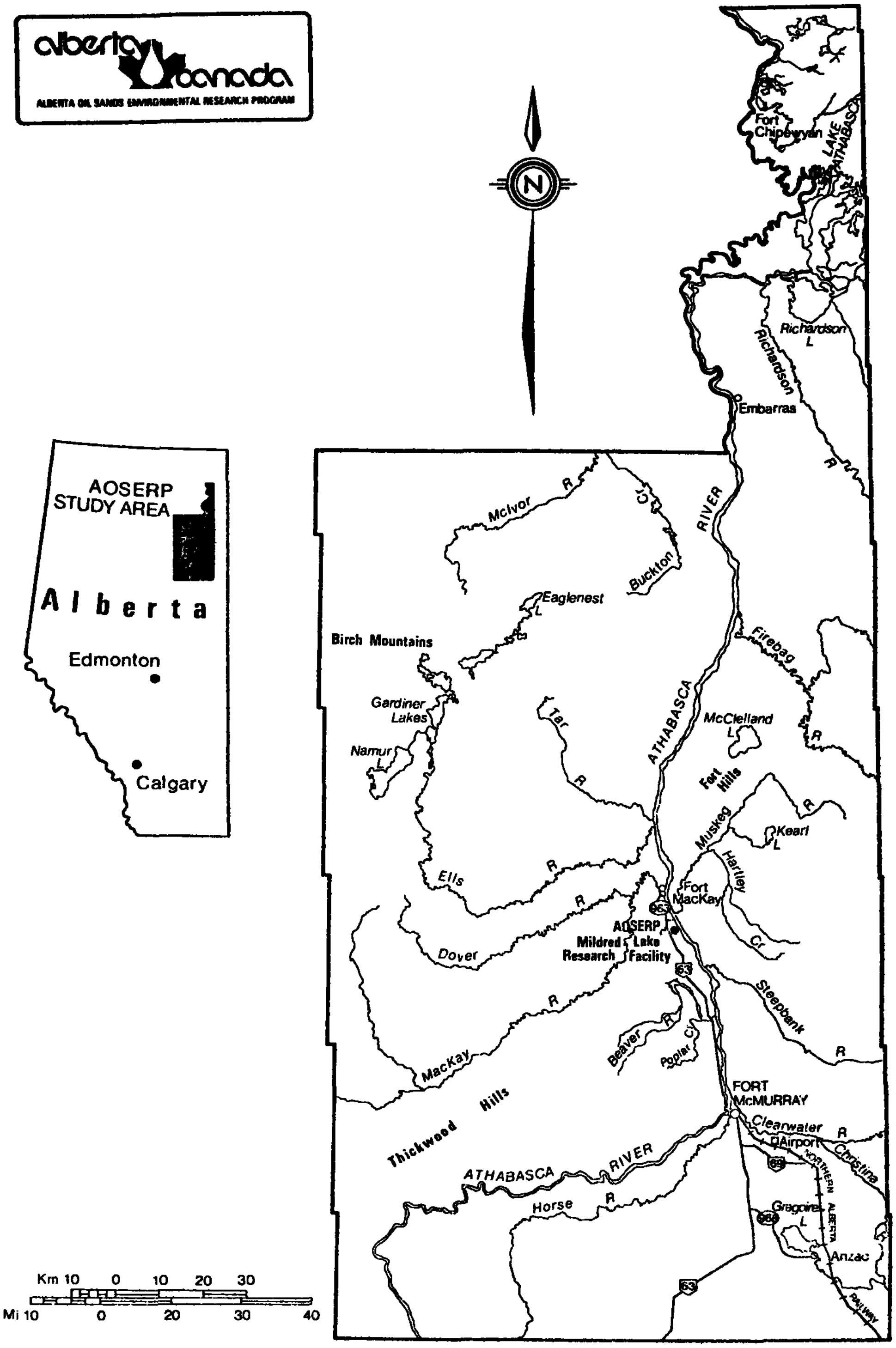

Fig. 1. Location of the Alberta Oil Sands Environmental Research Program Study Area.

Athabasca River system. The second general objective was to employ selective dissolution analyses (SDA) and measurement of other sedimentological and minerological parameters to better understand the forms in which these heavy metals occur in the bottom sediments. The specific objectives were:

1. To determine the concentration and distribution of various heavy metals in the bottom sediments of the mainstem Athabasca River from just above Fort McMurray to the Slave River confluence;
2. To comment on the historic input of metals to the drainage system and on any detected contamination;
3. To use selective dissolution analyses (SDA) to develop a better understanding of the forms in which heavy metals are held in the bottom sediments;
4. To recommend any necessary continuation of bottom sediment collection and analysis so as to monitor the toxic metal impact on the mainstem Athabasca River of extraction and processing of the Athabasca Oil Sands.

A knowledge of bottom sediment heavy metal concentrations will allow a future assessment of changes, if any, resulting from airborne or waterborne release of heavy metals to the drainage system.

The results are of general application and relevant to several Alberta Oil Sands Environmental Research Program (AOSERP) concerns, including:

1. What effect will extraction of the oil sands have on water quality of the Athabasca River, Delta and Lake?
2. What might be the effect of a tailings dike failure?
3. What effect will the addition of particulates have

on the chemistry of the Athabasca River, Delta and Lake?

1.1 HEAVY METAL POLLUTION OF WORLD RIVERS

Heavy metal contamination of rivers, lakes, deltas, estuaries, bays, coastal zones and oceans is being increasingly reported in the literature. Once heavy metals are in bottom sediments, cleaning up a contaminated river often simply results in a transfer of the problem, albeit at a less toxic level, down the drainage system. The reduction of Hg levels in Lake St. Clair in recent years is simply a reflection of natural transfer of contaminated sediments to Lake Erie (Thomas et al. 1975a). Accordingly the best protection is early detection and prevention. In a global review of heavy metal contamination of rivers (Forstner and Muller 1976) the problem of heavy metal contamination of bottom sediments is clearly common and extensive. The reader is referred to this excellent review as the best presently available on the subject. The total list is extensive, particularly for the U.S.A. and western Europe, and is more than enough to justify concern for waterways on a global scale. Every effort should be made to avoid adding the Athabasca-Slave-Mackenzie-Beaufort, river-lake-sea system to this rapidly expanding number of documented cases. Examples of studies of Canadian rivers already contaminated by heavy metals include the English and Wabigoon in Ontario (Armstrong and Hamilton 1973, Parks 1975 and Jackson 1978); the Ottawa in Ontario (Rust and Waslenchuk 1974, Oliver and Agemian 1974 and Merritt 1975); and the Quevillon in Quebec (Thomas et al. 1975b). All of these publications focused on mercury.

All of these publications and those in Forstner and Muller (1976) deal with those heavy metals, Hg, Cd, Pb, Zn and Cu which have to date received most attention in pollution investigation. They do not deal with vanadium (V) and nickel (Ni), the predominant heavy metals found in the bituminous oil sands. Data on Ni concentrations in drainage system sediments are available for lakes in Canada (Allan and Timperley 1975; Allan and Brunskill 1976) and Australia (Forstner 1976). Data on V concentrations in sediments of freshwater lakes and rivers in Canada (or elsewhere) are scarce and the only published values known to us are those for bottom sediments in Lake Winnipeg (Allan and Brunskill 1976) and Lake Erie (Kemp et al. 1976). For the oil sands area additional data on V and Ni in bottom sediments of the AOSERP study area can be found in reports on the Peace-Athabasca Delta (Water Quality Branch 1972) and in AOSERP Reports on heavy metals in water (Korchinski in prep.) and biota (Lutz and Hendzel 1977).

1.2 HEAVY METALS IN THE AOSERP STUDY AREA

In most of the examples given above, industrial sources for the heavy metals can be clearly identified. In the AOSERP study area, this is more complex because of the natural geological presence of heavy metals in the oil sands.

1.2.1 Natural Sources

The Athabasca Oil Sands, a natural source of heavy metals, is a lower Cretaceous formation overlain by extensive Pleistocene deposits of fluvio-glacial and glacial drift. Trace elements are associated with the oil sands proper (Table 1), the overburden, soils and their interstitial solutions. Korchinski (in prep.) notes that Scott et al. found 195 and 70 ppm V and Ni, respectively, in oil samples. Three samples of oil sand from different locations contained high concentrations of Fe, Ni, V, Zn, Mn, Co, and Cd (Korchinski in prep.). The oil sands, like many oils, are thus enriched in V, Ni, and Fe. Hodgson (1954) proposed that the V had been substituted for Mg, the central atom in the

Table 1. Some analyses of Athabasca Oil Sands.[1]

Analytical Method[2]	Element	Concentration Range
		---- % ------
X-ray fluorescence (XRF) on ashed sample (500°C for 3 hours)	SiO_2	90.90 - 97.30
	Al_2O_3	1.40 - 5.30
	Fe_2O_3	0.10 - 1.80
	P_2O5	<0.40 - 0.90
	CaO	0.02 - 0.22
	MgO	<0.10 - 0.57
	Na_2O	<0.40 - 0.90
	K_2O	0.34 - 1.20
	TiO_2	0.08 - 0.84
	Zr	0.00 - 0.23
	MnO	0.00 - 0.02
	Ba	0.01 - 0.05
	S	0.10 - 0.30
		--- -ppm- ---
DC arc on whole sample	V[3]	32 - 117
	Ni	12 - 20
	Cr	7 - 30
	Zn	61 - 109
	Cu	3 - 16
	Co	1 - 13
	Pb	6 - 52
	La	29 - 44
	Y	5 - 16
	Mo	1.3 1.7
	Be	0.5 2.1
Fluorimetry on ashed sample (500°C for 3 hours)	U	0.4 1.2

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1. Data provided from preliminary analyses by I. R. Jonasson, Geological Survey of Canada, Ottawa. Samples are a geographically representative suite covering the Athabasca oil sands area.

2. Analyses of these samples is difficult because of problems with decomposition of the tar and because of difficulty in grinding un-ashed samples.

3. V/Ni ratios ranged from 1.6 to 9.8.

chlorophyll-a of the plankton from which the oil was derived. Nickel is also present in these oils but the reason for its presence is more problematical. The ratio of V:Ni in the bitumen is 2.4:1 and is characteristic of other Cretaceous oils (Hodgson 1954). Some idea of heavy metal concentrations in overburden is obtained from the few analyses performed on this material by Korchinski (in prep.). In addition to heavy metals in the oil fraction, there are heavy metals associated with the sand fraction of the oil sands. Heavy minerals in the sand fraction include zircon, rutile and anastase, which contain Zr and Ti (Kramers and Brown 1976). Other sources of metals, particularly Zn and Pb might be the underlying bedrock and/or groundwater. Deposits of Zn and Pb are associated with similar Cretaceous bedrock north of the oil sands area at Pine Point on the shores of Great Slave Lake.

1.2.2 Anthropogenic Sources

During the extraction and processing of the Athabasca Oil Sands, airborne and waterborne heavy metals could be released to the environment. Possible sources of heavy metals include fly-ash, wastewater, cokes and sludges.

1.2.2.1 Airborne emissions. Stanley Associates Engineering Ltd. (1976) in a study of the magnitude of fog occurrence in the oil sands area, give data (Table 2) on the quantity of particulate emissions for the various existing and proposed oil sands extraction plants. The fly-ash produced by these plants is known to contain high quantities of various heavy metals. Stemerowicz et al. (1976) have even proposed that V and Ni may be economically recoverable from the fly-ash providing that suitable extraction methods can be developed. However, present world resources of vanadium well exceed demand (Brown et al. 1974). Data on the heavy metal content of fly-ash has been determined by different agencies (Tables 3 and 4)

Table 2. Annual Particulate Emission Rates from oil sands plants[1].

Plant	Particulates
	metric tons
GCOS	14,819[2]
Syncrude	4,635
Shell	4,380
Petrofina	4,380
Home	4,380
Total	32,594

1. Values calculated from Table 12 in Croft et al., 1976. They are likely to change as precipitator technology changes.
2. Value of 11,826 is given in Shelfentook (1978).

Table 3. Heavy Metal Concentrations in GCOS Fly-Ash.

Metal	Concentration[1]
	ppm
V	25,500
Ni	10,000
Zn	400
Cu	380
Co	190
As	7
Hg (ppb)	7
Fe	46,100
Mn	900

[1] Mean of 3 samples collected in Nov./Dec., 1975. (Data from Table 2 in Shelfentook (1978)).

Table 2. Annual Particulate Emission Rates from oil sands plants[1].

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and estimates of V and Ni emission rates calculated (Table 4). The values presented in these tables are from published reports or reports in review. As precipitator technology develops, emission rates may be radically changed. Tables 2 to 4 should be assessed in this context. Irrespective, the fly-ash produced in recent years by oil sands plants does contain appreciable quantities of heavy metals and is a potential source for these in the study area. Fly-ash and gaseous emissions could be spread over a wide area of the Athabasca River drainage system. The impact of the airborne fallout of heavy metals will not be confined simply to direct fallout on the Athabasca River, Delta, and other waterbodies in the study area but could be enhanced by leaching of heavy metals deposited on soils and vegetation in the area affected by such fallout.

The impact of airborne heavy metal fallout may also be compounded by synergistic effects associated with the sulphur dioxide (SO_2) released to the atmosphere by oil sands plants. The detailed effect of acidification of waterbodies on heavy metal sorbtion-release processes is not clearly understood but is the subject of investigation. A predicted annual emission rate of 64,000 to 106,000 metric tonnes SO_2 has been arrived at for the Syncrude Plant (Murray and Kurtz 1976). Blanket coverage of up to 1,200 km^2 is shown to occur. Depending on meteorological conditions, the effect could extend to an area of 9,800 km^2. It is not likely that particulates will be this widely dispersed. Alternatively, there will be some SO_2 fallout in all areas where particulates are deposited and this may contribute to mobilization of heavy metals from these particulates. Another aspect of SO_2 fallout is that it may increase the dispersion of naturally occurring heavy metals in overburden (see 1.2.1). Korchinski (in prep.) found that heavy metal concentrations were higher in bank overburden than in river bottom sediments. Although this appeared to be a function of differing clay contents, it does show that an additional source of heavy metals to the drainage system could result from enhanced leaching of the finer particle size range of such overburden materials. This discussion is based on SO_2 emissions and the assumption that these would make the precipitation in the study area more acidic. Barrie and Whelpdale (1978) showed that snow in the immediate vicinity of GCOS was relatively less acidic which might be the result of airborne fallout of Ca, Mg and Na oxides and hydroxides from coke combustion. The situation may thus be more complex than in other areas, such as those with smelters, where SO_2 and heavy metals alone are emitted.

The heavy metal concentration values reported in Tables 3 and 4 should be taken to represent low estimates for emissions. Evidence in the literature (Harrington 1974) suggests that heavy metals are concentrated in smaller particles or are released in gaseous form. Conventional inertial type control devices such as cyclones may thus be effective in reducing the mass rate of release of total particulates but have little effect on the removal of heavy metals. The low concentrations of Hg and As (Table 3) in scrubbed particulates could reflect a release of these primarily in fine particulate or gaseous form. Korchinski (in prep.) reports detecting Hg in GCOS fly-ash. However, neither Hg nor As are reported in Table 1 because they are both lost in analytical procedures which involve ignition of the samples and would also presumably be lost to the atomosphere on combustion of cokes. Over a long period of time, their release to the atmosphere could be cumulatively significant.

1.2.2.2 Waterborne emissions. In the past, there has been a minor release of drainage from the tailings pond to the river (Atkinson et al. 1976) but the present tailings handling procedure calls for recycling of this drainage. Prior to recycling, drainage flowed along the west bank of the river, and was rapidly diluted to 1/1000 and 1/2000, 3 km and 1/2800 and 1/5400, 24 km downstream (winter and summer dilutions respectively). The 1967 seepage released to the river was in the order of 0.7 to 1.3 m^3/day (Atkinson et al. 1976). This rate is possibly representative of the input between 1965 when construction of the dike began and 1976 when the recycling procedure for drainage water was installed. Analyses of all samples of dike discharge gave heavy metal results within the accepted Alberta surface water quality criteria. One exception (No. 7, 1973) had higher Zn, Cr, Pb, Cu and Cd (1750; 1500; 910; 190; 50 ppb respectively) concentrations (Atkinson et al. 1976). Problems with interpretation of heavy metal contents of contaminated water was touched upon in section 1.1. In any event, even with this one sample, dilution effects in the Athabasca River are high, background hardness, calcium and turbidity may reduce heavy metal toxicity, and 100% survival of rainbow trout was shown in 13 static bio-assays using river water from downstream of the dyke discharges (Atkinson et al. 1976). The only documented major release of tailings pond effluent was in 1968, when some 3 million m^3 of selective effluent was discharged to the Athabasca River during periods of high summer discharge.

One sample of tailings pond sludge (Korchinski in prep.) had high concentrations of V, Ni, Fe and Mn and significant concentrations of Zn, Pb, Cu, Co and Cd. A large deposit of these tailings is now enclosed by the GCOS tailings dike adjacent to the mainstem Athabasca River. The tailings dike has risen to elevations well above those originally planned and Alberta Environment has stated that serious environmental effects could result in the event of failure of the dike and spilling of the ponded tailings into the Athabasca River.

2. METHODOLOGY

2.1 COLLECTION METHODOLOGY

Bottom sediments were collected from sites (Table 5) in the Athabasca River from just south of Fort McMurray to Embarras (Figs. 2 and 3); from channels, lakes and sloughs in the Athabasca River Delta (Fig. 4); and from Lake Athabasca and Riviere des Rochers (Fig. 5). The length of continuous river system sampled exceeds 200 km from just south of Fort McMurray to the confluence of Riviere des Rochers with the Slave River.

The sediment samples were collected during late August to 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-litre Eckman or a stainless steel mini-Shipek dredge. Sediment cores were obtained by Phleger Corer. The cores obtained were short because of the compact nature of the bottom sediment material. All samples were shipped by air to Winnipeg within a few days. They were then frozen at -40°C until removed for freeze drying. Two freeze dryers were in continuous operation from September, 1976 to April, 1977. The entire freeze-dried sample suite is stored at the Freshwater Institute in Winnipeg.

2.2 ANALYTICAL METHODOLOGY

Twenty-one samples were selected to represent locations (Fig. 6) in the major units of the mainstem Athabasca River system. Duplicate sets of these twenty-one samples, along with five blind duplicates, were submitted to four laboratories for determination of total element concentrations. The laboratories were instructed

Table 5. Sample Numbers, Locations, Textures and Sites.

Station Number	Sample Location		Sample[1] Texture	Sample Site
	Longitude	Latitude		
A-D- 1[2]	111° 37' 12"	57° 09' 05"	sand	middle of Athabasca R.[6]
2	111° 35' 56"	57° 07' 20"	sand + clay	west edge "
3	111° 33' 01"	57° 05' 24"	"	middle "
4	111° 31' 00"	57° 04' 00"	sand + tar fragments	west edge "
5	111° 30' 15"	57° 02' 00"	"	west edge "
6	111° 29' 15"	57° 01' 10"	clay + sand	east edge "
7	111° 28' 00"	57° 00' 36"	sand	east edge "
8	111° 27' 02"	56° 59' 50"	sand + clay	west edge "
9	111° 26' 56"	56° 57' 00"	clay + sand	west edge "
10	111° 25' 01"	56° 52' 32"	sand	east edge "
11	111° 24' 45"	56° 48' 55"	clay + sand	west edge "
12	111° 29' 18"	56° 46' 24"	sand + clay	middle "
13	111° 22' 40"	56° 44' 30"	clay + sand	north edge of Clearwater R.
14	111° 19' 42"	56° 41' 40"	sand + clay	south edge "
15	111° 23' 50"	56° 44' 00"	sand	west edge of Athabasca R.
16	111° 26' 45"	56° 41' 40"	clay + sand	east edge "
17	111° 37' 48"	57° 10' 36"	"	west edge "
18	111° 37' 00"	57° 11' 40"	"	middle edge "
19	111° 37' 48"	57° 14' 15"	sand + clay	southeast edge of Ing Is.[7]
20	111° 34' 50"	57° 19' 20"	clay + sand	south edge of Sutherland Is.
21	111° 39' 40"	57° 21' 00"	sand + clay	north edge of McDermott Is.
22	111° 13' 00"	58° 42' 20"	clay	eastbank of R. des Rochers
23	111° 16' 00"	58° 50' 30"	"	westbank "
24	111° 10' 55"	58° 54' 20"	"	eastbank "
25	111° 17' 00"	58° 56' 50"	"	westbank "
26	111° 23' 20"	58° 59' 35"	clay + sand	eastbank "
27	111° 09' 10"	58° 42' 08"	"	north tip of Potato Is.
28	111° 07' 30"	58° 41' 05"	clay	Lake Athabasca
29	111° 02' 30"	58° 41' 10"	sand + clay	"
30	110° 55' 40"	58° 41' 00"	"	"
31	110° 50' 50"	58° 40' 50"	clay + sand	"
32	110° 48' 28"	58° 40' 45"	sand	"
33	110° 44' 10"	58° 40' 30"	sand + clay	"
34	110° 39' 30"	58° 39' 50"	sand	"
35	110° 38' 40"	58° 43' 15"	clay	"
36	110° 39' 58"	58° 44' 50"	sand + clay	"
37	110° 42' 30"	58° 43' 25"	clay	"

continued . . .

Table 5 (cont.) Sample Numbers, Locations, Textures and Sites.

A-D	38	110° 45' 00"	58° 43' 35"	sand + clay	"
	39	110° 45' 00"	58° 45' 23"	clay	"
	40	110° 50' 40"	58° 45' 23"	"	"
	41	110° 50' 50"	58° 43' 50"	"	"
	42	110° 45' 47"	58° 43' 50"	"	"
	43	110° 45' 47"	58° 43' 50"	"	"
	44	110° 55' 40"	58° 45' 30"	"	"
	45	111° 00' 00"	58° 43' 50"	"	"
	46	111° 02' 55"	58° 38' 50"	sand	eastbank of Embarras R.
	47	110° 59' 00"	58° 38' 00"	clay	eastbank of Fletcher Ch.[8]
	48	111° 03' 30"	58° 34' 28"	sand	westbank "
	49	111° 04' 40"	58° 34' 00"	"	eastbank of Embarras R.
	50	111° 03' 30"	58° 31' 30"	"	eastbank of Fletcher Ch.
	51	111° 04' 30"	58° 27' 50"	clay + sand	eastbank "
	52	111° 07' 20"	58° 27' 00"	clay	southbank of Athabasca R.
	53	110° 59' 20"	58° 26' 05"	sand + clay	north edge "
	54	111° 02' 50"	58° 23' 55"	clay	middle of Richardson L.
	55	111° 05' 30"	58° 23' 55"	"	middle "
	56	111° 04' 05"	58° 22' 50"	"	middle "
	57	110° 50' 35"	58° 28' 00"	sand	southeast bank of Athabasca R.
	58	110° 49' 42"	58° 31' 10"	clay	eastbank of Big Point Ch.
	59	110° 48' 18"	58° 33' 12"	"	eastbank "
	60	110° 48' 10"	58° 36' 15"	clay + sand	westbank "
	61	110° 49' 55"	58° 37' 25"	"	eastbank of Goose Is. Ch.
	62	110° 50' 35"	58° 33' 00"		westbank "
	63	110° 50' 35"	58° 29' 50"	sand + clay	eastbank "
	64	111° 26' 53"	58° 26' 30"	clay	northbank of Athabasca R.
	65	111° 31' 42"	58° 22' 12"	sand	eastbank "
	66	111° 26' 00"	58° 12' 30"	sand + clay	westbank "
	67	111° 22' 20"	58° 04' 55"	sand	eastbank "
	68	111° 26' 28"	57° 51' 30"	sand + clay	westbank "
	69	111° 22' 00"	57° 49' 45"	sand	northwest bank of Is.
	70	111° 27' 10"	57° 38' 30"	clay	northeast bank of Dalkin Is.
	71	111° 31' 30"	57° 34' 00"	sand + clay	westbank
	72	111° 37' 25"	57° 27' 10"	"	eastbank
D-	1[3]	111° 43' 15"	58° 32' 08"	organic	southwest edge of lake
	2	111° 36' 15"	58° 32' 45'	"	west edge of Otter Lake
	3	111° 28' 33"	58° 31' 00"	"	westside of Pair Lake
	4	111° 19' 20"	58° 32' 45"	"	eastside of lake

continued . . .

Table 5 (cont.) Sample Numbers, Locations, Textures and Sites.

D-	5	111° 26' 55"	58° 25' 15"	clay + organic	northeast edge of Dagmar L.
	6	111° 19' 00"	58° 25' 08"	"	eastedge of Limon L.
	7	111° 18' 02"	58° 23' 40"	"	northeast edge of Blanche L.
	8	111° 08' 55"	58° 25' 02"	clay	northwest edge of Richardson L.
	9	111° 03' 00"	58° 25' 30"	sand + clay	north edge "
	10	110° 59' 12"	58° 24' 57"	clay	southeast side of marsh area
	11	110° 59' 20"	58° 23' 20"	clay	east edge of Richardson L.
	12	111° 03' 00"	58° 21' 00"	sand + clay	south edge "
	13	111° 08' 20"	58° 39' 00"	clay + organic	south delta area of Lake Athabasca
	14	111° 07' 30"	58° 34' 20"	"	south edge of
	15	111° 09' 30"	58° 31' 40"	"	southeast corner of lake
	16	111° 08' 20"	58° 30' 25"	"	southeast edge of lake
	17	111° 11' 50"	58° 29' 30"	"	south edge of lake
	18	111° 01' 00"	58° 27' 20"	organic	west extremity in marsh
	19	110° 59' 20"	58° 26' 40"	"	southeast bank in marsh
	20	110° 57' 25"	58° 25' 50"	"	northwest side of Freezie L.
	21	110° 57' 25"	58° 25' 50"	"	"
	22			clay + sand	
	23	110° 49' 45"	58° 30' 18"	clay + organic	northwest side of lake
	24	110° 49' 50"	58° 28' 50"	organic	south edge of lake
	25	110° 47' 50"	58° 32' 15"	"	west "
	26	110° 54' 20"	58° 32' 08"	clay + sand	southwest "
	27	111° 00' 00"	58° 32' 40"	"	southeast "
	28	110° 59' 20"	58° 39' 45"	"	west outlet of Fletcher Ch.
	29	110° 54' 20"	58° 39' 00"	"	west side of Goose Is.
	30	110° 51' 58"	58° 36' 15"	clay	east side of delta
	31	110° 49' 30"	58° 38' 50"	"	top of outlet Goose Is.
	32	110° 47' 25"	58° 38' 22"	"	west side of outlet of Big Point Ch.
	33	110° 44' 35"	58° 37' 42"	"	east of Big Point Ch.
	34	110° 53' 30"	58° 35' 25"	clay + sand	east middle of lake
A-C	1[4]	111° 29' 15"	57° 01' 10"		east edge of Athabasca R.
	2	111° 26' 56"	56° 57' 00"		west edge "
	3	111° 24' 45"	56° 48' 55"		west edge "
	4	111° 29' 18"	56° 46' 24"		middle "
	5	111° 19' 42"	56° 41' 40"		south edge of Clearwater R.
	6	111° 26' 45"	56° 41' 40"		east edge of Athabasca R.

continued . . .

Table 5 (cont.) Sample Numbers, Locations, Textures and Sites.

A-C 7	111° 39' 50"	57° 19' 20"	south edge of Sutherland Is.
8	111° 13' 20"	58° 47' 00"	east edge of R. des Rochers
9	111° 20' 35"	58° 58' 25"	east edge "
10	110° 45' 05"	58° 42' 35"	Lake Athabasca
11	110° 53' 15"	58° 42' 58"	"
12	111° 02' 00"	58° 42' 58"	"
13	111° 16' 00"	58° 25' 48"	north edge of Athabasca R.
14	111° 17' 50"	57° 43' 50"	southeast side of island
1[5]	111° 43' 15"	58° 32' 02"	south edge of lake
2	111° 28' 33"	58° 31' 00"	west side "
3	111° 19' 20"	58° 32' 45"	east side "
4	110° 59' 12"	58° 24' 57"	southeast side of lake
C- 5	110° 54' 20"	58° 32' 08"	southwest edge of lake
6	111° 00' 00"	58° 32' 40"	southeast "
7	111° 08' 20"	58° 39' 00"	southwest corner of delta
8	110° 54' 20"	58° 39' 45"	west of outlet of Fletcher Ch.
9	110° 54' 20"	58° 39' 00"	west side of Goose Is.

1. Samples assigned to textural groups at time of collection. Clay + sand is mainly clay. Sand + clay is mainly sand. Clay + organic is mainly clay.
2. A-D = Athabasca River, Lake Athabasca and Riviere des Rochers sites; collected by dredge.
3. D = Athabasca River Delta; collected by dredge.
4. A-C = Athabasca River, Lake Athabasca and Riviere des Rochers; collected by corer.
5. C = Athabasca River Delta; collected by corer.
6. R. = river
7. Is. = island
8. Ch. = channel

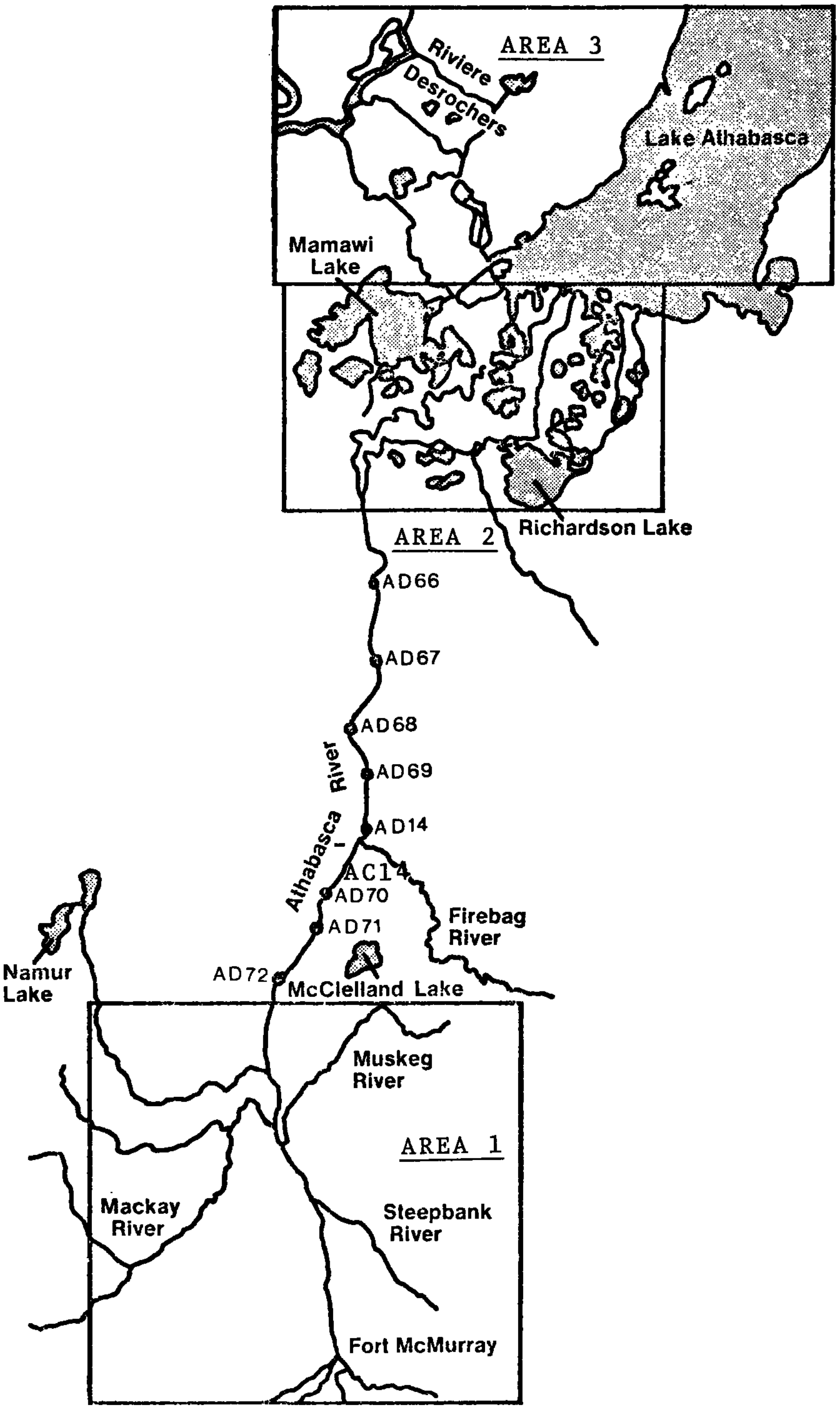

Fig. 2. Location of sample areas 1, 2 and 3 and location of samples collected from the Athabasca River outside these areas.

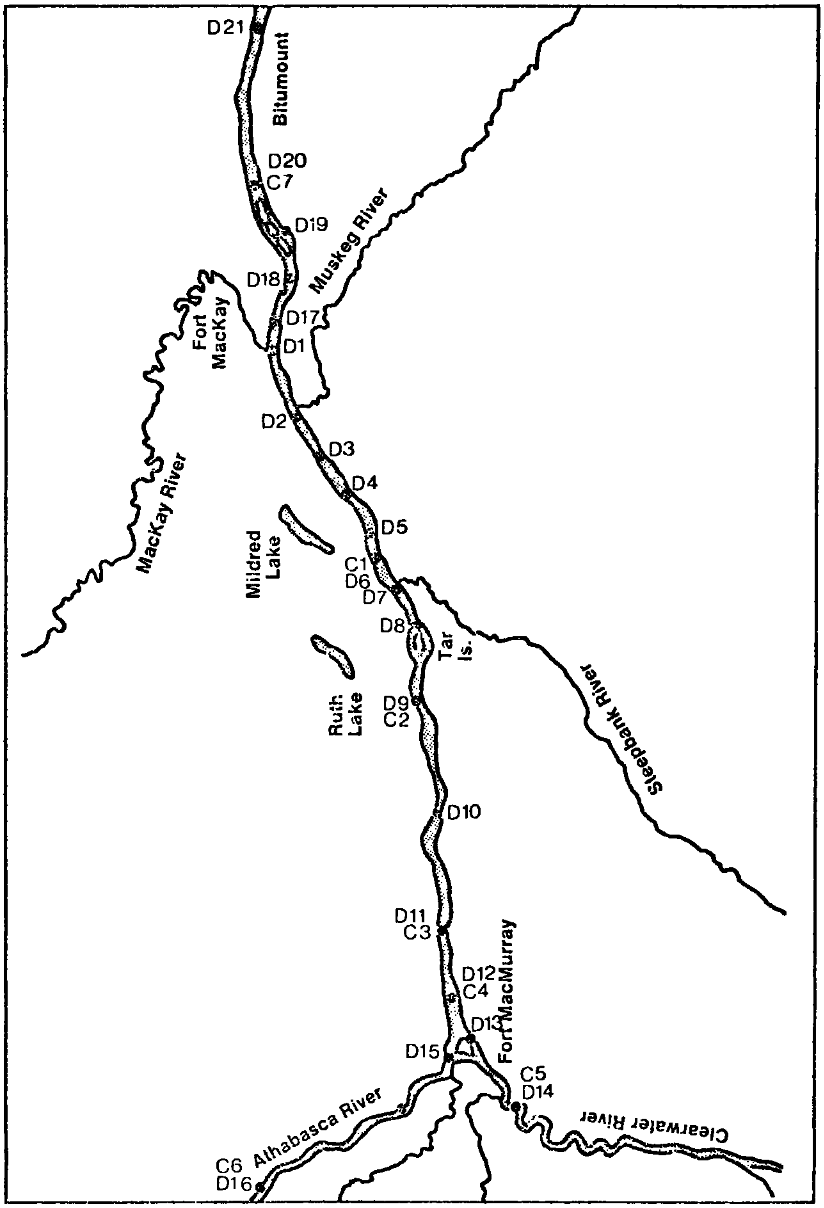

Fig. 3. Location of samples collected in area 1: Fort McMurray to Bitumount (these sites are prefixed AD and AC in the Tables — see Table 5).

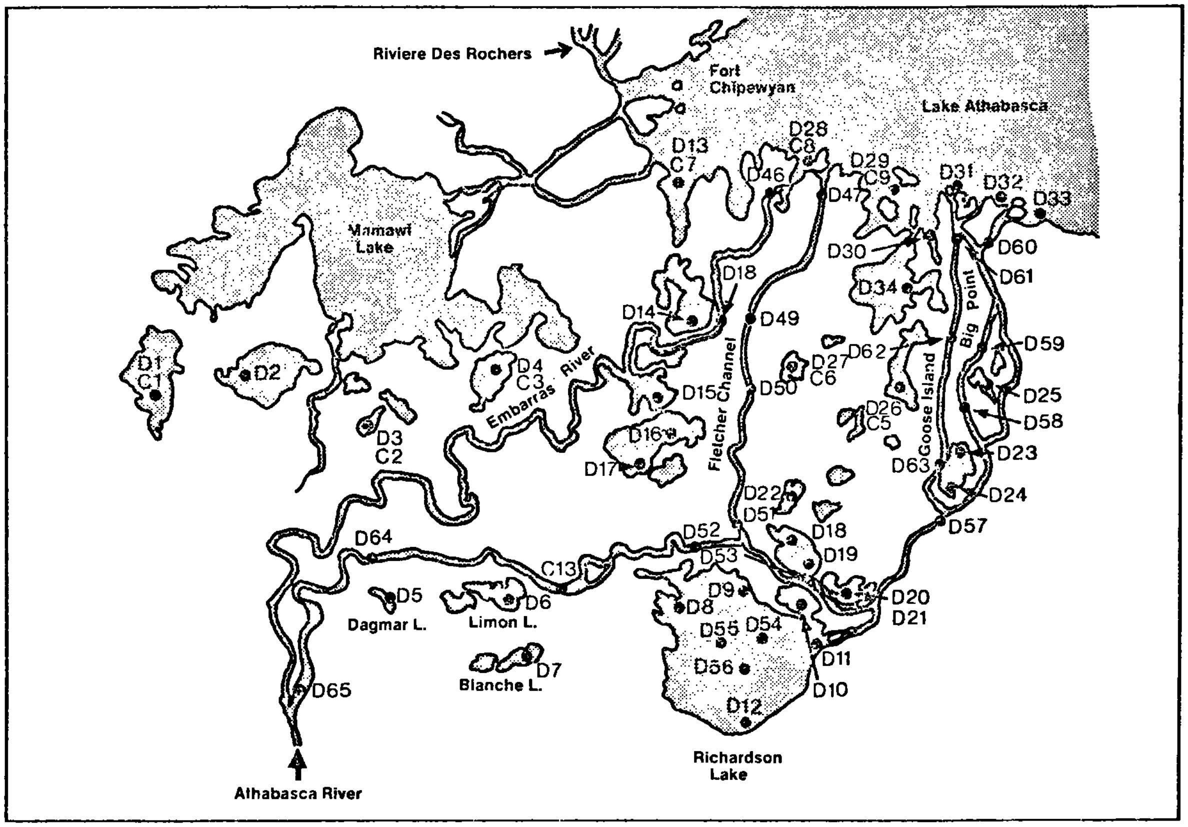

Fig. 4. Locations of samples collected in area 2: Athabasca River Delta (site numbers above D34 are prefixed AD and site C13 as AC13 in the Tables -- see Table 5).

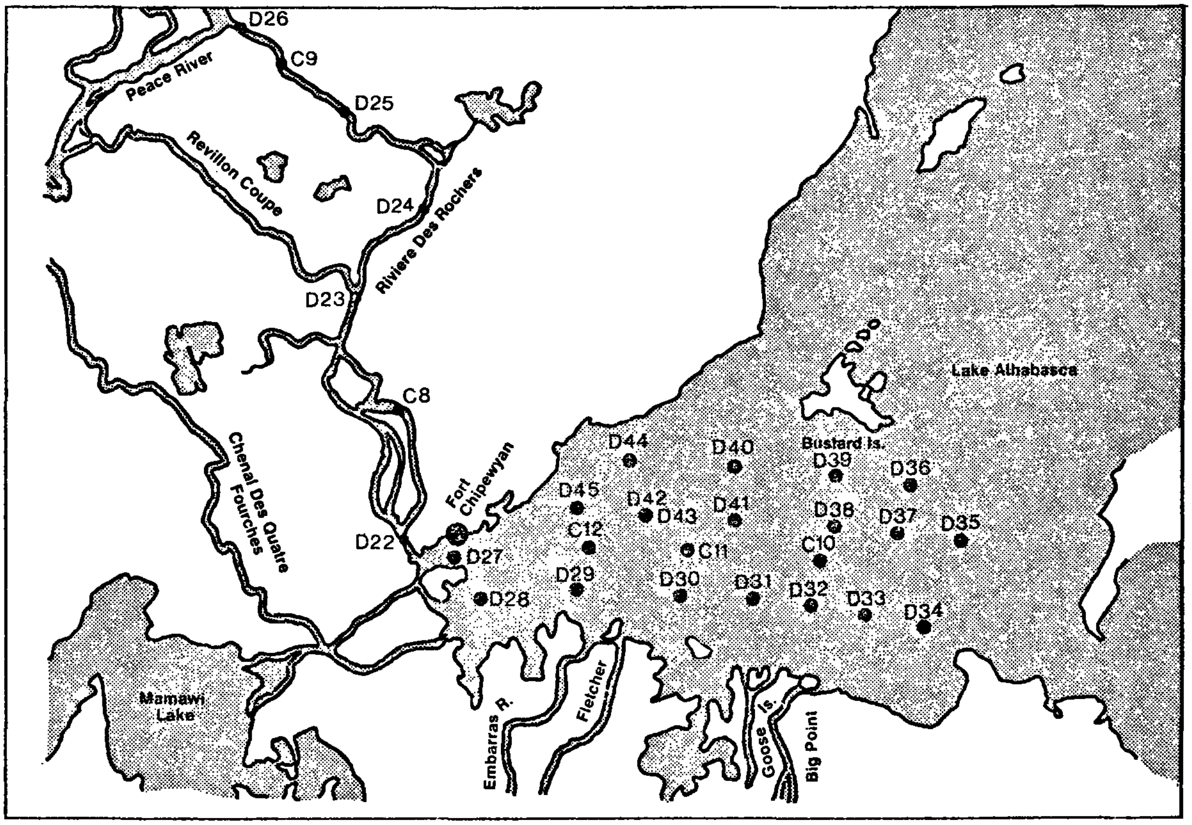

Fig. 5. Location of samples collected in area 3: Lake Athabasca and Riviere des Rochers (these sites are prefixed AD and AC in the Tables -- see Table 5).

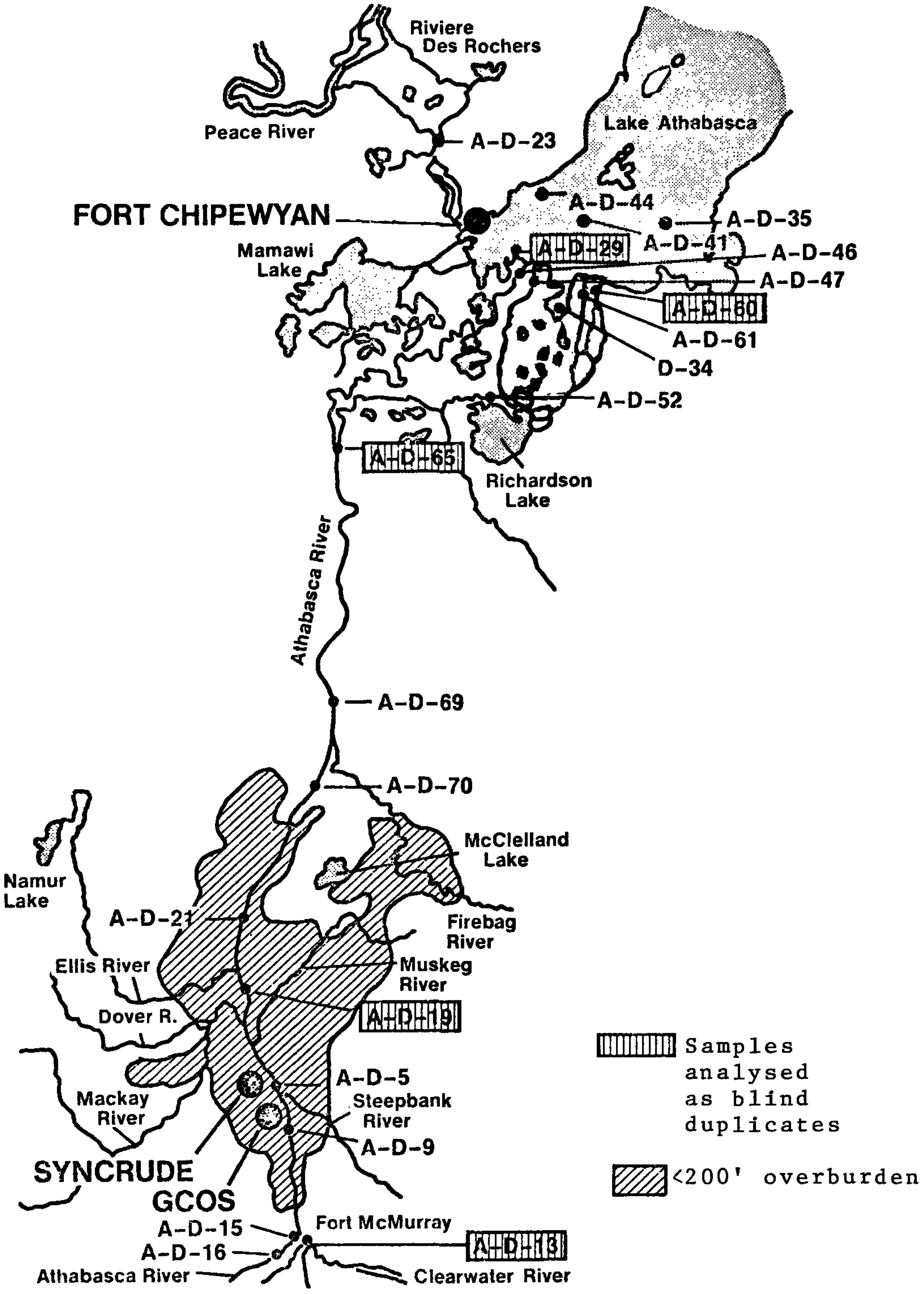

Fig. 6. Location of samples analysed for heavy metals and related parameters.

to employ their existing standard method and four separate analytical methodologies for total element estimation were thus employed. One of the laboratories (Laboratory 2) carried out determination of organic parameters and made three different partial element extractions of the sample suite.

2.2.1 Total Metals

The four laboratories employed the following procedures. Sample preparation in addition to freeze-drying was at the discretion of each laboratory.

2.2.1.1 Laboratory 1. The freeze-dried 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).

2.2.1.2 Laboratory 2. 100 mg of freeze-dried sediment was placed in a Teflon cup and 4 ml HNO_3, 1.0 ml $HCLO_4$ and 6 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 deionized water. The solutions were analysed for V, Ni, Cu, Co, Zn, Mn 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.

2.2.1.3 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 through the procedure. An aliquote of the digest was analysed for Hg by the semi-automated method of Armstrong and Uthe (1971). For As, an H_2SO_4-HNO_3-$HClO_4$ digest, diluted and with boronhydride added to liberate arsine, was purged with Ar and measured by atomic absorption.

2.2.1.4 Laboratory 4. Ten ml of aqua regia were added to 2 g of the freeze-dried 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 deionized 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.

2.2.2 Partial Metals

Laboratory 2 carried out an additional series of three selective dissolution analyses (SDA). These used 1:1 benzene-methanol, 0.1N NaOH and 0.5N HCl. The benzene-methanol and 0.5N HCl extractions were made on the freeze-dried sediment. The 0.1N NaOH extraction was performed on the residue from the benzene-methanol extraction. In all cases after reaction, the supernatant was removed by centrifugation and placed in a Teflon Bomb. From there on the metal analysis procedure was the same as that described above by Laboratory 2 for total metals.

2.2.3 Organics

Carbon was determined in the acidified samples by Leco analyser with CO_2 collection system. Nitrogen was determined by the standard Kjeldahl method with Zn powder reduction.

2.2.4 Inorganic Carbon

This was the difference in carbon content between non-acidified and acidified sediments. Carbon in both cases was determined by Leco analyser with CO_2 collection system.

3. RESULTS AND DISCUSSION

None of the heavy metal concentrations in any of the sediment samples were unusual. It is extremely unlikely that anthropogenic activities have enhanced concentrations in any of the analysed samples. Heavy metal concentrations were much lower than in sediments from contaminated drainage systems elsewhere in Canada (Allan and Timperley 1975) or other countries (Forstner and Muller 1976). The concentrations are also lower than found naturally in other geological terrains (Allan et al. 1974, Allan 1975 and Forstner 1976). The distribution of heavy metals does not evidence any point source inputs of anthropogenic origin. Variations in heavy metal concentrations between sample sites are largely controlled by sedimentological parameters including texture, carbonate content, organic content, and amorphous oxides. Mean concentrations represent natural geological background values that can be used for comparison with data obtained in the future.

3.1 PARTICLE SIZE

Samples were assigned to textural groups at the time of collection (Table 5). Many of the river samples were sandy whereas the delta and lake samples were predominantly of clay size. The delta and lakes are obvious sites of deposition of finer grain sized sediment. A Landsat image made on July 19, 1973 clearly shows the spread of silt from the Athabasca River Delta into Lake Athabasca and along its southern shore (Mercer and Charlton 1977). The finer textured sediments found in the Athabasca River Delta and Lake are also slightly richer in organic content as shown by carbon and nitrogen concentrations (Tables 6 and 7). In general the organic carbon contents are low (Table 7) and all of the sediments are dominated by mineral components.

3.2 TOTAL ELEMENT CONCENTRATIONS

Five blind duplicates were in the identical sample suites submitted for analyses to the four laboratories. The results (Table 8) from analyses of these blind duplicates show that in general 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 Teflon bombs used in this technique. However, this would require additional analyses of other samples before a firm conclusion could be drawn. Nickel is one of the elements with which extraction difficulties have been encountered in other studies of sediments from the Athabasca Oil Sands Area (Lutz and Hendzel 1977). A comparison of the four sets of total element analyses indicates that the technique used by Laboratory 1 may overestimate

Table 6. Duplicate Carbon and Nitrogen Analyses of Bottom Sediments.

Sample Number	Inorganic C	Organic C	Total N
	- - - - - %	- - - - -	ppm
A-D-13	0.42	1.40	830
	0.44	1.72	945
A-D-19	0.60	1.63	745
	0.61	1.24	920
A-D-29	0.64	0.99	660
	0.68	1.04	710
A-D-60	0.92	1.89	1070
	0.96	1.92	1380
A-D-65	0.08	0.16	400
	0.12	1.10	120

Table 7. Carbon and Nitrogen in Bottom Sediments.

Area	Sample Number	Organic Carbon	Inorganic Carbon	Nitrogen	C/N
		- - - - %	- - - - - -	ppm	
Athabasca River	A-D-13	1.40	0.42	830	22
	A-D-16	1.16	0.69	755	25
	A-D-15	0.19	0.25	110	40
	A-D- 9	1.74	0.84	975	26
	A-D- 5	0.20	0.21	110	37
	A-D-19	1.63	0.60	745	30
	A-D-21	0.33	0.46	205	39
	A-D-70	1.45	0.69	760	28
	A-D-69	0.18	0.35	530	10
	A-D-65	0.16	0.08	400	6
Athabasca River Delta	A-D-52	1.63	0.86	970	26
	D-34	1.87	1.25	1,620	25
	A-D-61	1.95	1.24	1,310	24
	A-D-60	1.89	0.92	1,070	26
	A-D-46	0.03	0.24	220	12
	A-D-47	1.09	0.86	870	22
	A-D-29	0.99	0.64	660	25
Lake Athabasca	A-D-35	2.00	0.78	1,345	21
	A-D-41	1.84	0.62	1,380	18
	A-D-44	1.57	0.56	1,210	18
Riviere des Rochers	A-D-23	1.27	0.69	1,050	19

Table 8. Duplicate Analyses by Four Laboratories for Total Heavy Metals in Bottom Sediments.

(a) Laboratory 1:

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

(b) Laboratory 2:

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

continued . . .

Table 8 (cont.) Duplicate Analyses by Four Laboratories for Total Heavy Metals in Bottom Sediments.

(c) Laboratory 3:

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

(d) Laboratory 4:

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

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 (Tables 9 to 13), we concluded that the results for V, Ni, Cu, Zn, Mn, Fe and Hg provided by Laboratory 3 appeared to be the most reliable, followed by those of Laboratory 1. In the discussion section, we rely primarily on the results of these two laboratories. However, the concentration levels and variations are such that the results from any of the four laboratories could have equally well been used to arrive at the main conclusions viz detection of anthropogenic inputs of heavy metals. Heavy metal concentrations are similar to those found in sediments analysed as part of other investigations in the same area (Tables 14 to 16).

Higher heavy metal concentrations are associated with the finer textured samples, those found downstream at sites where sediment deposition predominates. The relationship between finer textured, more organic and clay-rich sediments and slightly higher heavy metal concentrations can be seen for V and Ni (Table 17) and Hg and As (Table 18). This relationship is general in nature because surficial sediments including river bottom sediments are normally composed of quartz, feldspars, carbonates, layer silicates, small amounts of heavy minerals, amorphous inorganic oxide and hydroxide coatings, and organic material. In a system affected only by natural loadings of heavy metals, the sediment geochemistry at any one site should result from the availability of heavy metals in geological source materials and sedimentological and fluvial parameters. At high energy sites, sediment will be coarse grained, dominated by silica, feldspar, and heavy minerals and have a low organic content. At low energy sites, sediment will be fine grained, made up largely of clay sized layer silicates

Table 9. Total Major Elements in Selected Bottom Sediments -- Laboratory 1.

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

Table 10. Total Heavy Metals in Selected Bottom Sediments ---Laboratory 1.

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

Table 11. Total Heavy Metals in Selected Bottom Sediments -- Laboratory 2.

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

Table 12. Total Heavy Metals in Selected Dredged Bottom Sediments -- Laboratory 3.

Area	Sample Number	Element							
		V	Ni	Cu	Zn	Mn	As	Hg	Fe
		- - - - - - - - - -	ppm	- - - - - - - - - -				ppb	%
Athabasca River	A-D-13	97	15.3	11.6	48.0	324	4.2	46	1.74
	A-D-16	113	16.6	13.4	56.4	313	4.6	36	1.70
	A-D-15	32	6.8	1.9	16.0	248	2.7	10	0.74
	A-D- 9	118	21.3	16.4	60.2	406	5.2	70	1.81
	A-D- 5	27	7.1	2.6	16.8	189	1.6	29	0.79
	A-D-19	95	12.9	9.8	44.3	318	4.3	35	1.48
	A-D-21	43	8.1	3.5	22.9	201	2.7	11	0.93
	A-D-70	112	15.0	11.4	49.8	346	4.8	36	1.67
	A-D-69	38	8.8	1.8	20.7	179	2.1	9	0.83
	A-D-65	18	5.1	0.3	9.6	82	2.0	9	0.46
Athabasca River Delta	A-D-52	137	17.9	14.8	57.2	418	5.1	48	1.82
	D-34	133	20.8	16.7	64.0	603	4.4	45	2.07
	A-D-61	156	25.8	19.8	71.0	722	5.7	46	2.23
	A-D-60	128	21.1	17.2	64.8	531	4.4	51	2.11
	A-D-46	25	4.2	0.4	18.8	71	1.9	5	0.44
	A-D-47	105	15.7	10.2	44.1	350	4.2	25	1.49
	A-D-29	89	15.7	9.6	44.9	312	3.4	28	1.43
Lake Athabasca	A-D-35	152	25.3	19.9	73.4	450	5.4	66	2.32
	A-D-41	189	25.4	20.4	79.1	728	6.3	62	2.51
	A-D-44	207	30.7	24.9	92.7	620	6.6	69	2.50
Riviere des Rochers	A-D-23	156	26.3	19.5	81.0	484	6.2	57	2.27

Table 13. Total Heavy Metals in Selected Bottom Sediments -- Laboratory 4.

Area	Sample Number	Element					
		V	Ni	Ci	Zn	Pb	Fe
		ppm					%
Athabasca River	A-D-13	22.5	17.5	12.5	43.8	5.0	1.61
	A-D-16	21.3	20.0	13.8	47.5	6.3	1.25
	A-D-15	8.8	8.8	2.5	21.3	<1.0	0.68
	A-D- 9	25.0	22.5	17.0	53.8	7.5	1.66
	A-D- 5	5.0	6.3	2.0	18.8	<1.0	0.54
	A-D-19	15.0	16.3	10.1	37.5	5.0	1.34
	A-D-21	8.8	8.8	4.5	26.5	2.5	0.79
	A-D-70	27.5	18.8	12.8	43.8	5.0	1.42
	A-D-69	10.0	8.8	2.5	23.5	1.3	0.69
	A-D-65	<2.5	7.5	1.1	13.8	<1.0	0.41
Athabasca River Delta	A-D-52	30.0	20.0	14.8	47.5	7.5	1.52
	D-34	27.5	23.8	17.0	56.3	7.5	1.58
	A-D-61	32.5	25.0	18.8	56.3	8.8	1.84
	A-D-60	32.5	22.5	16.8	51.3	8.8	1.77
	A-D-46	5.0	2.5	1.5	13.8	1.3	0.33
	A-D-47	23.8	16.3	10.8	37.5	5.0	1.23
	A-D-29	20.0	15.0	10.5	40.0	5.0	1.33
Lake Athabasca	A-D-35	28.8	25.0	20.3	62.5	8.8	1.91
	A-D-41	35.0	30.0	20.8	71.3	8.8	2.13
	A-D-44	27.5	30.0	22.5	77.5	8.8	2.06
Riviere des Rochers	A-D-23	33.8	28.9	20.6	77.5	8.8	2.10

Table 14. Heavy Metals in Bottom Sediments from the Athabasca Delta Area (data from Water Quality Branch, 1971-72).

		Lake[1]								
	Extraction	Athabasca			Clair			Mamauri		Baril
Element		West	Centre	East	West	East	South	West	East	Centre
		ppm								
Hg[2]	Exch.	3	-	-	1	3	<1	<1	<1	8
	Sol.	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.[3]	1.9	2.7	2.5	1.6	0.5	0.5	1.9	1.7	3.0

1. All samples were of general clayey texture.
2. Hg values are ppb.
3. Soluble Fe values in %.

Table 15. Heavy Metals in Bottom Sediments from the Athabasca River System (data from Korchinski in prep.)[1].

Location	Sand	TOC[2]	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	ND[3]	<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

1. Analyses on <425 μ fraction.
2. Total organic carbon.
3. Not done.

Table 16. Heavy Metals in Bottom Sediments from the Athabasca River system (data 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

Table 17. Mean Vanadium and Nickel Concentrations and their relation to texture of Bottom Sediments from the Various Units of the mainstem Athabasca River System.

Area	Texture[2]	Number Samples	Mean Concentrations[1] V	Ni	Mean Ratio[3] V/Ni
			- - - - ppm	- - - -	
Athabasca River	S	3	29	7	4
	Sc	2	69	11	6
	St	1	27	7	4
	CS	3	109	18	6
	C	1	112	15	7
	All[4]	10	69	12	6
Athabasca River Delta	S	1	25	4	6
	Sc	1	89	16	6
	CS	2	139	24	6
	C	3	121	18	7
	All	7	101	17	6
Lake Athabasca	C	3	183	27	7
Riviere des Rochers	C	1	156	26	6
All Areas		21	103	17	6

1. Analyses by laboratory 3.
2. Visual estimate; S = Sand; Sc = Sand with some clay; St = Sand with Tar; CS = Clay with some Sand; C = Clay.
3. The ratio in Cretaceous oils is 2.4:1 (V/Ni) (Hodgson 1954).
4. All sample textures.

Table 18. Mean Mercury and Arsenic Concentrations and their Relation to Texture of Bottom Sediments from the Various Units of the Mainstem 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[4]	10	30	4
Athabasca River Delta	S	1	7	2
	Sc	1	31	3
	CS	2	54	5
	C	3	45	4
	All	7	40	4
Lake Athabasca	C	3	74	6
Riviere Des Rochers	C	1	61	6
All Areas		21	41	4

1. Visual estimate; acronyms as for Table 17.
2. Mean of analytical values from Laboratories 2 and 3.
3. Analyses by Laboratory 3.
4. All sample textures.

and have a higher organic content. Because of their affinity for clay sized materials via sorbtion and exchange processes heavy metal concentrations should be naturally higher at these low energy sites.

3.2.1 Major Elements

Limited data are available on element concentrations in river bottom sediments from the glaciated, forested, interior lowlands of western Canada. Comparison of the data with those for Lake Winnipeg bottom sediments (Allan and Brunskill 1976) may be applicable. Sediments in both areas are derived largely from Phanerozoic sedimentary strata of the Interior Platform and were analysed by the same method for major elements (RFPES).

3.2.1.1 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%). Variation is probably a reflection of different concentration of layered aluminosilicates in the different sediments.

3.2.1.2. Iron and Titanium. Both elements are found naturally in the oil sands (section 1.2.1) (Kramers and Brown 1976). Fe 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 fractionation followed by x-ray diffraction could resolve this question. The finer grained sediments have the higher Fe and Ti concentrations, probably a result of concentration in amorphous oxide-hydroxide coatings or present in the lattice of clay sized layer silicates. Ti concentrations of Lake Winnipeg sediments are slightly higher than in the Athabasca River and Delta sediments but similar (0.4%) to the Lake Athabasca sediments.

3.2.1.3 Sodium. This element can be present as sand and silt sized feldspars, in layer silicates, in organic materials, and 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%).

3.2.1.4 Calcium and Magnesium. In view of the abundance of Devonian limestone and dolomite in the study area, calcium and magnesium are most likely present as dolomite among the finer particles. For both Ca and Mg, concentrations are similar to those in sediments from the north basin of Lake Winnipeg.

3.2.2 Heavy Metals

On the basis of the blind duplicate analyses (Table 8) and the four independent determinations of total metals (Tables 9 to 13) the results from Laboratory 3 are the best in our estimate as regards absolute or most likely correct total element values. However, our main site for comparative purposes is Lake Winnipeg (Allan and Brunskill, 1976) and these samples were analysed by the RFPES technique of Laboratory 1. Thus, comparisons of heavy metal concentrations are better made on the basis of the Laboratory 1 analyses.

3.2.2.1 Vanadium and Nickel. The finer textured sediments have the higher concentrations (Table 17). In addition to decreasing particle size, increasing organic content down-drainage is also a factor causing concentration increases. The absolute concentrations do not appear to reflect an anthropogenic point source input such as industrial effluents from Athabasca oil sands plants 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 19). Some sediments from Lake Winnipeg have higher V concentrations (Allan and Brunskill 1976) than the Athabasca drainage system which could be related to the vanadium content of oil rich clays in the Red River basin. The Ni concentrations (Table 17) are low when compared to many lake sediments elsewhere (Allan and Timperley 1975 and Forstner, 1977). The ratio of V/Ni in one Athabasca oil sand was 2.91 (Hodgson 1954) and in general 1.6-9.8 (Table 1). The ratios of V/Ni in the Athabasca River drainage sediments were usually 4-7 (Table 17). These overlapping ratios indicate that relative enrichment of one or other element as a result of natural terrestrial geochemical processes has not taken place.

3.2.2.2 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 probably in amorphous inorganic-organic coatings. Concentrations are normal or even low in comparison with polluted river (Forstner 1976; Forstner and Muller 1976) and lake (Allan, 1975) sediments elsewhere.

3.2.2.3 Mercury. This element has received the most attention of all the heavy metal contaminants of drainage systems (see Proc. 1st. Internat. Mercury Congress, Barcelona, Spain 1974; Proc. Conf. on Transport of Persistent Chemicals in Aquatic Ecosystems, Ottawa,

Table 19. Comparison of Mean Vanadium Concentrations in the Mainstem Athabasca River System with other North American Sites.

Area	Number Samples	Vanadium Concentration Mean	Vanadium Concentration Range
		ppm	
Lake Erie[1]	6	55	10-110
Athabasca River (Ft. McMurray to Delta)	10	62	15-100
Athabasca River System (Ft. McMurray to Slave River)	21	84	15-148
Athabasca River Delta	6	90	22-127
Lake Athabasca	4	115	76-148
Riviere Des Rochers	1	136	136
South Basin Lake Winnipeg	21	191	63-232
North Basin Lake Winnipeg	21	158	53-214
Lake Winnipeg	50	169	53-232
Santa Barbara Basin,[2] California	13	150	148-152
Santa Monica Basin,[2] California	12	150	125-175
Soledad Basin,[2] California	16	120	90-175
San Pedro Basin,[2] California	16	125	100-130

1. Six sediment cores (Kemp et al. 1976) showed no clear surface enrichment.
2. 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.

Canada 1974; Proc. of Internat. Conf. on Heavy Metals in the Environment, Toronto, Canada 1975). Hg concentration in fly-ash was low (Table 3) and Hg concentrations in the oil sands may also be low. However, it is a well established fact that Hg from coal or coke combustion by thermal power stations is almost completely released to the atmosphere in gaseous form. The possibility that this may also be the case for oil sands plants has not been established but should not be overlooked. In any case, Hg concentrations in sediments from all units of the drainage system are presently very low (Tables 11, 12 and 18). Mercury contaminated sediments can have anything from 1 to 684 ppm Hg (Forstner and Muller 1976). None of the sediments from the Athabasca drainage system come close to such high concentrations (Tables 11 and 12). Mean values ranged from only 30 to 74 ppb and are considered to be normal geological concentrations for the area. There was an increase from river to delta to lake probably corresponding to changes to finer texture and greater organic content. It should be noted that this is opposite to the trend documented for rivers polluted with Hg in northwestern Ontario (Parks 1975). Lake Athabasca sediment had a mean concentration of 74 ppb. Such concentrations are much less than in surface sediment from many other Canadian lakes (Allan et al. 1974) or even from Lake Winnipeg (about 150 ppb) (Allan and Brunskill 1976).

3.2.2.4 Arsenic. As is not found in appreciable concentrations in precipitator fly-ash (Table 3) which could mean that if present in the coke, it may be released primarily in gaseous form to the atmosphere.

Bottom sediment concentrations of As were low and similar to those found in the surface sediments of many natural Canadian lakes (Allan et al. 1974).

3.2.2.5 Others.

Variations in concentrations of all of the elements analysed for but not discussed above seem to result from natural geological, geochemical, mineralogical, sedimentological or fluvial controls. There is no evidence of anthropogenic input. None of the concentration levels for any of the elements give reason to suspect contamination.

3.3 PARTIAL METAL CONCENTRATIONS

Partial element or selective dissolution analyses (SDA) were carried out by Laboratory 2. Generally, results for the blind duplicates (Table 20) show that precision was adequate in spite of low concentrations. Many of the results were beneath detection limits. This was not important because of the low concentrations recorded. Total heavy metal analyses should not be affected by sample composition because the entire sample should be dissolved. In contrast, partial extractions of heavy metals remove debatable operationally defined fractions. Our interpretation of the fractions selectively dissolved by the different extractions are summarized in the tables. However, each technique should still remove the same fraction every time. Precision with the benzene-methanol extraction is hard to comment on because most results are below detection limits. The NaOH results, where they exceed detection, are good, with the possible exception of Fe. Precision by the HCl extraction was good to very good.

3.3.1 Sequential Benzene-Methanol/NaOH Extraction

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 organic but not humic material (Jackson 1975b). The subsequent $0.1\overline{N}$ NaOH extractant is expected to remove humic material but not to significantly attack the mineral particles or amorphous inorganic coatings

Table 20. Duplicate Analyses for Partial Heavy Metals from Athabasca River Bottom Sediments -- Laboratory 2.

(a) 1:1 Benzene/Methanol Extraction:

Sample Number	Element						
	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

(b) 0.1N NaOH Extraction:

Sample Number	Element						
	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

continued . . .

Table 20 (cont.) Duplicate Analyses for Partial Heavy Metals from Athabasca River Bottom Sediments -- Laboratory 2.

(c) 0.5N HCl Extraction:

Sample Number	Element 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

on these particles.

All of the vanadium concentrations (Tables 21 to 24) were beneath detection in both extractions. Some 90% of the total V (Tables 10 to 13) thus appears present in a form that is not extractable by either of these reagents. Most of the other elements (Tables 21 to 24) were extracted in amounts beneath detection limits. In general, the low concentrations of heavy metals removed by the benzene-methanol/NaOH reagents imply that they are held primarily in more resistant forms. Benzene-methanol extracted little Fe or Mn. The NaOH removed some 10% to 30% of the Fe removed by the 0.5N HCl (Tables 21 to 24) and about 1% of the total iron (Tables 10 to 13). Thus, iron and Mn present in easily extractable organics is not a major component of the sediment.

3.3.2 Dilute Hydrochloric Acid Extraction

The extractant, 0.5N HCl, is thought to remove exchangeable and chemisorbed elements; amorphous inorganic coatings with their associated trace metal content; carbonates; low molecular weight fulvic acid; and certain polar organic compounds such as amino acids (Jackson, 1975a). Silicate mineral particles should not be significantly attacked. As expected lower concentrations for all elements were removed (Tables 21 to 24) than by the total extraction procedures (Tables 10 to 13). Less than 10% of the total vanadium was extracted. Several of the nickel concentrations were higher than those obtained by the total extracts of Laboratory 3 (Table 12). This may be related to accuracy of total Ni determination (Table 8) or to problems with extraction of this element from these sediments (Lutz and Hendzel 1977). Some 75% of the Mn was also extracted and about 40% of the Fe, indicating that these are probably present as sorbed ions or in amorphous inorganic or low molecular weight organic coatings as in the case for many drainage sediments (Whitney et al. 1975). Significant quantities of Cu

Table 21. Partial Extractions of Heavy Metals from Athabasca River Bottom Sediments.

Sample Number	Extraction Method	Metals						Expected Removal
		V	Ni	Cu	Zn	Mn	Fe	
A-D-13	1:1 Benzene/ Methanol	<5	<5	<1	12	<1	<4	lipids; some hydrocarbons
A-D-16		<5	<5	<1	<1	<1	<4	
A-D-15		<5	<5	1	8	<1	<4	
A-D- 9		<5	<5	<1	12	<1	<4	
A-D- 5		<5	<5	<1	<1	<1	4	
A-D-19		<5	<5	<1	2	<1	<4	
A-D-21		<5	<5	<1	1	<1	<4	
A-D-70		<5	<5	<1	<1	<1	6	
A-D-69		<5	<5	<1	<1	<1	9	
A-D-65		<5	<5	<1	<1	<1	<4	
A-D-13	0.1N NaOH[1]	<10	<5	4	1	6	255	fulvic and humic acids; some proteins, amino acids
A-D-16		<10	<5	8	1	2	173	
A-D-15		<10	<5	<1	1	<1	18	
A-D- 9		<10	<5	7	2	9	380	
A-D- 5		<10	<5	<1	1	2	93	
A-D-19		<10	<5	4	2	8	391	
A-D-21		<10	<5	1	1	1	81	
A-D-70		<10	<5	5	1	6	312	
A-D-69		<10	<5	<1	1	<1	40	
A-D-65		<10	<5	<1	1	<1	26	
A-D-13	0.5N HCl	11.0	17.0	8.0	24.0	250	7000	Fe + Mn coatings; exchangeable and sorbed cations; carbonates
A-D-16		9.0	24.0	9.0	34.0	240	6600	
A-D-15		<8.0	9.0	2.0	8.0	190	3300	
A-D- 9		<8.0	24.0	12.0	37.0	330	7400	
A-D- 5		<8.0	<5.0	2.0	6.0	160	2500	
A-D-19		<8.0	21.0	8.0	24.0	240	6500	
A-D-21		<8.0	11.0	3.4	13.0	160	3900	
A-D-70		<8.0	24.0	8.0	28.0	280	7000	
A-D-69		<8.0	11.0	2.2	12.0	150	3800	
A-D-65		<8.0	<5.0	<1.0	6.0	70	1900	

[1] On residue from 1:1 Benzene/Methanol Extraction.

Table 22. Partial Extractions of Heavy Metals from Athabasca River Delta Bottom Sediments.

Sample Number	Extraction Method	Metals						Expected Removal
		V	Ni	Cu	Zn	Mn	Fe	
A-D-52	1:1 Benzene/ Methanol	<5	<5	2	3	<1	<4	lipids; some hydrocarbons
D-34		<5	<5	<1	12	<1	5	
A-D-61		<5	<5	<1	3	<1	4	
A-D-60		<5	<5	<1	2	<1	<4	
A-D-46		<5	<5	<1	<1	<1	6	
A-D-47		<5	<5	<1	4	<1	<4	
A-D-29		<5	<5	<1	2	<1	<4	
A-D-52	0.1N NaOH[1]	<10	<5	7	1	9	363	fulvic and humic acids; some proteins, amino acids
D-34		<10	<5	12	1	8	242	
A-D-61		<10	<5	11	1	17	373	
A-D-60		<10	<5	9	1	11	322	
A-D-46		<10	<5	<1	1	<1	35	
A-D-47		<10	<5	6	1	12	413	
A-D-29		<10	<5	6	1	5	202	
A-D-52	0.5N HCl	12.0	27.0	11.0	40.0	340	8500	Fe + Mn coatings, exchangeable and sorbed cations; carbonates
D-34		13.0	28.0	14.0	45.0	480	12000	
A-D-61		14.0	29.0	14.0	44.0	580	10000	
A-D-60		14.0	27.0	12.0	40.0	430	8700	
A-D-46		<8.0	7.0	1.0	7.0	60	2200	
A-D-47		9.0	20.0	9.0	27.0	310	7500	
A-D-29		<8.0	19.0	8.0	28.0	250	7300	

1. On residue from 1:1 Benzene/Methanol Extraction.

Table 23. Partial Extractions of Heavy Metals from Lake Athabasca Bottom Sediments.

Sample Number	Extraction Method	Metals						Expected Removal
		V	Ni	Cu	Zn	Mn	Fe	
A-D-35	1:1 Benzene/ Methanol	<5	<5	<1	5	<1	5	lipids; some hydrocarbons
A-D-41		<5	<5	<1	5	<1	<4	
A-D-44		<5	<5	<1	<1	<1	<4	
A-D-35	0.1N NaOH[1]	<10	<5	11	1	5	283	(see Table 21)
A-D-41		<10	<5	12	2	7	252	
A-D-44		<10	<5	11	2	6	293	
A-D-35	0.5N HCl	15	33	15	47	360	11000	(see Table 21)
A-D-41		10	35	16	52	600	12000	
A-D-44		12	35	17	54	480	9400	

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[1] On residue from 1:1 Benzene/Methanol Extraction.

Table 24. Partial Extractions of Heavy Metals from Riviere Des Rochers Bottom Sediments.

Sample Number	Extraction Method	Metals						Expected Removal
		V	Ni	Cu	Zn	Mn	Fe	
A-D-23	1:1 Benzene/ Methanol	<5	<5	<1	1	<1	4	(see Table 21)
A-D-23	0.1N NaOH[1]	<10	<5	9	1	6	283	(see Table 21)
A-D-23	0.5N HCl	13	33	13	47	390	9300	(see Table 21)

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1. On residue from 1:1 Benzene/Methanol Extraction.

and Zn were extracted, in some cases all of the Cu and up to 50% of the Zn.

3.4 Organic Analyses

Organic carbon and nitrogen analyses were made by Laboratory 2. Analyses of blind duplicates showed precision to be satisfactory (Table 6) with the exception of A-D-65. The sandy texture of this sample and problems associated with sub-sampling are probably the reason. For the coarser grained, sandy samples the organic carbon content is less than the inorganic carbon content (Tables 5 and 7). In the finer textured, clayey sediments, the opposite applies and organic to inorganic carbon ratios are about 3:1. High C/N ratios indicate that the organic material has not undergone a great deal of alteration and if extracted and studied in detail, may be similar to the relatively poorly mineralized organic material which predominates in northern forest soils. Korchinski (in prep.) shows that fulvic to humic acid ratios in the waters of the Athabasca River mainstream and its tributaries vary from 4:1 to 10:1.

3.5 Element Forms in Sediments

Throughout this discussion, it has been implied that many of the easily extractable metals are probably present on or in inorganic amorphous hydroxide-oxide coatings on fine particle size minerals. The relatively simple selective extraction methods used here (0.1N NaOH; 0.5N HCl) cannot categorically resolve whether the heavy metals are sorbed by inorganic (Fe, Al, Mn) coatings, organic matter, or complex mixtures of the two. In uncontaminated sediments there is often a positive correlation between "clay" content and element concentration. This textural or sedimentological control of concentrations has been alluded to for most of the element concentration variations in sediments from the Athabasca drainage system. In the "clay" fraction there exists a complex mixture of fine particle size silicate minerals (dominated usually by layer silicates) and organic material. Both are often coated with sorbed organic-inorganic, Fe-Al-Mn rich oxide-hydroxide coatings. All of these sediment components if determined separately are likely to correlate to varying degrees with each other.

3.5.1 Metal-Organic Relationships

V and Ni are the two heavy metals most commonly associated with the bitumen fraction of the Alberta oil sands. Both V and Ni are strongly, and positively correlated with total organic carbon content of the bottom sediments (Figs. 7 and 8 respectively). The correlation is best for samples from the Athabasca River and from its channels in the delta. The samples from Lake Athabasca and Riviere des Rochers have the highest concentration of both V and Ni and plot at the upper, organically richer end of the correlation. The correlations support a hypothesis that V and Ni are both present in the sediments in the organic fraction. Neither V nor Ni are significantly removed by 0.1N NaOH (Tables 21 to 24) which should extract the more readily dissolved organic component of the bottom sediments. The combination of these results implies that both V and Ni are present in the sediments in a fairly resistant organic form.

3.5.2 Metal-Metal Relationships

V and Ni have both been positively correlated with total organic carbon. They are thus likely to correlate with each other. An excellent positive correlation (Fig. 9) does in fact exist. The slope of the correlation is a reflection of the analytical technique used in that relatively more Ni was removed by Laboratory 1 and more V by Laboratory 3. There is a clear progression in both cases to higher bottom sediment V and Ni concentrations from river to delta to lake. Good correlation between V and Ni would

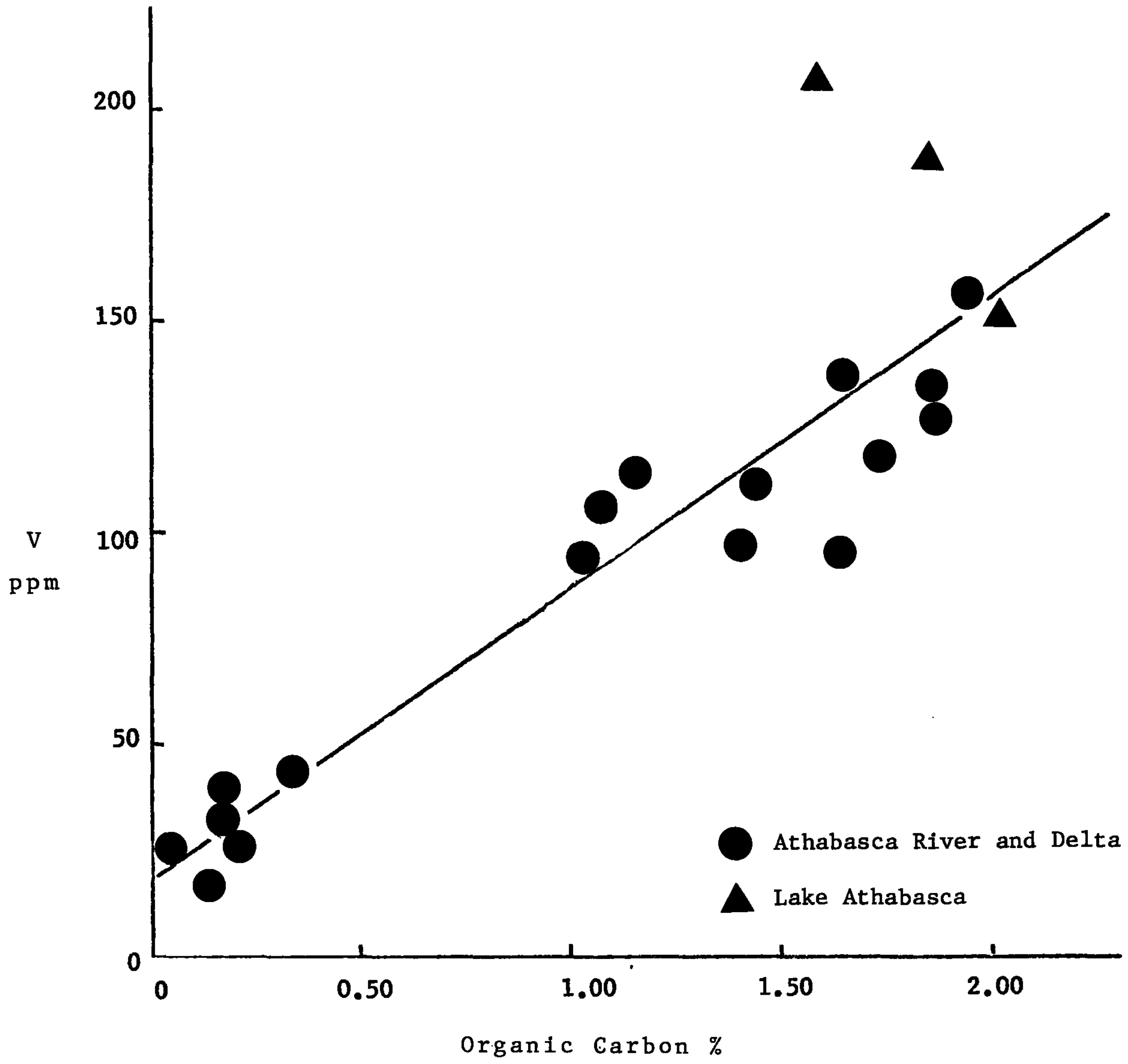

Fig. 7. Correlation between total vanadium and organic carbon concentrations in bottom sediments (data in Tables 7 and 12).

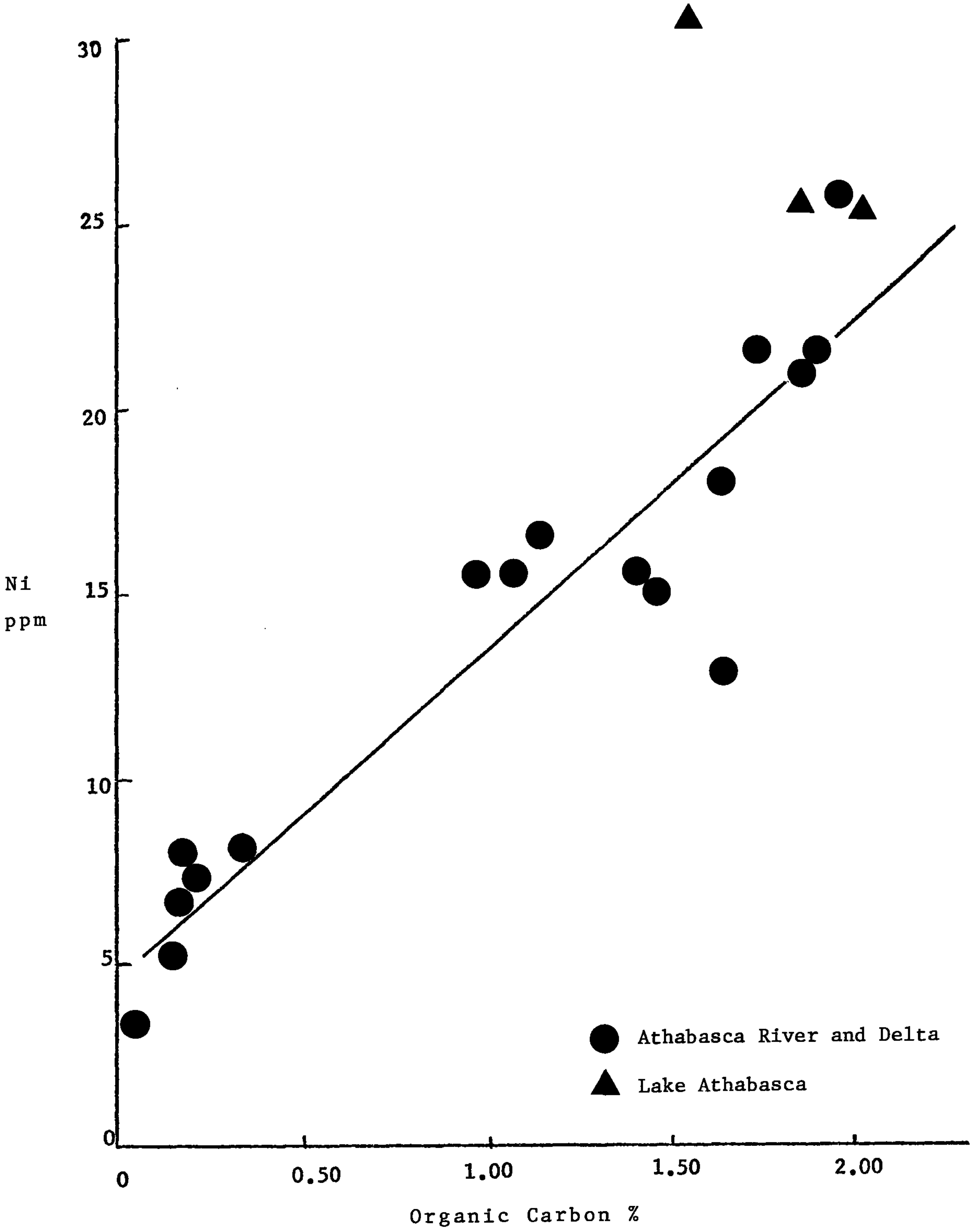

Fig. 8. Correlation between total nickel and organic carbon concentrations in bottom sediments (data in Tables 7 and 12).

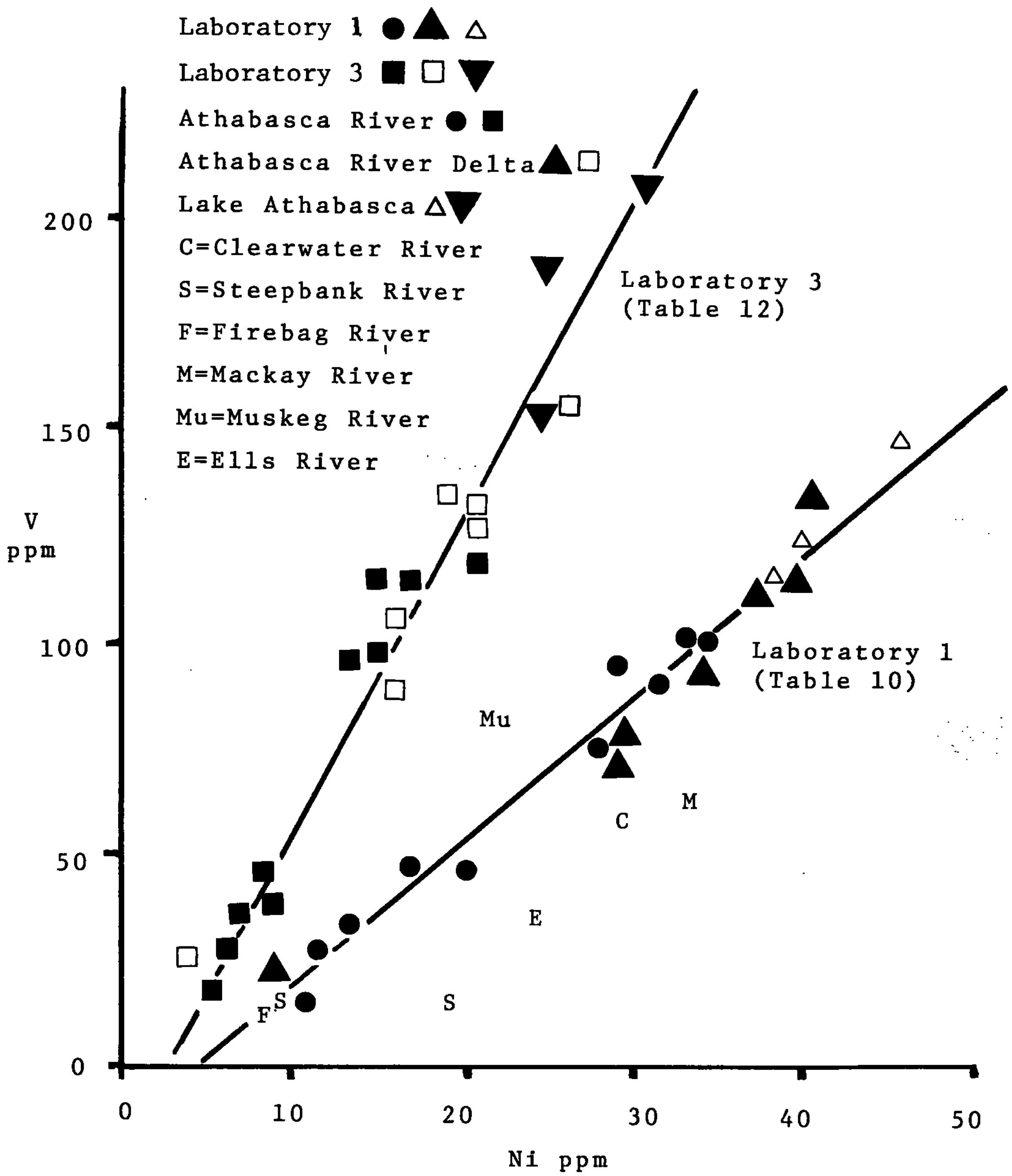

Fig. 9. Correlation between total vanadium and total nickel concentrations in bottom sediments (data for Athabasca River, its delta and Lake Athabasca in Tables 10 and 12 and data for tributary rivers from Lutz and Hendel (1977)).

be expected because of the short range of V/Ni ratios found in Cretaceous oils (Hodgson 1954) (Table 1). In a similar vein, Barry et al. (1975) have used high positive correlations for V and Ni in the atmosphere of the northeastern U.S.A. to relate the metals to residual fossil fuel combustion. The strong correlation between V and Ni (Fig. 9) could thus be indicative of their source as the bitumen fraction of the oil sands. This source for the elements is further supported by their strong positive correlation with total organic carbon content and relative resistance to extraction by 0.1N NaOH. The plots of V versus Ni (Fig. 9) determined by both Laboratories 1 and 3 intersect close to the origin. Such a relationship supports a theory of common origin in that neither V or Ni are present in the sediments individually. A similar argument viz source of V and Ni is used by Barry et al. (1975) in their atmospheric work in the northeastern U.S.A.

Lutz and Hendzel (1977) did not find such a good correlation between V and Ni. The reason is related to sample site. All of our samples come from the mainstem Athabasca River-Delta-Lake system. Many of their samples come from different rivers (Steepbank, Ells, Firebag, Clearwater, MacKay, Muskeg) draining into the Athabasca and each of these rivers (Fig. 9) appears to have its own characteristic V/Ni ratio which results in a poorer overall V to Ni correlation.

A strong correlation for V and Ni in bottom sediments should be reflected in their strong correlation in suspended loads. Korchinski (in prep.) has in fact shown that high concentrations of V and Ni occur in the Clearwater, Steepbank and Hangingstone (tributary of the Clearwater) Rivers (Fig. 1) following rainfall. He attributed this to higher suspended sediment loads following rainfall events.

In analyses of water from rivers in the study area, Lutz and Hendzel found values of 294, 528, 560 and 1010 ppb Zn in unfiltered, acidified samples from the Ells, Steepbank, Firebag and MacKay Rivers (Fig. 1) respectively, near their inflow to the Athabasca River. These unfiltered water samples were acidified with concentrated HNO_3 on collection and left for some time so that sediment could settle before analysis. The high Zn values in these waters are probably a result of leaching of Zn from suspended sediment because three of the four samples had much lower Zn concentrations (1 to 2 ppb) when filtered in the field at time of collection. Fe behaved similarily and supports an argument that Zn and Fe are transported as sorbed elements on suspended sediment. Because this suspended sediment is eventually deposited as bottom sediment, we plotted Zn versus iron as extracted from the bottom sediments by the 0.5N HCl (Fig. 10). The correlation was excellent indicating that the Zn and Fe extracted by this technique is probably in the form proposed. The general relationship between heavy metals such as Zn and Cu, with Fe and Mn rich coatings on drainage sediment fractions is now an accepted technique in geochemical prospecting (Whitney, 1975 and Nowlan, 1976).

Another example of metal-metal correlation is that between Ca and inorganic carbon (Fig.11). The strong positive correlation between all samples suggests that most of the Ca is present in carbonate particles.

4. CONCLUSIONS

The conclusions drawn from this study and pertaining to bottom sediment geochemistry are as follows:

1. There is presently no evidence of anthropogenically related loadings of heavy metals to bottom sediments of the Athabasca River Delta and Lake system, at least as far as can be determined from the relatively few analyses performed so far on selected samples

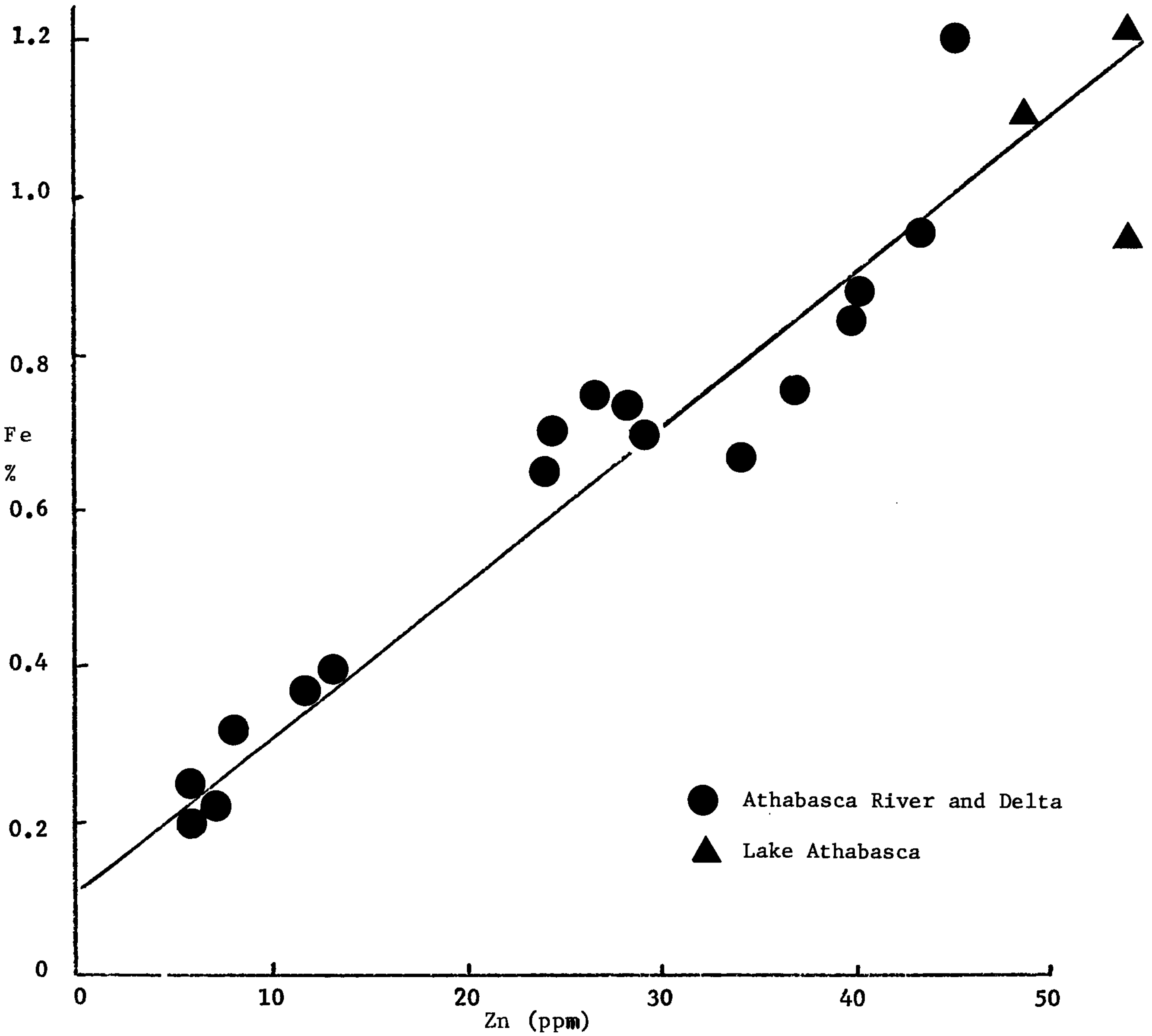

Fig. 10. Correlation between iron and zinc concentrations (partial extraction using 0.5N HCl) in bottom sediments (data from Tables 21 to 23).

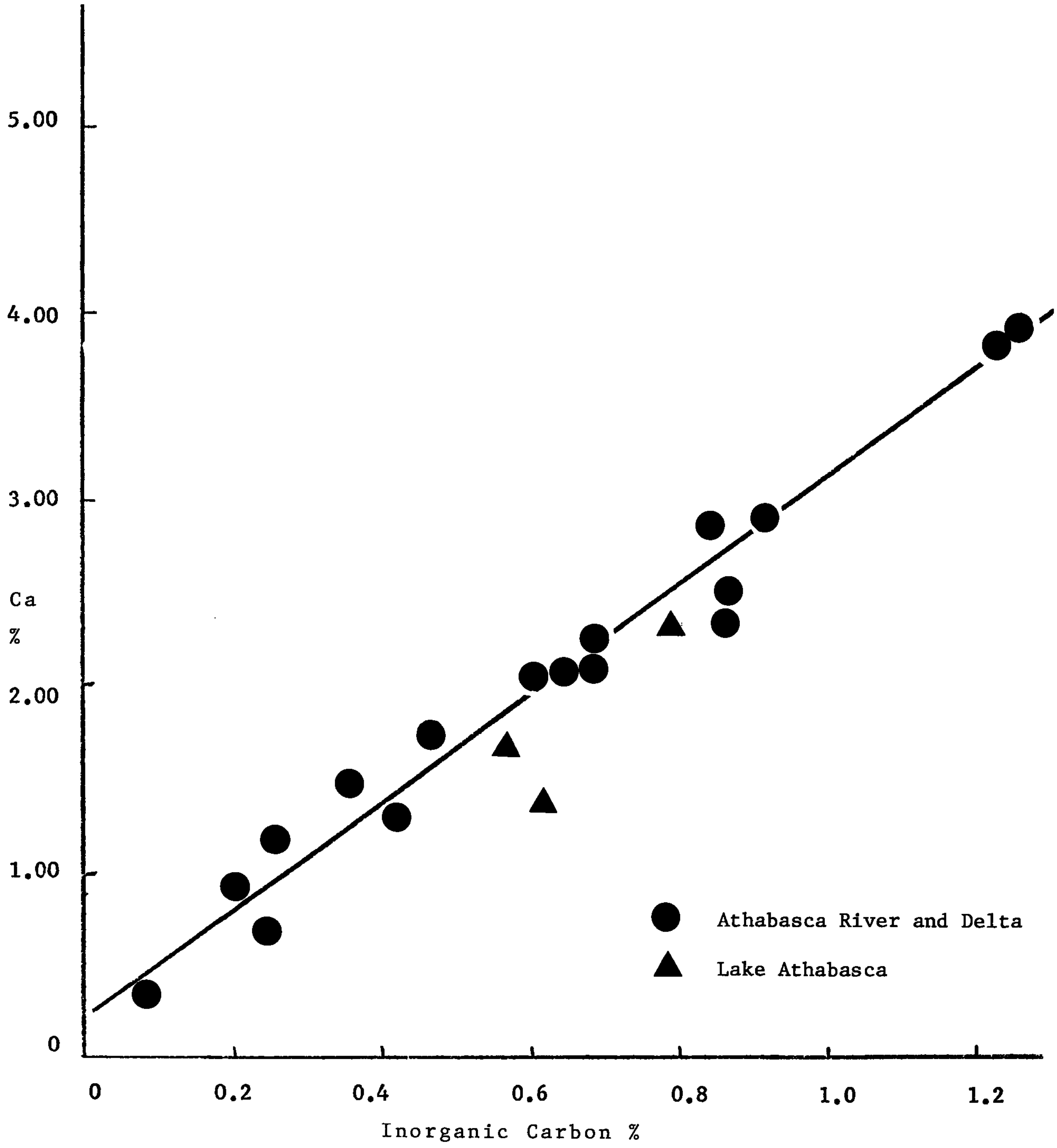

Fig. 11. Correlation between total calcium and inorganic carbon concentrations in bottom sediments (data in Tables 7 and 9).

from the total sample suite collected.

2. Variations in heavy metal concentrations are a result of natural sedimentological, geochemical, and fluvial controls. 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 silicate concentration, and organic content.
3. There is a progression towards higher concentrations of heavy metals from the Athabasca River to its delta to Lake Athabasca. Because of their deposition in low energy environments, fine textured sediments increasingly predominate from river to delta to lake and an associated increase in heavy metal concentrations can be expected.
4. V and Ni, the heavy metals most commonly associated with the Athabasca oil sands, are present in bottom sediments in the same or lower concentrations than in many unpolluted drainage sediments elsewhere. Caustic reagents only removed a small fraction of the total V. Total V correlates well with organic carbon as does total Ni. Total V and Ni are also strongly correlated with a zero intercept. In combination, these relationships support a conclusion that the V and Ni in the sediments are probably in a form similar to that in which they occur in the bitumen of the oil sands and have thus undergone little chemical or bacteriological alteration between source and site of deposition in drainage bottom sediments.

5. Heavy metals other than V and Ni are partly present in amorphous Fe and Mn rich coatings of mineral grains. For example, there is a strong correlation between the Fe and Zn removed from the bottom sediment suite by 0.5N HCl.

Conclusions 1, 2 and 3 relate to objectives 1 and 2 in the Introduction. Conclusions 4 and 5 relate to objective 3. Objective 4 and more detailed investigations relevant to objective 3 are dealt with in the recommendations made below.

The conclusions relative to anthropogenic sources for heavy metal concentrations of drainage sediments from the Athabasca River system are based on relatively few sample sites. The conclusions as to heavy metal forms in the sediments are based on limited extractions of a relatively small, selected, sample suite. In spite of this, we feel that the conclusions are adequate and unlikely to be significantly changed by further analyses.

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