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ABSTRACT

A study was carried out to determine the geochemistry of sediments in the Spanish River Area of Concern and its vicinity. Surficial sediments were collected at thirty-seven sampling stations in the study area to determine the distribution of major elements (Si, Al, Fe, Ca, Mg, K and Na) and trace elements (Co, Cu, Ni, Pb and Zn) in the sediments. Eight sediment cores were collected at selected sampling stations to determine background concentrations and concentration profiles of trace elements in the sediments. The sequential extraction procedure was carried out using sediments collected at three selected stations in the study area to determine associations of trace elements with different geochemical components in the sediments. Association of trace elements with different particle size of the sediments was determined to evaluate the potential for transport of the trace elements and for effects on benthic organisms through sediment digestion. Most of the collected sediments consisted of clay and silt particles (<63 um). The concentration ranges of major elements in sediments indicated a similar source of material deposited at the Area of Concern during past years. The concentrations of Ni and Cu ranged between 77 to 1,032 ug/g and 18 to 171 ug/g, respectively, in sediments in the Whalesback Channel, and between 45 to 865 ug/g and 16 to 201 ug/g, respectively, in the study area outside the Whalesback Channel. The results suggested there is transport of sediment-associated trace elements from the Spanish River Area of Concern into the

North Channel, Lake Huron. Concentration profiles of trace elements indicated increased inputs of Ni, Cu, Pb and Zn into the Area of Concern during the 1930's followed by a decrease of the inputs around the 1970's. These inputs most likely reflect mining and smelting of Ni and Cu ores in the Spanish River drainage basin. The results of the study indicated that 50 ug/g of Ni, 20 ug/g of Co, 40 ug/g of Cu, 10 ug/g of Pb and 100 to 120 ug/g of Zn can be considered the background concentrations in fine-grained sediments at the study area. Calculated sediment enrichment factors showed that surficial sediments at the study area are enriched to a greater extent by Cu, Pb and Ni than those in Lakes Huron, Erie and Ontario. Nickel was associated mainly with sediment particles <13 um in the Whalesback Channel. On the other hand, sediment particles >13 um contained greater concentrations of Cu (up to 1,959 ug/g) than the smaller particles. The results of the study suggested that changes in pH and redox potential in bottom sediments or at the sediment-water interface may increase the potential for toxity of Cu, Ni, Pb and Zn in the sediments. The results showed that the area containing sediments enriched by trace elements, particularly Ni and Cu, exceeds the area presently defined as the Spanish River Area of Concern.

INTRODUCTION

The lower Spanish River and its harbour area are among the forty-three Great Lakes Areas of Concern (AOC) designated by the U.S.-

Canada International Joint Commission for rehabilitation. There are collective efforts of the United States and Canadian federal governments, the eight Great Lakes States, the Province of Ontario, and local stakeholders to develop and implement remedial action plans (RAPs) to restore environmental quality in the Areas of Concern in the Great Lakes Basin Ecosystem (U.S. Environmental Protection Agency, 1994).

Deterioration of the ecosystem of the Spanish River AOC was described in detail in the Remedial Action Plan (Spanish River RAP Team, 1988). Increased concentrations of nutrients in the water, degradation of fish population, devoid of macroinvertebrates, and contamination of bottom sediments by Cu, Zn, Ni, Cr and PCBs were the major problems in the Spanish River AOC.

The Spanish River drains an area in size about 14,000 km^2 with the majority of the drainage basin located in the geographic District of Sudbury, Ontario. The river empties into the North Channel of Lake Huron (Figure 1). The upper part of the Spanish River drainage basin is underlain by Precambrian igneous rocks including the Sudbury Eruptive. The lower part of the drainage basin is underlain by sedimentary, volcanic and derived metamorphic rocks. Surficial deposits consist of a thin layer of undifferentiated silts, clays and sands with scattered swamps and bogs between bedrock ridges.

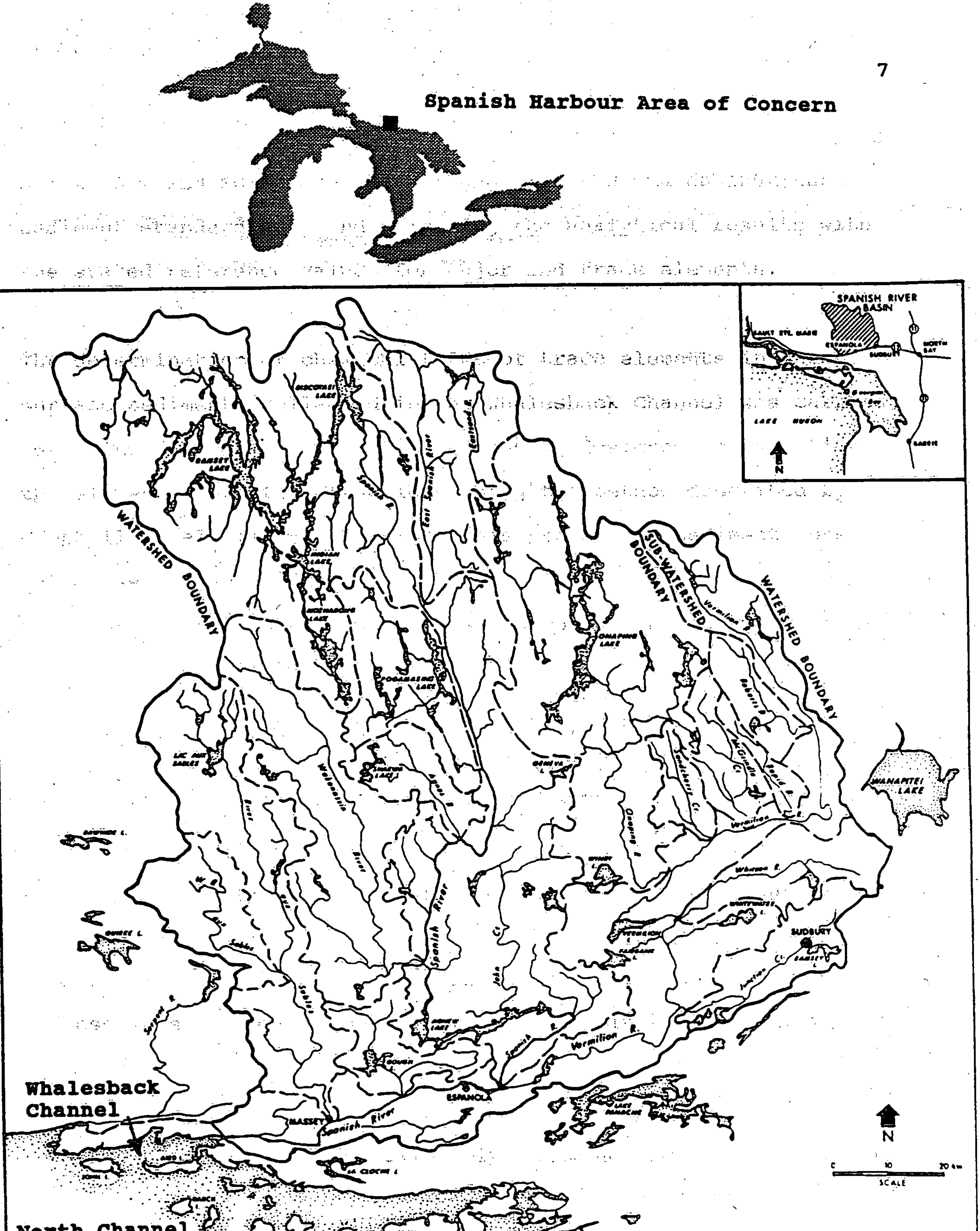

FIGURE 1. LOCATION AND WATERSHED OF THE SPANISH RIVER
(modified after Spanish River - Harbour Area, Remedial Action Plan, 1988)

Agriculture, industry, particularly metal mining and smelting and pulp and paper plant, forestry management and recreation are the major anthropogenic activities in the Spanish River drainage basin. The Vermilion River and Junction Creek, tributaries of the Spanish River, drain the metal mining and smelting/refining area in the Sudbury basin.

A multidisciplinary study was carried out from 1988 to 1991 to assess the quality of suspended and bottom sediments and the benthic community structure in the Spanish River AOC. The objective of the study was to provide information for planning the remedial action to rehabilitate the Spanish River AOC. This report describes the geochemical properties of the bottom sediments in the AOC and its vicinity. The results presented in the report have been used in the assessment of the effects of sediment quality on the benthic invertebrates community in the area. Further, the results will be used in the preparation of the summary report on the multidisciplinary study carried out between 1988 and 1991 in the Spanish River AOC and adjacent area in the North Channel of Lake Huron.

MATERIALS AND METHODS

Sediment sampling

Sediment samples were obtained at the Spanish River mouth and within the Whalesback Channel areas in 1988. At eighteen sampling stations, surficial sediments were collected by using a mini-

Ponar grab sampler. At an additional eight stations, a surficial 5 cm of sediments was collected by a modified Kajak-Brinkhurst corer equipped with a plastic liner. At four sampling stations, additional sediment cores were collected (two cores per station) for the separation of sediment pore water and determination of concentration profiles of major and trace elements in the sediments. The location of the 1988 sediment sampling stations is shown in Figure 2.

In 1990, a surficial 5 cm of sediments was collected at nineteen stations within the Whalesback Channel and at twenty-five stations outside the Whalesback Channel (Figure 2). In adition, surface sediments were collected using a mini-Ponar grab sampler in the vicinity of the 1988 grab sampling stations 8, 12 and 17 in the Whalesback Channel for the determination of chemical forms of trace elements in the sediments (Figure 2).

At four stations (603, 616, 638 and 644, Figure 2) cores were collected to investigate the background concentrations of the trace elements in sediments at the study area. Further, two surface sediment samples were collected in the western and southern parts of the Whalesback Channel by mini-Ponar grab sampler to investigate the association of the trace elements with sediment particles of different size.

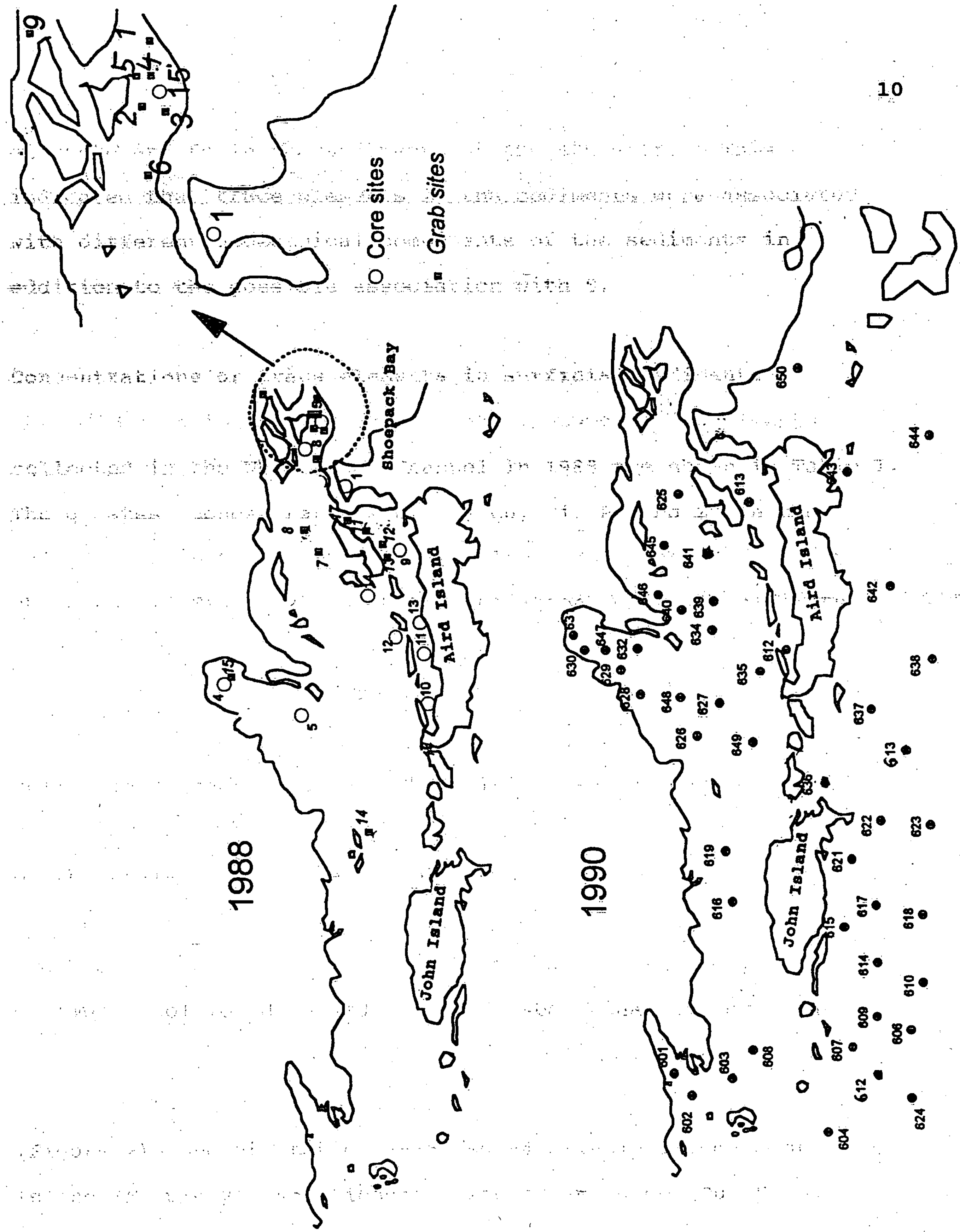

FIGURE 2. SAMPLING SITES - SPANISH RIVER STUDY AREA 1988, 1990

Sample storage and processing

With the exception of the three samples collected for the determination of chemical forms of trace elements in the Whalesback Channel, the surface sediment samples were manually homogenized in a plastic container using a plastic spoon, and divided into subsamples for the determination of particle size distribution and concentrations of major and trace elements. The subsamples for the determination of the particle size were collected into plastic bags and stored at 4°C prior to analysis. The subsamples for the determination of major and trace elements were collected into plastic jars prewashed by 5% HNO_3 and rinsed three times with distilled water, and freeze-dried prior to analysis. Sediment cores were subsampled in the field into 1-cm sections using a hydraulic extruder (Mudroch and MacKnight, 1994). Each section was collected in prewashed and rinsed plastic containers (washing method similar to that described above). All core sections were frozen and freeze-dried. Dried surface sediment samples and core sections were sieved using a 20-mesh screen to remove large objects, such as wood chips, etc. Sieved samples were homogenized by grinding using a mechanical grinder equipped with an agate grinding dish. The sediments collected at three sampling stations for the determination of chemical forms of the trace elements were stored in prewashed glass jars. The jars were filled completely to the top with the samples and tidily closed to avoid oxidation of the sediments, and stored at 4°C prior to analysis. Analysis of the samples was carried out within fourteen days of collection. Sediment cores collected at stations 3, 16, 38 and 44 were sectioned to obtain samples from the following depths: surface 1 cm, 9 cm and 15 cm. Two surface sediment samples collected in the western and southern parts of the Whalesback Channel were stored in plastic bags at 4°C. The samples were then separated into six different size fractions (<13 um, 13 to 20 um, 20 to 27 um, 27 to 35 um, 35 to 44 um and 44 to 53 um) using the Warman Cyclosizer following the method described by Mudroch and Duncan (1986). Each sediment size fraction was freeze-dried and manually homogenized prior to the determination of the concentrations of trace elements.

Analytical Methods

The concentrations of major elements (Si, Al, Fe, Mg, Ca, K and Na) and trace elements (Cu, Co, Cr, Ni, Pb, V and Zn) in sediment samples were determined by x-ray fluorescence spectrometry (Mudroch, 1985). The precision of the analysis was determined by analyzing five pellets made from a homogenized sediment sample. Relative deviations for major elements in sediment samples can be expected at the following levels: SiO_2 2%, K_2O and Al_2O_3 4%, Fe_2O_3 and CaO 2%, MgO and Na_2O 10%. Absolute deviations of 0.01% to 0.02% were found for MnO, TiO_2, and P_2O_5. Generally, the coefficient of variation for trace elements was less than 10% and continuously declining with increased trace element concentrations in the samples. The accuracy of the analyses was verified by running Canadian reference standards Syenite SY-2 and soils SO-2 and SO-4, and the National Water Research Institute sediment standard WQ1, and comparing the analytical results with the stated reference values for major and trace elements.

The determination of chemical forms of trace elements in three surface sediments collected in the Whalesback Channel was carried out using sequential extraction procedure designed to partition the elements into five fractions using the method described by Campbell *et al.* (1985). Prior to this procedure, sediment pore water was extracted from the sediments by a high-speed refrigerated centrifuge. The extraction of the pore water and the sequential extraction procedure were carried out under N_2-atmosphere to prevent oxidation of the sediments with subsequent changes of chemical forms of the investigated trace elements. The concentrations of trace elements in the extracts generated by the sequential extraction procedure were determined by graphite furnace atomic absorption spectrometry using internal standards. Particle size distribution was determined on wet sediment samples using the sedigraph method (Duncan and LaHaie, 1979). Data was expressed as percent of sand, silt and clay in the sample. The concentration of organic matter in the sediments was determined as loss on ignition (LOI) by heating dry sediment at 450°C to constant weight, i.e., approximately three hours.

RESULTS AND DISCUSSION

Particle size distribution and concentrations of major elements

With two exceptions, sediments collected at all sampling stations in 1988 and 1990 consisted of 90 to 95% of fine-grained (<63 um) particles. Therefore it was not necessary to standardize the concentrations of major and trace elements for particle size. The concentration ranges of major elements in surficial sediments and in sediment cores in the Whalesback Channel were as follows: 65 to 70% SiO_2; 10 to 11.7% Al_2O_3; 1.3 to 2.3% MgO; 1.7 to 2.2% CaO; 2.3 to 2.7% K_2O; and 3 to 3.4% Na_2O. Relatively narrow ranges of the concentrations of major elements in the sediments indicated a continuous input of geochemically similar material into the Whalesback Channel.

The concentration ranges of major elements outside the Whalesback Channel were as follows: 59 to 68% SiO_2; 11.2 to 13.5% Al_2O_3; 1.7 to 2.3% MgO; 1.7 to 7% CaO; 2.1 to 3% K_2O; and 1.5 to 2.3% Na_2O. The wider concentration ranges of the major elements, particularly CaO, in the sediments outside the Whalesback Channel indicated additional sources of material to those in the Whalesback Channel.

The greatest concentrations of organic matter in sediments (25.5%) were found at station 619 located between small islands, north of John Island, in the outlet from the Whalesback Channel (Figure 2). The concentrations of organic matter in sediments at the other three stations, i.e., 612, 613 and 616, in the outlet were 10.5, 9.3 and 11.7%. The range of concentrations of organic matter in the sediments was between 1.7 and 9.0% outside the Whalesback Channel and between 5.9 and 10.8% in the Channel. Generally, the concentrations were greater in the Whalesback Channel sediments than those outside the Channel. The concentrations of organic matter in sediments in the study area are typical for the Great Lakes sediments (Thomas and Mudroch, 1979). There was no relationship between the concentrations of organic matter and major and trace elements in the sediments in the study area.

The concentrations of S in sediments ranged between 0.14 and 0.30% in the Whalesback Channel, and between 0.11 and 0.50% in the sediments outside the Channel. The greatest concentrations of S (0.50%) were found in sediments at station 612 in the outlet from the Whalesback Channel. Further, the concentrations of S in sediments at station 638 (outside the Whalesback Channel, south of Aird Island, Figure 2) were 1.3% at the 9-cm and 16-cm sediment depths compared to 0.08% S in the 1-cm surface layer of the sediment. The sediments below the 5-cm depth are usually anoxic. Therefore it can be expected that the majority of S at the 9-cm and 16-cm depth will be present as sulfides. Generally, the distribution of S in the sediments at the study area varied from one station to the other showing no specific trends. There was no relationship between the concentrations of S and trace elements and Fe in the sediments at the study area. This indicated that trace elements in the sediments were associated with different geochemical components of the sediments in addition to the possible association with S.

Concentrations of trace elements in surficial sediments

The concentrations of trace elements in surficial sediments collected in the Whalesback Channel in 1988 are shown in Table 1. The greatest concentrations of Co, Cu, Ni, Pb and Zn in the sediments were found at station 14 located in the western part of the Channel (Figure 2). High concentrations of these elements also existed in the sediments collected at stations 10 to 13 (Table 1) in the vicinity of Aird Island in the southern part of the Whalesback Channel (Figure 2). Analysis of additional samples collected in the Whalesback Channel in 1990 indicated enrichment of surficial sediments by Ni, Cu, Pb and Zn over the major part of the Whalesback Channel (Table 2).

The greatest concentrations of Co, Cu, Ni, Pb and Zn in the sediments collected outside the Whalesback Channel were found at stations 612, 616 and 619 (Table 3) located near the main outlet from the Whalesback into the North Channel near John Island (Figure 2), and at stations 636 and 642 (Table 3) south of Aird Island (Figure 2). Relationship existed among Co, Cu, Fe, Ni, Pb and Zn concentrations in the sediments in the Whalesback Channel, indicating a similar source of the trace elements and Fe (Tables

TABLE 1

CONCENTRATIONS OF TRACE ELEMENTS IN SURFICIAL SEDIMENTS IN WHALESBACK CHANNEL, 1988
(in ug/g Co, Cu, Ni, Pb and Zn, in % Fe)

Stations	Co	Cu	Fe	Ni	Pb	Zn
			Ponar grabs:			
1	9	18	1.67	62	19	59
2	11	40	2.40	120	21	106
3	11	37	2.04	102	20	92
4	12	47	2.40	122	21	111
5	12	53	2.35	131	22	120
6	13	43	2.30	107	11	106
7	12	63	2.58	159	26	124
8	12	60	2.49	142	31	118
9	12	27	3.07	52	9	79
11	16	86	2.93	226	34	170
12	19	84	2.90	218	37	167
13	24	108	3.34	444	55	213
14	56	174	5.38	1032	104	339
15	32	141	6.42	317	63	224
17	15	76	2.45	171	32	131
			cores 0-5 cm:			
4	27	111	5.29	317	47	204
5	27	162	4.30	583	121	332
9	17	77	3.08	198	36	172
10	34	159	4.67	856	104	340
11	45	182	5.13	932	134	405
12	35	132	4.07	658	79	312
13	35	152	4.41	790	92	344
15	10	23	1.70	77	20	71

TABLE 2

CONCENTRATIONS OF TRACE ELEMENTS IN SURFICIAL SEDIMENTS IN WHALESBACK CHANNEL, 1990
(in ug/g Co, Cu, Ni, Pb and Zn, in % Fe)

cores 0-5 cm:

Stations	Co	Cu	Fe	Ni	Pb	Zn
620	65	140	6.50	637	101	353
625	73	170	6.10	839	108	375
626	59	135	6.00	626	86	323
627	65	150	5.97	741	92	339
628	58	124	6.61	683	77	311
629	51	132	6.25	712	91	319
630	42	118	5.50	476	74	256
631	40	90	4.53	457	58	217
632	52	154	5.75	683	121	366
634	54	143	5.45	786	79	324
635	53	128	6.01	607	74	300
639	23	48	5.35	372	34	229
640	52	124	4.85	743	75	306
641	43	105	5.25	535	60	256
645	15	46	3.55	215	38	150
646	27	63	4.45	291	33	173
647	43	100	6.61	469	58	242
648	63	139	5.78	785	100	311
649	58	147	6.20	653	83	313

TABLE 3

CONCENTRATIONS OF TRACE ELEMENTS IN SURFICIAL SEDIMENTS OUTSIDE WHALESBACK CHANNEL, 1990

(in ug/g Co, Cu, Ni, Pb and Zn, in % Fe)

cores 0-5 cm:

Stations	Co	Cu	Fe	Ni	Pb	Zn
601	12	41	2.72	117	41	155
602	39	76	3.24	321	90	269
603	41	77	4.60	310	94	277
604	30	78	4.55	300	108	267
606	34	67	4.92	210	66	191
607	19	55	6.40	217	60	184
608	35	86	4.51	339	89	259
609	20	49	4.43	182	47	162
610	33	80	5.75	251	97	222
612	58	201	6.29	757	146	452
613	47	120	5.55	498	117	329
616	67	129	6.30	721	117	372
617	17	33	9.54	231	23	147
618	27	66	5.20	252	87	217
619	77	170	6.20	865	110	404
621	11	27	3.25	45	15	75
622	9	28	3.26	63	17	84
623	44	34	8.04	73	15	103
636	61	151	3.89	687	86	341
637	30	65	4.55	274	66	223
638	29	72	4.31	321	88	243
642	46	123	4.30	779	72	308
643	20	57	1.70	253	59	197
644	23	16	2.55	52	19	60
650	39	104	5.45	453	108	292

TABLE 4

RELATIONSHIP AMONG TRACE ELEMENTS AND Fe IN WHALESBACK CHANNEL SURFICIAL SEDIMENTS COLLECTED IN 1988

(Correlation coefficients)

	Co	Cu	Fe	Ni	Pb	Zn
Co	1.0000 (24) .0000	.9249 (24) .0001	.8622 (24) .0001	.9490 (24) .0001	.8849 (24) .0001	.9175 (24) .0001
Cu	.9249 (24) .0001	1.0000 (24) .0000	.8755 (24) .0001	.9228 (24) .0001	.9507 (24) .0001	.9749 (24) .0001
Fe	.8622 (24) .0001	.8755 (24) .0001	1.0000 (24) .0000	.7476 (24) .0001	.7682 (24) .0001	.8057 (24) .0001
Ni	.9490 (24) .0001	.9228 (24) .0001	.7476 (24) .0001	1.0000 (24) .0000	.9411 (24) .0001	.9601 (24) .0001
Pb	.8849 (24) .0001	.9507 (24) .0001	.7682 (24) .0001	.9411 (24) .0001	1.0000 (24) .0000	.9730 (24) .0001
Zn	.9175 (24) .0001	.9749 (24) .0001	.8057 (24) .0001	.9601 (24) .0001	.9730 (24) .0001	1.0000 (24) .0000

Coefficient
(Sample size)
Significance

TABLE 5

RELATIONSHIP AMONG TRACE ELEMENTS AND Fe IN WHALESBACK CHANNEL SURFICIAL SEDIMENTS COLLECTED IN 1990

(Correlation coefficients)

	Co	Cu	Fe	Ni	Pb	Zn
Co	1.0000 (19) .0000	.9479 (19) .0001	.7305 (19) .0004	.9172 (19) .0001	.8682 (19) .0001	.9178 (19) .0001
Cu	.9479 (19) .0001	1.0000 (19) .0000	.6719 (19) .0016	.9198 (19) .0001	.9329 (19) .0001	.9396 (19) .0001
Fe	.7305 (19) .0004	.6719 (19) .0016	1.0000 (19) .0000	.6175 (19) .0048	.6097 (19) .0056	.7292 (19) .0004
Ni	.9172 (19) .0001	.9198 (19) .0001	.6175 (19) .0048	1.0000 (19) .0000	.8476 (19) .0001	.9226 (19) .0001
Pb	.8682 (19) .0001	.9329 (19) .0001	.6097 (19) .0056	.8476 (19) .0001	1.0000 (19) .0000	.9256 (19) .0001
Zn	.9178 (19) .0001	.9396 (19) .0001	.7292 (19) .0004	.9226 (19) .0001	.9256 (19) .0001	1.0000 (19) .0000

Coefficient
(Sample size)
Significance

TABLE 6

RELATIONSHIP AMONG TRACE ELEMENTS AND Fe OUTSIDE WHALESBACK CHANNEL SURFICIAL SEDIMENTS COLLECTED IN 1990

(Correlation coefficients)

	Co	Cu	Fe	Ni	Pb	Zn
Co	1.0000 (25) .0000	.8651 (25) .0001	.3254 (25) .1125	.8688 (25) .0001	.6943 (25) .0001	.8399 (25) .0001
Cu	.8651 (25) .0001	1.0000 (25) .0000	.2077 (25) .3191	.9465 (25) .0001	.8395 (25) .0001	.9601 (25) .0001
Fe	.3254 (25) .1125	.2077 (25) .3191	1.0000 (25) .0000	.2245 (25) .2806	.1435 (25) .4938	.2122 (25) .3085
Ni	.8688 (25) .0001	.9465 (25) .0001	.2245 (25) .2806	1.0000 (25) .0000	.7459 (25) .0001	.9265 (25) .0001
Pb	.6943 (25) .0001	.8395 (25) .0001	.1435 (25) .4938	.7459 (25) .0001	1.0000 (25) .0000	.9233 (25) .0001
Zn	.8399 (25) .0001	.9601 (25) .0001	.2122 (25) .3085	.9265 (25) .0001	.9233 (25) .0001	1.0000 (25) .0000

Coefficient
(Sample size)
Significance

4 and 5). There was a relationship among Co, Cu, Ni, Zn and Pb in the sediments outside the Whalesback Channel. However, no relationship was found between these trace elements and Fe concentrations in the sediments in this area (Table 6). The results indicated that the transport of sediment particles containing the trace elements from the Whalesback Channel affects the association of the trace elements with different sediment components. These associations need to be further investigated.

Concentration profiles of trace elements in sediments

The concentration profiles of Cu, Ni, Pb and Zn in sediment cores collected at stations 2, 8 and 14 in the Whalesback Channel and station 1 outside the Channel (Shoepack Bay, Figure 2) are shown in Figure 3. A gradual increase in the concentrations of Cu, Ni and Zn towards the sediment surface at station 1 indicated continuous recent inputs of these elements into the Shoepack Bay of the North Channel. On the other hand, the concentration profiles of Cu, Ni and Zn in sediments at stations 2 and 4 in the Whalesback Channel indicated an input of material recently less enriched with the trace elements than in the past. At station 8 in the Whalesback Channel (Figure 2), the concentrations of Cu, Ni, Pb and Zn fluctuated slightly within 27 cm sediment depth and did not indicate any major changes in the input of the trace elements in this area over the past years.

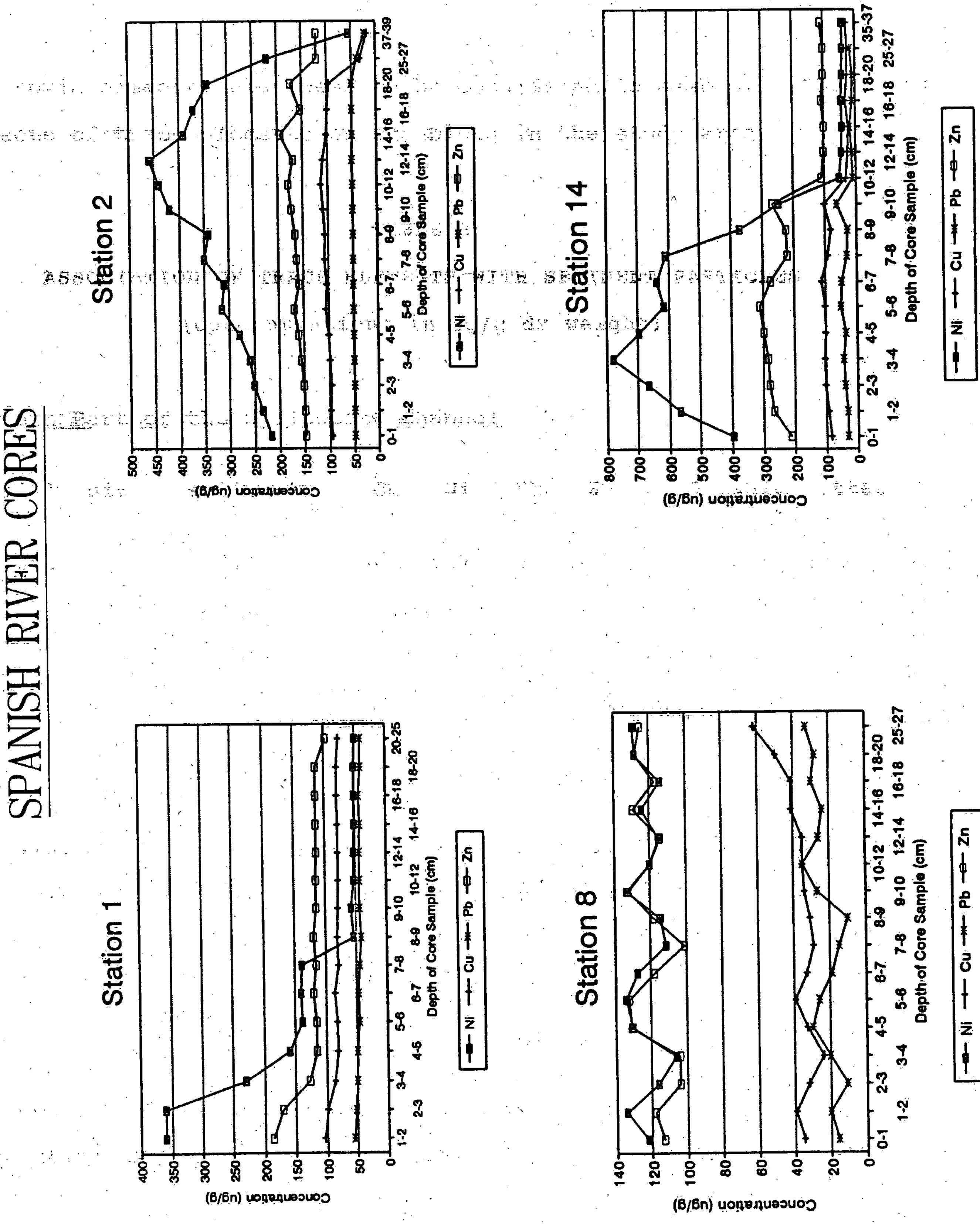

FIGURE 3. CONCENTRATION PROFILES OF TRACE ELEMENTS IN SEDIMENTS

Sedimentation rates were calculated from concentration profiles of Cs^{137} and Pb^{210} in sediment cores collected by the Ontario Ministry of the Environment at the Spanish River Area of Concern in 1988. The data were obtained from the Ontario Ministry of the Environment and used in the calculation. At the area north of Aird Island in the Whalesback Channel, the calculated sedimentation rate was approximately 0.32 cm per year. At the area adjacent to John Island in the Whalesback Channel, the calculated sedimentation rate was approximately 0.18 cm per year. However, low accumulation of sediments on the bottom of the Whalesback Channel and subsampling the cores into 2-cm sections prior to the determination of Cs^{137} and Pb^{210} allowed only an estimation of approximate sedimentation rates. On the other hand, the sedimentation rates calculated using a Cs^{137} concentration profile agreed well with those calculated from the Pb^{210} concentrations. Assuming that the sedimentation rate in the Whalesback Channel is about 0.20 to 0.30 cm per year and using the concentration profiles of trace elements at station 14 (Figure 3), the deposition of Ni, Cu, Pb and Zn started to increase around the 1940's followed by a decrease in the middle of the 1970's in the Whalesback Channel. This may reflect mining and smelting of Ni and Cu ores in the Spanish River drainage basin. However, the sedimentation rates and transport of fine-grained sediment particles may vary considerably from one area to the other in the Whalesback Channel as indicated by the concentration profiles of trace elements shown in Figure 3.

Background concentrations of trace elements in sediments

To investigate the background levels of Co, Cu, Ni, Pb and Zn in the sediments outside the Whalesback Channel, sediment cores were collected at stations 616 and 603, located near the main outlet from the Whalesback Channel at John Island, and at stations 638 and 644 in the North Channel, south of Aird Island (Figure 2).

The concentrations of Co, Cu, Ni, Pb, Zn and Fe in the surface 1 cm sediment, and at 9 and 15 cm sediment depth are shown in Table 7.

TABLE 7

CONCENTRATIONS OF METALS AT DIFFERENT SEDIMENT DEPTHS

(in ug/g Co, Cu, Ni, Pb and Zn, in % Fe)

Station	Sed. depth cm	Co	Cu	Fe	Ni	Pb	Zn
603	1	39	62	4.31	265	79	247
603	9	24	69	4.35	213	63	208
603	15	30	75	4.78	152	40	154
616	1	63	99	5.82	550	82	303
616	9	51	137	5.48	615	133	344
616	15	61	106	6.03	330	42	191
638	1	42	80	4.20	1042	87	456
638	9	27	41	5.80	68	11	113
638	15	19	43	4.53	54	12	117
644	1	21	50	3.79	409	72	208
644	9	18	40	4.80	51	10	95
644	15	19	41	4.78	52	10	95

The results indicated that about 50 ug/g of Ni, 20 ug/g of Co, 40 ug/g of Cu, 10 ug/g of Pb and 100 to 120 ug/g of Zn can be considered the background concentrations of these elements in fine-grained sediments at the study area in the North Channel. At stations 603 and 616, the concentrations of the trace elements were greater than the above suggested background levels at the 15-cm sediment depth. The results indicated a greater layer of enriched sediments deposited at this area than the area at stations 638 and 644. This is most likely due to a continuous long-term transport and deposition of trace elements-enriched material as well as greater sedimentation rates at the area near the outflow from the Whalesback Channel than in the other parts of the North Channel. There was no relationship between the concentrations of trace elements and Fe in the sediments collected at stations 603, 616, 638 and 644.

Results of many previous studies indicated that the background concentrations of Ni, Cu, Pb and Zn in fine-grained sediments in Lake Huron depositional areas ranged between 30 to 51, 31 to 48, 14 to 36 and 60 to 88 ug/g, respectively (Mudroch *et al.*, 1988). These background concentrations are in agreement with those found in this study. Using the results of the previous studies, the concentrations of Ni, Cu, Pb and Zn ranged from 5 to 132, 2 to 95, 1 to 151 and 6 to 233 ug/g, respectively, in surficial sediments in Lake Huron depositional areas and embayments (Mudroch *et al.*, 1988). The concentrations of Ni, Cu, Pb and Zn given by Thomas and Mudroch (1979) ranged between 8 and 100, 25 and 50, 5 to 50 and 50 to 100 ug/g, respectively, in surficial sediments collected in the 1970's in North Channel in the vicinity of the present study area. The concentrations of Ni, Cu, Pb and Zn in surficial sediments determined in this study exceeded those found in the 1970's. However, it should be noted that analytical methods used in the determination of the concentrations of trace elements in sediments can affect the results (Mudroch *et al.*, 1988).

Considering the background concentrations of Ni, Cu, Pb and Zn to be 50, 40, 10 and 120, respectively, calculated enrichment factors in the sediments ranged between 1 to 20 for Ni, <1 and 4.35 for Cu, <1 and 12.1 for Pb, and <1 and 3.13 for Zn in the Whalesback Channel. The enrichment factors ranged between <1 and 17.3 for Ni, <1 and 5.03 for Cu, 1.5 and 14.6 for Pb, and <1 and 3.77 for Zn in the sediments outside the Whalesback Channel. The enrichment factors were calculated for Cu, Pb and Zn in surficial sediments in Lakes Huron, Erie and Ontario in the 1970's (Kemp and Thomas, 1976). They ranged between <1 and 2.2 for Cu, <1 and 14.0 for Pb, and <1 and 6.2 for Zn in the three Great Lakes. In Lake Ontario, maximal enrichment factor for Ni was 3.0 (A. Mudroch, National Water Research Institute, unpublished data). According to this information, surface sediments in the study area were enriched more by Ni, Cu and Pb than those in Lakes Huron, Erie and Ontario. The enrichment factor for Ni was greater in sediments in the Whalesback Channel than in the rest of the study area.

Concentrations of trace elements in different particle size fractions of the sediments

The association of trace elements with different particle size fractions of sediments in the western and southern parts of the Whalesback Channel is shown in Table 8. The data indicated that Ni was associated mainly with particles <13 um in the sediments collected in both areas. On the other hand, sediment particles >13 um contained considerably greater concentrations of Cu than the smaller particles (Table 8). The concentrations of Pb and Zn decreased with the decreasing size of the particles in sediments collected at the western part of the Whalesback Channel, and increased with the decreasing size of the particles in sediments collected in the southern part of the Whalesback Channel. There was a relationship between the concentrations of Ni and organic matter in different sediment particle size in both locations. High concentrations of Cu in 5% and 43% of sediment particles in the western and southern part, respectively, of the Whalesback Channel should be considered in bioassessment of the sediment quality. Benthic organisms digesting preferably particles >13 um would be exposed to very high concentrations of Cu in their food source in the Whalesback Channel. On the other hand, organisms selecting particles <13 um for their food source would be exposed to very high concentrations of Ni. Synergistic effects of these two toxic elements also need to be considered in assessing the effects of trace elements on the biota in the study area.

TABLE 8

ASSOCIATION OF TRACE ELEMENTS WITH SEDIMENT PARTICLES

(concentrations in ug/g dr weight)

Western Part of the Whalesback Channel

Particle size µm	sediment %	Cu	Ni	Pb	Zn	Organic matter %
<35>27	0.5	1365	847	135	420	8.44
<27>20	2	1716	853	149	426	8.26
<20>13	5	1959	800	157	408	8.31
<13	90	170	1200	103	373	10.50

Southern part of the Whalesback Channel

Particle size µm	sediment %	Cu	Ni	Pb	Zn	Organic matter %
<44>35	4	189	61	13	163	1.05
<35>27	7	433	124	29	109	3.03
<27>20	10	591	150	56	123	3.68
>20<13	22	747	160	58	138	4.68
<13	57	71	229	79	215	7.59

Speciation of trace elements in sediments

The concentrations of trace elements in five fractions of the sequential extraction procedure are shown in Table 9.

TABLE 9

TRACE ELEMENTS SPECIATION

(in ug/g dry weight and % of total element concentrations)

STATION 8

Particle size: 0.5% sand, 80.2% silt, 19.3% clay

Element	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Cu	<0.1	<0.1	8.2	47.6	4.2
% total			13.7	79.3	7.0
Ni	16.1	34.8	18.3	110.8	38.8
% total	7.4	15.9	8.4	50.6	17.7
Pb	0.5	0.3	5.7	17.7	11.8
% total	1.4	0.8	15.8	49.2	32.8
Zn	2.7	19.6	17.4	57.9	30.7
% total	2.1	15.3	13.6	45.1	23.9

STATION 12

Particle size: 2.1% sand, 78.0% silt, 19.8% clay

Element	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Cu	<0.1	9.4	4.8	48.8	2.9
% total		14.3	7.3	74.1	4.4
Ni	20.6	78.1	8.9	106.1	35.9
% total	8.3	31.3	3.6	42.5	14.4
Pb	1.6	14.3	4.1	15.9	13.2
% total	3.3	29.1	8.4	32.4	25.1
Zn	1.8	55.0	10.0	57.1	28.6
% total	1.2	36.1	6.6	37.4	18.8

STATION 17

Particle size: 2.6% sand, 87.0% silt, 10.4% clay

Element	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Cu	<0.1	0.1	6.2	38.4	3.2
% total		0.2	12.9	80.2	6.7
Ni	11.7	19.6	12.4	90.9	32.8
% total	7.0	11.7	7.4	54.3	19.6
Pb	0.9	0.3	5.2	15.0	15.7
% total	2.4	0.8	14.0	40.4	42.3
Zn	0.3	11.5	14.4	56.0	30.3
% total	0.3	10.2	12.8	49.8	26.9

It should be noted that the distribution of individual trace elements among various fractions as obtained with the sequential extraction scheme used in this study, does not necessarily reflect the scavenging action of discrete sediment phases, but rather should be considered as operationally defined by the extraction method. Generally, the distribution of the trace elements in the five fractions of the sequential extraction procedure was similar in all three sediments collected for analysis in the Whalesback Channel.

Copper, Ni, Pb and Zn were associated mainly with organic matter and sulfides (Fraction 4) or were in the crystallinic lattice of the minerals (Fraction 5). However, considerable quantities of Cu, Ni, Pb and Zn were associated with carbonates or adsorbed on sediment particles (Fraction 2) in the sediments collected at station 12 in the Whalesback Channel. The concentrations of easily available Ni (Fraction 1) in all three sediment samples were greater than those of Cu, Pb and Zn.

The weakly bound trace elements may be considered more biochemically reactive and have the capacity to inhibit enzyme-catalyzed biochemical reactions in sediment biota, such as microbial and benthic organisms populations. Lowering the ambient pH of the sediments may solubilize trace elements associated with carbonates (Fraction 2). This may increase the potential for toxicity of these elements to sediment biota. Changes in the redox potential in the sediments or at the sediment-water interface may bring about oxidation of sulfides with subsequent solubilization of sulfide-associated trace elements. The ambient redox potential of the sediments may change, for example, during the resuspension of sediment particles and their transport through an oxic water column. Further, trace elements bound to Fe-Mn oxides (Fraction 3) may become released during lowering the sediment redox potential. This may occur in winter under ice cover in the Whalesback Channel or during decomposition of organic matter in the bottom sediments. With considerably large quantities of trace elements in the four fractions, the sediments in the Whalesback Channel appear to have the potential to become toxic with any physico-chemical changes within the sediments or at the sediment/water interface.

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