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Zonation of Contaminated Bottom Sediments in Hamilton
Harbour as Defined By Statistical Classification Techniques

By:

D. Poulton, W. Morris, J. Coakley

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**ZONATION OF CONTAMINATED BOTTOM SEDIMENTS IN HAMILTON HARBOUR
AS DEFINED BY STATISTICAL CLASSIFICATION TECHNIQUES**

D.J. Poulton ¹, W.A. Morris ², and J.P. Coakley ³

¹ Science and Technology Branch, Ontario Ministry of Environment and Energy,
Toronto, ON M4V 1L5;

² Department of Geology, McMaster University, Hamilton, ON L8S 4M1;

³ Aquatic Ecosystem Restoration Branch, National Water Research Institute,
Burlington, ON L7R 4A6

MANAGEMENT PERSPECTIVE

[Poulton, D.J., Morris, W.A., and Coakley, J.P. 1994: Zonation of contaminated bottom sediments in Hamilton Harbour as defined by statistical classification techniques].

Clean-up efforts in Hamilton Harbour under the Hamilton Harbour Remediation Plan require a reliable knowledge of the net transport patterns and depositional zones for contaminated sediments in the Harbour. Bottom sediments are known to act as storage media for many toxic contaminants and, even after source reduction has been implemented, they continue to release these elements back to the water column, and thus to the aquatic ecosystem. In the present report, chemical determinations of total and weak acid-extractable metals carried out on 40 sediment samples from the harbor were examined to deduce net transport patterns in the Harbour. The data were subjected to two multivariate statistical techniques to assess sources or transport processes (ratio matching followed by cluster analysis, and principal component analysis). The cluster analysis technique resolved six groups of samples related to contaminant sources, sandy relatively clean nearshore areas, and a large contaminated central area. The principal components technique supported this by identifying factors related to the large central area to be most likely due to sediment focusing; it also identified a factor related to contaminant source input and one related to input of silt-sized particles rich in Ca and Sr. Two "outlier" samples were noted and addressed in the analysis: one related to a heavily contaminated area near the steel industries in the south central shoreline, and one containing almost pure sand at the northeastern corner of the harbor.

ABSTRACT

Hamilton Harbour, a 2150 ha embayment at the western end of Lake Ontario, is the receiving water for a number of industrial and municipal effluents. Their accumulation over the past decades has resulted in a seriously degraded aquatic environment that is now being subjected to remedial actions. Chemical determinations of total and weak acid-extractable metals were carried out on 40 sediment samples from the harbor. These data were subjected to two multivariate statistical techniques to assess their ability to discriminate samples that could be associated with common sources or transport processes. The techniques used were ratio matching followed by cluster analysis, and principal component analysis. The cluster analysis technique resolved six groups related to contaminant sources, sandy relatively clean nearshore areas, and a large contaminated central area. The principal components technique supported this by showing factors related to the large central area as a result of sediment focusing, plus a factor related to contaminant source input and one related to input of silt-sized particles rich in Ca and Sr. Two "outlier" samples were noted, one related to a heavily contaminated area near the steel industries, and one containing almost pure sand at the northeastern corner of the harbor.

Keywords: Hamilton Harbour, sediment, metals, statistics.

INTRODUCTION

Hamilton Harbour is one of 43 Areas of Concern on the Great Lakes designated by the International Joint Commission (IJC) as having significant environmental degradation. Problems identified by the joint Environment Canada - Ontario Ministry of Environment and Energy working group [1] include loss of fisheries and wildlife habitat, restrictions on fish consumption, fish tumors and other deformities, beach closings, eutrophication and summer hypolimnetic dissolved oxygen depletion, interferences with drinking water, degradation of benthos, and exceedences of water and sediment quality criteria. Most of these problems can be traced directly to the presence of contaminated sediments in the harbor. The paper proposes a statistical approach to delineating sediment zones according to trace element distributions.

Physical setting

Hamilton Harbour (Figure 1) is a 21.5 km² embayment at the western end of Lake Ontario. It is separated from the lake by a natural sand bar through which a ship canal 107 m wide and 9.5 m deep passes. At the western end, the harbor is connected to Cootes Paradise by the Desjardins Canal. The harbor receives treated sanitary sewage from sewage treatment plants (STPs) serving the cities of Hamilton and Burlington, and (indirectly, through Cootes Paradise at the west end) the Dundas STP. Cooling water for the two large steel mills (Dofasco and Stelco) situated on the south side of the harbor is withdrawn from and recirculated to the harbor; process wastes from these steel mills are also treated at the Hamilton STP. The harbor also receives stormwater overflow drainage water from the untreated urbanized areas in its watershed.

Previous work

Previous information on contaminants in the harbor was summarized by Poulton [3] and also in the Hamilton Harbour RAP documents [1,2]. Toxic effects of metals, and their influence by the dissolved oxygen regime was also studied by Krantzberg [4]. She found that although sediment from regions within the harbor is highly contaminated with metals, not all contaminated sites were toxic to test organisms (fathead minnows and several benthic taxa). Availability of metals (as measured by weak acid extractions) and sediment oxygen demand both played a role in determining toxicity of individual sediment samples. Sediment toxicity should be reduced by improving the oxygen regime of the harbor, which will produce an improved regime for organisms less tolerant of anoxic conditions, and also indirectly by decreasing metal bioavailability, possibly through coprecipitation and adsorption of trace metals with iron and manganese hydroxides.

Multivariate statistical techniques have been used previously by numerous authors in order to discern groups of similar sediments and attempt to pinpoint sources and pathways of sediment movement. In Hamilton Harbour itself, Poulton [5] used ratio matching followed by cluster analysis to define sediment zones based on more limited surveys in 1980 and 1984. Principal components analysis was used by Eltzer [6] to separate point and nonpoint sources of polychlorinated dibenzo-p-dioxins and furans in sediments of the Housatonic River in Massachusetts and Connecticut. A related technique, principal factor analysis, was used by Buckley and Winters [7] to define zones in Halifax Harbour impacted by primary and secondary contamination, subsurface drainage, and sediment diagenesis.

FIELD AND LABORATORY METHODS

Field methods

Forty bottom sediment samples were collected on a quasi-equally-spaced grid over the entire harbor in December 1993 (Figure 1). The sampler used for most was a small gravity corer, but for those in deep water or consisting of sediments too loose for retention in the corer, a box-corer was used and core samples taken on the launch deck. The samples were kept as cool as possible onboard, then transferred to a cold storage chamber (5° C) at the Canada Centre for Inland Waters (CCIW) prior to freeze-drying. The samples were freeze-dried within 60 days of collection and stored thereafter at room temperature in plastic vials.

Laboratory analysis

The top 2 cm of each core was sub-sampled and, after freeze-drying, were analyzed for selected trace and major elements in the following manner:

1. Total elements. Ten elements were determined at the National Laboratory for Environmental Testing (NLET), Canada Centre for Inland Waters using an open digestion technique, followed by Atomic Absorption spectrography. This technique is generally used to determine the total concentration of the elements assayed, both surface-adsorbed and in the mineral structure.
2. Acid-extractable elements. Chemical determinations were carried out simultaneously on the 40 samples for a suite of 33 trace and other elements at the Centre de Recherches

Minérales (CRM), Ste-Foy, Quebec, using techniques adapted by Gagné [8], for use on sediment samples from those described in Standard Methods [9].

The analytical procedure involved the leaching of extractable metals from a 0.5 g subsample with 2 mL of 13.3% nitric acid reagent (500° C for one hour). The nitric acid reagent was prepared by first dissolving 1 g of mercuric nitrate into 2250 ml of concentrated nitric acid and diluting this solution to 13.3% (weight) by combining 266 ml of the above mixture with 2 L distilled water. The mercuric nitrate was added to prevent precipitation of silver in the sediment and thus to increase the resolution of the measurement. Quantitative determination was carried out using inductively-coupled plasma atomic emission spectrography. Detection limits for major elements, Al and Fe, were 0.02 and 0.01%, respectively, and were 1 to 3 $\mu\text{g g}^{-1}$ for all trace elements. Standard QA/QC procedures were incorporated in the determinations. In addition, target element concentration for duplicates samples inserted in the batch were all within reasonable limits of variation.

Detailed results of the chemical and physical analyses for all 40 samples are presented in [10].

STATISTICAL METHODS

Sediment Sample Zonation by Ratio Matching followed by Cluster Analysis

Zones representing sediment samples of similar origin were defined by ratio matching followed by cluster analysis [5]. This method helps to identify pollutant sources by identifying sediment samples of similar origins. Unique samples (of different origin from most) can be related to nearby sources or unique (e.g. high energy) sedimentary environments. The technique, originally developed by Anders [11], is based on the fact that sediment samples of similar origin tend to have similar ratios of concentrations of anthropogenic pollutants, even though they may be diluted with varying amounts of inert background materials such as silica, calcite, etc. Each possible combination of samples is compared together as follows: Ratios of the concentrations of all trace metals with each other are calculated for every sample, to form triangular matrices of size m by m , where m is the number of chemical parameters involved. The comparison is done by dividing the matrix for one sample by that for another, and repeated for all possible combinations of samples. For a perfect match, the ratios would be unity. To obtain a similarity coefficient for each pair of samples, 1.0 is added to the absolute values of the natural logarithm of each matrix element, and the elements summed and divided by their total number $(=\frac{m}{2})$ [5]. This expression is equal to:

$$\frac{m!}{(m-2)! 2!}$$

The similarity matrix is broken down into groups representing similar stations by average linkage cluster analysis [5]. This procedure was conducted separately on the data representing "total" and "total plus extracted" metals (as defined above). Ba, Ca, and Sr were omitted from the

analyses as potential diluents; Cd had to be omitted from the "total plus extracted" analysis due to several non-detected results.

Sediment Zonation by Factor Analysis

It is assumed that the chemical concentration of the trace metals in any unit volume of sediment represents a mixture of materials derived from a number of independent sources. The relative concentration of the trace metals depends upon both proximity to the source of the metal, and on the transport mechanism by which the metal is moved from the source to the sampling point. It is assumed that the amount of any given element present in the total sample can be expressed as the sum of contributions from each of the sources. Should the transport mechanism also involve a chemical reaction it would also give rise to a separate source effect [12]. In applying the factor analysis procedure we are attempting to describe a multivariate sample by a smaller number of variables which are combinations of the various elements. Prior to analysis the data were standardized to a mean value of zero and a standard deviation of unity for each variable. As in previous studies employing factor analysis [7, 12] the analysis was made on the matrix of correlations about the mean between the variables: R-mode factor analysis. Factor extraction was achieved using a Principal Component Analysis procedure taken from SPSS/PC 6.01 for Windows. A minimum eigenvalue of 0.9 was selected in order to restrict the number of factors to 4, or less. (It was assumed that factors with eigenvalues less than this number were related to noise present in the chemical analyses). Varimax factor rotation was used in all cases. Factor scores were calculated for each variable and a combined factor score was determined for each sample.

RESULTS

Ratio Matching followed by Cluster Analysis

Initial sensitivity testing of the statistical techniques was carried out on the total-metals data as these data were available earlier than the extractable metals data. Using an average linkage procedure, five groups were defined by this analysis (Figure 2). The largest group comprised most of the stations in the central harbor area. This result substantiated a previous sediment ratio matching study of a smaller suite of samples from Hamilton Harbour sediments [5]. A second group present in this collection comprises a number of near shore sampling points. This statistical procedure shows that the result for station 39 (Randle's Reef, offshore from previous Stelco process outfalls) is clearly divergent from any other samples examined from the harbor; this station has total Fe, Zn and Cd concentrations that are close to 3 times that found at any other station in the harbor. Including such an anomalous station can have profound effects on the results of multivariate statistical analysis [13, 14, 15]. For this reason, Station 39 was deemed an outlier and was deleted from the data set before statistical analysis on the "total plus extracted" metals was commenced.

The result of the cluster analysis from ratios including both total and extractable metals but excluding station 39 is shown in Figure 3. Five groupings are evident from this analysis, and are shown geographically in Figure 4. Group 1 comprises 25 stations that are generally located towards the center of the harbor. This group of stations, which is similar to that first observed in the analysis of the total metal concentrations, and in previous work [5], is typified by the

presence of mainly clay-organic muds, with significantly high levels of total and extractable trace metals. Group 2 consists of ten stations all of which, although coming from various parts of the harbor, are located fairly close to shore in various areas. Significantly, at each of this group of sites the sediment has a much higher sand content, and also noticeably lower concentrations of trace metals. Group 3, containing stations 32 and 32A is also sandy and close to shore; with the exception of Cd this group has systematically lower concentrations of trace metals than found in Group 2. Group 4 (not seen previously) is defined by site 40 in the Windermere Channel leading from the Hamilton STP. The particulate loadings introduced from this source have produced a group that is distinguished by abnormally high concentrations of Cr, Zn, Cu and Fe. Group 5 is also defined by a single station (1) which is located very close to the north shore, north of the Burlington STP. Examination of its composition indicated it to be extremely (99.5%) sandy. A direct consequence of the very high sand content is the extremely low concentration of contaminants. Site 1 also qualified as an outlier and hence was eliminated prior to the principal components analysis.

Principal Components Analysis

On the basis of the cluster analysis and preliminary factor analysis studies it was found that the results from samples 1 and 39 were so divergent that they significantly affected the factor solutions, hence these samples were eliminated prior to any further analysis. As with the cluster analysis the factor analysis was initially applied to the total trace metal data. This defined a simple two factor separation. The predominant factor comprises most of the trace metals Pb, Ni, Cu, Fe, V, Zn, Co, Cd, and Al. These are directly related to the presence of clay and

indirectly related to the presence of sand (Figure 5, Table 1). This defines a grouping of sites that is somewhat similar to Group 1 defined by the cluster analysis. A second group is defined by the presence of Ba, which is inversely correlated to the concentration of silt.

Inclusion of the extracted (-E) metals data with the total (-T) metals leads to the definition of three distinct factors. Like all other analyses this procedure confirms the strong inverse relationship between the presence of a sand substrate and trace metal concentrations; i.e. in regions of sand accumulation there are little or no trace metals. This observation further emphasizes the justification for eliminating site 1 from this analysis. Factor 1 which is defined by high loadings of Cr-E, Zn-T, Zn-E, Cd-E, Pb-E and -T, Cu-E, Fe-E and -T accounts for over 70% of the total variation (Figure 6, Table 2). Factor 2 with high loadings for other metallic species such as Co-E, Al-E and -T, Ni-E and -T, and V-E and -T, accounts for 14% of the total variation. Its distribution is also directly related to the concentration of clay and inversely related to sand (Figure 6, Table 2). Factor 3, which accounts for 11% of the total variation, is defined by the distribution of Ca-E, Sr-E and silt. Ba-T is inversely related to the presence of calcium and strontium.

DISCUSSION

Those sites which belong to Group 1 generally belong to the deeper parts of the harbor. In these areas fine-grained contaminated sediments from various sources have been mixed and deposited. This zone defines a broad region of sediment mixing (figure 4). The ten sites that define Group 2 are all located in near shore positions. It is believed that increased wave action in these near shore environments leads to a constant re-suspension of the finer particulates which in turn are

moved to deeper water. This in-turn leads to a reduction in the content of trace metals. An extreme example of this form of mineral separation by resuspension is defined by Group 5 (site 1) where the extremely shallow water depth and enhanced wave activity has removed all material except the sand. Group 3 (sites 32 and 32a) are from the north shore shallow water environment. Locally in this region there is an increased amount of longshore drift as defined by the nearby spit. It is felt that this group is defined by the presence of an increased concentration of silicate fragments. Group 4 (site 40) is intimately associated with the Windermere basin. This suggests there is a chemically distinct source feeding sediment into Windermere Basin. While the Hamilton STP is the most likely source, others such as the Dofasco dock, and numerous industrial plants may contribute.

*There is an outfall
there - see GKR*

By calculating the factor scores for each element it is possible to calculate a loading for each factor at each observation point. These have been contoured using Rangrid by Geosoft using a 100 metre grid cell size. This contouring produces spatial patterns of the distribution of the individual factors in the harbor. Factor 1 (Figure 7; Table 2) shows an interesting distribution pattern consisting of a plume extending from the Stelco docks northwest across the harbor to the north shore. This plume tends to follow the bathymetry and after impinging on the north shore moves down into the deeper part of the basin. There is a zone of high values along the north shore, although sources for the elements represented are hard to imagine to exist in this highly residential area. It is felt therefore that some of this pattern may be an artifact of the gridding technique and is related to the lack of samples from the nearshore areas. Input of metals from Stelco followed by transport across the harbor could explain the pattern for this factor. The

pattern defined by this factor is very similar to that reported by Murphy for sediment toxicity zones [16]; [1] (p. 84).

Factor 2 (Figure 8; Table 2) is associated with higher levels of clay, Al, V, Co, Ba, Ni, and Mn, and moderate levels of Cd, Cr, Cu, Fe, Pb, and Zn, favors mainly the offshore deeper sediment areas, with a slight bias toward the north shore. When the depth contours of the harbor are superimposed, it is clear that depth plays an important role here. Because the distribution is almost closed, it would appear that this factor loading is not directly related to a source, but more likely to a depositional process. Sediment focusing, that is the resuspension and mobilization of finer grained and more contaminated sediments followed by accumulation in deeper waters, offers the most likely explanation. Some justification for this interpretation may be found in the close association of this factor with the presence of clay particles (Table 2).

Factor 3 (Figure 9, Table 2) is best defined around the periphery of the harbor. There are three regions exhibiting significant levels of factor 3: at the western end of the harbor where there is input from Cootes Paradise; at the northeast portion of the harbor where there is input from the Burlington STP, and along Windermere Basin and along the south shore which correlates with input from the Hamilton STP and the steel industries. The predominant elements defining this pattern are Ca and Sr, and these are most commonly resident in silt size particles (Table 2). As the surrounding watershed is mainly composed of limestone and dolomite it is felt that this pattern is reflecting the input of surface runoff which is introduced to the harbor via inflowing streams and local shore erosion.

Exceedence

Average composition of the six identified groups (including the outlier stations) is given for selected extracted metals in Table 3. Extracted metals were selected because they are more likely to be bioavailable than total metals. This includes comparisons with the Ministry of Environment and Energy's Provincial Sediment Quality Guidelines (PSWG) [17]. For metals, two effect levels are identified: the Lowest Effect Level (LEL) indicates a contaminant level which has no effect on the majority of sediment-dwelling organisms. The Severe Effect Level (SEL) indicates heavy pollution, with the health of organisms in the sediment most likely to be affected. The guidelines recommend further testing to determine the acute toxicity of such sediments. Comparison of results in Table 4 with these guidelines indicates that nearly all the harbor is still highly contaminated with all these metals. Only station 1 (group 5) is below all LEL values. Group 3 (stations 32 and 32A) is above the LEL for all metals but chromium, copper, iron, and manganese (cobalt is not compared as no PSQG values are available). Even the relatively uncontaminated nearshore group 2 is above the LEL for all metals but copper and iron. Results in all other groups are above the LEL and exceed the SEL as follows: Group 1 (large central area), manganese and zinc; group 4 (Hamilton STP), chromium and zinc; group 6 (Randle's Reef), iron, manganese, lead, and zinc. These confirm the overall severe contamination of the harbor with heavy metals as noted before [2] but, as noted by Krantzberg [4] do not necessarily indicate acute toxicity to benthic organisms. The latter depends upon chemical speciation of metals in sediments, which is best tested by selective extraction schemes like that of Tessier et al. [18], but can be estimated roughly with a weak acid extraction such as 1 N HCl.

CONCLUSIONS

Two multivariate statistical methods have been used in Hamilton Harbour to study the distribution of contaminated sediments. These methods support each other in identifying interpretable zones in sediment chemical characteristics. In particular, certain locations, like station 1 (extremely high sand content) and 39 (highly polluted Randle's reef) were immediately classified as outliers respectively by their grain size and chemical composition.

Of the statistical techniques used, ratio matching with cluster analysis gave the simplest zonation, without identifying the factors that account most for the differentiation. Principal components analysis was able to provide a comparable zonation, but was also able to provide quantitative relationships between the parameters that gave the most separation. This hierarchy of statistical techniques enables one to locate regions characterized by anomalous sediment composition and to speculate about their sources. The distribution of trace metals within the harbor is controlled by the interaction between input sources, and depositional and resuspension processes which define the fate of mineral phases. The effects of specific input sources are identified by Groups 1, 4 and possibly Group 2, and Factors 1 and 3. Inputs from three source types (Steel Mill discharges, STP discharges, and watershed runoff) has produced these identifiable zones. Resuspension processes in regions of high current activity lead to the winnowing of fine grained particles, thus producing zones characterized by sand which typifies Groups 3 and 5. Preferred concentration of the fine grain phases with their enhanced trace metal contamination is isolated by Group 1 and Factor 2.

Most of the harbor continues to exhibit metal concentrations in excess of the Ontario Provincial Sediment Quality Guidelines, with exceedences of the Severe Effect Level occurring for several metals such as zinc, iron, manganese, chromium, and lead. The worst exceedences occur near Randle's Reef, and secondarily, in the Windermere Basin area. The statistical methods used in this study have helped to identify these "hot spots" as prime candidates for remediation, as well as defining on a more general level, the extent of impact zones for various pollutants in the harbor sediments.

REFERENCES

1. RAP 1992. Remedial Action Plan for Hamilton Harbour, Stage 2A. Prepared for Ontario Ministry of the Environment and Environment Canada. Toronto, ON.
2. RAP 1989. Remedial Action Plan for Hamilton Harbour, Stage 1. Prepared for Ontario Ministry of the Environment and Environment Canada. Toronto, ON.
3. Poulton, D.J. 1987. Trace contaminant status of Hamilton Harbour. *J. Great Lakes Res.* 13: 193-201.
4. Krantzberg, G. 1994. Spatial and temporal variability in metal bioavailability and toxicity of sediment from Hamilton Harbour, Lake Ontario. *Env. Toxicol. Chem.* 13(10): 1685-1698.
5. Poulton, D.J. 1989. Statistical zonation of sediment samples using ratio matching and cluster analysis. *Environ. Mon. Assessment* 12: 379-404.
6. Eltzer, B.D. 1993. Comparison of point and nonpoint sources of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans to sediments of the Housatonic River. *Environ. Sci. Technol.* 27: 1632-1637.

7. Buckley, D.E. and G.V. Winters. 1992. Geochemical characteristics of contaminated surficial sediments in Halifax Harbour: impact of waste discharge. *Can. J. Earth Sci.* 29: 2617-2639.
8. Gagne, R. 1990. Méthodes d'analyse de diverses substances minérales. Tome 1. Analyses par spectrométrie, d'absorption atomique, spectrométrie d'émission atomique au plasma, et fluorométrie. Centre de Recherches Minérales, Ste.-Foy, QC.
9. Clerceri, L.S., A.E. Greensberg, and R.R. Trussel. 1989. *Standard Methods for the Examination of Water and Waste Water, 17th Edition*. Joint publication by American Public Health Association, American Water Works Association, and American Pollution Control Federation.
10. Coakley, J.P., D.J. Poulton, and W. Morris. 1995 (in prep.). Trace metals and minor elements in surficial sediments from Hamilton Harbour. NWRI Contribution # ???, 94-43
Burlington, ON.
11. Anders, O.U. 1972. Ratio Matching -- A statistical aid for discovering generic relationships among samples. *Anal. Chem.* 44: 1930-1933.
12. Hopke, P.H.K., R.E. Lamb, and D.F.S. Natusch, 1980. Multielement characterization of urban roadway dust. *Env. Sci. & Tech.* 14: 164-172.

13. Jackson, D.A. and Y. Chen. 1994. Robust multivariate analysis: principal components with outliers. Abstracts, Fifth Conference on Environmetrics, Burlington, ON, August 11-15, 1994, p. 108.
14. Paatero, P. 1994. Application of robust factor analytic techniques for analyzing environmental time series. Abstracts, Fifth Conference on Environmetrics, Burlington, ON, August 11-15, 1994, p. 121-122.
15. Singh, A. 1994. Multiple outliers and robust regression. Abstracts, Fifth Conference on Environmetrics, Burlington, ON, August 11-15, 1994, p. 133.
16. Murphy, T.P., L. McArdle, H. Brouwer, A. Moller, and G. Krantzberg, 1994. Spatial variation in sediment toxicity and potential methods of in situ treatment. *Verhandlungen Internat. Verein. Limnol.* 25: 2036-2042.
17. Persaud, D., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Standards Development Branch and Environmental Monitoring and Reporting Branch, Ministry of Environment and Energy, Toronto, ON.
18. Tessier, A., P.G.C. Campbell, and M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51: 844-851.

TABLE 1

FACTOR SCORES FOR INITIAL PCA WITH TOTAL METALS ONLY

Metal	Factor 1	Factor 2
Pb	.97990	
Ni	.97508	
Cu	.95550	
Fe	.94404	
V	.94178	
Zn	.92466	
Co	.91915	
Cd	.89241	
Clay	.84502	
Sand	-.81953	.51707
Al	.62509	
Ba		.77287
Silt	.47288	-.69375

Note: Factor scores below an absolute value of 0.4 are omitted for clarity.

TABLE 2

FACTOR SCORES FOR SECOND PCA USING BOTH TOTAL AND EXTRACTABLE METALS

Metal	Factor 1	Factor 2	Factor 3
Cr_E	.87143	.43638	
Zn_T	.85965	.44487	
Zn_E	.84876	.43136	
Cd_E	.81964	.41256	
Pb_E	.81364	.56212	
Cd_T	.81059	.44616	
Cu_E	.80712		
Fe_T	.78100	.52297	
Pb_T	.77856	.59455	
Cu_T	.77624	.56974	
Fe_E	.70973	.67902	
Clay		.87666	
Al_E		.85835	
V_E	.52213	.81340	
Al_T		.80844	
Co_E	.47880	.80810	
V_T	.50816	.80518	
Ba_E	.47522	.78818	
Co_T	.50233	.78139	
Ni_T	.65347	.72721	
Ni_E	.63374	.71286	
Mn_E	.57102	.68491	
Sand	-.50922	-.64253	-.49115
Ca_E			.86424
Sr_E		.41312	.85020
Silt	.48574		.65339
Ba_T			-.46124

Note: Factor loadings less than an absolute value of 0.4 are omitted for clarity.

_T refers to total metals.

_E refers to extractable metals.

TABLE 3

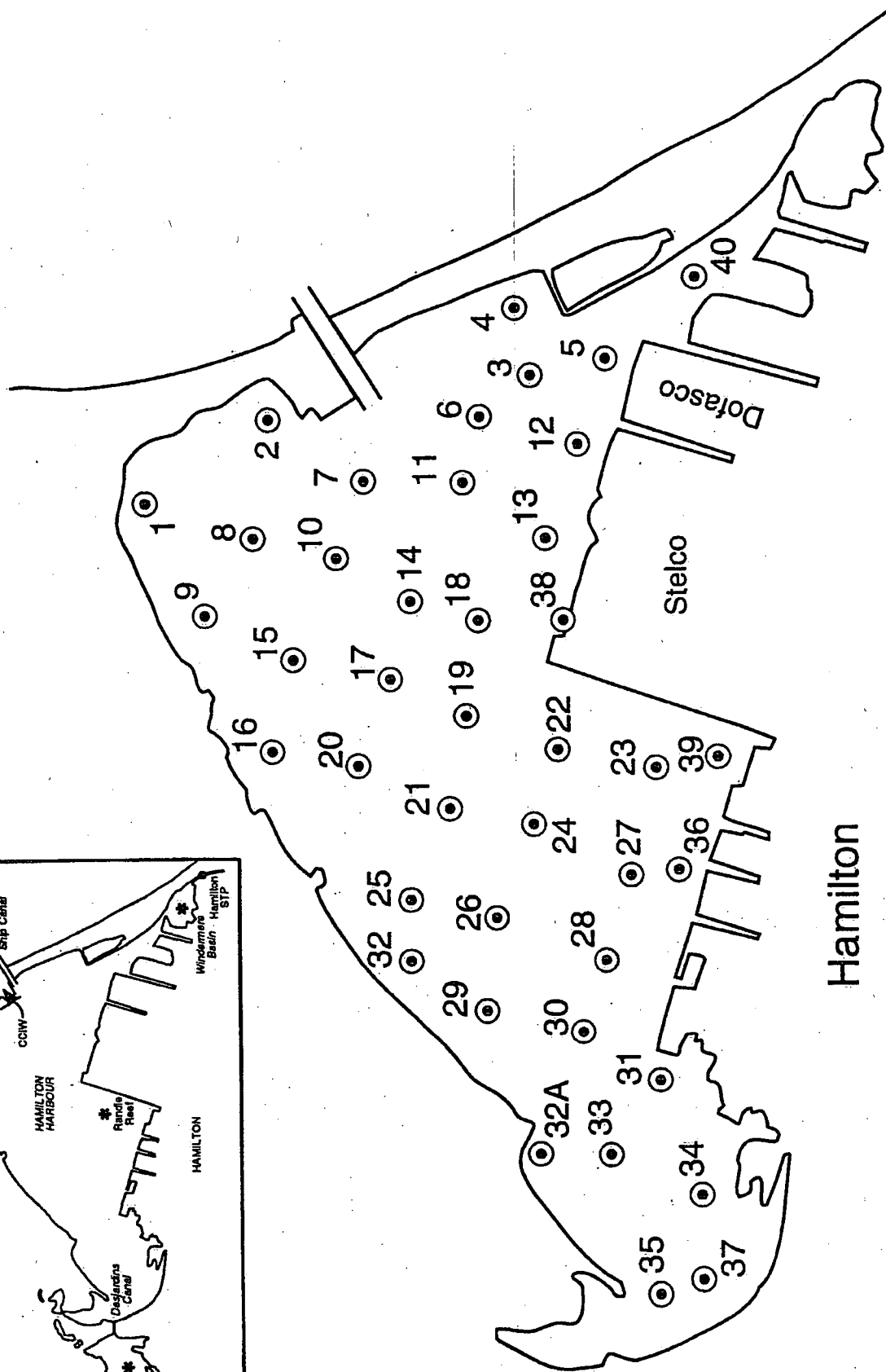
CONCENTRATIONS OF SELECTED HEAVY METALS IN HAMILTON HARBOUR SEDIMENTS, 1993

(ug/g unless otherwise noted)

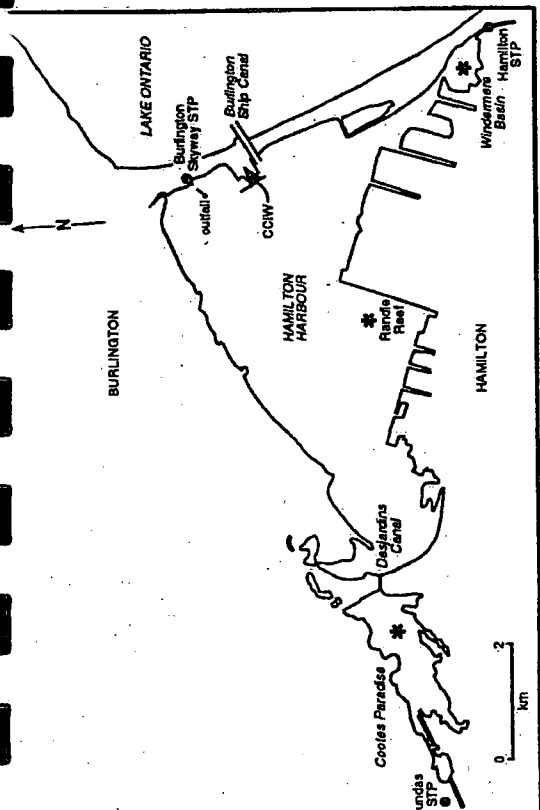
Group (location)	N	Cd	Co	Cr	Cu	Fe(%)	Mn	Ni	Pb	Zn
1 (central)	25 mean	3.66	10.2	102.0	27.8	2.96	1158	37.1	175	1272
	sd	0.91	1.3	23.2	4.9	0.39	161	4.4	36	288
2 (nearshore)	10 mean	1.13	6.3	33.1	14.9	1.55	697	19.3	57	437
	sd	0.53	1.5	11.0	3.4	0.28	156	5.0	17	170
3 (32 and 32A)	2 mean	1.70	5.0	19.0	6.5	1.17	440	17.0	36	598
	sd	0.14	0.0	11.3	3.5	0.08	42	5.7	13	75
4 (HSTP)	1	3.40	9.0	140.0	47.0	2.88	720	29.0	200	1300
5 (St. 1)	1	0.20	7.0	5.0	3.0	0.33	220	8.0	11	100
6 (Randle's Reef)	1	9.10	9.0	48.0	60.0	5.49	1500	20.0	1100	5100
Provincial Sediment	LEL	0.6	-	26	16	2	460	16	31	120
Quality Guidelines	SEL	10	-	110	110	4	1100	75	250	820

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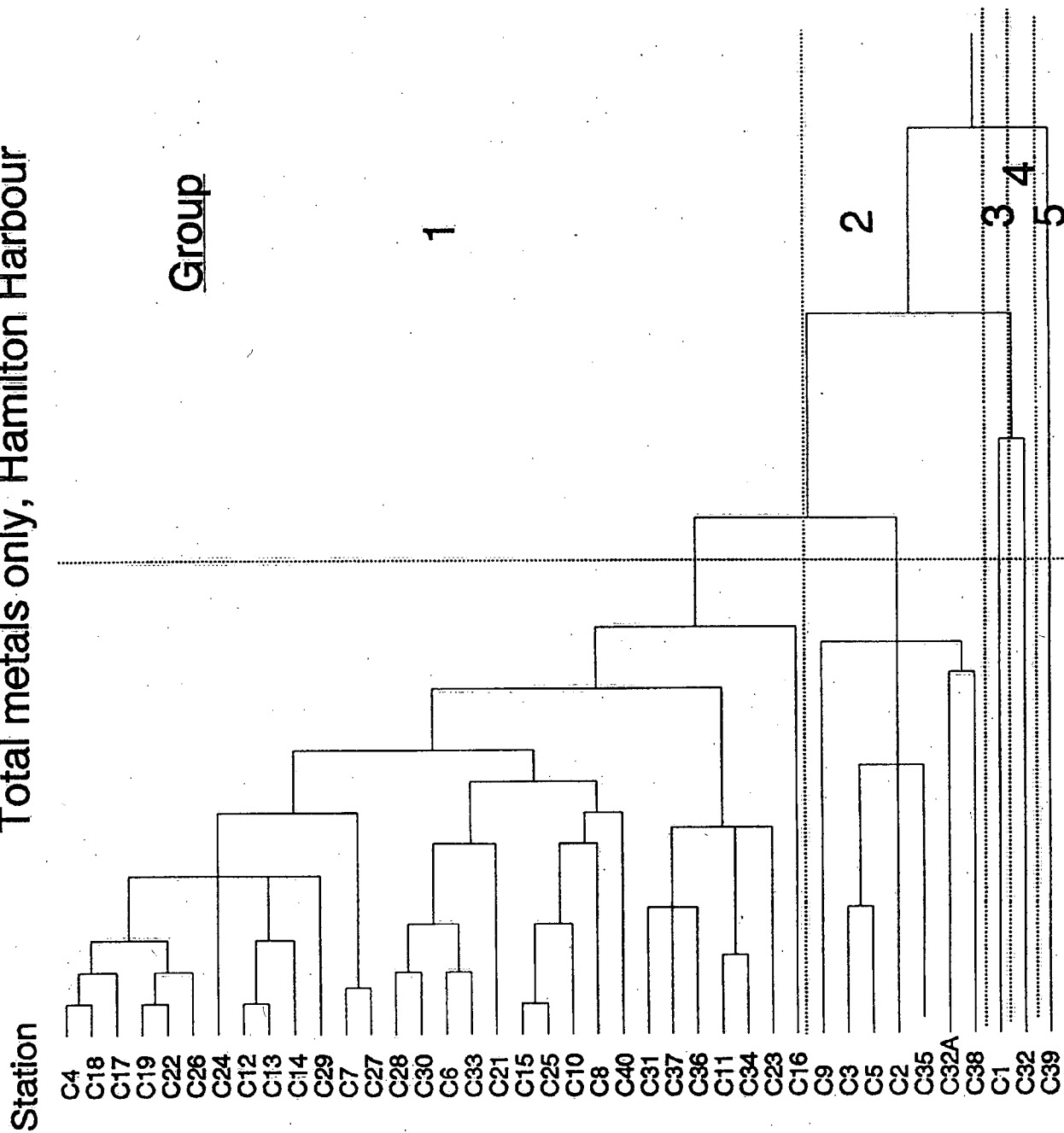


Hamilton



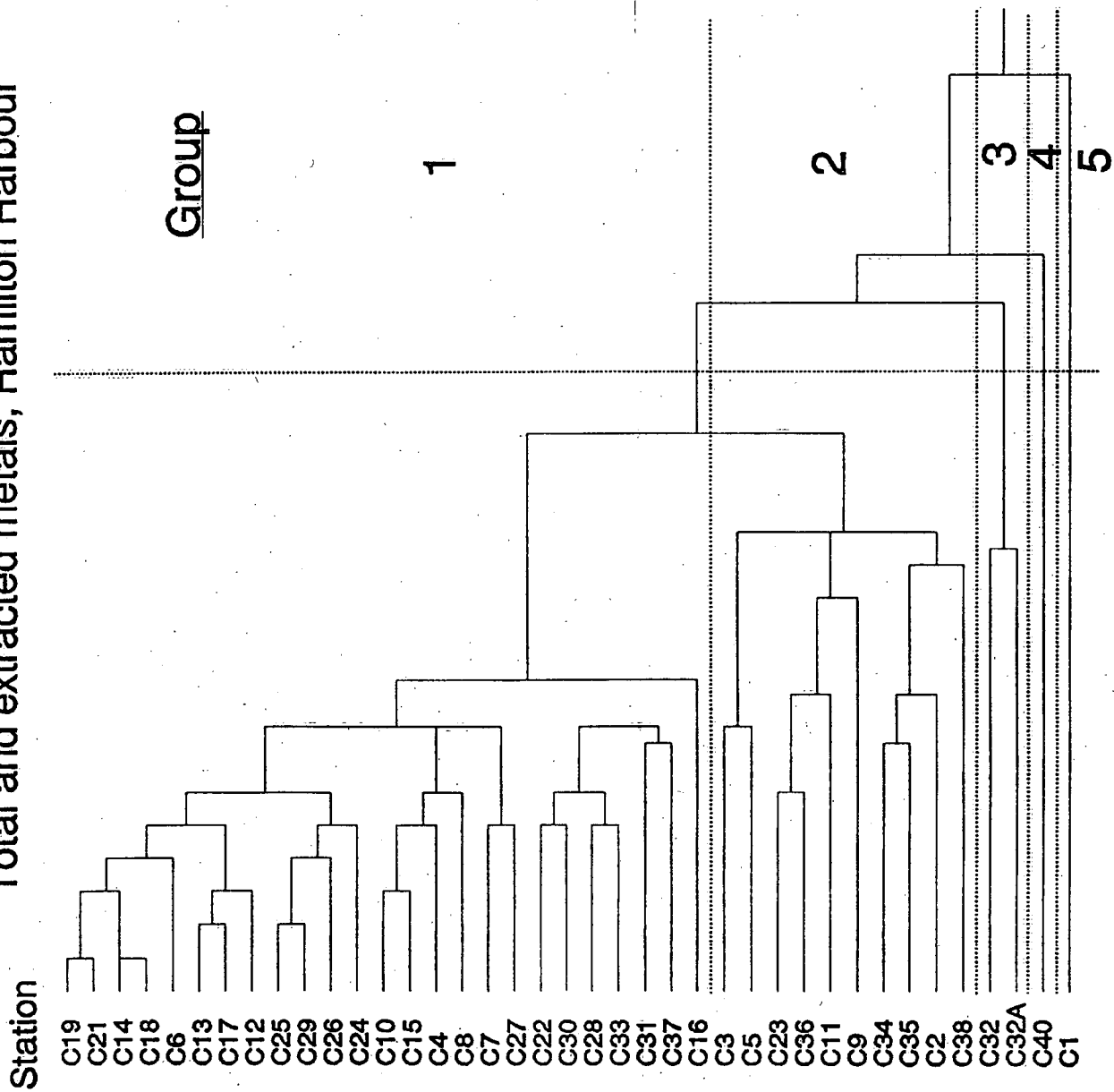
Average Linkage dendrogram, initial result

Total metals only, Hamilton Harbour



Average Linkage dendrogram, final result

Total and extracted metals, Hamilton Harbour



HAMILTON HARBOUR

Sediment Sampling

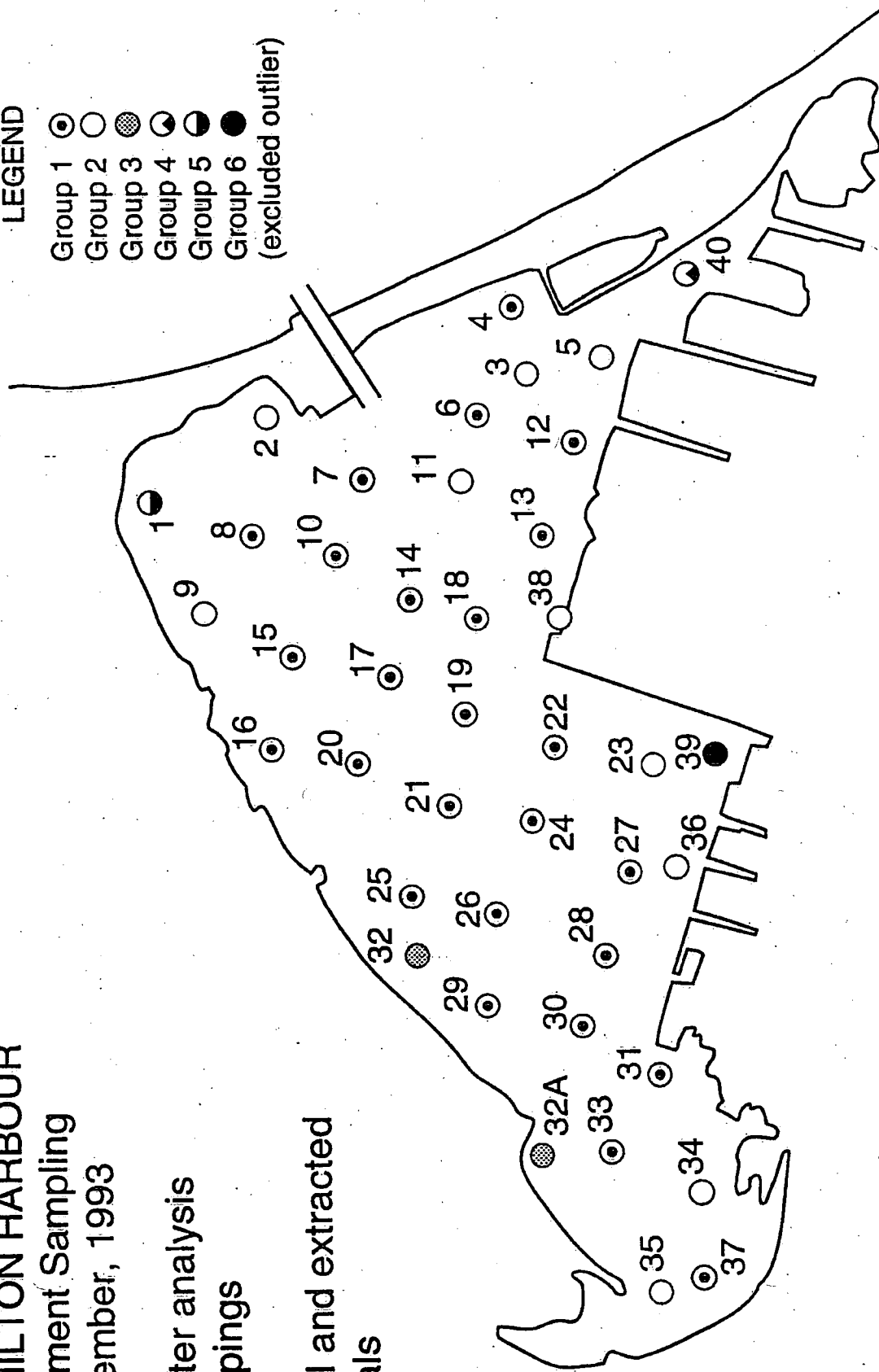
December, 1993

Cluster analysis
groupings

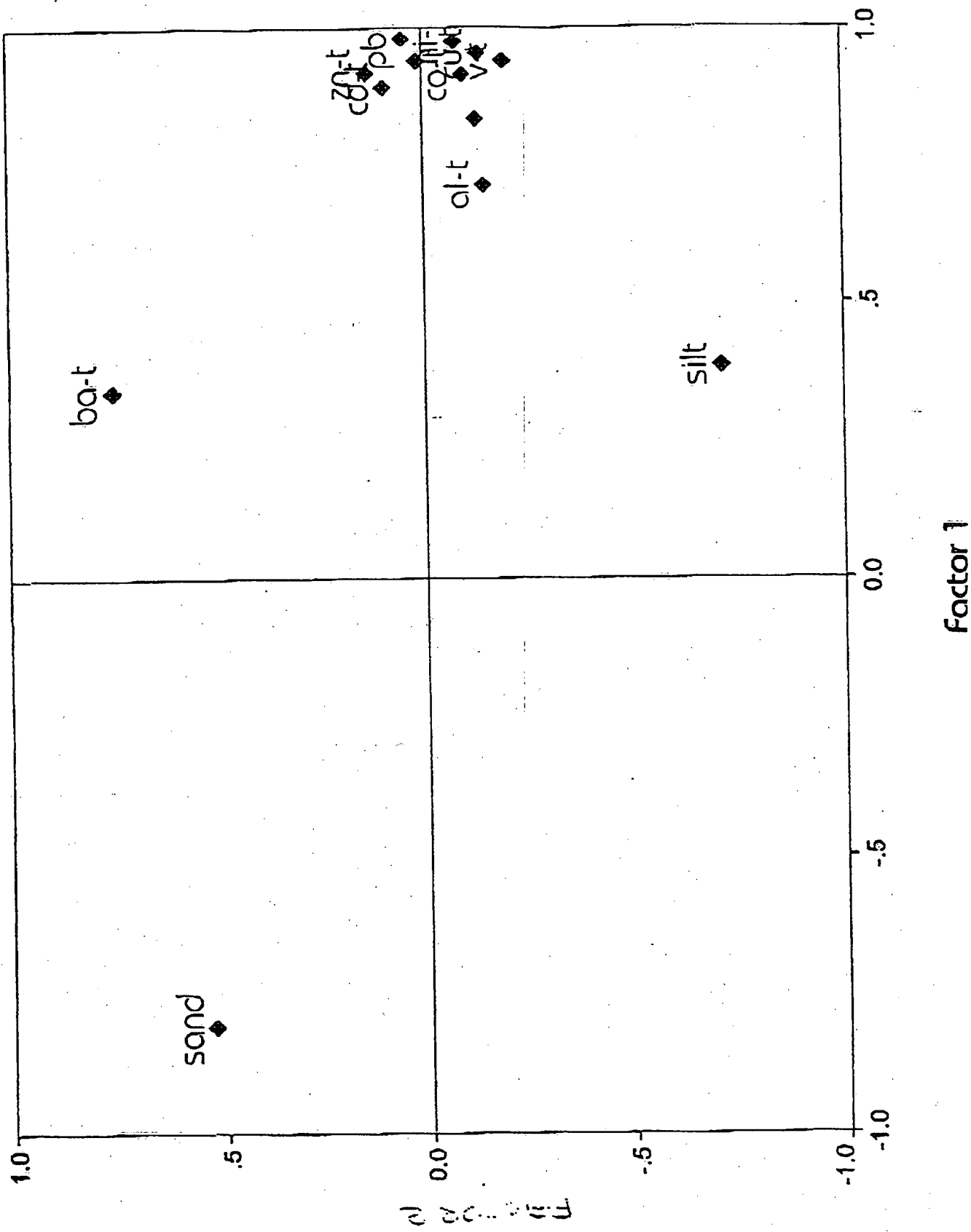
Total and extracted
metals

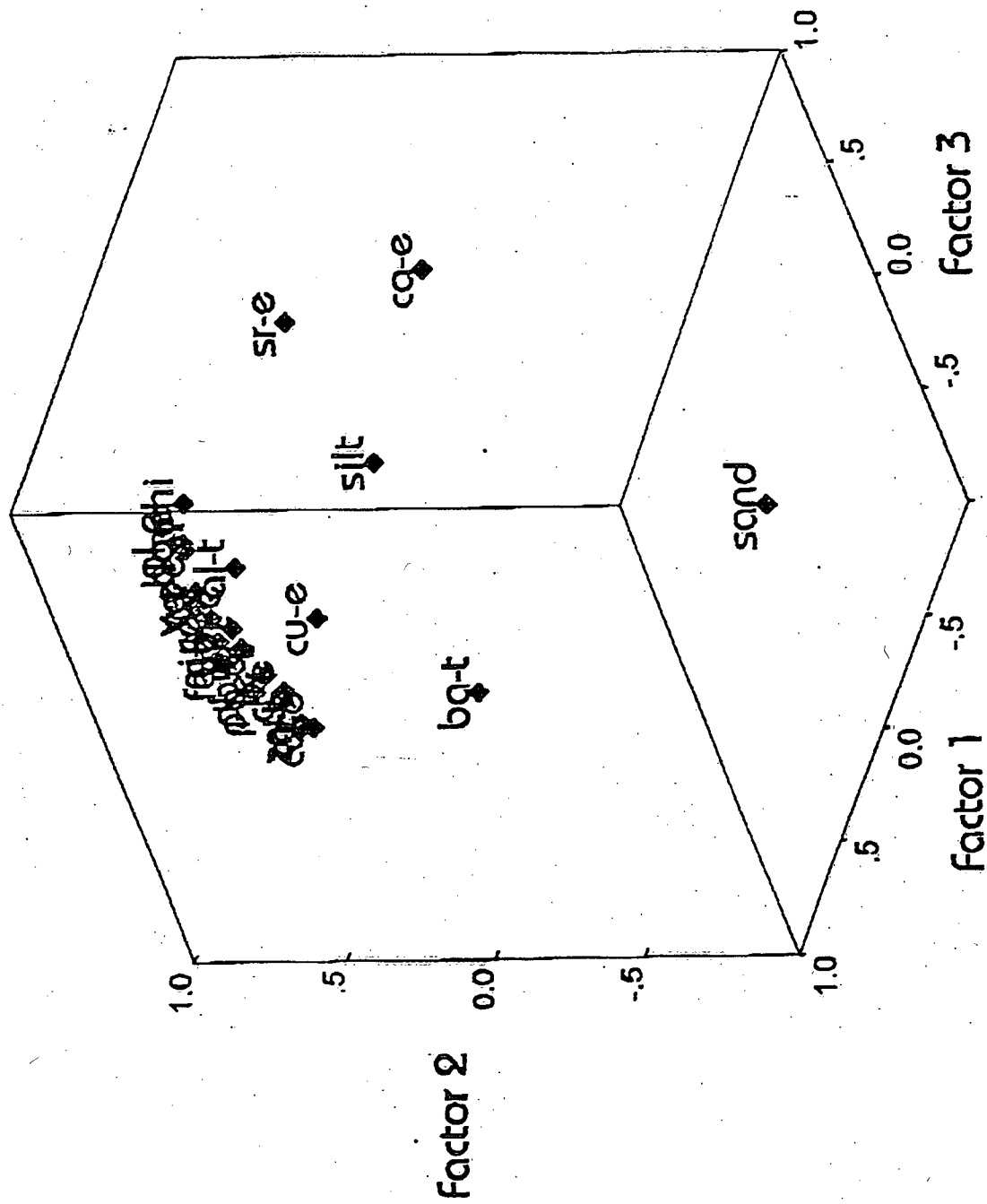
LEGEND

- Group 1 ○
- Group 2 ○
- Group 3 ●
- Group 4 ○
- Group 5 ○
- Group 6 ●
- (excluded outlier)



TOTAL METALS



[illegible]

97000N

4790000N



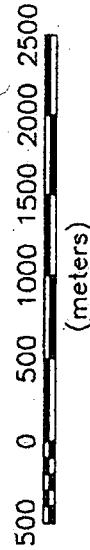
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595000E

590000E

Hamilton Harbour Factor 1

McMaster University Applied Geophysics Group



4797000

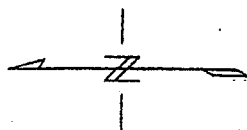
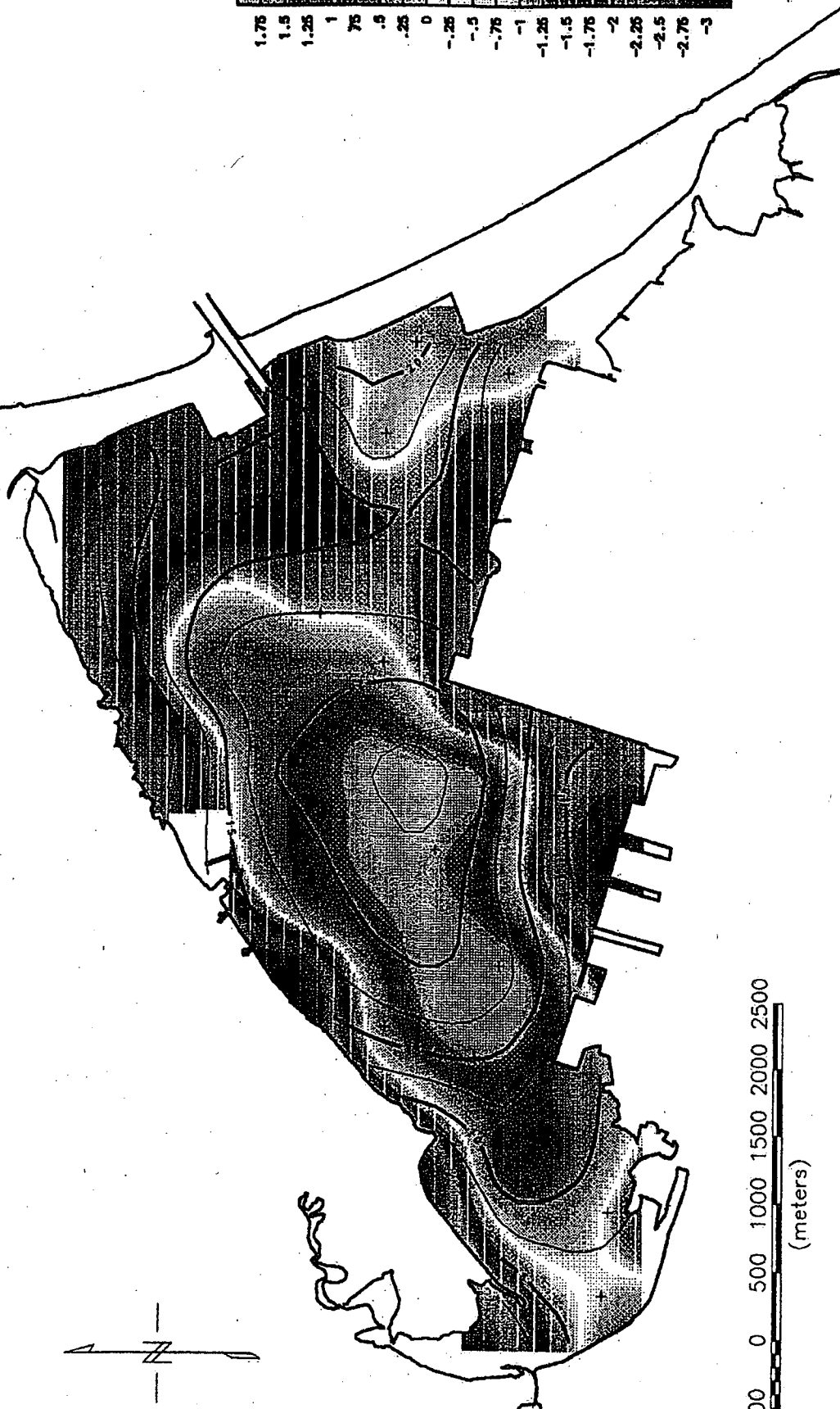
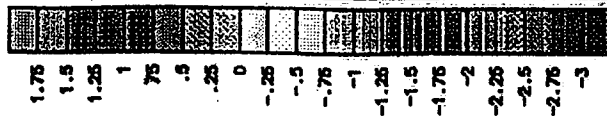
4790000N

4797000N

4790000N

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600000E



595000E

590000E

Hamilton Harbour
Factor 2

McMaster University Applied Geophysics Group

4797000N

4790000N

4797000N

4790000N

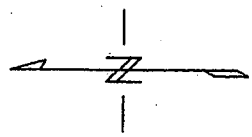


600000E

595000E

590000E

Hamilton Harbour
Factor 3
McMaster University Applied Geophysics Group



4797000

4790000N

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Environnement
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Canada Centre for Inland Waters

P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre

11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre

105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey

351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures

Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
L7R 4A6 Canada

Centre national de recherche en hydrologie

11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

Centre Saint-Laurent

105, rue McGill
Montréal (Quebec)
H2Y 2E7 Canada

Place Vincent-Massey

351 boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada