

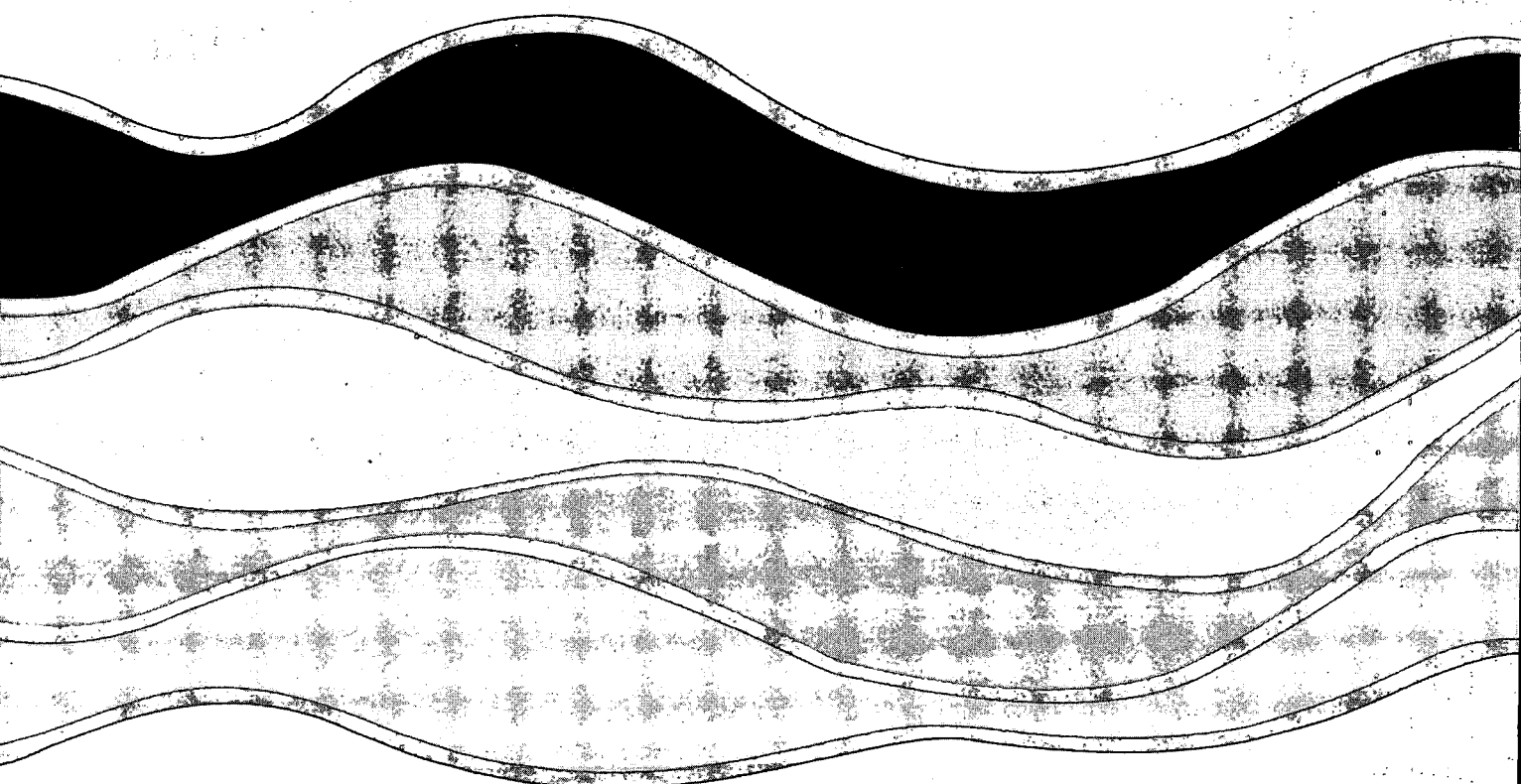
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**POLLUTION RANKING ANALYSIS AND  
DISTRIBUTION OF CHLOROBENZENES,  
PESTICIDES AND PCB ISOMERS IN  
LAKE ONTARIO OFF THE  
TORONTO WATERFRONT,  
MAY - OCTOBER 1987**

E. Halfon

NWRI Contribution No. 92-51

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**E. Halfon**

**National Water Research Institute  
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## MANAGEMENT PERSPECTIVE

The International Joint Commission has identified Toronto Harbour and Waterfront as an Area of Concern in the Great Lakes and this has lead to a combined federal and provincial effort to draw up a Remedial Action Plan (RAP). At the same time the Ontario Ministry of the Environment (OMOE) initiated its Municipal and Industrial Strategy for Abatement (MISA) program. The former activity examined conditions in the harbour and along the eastern and western waterfront while the latter program has focused on the assessment and control of pollution sources on land. There are four Sewage Treatment Plant (STP) effluent outfalls along the study area which are being evaluated by the MISA program. The study described in this report was co-funded by the National Water Research Institute and OMOE to assess the present extent of contamination of the nearshore zone by selected organochlorine compounds found in the STP effluents. This data will also serve as a baseline for evaluating the effectiveness of controls on chemical discharges to be promulgated by MISA in the near future.

This report presents concentration maps of 89 chlorinated organic chemicals found in samples collected in the lake along the Toronto waterfront area in spring, summer and fall of 1987. A novel ranking technique is used to analyze the overall pattern of chemical contamination. This ranking does not translate to an absolute risk scale for exposure to organochlorine compounds, but it identifies a number of contamination levels relative to this data set. Results show that the western waterfront, Humber Bay, the Inner Harbour, and areas near the Toronto Main STP discharge have the highest pollution rankings.

On several occasions, however, high rankings occurred offshore which indicate that other sources as well as the Toronto area could be contributing contaminants to the waterfront.

The pollution ranking technique used here could be applied to assess the effectiveness of pollution prevention initiatives in the Toronto area and assist in the Lake Ontario Toxics Management Plan.

## PERSPECTIVES DE LA DIRECTION

La Commission mixte internationale a désigné le port de Toronto et le secteur riverain comme secteur préoccupant dans les Grands Lacs; un Plan d'assainissement (PA) a donc été établi conjointement par les gouvernements fédéral et provincial. Au même moment, le ministère de l'Environnement de l'Ontario (MEO) mettait en oeuvre sa Stratégie municipale et industrielle de dépollution (SMID). La première initiative portait sur l'étude des conditions dans le port et le long des rives est et ouest tandis que la dernière était axée sur l'évaluation et la lutte contre les sources de pollution terrestres. Quatre exutoires d'effluents de stations d'épuration des eaux usées le long de la zone à l'étude sont évalués dans le cadre du programme SMID. L'étude décrite dans le présent rapport a été subventionnée conjointement par l'Institut national de recherche sur les eaux et le MEO afin d'évaluer l'ampleur actuelle de la contamination de la zone précôtière par certains composés organochlorés présents dans les effluents des stations d'épuration des eaux usées. Ces données serviront également de ligne de référence pour l'évaluation de l'efficacité des mesures de réduction des rejets de produits chimiques qui seront bientôt publiées par le SMID.

Le présent rapport contient des cartes de concentration de 89 produits chimiques organochlorés présents dans des échantillons prélevés dans le lac, le long du secteur riverain de Toronto, au printemps, à l'été et à l'automne 1987. Une nouvelle technique de classement est utilisée pour analyser le profil général de contamination chimique. Ce classement ne se traduit pas par une échelle de risque absolu d'exposition à des composés organochlorés, mais il détermine un certain nombre de niveaux de contamination relatifs à cet ensemble de données. D'après les résultats, le secteur riverain ouest, la baie Humber, le Inner Harbour et les régions à proximité du rejet de la station

principale d'épuration des eaux usées de Toronto se classent parmi les secteurs les plus pollués.

À plusieurs reprises, cependant, des zones au large se sont classées parmi les plus polluées, ce qui indique que d'autres sources aussi bien que la région de Toronto pourraient polluer le secteur riverain.

La technique de classement appliquée ici pourrait servir à évaluer les initiatives en matière de prévention de la pollution dans la région de Toronto et contribuer au Plan de gestion pour les toxiques dans le lac Ontario.

## ABSTRACT

This report presents concentration charts of 89 organochlorine compounds (25 compounds, including chlorobenzenes, pesticides, and PCBs (total + 64 PCB isomers)) found in Lake Ontario along the Toronto Waterfront area in late spring, summer and fall of 1987. A novel ranking technique is used to analyze the pattern of chemical contamination. The classification of polluted areas is relative, i.e., the ranking considers only the relative contamination by all chemicals at the 29 stations sampled during the three cruises. This ranking does not translate directly to absolute risk scale for exposure to these chemicals but it identifies a number of contaminant levels relative to a data set. The procedure discriminated between nine levels of contamination in this data set. Results show that the western waterfront, Humber Bay, the Inner Harbour, and areas near the Toronto Main Sewage Treatment Plant discharge were always at the sixth level or higher. While nearshore areas were usually ranked higher than offshore areas, some offshore areas were occasionally high in their ranking. As the water mass along the Toronto Waterfront is exchanged within seven days with water from offshore, the open lake can be a contaminant source to the waterfront. These open lake concentrations are maintained by inputs from the atmosphere, the lake sediment, the Niagara River and other tributaries as well as the sources identified along the Toronto Waterfront.

## RÉSUMÉ

Le présent rapport contient des graphiques de concentration de 89 composés organochlorés (25 composés, y compris des chlorobenzènes, des pesticides et des BPC (totaux + 64 isomères des BPC) présents dans le lac Ontario, le long du secteur riverain, à la fin du printemps, à l'été et à l'automne 1987. Une nouvelle technique de classement est utilisée pour analyser le profil de contamination chimique. La classification des zones polluées est relative, c'est-à-dire que le classement ne prend en compte que la contamination relative par tous les produits chimiques aux 29 stations échantillonnées au cours des trois campagnes d'étude. Ce classement ne se traduit pas directement en une échelle de risque absolu d'exposition à ces produits chimiques, mais il détermine plusieurs niveaux de contamination par rapport à un ensemble de données. La méthode a établi une distinction entre neuf niveaux de contamination dans ce jeu de données. D'après les résultats, le secteur riverain ouest, la baie Humber, l'Inner Harbour et les régions à proximité du point de rejet de la station principale de traitement des eaux usées se trouvait toujours au sixième niveau ou à un niveau plus élevé. Alors que le niveau de contamination des zones précôtières étaient en général plus élevé que celui des zones du large, le niveau de certaines régions du large était parfois plus élevé. Comme l'échange entre la masse d'eau le long du secteur riverain de Toronto et l'eau du large s'effectue en moins de sept jours, les eaux libres peuvent être une source de contamination pour le secteur riverain. Ces concentrations en eau libre sont maintenues par des apports atmosphériques, les sédiments lacustres, la rivière Niagara et d'autres affluents ainsi que par les sources reconnues le long du secteur riverain de Toronto.

## SUMMARY

This report presents an analysis of contaminants found in Lake Ontario waters off the Toronto Waterfront area during spring (May-June), summer (July-August) and fall (October) 1987. The spatial distribution of 89 chemicals (25 contaminants and 64 PCB isomers) has been plotted for the first time. Since the information contained in 271 figures is difficult to comprehend at a glance, a ranking method is used to classify the different areas of the Toronto Waterfront (Figs. i-iii). Zones that have a high ranking indicate that many different contaminants are found simultaneously in the same location while regions with a low ranking indicate that few contaminants are found concurrently. Therefore these latter zones are relatively clean. The presence of many chemicals, in different concentrations in the waters off Toronto, offers the challenge of classifying the areas near Toronto without disregarding the information about the pollutants present in low quantities. The classification of polluted areas is relative, i.e., the ranking considers only the relative pollution of the 29 stations sampled in Lake Ontario during the three cruises in 1987. This ranking does not translate to a quantitative risk for particular exposure but it represents the co-occurrence and relative concentrations of contaminants in a given area. Figures i, ii and iii show the areas where most contaminants are found simultaneously and also the idealized plumes of pollution. These plumes depict the relative concentrations and constituent mixtures of contaminants for the three surveys.



Results show that Humber Bay and the Eastern Beaches, near the outfall of the Toronto Main STP, are relatively the most polluted. A variety of contaminants impact on specific areas of the waterfront. Less impacted areas are significantly cleaner. Impacted areas are identified by a high ranking, 7 or 8, while less impacted areas have a lower rank. For a description of the method used for ranking see the main text.

Figures i, ii and iii, below, show that even if minor differences exist, the pattern of pollution is the same and that contaminants from the main body of the lake impact the Toronto Waterfront too. The waterfront area is polluted not only by local sources but significantly by contaminants present in Lake Ontario. Thus, even if all local sources of pollution were removed, lake waters in the Toronto Waterfront area would be impacted by other sources, mainly the Niagara River. This report points out areas of the waterfront that were affected by local sources of pollution in 1987. In general, the most contaminated sites are Humber Bay, the area near the discharge of the Toronto Main Sewage Treatment Plant (STP), the Inner Harbour, shallow bays and some nearshore areas where water exchanges with open lake waters is slow.

Several points must be pondered while appraising the information presented in this report: a) consumption of fish from Lake Ontario is a more significant route of human exposure to toxic chemicals in the lake, with respect to potential impact on human and ecosystem health, than drinking the water or swimming in it; b) some contaminants, such as the low chlorinated benzenes, e.g.,

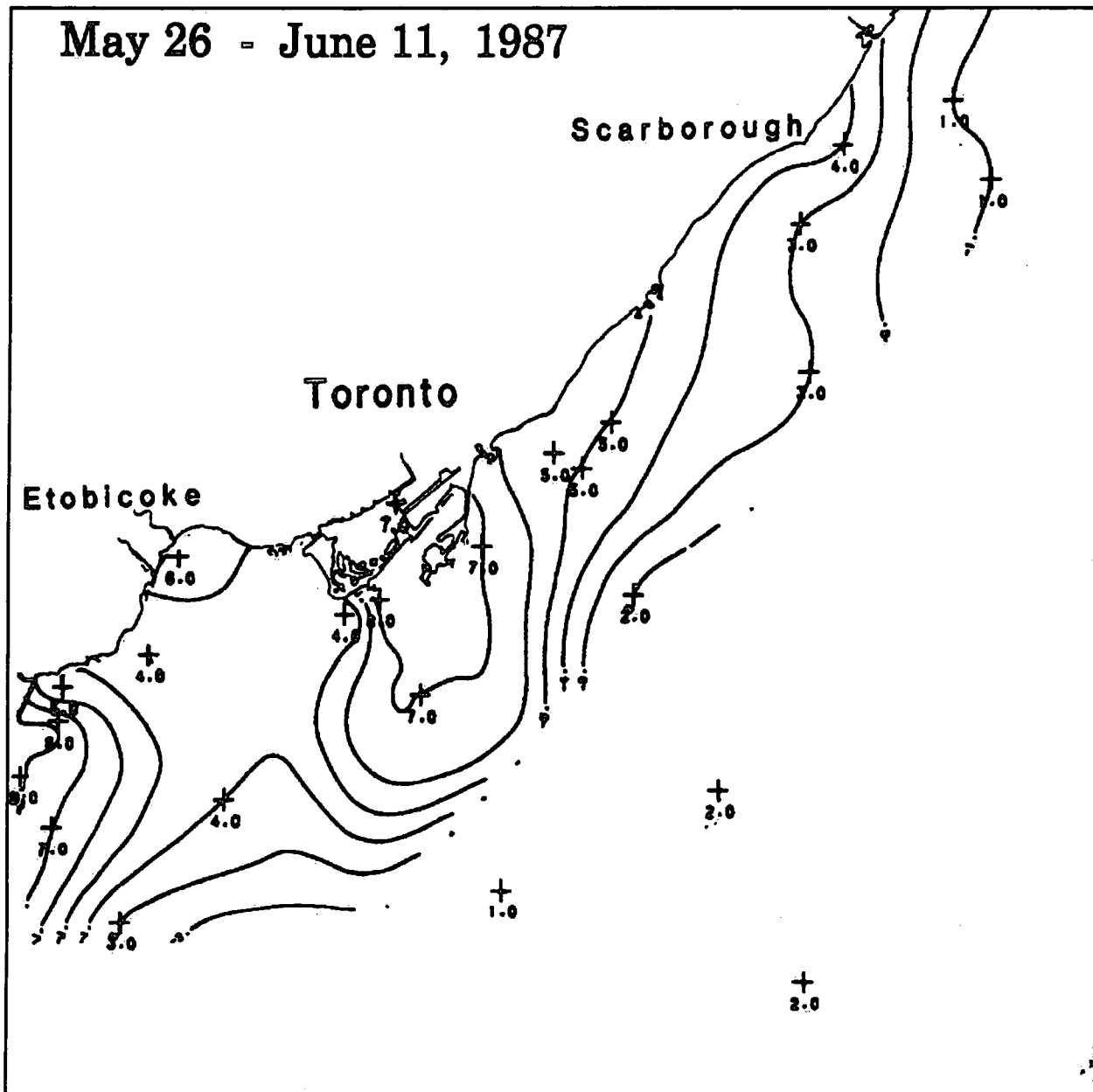


Figure i: The two most polluted areas are located on the western zone of the Toronto Waterfront and near the Lakeview STP station (rank 4 or higher). The offshore areas of the Lake and the Scarborough Bluffs are ranked at level 2 or lower.

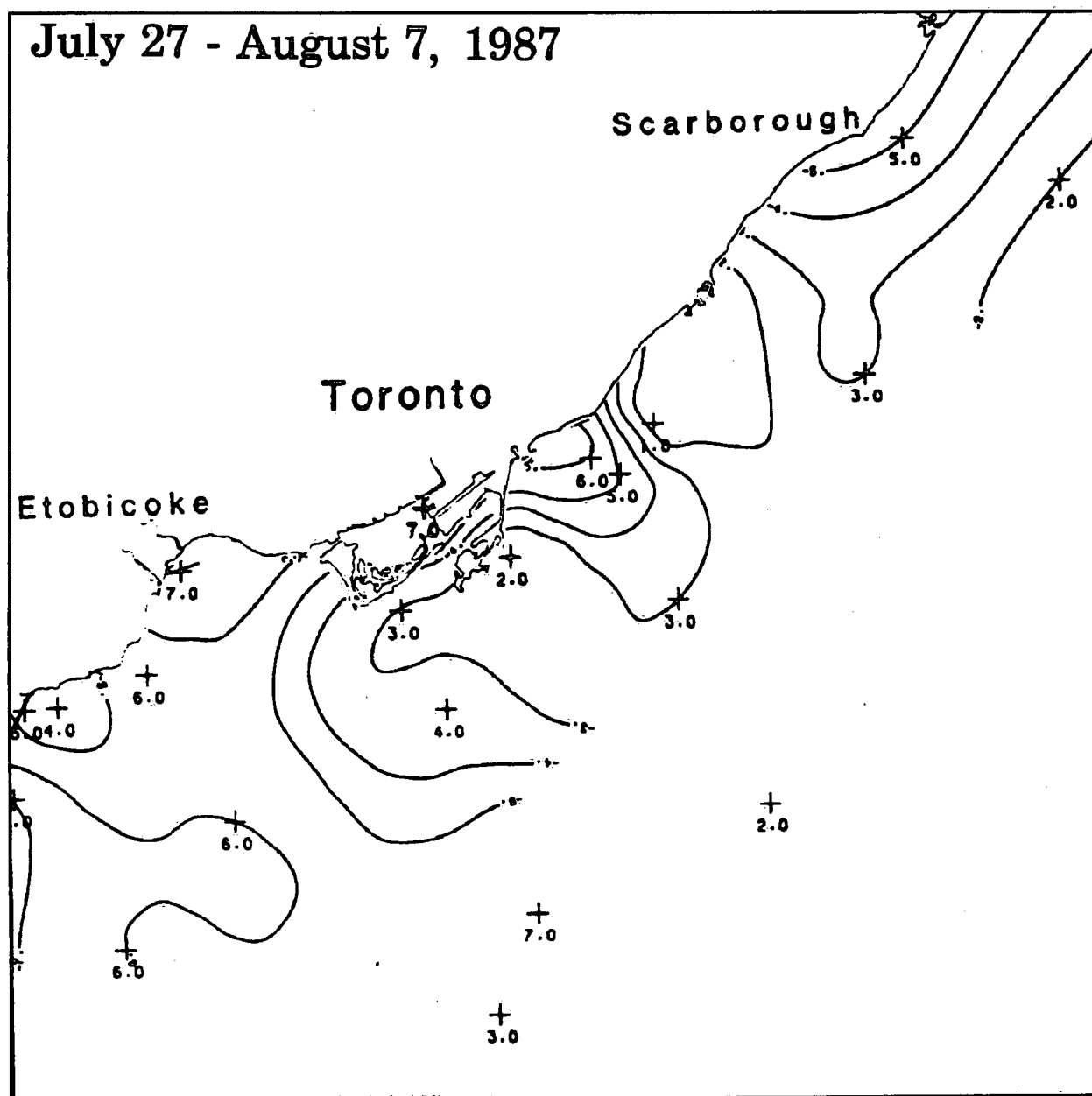


Figure ii: The pattern of pollution is similar to that one observed in May-June. The impact plume off the Toronto Harbour has shifted toward the eastern beaches while the plume in Humber Bay is practically unchanged.

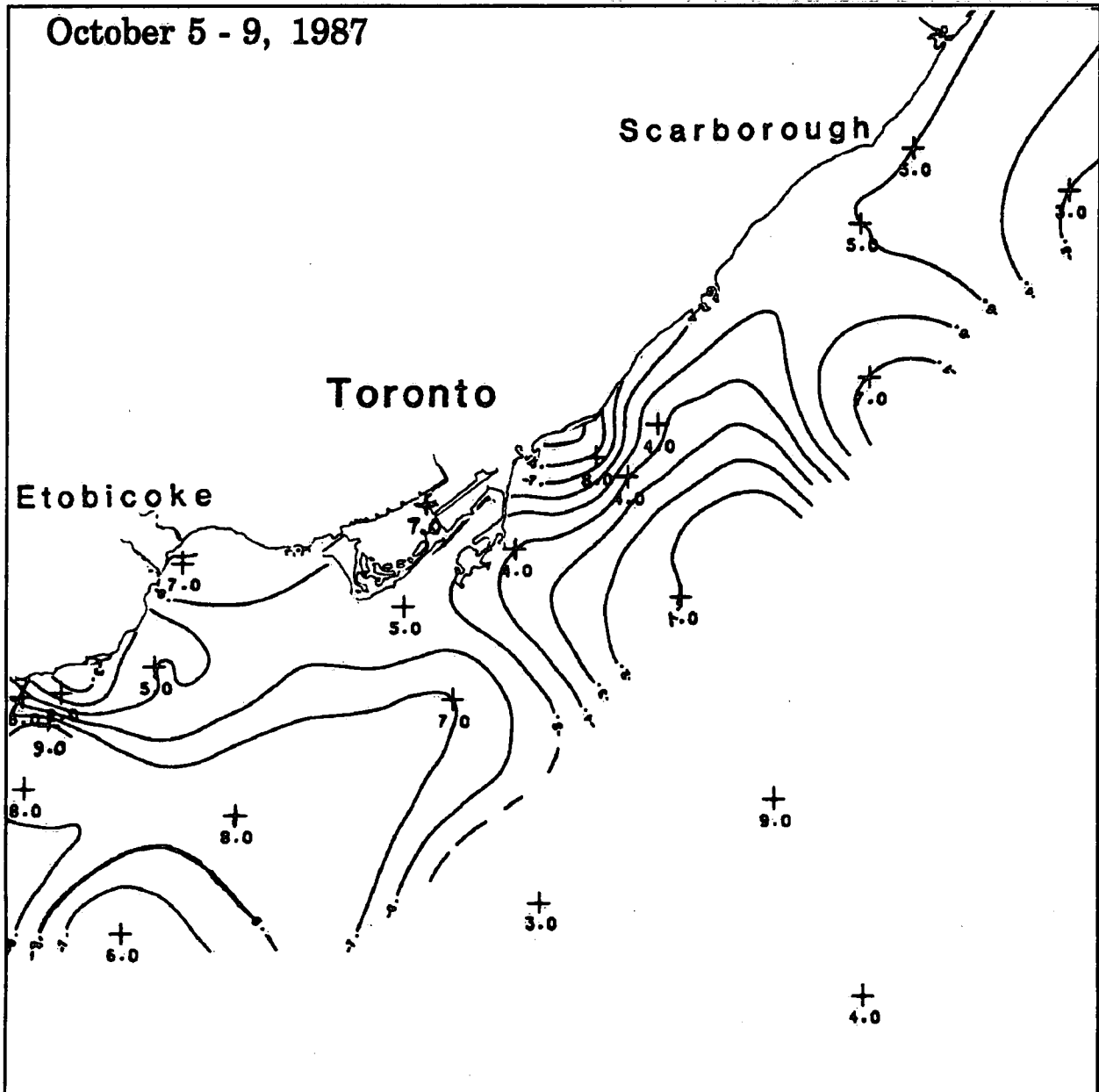


Figure iii: In October the same areas, identified in the previous two cruises as polluted, are impacted by local sources. Off the eastern beaches, hypolimnetic waters (Fig. 4) lower the impact by toxic contaminants from shore.

1,4-dichlorobenzene (1,4-DCB), from local sources near Toronto, are about 25% of the low chlorinated benzenes that enter Lake Ontario from the Niagara River; thus, for some chemicals Toronto is a significant source, c) total PCBs enter Lake Ontario mostly from the atmosphere and from the Niagara River; local sources are minimal; and d) Lake Ontario receives most of its pollutants from industry and waste dumps located near the Niagara River.

### The ranking method

The ranking method is based on the hypothesis that a set of numbers, here contaminant concentrations, is necessary to create a ranking file; these numbers can be considered as the elements of a vector, the "vector performance" or "vector distance". This "vector approach method" is different from the "scalar approach method", where a single number (a scalar performance index) is said to be sufficient to interpret the data, to compare sites, and rank them. Results are displayed using Hasse diagrams, a graph commonly used in lattice theory. Each station is located at a given level in the diagram. Stations near the top of the diagram are affected by a greater number of contaminants and their relative concentrations than stations near the bottom of the diagram. These levels are relative and the ranking refer only to the stations analyzed in this report. A section of the report is dedicated to the explanation of Hasse diagrams. The data to be analyzed can either be raw data or data classified into categories. This second option is chosen here since small differences in concentrations,

for example between 0.01 and 0.07 ng/L, are indistinguishable in terms of hazard. For this purpose the data are divided into three groups according to a logarithmic scale of concentrations [ $<0.1$  ng/L (including detection limits);  $0.1 \text{ ng} - 1 \text{ ng/L}$ ;  $>1 \text{ ng/L}$ ].

### Spatial distribution of the contaminated areas

Figures i to iii show charts of the Toronto Waterfront. Here stations located on the same level in the Hasse diagram (for example, see Fig. iv) are joined by an isopleth.

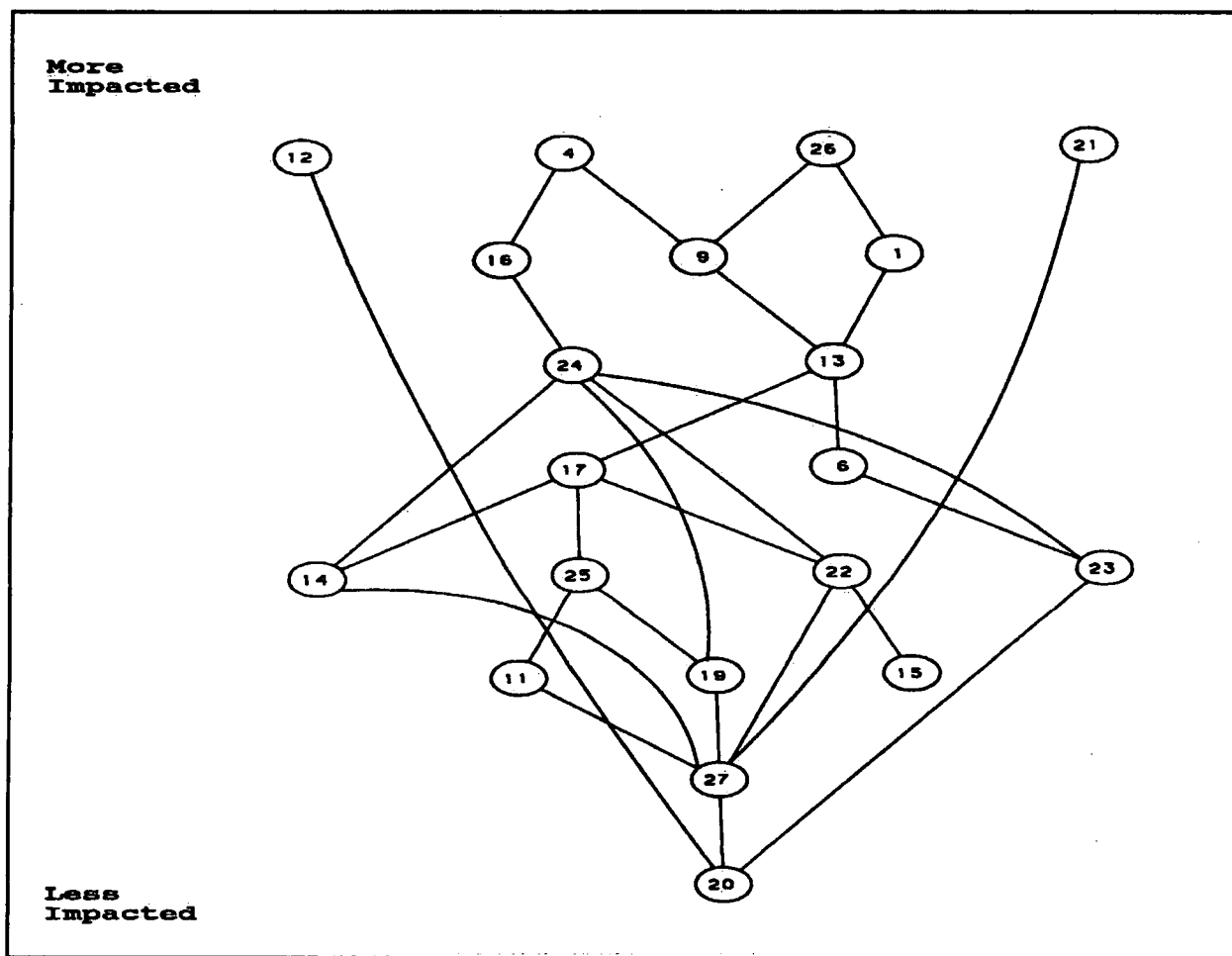


Figure iv: Twenty-six sites have been ranked according to the concentrations (criteria) of all chemicals present at that station. Circles represent the sites and labels are defined in Table 1.

In May-June 1987 we note two areas of impact by toxic contaminants; one located in the western zone of the Toronto Waterfront, namely Humber Bay and the Toronto Harbour, and one located near the Highland STP outfall. These stations are ranked at level 4 or higher. The offshore areas of the lake and the Scarborough Bluffs are ranked at level 2 or lower. In this area the water temperature (Fig. v) is low and contaminants might have been diluted in cleaner cooler hypolimnetic waters.

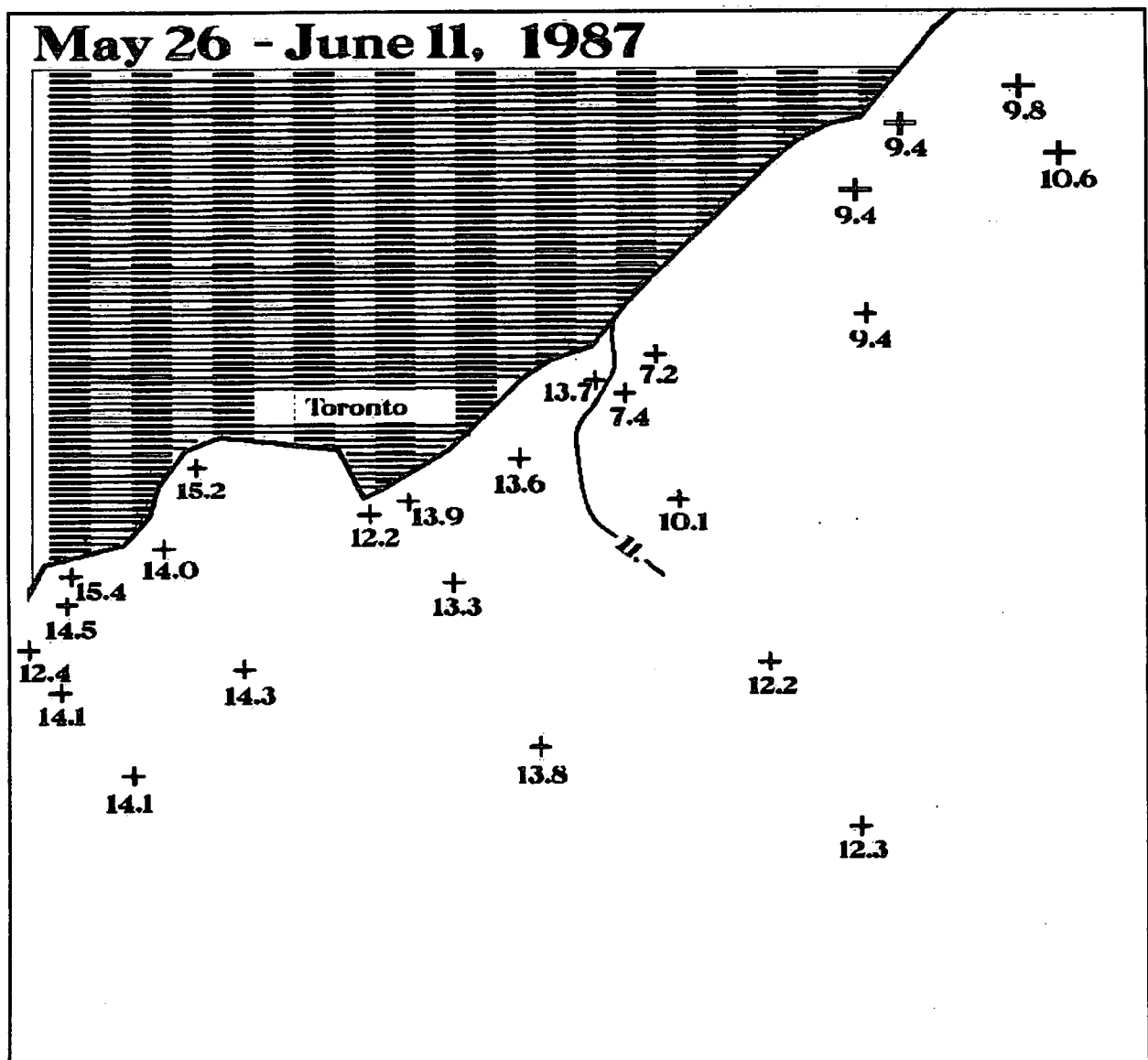


Figure v: Surface water temperature (in °C).

In July-August (Fig. vi) the pattern of pollution is similar to that one observed in May-June. During this survey, the contaminant plume off the Toronto Main STP trends toward the eastern beaches while the plume in Humber Bay is practically unchanged. Impacted zones occur in the east off Scarborough and at one station (#2889) offshore.

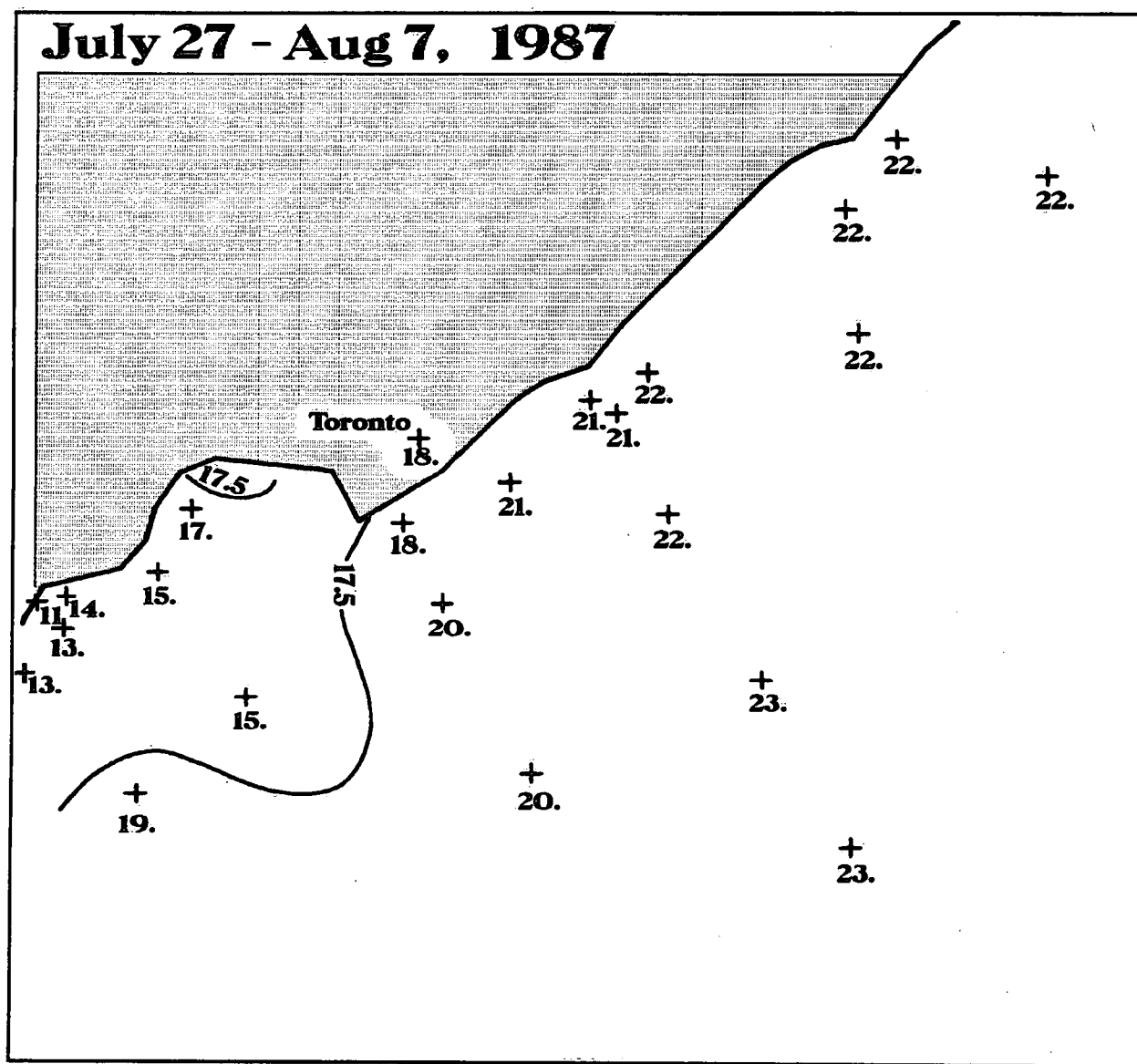


Figure vi: Surface water temperature (in °C).



Overall the whole waterfront has higher ranking than the open waters. In October (Fig. vii) the same impacted areas identified in the previous two cruises are present. Off the Eastern Beaches, hypolimnetic waters ( $<5^{\circ}\text{C}$ ; Fig. vii) lower the impact of local sources since pollutants in the lake are more diluted and at lower concentrations than nearshore.

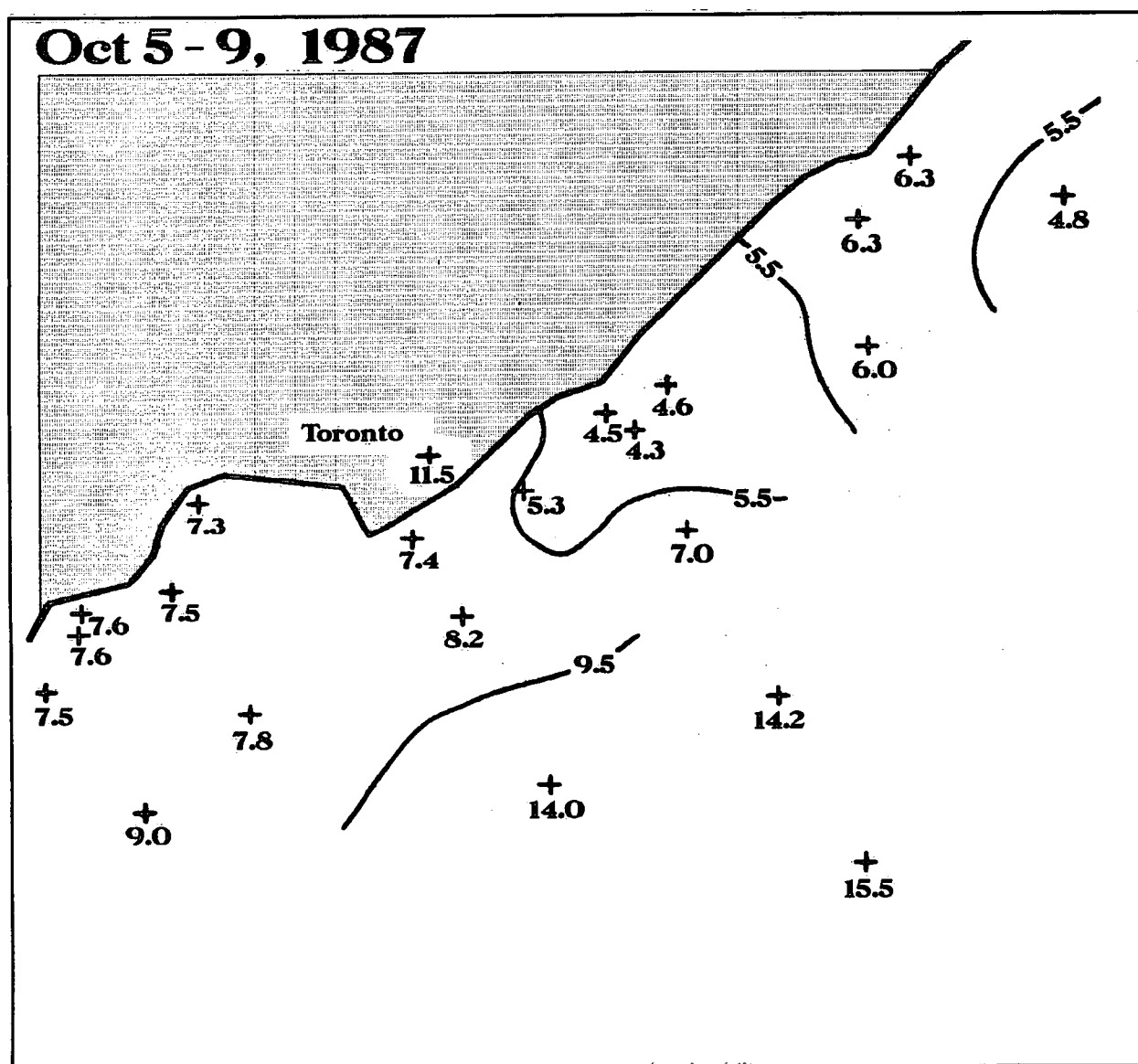


Figure vii: Surface water quality (in  $^{\circ}\text{C}$ ).

Toxic contaminants and water masses

Water concentrations of most contaminants are quite low and uniform. Local sources of pollution with resulting concentrations higher than 1 ng/L have been identified only for 1,4-DCB (in May-June and July-August only), 1,2-dichlorobenzene (1,2-DCB) and total PCBs. These higher concentrations are most evident in Humber Bay. The specific location of their sources, however, can not be pointed out by sampling only lake waters. In 1987 the Ontario Ministry of the Environment collected samples in rivers and at the end of STP effluents, and these data provide some information with regard to sources.

A correlation analysis between water temperature and contaminant concentrations (see Table 6 in the main text) points out possible local sources of other contaminants, namely in May-June, 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), hexachloroethane (HCE), lindane and the PCB isomers PCB-18, PCB-118 and PCB-138; in July-August 1,4-DCB, 1,2,4-trichlorobenzene (1,2,4-TCB), HCB (hexachlorobenzene), 2,3,6-trichlorotoluene (2,3,6-TCT), lindane, gamma-chlordane, pp'-DDE, pp'-DDD and the three isomers PCB-18, PCB-99 and PCB-153-132; in October, 1,2,3-TCB, 1,2,3,4-TeCB, pentachlorobenzene (QCB) and pp'-DDD. The concentrations of these contaminants in the receiving waters are quite low, <1 ng/L, and therefore the evidence from the correlation analysis is only circumstantial. Furthermore, the contaminant pattern varies with the sampling time, which points to intermittent sources of pollution.

Alpha-BHC is present in Lake Ontario at relatively high concentrations of 4-6 ng/L. This contaminant was observed uniformly distributed at concentrations far higher than all other contaminants and was not correlated with water mass temperatures. Lindane, total PCBs and occasionally the dichlorobenzenes were present in concentrations close to 1 ng/L.

The spatial patterns identified by the ranking analysis are fairly independent of water temperature conditions. The impact plumes change seasonally but the basic pattern does not change much. Humber Bay, Toronto Harbour and the area near the Toronto Main STP are the zones most impacted by toxic contaminants followed by an area in the east end near the Highland STP.

The Toronto Waterfront is part of Lake Ontario and therefore contaminant concentrations nearshore are affected both by local and remote sources. Our calculations show that the waters of the Toronto Waterfront have a mean residence time of six to seven days. Thus the Lake Ontario circulation is prominent in determining baseline levels of contaminants. If local shore sources were controlled or eliminated, concentrations of certain contaminants in the water, suspended sediments and plankton would diminish quickly to the levels of the main body of the lake. However, contaminant concentrations in fish, benthos and bottom sediments would decrease at a much slower rate if loadings were stopped since they retain contaminants. Because some contaminants (e.g., PCBs) have significant sources elsewhere there may not be much change.

### Temporal trends

The spatial distribution of individual contaminants changed seasonally. Some contaminants, like the dichlorobenzenes, were present in large concentrations in May-June and July-August but disappeared almost completely in October. Others, like the isomer PCB-1, were not present in May-August but were present in low concentrations in October.

Even if individual concentrations of contaminants change seasonally the overall pattern of pollution (as shown by the ranking analysis, Figs. i-iii) does not change substantially. Temporal trends are studied in more detail with mathematical modeling techniques in a companion report (Halfon ,1990).

### Comparison of results with existing guidelines/water quality objectives

The Ontario provincial water quality objective (PWQO) for total PCBs of 1 ng/L is exceeded in many locations of the Toronto Waterfront. The three dichlorobenzenes, alpha-BHC and Lindane are observed in concentrations of 1 - 5 ng/L. The three dichlorobenzenes and lindane have higher PWQO (lindane is 10 ng/L, 1,2-DCB and 1,3-DCB are 2500 ng/L and 1,4-DCB is 4000 ng/L) and therefore their concentrations are not considered to be crucial from an immediate ecosystem health perspective.

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## INTRODUCTION

In May-June, July-August and October 1987 the National Water Research Institute (NWRI) undertook an extensive fixed grid survey (Fig. 1) in Lake Ontario encompassing the entire Metro Toronto Waterfront area from Etobicoke to Scarborough. This project took

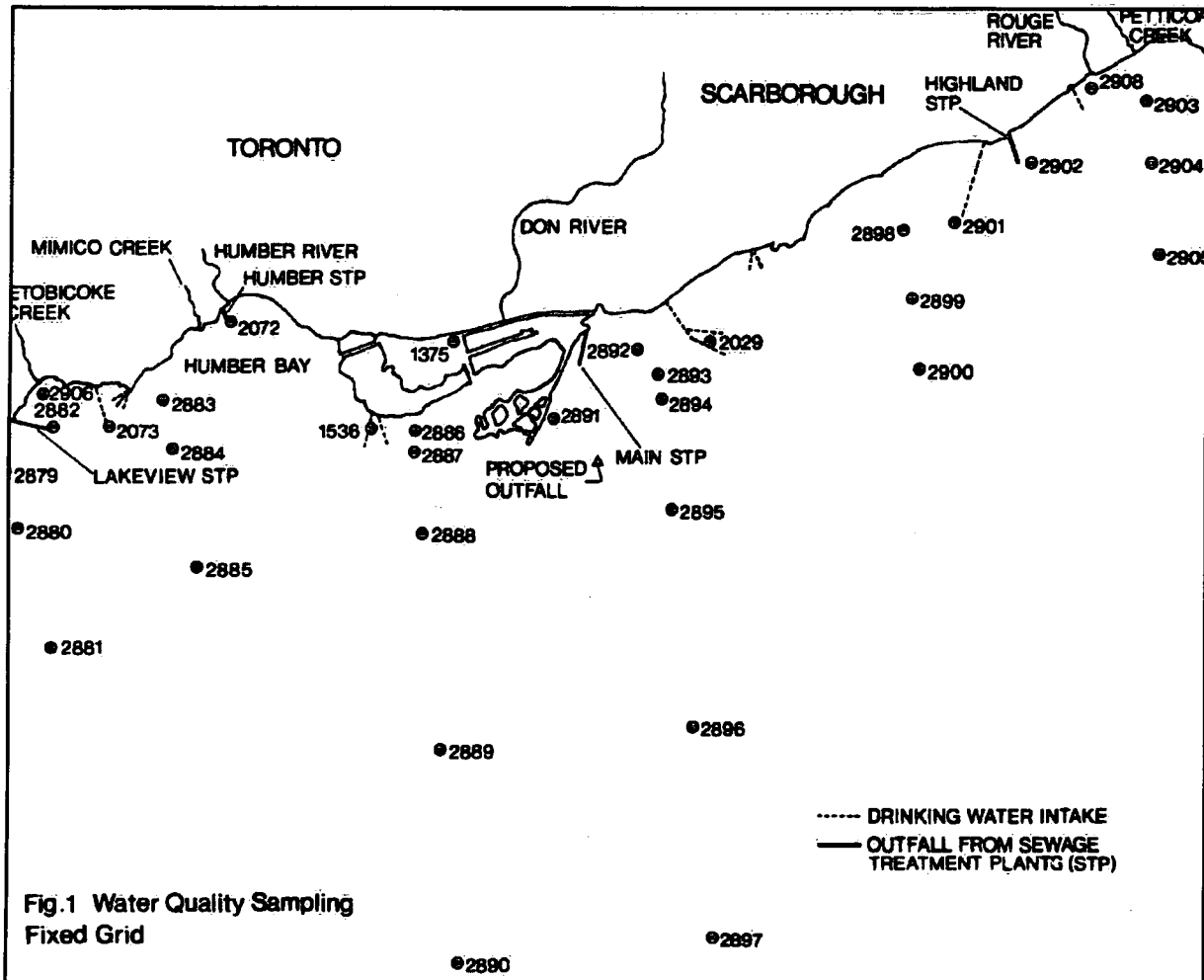


Figure 1: Station locations off the Toronto Waterfront in 1987.

place in support of both the Toronto Main Sewage Treatment Plant (STP) Municipal Industrial Strategy for Abatement (MISA) pilot area study and the Toronto Waterfront Remedial Action Plan (RAP). The purposes of this research are:

- (a) to provide a baseline data on toxic contaminant concentrations across the entire Metro Toronto Waterfront in support of the Toronto RAP and Toronto MISA pilot site project;
- (b) to update water quality zonation in the Toronto Waterfront;
- (c) to provide inputs for an organic contaminant modeling study;
- (d) to identify the relative contribution of Toronto sources and the Niagara River to organic contaminant pollution in the Toronto Waterfront; and
- (e) to verify the concern that Toronto drinking water might contain toxic pollutants that enter the lake from nearby rivers and the STPs.

This report presents results on the first two objectives. A companion report (Halfon, 1990) analyzes the last three and Gore and Storrie (1989) have developed a hydrodynamical model of the Toronto Waterfront to study current movements.

#### Toxic contaminants in Lake Ontario

Large amounts of toxic contaminants enter Lake Ontario from the Niagara River, thus, lake waters contain measurable concentrations of hundreds of toxic pollutants. Nevertheless, concerns exist that the local input of toxic pollutants may result in Toronto drinking water containing contaminants in concentrations higher than the average in Lake Ontario. To this end the National Water Research Institute (NWRI) and the Ontario Ministry of the Environment (MOE) in 1987 organized three cruises to sample the nearshore waters off Toronto as well as other sources. These

samples were analyzed by two independent laboratories (Eli-Eco Laboratories, Rockwood, Ontario and Zenon Laboratories, Burlington, Ontario) for the presence of toxic organic contaminants including chlorobenzenes, pesticides, mirex and total PCBs, including 64 PCB isomers.

Three sets of results are presented: (a) a set of 267 charts included in an Appendix (three cruises x 89 chemicals made up of 25 contaminants and including 64 PCB isomers) showing the concentrations of contaminants in Lake Ontario waters near Toronto; (b) three charts, each summarizing the results of the May-June, July-August and October cruises; and (c) an analysis of the relations between water masses, identified by their temperature, contaminant concentrations and possible sources. Water quality zonation is particularly challenging and is solved with the application of ranking technique (Halfon and Reggiani, 1986).

#### The ranking procedure

The 267 charts contain a large amount of detailed information difficult to comprehend by standard tabulation and isopleth mapping. For this purpose a ranking technique (described below), has been used to summarize the relative contaminant concentrations of all 25 contaminants, using one chart for each cruise (Figs. 8-10 below), in idealized composite plumes. A composite plume summarizes the concentration plumes of all contaminants. For each cruise the stations have been classified following the methods of Reggiani and Marchetti (1975), Halfon and Reggiani (1986) and



Halfon (1989). All stations at the same level have been connected with a line. The result is an idealized plume which shows the most polluted areas taking into account the concentrations of all 25 pollutants. A full discussion of the meaning of Figs. 8-10 takes place in the Results section.

#### METHODS

Three cruises took place on May 26-June 11, July 27-August 7 and October 5-7; Table 1 and Figure 1 show the locations of all 29 stations. Two ships were used for data collection. The Advent, a small ship, could only work during daylight hours, and collected three to four samples a day. Thus, on average, each of the first two cruises took two weeks. The Limnos, a large ship, collected water samples on the last cruise. This ship worked 24 hours a day and needed only three days to sample all stations.

At all lake stations 200-L Aqueous Phase Liquid-Liquid Extractor (APLLE) samples were collected. Coincidentally, during each cruise, 16-L samples, at least in duplicate, were collected by the MOE at four STPs which discharge directly into Lake Ontario - Highland (near the Rouge River), Toronto Main, Humber and Lakeview (Mississauga) on June 2, 4, 15 and 17, July 28 and 30, and October 5 and 6. The MOE also sampled river mouths during August and October with 200-L APLLE samplers.

Nearshore water samples were collected along six transects. All transects include three stations representative of water depths of approximately 15, 30 and 60 m, except at the two central

Table 1: Station locations in Lake Ontario.

Stat.ID	Lat.	Long.	Label	Crus. 1	Crus. 2	Crus. 3
2879	433316	793245	1	2879	2879	2879
2906	433457	793224	2		2906	2906
2880	433213	793154	3	2880		
2882	433420	793140	4	2882		2882
2073	433500	793131	5	2073	2073	2073
2881	433015	792957	6	2881	2881	2881
2883	433536	792858	7	2883	2883	2883
2072	433733	792802	8	2072	2072	2072
2885	433241	792649	9	2885	2885	2885
1536	433620	792311	10	1536		
2886	433637	792207	11	2886	2886	2886
1375	433838	792135	12		1375	1375
2888	433440	792054	13	2888	2888	2888
2891	433737	791859	14	2891	2891	2891
2889	433043	791836	15	2889	2889	2889
2892	433926	791647	16	2892	2892	2892
2890	432636	791614	17	2890	2890	2890
2893	433907	791557	18	2893	2893	2893
2029	434001	791503	19	2029	2029	2029
2895	433634	791429	20	2895	2895	2895
2896	433237	791204	21	2896	2896	2896
2897	432842	790941	22	2897	2897	2897
2901	434351	790922	23	2901		2901
2900	434054	790909	24	2900	2900	2900
2902	434524	790803	25	2902	2902	2902
2908	434730	790648	26		2908	2908
2903	434722	790526	27	2903	2903	2903
2904	434614	790446	28	2904		
2905	434438	790341	29	2905	2905	2905

transects where 30 and 60 m contours are very close together. The two central transects include two further offshore locations at 8 km distance intervals. In addition, samples were collected from stations 2891, about 3 km south of 1419 (Main STP outfall) and 2892, about 3 km east north-east of 1419, since the draft of the Limnos prevented entry into shallow waters, 2072 (Humber STP outfall), 2882 (Lakeview STP outfall), 2902 (Highland Creek STP outfall), 2029 (R.C. Harris filtration plant intake), 1536 (Island

filtration plant intake), 2901 (easterly filtration plant intake), 2073 (Etobicoke filtration plant intake), and 1375 (Inner Harbour).

The following collections took place at each station:

- (1) an EBT profile to the bottom;
- (2) surface water temperature (Figs. 2-4 show the surface temperature distribution);
- (3) in daylight hours a Secchi disk reading from the shaded side of the vessel;
- (4) a transmissometer profile to the bottom with a 25 cm path length transmissometer;
- (5) a large volume water APLLE sample (200 L) collected with a March pump; and
- (6) removed particulates with a Wesfalia continuous flow centrifuge.

Extraction of the APLLE sample was undertaken in the field with 8 L of dichloromethane (DCM). Water samples in the APLLE extractor were spiked at the parts per trillion level with the following surrogate chemicals: 1,3-dibromobenzene (1,3-DBB); 1,3,5-tribromobenzene (1,3,5-TBB); 1,2,4,5-tetrabromobenzene (1,2,4,5-TeBB); 2,3,5,6-tetrachlorobiphenyl (PCB-65); and octachloronaphtalene (OCN). The surrogate enabled the laboratories to check the chemical recoveries both in the field sampling and in the laboratory cleanup/concentration for each sample; this extract was stored on the ship for the duration of the cruise, returned to the Canada Centre for Inland Waters (CCIW), and forwarded by truck to Eli-Eco Laboratories in Rockwood, Ontario for analysis. Some

duplicate samples were sent to Zenon Laboratories in Burlington, Ontario.

At the four STPs 16-L effluent samples (4 x 4 L) were collected by MOE. Daily composites were obtained by collecting 8 L in the morning and 8 L in the afternoon. These samples were also spiked with the five surrogates and sent to Zenon Laboratories for analysis. The river mouths were sampled by MOE using APLLE samplers. These were also sent to Zenon Laboratories for analysis.

#### Water sample collection and extraction

Nearshore water samples were depth integrated. During unstratified conditions, samples were collected from the surface to 40 m, or if shallower than 40 m to 5 m from the bottom. During stratified conditions, samples were integrated from the surface to the top of the thermocline. To integrate a sample, the pump was set at a rate of 5 L per minute and was pumped at four equally spaced depths for a period of ten minutes for each depth until the 200 L APLLE sampler was full. At six stations the centrifuge bowl was cleaned and the particulate saved and placed in the containers provided. Duplicate water samples were also collected at a few stations.

#### Notes on the cruise May 26- June 11

Duplicate water samples were collected at a nearshore, an offshore and an intermediate station. Stations selected were 2883, 2890 and 2904. Suspended solids samples were collected at stations

2891, 2892, 2893, 2895, 2896 and 2897. Good weather was present throughout most of this cruise. On June 8, strong southwesterly winds of 25-30 knots caused the cancellation of any more stations that day. Strong northwesterly winds of 20-25 knots on June 9 caused some dragging of the anchor at deeper stations but also caused some extensive upwelling along the nearshore of the lake (Fig. 2). Surface water temperatures ranged from 12.3°C at station 2897 (mid lake) to 7.4°C at station 2893 nearshore. This upwelling effect was still taking place on June 10 and somewhat evident when the survey was completed on June 11. This effect might be important since this cruise was not short enough to be synoptic.

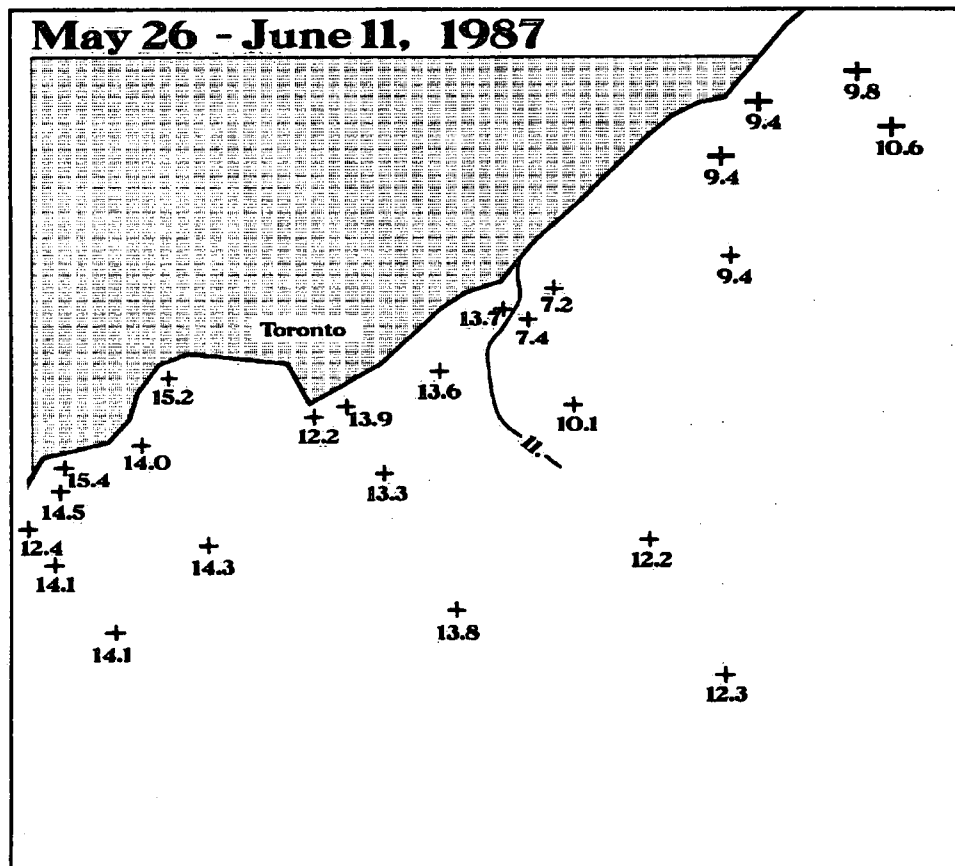


Figure 2: Surface water temperature (in °C)

Notes on the cruise July 27- August 7

Since the epilimnion layer was thin, samples were obtained at a mid-epilimnion depth or at a mid-column depth at shallow stations. At six stations, 2891, 2892, 2893, 2895, 2896 and 2897, the centrifuge bowl was cleaned and the particulate saved in the containers provided and stored at 4°C.

Duplicate water samples were collected from stations 2886, 2890 and 2905. Duplicate water samples were also obtained from stations 2072, 1375, 2906 and 2908 for analytical comparison of the two firms performing the sample analyses. Good weather was again present throughout most of this cruise. Water temperature was fairly uniform, but for an upwelling area in Humber Bay (Fig. 3). On July 31, strong easterly winds of 15-20 and increasing to 25-30 knots caused enough motion to cancel any more work on that day. Strong northeasterly winds between 15 and 25 knots caused cancellation of all sampling on August 5.

Notes on the cruise October 5-7

At six stations, 2891, 2892, 2893, 2895, 2896 and 2897, the centrifuge bowl was cleaned and the particulate saved in the containers provided and stored at 4°C. These stations are in a transect line from the Toronto Main Sewage Treatment Plant. Duplicate water samples were collected from stations 2886, 2890 and 2905. Duplicate water samples were also obtained from stations 2072, 1375, 2906 and 2908 for analytical comparison of the two firms performing the sample analyses. Fair to moderate weather was present throughout the cruise with moderate Southwesterly winds of

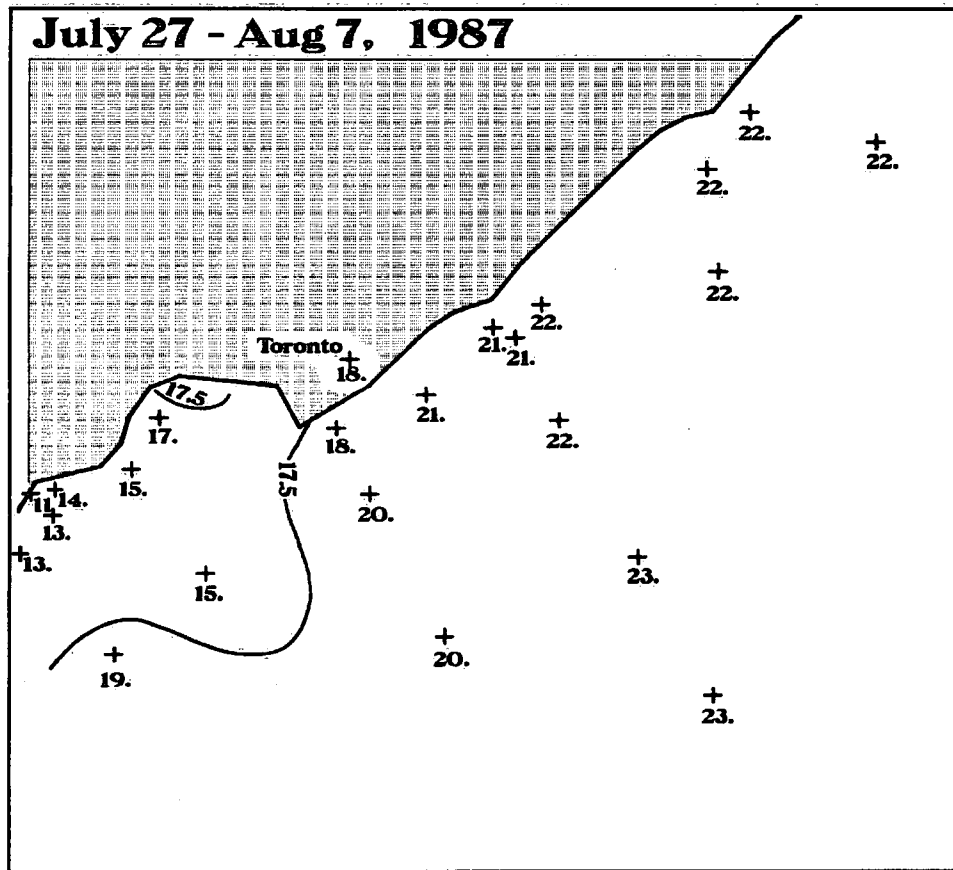


Figure 3: Surface water quality (in °C)

5-20 knots for the entire time. Different epilimnetic, mesolimnetic and hypolimnetic water masses were identified (Fig.4). The time taken to collect all the samples was minimal in that the LIMNOS is capable of working throughout an entire 24-hour day compared to the Advent working only during daylight hours. Large volume tubs, 600 L, stored the collected sample once it had been collected from depth. A small pump was put into each tub of collected water so that the water circulated to keep any suspended solids in suspension and from settling to the bottom of the tub.

#### Laboratory methods

Oliver and Nicol (1984) published the combined extraction and cleanup/concentration procedures. The report from Eli-Eco

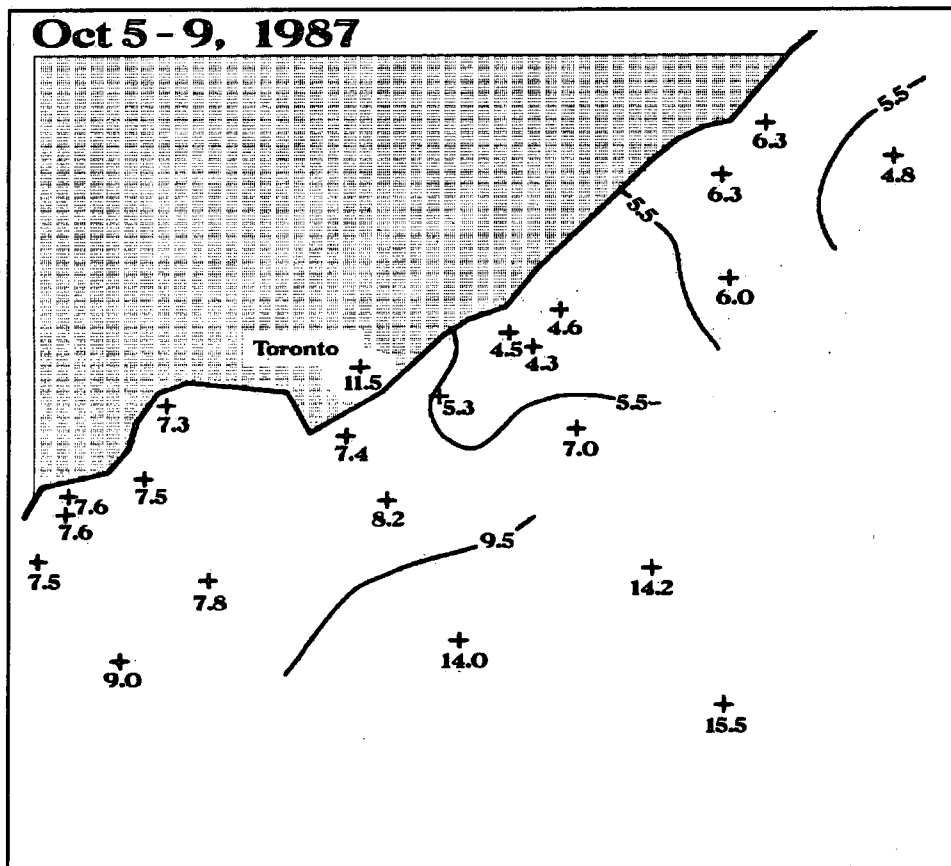


Figure 4: Surface water temperature (in °C)

Laboratories describes in detail the laboratory methodology. Detection limits for the 200-L water samples are 100 pg/L for dichlorobenzenes, 10 pg/L for trichlorobenzenes, 5 pg/L for tetrachlorobenzenes and 2 pg/L for pentachlorobenzene (QCB), hexachlorobenzene (HCB), most PCBs, and organochlorine pesticides.

#### THE RANKING METHOD

Classification of polluted areas (sites or stations) has been the subject of much research (Serat et al., 1965; Kaiser et al., 1984; Klein et al., 1984). Here a formal procedure (Reggiani and Marchetti, 1975), based on set theory and systems analysis, ranks the 29 stations using the information available from each of the three surveys. Partial ordering (Reggiani and Marchetti, 1975) is



a vectorial approach which recognizes that when concentrations of many chemicals are used to rank different sites, contradictions in the ranking are bound to exist. These contradictions might not be discovered using a single index. With the present approach contradictions are solved in a holistic way using decision theory. The computer program POSET (Reggiani and Marchetti, 1975) is used for this purpose. Results are displayed on paper or on a TV monitor driven by a desk top personal computer using Hasse diagrams (Preparata and Yeh, 1973; Warfield, 1973), a useful graphic tool commonly used in algebra to display lattices (e.g., a genealogical tree is a special case of a Hasse diagram). The results from the Hasse diagrams are then plotted on charts of Lake Ontario to identify plumes of pollutants.

A given number of criteria describe each site; these criteria may be called attributes. In this study, the attributes are the concentrations of the 25 chemicals (24 separate chemicals and total PCBs) at each station. The next step is the definition of weighting factors. The data to be analyzed can either be raw data or data classified into categories. The second option is chosen here since small differences in concentrations, for example between 0.01 and 0.07 ng/L, are indistinguishable in terms of hazard. For these purposes the data were divided into three groups according to a logarithmic scale of concentrations [ $<0.1$  ng/L (including detection limits);  $0.1$  ng -  $1$  ng/L;  $>1$  ng/L].

The formal mathematical and logical development of the ranking method can be found in Halfon and Reggiani (1986) and Halfon and

Brueggemann (1989); a program to display results with a desk top personal computer is available from the author. The rank levels are determined by comparing the data for each site with all the others according to prespecified logical rules. These rules are the definition of binary relations between pairs of set elements and are based on principles of lattice and graph theory developed during the 1970s (Harary, 1969; Preparata and Yeh, 1973; Reggiani and Marchetti, 1975). An example however will help explain the procedure used to create a Hasse diagram:

An example to describe the creation of a Hasse diagram

The ranking procedure can be explained by analyzing a small set of data (Table 2). The example classifies hypothetical sites rather than stations in Lake Ontario.

Table 2: Vector distance components of hypothetical sites. In this example each column represents a concentration of a contaminant; the lower the numerical value the lower the hazard. The identification number is the same number used in Figure 5 to identify each site in the Hasse diagram.

Identification Number	(1)	(2)	(3)	(4)	(5)	(6)
1 site A	2	2	1	1	1	2
2 site B	1	1	1	1	1	1
3 site C	2	2	1	1	1	1
4 site D	3	3	2	2	1	3
5 site F	3	3	1	1	2	2
6 site G	4	3	2	2	2	2
7 site H	5	3	2	2	2	3

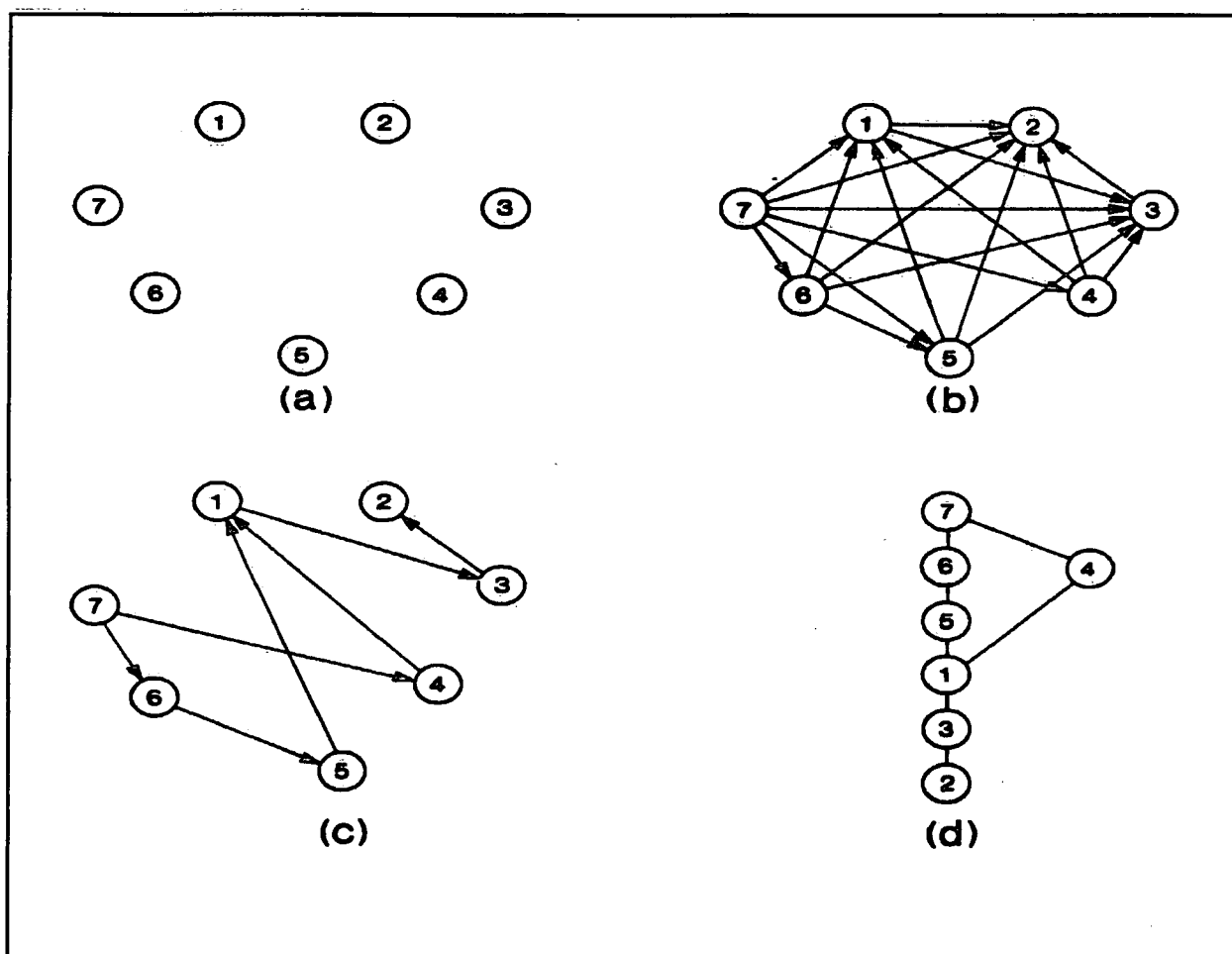


Figure 5: This figure shows the development of a Hasse diagram. The numbers within each circle identify the chemicals presented in Table 4.

The sites are identified as #1; #2; #3; #4; #5; #6 and #7. To derive the Hasse diagram for these seven sites, first assume that the seven sites are positioned at the vertices of a regular polygon, in this case a heptagon (see Fig. 5). Now, compare one site, e.g., #1 with all others (#2, #3, #4, #5, #6, #7) one at a time. In practice this comparison of sites implies the comparison of each individual test (each vector element) performed on one site with the respective tests on all the other sites, one site at the

time. In principle, there are four possible relationships to describe the outcome:

#1 = #2	case A
#1 ≥ #2	case B
#1 ≤ #2	case C
#1 and #2 are incomparable	case D

The notation  $\geq$  (greater or equal) of case B means that each element of site #1 is greater than or equal to each element of #2, i.e.,  $\#1_1 \geq \#2_1$ ;  $\#1_2 \geq \#2_2$ ; ... with the constraint that the sign = can not be valid for all elements, since this is case A or the two sites occupy the same place in the ranking scheme. If the symbol  $\geq$  is interpreted as a parental relation (father-son; father-grandson; grandfather-grandson, etc.) within a family, the Hasse diagram becomes a genealogical tree. The lines represent the direct relation father-son and each two successive levels represent the passage of a generation. For example, if we compare each element of #1 with each element of #2 (that is each element on line one in Table 2 with each element in line two) we find that

#1 <sub>1</sub> (2)	>	#2 <sub>1</sub> (1);
#1 <sub>2</sub> (2)	>	#2 <sub>2</sub> (1);
#1 <sub>3</sub> (1)	=	#2 <sub>3</sub> (1);
#1 <sub>4</sub> (1)	=	#2 <sub>4</sub> (1);
#1 <sub>5</sub> (1)	=	#2 <sub>5</sub> (1);
#1 <sub>6</sub> (2)	>	#2 <sub>6</sub> (1).

Since each element of #1 is greater than or equal to each respective element of #2, we can draw an oriented line in Fig. 5b from #1 to #2. This example reflects case B. Case C is the inverse of case B. If in the present example case C had been true

then #2 and #1 would have been connected with an oriented line from #2 to #1, the opposite of case B. If by chance the results of all tests were the same for #2 and #1 then we could say that #1 and #2 rank exactly the same or #1 = #2 (case A) and graphically the heptagon would then become a hexagon since #1 and #2 would occupy the same space.

Case D is most interesting from the point of view of data analysis. In the Hasse diagram two elements (for example #1 and #3 in Fig. 5b) are not connected because contradictions exist among the different tests; these elements are called "incomparable". This contradiction exists also between sites #4 and #6. From analysis of Table 2 we see that

$$\begin{array}{llll}
 \#4_1 (3) & < & \#6_1 (4); \\
 \#4_2 (3) & = & \#6_2 (3); \\
 \#4_3 (2) & = & \#6_3 (2); \\
 \#4_4 (2) & = & \#6_4 (2); \\
 \#4_5 (1) & < & \#6_5 (2); \\
 \#4_6 (3) & > & \#6_6 (2).
 \end{array}$$

Out of six experiments #4 is less hazardous than #6 (lower numerical value) in two experiments, more hazardous in one and the same in the other three. Therefore the results are inconclusive and overall we cannot say whether #4 is better than #6 or vice versa. The Hasse diagram (Fig. 5b) identifies #4 and #6 as incomparable by not connecting the two circles; lack of connection identifies contradiction in data or no predictable > or < relationship. By definition all sites located in the same ranking level in a Hasse diagram are incomparable. Similar contradictions exist between #4 and #5. The results of this analysis show that

this method is useful not only for ranking but also, and perhaps even more importantly, for data analysis to identify contradictions in the test results.

Continuing the analysis of the example, we compare the pairs #1-#3, #1-#4, #1-#5, #1-#6 and #1-#7 and oriented lines are drawn accordingly following the same rules explained in the previous paragraph. The next step is to compare the pairs #2-#3, #2-#4, #2-#5, #2-#6 and #2-#7; and so on until #5-#6; #5-#7 and finally #6-#7. When this analysis is completed, then we have Fig. 5b, or the relation diagram.

The next step is to eliminate all redundant oriented lines. For example the line #7-#1 in Fig. 5b is redundant since the lines #7-#6, #6-#5 and #5-#1 already exist. That is, we know that #1 is less hazardous than #7 since all tests in #1 have numerical values lower than in #7 and all test values of #1 are lower than those of #5 which in turn are lower than those of #6 and #7. Therefore, the line between #7 and #1 becomes superfluous since this information already is displayed in the Hasse diagram with the three lines #7-#6, #6-#5 and #5-#1. Likewise, we can eliminate #6-#2 (the information is contained in #6-#1 and #1-#2); #5-#2; #7-#2, #7-#3, etc. Figure 5c shows the simplified diagram after all eliminations have been done. The next step is to reorganize the diagram so that the oriented lines are directed towards the bottom of the page (Fig. 5d) so that the arrows become unnecessary. Sites with more contaminants in large concentrations are located above those with less. In the final drawing the number of horizontal levels which

contain the incomparable elements must be minimized and therefore the sites #6 and #4 are displayed in the same level.

## DATA

### Contaminant concentrations

All data are presented in Figs. 11-277. Data are also available in spreadsheet form from the author. Table 3 shows a list of all 89 (25 contaminants and 64 PCB isomers) chemicals found in the Lake Ontario waters off Toronto. These contaminants are 11 chlorobenzenes, 13 pesticides including DDT and Mirex, and total PCBs. Sixty-four PCB isomers are also separated.

### Water temperature distribution

As noticed above, upwelling episodes took place on the North shore of Lake Ontario. Upwelled water masses can be identified by their different temperatures; unfortunately, since all cruises progressed from west to east, we can not state when each upwelling event began. Hypolimnetic waters have lower temperatures than epilimnetic waters. Figure 2 shows the surface water temperature during the first cruise. The temperature in the western part of the waterfront is three to seven degrees higher than off the Scarborough Bluffs. The offshore water temperature is about twelve degrees. In July-August (Fig. 3), we note an upwelling in Humber Bay. In October (Fig. 4), with cooling air temperatures and strong winds, we observe three water masses. Offshore an epilimnetic mass at 14-15°C in Humber Bay and off Pickering a mesolimnetic water

mass of 6-8°C and off the eastern beaches a hypolimnetic water mass at 4-5°C.

**Table 3: List of toxic contaminants (divided into three groups) found off the Toronto Waterfront in concentrations higher than 0.01 ng/L.**

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**Chlorobenzenes**

1,2-dichlorobenzene	12-DCB
1,3-dichlorobenzene	13-DCB
1,4-dichlorobenzene	14-DCB
1,2,4-trichlorobenzene	124-TCB
1,3,5-trichlorobenzene	135-TCB
1,2,3-trichlorobenzene	123-TCB
1,2,4,5-tetrachlorobenzene	1245-TeCB
1,2,3,4-tetrachlorobenzene	1234-TeCB
pentachlorobenzene	QCB
hexachlorobenzene	HCB
hexachloroethylene	HCE
hexachlorobutadiene	HCBD

**Organochlorine pesticides - including**

2,4,5-trichlorotoluene	245-TCT
2,3,6-trichlorotoluene	236-TCT
pentachlorotoluene	PCT
alpha-hexachlorocyclohexane	A-BHC
gamma-hexachlorocyclohexane	Lindane
Octachlorostyrene	OCS
gamma-chlordane	G-CHLOR
DDT family	pp'-DDE
	pp'-DDD
	pp'-DDT
	pp-DDD
	pp-DDT
	pp-DDE

aldrin  
dielrin  
mirex  
Total PCB's

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Table 3 (continued)

## Individual PCB congeners

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PCB-1-	PCB-44-	PCB-128-
PCB-3-	PCB-42-	PCB-185-
PCB-4+10-	PCB-41+71+64	PCB-174-
PCB-7-	PCB-40-	PCB-177-
PCB-6-	PCB-74-	PCB-171+156-
PCB-19-	PCB-99-	PCB-173-
PCB-12-	PCB-87+97-	PCB-180-
PCB-13-	PCB-85-	PCB-170+190-
PCB-18-	PCB-110-	PCB-201-
PCB-17-	PCB-82-	PCB-203+196-
PCB-16+32-	PCB-151-	PCB-70+76-
PCB-26-	PCB-149	PCB-66+95-
PCB-25-	PCB-118-	PCB-91-
PCB-31+28-	PCB-146-	PCB-56+60+81
PCB-33-	PCB153+132+105	PCB-84+92-
PCB-53-	PCB-141-	PCB-101-
PCB-22-	PCB-138-	PCB-195-
PCB-45-	PCB-158-	PCB-194-
PCB-46-	PCB-129-	PCB-206-
PCB-52-	PCB-178-	PCB-209-
PCB-49-	PCB-187+182-	
PCB-47+48-	PCB-183-	

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## POLLUTION RANKING ANALYSIS OF THE TORONTO WATERFRONT

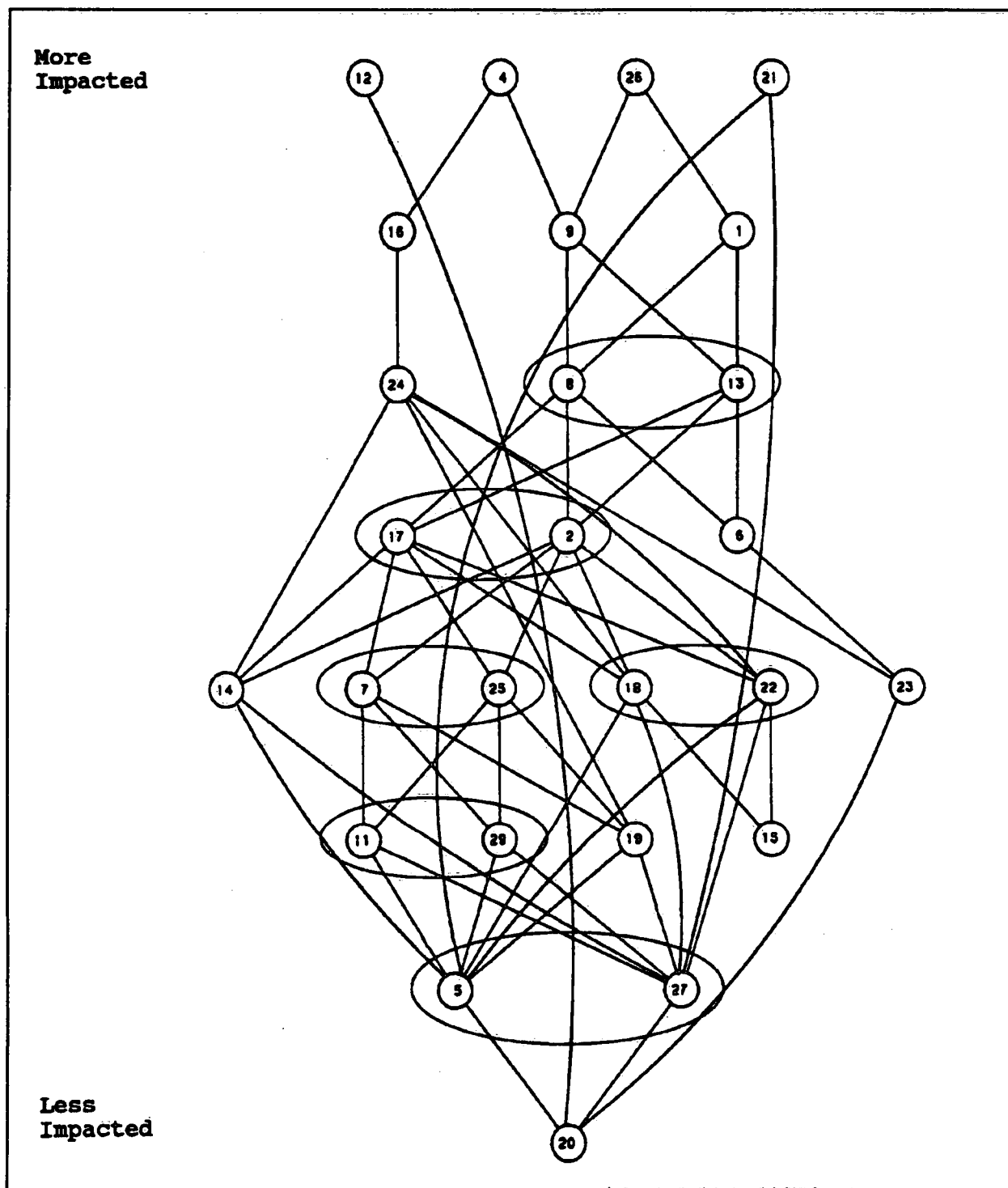
Analysis of contaminant distributions near Toronto has shown that few contaminants are present in relatively high concentrations, that is, higher than 1 ng/L. These contaminants are the dichlorobenzenes, alpha-BHC, gamma-BHC (lindane) and total PCBs. Nevertheless, lake waters contain a large number of other toxic contaminants at low concentrations. These contaminants must be taken into account in an analysis of relative impact because of possible additive and synergistic effects. To assess the impact of toxic contaminants on the drinking water of Toronto a holistic approach must be used. The approach follows a method (Halfon and

Reggiani, 1986) that can classify the sites off the Toronto Waterfront according to their relative contaminant concentrations.

#### Classification of impacted zones in the Toronto Waterfront

The presence of 25 chemicals in the waters off Toronto offers the challenge of classifying the areas near Toronto without disregarding the information about the pollutants present in low quantities. Figure 6 shows a Hasse diagram ranking the sampling stations according to the concentrations collected in July-August, 1987. In a Hasse diagram the stations closer to the bottom of the figure are the least impacted. The numbers in each circle are labelled (Table 1) and the lines between the circles mean that the given chemicals can be directly compared with each other following any path. By definition the stations on the same level are "incomparable" (see example above). Figure 7 shows that a Hasse diagram can be simplified if several stations occupy the same position (stations included in the oval are the same from a ranking point of view, thus one can be eliminated) in the ranking scheme. Figure 7 is therefore easier to understand than Fig. 6.

The ranking method is based on the hypothesis that a set of numbers, here contaminant concentrations, is necessary to create a ranking file; these numbers can be considered as the elements of a vector, the "vector performance" or "vector distance". This "vector approach method" is different from the "scalar approach method", where a single number (a scalar performance index) is said to be sufficient to interpret the data, to compare sites and rank



**Figure 6:** Twenty-six sites are ranked according to the concentrations (criteria) of all chemicals present at that station. The sites included in the ovals have the same ranking place and therefore one can be eliminated.

them. The ranking method used in this study only takes into consideration that at some sites, concentrations of some contaminants might be higher than at other sites, where other contaminants, equally toxic, might prevail. From a ranking point of view this condition leads to a contradiction, usually not resolved by other ranking techniques. Here, these contradictions are made explicit with the use of Hasse diagrams as they will be discussed later.

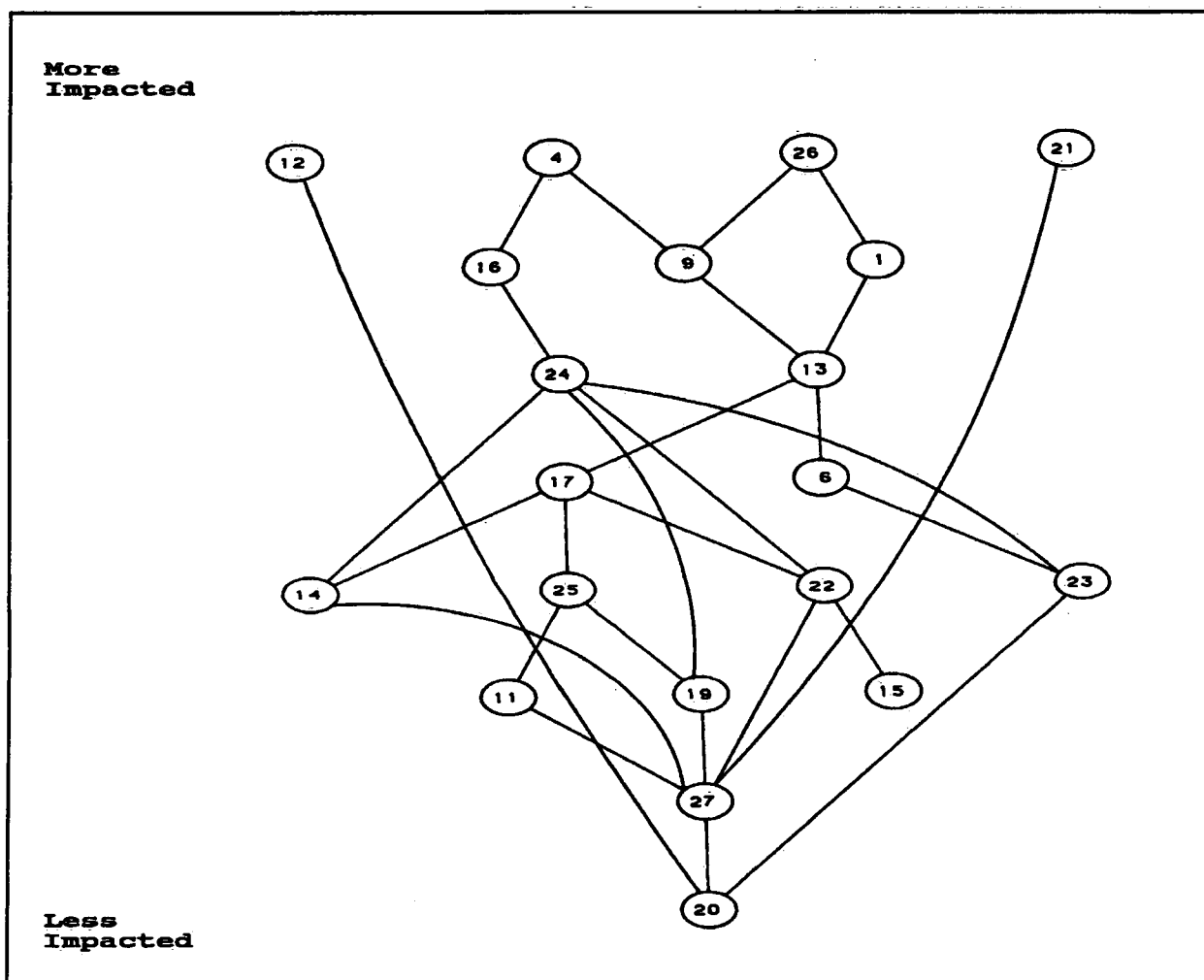


Figure 7: Twenty-six sites are ranked according to the concentrations (criteria) of all chemicals present at that station. Circles represent the sites and labels are defined in Table 1.

### Contaminated areas

Figures 8-10 show charts of the Toronto Waterfront where the stations located on the same level in the Hasse diagram (for example see Fig. 6) are joined by a line. In May-June 1987 we note two areas of impact by toxic contaminants; one located on the western zone of the Toronto Waterfront (which includes Humber Bay, Toronto Harbour and the Leslie Spit) and one located near the Highland STP station. These stations are ranked at level 4 or higher. The offshore areas of the Lake and the Scarborough Bluffs are ranked at level 2 or lower. In this area the water temperature (Fig. 8) is low and contaminants might have been diluted in cleaner cooler hypolimnetic waters. In July-August (Fig. 9) the pattern of pollution is similar to the one observed in May-June. The impact plume off the Toronto Harbour is located near the eastern beaches while the plume in Humber Bay is practically unchanged. Impacted zones exist in the east off Scarborough and at one station offshore. In October (Fig. 10) we see the same impacted areas identified in the previous two cruises. The only notable difference is an area offshore with rank 9. Off the eastern beaches, the intrusion of hypolimnetic waters (Fig. 10) lower the impact factor.

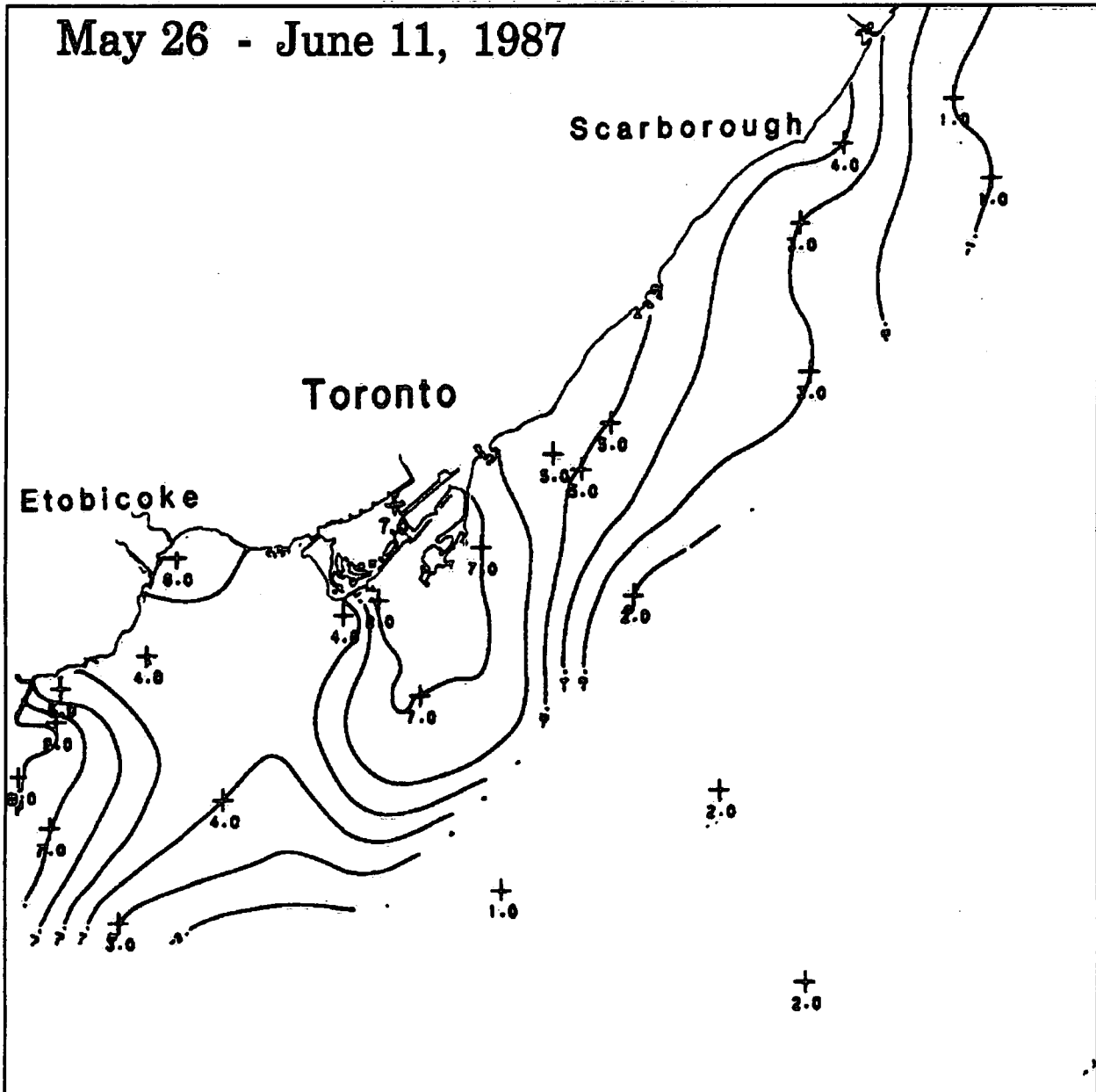


Figure 8: In May-June 1987, we note two polluted areas; one located on the western zone of the Toronto Waterfront and one located near the Lakeview STP station.

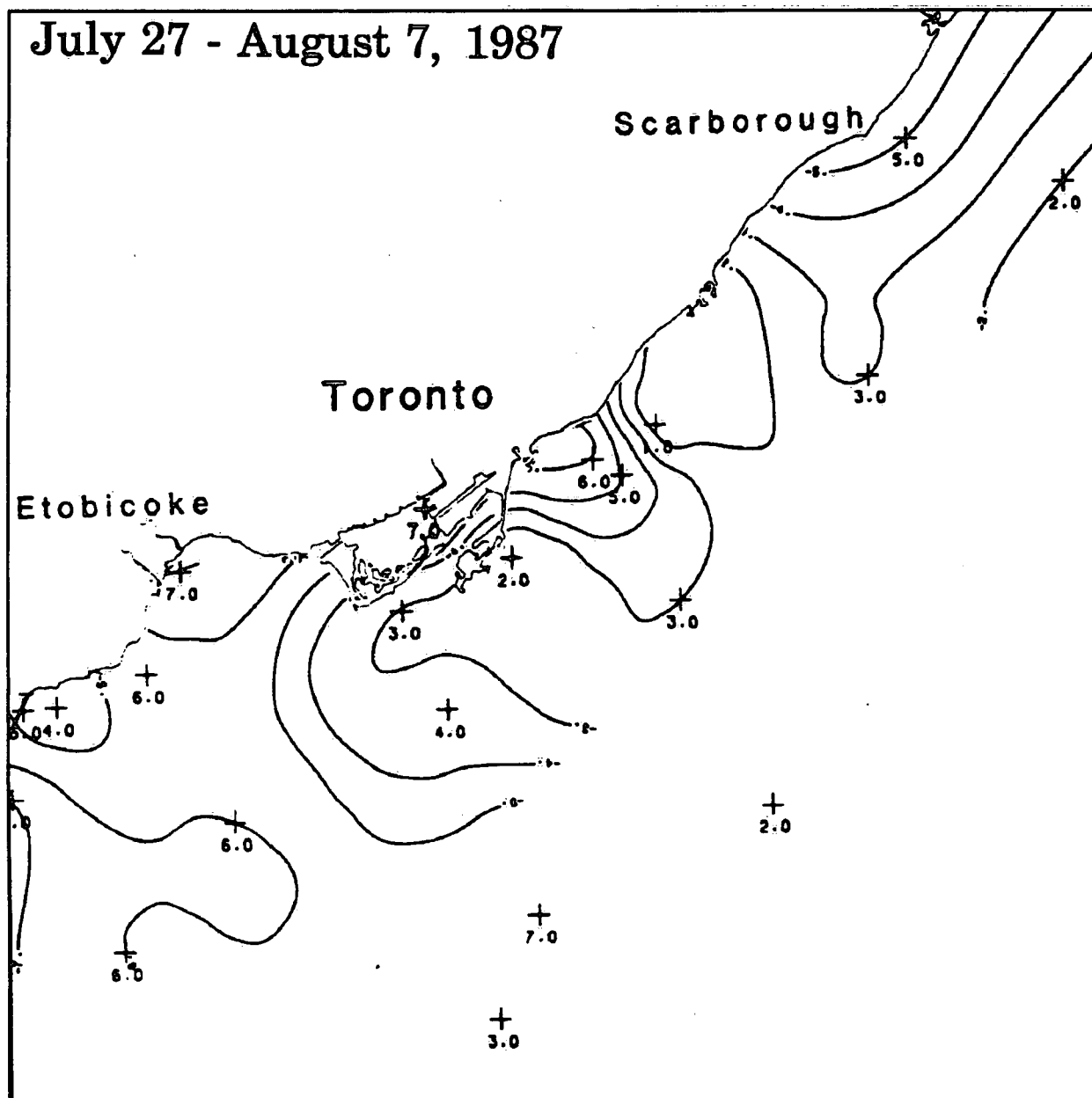


Figure 9: In July-August, the pattern of pollution is similar to that one observed in May-June. The impact plume off the Toronto Harbour has shifted toward the eastern beaches while the plume in Humber Bay is practically unchanged.

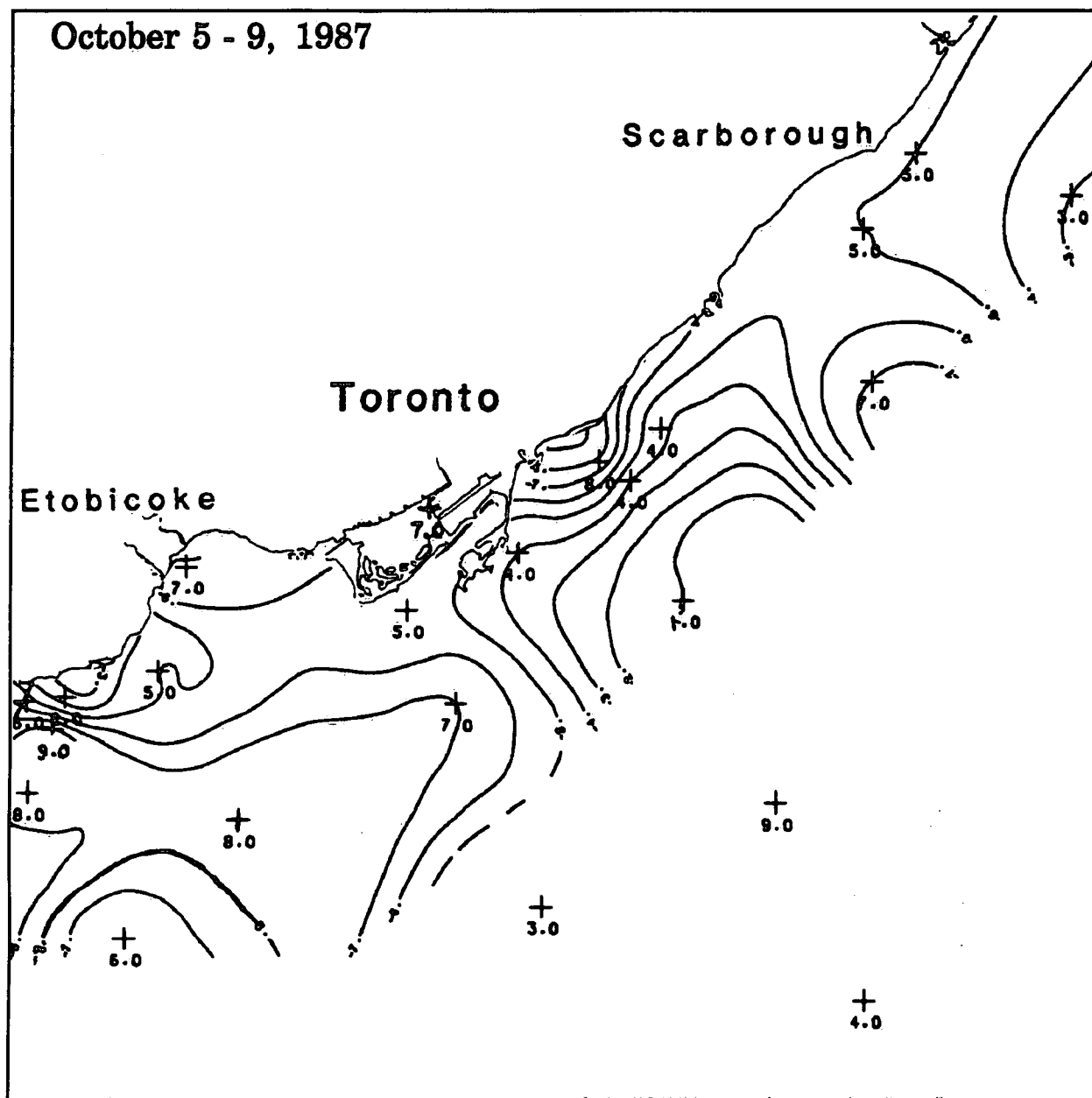


Figure 10: In October toxic pollutants impact the same areas identified in the June and August cruises.



### SPATIAL DISTRIBUTION OF CONTAMINANTS

Each water sample was analyzed for chlorobenzenes, organic pesticides and PCBs. The PCB analysis was conducted both for total PCBs and for most isomers, which is the first time Toronto Waterfront samples have been so analyzed. The main reason for this effort is to verify whether the same PCB sources were active during different periods in spring, summer and fall. Total PCB concentrations do not provide this level of resolution.

#### Chlorobenzenes

Dichlorobenzenes are present in relatively high concentrations while the trichlorobenzenes, tetrachlorobenzenes, QCB and HCB occur at much lower concentrations (0.1 ng/L or less). While the relative toxicity of chlorinated benzene isomers increases in proportion to the number of chlorine atoms in the benzene molecule (thus making HCB potentially more hazardous than dichlorobenzene) all the observed chlorinated benzene levels were well below existing Provincial Water Quality Objectives (PWQOs). Figures 11-13 show the distribution of 1,3-dichlorobenzene (1,3-DCB, PWQO = 2500 ng/L) in May, July and October. Offshore concentrations are in the order of 0.3-1 ng/L while in the nearshore we note concentrations of 1-2 ng/L in May; in July offshore concentrations are low and concentrations of 1-2 ng/L are only found in Humber Bay; in October concentrations are below 1 ng/L everywhere with the exception of mean 1 ng/L levels along the western boundary of the

study area. Figures 14-16 show the distribution of 1,4-DCB (PWQO = 4000 ng/L). In May-June offshore concentrations are in the order of 2-3 ng/L. Higher concentrations are present in Humber Bay (about 35 ng/L near the Lakeview STP outfall) and relatively high concentrations of 5-15 ng/L are observed along the entire Toronto Waterfront nearshore. In July concentrations are similar to those in June while in October no 1,4-DCB was detected anywhere, even offshore. Figures 17-19 show a spatial pattern of 1,2-DCB (PWQO=2500 ng/L) similar to that of 1,4-DCB with concentrations higher than the lake average (<1 ng/L) in Humber Bay (0.7-1 ng/L) and along the nearshore (0-3 ng/L) in May and August. In October, concentrations of the order of 2-4 ng/L still persist in Humber Bay while the offshore is below 1 ng/L. The higher chlorinated benzenes are present in low concentrations in Lake Ontario (Figs. 20-43). 1,3,5-trichlorobenzene (1,3,5-TCB; PWQO=650 ng/L) was generally below 0.1 ng/L; 1,2,4-TCB (PWQO=500 ng/L) was largely below 1 ng/L and 1,2,3-TCB (PWQO=900 ng/L) rarely exceeded 0.1 ng/L. 1,2,3,5-tetrachlorobenzene (PWQO=100 ng/L) was usually below 0.05 ng/L, 1,2,4,5-TeCB (PWQO=150 ng/L) was below 0.2 ng/L and 1,2,3,4-TeCB (PWQO=100 ng/L) was below 0.5 ng/L. As with the trichlorobenzenes, highest levels of tetrachlorobenzenes were found in Humber Bay, near the Toronto Main STP outfall, in the Toronto Inner Harbour and along the western boundary of the study area. QCB (PWQO=30 ng/L) was generally below 0.05 ng/L and as high as 0.18 ng/L in the Inner Harbour in August. Hexachlorobenzene (PWQO=6.5 ng/L) was generally below 0.1 ng/L and showed a much

weaker inshore-offshore gradient than the lower chlorinated benzenes.

#### Organic pesticides

Most organic pesticides (see Table 3) are in very low concentrations in the order of 0.1 ng/L or less (Fig. 44-58). Therefore, no plumes or sources can be detected. Nevertheless, alpha-BHC, the isomerized product of lindane (Fig. 59-61), is detected in concentrations of 3-5 ng/L but no obvious sources exist nearshore. Concentrations are fairly uniform in May-August while in October we note a mixing of different water masses (Fig. 61) varying concentrations between 0 and 8 ng/L. No obvious sources, however, exist. Lindane concentrations (Fig. 62-64) range between 0.5 and 1 ng/L in offshore waters. In May-August we notice a slightly higher concentration, 2 ng/L, in Humber Bay while in October concentrations are fairly uniform. Figures 65-82 show that concentrations for the other pesticides including DDT and mirex is fairly uniform over the lake and nearshore. No obvious sources exist and concentrations are lower than 0.1 ng/L.

#### PCBs

Figures 83-85 show the concentrations of total PCBs. In May-June concentrations are fairly uniform. Offshore concentrations are less than 0.5 ng/L while in the western part of the Toronto Waterfront, concentrations of 1-4 ng/L are observed; the PWQO is 1 ng/L. In July-August 1987 offshore concentrations

are not very different but we can note concentrations of 1-4 ng/L near the Humber River. In October several water masses are present near the north shore of Lake Ontario and concentrations very between 1 and 9 ng/L. No obvious source of PCB is present nearshore.

### PCB isomers

As mentioned in the introduction the analysis of PCBs included an analysis of 64 PCB isomers. A total of 209 PCB isomers exist but only about 100 are likely to be found in Lake Ontario; out of these 100 only 80 were actually found. However, 31 isomers co-elute on the gas chromatography and we therefore report on 39 isomers, 14 pairs of congeners and one triplet. The distribution of all isomers are shown in Figs. 86-277. Most concentrations are very low and patterns can not be easily identified. Nevertheless, this analysis is useful to point out whether any particular PCB isomers are in larger percentages than the others. Table 4 shows the percentages of all PCB isomers; the relative percentages vary more temporally than spatially. Five isomers are present in high percentages over time; they are PCB-52 (3-5% in all three cruises), PCB-70+76 (4-5%), PCB-66-95 (5-7%), PCB-84-92 (4-8%) and PCB-101 (2-8%). Totally they represent about 25% of all isomers. Other isomers appear in very large percentages, but only once during the year: PCB-180 (19% in May-June), PCB-22 (29% in July-August) and PCB-53 (27% in October). Other isomers were detected at significant percentages, but again only once during the period

Table 4: Percentages of total PCBs

PCB Name	May-June	July-August	October
PCB-1-	0.00	0.00	1.90
PCB-3-	0.00	0.00	4.06
PCB-4+10-	0.00	0.38	1.64
PCB-7-	0.05	0.85	0.91
PCB-6-	0.02	0.56	5.88
PCB-19-	0.00	0.00	0.55
PCB-12-	0.00	0.39	0.28
PCB-13-	0.02	1.39	0.21
PCB-18-	0.02	2.14	5.71
PCB-17-	0.00	0.31	0.49
PCB-16+32	0.01	3.22	1.13
PCB-26-	0.01	2.14	0.17
PCB-25-	0.00	0.99	0.09
PCB-31+28	2.11	2.03	1.09
PCB-33-	0.01	0.30	1.90
PCB-53-	0.00	0.00	27.33
PCB-22-	0.00	29.45	0.85
PCB-45-	0.00	0.23	0.10
PCB-46-	0.00	0.00	0.10
PCB-52-	4.37	3.16	5.20
PCB-49-	0.68	2.17	1.69
PCB-47+48	0.00	0.38	0.14
PCB-44-	0.00	0.10	3.76
PCB-42-	0.00	9.21	0.80
PCB-41+71	0.70	0.91	1.65
PCB-40-	0.05	0.28	0.45
PCB-74-	6.91	0.76	0.63
PCB-70+76	4.76	4.98	4.12
PCB-66+95	6.84	7.14	5.72
PCB-91-	0.01	0.14	0.78
PCB-56+60	1.90	0.70	0.93
PCB-84+92	7.94	7.54	3.80
PCB-101-	8.33	5.91	2.52
PCB-99-	5.12	2.91	0.87
PCB-87+97	2.44	0.74	2.30
PCB-85-	1.64	1.07	0.95
PCB-110-	2.45	3.45	2.54
PCB-82-	0.01	0.00	0.20
PCB-151-	0.00	0.00	0.25
PCB-149-	9.84	0.86	1.26
PCB-118-	3.20	0.64	0.82
PCB-146-	0.00	0.00	0.09
PCB153+132+105	7.94	1.70	1.28
PCB-141-	0.57	0.03	0.18
PCB-138-	2.11	0.32	0.59

Table 4 (continued)

PCB Name	May-June	July-August	October
PCB-158-	0.00	0.00	0.04
PCB-129-	0.00	0.00	0.02
PCB-178-	0.00	0.00	0.02
PCB-187+1	0.00	0.00	0.12
PCB-183-	0.00	0.00	0.01
PCB-128-	0.00	0.00	0.20
PCB-185-	0.00	0.00	0.00
PCB-174-	0.00	0.02	0.06
PCB-177-	0.00	0.00	0.38
PCB-171+1	0.00	0.00	0.26
PCB-173-	0.00	0.00	0.00
PCB-180-	18.89	0.47	0.43
PCB-170+1	1.02	0.00	0.23
PCB-201-	0.00	0.00	0.00
PCB-203+1	0.00	0.00	0.00
PCB-195-	0.00	0.00	0.14
PCB-194-	0.00	0.00	0.01
PCB-206-	0.00	0.00	0.07
PCB-209-	0.00	0.00	0.12
TOTAL PCB's	100.00	100.00	100.00

sampled: in May-June we see PCB-74 (7%), PCB-99 (5%), PCB-110 (2%), PCB-149 (10%), PCB-118 (3%) and PCB-153-132-105 (8%) for a total of 35%. In July-August we see PCB-13-32 (3%), PCB-42 (9%) and PCB-99 (3%) for a total of 15%. In October we see PCB-3 (4%), PCB-6 (6%), PCB-18 (6%) and PCB-44 (4%) for a total of 20%.

Overall we see that in May-June twelve PCB isomers out of sixty-four account for 79% of all PCBs, in July-August nine PCB isomers account for 69%, and in October ten isomers account for 72%. All the other isomers are found in very low percentages (less than 2% each).

## IDENTIFICATION OF SOURCES

One of the purposes of this study is to identify any local sources of the contaminants and relate their presence with the water masses. Contaminant concentrations were measured in river mouths and in the final effluent from Sewage Treatment Plants (STPs); Halfon (1990) presents the results of this sampling program. He concluded that, if one does not consider the impact of contaminants already present in the lake, the main sources of contaminants to the Toronto Waterfront are the Sewage Treatment Plants (STPs). The local rivers are only a minor source. The main problem of tracing the fate of toxic contaminants is the fact that Lake Ontario receives toxic contaminants from a variety of other sources, namely the atmosphere and the Niagara River. The lake is therefore full of contaminants and plumes from local sources can be followed only using mathematical models (Halfon, 1990). This reports deals mostly with data analysis rather than with simulations and therefore one way of tracing sources is to identify zones nearshore where concentrations are higher than average lake concentrations. Halfon (1990) computed the relative loadings from the Niagara River; he found that the lowest percentage is for 1,4-DCB (at 58%). The percentages for the Toronto Waterfront range between 0.5 and 25%. At the low end are the PCBs and at the high end 1,4-DCB. Thus, the Toronto Waterfront might be a significant source only for a few toxic contaminants, especially for the chlorinated benzenes. Elimination of chlorobenzene loadings from the Toronto Main STP would be quite beneficial to the Lake Ontario

ecosystem. The effect of removing these loads is discussed in Halfon (1990) with the use of simulation models. Conversely, loadings of PCBs and HCB from the Toronto Waterfront area are quite insignificant.

As noticed in the analysis of the map distributions, higher-than-average concentrations are detected only for a few contaminants like dichlorobenzenes. A method to trace the impact of contaminants is to correlate the contaminant concentrations with the water temperature; this correlation verifies whether an association exists between water masses and individual contaminants. Only large lake water masses can be identified since the sampling grid contains 26 stations per cruise. Water masses from the Humber River and the Don River, which enters the Toronto Harbour, can not be identified. Table 5 shows the correlations of the water temperature and contaminant concentrations during the three cruises. A positive correlation between contaminant concentrations and surface water temperature implies that contaminants are associated with warm epilimnetic water. A negative correlation implies that high concentrations of contaminants are associated with cold hypolimnetic water which has upwelled near the north shore. The temporal trend in correlations is also important to detect whether the pollutants are associated with the water masses (sign of significant correlations does not change in the three cruises), or whether local sources are important (sign of significant correlations changes in time).



In May-June the overall correlation of the 25 contaminants (including total PCBs but not all individual isomers) is 0.39. Since the water mass is warmer in Humber Bay than in the eastern shores, this correlation points out pollution sources in Humber Bay (a significant correlation factor does not imply a well defined source but only a generalized area of contamination; Halfon (1990) has identified the source in Humber Bay as the Humber STP rather than the Humber River). 1,4-DCB has a correlation of  $r=0.37$  and 1,2-DCB a correlation of  $r=0.40$ . Spatial distribution maps of these two contaminants (Figs. 14-19) show obvious sources nearshore. Other contaminants without well defined sources are 1,2,4,5-TeCB ( $r=0.35$ ), HCE ( $r=0.42$ ), lindane ( $r=0.43$ ) and octachlorostyrene ( $r=-0.50$ ). The negative correlation of octachlorostyrene implies that no sources of the chemical are present in Humber Bay; most of octachlorostyrene is present offshore, which points to a far source such as the Niagara River. PCB isomers have no significant correlations with water temperature but for PCB-18 ( $r=0.34$ ), PCB-118 ( $r=0.35$ ) and PCB-138 ( $r=0.38$ ).

In July-August the overall correlation was of  $r=-0.56$ . The upwelling takes place in Humber Bay, water is cooler than in May, and the negative correlation points to sources of pollution in the bay. The correlation has changed sign and is significant with the location rather than with the water mass. Large correlations can be observed for 1,4-DCB ( $r=-0.49$ ), 1,2,4-TCB ( $r=-0.48$ ), 1,2,3-TCB ( $r=-0.54$ ), HCB ( $r=-0.44$ ), 2,3,6-TCT ( $r=-0.62$ ), lindane ( $r=-0.37$ ), gamma-chlordane ( $r=-0.59$ ), pp'-DDE ( $r=-0.44$ ) and pp'-DDD ( $r=-0.44$ ).

Three PCB isomers are also significantly correlated and present in relative high percentages of total PCBs: PCB-18 ( $r=-0.38$ ; 2.1%), PCB-99 ( $r=-0.43$ , 2.9%) and PCB-153-132 ( $r=-0.69$ ; 1.7%).

In October the overall correlation is a non significant  $r=0.11$ . The correlation analysis is less meaningful than for the other two previous cruises: three different water masses are present near the Toronto Waterfront. Water masses with low temperature are present nearshore while the lake waters offshore are relatively warmer. Some individual contaminants however show significant correlations, 1,2,3-TCB ( $r=-0.40$ ), 1,2,3,4-TeCB ( $r=-0.43$ ), QCB ( $r=-0.49$ ), pp'-DDD ( $r=-0.43$ ) and Mirex ( $r=0.35$ ). The only positive correlation is for mirex, which shows that mirex is present in larger concentrations offshore, rather than inshore. Among the PCB isomers we can note PCB-44 ( $r=0.40$ ; 3.7%), PCB-70-76 ( $r=0.39$ ; 4.1%), PCB-66-95 ( $r=0.42$ ; 5.7%), PCB-84-92 ( $r=0.42$ ; 3.8%), PCB-101 ( $r=0.42$ ; 2.5%), PCB-87-97 ( $r=0.40$ ; 2.3%) and PCB-110 ( $r=0.41$ ; 2.5%). Total PCBs have a correlation of 0.38. For all significant correlations, both PCB isomers and total PCBs have positive correlations with water temperature. Thus PCBs are mostly found in warmer offshore waters in October 1987.

Table 5: Correlation of contaminant concentration with temperature.

Chemical	May-June	July-August	October
13-DCB	0.06	-0.08	-0.06
14-DCB	0.37	-0.49	0.00
12-DCB	0.40	-0.24	-0.11
135-TCB	0.32	-0.24	-0.20
124-TCB	0.33	-0.48	-0.22
123-TCB	0.25	-0.54	-0.40
1235-TECB	0.11	-0.30	0.00
1245-TECB	0.35	0.06	-0.15
1234-TECB	0.23	-0.23	-0.43
QCB	0.27	-0.25	-0.49
HCB	0.21	-0.44	-0.05
HCE	0.42	-0.26	-0.16
HCB D	0.09	-0.13	0.00
245-TCT	0.21	-0.31	-0.06
236-TCT	0.00	-0.62	0.00
PENTACHLOROTOLUENE	0.25	-0.30	-0.18
A-BHC	-0.09	-0.12	-0.12
Lindane	0.43	-0.37	-0.04
OCS	-0.50	0.00	0.05
G-CHLORDANE	0.16	-0.59	0.14
PP'-DDE	-0.15	-0.44	-0.05
PP'-DDD	0.34	-0.44	-0.43
PP'-DDT	0.00	-0.32	-0.29
MIREX	0.00	-0.27	0.35
TOTAL PCB'S	0.18	-0.23	0.38
TOTAL CHEMICALS	0.39	-0.56	.11
PCB-1-	0.00	0.00	0.35
PCB-3-	0.00	0.00	0.02
PCB-4+10-	0.00	-0.04	0.29
PCB-7-	-0.11	0.16	0.08
PCB-6-	-0.29	-0.19	0.18
PCB-19-	0.00	0.00	0.34
PCB-12-	-0.01	-0.23	0.08
PCB-13-	-0.16	-0.24	-0.22
PCB-18-	0.34	-0.38	0.18
PCB-17-	0.00	-0.14	-0.10
PCB-16+32-	0.10	-0.07	0.15
PCB-26-	0.17	0.25	0.02
PCB-25-	0.00	0.13	0.32
PCB-31+28-	0.09	-0.28	-0.07
PCB-33-	0.09	-0.37	0.17
PCB-53-	-0.01	0.00	0.18
PCB-22-	0.08	-0.13	-0.14
PCB-45-	-0.01	0.01	0.18

Table 5 (continued)

Chemical	May-June	July-August	October
PCB-46-	0.00	0.00	0.38
PCB-52-	0.14	-0.06	0.23
PCB-49-	-0.00	-0.25	0.23
PCB-47+48-	-0.01	0.20	0.42
PCB-44-		0.13	0.41
PCB-42-	-0.01	-0.06	0.02
PCB-41+71+64	0.12	-0.28	0.37
PCB-40-	-0.10	0.11	0.35
PCB-74-	0.20	-0.29	0.20
PCB-70+76-	0.12	-0.13	0.39
PCB-66+95-	0.10	-0.19	0.42
PCB-91-	0.07	-0.10	0.28
PCB-56+60+81	0.20	-0.35	0.25
PCB-84+92-	0.16	-0.23	0.42
PCB-101-	0.14	-0.18	0.42
PCB-99-	0.20	-0.43	0.34
PCB-87+97-	0.30	-0.49	0.40
PCB-85-	0.11	-0.25	0.30
PCB-110-	0.11	-0.13	0.41
PCB-82-	0.20	0.00	0.16
PCB-151-	0.17	0.00	0.14
PCB-149-	0.33	-0.60	0.12
PCB-118-	0.34	-0.36	-0.02
PCB-146-	0.14	0.00	0.05
PCB153+132+105	0.28	-0.69	0.32
PCB-141-	0.16	-0.10	0.32
PCB-138-	0.38	-0.32	0.13
PCB-158-	0.00	0.00	0.01
PCB-129-	0.00	0.00	-0.13
PCB-178-	0.00	0.00	-0.02
PCB-187+182-	-0.01	0.00	0.05
PCB-183-	0.00	0.00	-0.01
PCB-128-	-0.01	0.00	0.27
PCB-185-	0.00	0.00	0.00
PCB-174-	0.27	-0.10	0.19
PCB-177-	0.00	0.00	0.33
PCB-171+156-	0.23	0.00	0.13
PCB-173-	0.00	0.00	0.00
PCB-180-	0.20	0.17	0.10
PCB-170+190-	0.00	0.00	0.03
PCB-201-	0.00	0.00	0.00
PCB-203+196-	0.00	0.00	0.00
PCB-195-	0.00	0.00	0.39
PCB-194-	0.00	0.00	0.01
PCB-206-	0.00	0.00	0.33
PCB-209-	0.00	0.00	-0.04

## DISCUSSION

### Spatial patterns

Water concentrations of most contaminants are quite low and uniform. The presence of toxic contaminants in offshore waters shows that the lake is presently polluted by a variety of sources. Halfon (1990) identified the Niagara River as a major source, much larger than the local sources along the Toronto Waterfront. The percentages for the Toronto Waterfront range between 0.5 and 25%. At the low end are the PCBs and at the high end 1,4-DCB. The Toronto Waterfront might be a significant source of toxic contaminants, especially for the chlorinated benzenes. Elimination of chlorobenzene loadings from the Toronto Main STP would be quite beneficial to the Lake Ontario ecosystem. This action, however, might be impossible since low chlorinated benzenes are often used as disinfectants in urinals. Observability of the effect of removing these loads are discussed in Halfon (1990) by using simulation models.

Local sources of pollution with resulting concentrations higher than 1 ng/L have been identified only for 1,4-DCB (in May-June and July-August only), 1,2-DCB and total PCBs. All local sources of pollution are in Humber Bay; however the exact location of each source has not been identified.

A correlation analysis between water temperature and contaminant concentrations has pointed out possible local sources of other contaminants, namely in May-June, 1,2,4,5-TeCB, HCE, lindane and the PCB isomers PCB-18, PCB-118 and PCB-138; in

July-August 1,4-DCB, 1,2,4-TCB, HCB, 2,3,6-TCT, lindane, gamma-chlordane, pp'-DDE, pp'-DDD and the three isomers PCB-18, PCB-99 and PCB-153-132; in October, 1,2,3-TCB, 1,2,3,4-TeCB, QCB and pp'-DDD. But the concentrations of these contaminants are quite low, <1 ng/L, and therefore the evidence from the correlation analysis is only circumstantial. Furthermore, the contaminant pattern varies with the sampling time, which points to intermittent sources of pollution.

Alpha-BHC is present in Lake Ontario at relatively high concentrations (4-6 ng/L). This contaminant was observed uniformly distributed at concentrations far higher than all other contaminants. Lindane, total PCBs and occasionally the dichlorobenzenes were present at concentrations close to 1 ng/L. The spatial patterns identified by the ranking analysis are fairly uniform independent of water temperature conditions. The size and configuration of impact plumes change over the months but the basic pattern does not change much. Humber Bay and Toronto Inner Harbour are the zones most impacted followed by an area in the east end near Highland Creek.

#### Temporal trends

The distribution of some individual contaminants changed dramatically during the survey. As noticed above, some contaminants, like the dichlorobenzenes, were present in large concentrations in May-June and July-August but disappeared almost completely in October. Others, like the isomer PCB-1, were not

present in May-August but were present in low concentrations in October.

Even if individual concentrations of contaminants change seasonally, the overall pattern of pollution (as shown by the ranking analysis, Figs. 2-4) does not change much. Halfon (1990) has studied temporal trends in more detail with mathematical modeling techniques.

#### Comparison of results with existing guidelines/water quality objectives

PCB water quality objectives (PWQO) of 1 ng/L are exceeded in many locations of the Toronto Waterfront. This observation reflects the fact that the average concentration of PCBs in Lake Ontario is 1.3 ng/L. Local sources of PCBs do not have much impact on the nearshore waters. Other contaminants observed in concentrations between 1 and 5 ng/L, such as the three dichlorobenzenes, alpha-BHC and lindane have higher water quality objectives (lindane is 10 ng/L and 1,2-DCB is 2500 ng/L) and therefore occur in concentrations unlikely to have a serious deleterious effect.

#### Pollution ranking analysis

The reality that we wish to represent is difficult to classify and only when reality is simple (elements in a chain) no problems of visual display exist. The Hasse diagram is a solution to the understanding of large amounts of data (Table 3) while not

confounding the large amount of information in a simple chain. We should avoid procedures that are apparently simpler (scalar indices) because we may distort reality by gaining simplicity.

The ranking procedure with the vectorial approach is applicable to a variety of problems in environmental toxicology. Once data have been collected, a computer can process them in a few seconds and point out contradictions within a data set. A graphical display program has been developed for desk top computers and is available on request; a second program produces publication ready figures on a plotter. The number of different classification levels is directly proportional to the number of sites and inversely proportional to the number of criteria; in fact the more criteria considered at the same time, the higher the probability of contradictions in the data and therefore the fewer the discrimination levels. In this instance the number of ranking levels is quite high (8 or 9) in relation to the number of attributes used (25). This result points to pollution of the waterfront areas by the same variety of contaminants acting together. If the ranking analysis would have provided a much smaller number of ranks, 3 or 4, then our interpretation would have been that some areas were polluted by some contaminants and other areas by other contaminants. Because this pattern of pollution is not present in the Toronto Waterfront, we can surmise that the contaminants are already mixed together in a few sources (.e.g., STPs).



The availability of the ranking program in microcomputer form makes the routine applicability easy to this or other ranking problems, for example, ranking the effects of toxic contaminants (Halfon and Reggiani, 1986). If the relative toxicity of each of the contaminants and their relative retention in drinking water plants were available, techniques such as these will be powerful tools to prioritize the contaminants which require the most regulatory action.

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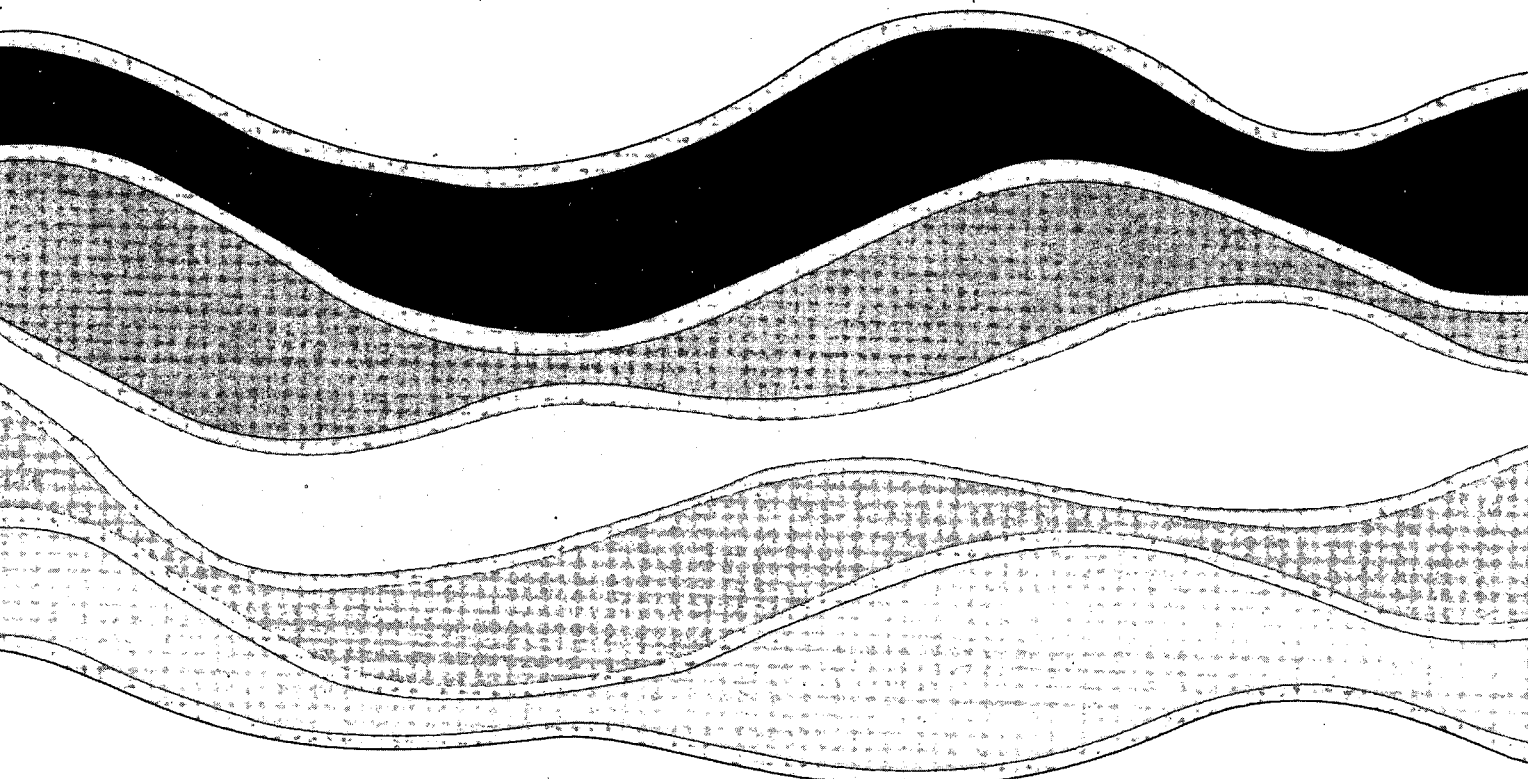
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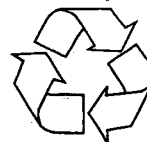


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