SURFICIAL SEDIMENTS OF WESTERN NIPIGON BAY, LAKE SUPERIOR, IN RELATION TO PULP MILL EFFLUENT

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R. G. Sandilands Canada Centre for Inland Waters Burlington, Ontario

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updating shorts incorporated april 176

	2:	X-RAY DIFFRACTOGRAMS OF TWO SAMPLES
	3:	PERCENT TOTAL SULPHUR
	4:	PERCENT ORGANIC CARBON
TABLE	1:	On site data and size analysis results
	2:	Percent occurrence of major element oxides in sediment samples
	3:	Trace elements, organic and inorganic carbon results
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SAMPLE LOCATIONS

FIGURE 1:

INTRODUCTION

This report forms part of a study being carried out, within the study plan of the International Joint Commission (I.J.C.) Upper Lakes Reference Group, to examine the influence of point source inputs of energy, nutrients and toxic materials on water quality and on aquatic communities. The composition and characteristics of the surficial sediments in the western section of Nipigon Bay, Lake Superior, have been investigated to provide insight into the effect of paper mill wastewater discharge and the zone of influence of the discharge plume.

Previous studies of the biology of Nipigon Bay by German (1968), found midge larvae throughout the area, mayflies only in the non-plume areas, and sludge worms throughout but with high concentrations in the plume area. Additional biological studies conducted by T. W. Beak Consultants (1970) and Brouzes (1971) found the following results: (1) a high concentration of worms occurred up to a mile from the mill outfall; (2) worm populations decreased, and more sensitive species increased with greater distance from the outfall. In addition, the Ontario Ministry of Environment has conducted a benthic sampling program during 1974 as a part of the I.J.C. study plan. The general distribution of Quaternary sediments in Nipigon Bay has been reported by Mothersill (1972) who used a widely spaced grid to cover the whole bay. The results suggested that the greatest accumulation of recent, fine grained, sediment was in the deeper water.

In the present study, bottom samples were taken to cover the

area which was expected to be effected by the discharge from the Kraft Paper Mill at Red Rock (Fig. 1). Since Thomas et al., (1972, 1973) and Allersma and de Groot (1974) have demonstrated the preferred occurrence of heavy minerals and organic material with the fine-grained size fraction (<16 microns), sample locations were also chosen to be in the deeper water areas where fine-grained sediments accumulate. The composition and characteristic associations of the samples are described by particle-size distribution, organic and inorganic carbon, major element and trace element analysis.

GENERAL DESCRIPTION OF THE STUDY AREA

The Nipigon River drains approximately 25,000 square kilometers (10,000 sq. miles) of the Canadian Shield, including Lake Nipigon. In 1972, the mean discharge of the river was reported at 15,000 cfs. (420 m³/sec) (Water Survey of Canada). South of the townsite of Nipigon, the river widens to form Nipigon Bay (Fig. 1) which extends about 16 km. south and 40 km. east of the river mouth. The western part of the Bay is divided into two deep channels. The south channel runs between Five Mile Pt. and Burnt Island (Fig. 1) and then parallels the western shoreline until it enters Lake Superior through the Nipigon Straits. The east channel runs parallel to the north shore between Hughes Pt. and Ile 1a Grange (Fig. 1) and then into the eastern half of the Bay.

Near its mouth, the Nipigon River cuts through erosional remnants of a thick sheet of sill of diabase, which overlies either flat lying sediment rock of the Silbey Series or in places, Algoman granitic rocks. The Sibley Series, red in colour due to the presence of small amounts of

hematite, consists of shales, shaley dolomites and dolomitic limestone with interbedded sandstone (Pye 1962).

Zoltai (1965) reported occurrences of glaciolacustrine deposits of varved clays in the Lake Nipigon basin area which contained 16 to 26% carbonate by weight. He also mentioned that the ground morainic till in this area, which generally reflects the composition of the bedrock, may contain up to 15% calcium carbonate in the fine matrix.

At the northwestern end of Nipigon Bay, a large paper mill at Red Rock discharges about 96,000 m³/day (21.1 million gallons per day) of wastewater effluent into the bay (average flows in July 1974 as reported by Polak (1975)). This effluent contained an average of 6.51 metric tons/day (approximately 14,000 lb/day) of suspended solids. T.W. Beak Consultants (1969) reported an average suspended solids loading of approximately 47. metric tons/day (96,000 lb/day) in 1969 before plant modifications.

METHODS

Sediment sampling was carried out on June 24-26, 1974 in conjunction with an O.M.E. benthic sampling program. Pre-determined sample locations were found by using a Furuno sounder and dead reckoning. Forty-five bottom samples and eight cores (up to 60 cm in length) were obtained using a ponar grab sampler and phleger corer respectively (Sly 1969). Temperature, Eh and pH readings were recorded and the top 1 cm of sediment was subsampled for the remaining analyses.

Two subsamples were frozen and later freeze-dried and lightly

ground. The concentration of the following major elements, Si, Al, K, Na, Mn, Fe, Ca, Mg, S, P, Ti, were determined by x-ray fluorescence, using a Phillips P.W. 1220 C automatic spectrometer. The percentage organic and inorganic carbon was determined using a Leco induction furnace carbon analyser and sulphurous acid digestion at room temperature. The trace elements, Ni, Pb, Cu and Cr were determined on a Techtron AA-5 atomic absorption spectrophotometer after hot concentrated HCl extraction. Mercury analysis was conducted on 20 samples by the Water Quality Branch at CCIW using flameless atomic absorption after acid extraction. Trace element concentrations are expressed relative to the dry weight of sediment.

One sediment subsample was retained wet and particle size distribution was determined using a Micromeritics sedigraph 5000 analyser (Duncan and Rukavina 1972). Coarse organic material and clumping of organic fibers, which blocked the flow, prevented the analysis of seven samples. These samples were located close to the mill outfall. A computer program (Rukavina and Dolling 1973) was used to process the sedigraph results to provide the percentage size composition and moment measures.

RESULTS AND DISCUSSION

Table 1 shows the station locations, on site data and size analysis results. Most samples consisted of a thin (1/2-1 cm) oxidized surface layer of brown mud overlying structureless grey mud. Near the

river mouth, mean sediment size was approximately 7 phi (8 microns) and averaged about 66% silt size and 33% clay size material. At the downstream ends of both east and south channels, mean sediment size was approximately 8.25 phi (3-4 microns) and consisted of about 40% silt size and 60% clay size material.

Figure 2 shows traces of x-ray diffractograms from the less than 2 micron fraction of samples 13 and 38. Sample 13 is one kilometre east of the outfall while sample 38 is in the south channel approximately six kilometres from the outfall. Both samples showed similar analytical peaks relating to the inorganic composition of the sediment. However, a repeat analysis of a bulk sub-sample of sample 13 (figure 2) gave a strong peak for dolomite that wasn't recorded in the less than 2 micron fraction. This would suggest a correlation with silt size particles and carbonates as has been observed in the Great Lakes (Thomas et al 1972, 1973). Eroded glacial sediments upstream provide a likely source for this silt size dolomite.

Cores taken at stations 13, 20, 31 and 41 (figure 1) generally consisted of structureless muds. Some thin layers of sandy silt were observed in predominantly mud cores at locations 3 and 24. The core at station 35 penetrated through a thin mud layer into glacial sediment. At station 12, approximately 500 m east of the mill outfall, the core consisted of 30 cm of coarse organic material over structureless mud. Organic fibers were visible in all the bottom samples within 1.5 km of the outfall. Bark and/or wood chips were found in the top 10 cm of

most bottom samples within 6 km of the outfall.

The redox potential (Eh) of sediment samples was measured at a depth of 1.5 cm at most stations (table 1). Considerable variation was observed with values ranging from +0.050 to +0.275 V.with a mean of +0.102V. and a standard deviation of 0.042. There was no apparent pattern to the results or correlation with other factors. Redox potentials below +0.200 V. indicate a reducing environment at most of the sample locations.

The hydrogen ion concentration (pH) was measured similarly at a depth of 1.5 cm in most samples. The pH ranged from 5.3 to 7.3 with a mean of 6.8 and a standard deviation of 0.28. Stations up to one kilometre east and south of the outfall had pH values less than 6.0 with the minimum (5.3) at station 22 (500 m south east of outfall). These observations would suggest that organic matter from the outfall is being decomposed on the bottom with the production of organic acids which are lowering the pH. It is noted that the organic content of the sediment at these locations was high and that wood fibers were observed.

The sediment temperature in the river mouth and in the south channel was between 8.0 and 9.0°C. It was about 6.0°C in the east channel. This suggested that a temperature stratification has not developed in the southern channel because of the influence of mixing or flushing by river water. Results from current meters (Polak 1975) showed that currents near the outfall generally travelled along the shore. In the east channel, between Hughes Pt. and Ile la Grange, the current was

somewhat stronger, mainly in the east-west direction with currents from the east more prevalent. This supports the assumption that most of the river water flowed down the south channel.

The concentration of all the major elements was fairly constant throughout the area with the exception of sulphur (table 2).

Most elements showed a reduction in concentration nearer the outfall.

This was presumably related to the increasing amount of organic matter which diluted the amount of inorganic material. Total sulphur (figure 3), which ranged from undetectable amounts in the south channel to 0.35% at station 22 (500 m S.E. of outfall), shows a direct correlation with proximity to the mill outfall. Organic carbon and mercury also increased towards the outfall.

Nine samples (#17 - 21) in the east channel compared with five samples (#17 - 21) in the east channel showed an average increase of 1.5, 0.8 and 0.6 percent in the occurrence of calcium magnesium and inorganic carbon. This enrichment of carbonate in the sediments of the south channel appears to be related to the river water which flows predominantly down the south channel. The core at station 20 in the east channel also shows substantially lower values for calcium (table 4) throughout its entire 50 cm length. This suggests that the carbonate enrichment in the south channel relative to the east channel has been a long-term relationship.

The organic carbon (figure 4) had an average background level of 1.5 - 2.0% in the river mouth and both channels. It increased with proximity to the outfall, until a value of 31% organic carbon was

obtained 500 m east of the outfall.

The trace elements copper, nickel and lead (table 3) were fairly constant across the area ranging from 29 - 41, 6 - 69 and 11 - 42 ppm, respectively. The trace element concentration were closely proportional to the clay content. Chromium ranged from 11 - 132 ppm, with greater variation than the others (table 3). Mercury ranged from 30 - 420 ppb. Mercury values averaged 50 ppb in the river mouth, 130 ppb in the east channel and 110 ppb in the south channel. The highest values were found off the mill outfall (350 ppb). The core, one kilometre east of the outfall, had 360 ppb of mercury in the top five centimetres. The rest of the core (5 - 55 cm) averaged at or near background level with 80 ppb.

X.R.F. analyses for major elements were also conducted on 56 subsamples from the eight cores (table 4). In core 12, with a high amount of organic material at the top, most elements had a lower percentage of occurrence. The exceptions were Mn and P which were slightly higher, and S which was substantially higher (0.275%). The whole of core 20 in the east channel showed a reduction in calcium by approximately 2% and an increase in clay forming and associated elements (Al, K, Ti, Mn, Fe). The glacial material in core 35 had an increase in calcium (2-3%) and a decrease in silicon (6%). In cores 3, 12, 13, 20 and 31, total sulphur was detectable only in the top one or two subsamples. This was probably related to the occurrence of organic material at the top of these cores. However, in cores 24, 35 and 41, total

sulphur levels ranged from 0.05 to 0.06% throughout the entire core and may indicate the presence of sulphide compounds rather than organic sulphur.

MATHEMATICAL INTERPRETATION

A statistical evaluation of the results was carried out using linear correlation coefficient matrices and r-mode factor analysis (Cameron 1967). Since this procedure requires a normal distribution of results, stations 12 and 22, with the anomalously high organic values, were left out and the data did not require log transformation. Table 5 is a correlation matrix using 43 samples for the geochemical data, 38 samples for size data, and 17 samples for mercury data. The critical value of coefficient of correlation, 'r', for a 95% confidence level for these numbers of samples is 0.304, 0.325 and 0.482 respectively (Freund 1970).

Examination of table 5 shows a good correlation between organic carbon and sulphur. The frequently reported relationship of organic carbon with clay size fraction and trace elements (Thomas 1972, 1973, Thomas et al 1972, 1973) does not exist. This is presumably due to the influence of organic fibers. There is a strong relationship between organic carbon, sulphur and mercury. Most of the sulphur is presumably organic sulphur and not as sulphides as the Fe/S relationship is poor. Two of the adsorption processes by which mercury may be bound in a sediment as given by Jonasson (1970), may explain the

association of mercury with organic carbon and sulphur. They are:

- (1) irreversible adsorption of mercury by sulphide surfaces
- (2) covalently bonded sulfo-organometallic compounds

There is a strong correlation between calcium and inorganic carbon (r=0.840) and between calcium and percent silt size material (r=0.641). This agrees with the report by Thomas et al (1972, 1973) that calcium is held predominantly in the form of calcium carbonate in the silt size fraction; in addition, there are reports of calcium carbonate in glacial sediments of the area (Zoltai 1965).

the following two interpretations of table 5 are based on a summary of major element relationships in Great Lake sediments by Sly and Thomas (1974). (1) The strong Fe/Ti correlation (r=0.908) indicates the presence of ilmenite and/or rutile, while the Al/Fe correlation (r=0.910) suggests that these iron compounds are probably bound to the clay minerals. (2) The correlation of K/%clay size (r=0.918) and K/Al (r=0.944) suggest the predominance of illite clay minerals and only a minor amount of chlorite (Mg/Al, r=0.344). The strong Al/Fe correlation does agree with results of Williams et al (1971) and Vernet and Thomas (1972) who suggest that iron is predominantly in the form of hydrated iron oxide occurring as coatings on individual clay particles.

The trace elements Cr and Ni are strongly related (r=0.828), and have secondary relationship to elements associated with clay minerals (Fe, Ti, Al, K, Mn). Pb correlates strongly with K and

Al and suggests an association with illite; while Cu correlates with K, Al (illite) and organic material. The Si/Na correlation suggests the presence of detrital quartz and alkali feldspar.

The core subsamples and associated surface samples, excluding the top of core #12, were also analysed and showed similar correlations. (1) Al/K correlation (r=0.925), suggesting illite clay minerals,

- (2) Fe/Ti correlation (r=0.944), suggesting presence of ilmenite or rutile,
- (3) high correlation of Fe and Mn to Al, K, and Ti, suggesting hydrated oxides bonded to illite clay particles.

CONCLUSIONS

From the analyses in this report, it may be seen that the effects of mill discharge, on the sediments in the Bay, are related to a decrease in sediment pH, and an increase in both temperature and organic material. The organic material appears to have retained a higher than average concentration of sulphur and mercury. Figures 3 and 4 for sulphur and organic carbon concentrations, show the area where mill effluent significantly effects these bottom sediment characteristics. Beyond this area there are samples which show minor anomalies but which cannot be said to depart markedly from background values.

The average concentrations of the trace elements (Cr, Cu, Ni)

are slightly less than reported by Mothersill (1972) for sediments of northern Lake Superior and are closer to those results reported for Lake Michigan by Shimp et al (1971). The normal results for most major elements reflect the presence of illite clay and detrital quartz and feldspar within the survey area. Carbonates show a preferential relationship with the silt size fraction and with the south channel.

As a result of this survey, the effect of pulp mill effluent upon bottom sediment characteristics appears to be rather localized. However, other studies on mill related organic compounds, which are to be reported elsewhere, may show a greater zone of influence of mill effluent as well as a greater effect on the water quality and the aquatic community.

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35.2	31.2	35.9	45.7	38. 3	46.9	43.8	42.8	46.3	45.9	57.1	58.3	52.7	9.44	65.3	4-8 8	ZIIIS %
64.8	68.8	64.1	5 1 .3	60.7	52.3	56.2	57.2	53.7	53.4	12.9	41.7	7.91	55.4	34.7	v 80	% CLAY
8.3	8.59	8.36	7.90	8.17	7.65	7.92	8.13	7.92	7.74	7.39	7.29	7.30	7.95	6.88	ю	MEAN
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Table 2: Major Element Results for Grab Samples

St'n	SiO ₂	A1 ₂ 0 ₃	MgO	CaO	Na ₂ O	к ₂ 0	TiO ₂	P ₂ 0 ₅	MnO	S	Fe ₂ 03
1	62.9	8.39	5.31	8.03	2.74	1.93	0.51	0.22	0.08	.028	4.03
2	63.5	9.24	5.05	6.24	2.85	2.17	0.57	0.21	0.14	.027	4.51
3	62.8	9.10	5.17	6.75	2.74	2.16	0.56	0.21	0.10	.023	4.53
Ĭ,	62.8	8.85	5.05	7.26	2.88	2.07	0.55	0.22	0.12	.025	4.24
5	62.8	8,98	5.02	7.18	2.91	2.11	0.56	0.21	0.13	.023	4.39
6	62.4	9.44	5.49		2.78	2.25	0.58	0.22	0.12	.028	4.76
7	62.0	10.30	5.37	5.23	2.95	2.46	0.65	0.20	0.13	.041	5.47
8	53.0	8.06	4.48	5.66	2.09	1.90	0.55	0.21	0.09	.110	4.21
9	61.4	9.67	5.42	5.52	2.82	2.35	0.62	0.22	0.12	.046	5.42
10	61.9	10.12	5.45	5.42	3.08	2.42	0.64	0.19	0.14	.035	5.38
11	62.0	10.36	5.41	4.97	2.82	2.42	0.69	5.2.0	0.14	.041	5.64
12	FÓ 0	0.00	-	606	2.62		- 0		- 0 00	- 056). En
13 14	59.9 61.4	9.00 9.74	5.10 5.66	6.06	2.63	2.12	0.57	0.20	0.08	.056	4.51
15	61.8	10.07	5.49	5.79 5.56	2.87 3.00	2.31 2.41	0.62 0.64	0.20 0.19	0.10 0.13	.024 .018	5.15 5.30
16	61.5	10.20	5.32	5.23	2.91	2.36	0.67	0.19	0.13	.012	5.41
17	62.8	10.56	4.92	4.09	2.83	2.51	0.70	0.19	0.13	.012	5.80
18	62.2	10.56	4.85	4.06	2.73	2.51	0.72	0.19	0.16	.029	5.91
19	62.2	10.85	4.92	3.85	2.78	2.64	0.72	0.18	0.17	.034	6.10
20	61.0	10.46	5.27	4.62	2.81	2.56		0.19	0.14	.031	5.77
21	60.3	10.17	5.12	4.64	2.69	2.49	0.69	0.19	0.17	.040	5.69
22	25.1	4.17	1.72	2.51	0.61	1.25	0.37	0.17	0.16	.352	3.44
23	53.2	7.76	4.50	5.26	2.01	1.97	0.55	0.20	0.08	.157	4.38
24	60.5	9.01	4.99	6.08	2.58	2.00	0.61	0.21	0.08	.053	4.62
. 25	60.7	9.10	5.49	6.47	2.72	2.05	0.61	0.22	0.08	049	4.66
26	55.1	8.13	4.71	5.47	2.15	1.85	0.59	0.21	0.08	.118	4.51
27	55.6	8.32	4.80	6.78	2.33	1.63	0.68	0.22	0.09	.049	4.91
28	59.8	8.83	5.03	6.22	2.55	1.90	0.62	0.21	0.08	.060	4.70
29	61.3	9.49	5.64	6.12	2.83	2.14	0.62	0.21	0.09	.035	4.92
30	61.7	10.02	5.69	5.45	2.91	2.41	0.64	0.20	0.13	.028	5.49
31	60.1	8.66	6.40	6.13	2.51	2.04	0.61	0.21	0.09	.056	4.75
32.	61.4	9.89	5.76	5 - 59	2.89	2.37	0.63	0.21	0.13	.037	5.40
33	61.2	10.08	5.44	4.98	2.76	2.34	0.67	0.19	0.15	.034	5.48
34	59.4	8.97	6.36	7.44	2.73	2.04	0.62	0.32	0.12	.035	5.05
35	61.1	9.37	5.71	6.61	2.78	2.14	0.61	0.29	0.08	.048	4.74
36	61.2	10.02	5.80	5.77	2.81	2.31	0.66	0.26	0.13	.023	5.43
37 38	60.7 61.0	9.77	5.85	6.26	2.90	2.30	0.62	0.29	0.12	.029	5.28
39	61.0	9.89	5.65 5.67	5.56 5.42	2.88	2.35	0.62	0.26	0.12	.003	5.45
کو 40	60.6	10.06 10.07	5.64	5.50	2.95 2.82	2.37	0.66	0.25	0.15	.001	5.57
41	60.8	10.07	5.84	5.66	2.92	2.32	0.66	0.26	0.14	.021	5.56
42	60.7	9.90	5.74	6.18	3.01	2.39 2.32	0.65 0.64	0.25 0.27	0.13 0.14	.002 .001	5.62 5.37
43	60.5	10.06	5.95	5.99	3.04	2.43	0.64	0.26	0.10	.018	5.49
44	60.2	10.08	5.85	5.64	2.95	2.44	0.64	0.25	0.10	.001	5.56
45	60.6	10.25	6.00	5.71	2.96	2.47	0.64	0.26	0.10	.001	5.60
		/	2.0)- <u> </u> -	,		3.0.	J. L. O	3.10	•004	<i>)</i> .00
Mean	59.9	9.46	5.32	5.72	2.72	2.23	0.62	0.22	0.12	. 04	5.10
Standard			. .								•
Deviation	5.8	1.11	0.71	1.00	0.40	0.27	0.06	0.03	0.03	.06	0.58

Table 3: Trace Element Results for Grab Samples

Station Number	Cr ppm	Cu ppm	Ni ppm	Pb ppm	Hg ppb	% Organic Carbon	% Inorganic Carbon
1 2 3 4 5 6 7 8 9 10 11 12	84.5 51.8 20.7 21.0 23.9 34.2 40.4 13.7 35.3 45.6 43.0	29.3 28.8 31.5 28.8 31.0 34.3 35.8 40.8 37.6 37.8	44.7 29.6 26.7 27.3 31.1 28.5 36.0 19.9 35.6 42.3 37.1	24.2 25.2 27.8 25.5 26.5 32.0 35.1 27.1 36.8 30.9	30 70 60 40 40 60 140 300 160 90	1.94 1.87 1.81 1.92 1.95 1.75 1.63 9.77 2.37 1.62 1.35	1.72 1.31 1.59 1.36 1.29 1.55 1.07 1.53 1.20 1.18 0.98
13 14 15 16 17 18 19 20 20 20 20 20 20 20 20 20 20 20 20 20	25.2 37.8 30.0 55.3 76.5 11.2 51.2 61.6 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.3 47.0 57.0 57.0 57.0 57.0 57.0 57.0 57.0 5	36.7 39.4 36.1 37.8 36.1 40.8 5.7 30.8 40.3 47.3 35.8 37.5 40.4 34.7 35.8 37.5 37.5 38.3 37.5 38.3 37.3 38.3 38.3 38.3 38.3 38.3 38.3	212.338.47.4485.7865.636.947.73049.116975.274 223.847.4485.7865.636.947.73049.116975.274 2233845.7558.7558.7555.665.7558.7555.7558.7555.7555	24.5 32.5 34.4 30.7 34.2 24.5 35.5 24.5 24.6 24.6 24.6 24.6 25.6 26.8 32.6 32.6 32.6 32.6 32.6 32.6 32.6 32.6	420 90 140 80 130 100 140 210 80 330 180 110 150 190 80 110 150 70 80 70 150 90 80 110 150 90 80 80 80 80 80 80 80 80 80 8	5.04 2.42 1.54 1.49 1.44 1.36 1.30 1.17 31.2 12.25 3.49 3.43 9.46 3.23 3.86 2.83 1.58 3.54 1.96 1.12 1.78 2.08 1.17 2.66 1.12 1.78 2.08 1.55 1.18 1.67 1.24 1.25 1.30 1.27	1.33 1.35 1.28 1.00 0.65 0.62 0.66 0.93 0.88 1.32 1.38 1.10 1.32 1.22 1.34 1.23 0.86 1.65 1.45 1.67 1.47 1.19 1.05 1.47 1.19 1.05 1.47 1.42 1.43 1.31 1.34
Mean	55.2	36.2	42.2	29.5	125:	3,22	1.24
Standard Deviation	25.7	4.2	13.8	6.5	77.	4.92	0.26

Table μ : Major Element Results of core subsamples and associated grab samples

								_			_	-
St	** cm.	sio ₂	803	MgO	CaO	Na ₂ 0	к ₂ 0	TiO ₂	P205	MnO	S	Fe ₂ 03
	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	62.8 62.3 62.1 62.1 62.2 62.2 62.3 62.0	9.10 9.22 9.34 9.59 9.93 10.05 10.17 9.93	5.17 5.53 5.42 5.44 5.34 5.30 5.23 5.35	6.75 6.45 6.36 5.95 5.53 5.41 5.35 5.73	2.74 2.80 2.85 2.83 2.79 2.90 2.85 2.95	2.16 2.21 2.22 2.30 2.39 2.38 2.42 2.40	0.56 0.58 0.59 0.62 0.62 0.63 0.61	0.21 0.20 0.19 0.20 0.18 0.18 0.25	0.10 0.11 0.10 0.10 0.10 0.09 0.09	.023 * * * * * *	4.53 4.56 4.55 4.77 5.05 5.00 5.04
12	0-5 5-10 10-15 15-20 20-25 25-30 30-40 40-50	30.0 25.7 23.5 47.8 60.7 62.3 61.7	4.74 4.24 3.88 6.87 9.62 10.27 10.22	2.21 1.62 1.94 4.08 5.41 5.36 5.41 5.56	3.51 2.70 3.81 6.34 5.89 5.23 5.52 5.63	0.78 0.60 0.68 1.80 2.84 2.92 2.93 2.94	1.42 1.34 1.25 1.79 2.27 2.41 2.42 2.44	0.42 0.40 0.36 0.50 0.63 0.65 0.65	0.24 0.21 0.25 0.31 0.25 0.24 0.24	0.14 0.16 0.16 0.10 0.09 0.09 0.09	.274 .275 .264 .165 .026 *	3.59 3.53 3.36 4.11 5.08 5.24 5.14 5.19
13	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	59.9 59.6 61.3 61.6 61.4 61.5 60.9	9.00 9.11 10.01 10.29 10.04 10.31 10.36	5.10 5.27 5.67 5.78 5.66 5.77 6.07	6.06 6.37 5.72 5.48 5.49 5.59 5.59	2.63 2.69 2.81 2.92 2.81 2.90 2.97 2.96	2.12 2.13 2.38 2.43 2.40 2.43 2.47 2.47	0.57 0.58 0.64 0.67 0.66 0.66 0.65	0.20 0.20 0.19 0.19 0.19 0.19 0.19	0.08 0.09 0.10 0.10 0.11 0.10	.056 .048 * * * *	4.51 4.61 5.30 5.44 5.32 5.31 5.33 5.28
20	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	61.0 61.7 61.5 62.3 62.1 61.8 61.6	10.46 10.91 10.90 10.98 10.99 10.93 10.82	5.27 4.97 5.21 5.12 5.24 5.27 5.43 5.36	4.62 4.16 4.18 3.94 3.86 4.00 4.23 4.15	2.81 2.82 2.81 2.93 2.90 2.79 2.89	2.56 2.62 2.62 2.66 2.71 2.68 2.65 2.66	0.70 0.71 0.72 0.72 0.73 0.73 0.73	0.19 0.18 0.18 0.17 0.17 0.17 0.17	0.14 0.14 0.13 0.12 0.12 0.12 0.12	.031 .009 * * *	5.77 5.97 5.94 5.98 6.00 5.95 5.94 5.93
24	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	60.5 61.3 61.2 60.4 64.3 60.5 60.9 61.5	9.01 9.29 9.64 9.96 10.10 9.83 10.20	4.99 5.51 5.56 5.74 4.84 5.66 5.91 5.86	6.08 6.66 6.37 5.93 5.15 6.34 5.56 5.46	2.58 2.85 2.92 2.98 2.95 2.84 3.00 2.95	2.00 2.06 2.25 2.37 2.16 2.32 2.45 2.46	0.61 0.60 0.59 0.61 0.60 0.61 0.65	0.21 0.20 0.20 0.19 0.16 0.18 0.19	0.08 0.08 0.09 0.10 0.09 0.10 0.10	.053 .080 .067 .052 .044 .049	4.62 4.61 4.80 5.20 4.76 5.08 5.45 5.39
31	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	60.1 61.5 60.5 61.0 61.1 61.0 61.2	8.66 9.56 9.72 9.78 10.01 10.07 10.00	6.40 5.57 5.78 5.82 5.90 6.06 6.09 5.99	6.13 6.69 6.92 6.87 5.99 6.22 6.08 6.32	2.51 2.96 3.09 3.10 2.86 3.01 2.95 2.88	2.04 2.21 2.29 2.25 2.32 2.32 2.32 2.32	0.61 0.58 0.60 0.62 0.65 0.65 0.66	0.21 0.19 0.20 0.19 0.19 0.19 0.20	0.09 0.08 0.09 0.10 0.10 0.10 0.10	.056 .017 .005 *. .001 *	4.75 4.68 5.00 5.09 5.39 5.34 5.33 5.33

Table 4 continued

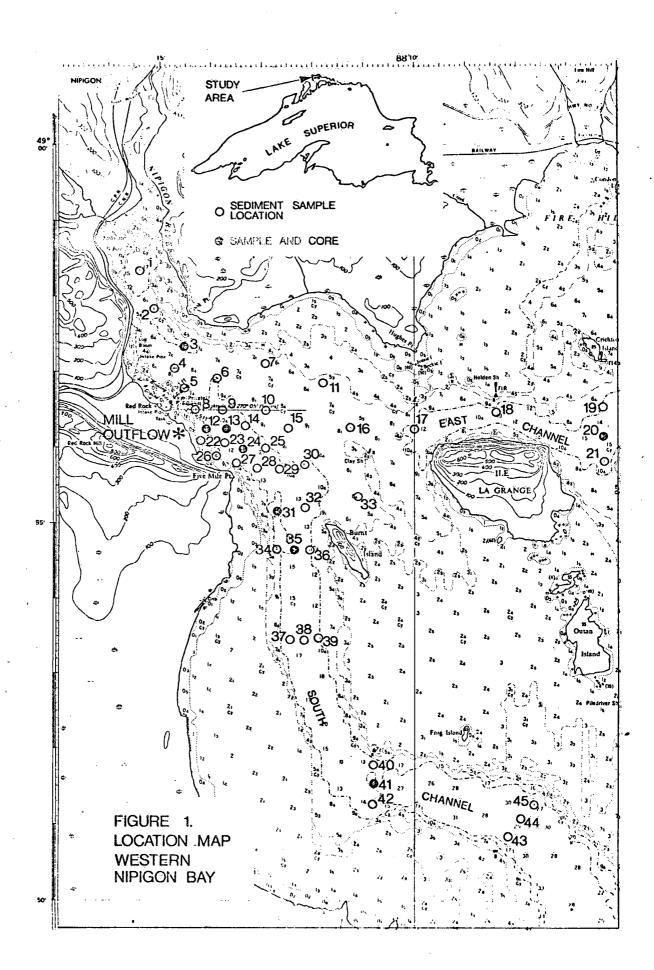
St 1	n em.	sio ₂	A1 ₂ 0 ₃	MgO	CaO ₁	Na ₂ 0	_K 20	TiO ₂	P ₂ O ₅	MnO	S	Fe ₂ O ₃
35	0-1 0-5 5-10 10-15 15-20 20-30 30-40 40-50	61.1 63.2 56.3 56.9 55.3 55.3 54.8	9.37 9.30 9.79 10.21 10.20 9.87 9.66 9.84	5.71 5.08 6.03 6.22 6.02 5.93 5.97 5.89	6.61 5.20 7.92 7.83 7.40 8.35 8.84 8.92	2.78 2.57 3.00 2.98 2.99 2.94 2.92 3.00	2.14 1.99 2.26 2.41 2.43 2.40 2.31 2.34	0.61 0.71 0.69 0.69 0.69 0.68 0.66	0.29 0.17 0.21 0.21 0.20 0.21 0.21	0.08 0.09 0.12 0.11 0.11 0.10 0.11	.048 .069 .060 .060 .054 .057 .066	4.74 5.32 5.51 5.66 5.68 5.48 5.32 5.34
41	0-1 0-5 5-10 10-15 15-20 20-30 30-40- 40-50	60.8 60.5 60.8 60.9 60.6 59.7 59.8 59.7	10.07 9.99 10.13 10.21 10.30 10.09 10.01 10.00	5.84 5.99 6.16 6.16 5.96 6.24 6.25 6.41	5.66 5.95 5.94 5.90 6.11 6.46 6.61 6.72	2.92 2.92 2.90 2.93 2.87 2.92 2.90 2.87	2.39 2.36 2.35 2.28 2.31 2.30 2.27 2.29	0.65 0.65 0.67 0.68 0.68 0.68 0.66	0.25 0.19 0.18 0.18 0.19 0.19 0.19	0.08 0.09 0.12 0.11 0.11 0.11 0.10	.002 .060 .050 .043 .046 .047 .046	5.62 5.37 5.50 5.43 5.34 5.36 5.26 5.32

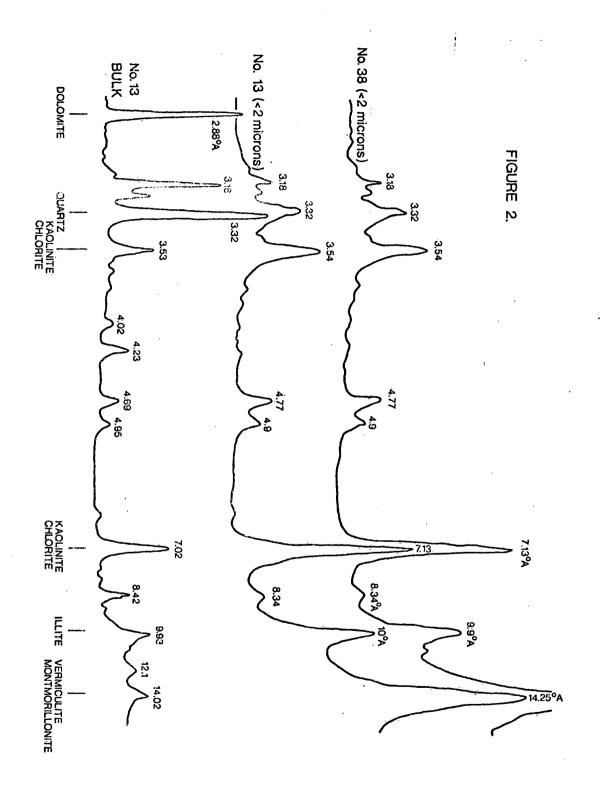
^{*} undetectable amount

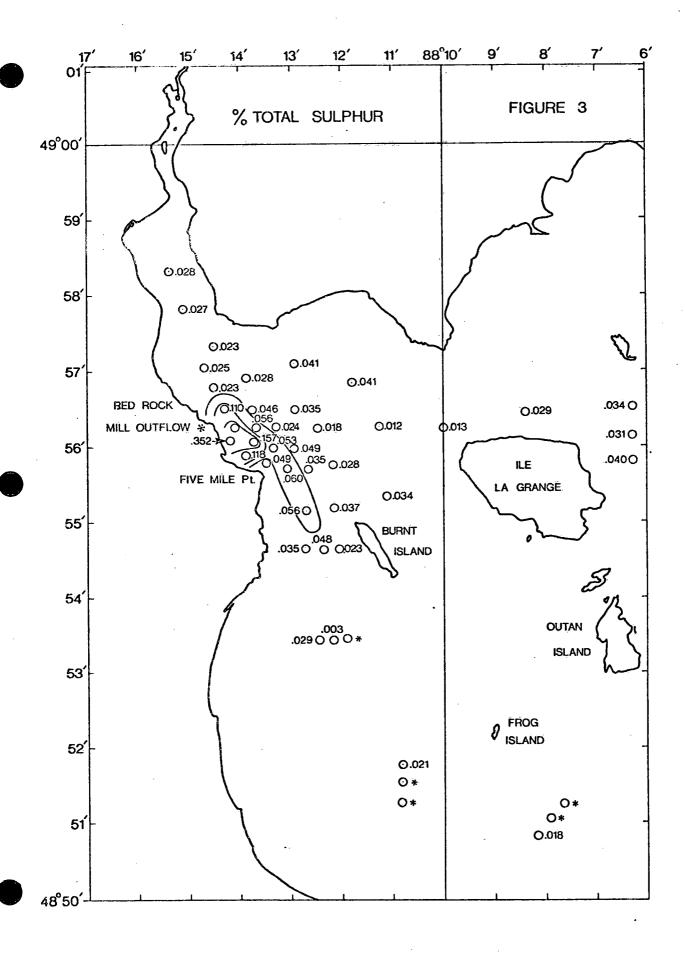
^{** 0-1} results from grab sample at this station 0-5 cm. first core subsample

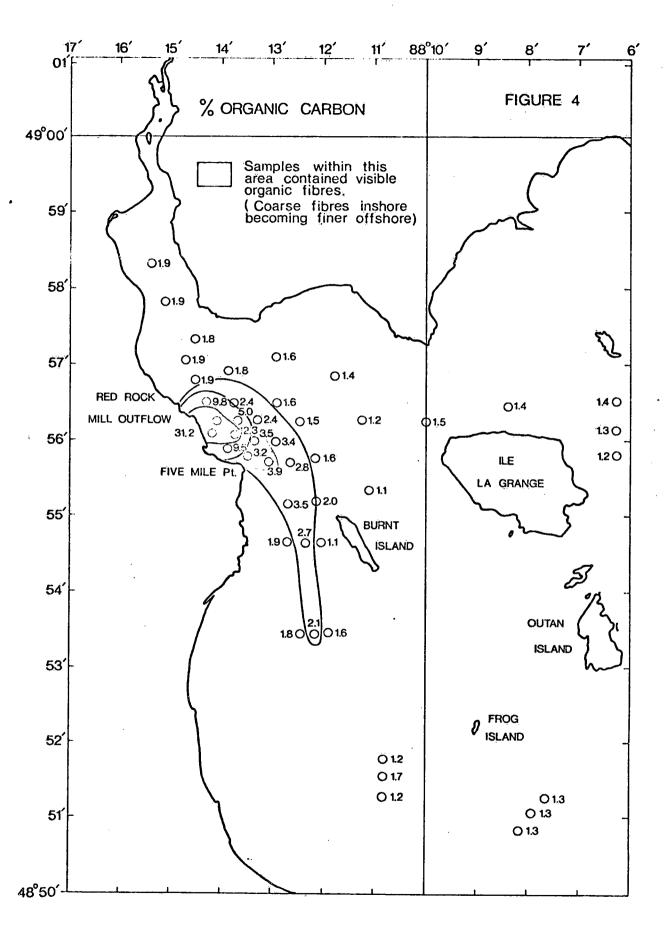
Table 5 : Correlation Matrix of 43 sediment samples from Western Nipigon Bay

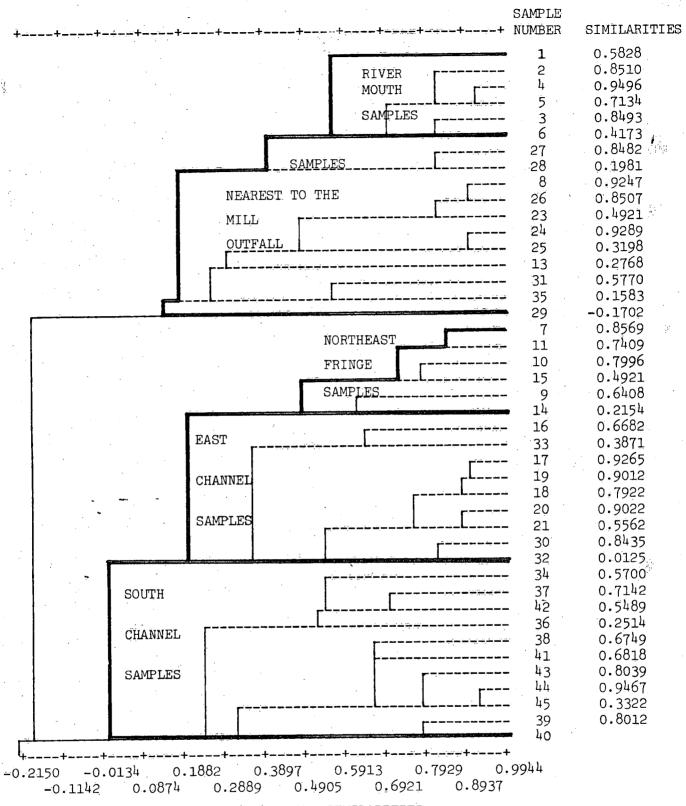
1.000 .611 .350 .020 .834 .553 .185058 .434769 .305 .161315 .321 .430847225188 .611 1.000 .344632 .754 .944 .782035 .724691 .910 .452 .230 .698 .823747601871 .350 .344 1.000 .224 .583 .306 .140 .627 .021554 .324 .151 .023 .458 .227532 .290 .326 .200 .696 .803747601871 .350 .344 1.000 .224 .583 .306 .140 .627 .021554 .324 .151 .023 .458 .227532 .290 .326 .200 .696 .315 .214 .472888 .521 .192157 .518 .561 .879133 .708 .484 .754 .583025 1.000 .696 .315 .214 .472888 .521 .192157 .518 .561 .879133 .708 .553 .944 .306669 .696 .000 .641079 .719571 .852 .440 .424 .660 .926 .608573914 .185 .782 .140742 .315 .641 1.000115 .631368 .908 .520 .216 .625 .525484701 .508 .000 .494 .701 .508 .908 .500 .216 .625 .525 .484 .701 .500 .494 .701 .508 .908 .500 .216 .625 .525 .484 .701 .500 .495 .608 .571 .948 .724 .021 .558 .472 .719 .631146 1.000439 .699 .383 .092 .530 .646 .547 .603 .485 .711 .083 .496 .711 .287 .309 .546 .429 .921 .106 .485 .709 .709 .709 .701 .708 .701 .708 .701 .701 .708 .701 .701 .701 .701 .701 .701 .701 .701	Clay	IC	8 9	TH CH CT	9 B C	? <u>F</u>	P. H	X Ne	a 2	¥ A	ş
1. 350 . 020 . 834 . 553 . 185058434769 . 305 . 161315 . 321430847225182344632754944782035724691910452230698823747601871400224583 . 306140627021554324151023458227532290326224 1.000025669742448558028741408608404672033840641583025 1.000696315214472888521192157518561879133708404742315641 1.000115631368921924660926608573914406669669712115 1.000115631368908520216625626404701508627448214079115 1.000146277022056055176136164517083627448214079115 1.000146277022056055176136164517083627448511568771439 1.000511257 . 309546429921 . 1.06485551028988571368277439 1.000521257309546429921 . 1.0648522400022423523533146629722757256192652513646424992105625725025825824420520625220525725025425335931977657625025425325125225625	.213 566			315 321	305	.434					1.000
0.020 .834 .553 .185 .058 .434 .769 .305 .161 -315 .321 .430847 -225182632 .754 .944 .782035 .724691 .910 .452 .230 .698 .823747601 .871 .224 .583 .306 .140 .627 .021554 .324 .151 .023 .458 .227532 .290 .326 .1000025669742 .448556028741408608404672 .033 .840 .641 .025 1.000 .696 .315 .214 .472888 .521 .192157 .518 .561879133708 .469 .696 .1000 .641079 .719571 .852 .440 .424 .660 .926608573914 .742 .315 .472 .315 .471 .000146277 .022056055 .176136164 .577083 .558 .472 .719 .631146 .000 .413 .277 .022056055 .176136164 .517083 .558 .127 .393 .840 .641 .571 .308 .277 .399 .546 .429 .921 .106 .485 .297 .560 .122 .440 .520 .226 .525 .484 .701 .598 .227 .503 .469 .573 .914 .521 .521 .522 .908 .022 .699 .511 .000 .511 .257 .399 .546 .429 .921 .106 .485 .297 .560 .127 .424 .216 .055 .327 .327 .000 .527 .334 .738 .755 .569629795 .406 .127 .528 .389 .571 .328 .329 .334 .335 .441 .708 .525 .136 .646 .429 .755 .360 .527 .331 .466 .297 .560 .124 .510 .625 .525 .136 .646 .429 .755 .360 .523 .359 .319 .776 .576 .383 .879 .608 .484 .717 .511 .603 .106 .629 .755 .360 .523 .546 .1000 .546 .582 .399 .577 .569 .629 .776 .526 .333 .879 .608 .484 .710 .503 .486 .429 .755 .360 .523 .546 .1000 .546 .582 .399 .577 .569 .629 .776 .560 .523 .776 .508 .484 .710 .503 .486 .297 .776 .526 .529 .781 .500 .388 .571 .708 .584 .708 .708 .708 .708 .708 .708 .708 .708				. 452 . 230 . 698			.782	.75 ¹			A1 .611
182		. 326		.023 .023	. 324	.021	.140	.583 .306			.350
1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	. 130	- 119. - 018.	. 672 . 033 -				- 7 ¹ 2	025 669		632	Ca .020
3 .185 - 0.58 . h 3h769 . 305 . 1.61315 . 321 . h 308h 7225182 4 .782 - 0.35 . 724691 . 910 . h 52 . 230 . 698 . 8237h 76018h 7 5 .1h 0 .627 . 0.2155h . 32h . 1.51 . 0.23 . h 58 . 227532 . 290326 97h 2 . h 18558 - 0.287h 1h 08608h 0h672 . 0.338h 06h 1 5 .315 . 21h . h 72888 . 521 . 192157 . 518561879133708 9 .6h 1079719571852 . h h 0 . h 2h66092660857391h 1 .1000115 . 631368 . 908 . 520216625525h 8h701508 9115 . 1000h 6277 . 0.2205605517613616h517083 9 . 631h 6 1.000h 39 . 699383 . 0.925306h 65h 7603h 69 9368277h 39 1.000511257 . 3095h 6h 29921 . 106h 85 9 .008 . 0.22699511 1.000527354738755569629795256055176331h 6629721605502230935h2h 60002h 6582399567525136h 1531h 66297256125569629795256125569331h 66297256328359331h 66297256258341 1 .000205588368300311531862258305331h 66297256063459569529561000h 1531862288300311531862288300331862288300331862288300331368388000385998300385998300385998300388000300				.192 157 .518						.754	Na.
Fe Cr Cu Ni Pb Oc Ic Silt Size058 . h3h769 . 305 . 161315 . 321 . h308h7225182 2035 . 724691 . 910 . h52 . 230 . 698 . 8237h7601871				.424				1.000		.944	.553
### S Fe Cr Cn M1 Pb OC IC S11x 134769 .305 .161315 .321 .430847225182 .724691 .910 .452 .230 .698 .823747601871 .021554 .324 .151 .023 .458 .227532 .290326558028741408608404672 .033 .840 .641 .472888 .521 .192157 .518 .561879133708 .719571 .852 .440 .424 .660 .926608573914 .631368 .908 .520 .216 .625 .525484701508146277 .022056055 .176136164 .517083 1.000439 .699 .383 .092 .530 .646547603469439 1.000511257 .399546429 .921 .106 .485 .699511 1.000 .527 .354 .738 .755569629795 .383257 .527 1.000 .246 .828 .360331466297 .646429 .755 .360 .523 .546 1.000 .441 .531862 .547 .666399567 .646429 .755 .360 .523 .546 1.000 .441 .531862 .547 .663 .469 .469 .465429 .755 .360 .523 .546 1.000 .441 .531862 .588 .388 1.000 .467480 .779 .290 .787 .558 .867562385 .998 .275 .596153340 .384432140 .639 .042 MA			. 525 .		368 .908	.631	1.000	.641	.140 742		
### S Fe Cr Cn M1 Pb OC IC S11x 134769 .305 .161315 .321 .430847225182 .724691 .910 .452 .230 .698 .823747601871 .021554 .324 .151 .023 .458 .227532 .290326558028741408608404672 .033 .840 .641 .472888 .521 .192157 .518 .561879133708 .719571 .852 .440 .424 .660 .926608573914 .631368 .908 .520 .216 .625 .525484701508146277 .022056055 .176136164 .517083 1.000439 .699 .383 .092 .530 .646547603469439 1.000511257 .399546429 .921 .106 .485 .699511 1.000 .527 .354 .738 .755569629795 .383257 .527 1.000 .246 .828 .360331466297 .646429 .755 .360 .523 .546 1.000 .441 .531862 .547 .666399567 .646429 .755 .360 .523 .546 1.000 .441 .531862 .547 .663 .469 .469 .465429 .755 .360 .523 .546 1.000 .441 .531862 .588 .388 1.000 .467480 .779 .290 .787 .558 .867562385 .998 .275 .596153340 .384432140 .639 .042 MA				056 055	277	146	115	.214 079		035	P058
Fe Cr Cu Ni Pb OC IC Silt Size 9		469			439 . 699	1.000	.631	.472 .719			Mn 434
Fe Cr Cu M Pb OC IC Silter Size -305	- 1480 - 596 -		. 129	.309		439	368	888 571	554 028	691	s 769
Cu Ni Pb OC IC Silt Size 1315	.779							. 852	.324 741	.910	. 305
N1 Pb OC IC Silt Size 5 .321 .430847225182 0 .698 .823747601871 3 .458 .227532 .290326 8404672 .033 .840 .641 7 .518 .561879133708 4 .660 .926608573914 5 .625 .525484701508 .176136164 .517083 2 .530 .646547603469 546429 .921 .106 .485 .738 .755569629795 .828 .360331466297 .224 .523 .359319776 1.000 .546582399567 .546 1.000441531862 582441 1.000 .205 .588 399531 .205 1.000 .388 567862 .588 .388 1.000 .558 .867582385998			.331		257 .527			.192	.151 408	.452	.161
Pb OC IC Silt Size 1 .430847225182 8 .823747601871 8 .227532 .290326 4672 .033 .840 .641 8 .561879133708 0 .926608573914 5 .525484701508 6136164 .517083 0 .646547603469 5429 .921 .106 .485 8 .755569629795 1.000441531866 546582399567 1.000441531862 441 1.000 .205 .588 862 .588 .388 1.000 .867582385998 140 .639 .042 NA	.787		. 523 . 359		. 309 . 35 ⁴	.055	.216			.230	Cu 315
OC IC Silt Size 847225182 747601871 532290326 .033840641 879133708 608573914 484701508 164517083 547603469 .921106485 569629795 331466297 .359319776 582399567 441531862 1.000 .205 .588 .205 1.000 .388 .205 1.000 .388 .588 .388 1.000 582385998		4 O 10	. 285 ·	.828	546 .738	.530	.625	.518		.698	30 M
IC Silt Size225182601871290326840641133708573914701508517083603469106485629795466297319776319567399567531862205588 1.000388385998			. tht. - 000 .1 - 946	.360 ·	429 .755	136	.525	.561	.227	. 823	Pb
IC Silt Size225182601871290326840641133708573914701508517083603469106485629795466297319776319567399567531862205588 1.000388385998	. 582			331 · . 359 ·	.921	547	-,484	879	.033	747	1 OC
Silt Size 182 871 326 .641- 708 914 508 083 469 .485- .776 297 776 567 567 567 568 588	.385	. 388 . 388	- 399 - 531 - 205	319	.106	.517 603	701	133	. 840 . 290	601	10
	. 998 :	. 388 . . 300 .			.485	083 469	508	708	326	871	Silt
		582		.290 .787	480 779	.090 .467	.485	717.	.340	. 866	Clay
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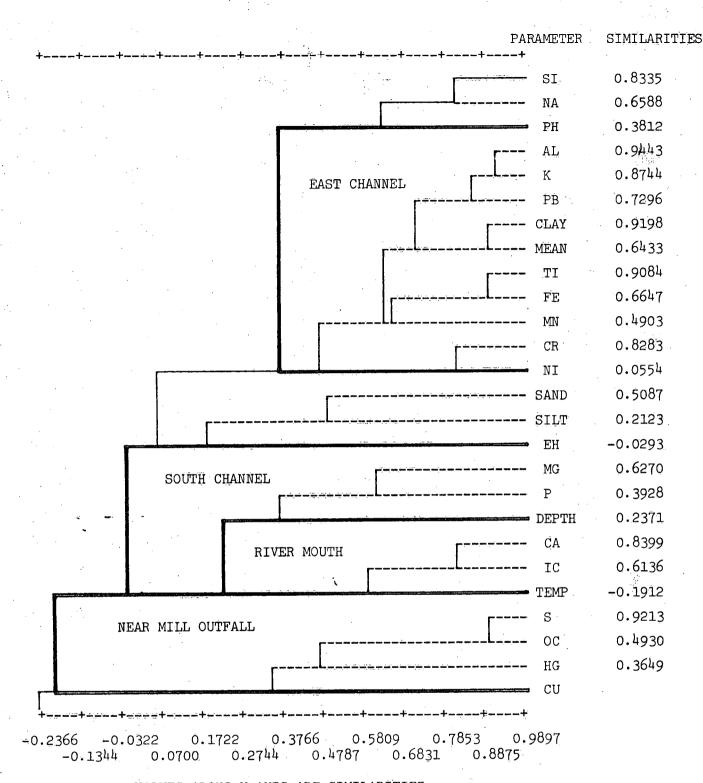








VALUES ALONG X-AXIS ARE SIMILARITIES



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France 2