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DISTRIBUTION OF CONTAMINANTS IN CLAMS AND SEDIMENTS FROM THE HURON-ERIE CORRIDOR. I—PCBs and OCTACHLOROSTYRENE

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ABSTRACT. Samples of surficial sediments and the clam species Lampsilis radiata siliquoidea were collected from 102 sites covering all of Lake St. Clair and the Canadian shoreline of the St. Clair and Detroit rivers. The distribution patterns of both octachlorostyrene (OCS) and PCBs were mapped throughout this area. The mean level of PCBs in sediments of 3.9 µg kg⁻¹ (Aroclor 1254) was much lower than values for "total PCBs" reported in studies carried out in the early 1970s. This reduction does not appear to reflect a real decrease in PCB levels in the environment, but rather changes that have been made in sampling procedures and analytical techniques. Highest levels of PCBs in both sample types were found along the western shore of Lake St. Clair. Mean levels of OCS in whole clam tissue and surficial sediment (0–10 cm) were 43.0 and 5.1 µg kg⁻¹, respectively. The distribution pattern of OCS in the Huron-Erie corridor in both clams and sediments suggests that the primary source is in the St. Clair River. The mean chemical concentration factor was 59 for OCS, indicating considerable bioaccumulation in the biota of Huron-Erie corridor.

ADDITIONAL INDEX WORDS: Toxic substances, chlorinated hydrocarbons, lake sediments, mollusks, bioindicators.

INTRODUCTION

Sediments have been widely used to locate contaminant discharges into the Great Lakes, with interest usually focusing on the chlorinated hydrocarbons. Although fish have also been used extensively in contaminant monitoring studies, there has been relatively little work on less mobile, in situ organisms. In this study both sediments and the Unionid clam *Lampsilis radiata siliquoidea* were chosen to monitor levels and distribution patterns of two contaminants in the Huron-Erie corridor.

There has been much debate as to the requirements of an ideal indicator species for monitoring trace levels of contaminants in aquatic environments (Phillips 1978, National Research Council (United States) 1980). For studies which aim to determine the levels and distribution patterns of trace contaminants, indicator organisms have direct advantages over the monitoring of sediments or water in that they provide some integration of fluctuations in contaminant levels over time, thus avoiding the need for frequent sampling. The use of biota also circumvents the need for any assump-

tions to be made about the bioavailability of contaminants, as is the case if water or sediments alone are monitored.

Clams are long-lived filter feeders which move little (Imlay 1982). They quickly accumulate both organic compounds and heavy metals from polluted environments (Imlay 1982), both as a result of feeding activity and direct absorption (Coker et al. 1921, Hart and Fuller 1974). In fact, bivalve molluscs meet most of the criteria desirable for an indicator species (Phillips 1978). As a result bivalves were selected for use in a monitoring program (international mussel watch) to measure trace contaminants in marine coastal environments (National Research Council (United States) 1980).

L. radiata is a common native clam species, with a wide distribution in both lakes and rivers across Canada (Clarke 1981). It would therefore appear to be a particularly suitable indicator species for monitoring trace contaminants in the Canadian freshwater environment. A major consideration in our choice of this particular species was the fact

that it was also the most abundant and ubiquitous Unionid present in the Huron-Erie corridor.

The aim of this study was to measure the levels and distribution patterns of PCBs and octachlorostyrene (OCS). These two contaminants were selected in part because of the contrast between PCBs, for which there were many known sources and high background levels, and OCS for which there was only one known source, and low background levels.

As far as we are aware this is the first time that contaminant levels have been measured simultaneously in both sediments and biota throughout the corridor. Intensive studies by the Ontario Ministry of Environment, such as the St. Clair Organics Study (OME 1979), or the sediment surveys carried out by the Canadian Centre for Inland Waters (Frank et al. 1977, Thomas et al. 1975, Thomas and Mudroch 1979) have focused on only one part of the system at a time.

METHODS

Field samples from 102 sites were collected between May and November 1983. Nine sites were in the Detroit River, 24 in the St. Clair River, and 69 sites in Lake St. Clair (Fig. 1, Table 1). All river sites were in Canadian waters, with the exception of station 90. Using latitude/longitude grid coordinates at 2.5' intervals, both U.S. and Canadian portions of Lake St. Clair were sampled. At each site SCUBA divers searched for clams, and took samples of the upper 10 cm of bottom sediment. The 500-mL amber glass jars used to collect the sediment, together with the aluminum foil liner used to cap them, were cleaned according to procedures described later. Batches of 10 cleaned jars were selected at random and analysed for traces of organic contaminants to ensure quality control over the cleaning procedures.

At least five specimens of L. radiata from each station were shucked immediately after collection. After draining any excess liquid from the shell, the soft tissues were wrapped in aluminum foil and labeled. Both valves were coded using a glass marker pen. Clam tissues, shells, and sediments were stored in ice until transfer to a freezer (-20°C) at the end of each day. At least one L. radiata aged 9-12 years was selected for trace organic analysis from the five or more specimens taken at each station.

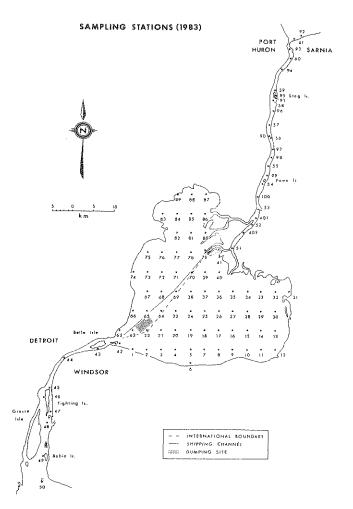


FIG. 1. Location of sampling sites (1983) along the Huron-Erie corridor.

Reagents—Acetonitrile, hexane, acetone, benzene, and petroleum ether (30-60°C) were pesticide grade obtained from Caledon Laboratories Ltd., Georgetown, Ontario. Florisil (60-100 mesh, Sigma) and anhydrous sodium sulfate (J. T. Baker) were heated to 600°C overnight and stored at 130°C before use. Celite 545 was obtained from Fisher Scientific.

Cleaning of Glassware

All glassware used in analysis was first cleaned in hot soapy (Contrad 70, Canlab) water, rinsed successively with large volumes of hot tap water, three portions of acetone, three portions of petroleum ether, and finally with pesticide grade hexane. Rinses with organic solvents used about 3% of the volume of the container. Except for sintered glass funnels, no chromic acid was used.

TABLE 1. Location of 1983 sampling sites in the Huron-Erie corridor. (I = Canada, 2 = U.S.A., LSC = L. St. Clair, SCR = St. Clair R., DR = Detroit R., LH = L. Huron.)

				Latitude				Longitude		
Station	Country	Location	Deg.	Min.	Se	c.	Deg.	Min.	Dε	g.
1	1	LSC	42	20	00	N	82	52	30	W
2	1	LSC	42	20	00	N	82	50	00	W
3	1	LSC	42	20	00	N	82	47	30	W
4	1	LSC	42	20	00	N	82	45	00	W
5	1	LSC	42	20	00	N	82	42	30	W
6	1	LSC	42	18	10	N	82	42	30	W
7	1	LSC	42	20	00	N	82	40	00	W
8	î	LSC	42	20	00	N	82	37	30	W
ğ	î	LSC	42	20	00	N	82	35	00	W
10	î	LSC	42	20	00	N	82	32	30	W
11	1	LSC	42	20	00	N	82	30	00	W
12	1	LSC	42	20	00	N	82	27	30	W
13	1	LSC	42	22	30	N	82	27	30	W
13	1	LSC	42	22	30	N	82 82	30	00	W
15	1	LSC	42 42	22	30	N	82 82	32	30	W
		LSC	42 42	22	30	N TA	82	35	00	W
16	1									
17	1	LSC	42	22	30	N	82	37	30	W
18	1	LSC	42	22	30	N	82	40	00	W
19	1	LSC	42	22	30	N	82	42	30	W
20	1	LSC	42	22	30	N	82	45	00	W
21	1	LSC	42	22	30	N	82	47	30	W
22	2	LSC	42	22	30	N	82	50	00	W
23	1	LSC	42	25	00	N	82	45	00	W
24	1	LSC	42	25	00	N	82	42	30	W
25	1 .	LSC	42	25	00	N	82	40	00	W
26	1	LSC	42	25	00	N	82	37	30	W
27	1	LSC	42	25	00	N	82	35	00	W
28	1	LSC	42	25	00	N	82	32	30	W
29	1	LSC	42	25	00	N	82	30	00	W
30	1	LSC	42	25	00	N	82	27	30	W
31	1	LSC	42	27	30	N	82	25	00	W
32	1	LSC	42	27	30	N	82	27	30	W
33	1	LSC	42	27	30	N	82	30	00	M
34	1	LSC	42	27	30	N	82	32	30	W
35	1	LSC	42	27	30	N	82	35	00	M
36	ī	LSC	42	27	30	N	82	37	30	M
37	1	LSC	42	27	30	N	82	40	00	W
38	1	LSC	42	27	30	N	82	42	30	W
39	Î	LSC	42	27	30	N	82	40	00	W
40	Î	LSC	42	30	00	N	82	37	30	W
41	i	LSC	42	31	45	N	82	37	30	W
42	1	DR	42	20	37	N	82	54	58	Ŋ
43	ì	DR	42	19	50	N	82	58	41	V
44	1	DR DR	42	18	44	N	83	04	07	V
45	1	DR DR	42	14	47	N	83	07	04	N
43 46		DR DR	42	13	28	N	83	07	36	N
	1							06		
47 49	1	DR	42	11	58	N N	83		34 13	N N
48	1	DR	42	10	33	N	83	07		
49	1	DR	42	05	59	N	83	07	33	V
50	I	DR	42	03	29	N	83	07	51	V
51	1	SCR	42	33	06	N	82	35	08	N
52	1	SCR	42	36	13	N	82	31	30	M

TABLE 1. continued

Station				Latitude			Longitude		
	Country	Location	Deg.	Min.	Sec.	Deg.	Min.	Deg.	
53	1	SCR	42	38	09 N	82	30	27 W	
54	1	SCR	42	41	42 N	82	29	40 W	
55	1	SCR	42	44	02 N	82	28	44 W	
56	1	SCR	42	47	40 N	82	28	23 W	
57	1	SCR	42	49	17 N	82 82	48	23 W 27 W	
58	1	SCR	42	52	09 N	82	28	00 W	
59	1	SCR	42	53	51 N	82	27		
60	1	SCR	42	57	35 N	82	25	40 W 10 W	
61	1	LH	43	00	31 N	82	23 24	28 W	
62	2	LSC	42	22	30 N	82 82	55	20 W	
63	2	LSC	42	22	30 N	82 82	52	30 W	
64	2	LSC	42	25	00 N	82	47	30 W	
65	2	LSC	42	25	00 N	82	50		
66	2	LSC	42	25	00 N	82 82	52		
67	2	LSC	42	27	30 N	82 82	50		
68	2	LSC	42	27	30 N	82 82		00 W	
69	2	LSC	42	27	30 N	82	47	30 W	
70	1	LSC	42	30	00 N	82 82	45	00 W	
71	2	LSC	42	30	00 N	62 82	42	25 W	
72	2	LSC	42	30	00 N		45	00 W	
73	2	LSC	42	30	00 N	82	47	30 W	
74	2	LSC	42	30		82	50	00 W	
75	2	LSC	42	32	00 N 30 N	82	52	30 W	
76	2	LSC	42	32		82	50	00 W	
77	2	LSC	42	32 32	30 N	82	47	30 W	
78	2	LSC	42	32 32	30 N 30 N	82	45	00 W	
79	2	LSC	42	32		82	42	30 W	
80	2	LSC	42	35 35	50 N 00 N	82	39	56 W	
81	$\overline{2}$	LSC	42	35 35		82	40	00 W	
82	$\frac{\overline{2}}{2}$	LSC	42 42		00 N	82	42	30 W	
83	2	LSC	42	35	00 N	82	45	00 W	
84	$\overline{2}$	LSC	42	37	30 N	82	47	30 W	
85	2	LSC		37	30 N	82	45	00 W	
86	2	LSC	42	37	30 N	82	42	30 W	
87	2	LSC	42	37	30 N	82	40	00 W	
88	2	LSC	42	40	00 N	82	40	00 W	
89	$\bar{\tilde{z}}$	LSC	42	40	00 N	82	42	30 W	
90	2	SCR	42	40	00 N	82	45	00 W	
91	1	SCR	42	47	44 N	82	28	45 W	
92	1	I.H	42	52	28 N	82	27	54 W	
93	1		43	00	58 N	82	23	23 W	
94	1	SCR	42	59	15 N	82	25	12 W	
95	1	SCR	42	55	49 N	82	26	59 W	
96	1	SCR	42	53	04 N	82	27	23 W	
97	1	SCR	42	50	54 N	82	27	59 W	
98		SCR	42	46	22 N	82	27	53 W	
99	¥ 4	SCR	42	45	17 N	82	27	56 W	
100	1	SCR	42	43	06 N	82	28	48 W	
401	1	SCR	42	40	02 N	82	30	22 W	
	1	SCR	42	37	24 N	82	30	43 W	
402	1	SCR	42	35	04 N	82	33	07 W	

Clam Analysis

Frozen samples of whole clam tissue were weighed, placed in a beaker, and homogenized in 120 mL of acetonitrile using a Polytron for 1-1.5 minutes. The homogenate was filtered with suction through a sintered glass funnel, the homogenization was then repeated with a fresh portion of acetonitrile plus 40 mL of water, and finally the homogenate was treated a third time with 50 mL of acetonitrile. The combined extracts were made up to 20\% agueous with water and back-extracted with 300 mL of petroleum ether in three portions. The combined petroleum ether extracts were then washed with 200 mL water and dried by passage through columns containing 15 g of anhydrous sodium sulfate. The dried extracts were concentrated to 5 mL using a Kuderna-Danish evaporator and then applied to 20 mm \times 40 cm glass columns containing 30 g of Florisil and a top layer of 1-2 cm of anhydrous sodium sulfate. Elution of the column with 200 mL of petroleum ether, concentration of the elutant in a Kuderna-Danish evaporator to 10 mL and injection of 1 µL on the gas chromatography column complete the process.

Sediment Analysis

The sample in its original 500-mL amber jar was thawed. Large stones were set aside and the remaining sediment mixed in a Waring blender for 3-5 minutes. Three weighed subsamples of about 10 g each were placed in 50-mL amber jars, the remaining sediment replaced in the original jar, and all four jars refrozen. A subsample was prepared for extraction by thawing and transferring to a 250-mL thick walled beaker using water to rinse the jar. Mixed solvent (100 mL of 1:1 hexane:acetone) was added, and the mixture sonicated for 2 minutes at a duty cycle of 60% (Sonicator Sonic 300 Desmembrator, Systems Corporation, Farmingdale, N.Y.). Sonication was repeated with fresh portions of solvent for periods of 4 and 3 minutes, respectively. The resulting mixtures were filtered through a sintered glass filter containing a 3-cm layer of Celite which had been prewashed with 100 mL of benzene and rinsed with 1:1 hexane acetone prior to use. The funnel was finally rinsed with 10-20 mL of hexane, the contents dried under vacuum and left overnight to air dry before the weight was recorded.

Combined filtrates were transferred to a 500-mL separatory funnel and washed with 100 mL water.

The aqueous layer was extracted with 100 mL benzene and the combined organic layers were concentrated on a Kuderna-Danish evaporator and added to a Florisil column as described for the clam sample. The eluant from this column was concentrated to 5 mL and treated with activated copper (copper powder washed with 5% nitric acid until the reaction had stopped, then washed with distilled water, acetone, and hexane). The treated solution was diluted to 10 mL from which 1 μ L was injected for GC-ECD determination.

Gas Chromatography

A Hewlett-Packard Model 5790A capillary column GC-ECD fitted with a 15 m \times 0.25 mm fused silica column containing a cross-linked DB-1 stationary phase supplied by J & W Scientific was used for the analyses. A Hewlett-Packard auto-injector and a Model 3390A integrator completed the instrument.

Injector temperature: 250°C

Column temperature programming: 0.5 min at 50°C,

50-250°C at 7°C min-1, 10 min at 250°C

Detector temperature: 300°C Carrier gas: helium at 1.5 mL min⁻¹

Detector make-up gas: 5% methane – 95% argon at 60 mL

 min^{-1}

Injection mode: splitless

Cleaning of glassware and purity of reagents were checked by analysis of appropriate blanks. In addition, each set of four samples presented for analysis was accompanied by a solvent blank which had been submitted to the complete isolation procedure.

Recovery of OCS was determined in a concurrent study for samples of goldenrod (Solidago canadensis) leaves extracted by the same procedure as the clams. The recovery ranged from 75–100% over the range 3–30 μ g kg⁻¹, with the lower values for the smallest spikes. In a further test of precision and accuracy for PCB determination at low levels, a standard sample of marine sediment (Atlantic Regional Laboratory, National Research Council of Canada) was found to yield 18.1 μ g kg⁻¹, n = 5, S.D. = \pm 1.5 compared to the accepted value of 21.8 \pm 1.1 μ g kg⁻¹ (recovery—83%).

Quantification of OCS was done by comparison of peak areas against a set of standards containing OCS at known concentrations. The limit of quantification for OCS was 0.2 µg kg⁻¹. The quantification of PCBs as Aroclors 1254 and 1260 in clam

tissues was based on levels of two specific congeners found in the preparations. Using previously determined (% w/w) levels of these components in the commercial mixtures (Albro et al. 1981, Tuinstra et al. 1983), the amount of a particular Aroclor in a sample is estimated from the detected levels of these marker species. The congeners used are listed in Table 2.

The general equations used to quantify the Aroclors were as follows:

Isomer X (ng mL⁻¹) =
$$\frac{A/RF \times F}{\sqrt[9]{6} \text{ w/w}} \times C$$
 (1)

Where A = Chromatographic peak area (sample)

RF = Response factor

C = Contribution of isomer X (from Aroclor being quantified), to the total peak area

= Empirical factor accounting for contributions to total peak area by unresolved conge-

Aroclor (
$$\mu$$
g kg⁻¹) = $\frac{\text{Isomer 1 + Isomer 2}}{2}$
 $\times \frac{10 \text{ mL}}{Y}$ (2)

Where Y = Sample weight-dry (g)

With this approach, limits of quantitation of 10-50 μg kg-1 were attainable for Aroclor 1254 and 1260 in clams (Obal 1983). For statistical purposes the limit of detection in sediments was taken as being 2.3 and 0.5 μ g kg⁻¹ for Aroclor 1254 and 1260. respectively. Trace levels of Aroclor 1254 and 1260 in sediments were taken as 7.6 and 1.6 µg kg⁻¹, respectively. Reported values for both OCS and PCBs were not corrected to compensate for recovery losses.

TABLE 2. Congeners used to quantify PCBs as Aroclors 1254 and 1260., PCB No. after Zell and Ballschmiter (1980).

Isomer	PCB No.	% w∕w	Aroclor Quantified
2,4,5,2',5'-Hexachlorobiphenyl	153	7.4	1254
2,3,4,5,6,2',5'-Heptachlorobiphenyl	185	1.32	1254
2,3,4,2',4',5'-Hexachlorobiphenyl	138	9.8	1260
2,3,4,5,6,2',5'-Heptachlorobiphenyl	185	6.14	1260

Mass Spectrometry

Confirmation of the identification of OCS in a composite clam sample was done on a Finnigan Model 4000 GC/MS operating with a $6' \times 4 \text{ mm}$ (i.d.) glass column packed with 3% OV-1 on Chromosorb W (HP). The peak which co-eluted with a synthetic OCS standard showed ions at m/z 376, 378, 380, etc. in the expected ratio.

RESULTS

Levels of PCBs and OCS found in clams and sediments for each section of the Huron-Erie corridor are summarized in Table 3. Average sediment concentrations of the two contaminants were similar, although OCS levels in St. Clair River sediments were considerably higher than elsewhere in the corridor (Table 3). The mean concentration of PCBs (Aroclor 1254) in clams was approximately twice as high as that of OCS. Aroclor 1254 was the predominant Aroclor mix in both clams and sediments (Table 3). The Aroclor ratio (1254/1260) for clams was highly variable, ranging from 0.7 to 9.1. There was no significant change in clam Aroclor ratios between the St. Clair River, Lake St. Clair, and the Detroit River. There was a highly significant correlation between the levels of Aroclor 1254 and 1260 in clam tissue (r = 0.86, p = 0.0001, n =49).

The chemical concentration factor (i.e., chemical concentration in clam dry weight/chemical concentration in sediment dry weight) for OCS based on 72 stations (no trace or non-detectable values) was 67.6, n = 72, S.D. = \pm 81.3. The C.F. for OCS was lowest (52) in the St. Clair River. increased to 64 in Lake St. Clair, and was highest (146) in the Detroit River. Chemical concentration factors were not calculated for PCBs because of the high number of non-detectable and trace values of Aroclor 1254 and 1260 found in the sediments.

A map of PCB levels showed highest values were present in clams and sediments near the western shore of Lake St. Clair, possibly originating from the Clinton River area. (Figs. 2, 3). However, PCB levels in sediments were in general very low, with only three stations having more than trace levels (Fig. 3).

Highest OCS levels were found in St. Clair River sediments (Table 3), with relatively high concentrations in both clams and sediments extending as a plume from the delta, diagonally across the centre of the lake (Figs. 4, 5). The rarity of clams in the St. Clair River made it impossible to draw any

TABLE 3. Summary statistics for levels of PCBs and OCS found in whole clam tissue and sediments collected from the Huron-Erie corridor during 1983. All values expressed as $\mu g \ kg^{-1}$ dry weight. For clams, wet weight = dry weight \times 6.667. Aroclor ratios = Concentration of Aroclor 1254/concentration of Aroclor 1260. C.F. = Chemical concentration factor, i.e., chemical concentration in clam dry weight/chemical concentration in sediment dry weight. All trace (tr.) and non-detectable (n.d.) values excluded from calculations of C.F.'s and Aroclor ratios.

	n	Mean	S.D.	Maximum	Minimum
All Stations					
Clam Aroclor 1254	72	88.9	118.0	700.0	n.d.
Clam Aroclor 1260	72	43.9	40.2	224.0	n.d.
Clam Aroclor ratio	49	2.3	1.4	9.1	0.7
Sediment Aroclor 1254	99	3.9	4.6	34.0	n.d.
Sediment Aroclor 1260	99	0.7	1.5	15.0	n.d.
Clam OCS	72	43.0	42.1	192.7	2.0
Sediment OCS	99	5.1	11.6	79.5	n.d.
C.F. OCS	72	67.6	81.3	443.4	2.2
St. Clair River					
Clam Aroclor 1254	6	43.9	31.8	104.7	n.d.
Clam Aroclor 1260	6	35.4	29.3	90.7	9.3
Clam Aroclor ratio	2	1.5	0.4	1.8	1.1
Sediment Aroclor 1254	21	3.3	2.1	tr.	n.d.
Sediment Aroclor 1260	21	0.5	0.2	tr.	n.d.
Clam OCS	6	35.9	76.8	192.7	2.9
Sediment OCS	21	14.8	21.4	79.5	n.d.
C.F. OCS	6	52.0	46.5	138.9	11.8
Lake St.Clair					
Clam Aroclor 1254	62	90.6	124.8	700.0	n.d.
Clam Aroclor 1260	62	44.2	41.6	224.0	n.d.
Clam Aroclor ratio	44	2.4	1.4	9.1	0.7
Sediment Aroclor 1254	70	4.1	5.3	34.0	n.d.
Sediment Aroclor 1260	70	0.8	1.7	15.0	n.d.
Clam OCS	62	43.3	39.6	154.0	2.0
Sediment OCS	70	2.7	4.8	26.2	n.d.
C.F. OCS	62	64.0	81.0	443.3	2.2
Detroit River					
Clam Aroclor 1254	4	130.0	55.9	196.0	72.7
Clam Aroclor 1260	4	51.8	38.7	95.3	tr.
Clam Aroclor ratio	3	2.3	0.6	2.9	1.6
Sediment Aroclor 1254	8	4.3	2.7	tr.	n.d.
Sediment Aroclor 1260	8	0.9	0.6	tr.	n.d.
Clam OCS	4	48.7	12.3	57.3	31.3
Sediment OCS	8	1.0	1.2	3.5	n.d.
C.F. OCS	4	146.0	102.1	286.7	69.5

conclusions about distribution or levels of contaminants in these organisms north of Lake St. Clair.

Although sediment results suggest a source of OCS in the St. Clair River north of Stag Island, our data show considerable station-to-station variability downstream of this point (Fig. 5). For example, sites 59, 91, and 58 around Stag Island

have very low values, compared to upstream areas (Fig. 5). Again, further downstream at Fawn Island, station 54 has sediment OCS levels ten times greater than at station 99, just upstream of the island.

There was a significant correlation (r = 0.48, p = 0.0001, n = 72) between OCS levels in clam tis-

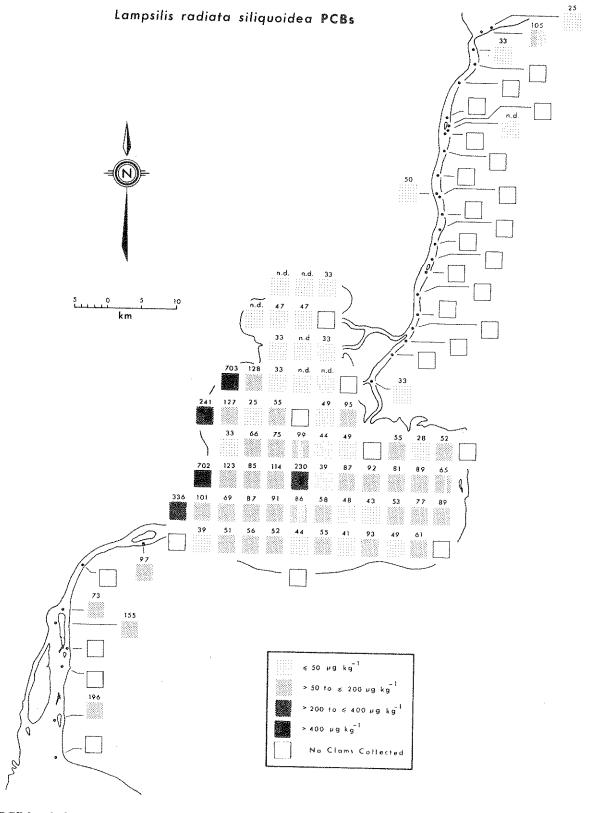


FIG. 2 PCB levels for 1983 samples of Lampsilis radiata siliquoidea whole tissue extract expressed as Aroclor 1254 on a dry weight basis (wet/dry weight = 6.667).

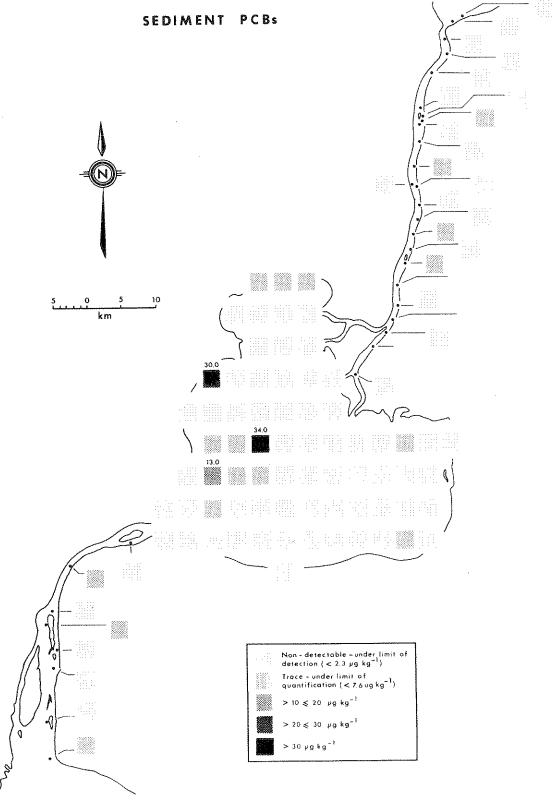


FIG. 3. PCB levels in surficial (0-10 cm), diver-collected sediments for 1983 expressed as Aroclor 1254 on a dry weight basis.

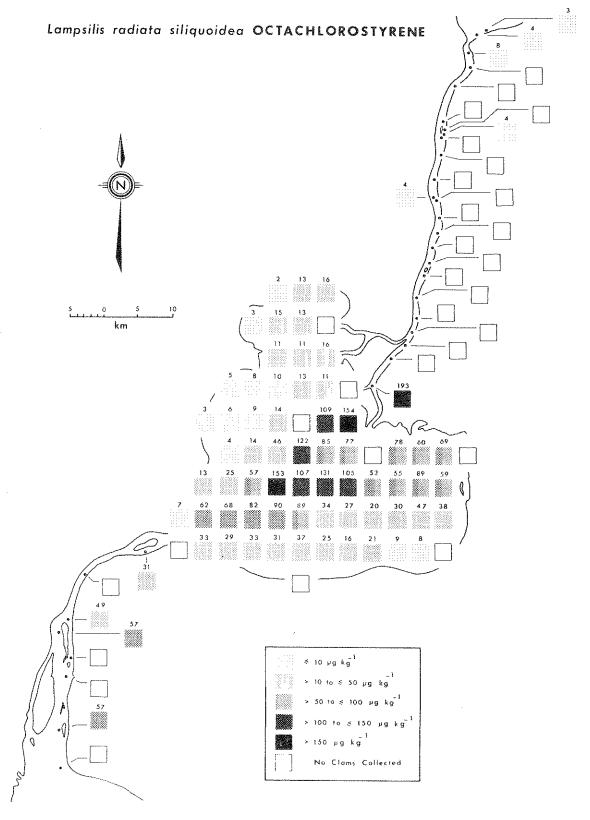


FIG. 4. Octachlorostyrene (OCS) levels for 1983 samples of Lampsilis radiata siliquoidea whole tissue extract expressed on a dry weight basis (wet/dry weight = 6.667).

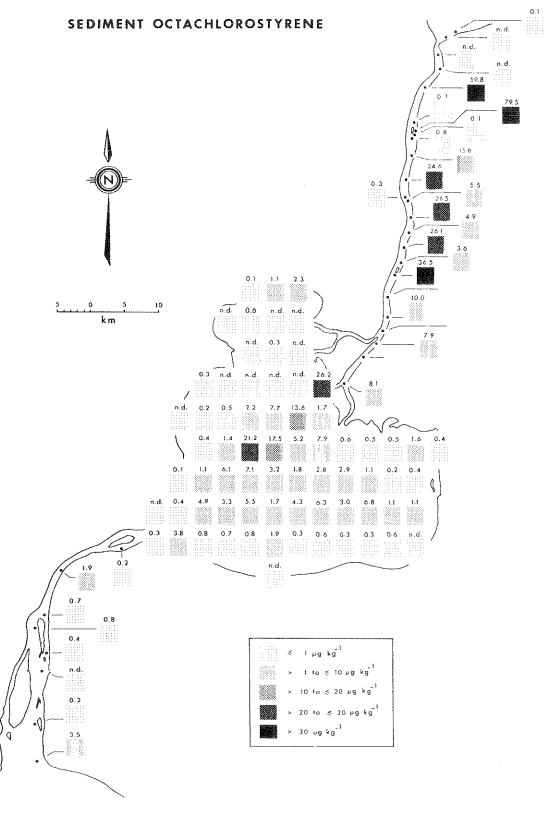


FIG. 5 Octachlorostyrene (OCS) levels in surficial (0-10 cm), diver-collected sediments for 1983 expressed on a dry weight basis.

sue and the concentration of OCS in the surrounding sediments (Fig. 6), but some conspicuous outliers were evident. Whether such variation reflects variation in physiological state of the clams remains to be investigated.

DISCUSSION

PCBs - Biota

The highest concentration of PCBs reported for a 16-day exposure to Niagara River water in clam caging experiments done in 1980 with *Elliptio complanatus* (Kauss *et al.* 1983) was 532 μg kg⁻¹ dry wt. (calculated using a wet-dry weight conversion factor of 5.6, P. Kauss, personal communication). Direct comparison with our data for the Huron-Erie corridor is difficult, because Kauss *et al.* (1983) expressed PCB levels as "total PCBs" rather than as Aroclor mixture (e.g., Aroclor 1254) and had a detection limit of 112 μg kg⁻¹ dry wt.). This value is well above both our detection limit and mean clam tissue level (88.9 μg kg⁻¹ dry wt.) for Aroclor 1254.

In 1979, levels of "total PCBs" in spottail shiners from three sites in Lake St. Clair ranged from non-detectable to 114 μ g kg⁻¹ wet wt. (Suns *et al.* 1981). The highest level of PCBs (as Aroclor 1254) in *L. radiata* found in this study was 105 μ g kg⁻¹ wet wt., i.e., similar to the highest levels (expressed as "total PCBs") found in the spottail shiners. However, as we had no samples from the U.S. side of the Detroit River, where PCB levels in sediments

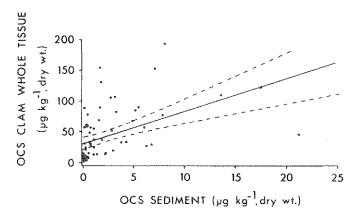


FIG. 6. Octachlorostyrene (OCS) levels in Lampsilis radiata siliquoidea as a function of OCS concentrations in the surrounding sediments. Linear regression with 95% confidence limits on mean predicted values—regression coeff. = 5.3, intercept = 30.8, correlation coeff. (r) = 0.48, p = 0.0001, n = 72.

indicate major sources (Thornley and Hamdy 1984), native clams, if present, are likely to have even higher values than found in our survey.

PCBs-Sediments

Because of differences in analytical procedure, location of sampling site, and sample collection methods, our sediment PCB levels appear much lower than the "total PCB" levels of 1,370 µg kg⁻¹ from the Canadian shoreline, and 1-3,800 µg kg⁻¹ from the U.S. shoreline of the Detroit River for 1980, reported by the Ontario Ministry of the Environment (Thornley and Hamdy 1984). In the OME study sediment samples were taken with a Shipek bucket and only the upper 3 cm of sediment analyzed. Therefore our samples of the upper 10 cm of sediment may well contain lower amounts of PCB, if as previous studies suggest (Durham and Oliver 1983), most of the PCBs are located in the upper sediment layers. However, five of our Detroit River sites (42, 44, 45, 46, 50) coincided with the 1980 OME sites. At three of these sites. PCB levels were at or near the detection limits on both studies, although at stations 44 and 50 we detected no Aroclor 1254, whereas the OME study found 260 and 110 µg kg-1 "total PCBs" respectively.

In a 3-year survey (1976–1978) at up to 90 sites along the St. Clair River (OME 1979), "total PCB" levels in sediments (Ponar grab, approx. 0-5 cm sediment sampled – S. Thornley, personal communication) averaged 491 µg kg-1, with a range of 0-10,000 μg kg⁻¹. Aroclor 1254 was reported as being the predominant Aroclor (OME 1979), with higher levels of PCBs occurring along the Canadian shoreline of the St. Clair River. These high levels of "total PCBs" were well above the 50 μg kg-1 limit for open water disposal of dredged materials (OME 1979). Levels of "total PCBs" in fish from the St. Clair River at 2,000 µg kg⁻¹ were sufficiently high to pose a threat to human health (OME 1979). Eight of our sampling stations (55, 56, 59, 60, 93, 95, 97, 98) coincided with OME sites sampled for PCBs during 1977 and 1978. Levels of "total PCBs" reported for 1977 and 1978 at these sites fell below 100 µg kg⁻¹ (OME 1979). Similarly in our study, only trace levels of Aroclor 1254 were found at these eight sites.

Frank et al. (1977) used packed column gas chromatography to estimate "total PCBs" in the upper 3 cm of lake sediment (collected with a Shipek bucket) at more than 50 stations in Lake St.

Clair. Their 1970 survey revealed mean concentrations of 19 μ g kg⁻¹, but this had dropped to 10 μ g kg⁻¹ in 1974. The 1974 study showed that PCBs were highest along both the western shore and in the middle of the lake. Our failure to detect a midlake peak may represent a real decline in PCBs levels in Lake St. Clair sediments. Alternatively the fact that we collected the upper 10 cm of sediment may have "diluted" the PCBs if in fact only the uppermost layers of sediments in the corridor area contained PCBs (Durham and Oliver 1983).

Oliver and Bourbonniere (1985) collected surficial samples (0-3 cm) from two box cores taken from Lake St. Clair in 1980. Using capillary column gas chromatography, they reported levels of PCB 118 (which after Zell and Ballschmiter (1980) corresponds to 2,4,5,3',4' pentachlorobiphenyl, the major congener of Aroclor 1254) in these two cores of 0.9 and 1.0 µg kg⁻¹. Total PCBs for these two cores were reported as 29 $\mu g \text{ kg}^{-1}$. In similar cores taken from the western basin of Lake Erie, Oliver and Bourbonniere found mean levels of PCB 118 and "total PCBs" of 6.1 μ g kg⁻¹ (n = 9, range 3.6–10 μ g kg⁻¹) and 300 μ g kg⁻¹ (n = 9, range 140-660) respectively. These values for Aroclor 1254 are in close agreement with ours (both their sites were near the centre of the lake). However their values for "total PCBs" are similar to those reported in the earlier studies already discussed. Our PCB values simply reflect the fact that although Aroclor 1254 was the most abundant PCB mixture we found, it did not constitute the majority of the "total PCBs" present. Using our sediment PCB data we cannot say whether sediment PCB levels have decreased or remained reasonably static over the last 10 years.

OCS - Biota

Since OCS is not routinely analysed in environmental samples, little information is available on levels in the biota from the corridor area. Reichel et al. (1977) appear to have been the first to report OCS from environmental samples in the U.S.A. They found that, from at least 1,500 samples of eggs and carcasses from herons and other estuarine birds, only those taken from the Lake St. Clair area contained detectable levels of OCS. Their reported values varied from non-detectable to 430 $\mu g \ kg^{-1}$ wet weight.

Kuehl *et al.* (1981) found OCS in whole carp taken from Anchor Bay (Lake St. Clair) at 227 μ g kg⁻¹ wet wt., i.e., above the highest levels of OCS found in clams, 32 μ g kg⁻¹ wet wt.

Ofstad *et al.* (1978), analyzing fish used for human consumption from Frierfjord in Norway, found mean OCS levels of between 3.1 and 431 mg kg⁻¹ (fat phase). Ernst *et al.* (1984) reported OCS levels in North Sea fish livers that ranged from 20 to 30,000 µg kg⁻¹ expressed on a lipid basis (2–58.8 µg kg⁻¹ on a liver wet weight basis). Heptachlorostyrene was also found. Levels of OCS were as high as PCB levels reported in other studies. There was no striking change in OCS levels in fish collected between 1972 and 1983. Very low levels of OCS in estuarine and sea water of 0.03–1.94 pg 1⁻¹ suggested to the authors the very high bioconcentration and absorption potential of this compound (Ernst *et al.* 1984).

In a laboratory study with oligochaetes and contaminated field-collected sediments, Oliver (1984) found that the uptake of OCS had not plateaued after 110 days' exposure. The chemical concentration factor (C.F.) of 6.7 for OCS was the highest in the group of 24 chlorinated compounds studied. With a octanol-water partition coefficient (Kow) of 6.29, OCS lay in the mid range of the contaminants tested. PCBs are in the same K_{ow} range (5-6), and Oliver suggested that such contaminants have a relatively long half life in biota. Therefore in his experiment, equilibrium was difficult to achieve for either OCS or PCBs. He also found that substances with Kow's below 5 easily equilibrated in worms during the 110-day study, while contaminants with Kow's above 6 were not easily taken up by the worms, perhaps because they were too strongly bound to the sediments to be available to biota. Alternatively, being larger molecules, contaminants with high Kow's were perhaps difficult to transport across biological membranes.

On the basis of Oliver's laboratory study it is not surprising that the CF for OCS found in clams in the Huron-Erie corridor was 59, i.e., equilibrium between contaminant levels in the clam tissues and the surrounding sediments was perhaps complete compared to Oliver's 110-day laboratory experiments. However we do not yet know the relative effect of sediment, versus ambient water concentration of organic contaminants on clam CF's.

Until laboratory procedures are standardized, and unless contaminant levels are expressed, or can be converted to a dry weight basis, attempts to compare the results of different studies are difficult. It is worth stressing that there is considerable variation in the percentage of water in biological or sediment samples and the data expressed in terms of wet weights only, without conversion factors,

are difficult to evaluate. In addition, there is also a need for the development of a standard reference sample to be used for intercalibration of analytical results for studies involving *L. radiata* as a monitoring organism. The development of a similar standard has been suggested by the international mussel watch program (National Research Council (United States) 1980).

OCS - Sediments

There are no published data from the corridor area on sediment levels of OCS. However Oliver and Bourbonniere (1985) found OCS in two cores collected near the middle of Lake St. Clair at concentrations of 8.1 μ g kg⁻¹, a value comparable to our mean for Lake St. Clair sediments of 2.7 μ g kg⁻¹. Oliver and Bourbonniere (1985) reported much lower levels in cores taken from southern Lake Huron (0.06 μ g kg⁻¹, n = 9, range 0.02 – 0.1), and low levels (2.3 μ g kg⁻¹, n = 9, range 0.8 – 5.9) from the western basin of Lake Erie. They concluded from this that the primary source for OCS must be in the St. Clair River.

Durham and Oliver (1983), using a sediment core taken from Lake Ontario, found nondetectable levels of OCS, i.e., less than 2 µg kg⁻¹, in sediment laid down before the 1920s. The highest concentrations of OCS (166 µg kg⁻¹) were found in sediment laid down in 1959-1962 (9-10 cm depth interval). The OCS content, averaged over the upper 10 cm of their core, was 35.7 μg kg⁻¹. Only four of our stations (54, 57, 94, 95), all in the St. Clair River, had levels above this value. In a similar study, Kaminsky and Hites (1984) focused exclusively on the analysis of OCS from 2-cm depth intervals from Lake Ontario sediment cores. The depth distribution of OCS was similar to that reported by Durham and Oliver (1983), with no detectable OCS in sediments laid down before about 1945. Peak levels of OCS in nine cores ranged from 4 - 137 µg kg⁻¹ for sediments laid down in the early 1970s. They demonstrated that significant amounts of the three isomers of heptachlorostyrene were also present when OCS levels exceeded about 5 µg kg⁻¹.

Burrows et al. (1981), working on marine sediments from Commencement Bay, Puget Sound (near an industrial area of Tacoma, Washington), found $20 \mu g \text{ kg}^{-1}$ dry wt. OCS in their samples, i.e., similar to the levels of OCS we found in the centre of Lake St. Clair.

Kaminsky and Hites (1984) deduced, by linking the history of industrial chlorine manufacture with OCS profiles in the sediments, that the main source of OCS was from waste (referred to as Taffy Tars in the industry) produced by the chlorination of tars used as binding agents in graphite electrodes, which were used in the production of chlorine from brine feedstocks. These electrodes were used extensively until they were replaced with metal electrodes in the early 1970s. The only major chlorine producer in the Huron-Erie corridor is the Dow Chemical plant in Sarnia (Kaminsky and Hites 1984). The distribution of OCS found in sediments in the present study supports Kaminsky and Hites' deduction that waste from the chlorine production industry could be the primary source of OCS in the Great Lakes.

The checkerboard distribution pattern of OCS in the St. Clair River sediments, downstream from Sarnia, illustrates the effect of sample site location when mapping contaminant distribution patterns. The reasons for such a patchy distribution of OCS in St. Clair River sediments are unknown. However we suggest that hydraulic transport mechanisms and the location of depositional zones in the river are important contributory factors.

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