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**CHLORINATED ORGANICS IN NEARSHORE WATERS
AND TRIBUTARIES OF THE ST. CLAIR RIVER**

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SUBSTANCES ORGANOCHLORÉES DANS LES EAUX DES RIVES
DE LA RIVIÈRE STE-CLAIRE ET DE SES TRIBUTAIRES

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RÉSUMÉ ADMINISTRATIF

D'après les concentrations d'hexachloroéthane (HCE) d'hexachlorobutadiène (HCBD), de pentachlorobenzène (QCB), d'hexachlorobenzène (HCB) et d'octachlorostyrène (OCS) trouvées dans des échantillons d'eau volumineux, il appert que les effluents de la Dow Chemical et, à un degré moindre, les eaux du fossé de la municipalité de Sarnia drainant une des décharges de cette compagnie sont à l'origine de la présence de ces substances chimiques dans la rivière Ste-Claire. On a trouvé que des panaches de ces substances persistaient sur des distances considérables en aval des industries et qu'ils avaient tendance à demeurer près de la rive canadienne. Les tributaires se déversant dans la rivière des deux côtés de la frontière Canada/É.-U. renferment des concentrations mesurables de ces substances, une indication de l'ampleur de la pollution à faibles concentrations dans la région. Le partage des substances dans les eaux et les sédiments en suspension fait l'objet d'une étude. Les composés les moins solubles dans l'eau ont davantage tendance à se fixer sur les matières en suspension dans la rivière.

PERSPECTIVE GESTION

Il appert que les deux principales sources de HCE, de HCBD, de QCB, de HCB et d'OCS dans la rivière Ste-Claire sont les effluents de la Dow Chemical et, à un degré moindre, le fossé de la municipalité de Sarnia. Les substances chimiques déversées dans la rivière ont tendance à persister, créant des panaches de concentrations parallèles à la rive canadienne sur des distances considérables en aval de la source. Cet état de chose pourrait avoir des répercussions graves pour les usagers de cette eau.

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RÉSUMÉ

D'après les concentrations d'hexachloroéthane (HCE) d'hexachlorobutadiène (HCB_D), de pentachlorobenzène (QCB), d'hexachlorobenzène (HCB) et d'octachlorostyrène (OCS) trouvées dans des échantillons d'eau volumineux, il appert que les effluents de la Dow Chemical et, à un degré moindre, les eaux du fossé de la municipalité de Sarnia drainant une des décharges de cette compagnie sont à l'origine de la présence de ces substances chimiques dans la rivière Ste-Claire. Les tributaires se déversant dans la rivière des deux côtés de la frontière Canada/É.-U. renferment des concentrations mesurables de ces substances, une indication de l'ampleur de la pollution à faibles concentrations dans la région. Le coefficient de partage (K_p) des substances dans les eaux et les sédiments en suspension a fait l'objet d'une étude. Les variations de K_p des diverses substances correspondant aux variations de leurs propriétés physico-chimiques.

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ABSTRACT

The concentrations of hexachloroethane (HCE), hexachlorobutadiene (HCBD), pentachlorobenzene (QCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS) in large volume water samples show that the major sources of these chemicals to the St. Clair River are Dow Chemical Company effluents and, to a lesser degree, Sarnia's Township ditch which drains one of Dow's waste disposal sites. Tributaries entering the river on both sides of the Canada/United States border contain measurable concentrations of these chemicals indicating low level contamination throughout the area. The degree of water/suspended sediment partitioning of the chemicals (K_p) was studied. K_p values for the individual chemicals changed in a manner consistent with changes in their physical-chemical properties.

INTRODUCTION

The presence of halogenated organic chemicals in industrial discharges to the St. Clair River has been documented by Bonner and Meresz (1981). Kaiser and Comba (1986a, 1986b) showed that plumes of volatile chlorinated chemicals could be traced in the river from the Sarnia area into Lake St. Clair. The severity of river contamination has been demonstrated from bottom sediment and clam investigations (Pugsley et al 1985, Oliver and Pugsley 1986, Kauss and Hamdy 1985). In this note we report the concentrations of several chlorinated hydrocarbons in nearshore waters and tributaries of the St. Clair River. The study was conducted to pinpoint sources and to investigate partitioning of the chemicals to suspended solids.

METHODS

During the week of April 22 to 25, 1985, large volume water samples and their associated suspended sediments were collected from 21 locations (C_1 to C_{16} , U_1 to U_5) shown in Figure 1. The samples were collected from mid-depth with a submersible pump and passed through a continuous flow centrifuge at 6 L/min to remove the suspended solids. The output from the centrifuge was placed in a large 200 L stainless steel liquid-liquid extractor and extracted with 8 L of high purity dichloromethane (DCM). The details and compound recoveries of this procedure have previously been published (Oliver and Nicol 1986). Briefly the DCM extracts were evaporated to 10 mL using a Snyder condenser. One mL of this extract was passed through a small pasteur disposable pipette column containing 1 cm Na_2SO_4 , 4 cm 40% H_2SO_4 on silica gel and 2 cm 5% water deactivated Florisil. A final volume of 10 mL was collected from this column and concentrated to 1 mL using a Kuderna-Danish condenser. The suspended solids were Soxhlet extracted with acetone/hexane and, after removal of the acetone with water, were concentrated and cleaned up with silica gel/Florisil as above.

The GC determinations were made on dual 30 m capillary columns (DB5 and DB17) with a Varian 4600 gas chromatograph equipped with electron capture detectors (Oliver and Nicol 1982).

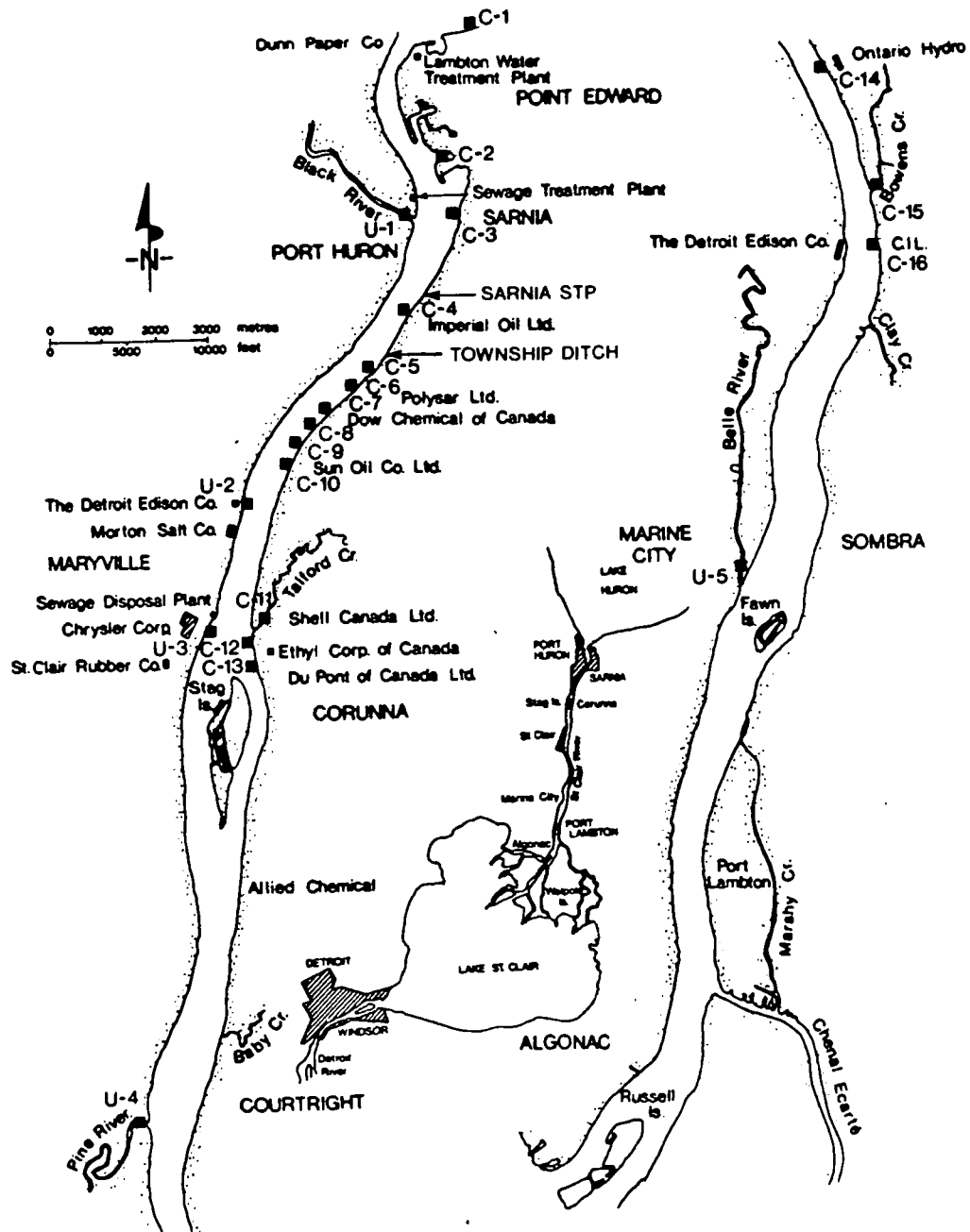


Fig. 1 Map of St. Clair River Sampling Stations

The chemicals quantified were the chlorobenzenes, including pentachlorobenzene (QCB) and hexachlorobenzene (HCB), hexachloroethane (HCE), hexachlorobutadiene (HCBd), octachlorostyrene (OCS), α - and γ -BHC, α -chlordane, pp-DDE, pp-DDD, pp-DDT and PCB's.

RESULTS AND DISCUSSIONS

(a) Concentration Distribution

The concentrations of α - and γ -BHC were fairly constant in all samples - with mean values of 2.0 and 0.3 ng/L, respectively. DDT-type residues and γ -chlordane were found to be near or below detection limits (≈ 0.1 ng/L) in all samples. PCB concentrations were also low throughout the study area and ranged from non-detected (ND) to 7.7 ng/L, with a mean of 1.7 ng/L. The concentrations of di-, tri- and tetrachlorobenzenes did show some minor increases near industrial sources but were mostly low throughout the river - with mean values of 6, 1.4 and 0.5 ng/L, respectively. The other five chemicals HCE, HCB, QCB, HCB and OCS were detected in most samples and all exhibited major increases along the river. The data for these chemicals are shown in Table 1.

The changes in HCB concentrations along the Canadian shoreline of the river in Figure 2 illustrate the behavior of these chemicals. Dramatic increases in HCB concentrations (as well as the other four contaminants) occurred after the Township Ditch, with the highest values observed near Dow similar to changes in bottom sediments (Oliver and Pugsley 1986). Peak concentrations in whole water were HCE 1700, HCB 150, QCB 3, HCB 87 and OCS 7.2 ppt, and on suspended sediments were HCE 0.53, HCB 24, QCB 0.6, HCB 40, and OCS 3.1 ppm. Elevated concentrations persist for at least 25 km downstream. Since no other sources of these chemicals were apparent, these raised downstream concentrations indicate that the effluent plume hugged the Canadian shoreline for a considerable distance. This is in agreement with the data of Chan et al (1986) and Kaiser and Comba (1986a and b).

Low but measureable concentrations of these five chemicals were observed upstream of the major sources and along the American side of the river. The concentrations of these chemicals on the suspended solids from these sites were much higher than those observed for bottom sediments for southern Lake Huron (Oliver and Bourbonniere 1985), the major source of sediments to the river. Thus it is unlikely that the bulk of these chemicals come from long range transport from distant sources. A more probable explanation is short range atmospheric and watershed transport emanating in all directions from the Sarnia point source.

Both tributaries on the Canadian side of the river, Telford and Bowens Creeks, contained measureable concentrations of all five contaminants in approximately the same ratios as the river samples. The highest values were found in Telford Creek which flows through a portion of Sarnia's industrial area. The highest concentrations in the American tributaries were in the Pine River which flows into the St. Clair River about 18 km downstream of Sarnia. We have no explanation for this observation other than the presence of a visible oily surface slick and comparatively high suspended sediment levels at the time of sampling.

(b) WATER/SUSPENDED SEDIMENT PARTITIONING

The partitioning between the "dissolved" and "suspended sediment" phases can be seen for individual samples in Table 1. Suspended sediment concentrations in the samples were quite low ranging from 0.4 to 9.9 mg/L with a mean of 3.6 mg/L. A summary of the data presented as percentage dissolved and as water/suspended sediment partition coefficient, K_p , (concentration (ng/Kg) on solids/concentration (ng/L) dissolved) is shown with literature octanol/water partition coefficients, K_{ow} , in Table 2. As the hydrophobicity and K_{ow} of the chemicals increase, the percentage of the chemical found in the "dissolved" state markedly decreases.

Table 1. Contaminant concentrations in the "dissolved" fraction (ng/L), in the suspended sediment or particulates (ng/g) and in whole water (ng/L) for St. Clair River nearshore and tributary samples; SS indicates concentrations of suspended sediments.

Compound	C-1 (SS = 0.42 mg/L)			C-2 (SS = 6.4 mg/L)			C-3 (SS = 0.54 mg/L)			C-4 (SS = 1.9 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	0.89	110	0.94	2.1	12	2.2	2.7	68	2.7	5.0	9.2	5.0
HCBD	0.09	440	0.25	0.54	16	0.64	0.40	83	0.45	0.68	110	1.1
QCB	ND	63	0.03	0.10	26	0.27	0.02	42	0.05	0.05	8.5	0.09
ECB	0.07	1400	0.59	0.24	46	0.53	0.10	250	0.30	0.47	290	1.7
OCS	ND	73	0.03	0.02	8.7	0.08	ND	29	0.02	0.02	28	0.13
Compound	C-5 (SS = 1.8 mg/L)			C-6 (SS = 0.8 mg/L)			C-7 (2.0 mg/L)			C-8 (SS = 2.1 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	1.8	1.4	1.8	4.7	2.6	4.7	530	120	530	1700	530	1,700
HCBD	4.2	120	4.4	7.4	140	7.5	80	17,000	114	130	9,300	150
QCB	0.09	15	0.12	0.11	8.2	0.12	0.63	260	1.2	1.8	600	3.0
ECB	0.21	250	0.67	0.18	190	0.33	6.9	40,000	87	13	23,000	61
OCS	0.03	130	0.27	0.02	6.9	0.03	0.64	3,300	7.2	0.71	2,100	5.0
Compound	C-9 (SS = 1.3 mg/L)			C-10 (SS = 1.8 mg/L)			C-11 (SS = 4.2 mg/L)			C-12 (SS = 7.6 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	110	37	110	85	27	85	41	41	41	67	4.2	67
HCBD	30	24,000	60	7.7	970	9.4	31	6,700	59	3.5	21	3.7
QCB	0.21	120	0.36	0.36	55	0.46	0.13	60	0.38	1.0	23	1.2
ECB	2.1	23,000	31	3.0	4,100	10	1.1	7,900	34	1.9	760	7.6
OCS	0.17	1,800	2.5	0.14	340	0.75	0.13	390	1.6	0.13	28	0.34
Compound	C-13 (SS = 3.7 mg/L)			C-14 (SS = 1.6 mg/L)			C-15 (SS = 9.4 mg/L)			C-16 (SS = 4.0 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	17	7.3	17	38	26	38	27	8.1	27	14	9.2	14
HCBD	1.4	270	2.4	7	250	7.4	4.2	64	4.8	2.3	110	2.7
QCB	0.10	65	0.34	0.12	27	0.16	0.12	11	0.22	0.11	8.5	0.14
ECB	0.38	2,300	9.0	1.0	760	2.2	0.85	200	2.8	1.1	290	2.3
OCS	0.02	140	0.54	0.06	79	0.19	0.08	30	0.36	ND	28	0.11

Table 1. Continued

Compound	U-1 (SS = 6.9 mg/L)			U-2 (SS = 1.4 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	1.0	2.0	1.0	2.8	11	2.8
ECBD	0.14	4.9	0.17	0.22	42	0.28
QCB	ND	6.3	0.04	0.03	12	0.05
ECB	ND	12	0.08	0.25	83	0.36
OCS	ND	1.1	0.01	ND	ND	ND

Compound	U-3 (SS = 1.2 mg/L)			U-4 (SS = 5.8 mg/L)		
	Dissolved	Particulates	Whole	Dissolved	Particulates	Whole
HCE	4.4	32	4.4	20	3.8	20
ECBD	0.25	55	0.31	1.2	8.1	1.3
QCB	0.03	38	0.07	0.05	4.8	0.08
ECB	0.10	180	0.31	0.47	56	0.79
OCS	ND	8.4	0.04	0.02	6.3	0.05

Compound	U-5 (SS = 9.9 mg/L)		
	Dissolved	Particulates	Whole
HCE	ND	2.1	0.02
ECBD	0.2	5.1	0.26
QCB	ND	2.3	0.02
ECB	0.55	19	0.74
OCS	ND	2.3	0.02

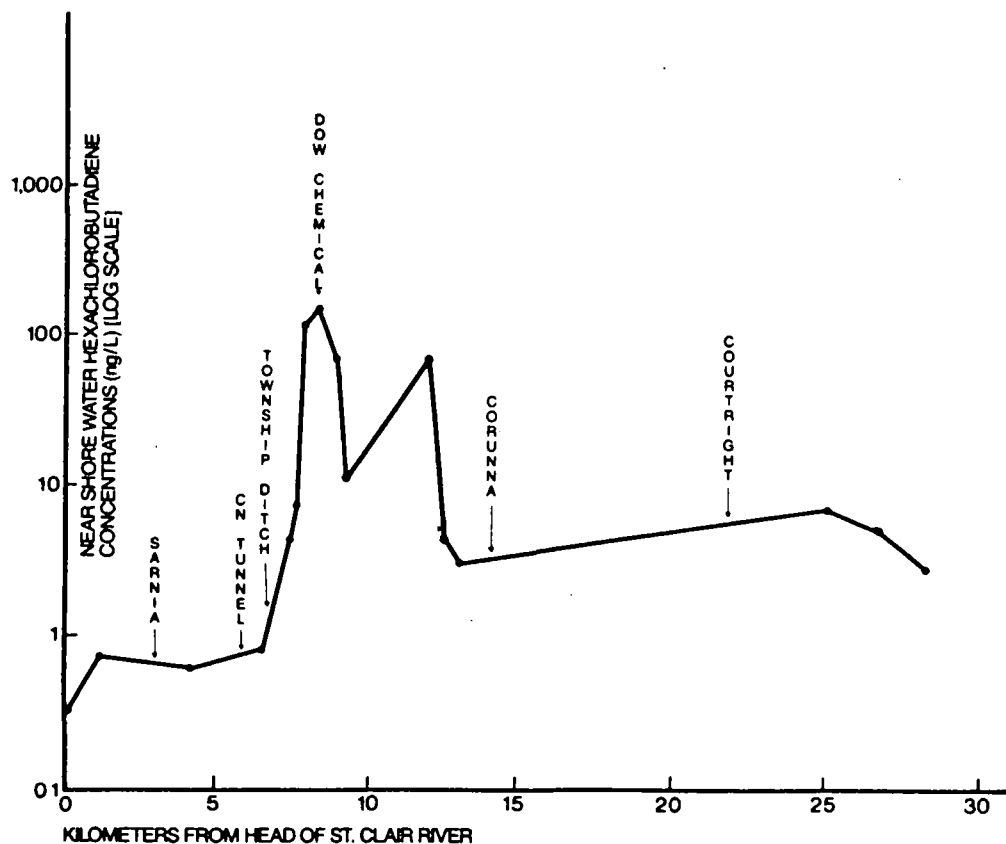


Fig. 2 Concentration of hexachlorobutadiene concentrations (ng/L) on a log scale versus distance (km) from head of St. Clair River.

Table 2. Percentage of chemicals "dissolved", sediment water partition coefficients, K_p , and octanol/water partition coefficients, K_{ow} for studied chemicals.

	% Dissolved		Log K_p		Log K_{ow}
	Range	Mean	Range	Median	
HCE	95 - 100	99	1.8 - 5.1	2.8	3.6
HCBd	33 - 99	78	3.8 - 6.7	4.9	4.8
QCB	29 - 94	60	4.4 - 6.3	5.4	4.9
HCB	4 - 74	33	4.5 - 7.3	6.0	5.5
OCS	4 - 43	20	5.3 - 7.0	6.3	6.2

The partition coefficients, K_p , vary widely with the individual samples. Some of this variation is likely due to analytical difficulties in the low concentration samples where the levels are close to the detection limits. A much smaller K_p range is observed in samples containing high concentrations. Median rather than mean K_p values are presented in Table 2 to minimize the impact of some of the very high values. In most cases the median K_p falls in the range found in the high concentration samples. The K_p values observed in this study are much higher than those observed at the Niagara River (Stepien et al 1986) and those calculated using semi-empirical equations (Karickhoff 1981). This may indicate that the contaminated suspended solids may not have reached equilibrium with the surrounding water at the time of sampling. As some of the samples were taken close to major outfalls, the available time to mix and equilibrate with river water would have been in the order of seconds to minutes. The time necessary for equilibration is expected to range from several minutes to a few hours.

KEY WORDS

Chlorinated organics, water, suspended sediments, St. Clair River, tributaries, water/sediment partitioning.

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