Chlorinated Organic Contaminants on Settling Particulates in the Niagara River Vicinity of Lake Ontario

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■ The concentrations of 26 chlorinated organic contaminants have been determined in settling particulates from sediment traps in Lake Ontario in the vicinity of the Niagara River and in two offshore stations. In addition, the same compounds have been analyzed in some Niagara River water and surficial Lake Ontario sediment samples. Compounds studied include chlorinated benzenes and toluenes, some PCB congeners, several pesticides, and miscellaneous compounds such as mirex and octachlorostyrene. Contaminant profiles have been used to distinguish between freshly settling particulates and resuspended bottom sediments found in the traps from various depths. From the sediment trap and river contaminant data a crude estimate of the relative proportion of contaminants sorbed on settling particles in the vicinity of the river was made. For most compounds poor agreement was found when field sediment–water partition coefficients were compared to coefficients estimated from octanol–water partition coefficients.

Introduction

The contamination of Lake Ontario with chlorinated organics from the Niagara River has been thoroughly documented (1). Chemicals such as chlorobenzenes, chlorotoluenes, mirex, etc. are of industrial origin and enter the Niagara River by direct discharges (2) or by leaching from chemical dump sites along the river (3). The sources of pesticides and PCB's in the river are more diffuse. Water and sediments from Lake Erie contain measurable concentration of these compounds but invariably a significant incremental increase in their concentration is observed in the Niagara River watershed (4).

Sediments in Lake Ontario contain many of the compounds identified in the river (2, 5–7), but little work has been done on tracing the pathway of contaminants from the river to bottom sediments in the lake. Simplisiticaly, contaminants enter the lake either adsorbed on particulates or dissolved; some fraction of the dissolved material is adsorbed onto particulates in the lake; finally, the contaminated particulates settle to the bottom. The most common method used for quantifying the amount of settling particulates in lakes are sediment traps (8) which are usually suspended at various depths in the water column. These traps have been used to measure trace metal, phosphorus, and organic matter downfluxes in lakes (8–12) and in the oceans (13). In the Great Lakes, sediment traps near the bottom catch higher amounts of settling solids than near surface traps due to the presence of a layer of higher turbidity and lower transmittance known as the nepheloid layer (9–10). The thickness of this layer, which is thought to be caused by resuspended bottom sediments, varied from about 22 m in Aug–Sept 1981 to about 45 m in Oct 1981 for Lake Ontario (14). Thus, while contaminants may settle to the bottom on particulates, some resuspension of the particles by strong currents in the lake (15) seems to occur. Some fraction of the material caught in sediment traps will likely be resuspended bottom sediments.

In this paper we describe the use of sediment traps for quantifying chlorinated contaminant downfluxes in Lake Ontario. Because of dramatic changes in loading patterns of these chemicals in recent years (16), we will also show how contaminant profiles can be used to fingerprint and distinguish freshly settling particulates from the resuspended sediments found in the traps.

Experimental Section

The sediment trap assembly used here has been described in detail previously (8). Briefly, each trap consisted of five plexiglass tubes (7 cm in diameter by 106 cm long) fitted at the bottom with removable cups. The traps were suspended in holders on a cable at 20-m intervals from the surface. The lower most trap was placed 2 m above the lake bottom. Traps were kept in the lake from early May to late November in both 1981 and 1982, and samples were collected from the traps monthly. Figure 1 shows a map of sample locations used for the study. Stations 207, 208, and 209 (water depth 70 m) are situated 8–10 km from the mouth of the Niagara River at the edge of the river plume as delineated by transmission and temperature profiles (8). Station 210 (water depth 70 m) is located a further 14 km to the east of these stations along the pathway of proposed PCB and mirex contamination drift (5, 6). Offshore stations were located in a region of rapid sediment accumulation (station 206, water depth 101 m) and on a sill of glaciolacustrine clay where modern sediment is not accumulating (station 211, water depth 135 m) (17).

Particulate matter collected in the sediment traps (0.2–2.0 g dry weight) was transferred into solvent–rinsed glass jars and frozen until analysis. The organic carbon content of the sediment trap material was estimated by measuring the total carbon at 950 °C (Hewlett–Packard C/H/N analyzer) and then subtracting the carbon present as $CaCO_3$. The analytical procedure, which has been described previously (18), consisted of Soxhlet extraction overnight with acetone/hexane, back-extraction of the extract with water to remove the acetone, and evaporation of the hexane extract to 1 mL using a Kuderna-Danish type condenser, followed by cleanup of this extract using a small H_2SO_4/silica gel column. Whole water samples were analyzed by liquid–liquid extraction with hexane (18). Centrifugation and filtration studies on river and lake water in the vicinity showed most of the contaminants (>70%) were in the water phase. All 26 study compounds were spiked into Niagara River water and sediment samples at different concentrations and recovery efficiencies determined. Values reported were corrected for recoveries which averaged 93% (85–99) for the sediments (18) and 65% (50–78) for the river water (20). Compounds were analyzed on dual 25-m fused silica capillary columns of different polarity, OV1 and SE54, with electron capture detectors. The average concentration on the two columns was used except, infrequently, when there was a significant discrepancy between the columns, in which case the lowest concentration was taken. A 2-μL injection with a Varian

Table I. Concentrations (ng/g) and Downfluxes (ng/(m² days)) (in Parentheses) for 20-m Sediment Traps (Sept 7–Oct 5, 1982) and Chemical Concentrations (ng/L) in Niagara River over This Period

compd	station 206	207	208	209	210	211	Niagara River water,[a] ng/L
1,3-DCB	ND[b]	14 (62)	15 (150)	9 (43)	ND	ND	15
1,4-DCB	ND	160 (710)	140 (1400)	110 (530)	66 (120)	79 (80)	48
1,2-DCB	ND	28 (120)	47 (490)	40 (190)	20 (38)	32 (32)	20
1,3,5-TCB	ND	4.2 (19)	5.2 (54)	5.0 (24)	3.8 (7.1)	2.4 (2.4)	1.1
1,2,4-TCB	55 (18)	39 (170)	39 (400)	30 (140)	22 (41)	23 (23)	11
1,2,3-TCB	36 (12)	9.9 (44)	8.5 (88)	9.6 (46)	9.9 (19)	5.3 (5.4)	2.4
1,2,4,5-TeCB	24 (7.7)	13 (58)	14 (140)	14 (67)	7.0 (13)	13 (13)	2.0
1,2,3,4-TeCB	15 (4.8)	22 (98)	27 (280)	22 (110)	12 (23)	12 (22)	3.7
QCB	7.7 (2.5)	11 (49)	12 (120)	8.9 (43)	7.0 (13)	5.3 (5.4)	1.2
HCB	12 (3.8)	19 (84)	21 (220)	40 (190)	20 (38)	13 (13)	0.71
PCB 18	17 (5.4)	5.6 (25)	4.7 (49)	5.2 (24)	5.6 (11)	6.8 (6.9)	0.46
PCB 40	5.6 (1.8)	2.2 (9.8)	1.4 (14)	1.9 (9.2)	1.7 (3.2)	1.7 (1.7)	0.14
PCB 52	48 (15)	24 (110)	17 (180)	16 (77)	27 (51)	23 (23)	0.90
PCB 101	31 (9.9)	15 (67)	17 (180)	13 (63)	15 (28)	14 (14)	0.83
PCB 153	15 (4.8)	10 (44)	12 (120)	9.9 (48)	7.5 (14)	7.4 (7.5)	0.32
PCB 194	4.9 (1.6)	3.0 (13)	1.5 (15)	1.7 (8.2)	1.0 (1.9)	1.0 (1.0)	ND
α-BHC	27 (8.6)	9.2 (41)	5.9 (61)	8.0 (39)	11 (21)	10 (10)	21
γ-BHC	6.0 (1.9)	1.9 (8.4)	1.0 (10)	1.7 (8.2)	2.2 (4.1)	1.8 (1.8)	3.5
α-chlor	4.5 (1.4)	1.6 (7.1)	1.4 (14)	1.5 (7.2)	1.7 (3.2)	1.4 (1.4)	0.14
γ-chlor	4.5 (1.4)	2.6 (12)	2.4 (25)	2.0 (9.6)	1.8 (3.4)	1.8 (1.8)	0.13
p,p'-DDE	18 (5.8)	8.5 (38)	9.1 (94)	7.6 (37)	7.5 (14)	5.8 (5.9)	0.28
p,p'-DDT	7.4 (2.4)	5.3 (24)	4.9 (51)	6.6 (32)	4.0 (7.5)	2.9 (2.9)	ND
HCBD	ND	11 (49)	6.9 (71)	7.3 (35)	7.5 (14)	2.9 (2.9)	0.82
PCT	ND	2.0 (8.9)	2.6 (27)	2.0 (9.6)	1.5 (2.8)	1.1 (1.1)	0.46
OCS	ND	2.4 (11)	2.5 (26)	2.5 (12)	1.4 (2.6)	2.7 (2.7)	0.06
mirex	18 (5.8)	5.3 (24)	5.3 (55)	4.3 (21)	5.9 (11)	3.9 (3.9)	ND

[a] Average of five weekly samples collected at Niagara-on-the-lake over period traps were deployed. [b] Not detected.
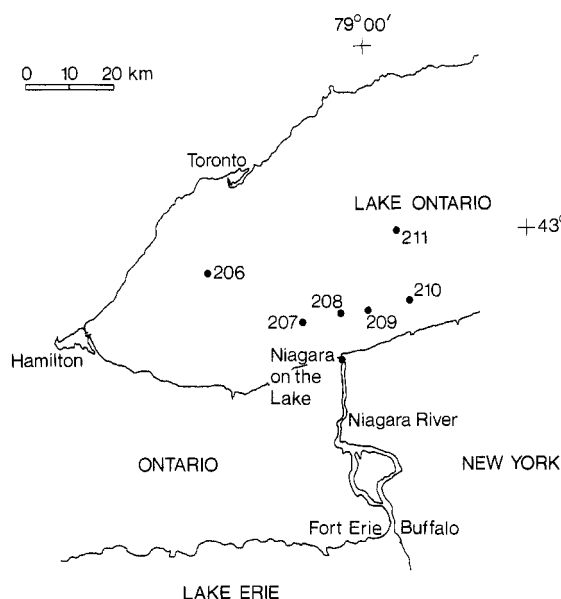

Figure 1. Location of sediment trap stations.

autosampler, a Varian 4600 gas chromatograph, and a Vista 401 integrator were used. Gas chromatographic conditions were the following: injector 250 °C; column 50–150 °C at 1 °C/min and 150–250 °C at 2 °C/min; final hold 15 min. Reproducibility of the analysis on replicate samples was ±10%.

The following abbreviations were used for the 26 compounds studied: (*chlorobenzenes, CB's*) 1,3-dichlorobenzene, 1,3-DCB; 1,4-dichlorobenzene, 1,4-DCB; 1,2-dichlorobenzene, 1,2-DCB; 1,3,5-trichlorobenzene, 1,3,5-TCB; 1,2,4-trichlorobenzene, 1,2,4-TCB; 1,2,3-trichlorobenzene, 1,2,3-TCB; 1,2,4,5-tetrachlorobenzene, 1,2,4,5-TeCB; 1,2,3,4-tetrachlorobenzene, 1,2,3,4-TeCB; pentachlorobenzene, QCB; hexachlorobenzene, HCB; (*polychlorinated biphenyls, PCB's*) (*19*) 2,5,2'-trichlorobiphenyl, PCB 18;

2,3,2',3'-tetrachlorobiphenyl, PCB 40; 2,5,2',5'-tetrachlorobiphenyl, PCB 52; 2,4,5,2',5'-pentachlorobiphenyl, PCB 101; 2,4,5,2',4',5'-hexachlorobiphenyl, PCB 153; 2,3,4,5,2',3',4',5'-octachlorobiphenyl, PCB 194; (*pesticides*) α- and γ-1,2,3,4,5,6-hexachlorocyclohexane, α-BHC and γ-BHC; α- and γ-chlordane, α-chlor, γ-chlor; 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene, p,p'-DDE; 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, p,p'-DDT; (*miscellaneous*) hexachlorobutadiene, HCBD; pentachlorotoluene, PCT; octachlorostyrene, OCS; mirex.

Results and Discussion

General Observations. A detailed discussion on the downflux of sediment, organic matter, and phosphorus from Lake Ontario sediment traps has already been reported by Charlton (*8*). The contaminants in sediment trap material and their relationship with contaminants in the Niagara River and in Lake Ontario bottom sediments will be examined in this paper. Table I shows some typical contaminant data for 20-m traps at the six stations. Contaminant concentrations are usually somewhat higher at stations near the Niagara River, but in some cases, higher concentrations are observed for the offshore stations. When the concentrations are converted to downflux by multiplying by sediment trap catches in g/(m² day) the strong influence of the Niagara River becomes readily apparent. For example, HCB concentrations average about 13 ng/g for the offshore stations and 27 ng/g for stations in the vicinity of the river, but HCB downfluxes average 8 ng/(m² day) compared to 160 ng/(m² day) for the offshore and near river stations, respectively. Similar behavior is apparent for the other chlorinated compounds. The contaminant downfluxes at nearshore station 210 (24 km from the river mouth) are lower than those of stations closer to the river but are somewhat elevated compared to offshore stations 206 and 211. Although many chlorinated hydrocarbons have been detected, the most prevalent class of compounds present in the sediment trap

Table II. Hexachlorobenzene Concentrations (ng/g) and Downflux (ng/(m² day)) (in Parentheses) for 40-m Sediment Traps

period	station 206	207	208	209	210	211
May 26–June 23, 1981	4.9 (10)	48 (230)	21 (210)	23 (170)	15 (21)	11 (10)
June 23–July 20, 1981	6.8 (19)	32 (300)	41 (400)	49 (400)	11 (53)	1.8 (11)
July 20–Aug 18, 1981	4.4 (6.7)	25 (190)	NS[a]	10 (120)	12 (84)	2.5 (4.8)
Aug 18–Sept 23, 1981	1.2 (1.5)	14 (190)	22 (250)	41 (490)	17 (100)	2.2 (2.6)
Sept 23–Oct 26, 1981	13 (12)	20 (200)	18 (84)	30 (140)	260 (1200)[b]	8.2 (5.5)
Oct 26–Nov 23, 1981	11 (8.1)	41 (430)	25 (450)	39 (480)	34 (340)	16 (16)
Nov 23, 1981–May 11, 1982	59 (180)	NS	NS	NS	NS	NS
May 11–June 7, 1982	44 (70)	35 (150)	160 (1500)	27 (200)	29 (130)	39 (73)
June 7–July 5, 1982	NS	33 (150)	NS	35 (260)	NS	NS
July 5–Aug 11, 1982	1.2 (2.8)	46 (300)	14 (120)	15 (59)	17 (34)	4.0 (12)
Aug 11–Sept 8, 1982	3.1 (2.6)	16 (89)	NS	12 (90)	6.4 (22)	3.2 (4.1)
Sept 8–Oct 5, 1982	12 (3.8)	12 (52)	29 (360)	21 (140)	20 (38)	13 (13)
Oct 5–Nov 10, 1982	12 (5.0)	33 (370)	42 (520)	25 (170)	20 (59)	1.1 (0.4)

[a] NS, no sample. [b] Outlier, concentrations of other components not elevated in this sample.

Table III. Mean Sediment Trap Depth Profile at Stations 207–209 (May 11–Nov 10, 1982): Contamination Concentrations (ng/g), Downflux (ng/(m² day)) (in Parentheses), and Mean Concentrations in Niagara Basin, Lake Ontario Surficial Sediments

compd	depth 20 m	40 m	60 m	68 m	lake ontario bottom sediments[a]
1,3-DCB	16 (150)	17 (150)	17 (210)	19 (250)	15 ± 10
1,4-DCB	110 (850)	120 (960)	150 (1500)	150 (1900)	63 ± 13
1,2-DCB	38 (300)	40 (340)	44 (560)	32 (500)	10 ± 5
1,3,5-TCB	5.5 (44)	7.0 (64)	8.6 (95)	9.5 (120)	53 ± 38
1,2,4-TCB	34 (260)	35 (270)	40 (380)	41 (530)	110 ± 33
1,2,3-TCB	7.7 (57)	6.9 (52)	64 (62)	7.8 (95)	9 ± 3
1,2,4,5-TeCB	13 (100)	15 (110)	19 (190)	21 (270)	68 ± 34
1,2,3,4-TeCB	23 (170)	23 (170)	21 (200)	20 (250)	41 ± 13
QCB	12 (93)	13 (99)	14 (130)	13 (170)	42 ± 19
HCB	27 (210)	26 (200)	42 (400)	41 (540)	110 ± 65
PCB 18	4.8 (36)	4.9 (36)	4.8 (43)	4.1 (52)	5 ± 2
PCB 40	1.9 (14)	2.1 (15)	1.8 (16)	2.2 (26)	3 ± 2
PCB 52	17 (130)	13 (96)	13 (120)	14 (180)	23 ± 8
PCB 101	14 (100)	11 (79)	11 (100)	13 (160)	23 ± 8
PCB 153	9.5 (73)	11 (80)	11 (100)	13 (160)	23 ± 7
PCB 194	1.8 (14)	2.1 (16)	1.9 (21)	2.8 (38)	4 ± 2
α-BHC	9.4 (70)	14 (94)	6.8 (56)	5.7 (71)	1.6 ± 0.5
γ-BHC	2.3 (17)	3.2 (22)	2.5 (21)	1.5 (19)	1.1 ± 0.5
α-chlor	1.8 (13)	2.1 (15)	2.2 (20)	2.4 (29)	2.6 ± 0.7
γ-chlor	2.4 (18)	2.7 (20)	2.8 (26)	3.0 (37)	3.5 ± 1.0
p,p′-DDE	10 (75)	12 (89)	13 (120)	15 (190)	87 ± 30
p,p′-DDT	5.8 (45)	6.3 (50)	8.5 (87)	12 (150)	45 ± 34
HCBD	5.9 (43)	5.6 (41)	6.9 (72)	7.4 (98)	32 ± 27
PCT	4.1 (33)	5.1 (42)	7.1 (81)	11 (150)	32 ± 40
OCS	2.9 (19)	2.5 (18)	3.7 (39)	4.6 (62)	15 ± 7
mirex	5.2 (38)	7.3 (55)	9.3 (95)	16 (200)	48 ± 32

[a] Average of 12 surficial sediment samples from the Niagara Basin of Lake Ontario ± standard deviation.

material is the chlorobenzenes.

To illustrate the type of variability in contaminant concentrations and downfluxes encountered during the study, Table II shows the HCB data for the six stations over the period May 26, 1981, to Nov 10, 1982. A total of 12 monthly samples from all stations and one overwinter sample from station 206 were collected. Stations under the greatest influence of the Niagara River (stations 207, 208, and 209) showed the least variability in concentrations and downfluxes. Offshore stations and station 210 showed the highest variability. This is not too surprising, since during a 2-year weekly sampling program in the river near its mouth, we have observed a reasonably steady input of contaminants to Lake Ontario (20) (although occasional spikes for some compounds have been observed). Highly variable sediment catches were observed for stations 206, 210, and 211, indicating that they may be more susceptible to changes in climatic conditions. For example, the overwinter sample at station 206 had by far the highest HCB

concentration and downflux for that location. Winter is a time of violent storms on the lake, and due to isothermal conditions, wind-driven currents may penetrate deeply and cause a significant resuspension of bottom sediments in the lake.

The mean depth profile of contaminant concentrations and downfluxes for stations 207–209 between May 11 and Nov 10, 1982, is shown in Table III. For many contaminants such as 1,3-DCB, 1,2,3-TCB, and PCB 18 very little change in concentrations with depth is observed. For contaminants such as PCT, HCB, and mirex concentrations increase substantially in the bottom traps as compared to traps closer to the surface. When downfluxes are compared, the bottom two traps show significantly higher quantities for all contaminants because of higher catches in these traps. From these results it appears that a significant amount of resuspension of bottom sediment is occurring, which gives rise to higher catches in the lower traps. The mean concentrations for study compounds in

12 samples of surficial sediments from the Niagara Basin of Lake Ontario are shown in the last column of Table III. Comparing this data to the sediment trap data readily indicates why the concentration of some contaminants change in the lower traps while other contaminant concentrations do not. The concentrations of 1,3-DCB, 1,2,3-TCB, and PCB 18 are virtually the same for settling particulate (20-m trap) as for bottom sediments. On the other hand, PCT, HCB, and mirex concentrations are substantially higher in bottom sediments, so sediment resuspension will cause the concentration of these contaminants to increase in lower traps where a significant portion of trap material is resuspended bottom sediments.

Estimating the Amount of Resuspended Bottom Sediments in Traps from Contaminant Ratios. The three main origins of material in the sediment traps are (1) contaminated sediment and detritus from the Niagara River, (2) resuspended contaminated bottom sediments from Lake Ontario, and (3) largely uncontaminanted inorganic clays and soils from shoreline erosion in the lake and lake seston. The best estimate of contaminant concentration of component 1 can be obtained from the analysis of 20-m sediment traps at stations 207–209 where the strongest influence of the river is felt. Contaminants in component 2 can be estimated from the analysis of surficial bottom sediments from the Niagara Basin of Lake Ontario (Table III). Component 3 will act as a diluent to the contaminant contributors. Unfortunately because of the large variability in sample concentrations (see, for example, Table II), it is difficult to obtain reliable estimates of the absolute contaminant concentrations for component 1 and 2. But, it should be possible to use contaminant ratios to differentiate between components 1 and 2 if discharge of specific contaminants over time has changed significantly. Durham and Oliver's (16) analysis of a sediment core in a high sedimentation zone near the river has shown that a dramatic change in the ratio of 1,2,4,5-TeCB to 1,2,3,4-TeCB has occurred in recent years, caused mainly by a large decrease in discharge of 1,2,4,5-TeCB. A careful examination of Table III reveals the 1,2,4,5-TeCB/1,2,3,4-TeCB ratio is 0.57 for 20-m traps at stations 207–209, 1.1 for the bottom traps at these stations, and 1.66 for bottom sediments. The 1,2,4,5-TeCB/1,2,3,4-TeCB ratio in the 20-m traps near the river is close to their ratio in Niagara River water, 0.54 (Table I). Core samples collected from the six sediment trap stations were gently agitated to resuspend the surface layer of sediments. The mean ratio of 1,2,4,5-teCB/1,2,3,4-TeCB in these resuspended sediments was 1.64 which is close to the mean ratio observed for the bottom sediments.

Thus, the following equation can be used to estimate fractional contributions of components 1 and 2 to the trap contaminant concentrations:

$$\frac{[C_{1245}]_{\text{sed trap}}}{[C_{1234}]_{\text{sed trap}}} = f_s \frac{[C_{1245}]_{\text{NR solids}}}{[C_{1234}]_{\text{NR solids}}} + f_B \frac{[C_{1245}]_{\text{bottom sed}}}{[C_{1234}]_{\text{bottom sed}}} =$$
$$0.57(1 - f_B) + 1.66f_B \quad (1)$$

where f_s is the fractional contaminant contribution from Niagara River settling particulates and f_B is the fractional contaminant contribution of the bottom sediments. The use of this equation to determine fractional contributions at various sites and depths is shown in Table IV. The data show that sediment traps at the 20- and 40-m depths at sites 207–210 from May to June 1982 caught mainly fresh sediment from the Niagara River, but the traps at the 60- and 68-m depth at these locations caught considerable quantities of resuspended bottom sediments. A completely different picture emerges for offshore sites 206 and 211

Table IV. Percent Contaminant Contribution from Bottom Sediments in May–June 1982 Sediment Trap Samples

	depth, m	bottom sed, %		depth, m	bottom sed, %
station 206	20	62	station 211	20	67
	40	57		60	64
	80	48		100	84
	90	70		120	74
	98	52		132	68
station 207	20	0	station 209	20	0
	40	6		40	0
	60	51		60	22
	68	82		68	41
station 208	20	0	station 210	20	0
	40	18		40	3
	60	48		60	47
	68	62		68	72

where the major contaminant contributor at all depths was resuspended bottom sediments. This interpretation is supported by mirex concentrations in the samples. The production and use of mirex has been limited since 1976 (21), and this has led to dramatic declines in mirex loading to Lake Ontario (16). In many cases, mirex concentrations from traps at the offshore stations and from the bottom traps at stations near the river are much higher (approaching bottom sediment values) than concentrations from 20- and 40-m traps at stations close to the river (see Tables I and III).

Thus, these observations indicate that sediments and detritus from the Niagara River adsorb contaminants from the river water and settle temporarily in the vicinity of the river. Currents in Lake Ontario, especially during fall and winter, resuspend much of this freshly sedimented material and redistribute it to the various sedimentation basins in the lake. This scenario is supported by bottom sediment studies showing contaminants characteristic of the Niagara River in all lake basins (2, 7). Also, samples from sediment traps and centrifuged particulates from the mid and eastern basins of the lake ≈ 100–200 km from the river mouth contain unusual contaminants which seem to be characteristic of the Niagara River (e.g., pentachlorotoluene) (20). The existence of a nepheloid layer in Lake Ontario as described by Sandilands and Mudroch (14) is confirmed by higher sediment catches in the lower traps. The present contaminant analysis strongly suggests that this layer is due to resuspended bottom sediments.

Portion of Niagara River Contaminants Sorbed on Settling Particles in Lake Ontario in the River's Vicinity. A comparison of contaminant downfluxes for stations near the river to the offshore stations shows contaminants that reach the sediment are likely to do so in the vicinity of the river. Not only are the contaminant downfluxes small for the offshore stations but also, from the above discussion, much of this downflux is due to the settling of resuspended bottom sediments. If it is assumed that stations 207–209 are representative, it is then possible to calculate mean sediment and contaminant downfluxes in the vicinity of the river from the data for these stations. Then a rough estimate can be made of the proportion of specific contaminants entering Lake Ontario via the Niagara River which reach the lake's bottom sediments in the river's vicinity. The flow in the Niagara River is largely invariant at 6400 m³/s (4), and sediment concentrations in the river at Niagara-on-the-lake have been monitored weekly (4, 22). Thus, the approximate amount of sediment entering Lake Ontario from the river can be calculated, and if the sediment catches at stations 207–209 are representative, the area required for deposition of this sedi-

Table V. Niagara River Contaminant Loadings to Lake Ontario and to the Lake Sediments (20-m Sediment Traps at Stations 207-209) and the Percentage of Input on Sedimenting Particles (May 11-Nov 10, 1982)

compd	Niagara River loading, g/day	downflux to sediments, g/day	downflux as a % of loading
1,3-DCB	6600	53	0.8
1,4-DCB	23000	300	1
1,2-DCB	14000	310	2
1,3,5-TCB	610	16	3
1,2,4-TCB	8800	93	1
1,2,3-TCB	2000	20	1
1,2,4,5-TeCB	1300	36	3
1,2,3,4-TeCB	2900	61	2
QCB	830	33	4
HCB	510	75	15
PCB 18	270	13	5
PCB 40	77	5.0	7
PCB 52	480	46	10
PCB 101	400	36	9
PCB 153	240	26	11
PCB 194	<55[a]	5.0	>9
α-BHC	9400	25	0.3
γ-BHC	1500	6.1	0.4
α-chlor	94	6.4	7
γ-chlor	88	4.6	5
p,p'-DDE	140	27	19
p,p'-DDT	<50[a]	16	>32
HCBD	530	15	3
PCT	250	12	5
OCS	30	6.8	23
mirex	<40[a]	14	>35

[a] These compounds were not detected (ND) in most of the Niagara River water samples. For these chemicals all ND values were set at the detection limit (0.05 ng/L) to estimate the upper loading limit.

Table VI. log K_{OC} Values Calculated from Sediment Trap (20-m, Stations 207-209) and Niagara River Contaminant Concentrations (May-Nov 1982), from Organic Matter Data in the Niagara River (25), and from the Semiempirical K_{OW} Equation of Karickhoff (24)

compd	field[a] log K_{OC}	Niagara River[b] organic matter log K_{OC}	log K_{OC}[c] from log K_{OW}	log K_{OW} (source)
1,3-DCB	4.5	4.1	3.0	3.4 (26)
1,4-DCB	4.8	5.0	3.0	3.4 (26)
1,2-DCB	4.6	4.6	3.0	3.4 (26)
1,3,5-TCB	5.1	4.2	3.8	4.2 (27)
1,2,4-TCB	4.7	4.4	3.6	4.0 (28)
1,2,3-TCB	4.7	4.1	3.7	4.1 (27)
1,2,4,5-TeCB	5.1	4.7	4.1	4.5 (27)
1,2,3,4-TeCB	5.0	4.9	4.1	4.5 (27)
QCB	5.3	5.4	4.5	4.9 (26)
HCB	5.9	5.5	5.1	5.5 (28)
PCB 18	5.4	5.5[d]	5.2	5.6 (29)
PCB 40	5.5	5.5[d]	5.2	5.6 (29)
PCB 52	5.6	5.5[d]	5.7	6.1 (29)
PCB 101	5.6	5.5[d]	6.6	7.1 (29)
PCB 153	5.6	5.5[d]	7.3	7.8 (29)
α-BHC	4.1		3.5	3.9 (30)
γ-BHC	4.3		3.5	3.9 (30)
α-chlor	5.5		5.6	6.0 (30)
γ-chlor	5.4		5.6	6.0 (30)
p,p'-DDE	6.0		5.3	5.7 (30)
HCBD	5.2	4.9	4.4	4.8 (26)
PCT	5.3		5.1	5.5[e]
OCS	6.1		5.9	6.3 (30)

[a] Mean organic carbon content of sediment trap material, 4.1%. [b] From July 1981 Niagara River data of Fox et al. (25) assuming the organic matter in the river was 50% organic carbon. [c] Using the semiempirical equation log K_{OC} = 0.989 log K_{OW}-0.346 (24). [d] For total PCB's. [e] Assumed to have approximately the same K_{OW} as HCB.

ment can be computed. For the May 11-Nov 10, 1982, period the suspended solids concentration in the river averaged 5.0 mg/L, and the average downflux at stations 207-209 (20-m traps) was 7.8 g/(m² day). The deposition area is calculated by dividing the sediment loading from the river by the downflux:

$$(0.005 \text{ g/L})(5.53 \times 10^{10} \text{ L/day})/7.8 \text{ g/(m}^2 \text{ day)} =$$
$$360 \times 10^6 \text{ or } 360 \text{ km}^2$$

By use of the average contaminant downfluxes at stations 207-209 and the calculated deposition area, a crude estimate of the total quantity of various contaminants deposited to the sediments in the vicinity of the river can be made. The total contaminant loading can be estimated from weekly analysis of Niagara River water at Niagara-on-the-lake over the period over which the traps were deployed. These data together with the percentage of compound deposition to the sediments in the river's vicinity is shown in Table V.

Although these estimates are crude because of our few stations and our lack of proper composite river sampling to obtain accurate compound loadings, some observations can be made regarding the *relative* tendency of compounds to become incorporated on settling particles. Of the chlorobenzenes, HCB appears to have the highest tendency to be incorporated on settling sediment (15%), whereas only a small percentage of lower CB's are sorbed. Qualitatively, this observation agrees with the different physical-chemical properties of the CB's. Lower CB's have higher water solubilities so they are more likely to remain dissolved; they also have higher vapor pressures so they have a greater tendency to volatilize out of the lake. Schwarzenbach et al. (23) showed that for Lake Zurich in Switzerland, a maximum of 2 kg of the 60 kg of 1,4-DCB

eliminated from the lake yearly was incorporated in bottom sediments with most of the rest lost by volatilization. According to our calculation, only about 10% of the PCB's entering the lake appear to be sequestered on settling particles in the river's vicinity. Surprisingly, only a small percentage of most of the pesticides appear to be associated with the settling sediments. Thus, in the Niagara River/Lake Ontario vicinity where suspended solid concentrations are fairly low ($\approx$5 mg/L of river water, <1 mg/L of lake water), the common assumption that the bulk of organic contaminants with low water solubility becomes associated with suspended sediments appears to be incorrect. Since most of the study chemicals are persistent in the aquatic environment, volatilization would appear to be a major loss mechanism in this area.

Comparison of Sorption Coefficients with Literature Empirical Equations. Karickhoff (24) has shown that the sorption of hydrophobic pollutants by sediments is linear, reversible, and characterized by a partition coefficient. Partition coefficients must be normalized to organic carbon as shown in the following equation:

$$K_{OC} = \frac{K_p}{f_{OC}} = \frac{[C]_{sed}/[C]_{H_2O}}{f_{OC}} \quad (2)$$

where K_p is the partition coefficient, K_{OC} is the partition coefficient normalized for organic carbon, f_{OC} is the fraction of organic carbon in the sediment, and $[C]_{sed}$ and $[C]_{H_2O}$ are contaminant concentrations in sediment and water, respectively. This equation applies at low sediment and low contaminant concentrations. K_{OC} (Table VI) has been computed for the study chemicals by using the average 20-m sediment trap data for stations 207-209 from May

to Nov 1982 and using mean Niagara River water contaminant concentrations for this 6-month period (20). As rational for using river water chemical concentrations in the K_{OC} calculations instead of lake water values (which are approximately one-tenth river concentrations at the trap locations), we propose the following behavior for chemicals entering the Niagara River: The contaminants enter the river just above or below Niagara Falls and pass through a strong mixing zone, the Whirlpool Rapids. By the time the chemicals reach Lake Ontario, an equilibrium between "dissolved" and "particle-associated" material is established. The plume of the Niagara River has been traced out to the location of the sediment traps (stations 207–209). The particles from the plume likely settle into the trap and finally into the cup at the base of the trap where they form a bed. In this high solid environment it is unlikely that reestablishment of equilibrium to that of the lake water would occur since exchange would be limited by diffusion.

To support this argument, column 3 in Table VI shows log K_{OC} values calculated for organic matter collected with a plankton net directly from the Niagara River (25). This material was largely algae, zooplankton, and other organic detritus, and it was assumed to have an organic carbon content of about 50%. Fairly good agreement between log K_{OC} values for the Niagara River and the sediment trap material is seen. The sediment traps catch seston such as algae, zooplankton, diatoms, and detritus as well as inorganic particles from the river (the organic carbon content of the 20-m trap material is about twice that of bottom sediments). Thus, the nature of the adsorbing organic material in the two studies appears to be similar. The effect of the trap's living biological "soup" (the traps were not "poisoned" to limit biological growth) on contaminant partitioning processes is completely unknown.

log K_{OC} values calculated by using Karickhoff's empirical equation, which relates K_{OC} to K_{OW}, the octanol–water partition coefficient, are shown in column 4 of Table VI. For compounds with high log K_{OW} values (>5.5), predicted and field values are in fair agreement, but for compounds with lower partition coefficients the field values are considerably higher than the predicted values. The lower the K_{OW}, the larger the observed deviation—field K_{OC} values for the dichlorobenzenes are approximately 40 times higher, and for HCB about 8 times higher, than the predicted K_{OC} values. This pronounced deviation could in part be due to the biological component of the trap material (Karickhoff used "stabilized" bottom sediments in his studies) or to equilibrium (lack of equilibrium) considerations. Why the empirical relationship works for some of the compounds and not for others is not apparent, because Karickhoff used chemicals with a wide range of K_{OW} values to develop his equation.

In summary, the study of contaminant concentrations in material caught in sediment traps has provided interesting information regarding the dynamics of contaminant movement and deposition in Lake Ontario. Contaminant ratios in the material have been used to compute the degree of sediment resuspension in the lake and show that considerable resuspension is occurring particularly during winter months. Surprisingly, our calculations indicate that only a small portion of most study chemicals entering the lake are adsorbed by settling particles and reach the bottom sediments. The general lack of agreement between field partition coefficients and coefficients derived from semiempirical equations based on physical and chemical properties of the contaminants shows the difficulties that can be encountered in applying laboratory predictions to field situations.

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