DYNAMICS OF PLUME DISPERSON OF
1,2,3,4-TETRACHLOROBENZENE FROM
THE NIAGARA RIVER INTO LAKE ONTARIO

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ABSTRACT

The dynamics of dispersion of 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) was examined in the Niagara River mouth area of Lake Ontario. A specific water mass was was tracked for 42 hours directly and 72 hours accumulation of suspended solids using sediment traps. Organic carbon normalized partition coefficients were calculated to describe the relationship between the dissolved phase and suspended solids. The coefficients were significantly higher than predictions from octanol-water partition coefficients and appeared to exhibit a decrease with plume aging. These observations support the proposal (Carey and Fox, 1987) that the elevated values are due to the large lipid pool of the living seston in the Niagara River. 1,2,3,4-TeCB concentrations in all compartments examined were >2x lower than 2-3 years previously. Sediment trap and surficial sediment concentrations of 1,2,3,4- TeCB suggested a resuspension mechanism for frequently observed patches of anomalously high levels in the near-shore plume area.

EXECUTIVE SUMMARY

The dynamics of dispersion of a chlorobenzene contaminant of the Niagara River in the nearfield region of Lake Ontario in 1985 was determined. The distribution of the chlorobenzene between the water phase and the suspended solids was determined for a 72 hour period in the nearfield area. The observations were related to concurrent surficial sediment measurements. Chlorobenzene concentrations in all compartments examined were more than 2x lower than 2-3 years previously.

MANAGEMENT PERSPECTIVE

The experiments reported here were undertaken to extend the physical scope of the previously reported Niagara River plume dispersion studies. No further field measurements are planned and the results and conclusions herein reported will be incorporated into a " State of Lake Ontario Ecosystem" special issue based largely on the symposium of that name, held at the 1988 International Association for Great Lakes Research Conference.

RÉSUMÉ

On a examiné la dynamique de dispersion du 1,2,3,4-
tétrachlorobenzène (1,2,3,4-TCB) dans le lac Ontario à
l'embouchure de la rivière Niagara. Une masse déterminée
d'eau a été suivie directement pendant 42 heures et, à l'aide
de pièges à sédiments, on a observé pendant 72 heures
l'accumulation des solides en suspension. On a calculé le
coefficient de distribution normalisé selon la teneur en
carbone organique pour décrire la relation entre la phase
dissoute et les solides en suspension. Les coefficients
étaient sensiblement plus élevés que les prévisions d'après
les coefficients de distribution octanol-eau et semblaient
présenter une diminution avec le vieillissement du panache.
Ces observations appuient l'hypothèse (Carey et Fox, 1987)

selon laquelle les valeurs élevées sont dues à la forte masse

lipidique de seston vivant dans la rivière Niagara. Les

concentrations de 1,2,3,4-TCB dans toutes les phases

observées étaient plus de deux fois moins élevées que celles

relevées 2 à 3 ans auparavant. Les concentrations de

1,2,3,4-TCB dans les sédiments superficiels et ceux à

l'intérieur des pièges indiquent l'existence d'un mécanisme

de remise en suspension dans le cas des zones de

concentrations anormalement élevées observées fréquemment

dans la région du panache à proximité du rivage.

RÉSUMÉ

On a déterminé, en 1985, la dynamique de dispersion d'un contaminant au chlorobenzène de la rivière Niagara, dans la zone proche des eaux du lac Ontario. La distribution du chlorobenzène dans l'eau et les solides en suspension a été établie pour une période de 72 heures dans la région concernée. On a comparé les relevés à des mesures concurrentes de sédiments superficiels. Dans toutes les phases examinées, les concentrations étaient plus de deux fois inférieures aux valeurs relevées 2 à 3 ans auparavant.

PERSPECTIVES DE GESTION

Les travaux expérimentaux décrits dans ce document ont été
entrepris pour élargir la portée des études antérieures de
dispersion du panache de la rivière Niagara, dont les
résultats ont déjà été publiés. On ne prévoit pas d'autres
mesures sur place, et les résultats ainsi que les conclusions
présentés dans ce document figureront dans une publication
spéciale intitulée "State of Lake Ontario Ecosystem" fondée
en grande partie sur le symposium du même nom, qui a eu lieu
dans le cadre de la Conférence de 1988 de l'International
Association for Great Lakes Research.

INTRODUCTION

Previous reports (Fox and Carey, 1986, Carey and Fox, 1987) have demonstrated the utility of chlorobenzenes as model compounds for determining the dynamics of plume dispersion of persistent organic contaminants from the Niagara River into Lake Ontario. From these compounds, 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) was selected as the most appropriate single compound to represent contaminants entering the Niagara River from industrial waste sites. The hexachlorohexanes, including lindane and a-HCH (a-BHC) were selected to represent ubiquitous contaminants without any site specific origin. Although the bulk of the 1,2,3,4-TeCB loading to Lake Ontario from the Niagara River was carried out of the study area in dissolved form, there was a significant removal from the surface water onto suspended solids. Carbon normalized partition coefficients suggested that contaminants are sorbed more strongly to river suspended solids than to lake suspended solids and bottom sediments.

The aim of the final field study in 1985, was to repeat the previous plume dynamics studies over a significantly longer time duration, and to investigate the dynamics of contaminant-particle association by the additional collection of settling particles and surficial sediments in the usual plume path. A simultaneous time series of water samples at the Niagara River mouth and the Welland Canal mouth were planned to check the short term variability of contaminant discharge into Lake Ontario. Procedural changes were made: principally, an increased sample

2

size to 18 L and direct measurement of contaminants on suspended solids. These changes were necesssary, due to the continuing reductions of organic contaminant levels in the Niagara River, which range up to 100 fold over the three years of observations.

Time series outflow monitoring

In previous studies, the short term variability of chloro-benzene concentrations in the Niagara River was not determined. In addition, the possibility of chlorobenzenes merging with the plume from the outflow of the Welland Canal was not investigated. In June 1985, automatic water samplers were installed at both of these locations and adjusted to collect 1 L whole water samples at 1 hour intervals over a 48 hour period starting 18 hours prior to the plume study. The samples were returned to the laboratory immediately after the period, combined into 2 hourly 2 L samples, extracted twice with dichloromethane (DCM), after adding an internal standard (1,3,5-tribromobenzene) and analysed for 1,2,3,4-TeCB and a-HCH as described later for the plume water samples.

Sediment traps

An attempt was made to collect suspended solids in the plume over the duration of the plume sampling period. The suspended solids were collected in traps moored at predetermined depths in the anticipated track of the plume. The traps were designed and used as described in detail by Charlton (1983). Location of the traps was based on several years of observations which have shown the predominant direction of the Niagara River plume to be eastward and close to the south shore of Lake Ontario. The traps were deployed 12-18 hours prior to plume observations at 10 m, 12 m, bottom - 4 m and bottom - 2 m at six sites as shown in Figure 1. They were removed after approximately 72 hours deployment.

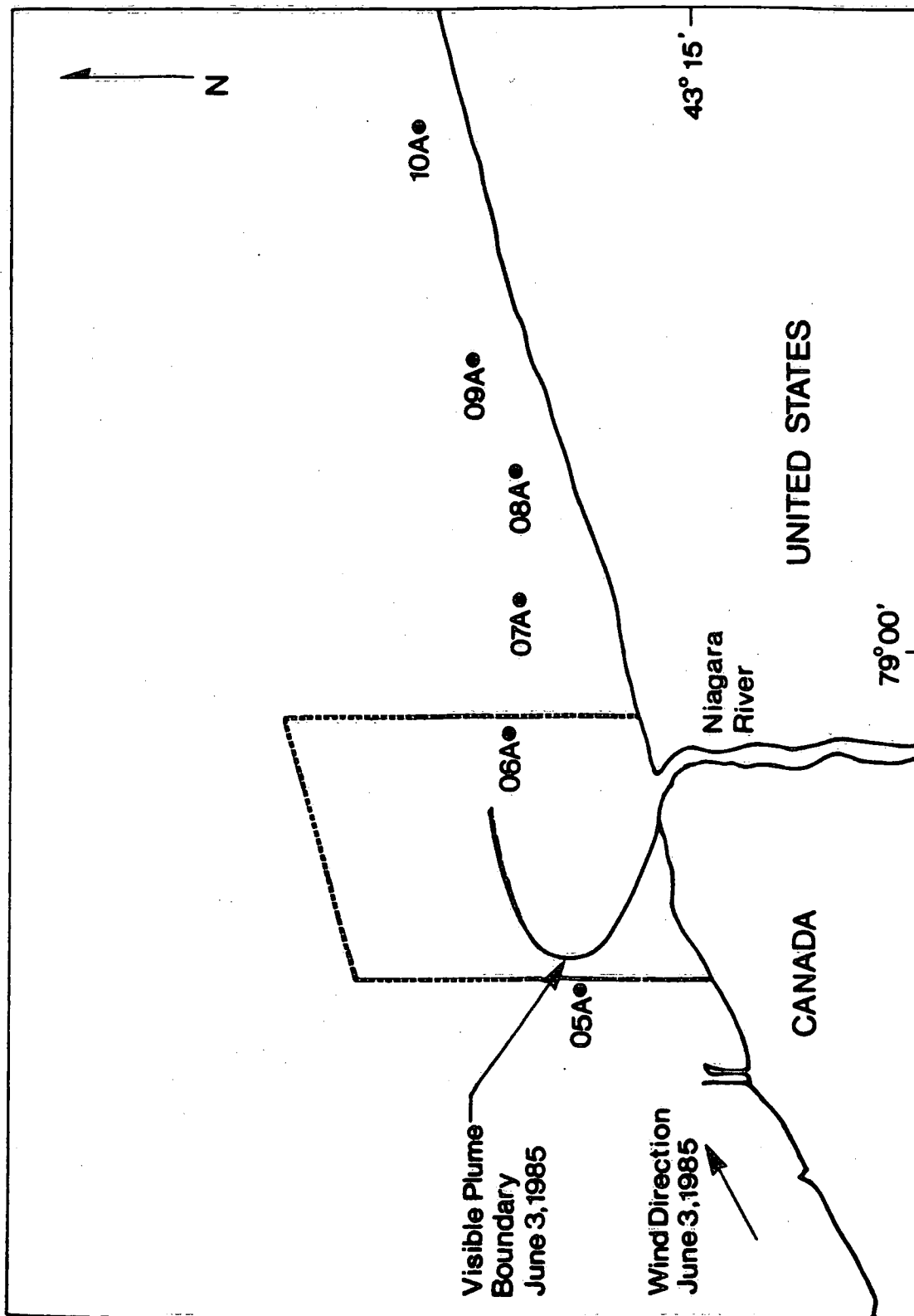Figure 1. Sediment trap sites and plume boundary, June 3, 1985.

Fig.1. SEDIMENT TRAP INSTALLATION AND PLUME, JUNE 3, 1985.

Each sediment trap device contained 5 trap tubes. One of these was used for weight determinations and physical evaluation, the other four were combined after decanting off excess water. The resulting slurry was filtered under 10 psi nitrogen pressure through prefired Gelman type A/E glass fibre filters of 1 um nominal pore size. The semidry filters were folded and placed in 50 mL culture tubes to which 100 uL internal standard and 20 mL DCM was added. The filters were extracted into the DCM by shaking and the extract dried over sodium sulphate with 3 additional 20 mL DCM rinses. The combined extract was evaporated to 2 mL and cleaned up on a Pasteur pipet minicolumn containing 2 cm deactivated Florisil and 2 cm 40% sulphuric acid on Biosil A. The column was eluted with 3 x 2 mL pesticide grade hexane. The final extract was was stored cold in sealed vials prior to gas chromatographic analysis as described later.

Surficial sediments

After completion of the plume sampling and sediment trap removal, cores were collected at the sediment trap sites. A Benthos box corer was used which collects a core of 0.5 m x 0.5 m and variable depth depending on the nature of the sediments (up to approx. 0.5 m). Duplicate 0-3 cm subsamples were removed from the box cores and stored frozen.

About 10 g of the surficial sediments was weighed, mixed with approximately 50 g sodium sulphate and extracted with 250ml of DCM and internal standard in a Soxhlet extractor for 8 hours. The extract was evaporated to 50 mL, 4 mL isooctane added as a keeper and further evaporated to 2 mL. The extract was cleaned up as described above. Dry weights were determined from small

separate subsamples.

Plume observations and sampling

The sampling grid of 1983 was used, with six transects sep-
arated by 3 km, each containing six sample sites at 2 km inter-
vals, as shown in Figure 2. Sampling cruises were carried out in
June, July and September of 1985. The June cruise, for which the
largest data set exists, was chosen to illustrate the dynamics of
plume dispersion of 1,2,3,4-TeCB in Lake Ontario.

Figure 2. Map of study area showing sampling grid.
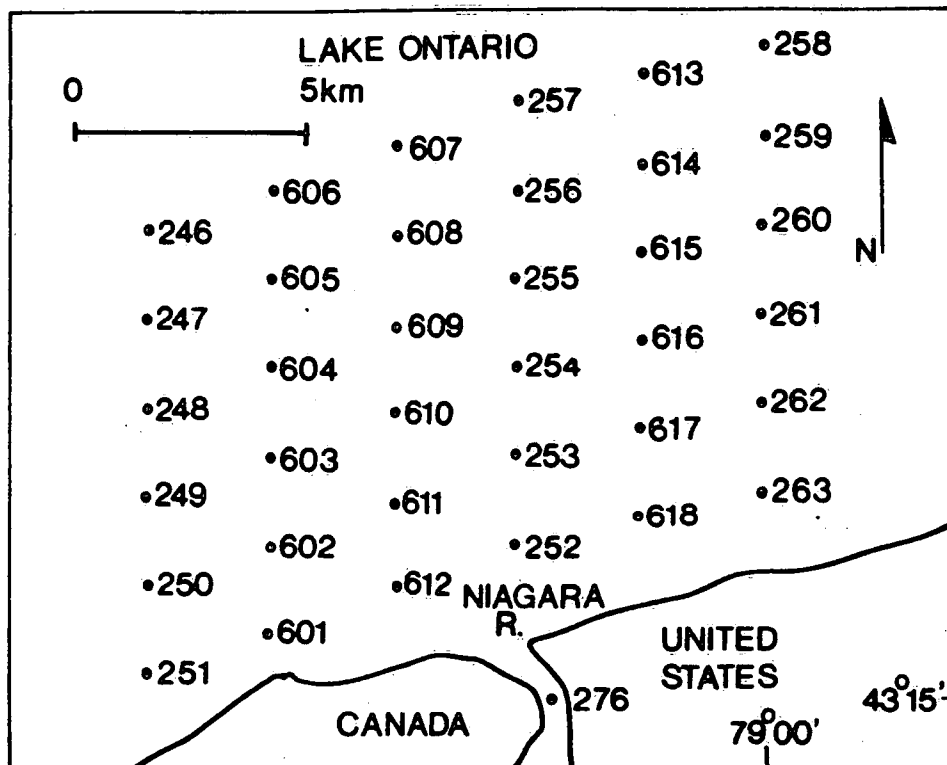
Duplicate 18 L water samples were collected in the Niagara
River mouth at about 6 am, June 4, while 10 visually tracked

"roller blind" type drifters (Murthy et al., 1987) were released in the nearshore area of the plume, just beyond the shallow sand bar. Additional 1 L water samples were also collected for suspended solids weight determination. Sampling and observations then commenced on the sample grid (Figure 2), starting from the offshore station on the westernmost transect. Temperature, conductivity and light transmission measurements were made at all grid stations. Water samples were collected at grid sites within the plume as defined by physical observations and close proximity to the drifters. After approximately 12 hours of visual tracking, the drifters were removed and replaced by 4 satellite tracked drifters (Murthy et al., 1987). Further water samples were collected over a 30 hour period at sites close to the satellite drifters. Duplicate water samples were also collected at a reference site beyond the plume boundary.

The 1 L water samples were filtered on site through pre-weighed 47 mm Whatman GFC glass fibre filters for suspended solids weight determination. The filters were later ashed for determination of loss on ignition. The 18 L water samples were filtered on site under nitrogen pressure through 142 mm prefired Gelman A/E glass fibre filters. The filters and filtrate were further treated as described in Fox (1987) after the addition of internal standard. The extracts were cleaned up as described earlier. The final extracts were adjusted to a volume of 1.0 mL and stored at $4^{\circ}C$ prior to gas chromatographic analysis.

Gas chromatographic analysis was performed on all sample extracts using dual column quantification and confirmation on a Hewlett Packard 5890 gas chromatograph with dual electron capture

8

detectors. The columns were 30 m x 0.24 mm ID HP Ultra 2 and HP-17 fused silica.

Mean reproducibility of the analysis on four replicate samples was:

1,2,3,4-TeCB (water)	19%
1,2,3,4-TeCB (suspended solids)	42%
a-HCH (water)	10%
a-HCH (suspended solids)	37%

RESULTS AND DISCUSSION

Sediment traps were installed at the predetermined locations shown in Figure 1 on June 3 1985 about 12-18 hours prior to plume sampling and observation. Visual observations showed the plume overlying the trap sites. The depths at which the traps were installed, along with temperature and transparency measurements, are shown in Table 1. Due to insufficient depth, only two trap depths were used at station # 06A and three at station # 07A. Winds were from the southwest and the westernmost edge of the plume was very distinct just to the east of station # 05A (# 249 on the grid).

Table 1. Sediment trap installation with depth, temperature and
% light transmission.

St. #	10 m °C	10 m %T	12 m °C	12 m %T	B-4 m °C	B-4 m %T	B-2 m °C	B-2 m %T
05	9.3	84	9.2	83	8.8	80	8.0	82
06	14.2	42	14.0	44	---	--	---	--
07	13.5	52	12.5	72	---	--	9.8	80
08	13.0	63	11.6	70	10.3	80	10.0	85
09	12.5	66	11.6	73	10.0	87	10.0	86
10	12.0	66	11.2	78	10.8	80	10.6	80

Plume tracking and sampling started at 0700 hrs on June 4, 1985 with duplicate water sampling at the river mouth station, # 276 and release of ten visual sighting drifters just off the mouth of the river. The vessel then followed the prearranged grid pattern from the southwest corner, taking surface temperature, conductivity and light transmission readings at each grid site. The results of the temperature and conductivity measurements are shown in Figure 3. Water samples for contaminant

Figure 3. Niagara River plume, June 4, 1985.
(A) temperature, 1 m; (B) % transmission, 1 m.

Fig.3A

Fig.3B

11
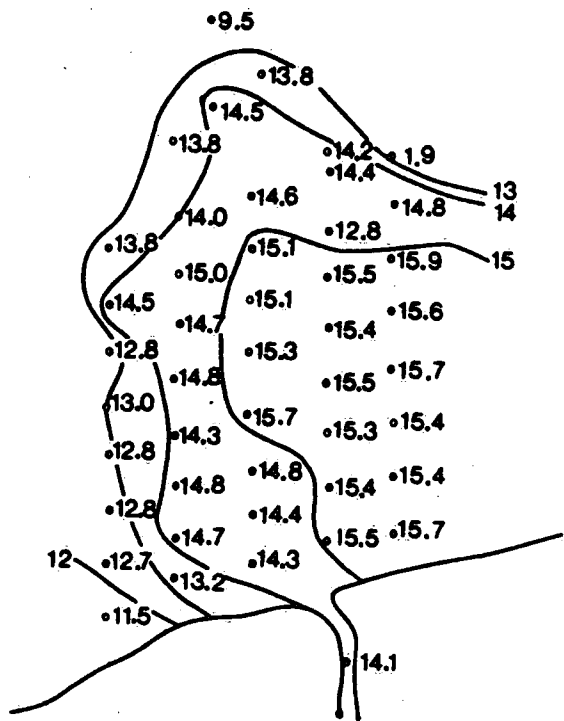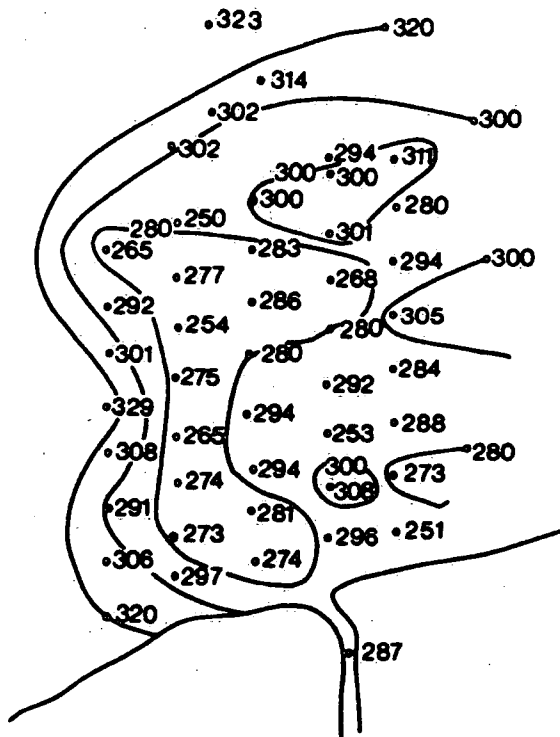
analysis were collected at up to three depths from grid stations 249, 611 and 256. Visual sighting of drifters near these locations, in addition to physical observations, confirmed that these samples could be related to the water mass sampled earlier in the river mouth. After several hours of plume observation it became apparent that an earlier wind shift to the south was changing the plume trajectory, which was now headed almost due north. In response to this change, the sampling grid was modified, with the now redundant easternmost transect removed, and two additional stations added to the offshore ends of the remaining transects (Figure 4).

Figure 4.   Map of modified sampling grid.
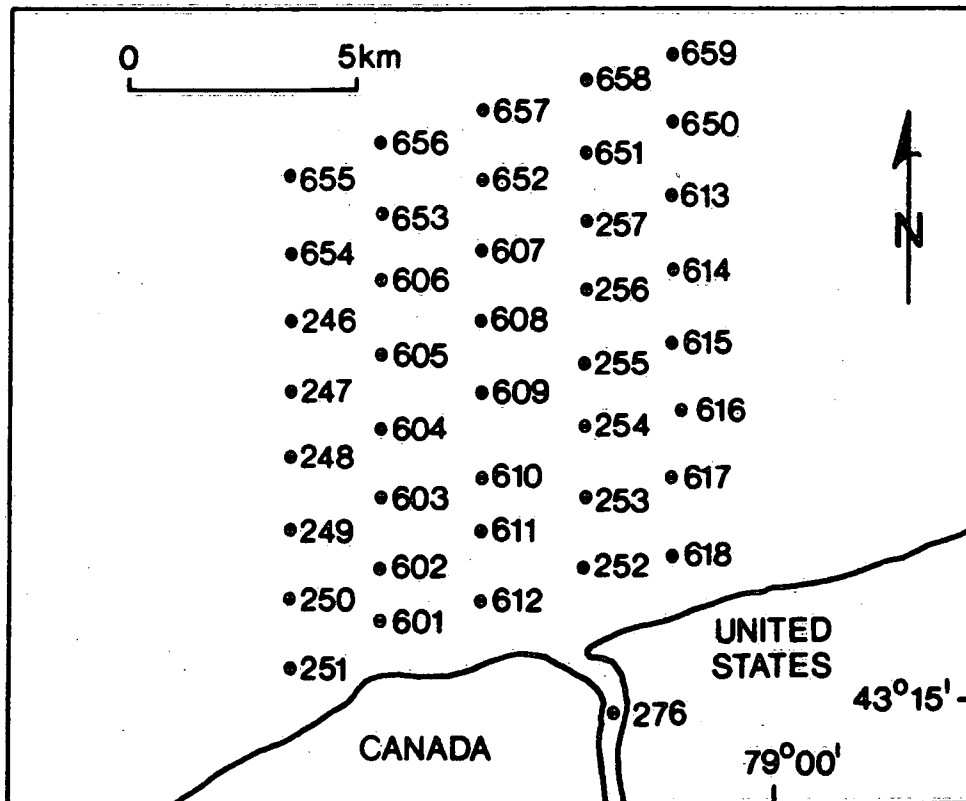
The temperature and conductivity profiles at 1 m similarly delineate the plume profile (Figures 3 and 4). The conductivity profile (Figure 4), clearly indicates the complexity arising from recent shifts in wind direction. Light transmission was relatively uniform at approximately 40% throughout the study area, indicative of relatively high suspended solids. At the end of daylight hours, the visual drifters were removed and four satellite tracked drifters were deployed. The drifter studies on Niagara River plume dispersion are described in detail in Murthy et al. (1987). The satellite drifters were followed for a further 30 hours and four water sampling sites near the drifters were selected during this period. A duplicate reference water sample was also collected at this time from a site to the north of the plume, determined by physical observations. Sample were collected at 1 m, 5 m and 2m above the bottom. The results of 1,2,3,4-TeCB and a-HCH analysis on the filtered water and suspended solids from these sites are shown in Table 2.

Although a number of chlorobenzenes were monitored, 1,2,3,4-TeCB was found to be the most appropriate chlorobenzene as a site specific marker, with physicochemical properties typical of many organochlorine contaminants, good detectability and a high degree of site specificity. a-HCH was two to three times more abundant than lindane (a-HCH) and was selected to represent organic contaminants with no site specific origin. The distribution of 1,2,3,4-TeCB and a-HCH in filtered water and suspended solids at 1 m is shown in Figures 5 and 6. Levels of 1,2,3,4-TeCB in the river mouth were 4-5 times lower than those observed in 1983. Only a slight decrease in 1,2,3,4-TeCB concen-

Table 2.   Concentration of 1,2,3,4-TeCB and a-HCH in water and suspended solids, Lake Ontario and Niagara River, June 4-6, 1985

Station	Depth (m)	Matrix	TeCB (ng/L)	a-HCH (ng/L)
276	1	FW	1.59	2.66
276	1	SS	0.09	0.03
276*	1	FW	1.31	2.06
276*	1	SS	0.19	0.05
611	1	FW	1.52	2.02
611	1	SS	0.09	0.03
611	6	FW	1.59	2.37
611	6	SS	0.09	0.03
249	1	FW	0.48	2.46
249	1	SS	0.01	0.05
249	4	FW	NM	NM
249	4	SS	NM	NM
249	18	FW	0.16	2.62
249	18	SS	NQ	0.05
256	1	FW	1.61	1.98
256	1	SS	0.06	0.05
256	5	FW	1.64	2.54
256	5	SS	0.07	NQ
256	78	FW	0.23	2.44
256	78	SS	NQ	0.06
666	1	FW	1.32	1.80
666	1	SS	NQ	0.03
666	5	FW	0.55	2.27
666	5	SS	0.06	0.09
666	110	FW	0.23	2.10
666	110	SS	NQ	0.06
667	1	FW	0.20	2.40
667	1	SS	NQ	0.05
667*	1	FW	0.15	2.46
667*	1	SS	NQ	0.02
667	60	FW	0.24	2.29
667	60	SS	NQ	0.03
667*	60	FW	0.17	2.64
667*	60	SS	NQ	NQ
668	1	FW	1.18	2.37
668	1	SS	0.06	0.04
668	5	FW	1.06	2.02
668	5	SS	0.08	0.03
668	110	FW	0.23	2.34
668	110	SS	NQ	NQ
669	1	FW	0.82	1.82
669	1	SS	0.07	0.03
669	5	FW	0.27	2.19
669	5	SS	NQ	0.02
669	100	FW	0.17	2.82
669	100	SS	NQ	NQ
670	1	FW	1.18	2.27
670	1	SS	0.10	0.03
670*	1	FW	1.19	2.14
670*	1	SS	0.07	0.04
MB	-	FW	ND	ND
MB	-	SS	ND	ND

FW = Filtered water; SS = Suspended solids; MB = Method blank;
NM = Not measured; NQ = Not Quantified; * = Replicate
ND = Not detected

14

Figure 5. Concentration of 1,2,3,4-TeCB in filtered water (top) and suspended solids (bottom), ng/L and % in dissolved phase,.June 4, 1985.
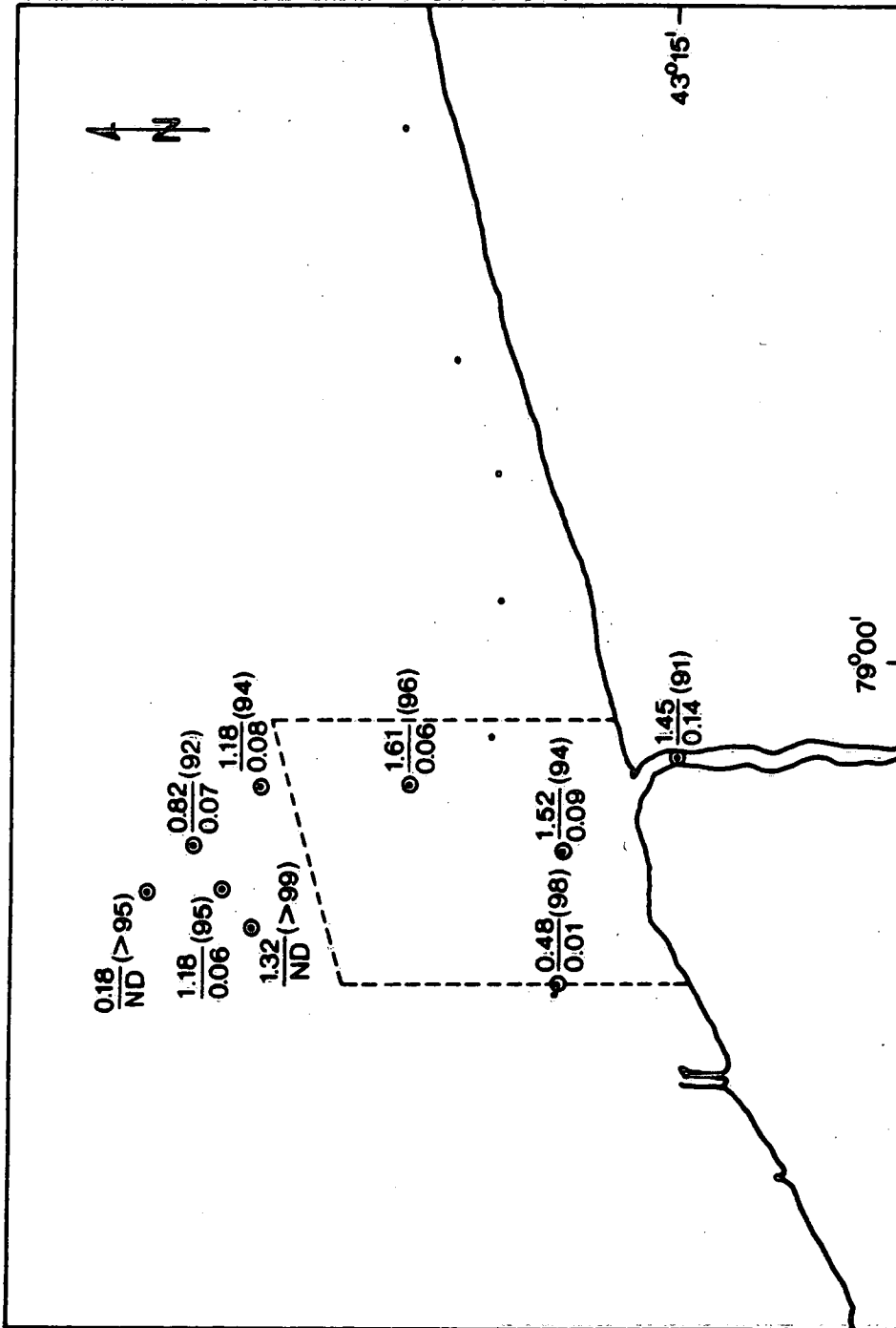

Figure 5. June 4-6 1985 1,2,3,4-TeCB 1m
$$\frac{\text{ng/L filtered water}}{\text{ng/L suspended solids}} \quad (\text{% in water phase})$$

Figure 6.   Concentration of a-HCH in filtered water (top) and
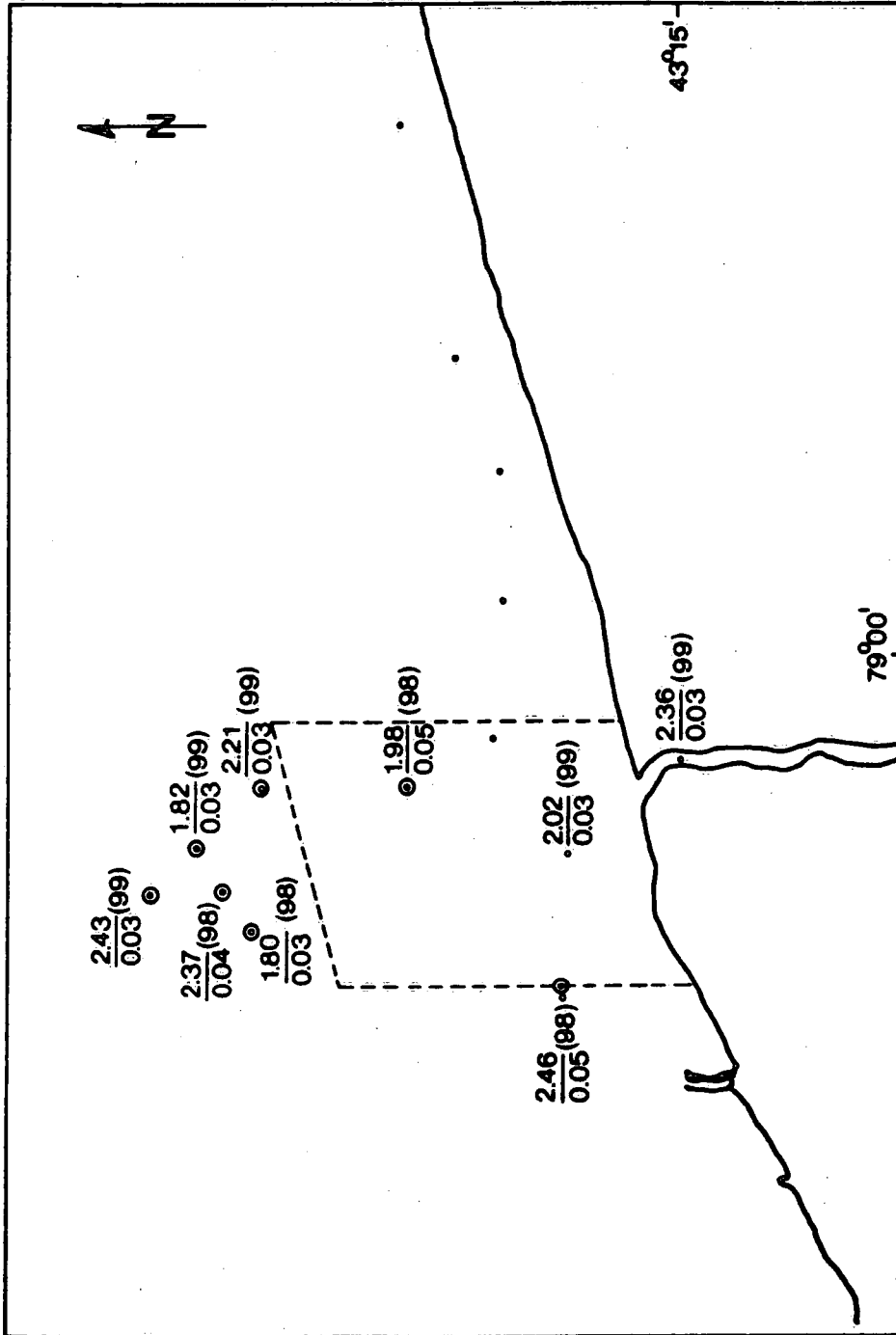suspended solids (bottom), ng/ L and % in dissolved phase, June
4, 1985.

Figure 6. June 4-6 1985 α HCH 1m

$$\frac{\text{ng/L filtered water}}{\text{ng/L suspended solids}} \quad (\% \text{ in water phase})$$

tration was observed from the river mouth level of 1.59 ng/g (total) to the last observation 46 hours later at satellite drogue site 670, of 1.26 ng/g. Grid station # 249 was clearly on the western margin of the plume with 0.49 ng/g 1,2,3,4-TeCB while the reference site, # 667, exhibited a near background concentration of 0.18 ng/g. An examination of 1,2,3,4-TeCB concentrations at 5 m and 2 m from the bottom showed similar or lower levels at 5 m and near background levels at 2 m from the bottom at the deeper stations. These observations are in agreement with detailed temperature transects made by Murthy et al. (1987), which showed a sharp thermocline at 10-15 m in the grid area. In the discussion which follows, the plume origin 1,2,3,4-TeCB will be assumed to occupy an approximately 5 m thick layer on the surface of the lake. The % of total 1,2,3,4-TeCB found in the water phase is also shown on Figure 6, and while this number is consistently in excess of 90%, the rather large variability on suspended solids replicates makes interpretation of the differences in these numbers difficult. A rather higher proportion of 1,2,3,4-TeCB on suspended solids was found in 1983, with an average of 12% on all samples and a maximum of up to 50% (Carey and Fox, 1987). However, the 1983 suspended solids values are inherently less reliable, being derived indirectly, from the difference between unfiltered and filtered water, which resulted in negative values for some of the suspended solids concentrations. Nevertheless, it is qualitatively clear that more of the 1,2,3,4-TeCB was associated with the suspended solids in previous years with significantly higher loadings.

The distribution of a-HCH (Figure 6) is that of a ubiquitous contaminant where the discharge concentrations from the Niagara River are similar to those in the receiving water. No significant differences are observed in the measurements, and 98-99% of the total a-HCH is associated with the aqueous phase.

In previous studies of the dynamics of the Niagara River plume, areas of higher concentration of 1,2,3,4-TeCB in the plume than in the river mouth were often observed (Fox and Carey, 1986, Carey and Fox, 1987). Once again this phenomenon was observed, but the 10% increase was probably not significant. In order to determine whether short term variations in river mouth concentrations, or intrusive inputs from the Welland Canal, could account for this anomaly, a time series of water samples was collected through the whole study period at the mouths of the Niagara River and the Welland Canal. The results of the analyses of these samples for 1,2,3,4-TeCB, along with the corresponding Niagara River discharges are shown in Figure 7. While there was no relationship between 1,2,3,4-TeCB concentrations and river flow, a gradual increase in 1,2,3,4-TeCB levels from just below 1 ng/L to almost 2 ng/L with spikes to almost 3 ng/L was observed at Niagara on the Lake over the 48 hour sampling duration. These time series data do not appear to account for the increased 1,2,3,4-TeCB levels offshore, since the increasing trend was the opposite to that required. The 1,2,3,4-TeCB concentrations measured at the mouth of the Welland Canal were too low to exert any effect on plume concentrations and were frequently below the detection limit of 0.1 ng/L.

Figure 7.   Time series 1,2,3,4-TeCB concentrations at Niagara River mouth and Port Weller and Niagara River discharge volumes, June 3-5, 1985.

19
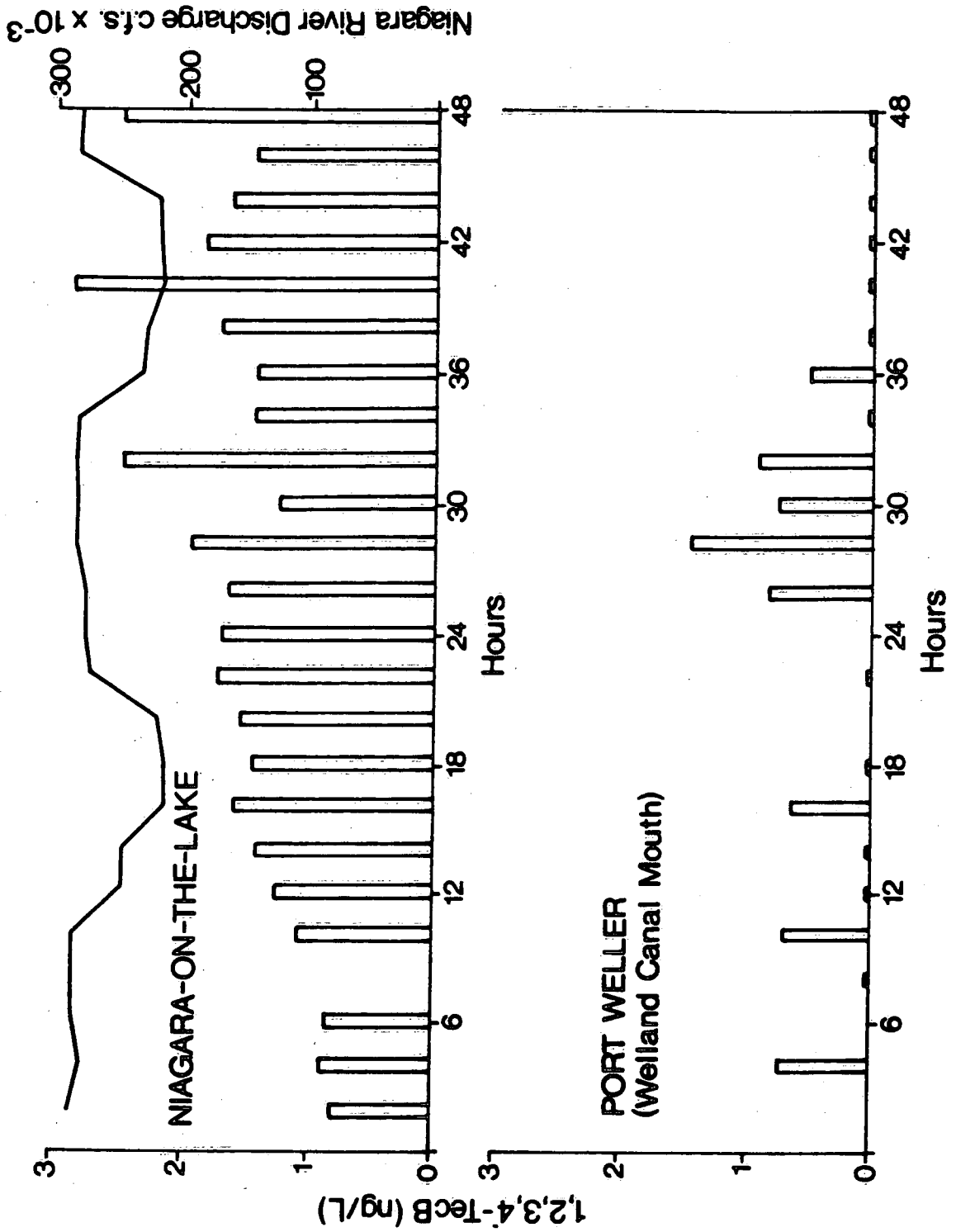
Separate 1 L water samples were analysed for suspended solids and the fraction of organic carbon (f_{oc}) was estimated from the measured loss on ignition using a factor of 0.5 based on empirical observations of Charlton (pers. comm.). The results of these calculations are shown in Table 3.

Table 3. Concentration, loss on ignition and estimated fraction organic carbon (f_{oc}) for Lake Ontario and Niagara River suspended solids, June 4-6, 1085.

Station	Depth (m)	Sus. solids concn. mg/L	Loss on ign. mg/L	F_{oc}
276	1	5.57	1.43	0.13
276*	1	6.00	1.42	0.12
611	1	5.01	1.25	0.12
611	6	5.17	1.25	0.12
249	1	2.82	1.25	0.22
249	4	2.72	1.31	0.24
249	18	1.68	1.44	0.43
256	1	3.93	1.50	0.19
256	5	4.38	1.50	0.17
256	78	1.65	0.75	0.23
666	1	4.08	1.56	0.19
666	5	3.30	2.22	0.34
666	110	1.14	0.83	0.37
667	1	1.88	1.69	0.45
667	60	0.44	NW	NC
668	1	3.69	1.79	0.24
668	5	4.06	1.99	0.25
668	110	0.62	NW	NC
669	1	3.67	1.93	0.26
669	5	2.48	1.56	0.31
669	100	0.79	0.69	0.44
670	1	3.31	1.49	0.23
670*	1	3.22	1.33	0.21

* = Replicate; NW = No weight; NC = No calculation

The sediment-water partition coefficient was then calculated from

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

where C_s = contaminant concentration on sediment

and C_w = contaminant concentration in water

K_{oc}, the organic carbon normalized partition coefficient could

then be calculated from

$$K_{oc} = K_{sw}/f_{oc}$$

(Karikhoff et al.,1979, Karikhoff, 1981).

These calculations, and the resulting organic carbon normalized partition coefficients expressed as log K_{oc}, are presented in Table 4.

Table 4. Sediment -water partition coefficient (K_{sw}) and log organic carbon normalized partition coefficient (log K_{oc}) for 1,2,3,4-TeCB in the Niagara River and Niagara River plume, June 4-6, 1985.

Station	Depth (m)	Dissolved conc. ng/g	Adsorbed conc. ng/g	K_{sw}	log K_{oc}
276	1	1.59E-3	15.44	9.71E+3	4.91
276*	1	1.31E-3	32.66	2.49E+4	5.28
611	1	1.52E-3	18.76	1.23E+4	5.01
611	6	1.59E-3	16.25	1.02E+4	4.93
249	1	4.8 E-4	4.26	8.87E+3	4.60
249	4	NM	NM	-------	----
249	18	1.6 E-4	NQ	-------	----
256	1	1.61E-3	16.03	9.96E+3	4.72
256	5	1.64E-3	16.21	9.88E+3	4.76
256	78	2.3 E-4	NQ	-------	----
666	1	1.32E-3	NQ	-------	----
666	5	5.5 E-4	19.09	3.47E+4	5.01
666	110	2.3 E-4	NQ	-------	----
667	1	2.0 E-4	NQ	-------	----
667*	1	1.5 E-4	NQ	-------	----
667	60	2.4 E-4	NQ	-------	----
667*	60	1.7 E-4	NQ	-------	----
668	1	1.18E-3	17.34	1.47E+4	4.79
668	5	1.06E-3	19.95	1.80E+4	4.88
668	110	2.3 E-4	NQ	-------	----
669	1	8.2 E-4	18.80	2.29E+4	4.95
669	5	2.7 E-4	NQ	-------	----
669	100	1.7 E-4	NQ	-------	----
670	1	1.18E-3	29.00	2.46E+4	5.03
670*	1	1.19E-3	22.67	1.91E+4	4.96

* = Replicate; NM = No measurement; NQ = Not quantified

As was found in the 1983 study, the values were significantly higher than theoretical value of 4.06 based on octanol-water partition coefficients, ranging from 4.60 on the western

21

margin of the plume, to 5.28 in the Niagara River mouth and a mean value of 4.91.

These findings strengthen the conclusions of the previous study, that higher than predicted log K_{oc} values for 1,2,3,4-TeCB are consistently observed in the Niagara River plume discharge, since the new measurements have better accuracy and precision despite the significantly lower concentrations observed. Unfortunately, the measurements were not sufficiently precise to demonstrate unequivocally the presence or absence of a lowering of K_{oc} as the plume material weathered and settled over the two days of direct observation. Levels of 1,2,3,4-TeCB on suspended solids were near, or below, the detection limits on the margins of the plume and at the reference site # 667. Larger samples of suspended solids collected by continuous flow centrifugation would have made such measurements more precise but the time requirements were too large for this study.

The settling solids, which were collected in the sediment traps over an approximately 72 hour period, do provide sufficient material for reliable analysis. The movement of the initial water mass in the plume over this period is shown in Figure 8, with the sediment trap stations superimposed. The drifter tracks are from the concurrent study of Murthy et al., (1987) and show the plume occupying the trap positions towards the end of the deployment period. The concentration of contaminants on the suspended solids is shown in Table 5.

As in case of the water samples, 1,2,3,4-TeCB is clearly shown to have a site specific origin in the Niagara River, while

22

Figure 8. Lagrangian drifter trajectories, June 4-9, 1985 (
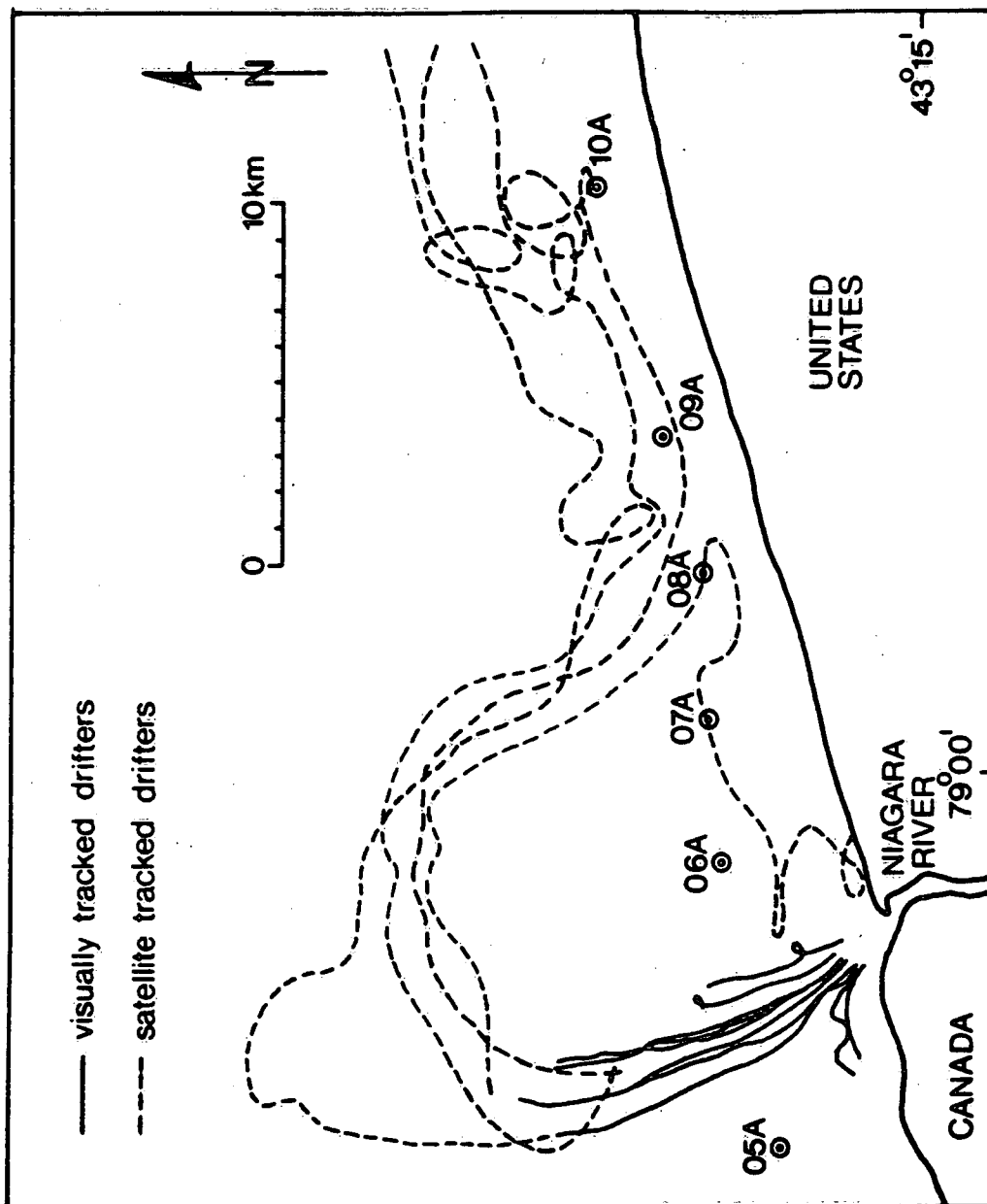after Murthy et al., 1987) and sediment trap sites.

Table 5.   Concentration of selected organochlorine contaminants (ng/g) observed in sediment traps placed in Lake Ontario near the Niagara River mouth, June 3-6, 1985.

Station	Depth (m)	sed. rate $g/m^2/d$	1,2,3,4- TeCB	a-HCH	p,p'- DDE
5A	10	11.9	7.6	1.1	5.8
5A	19*	19.3	13.7	0.9	4.9
6A	10*	15.5	16.4	0.8	4.5
7A	10	15.1	5.4	0.8	4.3
7A	13*	22.1	5.6	1.0	4.6
8A	10	12.2	4.3	1.1	4.6
8A	16*	20.3	4.3	1.0	4.5
9A	10	8.8	3.0	1.5	7.4
9A	21*	12.9	5.1	1.3	5.1
10A	10	7.2	3.0	1.8	6.0
10A	16*	13.2	2.9	1.3	3.9

* = B-2m

a-HCH and p,p'-DDE appear to be ubiquitous contaminants.

From these data, it is possible to make an estimate of log K_{oc} for 1,2,3,4-TeCB after 72 hours transit in the plume, using the last available water concentration at site # 670 and an estimated 4% organic carbon (Charlton, pers. comm.). Using these values at sediment trap site # 08A (the first trap site occupied by the extended plume), log K_{oc} for 1,2,3,4-TeCB is 4.95, which is essentially the same as that calculated for drifter site # 670. After a further 24 hours, the satellite drifters were occupying the region of sediment trap site 10A where log K_{oc} was estimated to be 4.80 using the same water concentration and f_{oc} values. As with the log K_{oc} values based on direct plume observations, a gradual decrease as the plume aged is suggested but not proven, due to assumptions made and

analytical inprecision. These log K_{oc} values are similar to the value of 5.0 for 1,2,3,4-TeCB reported by Oliver and Charlton (1984), which was based on sediment trap material collected in 1981 and 1982. The sediment trap 1,2,3,4-TeCB concentration reported by those authors of 23 ng/g (mean of 3 sites), can be compared to the mean of sites 05A, 06A and 07A in this study of 9.8 ng/g. Thus, a more than twofold reduction in 1,2,3,4-TeCB concentration has occured over the 3 year span between 1982 and 1985. This dramatic reduction in chlorobenzene discharge from the Niagara River to Lake Ontario is also documented elsewhere (McMahon, 1987, El Shaawari et al., 1988).

Surficial sediment (1-3 cm) was collected at the sediment trap sites and the concentrations of selected organochlorine contaminants are presented in Table 6.

Table 6.   Concentration of selected organochlorine contaminants (ng/g) observed in surficial sediments collected at sediment trap sites in Lake Ontario near the Niagara River mouth, June 10 1985.

Station	Depth (m)	1,2,3,4-TeCB	a-HCH	p,p'-DDE
5A	21	1.03	0.68	0.47
6A	14	8.19	1.32	24.53
7A	15	28.51	1.04	1.67
8A	18	36.95	1.18	4.24
9A	23	19.71	1.13	1.53
10A	18	24.52	1.33	1.88

The concentrations of 1,2,3,4-TeCB clearly support a long term, time integrated plume profile which is consistent with the one observed during this study.   Site 05A, although close to the river mouth, is clearly outside the predominant plume path, sites 07A-10A appear to lie directly in the main path with little

diminution of settled particle associated 1,2,3,4-TeCB at the most easterly site (10A). The intermediate value observed at site 06A might best be explained by the often observed trend (Murthy et al., 1987) of the plume initially moving directly offshore as a result of high discharge velocity. Thus, the plume often entirely misses site 06A before the combination of lower plume velocities, prevailing southwesterly winds and lake currents move the plume inshore and in an easterly direction. The mean concentration of 20 ng/g 1,2,3,4-TeCB is approximately half of the 1982 Niagara Basin concentration of 41 ng/g reported by Oliver and Charlton (1984). Since many of the Niagara Basin locations were more distant from the Niagara River, the twofold reduction in surficial sediment 1,2,3,4-TeCB concentrations since 1982 is probably an underestimate. Once again the a-HCH and p,p'-DDE concentrations are relatively uniform with the exception of the high p,p'-DDE value at site 06A which remains unexplained.

Site 06A is very shallow, situated near the Niagara River Bar and is in the region where elevated 1,2,3,4-TeCB concentrations in the plume, relative to the river mouth, have been observed in this and previous studies. The 1,2,3,4-TeCB concentration in the trap at this site is relatively high at 16.4 ng/g, while that in the surficial sediment is low, relative to the other sites. Vigorous resuspension of surficial sediments in this shallow area could explain all of these seemingly disparate observations.

The study has extended the observation of the dynamics of plume dispersion of a model persistent organic contaminant,

1,2,3,4-TeCB, to 42 hours directly, and 72 hours using sediment traps and satellite tracked drifters. Organic carbon normalized partition coefficients were calculated to describe the distribution of 1,2,3,4-TeCB between the solid and liquid phases. Log K_{oc} values ranged from 5.28 at the river mouth to 4.60 on the western fringe of the plume with a mean value of 4.9. The values were significantly higher than theoretical predictions based on octanol-water partition coefficients, confirming observations of earlier studies (Oliver and Charlton, 1984, Carey and Fox, 1987). Although no significance could be ascribed to their variance, a trend to lower values with plume aging appeared to be present. This is consistent with the proposal (Carey and Fox, 1987) that the elevated log K_{oc} values for 1,2,3,4-TeCB in the Niagara River resulted from the presence of significant amounts of 'living' organic carbon with it's associated lipid pool.

The plume has been shown to follow a predominantly easterly path, close to the south shore of Lake Ontario. More than 90% of the loading of 1,2,3,4-TeCB is transported in solution out of the river mouth area and into the general lakewide circulation patterns. Concentrations of 1,2,3,4-TeCB in all compartments sampled showed at least a twofold reduction over a span of two to three years. The elevated concentrations of 1,2,3,4-TeCB in the nearshore plume (relative to the Niagara River mouth) could not be explained by short term variations in river mouth concentrations. Resuspension from the more highly contaminated surficial sediments in this shallow, high energy sand bar zone remains the most likely explanation.

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