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**DISTRIBUTION OF CHLORINATED BENZENES
IN THE NIAGARA RIVER PLUME**

by

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EXECUTIVE SUMMARY

The dispersion of two chlorobenzenes from the Niagara river into Lake Ontario was measured on three occasions in 1983. Despite modifications in study design over the previous year, anomalies in chlorobenzene distribution were again observed. It is concluded that some unidentified factor and not flow fluctuations is causing this effect. Partition coefficients derived from the current results are higher than predicted but can be explained if the nature of the suspended material is examined.

MANAGEMENT PERSPECTIVE

The experiments reported here were one component of the joint ECD-APSD Niagara River Plume Project. All field and experimental work for this project is complete and once the various reports on each component are written, a publication analysing the management significance of the overall project is planned.

RÉSUMÉ DE L'ÉTUDE

A trois occasions, en 1983, on a mesuré la dispersion dans le lac Ontario de deux chlorobenzènes provenant de la rivière du Niagara. Malgré les modifications apportées à la conception de l'étude par rapport à l'année précédente, on a de nouveau observé des anomalies dans la distribution du chlorobenzène. On les a attribuées à un facteur inconnu, plutôt qu'aux fluctuations du débit. La valeur de partage dérivée des résultats actuels est plus élevée que prévu mais on peut l'expliquer en examinant la nature des matières en suspension.

PERSPECTIVE DE GESTION

Les expériences dont on fait état ici étaient un élément du projet conjoint connu sous le nom de ECD-APSD Niagara River Plume Project. On a terminé toutes les expériences et travaux sur le terrain entrepris dans le cadre de ce projet; une fois que les divers rapports sur chaque élément auront été rédigés, on projette de faire paraître une publication où l'on analysera l'importance de tout le projet pour la gestion.

ABSTRACT

The dispersal of 1,2,4-trichlorobenzene and 1,2,3,4-tetrachlorobenzene into Lake Ontario from the Niagara River plume was examined on three occasions in 1983. On each of these occasions, simple sail drogues were deployed in the river mouth to mark a specific water mass and water samples were collected periodically over the day at sites known to be in the plume based on physical measurements and drogue positions. This procedure was a significant modification of the sampling design used in the previous year. This modification was made necessary by the observation that contaminant concentrations at some sites in the plume were higher than in the river. This anomaly was thought to be due to flow fluctuations in the river. Despite modifications in sampling design to minimize the effects of flow fluctuations, concentrations of chlorobenzenes were found to be higher at some stations in the plume than in the river. It was concluded that some other unidentified factor and not flow fluctuations must be causing this effect.

Carbon normalized partition coefficients for the two chlorobenzenes suggest that contaminants are sorbed more strongly to the material suspended in the river than they are to sediment trap material and to bottom sediments. This is presumably due to its predominantly biological origin. Thus the nature of suspended solids in this system must be considered in attempts to describe the partitioning of contaminants between dissolved and sorbed states.

RÉSUMÉ

À trois occasions, en 1983, nous avons examiné la dispersion dans le lac Ontario du 1,2,4, - trichlorobenzène et du 1,2,3,4 - tétrachlorobenzène provenant du panache de la rivière du Niagara. À chacune de ces occasions, nous avons déployé des bouées stationnaires à voile simple dans l'embouchure de la rivière pour délimiter une certaine masse d'eau et nous avons recueilli des échantillons d'eau périodiquement tout au long de la journée dans des sites que l'on sait être dans le panache en se basant sur les mesures physiques et les positions des bouées. Cette procédure était très différente de la conception de l'échantillonnage utilisée l'année précédente. Il a fallu modifier la procédure parce qu'on s'est rendu compte que les concentrations de contaminants à certains sites du panache étaient plus fortes que dans la rivière. Nous avons attribué cette anomalie aux fluctuations du débit de la rivière. Malgré les changements apportés à la conception de l'échantillonnage pour minimiser ces fluctuations, nous avons constaté que les concentrations de chlorobenzènes étaient plus fortes à certaines stations dans le panache que dans la rivière. Nous en avons conclu qu'un autre facteur inconnu, plutôt que les fluctuations du débit, devait être responsable de cette anomalie.

La valeur de partage normalisée du carbone pour les deux chlorobenzènes laisse supposer que les contaminants sont plus fortement adsorbés par les matières en suspension dans la rivière que par les matières des fosses à sédiments et par les sédiments du fond. Cela est probablement dû à leur origine qui, de façon prédominante, est biologique. Il faut donc considérer la nature des matières solides en suspension dans ce système lorsqu'on essaie de décrire le partage des contaminants entre ceux qui sont dissous et ceux qui sont adsorbés.

INTRODUCTION

The Niagara River Toxics Committee (NRTC) has recently demonstrated that the Niagara River contributes a significant load of synthetic organic contaminants to Lake Ontario (NRTC, 1984). There is considerable public concern over the presence of these contaminants and their possible effects on human health and the Lake Ontario ecosystem. In 1982, we began a study of the physical transport and fate of Niagara River contaminants from the river into Lake Ontario. The results of this study are being combined with the results of concurrent studies of the factors controlling the direction and magnitude of the Niagara River plume and the extent of its interaction with Lake Ontario carried out by physical limnologists in the Aquatic Physics and Systems Division (APSD) of NWRI (Murthy et al., 1984 & 1987).

The focus of our efforts during the first year of the study was to determine which contaminants were suitable markers of Niagara River water in the lake and to determine methods of detecting and sampling water in the Niagara River plume. Light transmission at the surface, as measured with a transmissometer, and surface water temperature were found to be good physical parameters of use in locating the plume. On some occasions, only one of the parameters was useful due to a similarity between the river and the open lake for the other. Thus, to be assured of locating the plume, it is advisable to determine both surface transmission and temperature. On the seven occasions that the Niagara River plume was sampled the most common orientation was in an easterly direction, usually remaining close to the south shore. This agrees with the observations of Murthy (1969) and is

a consequence of the most common wind direction (generally westerly) and the semipermanent easterly flowing currents along the south shore of Lake Ontario (Simons, 1972). This orientation also produced the most coherent plumes.

The best contaminant tracers of Niagara River water into the lake were found to be 1,2,4-TCB and 1,2,3,4-TeCB. However, interpretation of the concentration patterns was made difficult by the fact that on five of the seven occasions, the concentration of 1,2,3,4-TeCB at a location in the plume was approximately two times higher than in the river. It was suggested that these effects were due to the daily fluctuations in water diversions from the upper Niagara River by U. S. and Canadian power authorities. Unfortunately, this behaviour was unanticipated and therefore the sampling design did not take it into account. For all seven cruises in 1982, the lake samples were obtained prior to sampling the river. This sampling strategy would tend to maximise these diurnal differences if they occur.

The results of this initial study led to the following recommendations regarding further studies of contaminant transport in the Niagara River plume;

i) The sampling strategy should take into account the possibility of diurnal fluctuations in contaminant concentration. For example, a sound strategy would be to follow contaminant transport and fate in a 'plug' of water from the river into the lake.

ii) The two chlorobenzenes, 1,2,3,4-TeCB and 1,2,4-TCB,

appear to be suitable as contaminant tracers of Niagara River water. However, at some sites, their concentrations are close to detection limits giving rise to analytical imprecision. The importance of this problem could be reduced by sampling larger volumes and using a suitable internal standard.

In this report, we describe the results of the following year's work in which we attempted to put some of the above recommendations into practice.

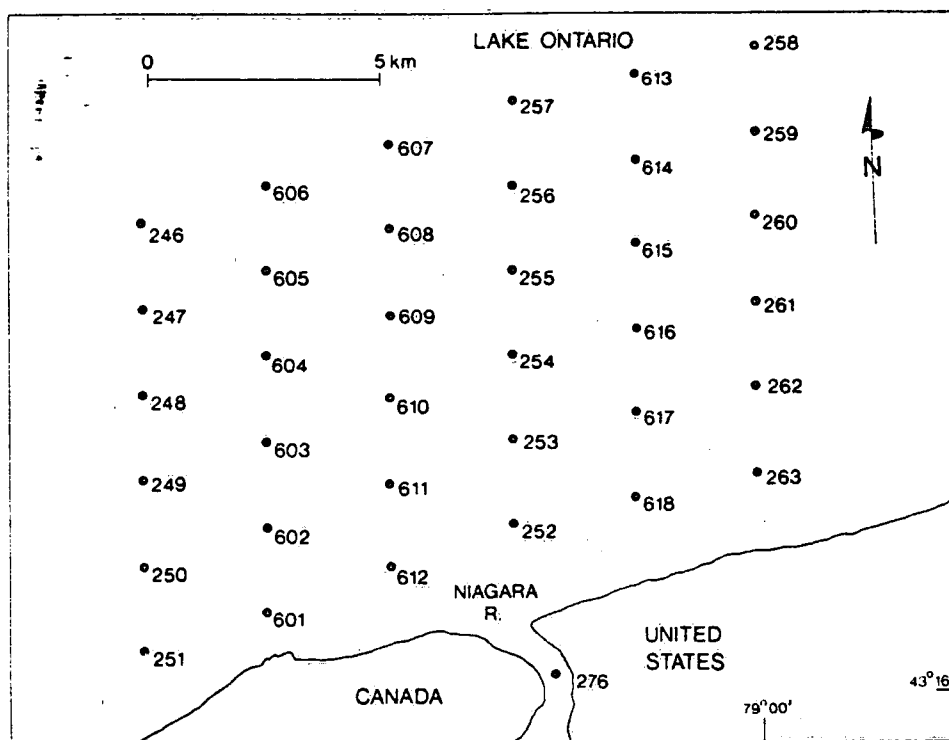


Fig 1. Map of study area showing sampling locations.

PROCEDURES

The study area and sampling procedures were similar to that described in the report of our earlier studies (Fox and Carey, 1986). The original sampling grid was modified for this study by removing the westernmost and easternmost transects and inserting two new transects to produce a uniform array of six transects separated by 2 km each containing six sampling sites at 3 km intervals as shown in Figure 1.

Sampling cruises were carried out in May, August and October in 1983. On each of these occasions, water samples were collected in the river mouth while drogues were being released at the Niagara River bar area for use as markers of specific water masses. The vessel then proceeded to the inshore station on the

westernmost transect. Temperature and light transmission measurements were then made systematically at each site on the sampling grid. Water samples for organochlorine contaminant analysis were collected at 1 m depth from grid stations known to be in the plume based on the results of the light transmission and temperature measurements and on drogue positions. On two occasions, nearshore and offshore stations out of the plume were sampled as reference sites. Water samples were also collected at depths of 2 m from the bottom in May and 5 m from the bottom in August and October at the same sites as the 1 m samples. On each sampling occasion, duplicate samples were collected from the river mouth site to check sampling and analytical variability.

Sampling and extration techniques were also modified from the 1982 procedures. Two separate samples were collected at each site and depth in amber glass 4L solvent bottles. One of the samples was immediately filtered with 10-15 psi nitrogen pressure through preweighed Gelman type A/E glass fibre filters (nominal pore size 1µm) that had been prefired at 400° C overnight. In order to inhibit biological processes and to initiate extraction, 150 ml of pesticide grade dichloromethane (Caledon Laboratories) was added to each sample in the field. The preweighed glass fibre filters were saved to determine the amount of suspended solids on the first two sampling cruises. This was found to be inadequate since small amounts of filter paper fibres were lost by adhesion to the filter holder. This small loss was of the same order of magnitude as the suspended solid weight. Therefore for the last sampling cruise, a separate 1L sample was collected and filtered through a preweighed Whatman GFC filter which was

reweighed after air drying and again after ashing to obtain suspended solid and loss on ignition weights.

The water samples were returned to the laboratory and stirred for 1 hour with a teflon coated stir bar at low speed. The dichloromethane was transferred to a 250 ml separatory funnel. A further 50 ml was added to the sample and the extraction repeated. A final 25 ml was used to complete the extraction. The extracts were combined, separated from residual water and dried by passing through a 5cm bed of anhydrous sodium sulfate. After addition of 3 ml of pesticide grade isooctane as a keeper, the extract was evaporated to 1-2 ml on a rotary evaporator at 40° C. The extract was further concentrated by nitrogen blowdown to exactly 1 ml and transferred to a crimp top vial for analysis by gas chromatography. In August and October, 93 ng of 1,3,5-tribromobenzene was added in 1 ml of methanol as an internal standard.

RESULTS AND DISCUSSION

The first sampling cruise of 1983 for this study occurred on May 11. Early in the morning, drogues were deployed in the bar area to track a specific water mass which was sampled in the river mouth area at that time. The ship then proceeded to the westernmost transect and began making temperature and transmission measurements at each station on the grid. The results of the temperature and transmission measurements are shown in Figure 2. The easterly flowing plume of warm turbid Niagara River water is clearly evident. These observations were used to define the plume and to select two sites clearly out of the plume for background contaminant measurements.

The water mass identified by the drogues was sampled at 1m depth at nine sites on the grid as it progressed from the bar area to the easternmost transect over a twelve hour period. At five of the deeper sites, water samples were also collected at a depth of 2m from the bottom. The results of the contaminant analysis are presented in Table 1. Members of the chlorobenzene and lindane families were the most significant of the organochlorines in agreement with results from the previous year (Fox & Carey, 1986) in which 1,2,4-trichlorobenzene (1,2,4-TCB) and 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) were suggested as the most suitable chemical tracers of Niagara River water. The distribution of one of these tracers, 1,2,3,4-TeCB, in filtered and unfiltered water at depth 1m is shown in Figure 3.

As expected, 1,2,3,4-TeCB was not detected at significant

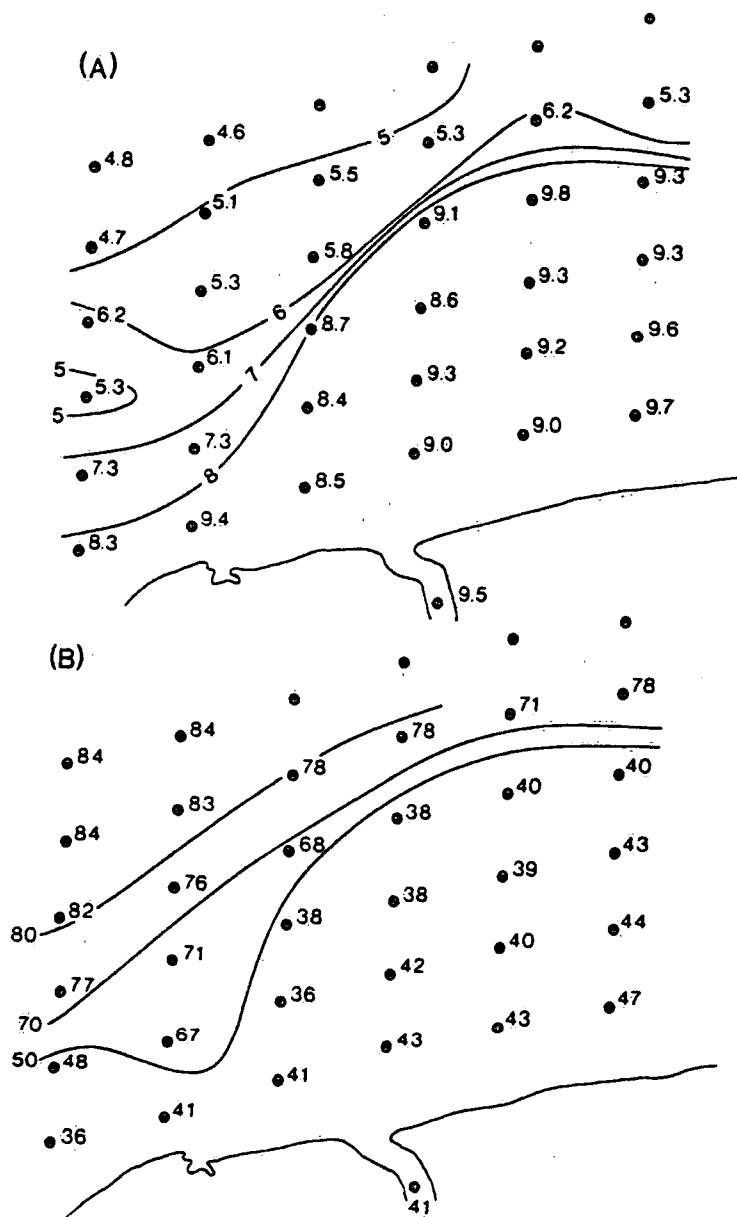


Fig. 2. Niagara River Plume. May 11 1983.
 (A) surface temperature; (B) % transmission

Table 1. Concentrations of organochlorine contaminants (ng/L) observed in Lake Ontario and the Niagara River, May 11, 1983.

Station	Depth (m)	f/u	1,2,4- TCB	1,2,3- TCB	1,2,3,4- TeCB	PeCB	Lindane
276	1	u	24.1	7.7	10.7	1.5	1.6
276	1	f	13	4.8	5.2	1.4	3.1
606	1	u	3.6	2	<1	<0.5	3.8
606	1	f	6	2.6	ND	ND	5.4
601	1	u	4	2.2	ND	ND	3.8
601	1	f	2.5	1.2	ND	ND	2.7
611	1	u	16.7	6.1	7.5	1.9	3.3
611	1	f	18.1	6.5	6.9	1.5	3.6
610	1	u	12.3	3.9	5.1	1.4	2
610	1	f	9.8	3.1	3.3	0.5	2.3
610	12	u	2.5	1	ND	ND	1.9
610	12	f	3.2	<1	ND	ND	2
254	1	u	16.5	5.4	5.8	1.9	3.9
254	1	f	13.7	4.6	5.2	0.9	2.1
254	13	u	11.8	4.3	5.3	1.3	2.8
254	13	f	10.8	4.3	4.3	<0.5	4.2
253	1	u	18.4	6.6	7.5	1.8	3.3
253	1	f	21.2	7.3	6.7	1.1	2.8
253	7	u	13.1	5.2	4.6	1.7	2
253	7	f	ND	2	ND	ND	2
252	1	u	22.1	7.9	7.4	1.9	3.7
252	1	f	16.4	5.1	4.1	0.6	1.5
617	1	u	23.7	8	10.3	1.9	2.9
617	1	u(rep)	20.6	6.4	9.4	2	3.2
617	1	f	21.7	7.9	8.8	2.2	4.4
616	1	u	13.9	5	6.3	1.3	2.1
616	1	f	12.6	3.8	4	0.7	1.7
616	12	u	8.6	3.6	3.3	0.5	0.5
616	12	f	12.5	4.6	4.4	1.1	2.9
261	1	u	15.6	5.4	5.6	1.1	1.9
261	1	f	22.3	7.8	7.1	1.5	3.8
261	20	u	3.6	1.7	1.3	ND	2.7
261	20	f	3.6	1.7	1.2	ND	2.4
262	1	u	16.8	5.4	5.5	0.8	1.2
262	1	f	10.3	4.4	4.1	1.9	2
Proc. Bl.	-	u	1.1	ND	ND	ND	0.6
Proc. Bl.	-	f	ND	ND	ND	ND	0.7

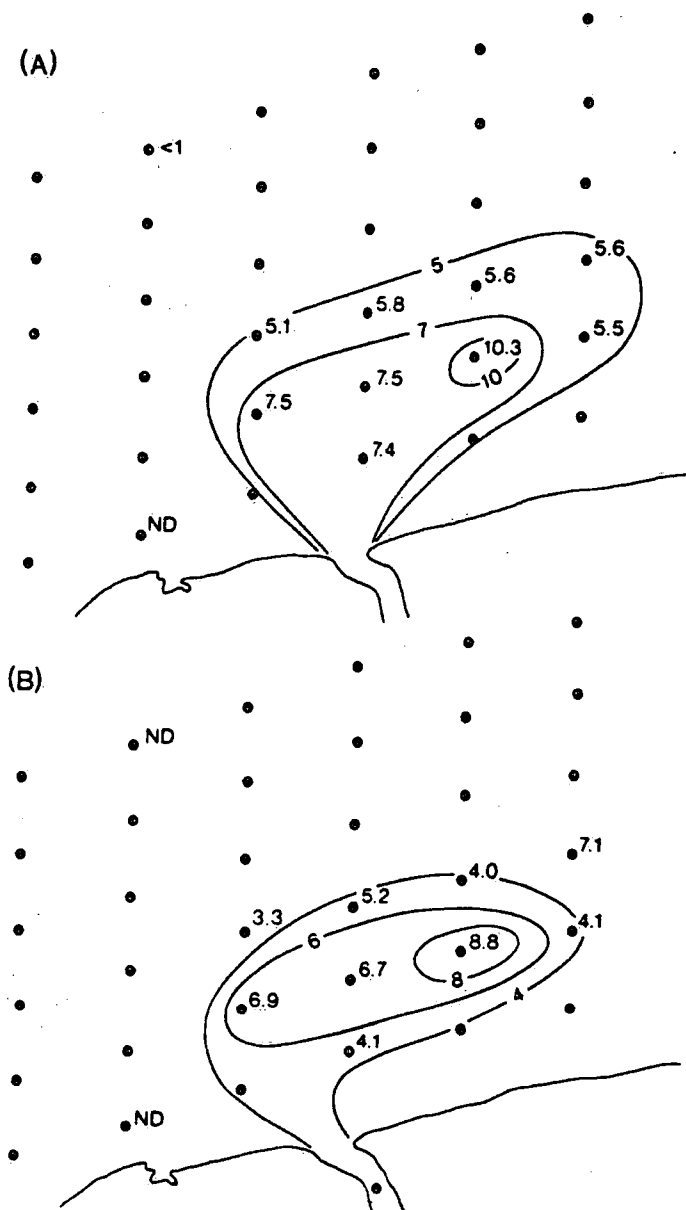


Fig. 3. Concentration of 1,2,3,4-TeCB in (A) unfiltered and (B) filtered samples, May 11 1983.

levels at the two out-of-plume sites confirming its usefulness as a chemical marker of the plume. The concentration of 1,2,3,4-TeCB in unfiltered water from the Niagara River mouth (site 276) was 10.7 ng/L while the concentration in filtered water from the same site was 5.2 ng/L. Thus approximately 50 % of the 1,2,3,4-TeCB was dissolved and 50 % adsorbed on suspended solids. This distribution was also observed at the next sampling site nearest to the river mouth (site 252). Further from the river mouth, the relative proportion dissolved increased to >70 %. For example, at site 262 on the easternmost transect the unfiltered concentration of 1,2,3,4-TeCB was 5.5 ng/L and the corresponding concentration in filtered water was 4.1 ng/L (75 % dissolved). One puzzling feature of these results is the existence of a patch of higher concentration at site 617. Such locally high patches were observed in previous work and interpreted as resulting from diurnal flow variations in the river due to water diversions for hydro generation (Stepien et al., 1987). The use of drogues to mark a specific water mass for sampling was expected to eliminate this factor. The observed differences were well outside of the analytical imprecision for these analyses which was estimated to be less than 5 % from the analysis of replicate samples. Despite this good precision, it was decided to add 1,3,5-tribromobenzene as an internal standard to each sample on subsequent cruises.

The second sampling cruise occurred on August 10. The surface temperature and transmission values determined at the grid sites are shown in Figure 4. The presence of a strong wind from the south resulted in a northerly flowing plume as clearly indicated in the temperature data. The transmission data was not

of use in determining the plume location because of the very turbid conditions prevailing all over the grid, especially in the southwest corner near the Welland Canal. Because of the speed at which the drogues were carried to the north, it was not possible to complete temperature and transmission measurements at sites on the grid and simultaneously conduct water sampling coincident with drogue positions. Water for contaminant analysis was collected 1 m from the surface and 2 m from the bottom at nine sites. The results of the contaminant analyses are listed in Table 2. The distribution of the plume tracer 1,2,3,4-TeCB for this cruise is shown in Figure 5. There is no obvious pattern to the results and none of the sites at which samples were collected were clearly outside the influence of the plume. It is likely that the resuspended sediments in the southwest corner of the grid significantly affected these results. This suggestion is supported by the percent of 1,2,3,4-TeCB dissolved at the sites. In the river (site 276) and in the easternmost samples (sites 252 and 256) between 75 and 90% of the 1,2,3,4-TeCB is dissolved, whereas at the westernmost site (site 248) only 55 % was dissolved. These results indicated a need for quantitative suspended solids data and it was decided to include measurements of suspended solids on the next sampling cruise. In addition, in both this and the previous cruise, the samples taken at a depth of 2 m from the bottom contained very little of the plume markers and profiles of temperature and transmission indicated that away from the bar area, the plume was only a few metres thick. It was therefore decided that on the next cruise samples

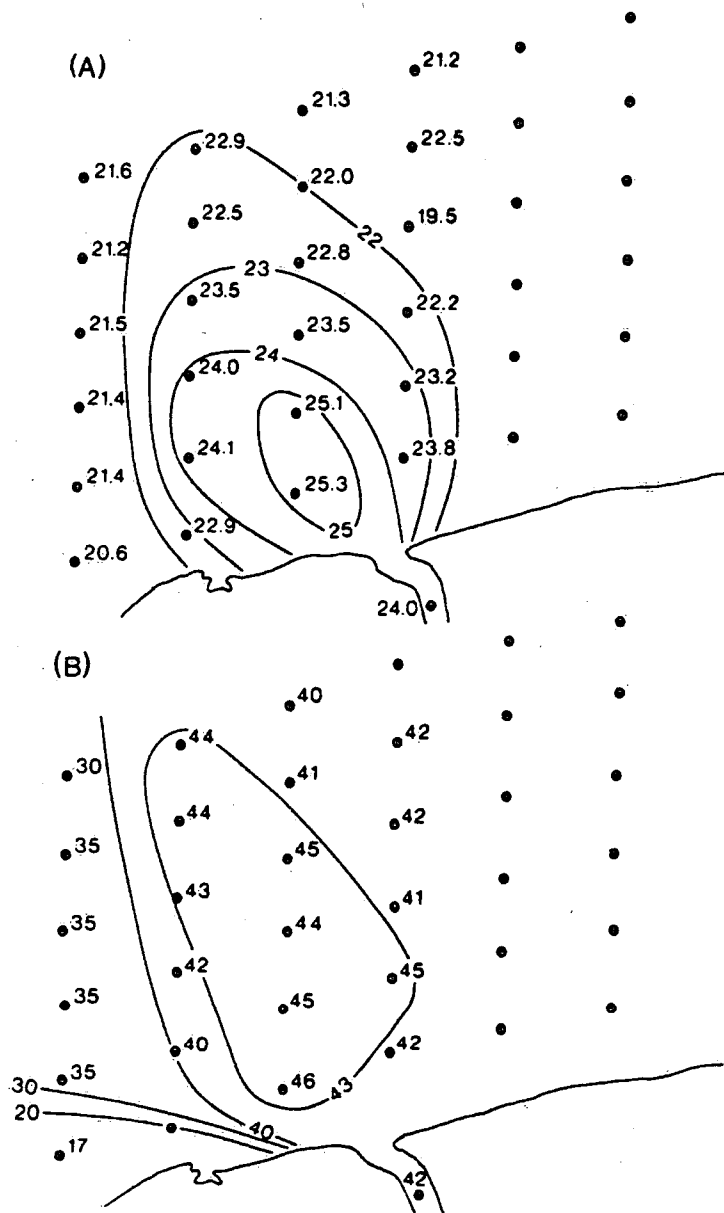


Fig. 4. Niagara River Plume. August 10 1983.
 (A) surface temperature; (B) % transmission

Table 2. Concentrations of organochlorine contaminants (ng/L) observed in Lake Ontario and the Niagara River, August 10 1983.

Station	Depth (m)	f/u	1,2,4-	1,2,3,4-	Lindane
			TCB	TeCB	
276	1	u	15	6.3	2.6
276	1	f	14	4.8	2.8
248	1	u	4.6	3.4	3.5
248	1	f	4.4	1.9	4.7
248	5	u	0.6	0.5	4.5
248	5	f	1.7	0.5	3.3
606	1	u	NM	NM	2.4
606	1	f	2.9	1.7	3.1
606	5	u	1.6	0.5	3.7
606	5	f	1	0.3	2.7
603	1	u	3.7	3.1	3
603	1	f	9.2	3.8	3.1
603	5	u	2	0.6	1.7
603	5	f	2.4	0.4	1.4
601	1	u	12.4	5.1	2.6
601	1	f	6.4	4.5	4.1
601	5	u	2.6	1.8	1.8
601	5	f	4	1.2	2.6
612	1	u	9.9	4.5	2.5
612	1	f	5.2	3.1	2.5
612	5	u	9.2	4.7	3
612	5	f	7.8	3.4	2.1
611	1	u	11	4.9	2.1
611	1	f	9.7	4.1	2.3
611	5	u	8.6	4	1.8
611	5	f	9.2	3.9	2.1
256	1	u	7	3.4	2.9
256	1	f	5.4	3.1	2.5
256	5	u	2	0.4	2.2
256	5	f	2.8	0.5	3.4
252	1	u	16	7.1	3.8
252	1	f	13	5.8	4.2
252	5	u	2.8	3.2	2.7
252	5	f	6.4	3.4	2.7
Proc. Bl.	-	u	ND	ND	0.7
Proc. Bl.	-	f	ND	ND	0.4

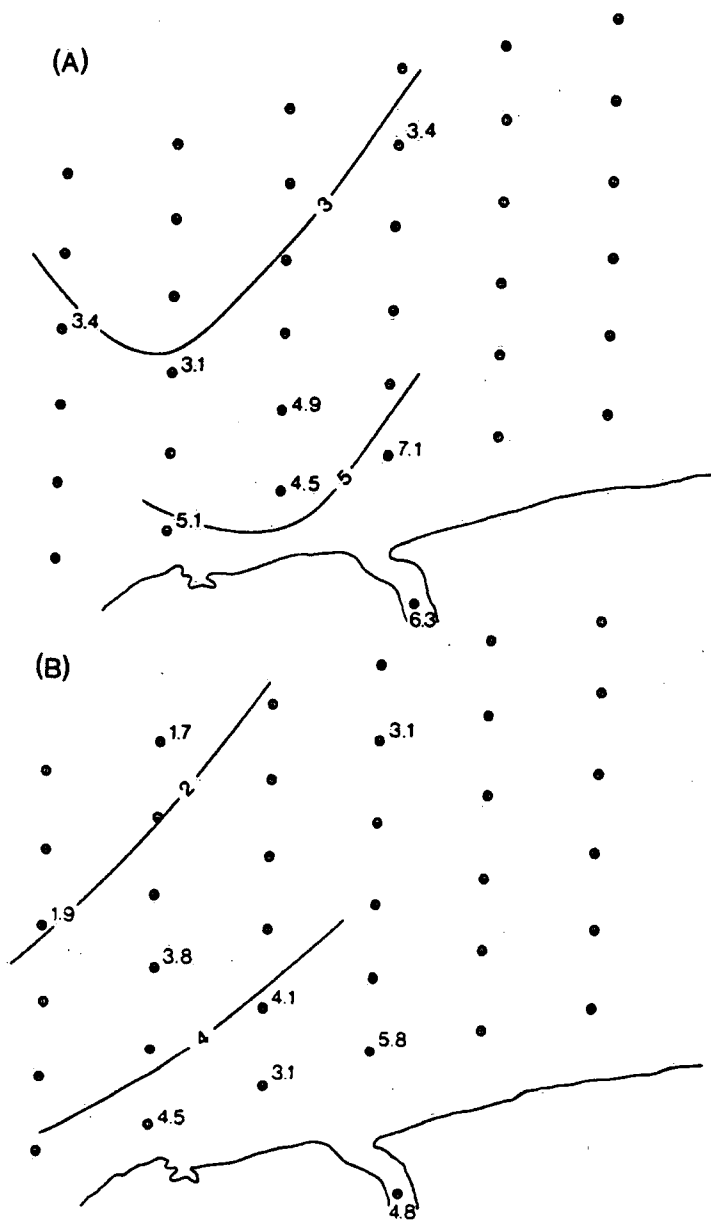


Fig. 5. Concentration of 1,2,3,4-TeCB in (A) unfiltered and (B) filtered samples, August 10 1983.

for contaminant analysis should be collected at 1 and 5 m depths.

The final sampling cruise of 1983 was conducted on October 4th and a well defined, easterly flowing plume was encountered. The temperature and transmission data collected on this cruise are shown in Figure 6. The % transmission in the river was significantly higher than in the two previous cruises indicating significantly lower suspended solids. The results of the suspended solids analyses are given in Table 3. These results confirm that the levels of suspended solids in the river on this occasion were relatively low (~5mg/L). Suspended solids in the plume at the easternmost transect were about 30% lower, indicating a small loss during transit while levels to the west of the plume at the two control site were more than 50 % lower.

In addition to two samples from the river mouth (site 276) collected in the morning and afternoon, water for contaminant analyses was collected at 1 and 5 m at 11 sites in the plume and two reference sites outside the plume. The results of the contaminant analyses for these samples are listed in Table 4 and the distribution of the plume marker 1,2,3,4-TeCB is shown in Figure 7. The level of 1,2,3,4-TeCB in the river mouth was about 10x higher than the levels observed at the two western sites out of the plume. A patch of higher concentration was again observed offshore and to the east of the river mouth. Since there was excellent coincidence between drogue position and plume water sampling throughout this cruise it is apparent that the existence of these higher patches cannot solely be due to diurnal fluctuations in concentration in the river.

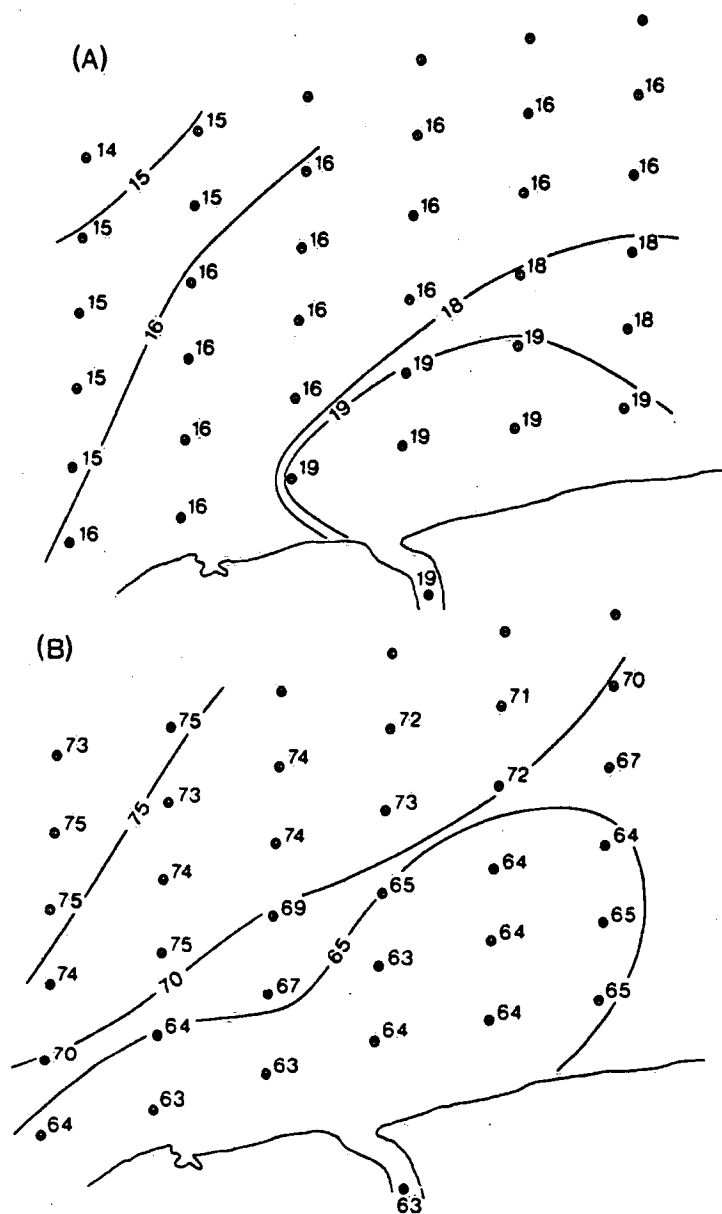


Fig. 6. Niagara River Plume. October 4 1983.
(A) surface temperature; (B) % transmission

Table 4. Concentrations of organochlorine contaminants (ng/L) observed in Lake Ontario and the Niagara River, October 4 1983.

Station	Depth (m)	f/u	1,2,4-	1,2,3,4-	Lindane
			TCB	TeCB	
276	1	u	12.8	6.3	3.3
276	1	f	16	6.9	2.8
251	1	u	3.1	0.7	3.4
251	1	f	3.1	0.8	3.1
246	1	u	1.8	0.6	3.4
246	1	f	2	0.6	3.6
612	1	u	NM	NM	NM
612	1	f	11	4.2	3.5
612	5	u	13	4.8	4.1
612	5	f	8.2	3.5	3.5
254	1	u	2.6	0.7	2.7
254	1	f	2.4	0.6	3.7
254	5	u	2.2	0.5	3.6
254	5	f	2.2	0.5	2.5
253	1	u	11	6.7	2.4
253	1	f	10	5.4	2.4
253	5	u	15	7.3	2.4
253	5	f	15.8	6.4	2.3
252	1	u	5.8	6.6	3.7
252	1	f	4.6	6.4	4.9
252	5	u	12	6.1	2.6
252	5	f	14.2	5.4	2.2
618	1	u	14.6	8.2	3
618	1	f	NM	NM	2.6
618	5	u	7.2	6	3
618	5	f	11	6.7	3.3
617	1	u	19.8	6.9	3
617	1	f	16.8	7.4	3
617	5	u	9.6	5.7	2.2
617	5	f	9.6	3.6	2.7
616	1	u	7	2.7	2.6
616	1	f	13.4	5.5	6.2
616	5	u	3.6	1.1	2.3
616	5	f	4	0.9	2.5
260	1	u	2.4	0.7	5.2
260	1	f	2.9	0.6	6.8
261	1	u	7	2.9	2
261	1	f	8.1	3	3.2
261	5	u	9.9	3.7	2.8
261	5	f	6.2	2.1	3.2
262	1	u	4.6	5.2	2.8
262	1	f	10.7	4.7	3.2
262	5	u	12.6	4.8	2.3
262	5	f	8.2	3.2	1.8
263	1	u	18.7	7.6	3.5
263	1	f	12.6	5.3	2.6
263	5	u	14.2	5.5	2.2
263	5	f	11.8	4.7	2.6
Proc. Bl.	-	u	ND	ND	0.3
Proc. Bl.	-	f	ND	ND	0.6

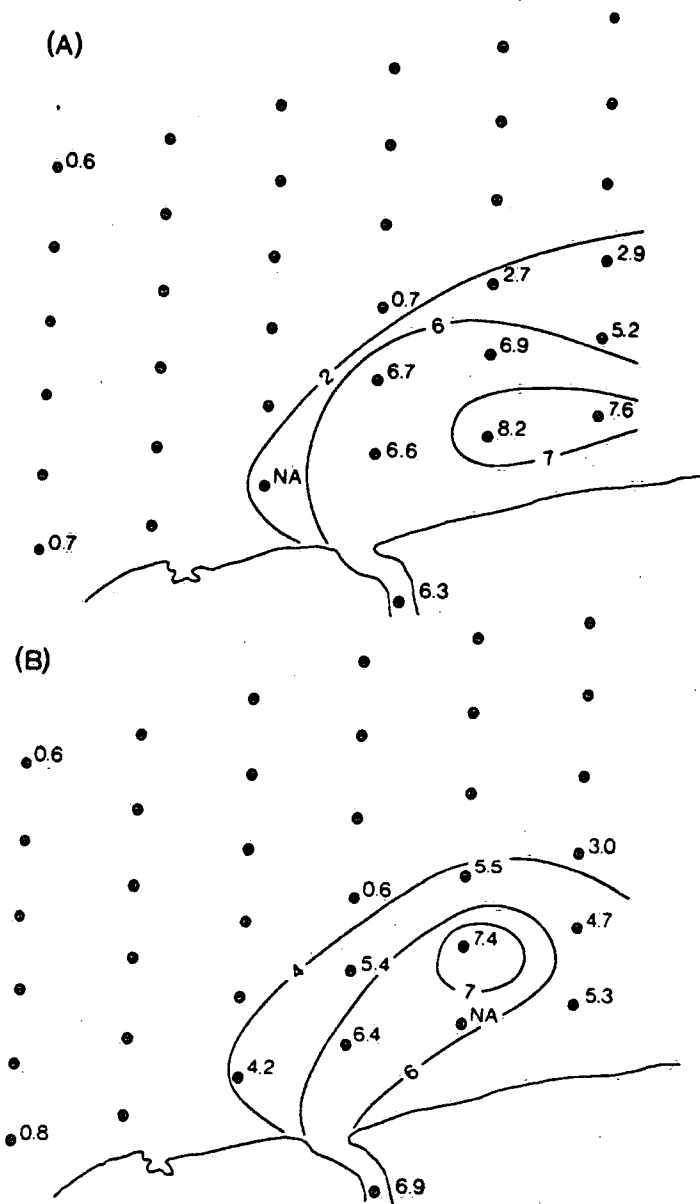


Fig. 7. Concentration of 1,2,3,4-TeCB in (A) unfiltered and (B) filtered samples, October 4 1983.

Table 3. Concentration, loss on ignition and estimated fraction organic carbon (f_{oc}) for Lake Ontario and Niagara River suspended solids on October 4, 1983.

Station	Depth (m)	conc. mg/L	LOI mg/L	f_{oc}
276	1	4.8	1.8	0.19
251	1	2.2	1.1	0.27
246	1	1.5	1.1	0.4
612	1	2.8	1.2	0.21
612	5	3.5	2.5	0.37
254	1	1.9	1.8	0.47
254	5	3.9	1.7	0.23
253	1	3.7	1.2	0.15
253	5	4.2	1.4	0.17
252	1	3.8	2	0.26
252	5	4.2	1.4	0.17
618	1	3.5	1.9	0.29
618	5	3.9	1.3	0.18
617	1	3.9	1.4	0.26
617	5	3.3	1.9	0.3
616	1	2.2	0.9	0.19
616	5	3.4	1.4	0.21
261	1	3.5	1.6	0.23
261	5	4	1.8	0.23
262	1	3.4	1.6	0.24
262	5	3.6	0.8	0.11
263	1	3.7	1.6	0.22
263	5	4.6	2.3	0.26
avg.				0.24
S.D.				0.08

Karickhoff and coworkers (1979; 1981) have discussed the sorption of hydrophobic contaminants to natural sediments in terms of the sediment-water partition coefficient, K_{sw} , defined as

$$K_{sw} = C_s / C_w$$

where C_s = contaminant concentration on sediment (ng/g dry weight)

C_w = contaminant concentration in water (ng/g)

They found that partition coefficients normalized to organic carbon content using the relationship

$$K_{sw} = K_{oc} \times f_{oc}$$

where K_{oc} = organic carbon normalized partition coefficient

f_{oc} = fraction of organic carbon in the sediment

were highly invariant over a set of soils and sediments from a range of geographically distinct areas. To evaluate the agreement of our data with these empirical expressions, the data from Tables 3 and 4 for all sites in the plume were used to calculate K_{sw} and K_{oc} . The results of these calculations are presented in Table 5. It should be noted that the adsorbed concentrations were calculated by difference between filtered and unfiltered samples. Since the overall uncertainty of the analytical procedure was in some cases the same order of magnitude as the differences between filtered and unfiltered samples, some of the filtered samples had higher levels than the unfiltered samples. This resulted in negative values for some of

Table 5. Sediment-water partition coefficient (K_{sw}) and organic carbon normalized partition coefficient (K_{oc}) for 1,2,3,4-TeCB and 1,2,4-TCB in the Niagara River plume, October 4, 1983.

1,2,3,4-TeCB

Station (d)	dissolved conc ng/g	adsorbed conc ng/g	K_{sw}	f_{oc}	K_{oc}
276 (1)	6.9E-03	-1.3E+02	-1.8E+04	0.19	-9.5E+04
612 (5)	3.5E-03	3.7E+02	1.1E+05	0.37	2.9E+05
253 (1)	5.4E-03	3.5E+02	6.5E+04	0.16	4.1E+05
253 (5)	6.4E-03	2.1E+02	3.3E+04	0.17	2.0E+05
252 (1)	6.4E-03	5.3E+01	8.2E+03	0.26	3.2E+04
252 (5)	5.4E-03	1.7E+02	3.1E+04	0.17	1.8E+05
618 (5)	6.7E-03	-1.8E+02	-2.7E+04	0.18	-1.5E+05
617 (1)	7.4E-03	-1.3E+02	-1.7E+04	0.18	-9.6E+04
617 (5)	3.6E-03	6.4E+02	1.8E+05	0.3	5.9E+05
616 (5)	9.0E-04	5.9E+01	6.5E+04	0.21	3.1E+05
261 (1)	3.0E-03	-2.9E+01	-9.5E+03	0.23	-4.1E+04
261 (5)	2.1E-03	4.0E+02	1.9E+05	0.23	8.3E+05
262 (1)	4.7E-03	1.5E+02	3.1E+04	0.24	1.3E+05
262 (5)	3.2E-03	4.4E+02	1.4E+05	0.11	1.3E+06
263 (1)	5.3E-03	6.2E+02	1.2E+05	0.22	5.3E+05
263 (5)	4.7E-03	1.7E+02	3.7E+04	0.26	1.4E+05
			Avg. 5.8E+04		Avg. 2.82E+05

1,2,4-TCB

Station (d)	dissolved conc ng/g	adsorbed conc ng/g	K_{sw}	f_{oc}	K_{oc}
276 (1)	1.6E-02	-6.7E+02	-4.2E+04	0.19	-2.2E+05
612 (5)	8.2E-03	1.4E+03	1.7E+05	0.37	4.5E+05
253 (1)	1.0E-02	2.7E+02	2.7E+04	0.16	1.7E+05
253 (5)	1.6E-02	-1.9E+02	-1.2E+04	0.17	-7.1E+04
252 (1)	4.6E-03	3.2E+02	6.9E+04	0.26	2.6E+05
252 (5)	1.4E-02	5.2E+02	4.4E+04	0.17	2.6E+05
618 (5)	1.1E-02	-9.7E+02	-8.9E+04	0.18	-4.9E+05
617 (1)	1.7E-02	7.7E+02	4.6E+04	0.18	2.5E+05
617 (5)	9.6E-03	0.0E+00	0.0E+00	0.3	0.0E+00
616 (5)	4.0E-03	-1.2E+02	-2.9E+04	0.21	-1.4E+05
261 (1)	8.1E-03	-3.1E+02	-3.9E+04	0.23	-1.7E+05
261 (5)	6.2E-03	9.3E+02	1.5E+05	0.23	6.5E+05
262 (5)	8.2E-03	1.2E+03	1.5E+05	0.11	1.4E+06
263 (1)	1.3E-02	1.6E+03	1.3E+05	0.22	5.9E+05
263 (5)	1.2E-02	5.2E+02	4.4E+04	0.26	1.7E+05
			Avg. 4.1E+04		Avg. 2.05E+05

the adsorbed concentrations and therefore negative values for the corresponding partition coefficients. Despite the fact that neither concentrations nor partition coefficients can actually be negative, the negative values were all used in calculations of the average values for K_{sw} and K_{oc} . As listed in Table 6, the average values for K_{oc} reported in Table 5 are significantly higher than those calculated using the empirical relationships of Karickhoff et al (1979, 1981) and those reported by Oliver and Charlton (1984) for material collected in sediment traps off the Niagara River bar. In view of the uncertainties in the present calculation and the fact the Oliver and Charlton used an average value for the water concentration derived from loading calculations, it would be dangerous to draw too many conclusions from the data in Table 6. Nevertheless, the differences between the three values for K_{oc} may be understandable if the nature of the solid phase is considered. As we have previously reported, the suspended material in the Niagara River contains significant amounts of algae and zooplankton from upstream Lake Erie that can rapidly accumulate significant concentrations of contaminants during the passage from Lake Erie to Lake Ontario (Fox et al., 1980). In the sediment traps, Oliver and Charlton collected material of recent biological origin some of which had been at least partially degraded. The empirical relationships of Karickhoff are based on sediment containing 'stabilised' organic carbon that has undergone substantial biodegradation. The conclusion derived from these observations is that as biological material undergoes degradation in aquatic systems, its general hydrophobicity is decreased and partitioning of hydrophobic

Table 6. Comparison of $\log K_{oc}$ values.

	$\log K_{oc}$ 1,2,4-TCB	$\log K_{oc}$ 1,2,3,4-TeCB
calculated from K_{ow}	3.63	4.06
sediment traps (*)	4.42	4.72
Niagara River solids (#)	5.31	5.45

(*) from Oliver & Charlton, 1983.

(#) this work

contaminants between it and the water phase becomes less favourable. This may be expected since the lipids that form a significant component of the energy pool of organisms and are therefore valuable as food for consumer species are also the phase into which contaminants partition most strongly. The implication of these observations is that models describing the fate of contaminants in surface waters should take into account the nature of the suspended solids present when calculating the extent of partitioning between the solid and water phases.

A second point worthy of mention concerns the patches of higher contaminant concentration observed in the plume relative to the river. In our earlier reports, we ascribed these patches to a the fact that the sampling strategy didn't take into account the possibility of diurnal variations of contaminant concentrations in the river. Despite the fact that the strategy of using drogues to mark specific water masses and sampling that water as it moved into the lake should have minimised variations due to diurnal changes in concentration, the patches of higher concentration were again observed in the current study on the two occasions when the plume turned eastward. It seems likely therefore that some other as yet unidentified effect must be

causing these patches. It is likely significant that when the plume turns east, a large, semi-permanent clockwise eddy often forms to the east of the river mouth. Although the fact that this eddy forms in the same general area as the patch of higher concentration is suggestive, the actual mechanism whereby it could cause an apparent increase in concentration of river contaminants out in the lake is not clear. Intensive scrutiny of recirculation, sediment transport and resuspension processes in this complex transition region will likely be required to resolve the question.

In the current study, there was a significant removal from the surface water of chlorobenzenes adsorbed onto suspended material as the Niagara River water moved into the lake. The contaminants that were present in the river in dissolved state were carried with the Niagara River water out of the study region. The results of the physical studies indicate that the immediate direction of this transport depends strongly on wind direction. (Murthy et al., 1987). Thus the factors controlling the fate of Niagara River contaminants in the river mouth area are the nature and quantity of suspended solids, both of which control extent of partitioning between solid and liquid phases, and the wind direction, which controls the plume direction. Other factors controlling the fate of the Niagara contaminants involve processes occurring once the Niagara River water has lost its initial momentum and becomes entrained in the general lakewide circulation (Murthy et al., 1987). These processes will be the subject of a future report.

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