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# BIOLOGICAL MONITORING OF ORGANOCHLORINE CONTAMINANTS IN THE ST. CLAIR AND DETROIT RIVERS USING INTRODUCED CLAMS, Elliptio complanatus

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ABSTRACT. Introduced clams (in cages) were effective biomonitors in determining the distribution, biological availability, and source areas of a number of chlorinated organic contaminants in the St. Clair River-Detroit River corridor during 1982 and 1983. In the St. Clair River, hexachlorobenzene (HCB), octachlorostyrene (OCS), pentachlorobenzene (OCB), hexachlorobutadiene (HCBD), 2.3,6trichlorotoluene (TCT), and alpha-BHC were most frequently identified in tissues after 3 weeks' exposure. When compared to other locations in the St. Clair and Detroit rivers, significantly (p<0.05) higher levels of QCB, HCB, OCS, and HCBD were found in clams exposed along the Sarnia to Corunna, Ontario, shoreline. Elevated concentrations of HCB and OCS were also detected in water samples from this section of the river. TCT was found in clams from most locations, at low levels, with no obvious source area. Low levels of polychlorinated biphenyls (PCBs) were restricted to clams from the Sarnia area. In the Detroit River, PCBs, HCB, and OCS were most frequently detected in clams. PCB levels were significantly (p < 0.05) higher along the Michigan shore and the highest concentrations were found in the Rouge River area. PCBs were also detected in some water samples from urbanized areas of the river. HCB and OCS were found at near-detection levels in clams from most stations. Contaminant levels in clams from around Fighting Island were low or nondetectable, indicating an absence of biologically available organochlorine contaminants in this area of the river. In the St. Clair River, p,p-DDE was only detected in the Sarnia area, whereas it was found in clams from both sides of the Detroit River, also at low levels. Aldrin, chlordane, and DDT were only sporadically detected in both rivers.

ADDITIONAL INDEX WORDS: Polychlorinated biphenyls, pesticides, chlorinated hydrocarbons, bioindicators, bioassay.

### INTRODUCTION

The St. Clair and Detroit rivers support an extensive sport fishery and a wide variety of water-related activities such as boating, swimming, and waterskiing. These two rivers, as well as their connecting waterbody, Lake St. Clair, provide spawning grounds for numerous fish species (Goodyear et al. 1982), and nesting colonies of piscivorous birds are located in Fighting Island, in the Detroit River (Blokpoel and McKeating 1978). Moreover, the lower Detroit River as well as the extensive "flats" of the lower St. Clair River delta contain important marshland habitat areas for waterfowl (Dennis et al. 1984, Mudroch 1981). These two rivers are also water sources for communities and

industries, including cooling water for electric power generating plants.

Urban centres are found along the length of the St. Clair River, and a major petroleum refining and petrochemical complex is concentrated along the Ontario side in the Sarnia-Corunna area (Fig. 1). Detroit and Windsor are the major population centres along the Detroit River. On the Ontario side, industries include automobile manufacturing, automotive components, chemicals, salt refining, food processing, pharmaceuticals, and distilled products in Windsor, as well as soda ash and distilled products in the Amherstburg area. In Michigan, heavy industry, including automobile manu-

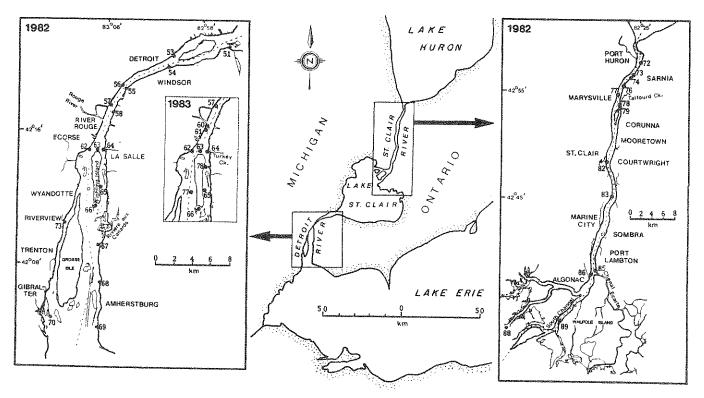


FIG. 1. Clam biomonitoring study areas and stations, 1982 and 1983.

facturing, steel, rubber, pharmaceuticals, and pesticides, are located in the Zug Island (Detroit) area and downstream as far as the rivers' outlet to Lake Erie (Trenton). Although now discontinued, waste caustic soda and soda ash from one of these industries (BASF, located in Wyandotte) were disposed of on Fighting Island until 1981 (Fig. 1).

The St. Clair and Detroit rivers are subject to heavy commercial shipping during the navigation season, since they are connecting channels between Lakes Huron, St. Clair, and Erie. This, in combination with wastes received from the numerous communities and industries, has contributed to a degradation in water quality. Indeed, water quality problems related to municipal and industrial discharges, combined sewer overflows, and pollutants in sediments have led to both rivers being categorized as International Joint Commission Class "A" Areas of Concern. This designation is assigned to those areas exhibiting significant environmental degradation and where impairment of beneficial uses is severe.

In recent years, improvements attributable to control measures have been noted in these waterways, mainly with respect to benthic communities and more conventional pollutants such as nutrients

and phenols, but also in levels of persistent contaminants such as mercury (Thornley 1985, Thornley and Hamdy 1984, International Joint Commission 1983). However, a number of persistent chlorinated organics have also been detected in the ecosystem of these rivers. For example, sediments along the Ontario shoreline of the upper St. Clair River and mainly along the Michigan side of the Detroit River contain levels of polychlorinated biphenyls (PCBs), rendering them unsafe for open water disposal if dredged (Thornley and Hamdy 1984, International Joint Commission 1982, Ontario Ministry of the Environment 1979). Also, concentrations of PCBs above the Canadian guideline have necessitated limited consumption advisories on larger sizes of some sport fish species from the St. Clair River, Lake St. Clair, and the western basin of Lake Erie (Ontario Ministries of the Environment and Natural Resources 1982, 1984-5).

Elevated levels of hexachlorobenzene (HCB) have been found in samples of carp from western Lake St. Clair (Kuehl et al. 1981) and in herring gull eggs (IJC 1978b) and some surficial sediments (Thornley and Hamdy 1984) from the Detroit River. In addition, octachlorostyrene (OCS) has been identified in Lake St. Clair great blue heron

(Reichel et al. 1977) and carp (Kuehl et al. 1981), as well as in walleye (Kuehl et al. 1976) from the Detroit River.

The objective of the present investigation was to better define the distribution of biologically available organochlorine contaminants in the St. Clair and Detroit rivers using biological and water quality monitoring. Furthermore, it was hoped that this information would aid in the identification of sources or source areas necessitating more detailed investigation. The organism chosen was the Unionid clam Elliptio complanatus Dillwyn. This species has been used as an indicator organism in previous Ministry investigations of Ontario lakes and rivers (Curry 1977/78, Suns et al. 1980) and been found to rapidly accumulate (within 2 to 4 days) detectable levels of organochlorine contaminants such as PCBs (Kauss et al. 1981). In these studies, it was introduced (in cages), which permitted a pre-selected exposure period of individuals with a similar physical, chemical, and biological background in a specified area. In general, the clams' identification of organochlorine sources has been consistent with that of native species such as filamentous algae (Cladophora glomerata) and young fish (Notropis hudsonius) despite differences in life habits, exposure periods, physiology, lipid content, and trophic status (for example, see Niagara River Toxics Committee 1984).

#### MATERIALS AND METHODS

#### Station Locations

Station locations were selected largely on the basis of concentration of industry and with a view to allowing cross-channel comparisons of contaminant levels. Previous studies (Hamdy and Kinkead 1979) have shown that, despite the large volumes of water carried by connecting waterways such as the St. Clair River, plumes of shore-based discharges may hug the shore for a considerable distance downstream. Therefore, cages were in most instances anchored in the nearshore (1 to 50 m from shore) and the clams were in relatively shallow depths (1 to 4 m) similar to their natural habitat.

Clams were exposed at 13 stations in the St. Clair River and its delta and 17 stations in the Detroit River for 3 weeks in 1982 (16 August to 9 September). A follow-up study was conducted at 10 stations in the Detroit River during 1983 (17 June-8 July) to supply additional data on the River

Rouge and Fighting Island areas. These stations are shown in Figure 1.

#### Field Methods

E. complanatus specimens of a restricted size class (maximum shell length of 6.5 to 7.2 cm) were collected from a healthy population in Balsam Lake. This well-buffered lake lies in an area of Palaeozoic limestones and is part of the Trent River system (Chapman and Putnam 1966). Concentrations or organochlorine contaminants in these clams are typically at low (near or below detection) levels (Curry 1977/78, Suns et al. 1980, Kauss et al. 1981). A representative subsample of these clams was sacrificed and processed for later analysis (see below). Live clams were transported to the study sites in bags of lake water within about 24 h of collection.

At each monitoring station, five clams were placed in a galvanized steel cage which was then anchored or tethered to a permanent, submerged structure so that the clams were in contact with bottom sediments. At the beginning and end of the 3-week exposure period, subsurface (0.1 m) field measurements were taken of water temperature, conductivity, dissolved oxygen, pH, and current speed (subsurface and bottom) at each station and water samples (unfiltered) were also obtained for later analysis. Water samples for hardness, calcium, magnesium, and suspended solids analysis were collected in 1-L glass bottles. Water for PCBs, OCS, and organochlorine pesticides analysis was collected in solvent-rinsed 1-L amber glass bottles with foil-lined caps and kept refrigerated until analyzed.

After an exposure period of 3 weeks, individual clams were retrieved, shucked, rinsed, and the drained soft tissues wrapped in pre-weighed, hexane-rinsed aluminum foil, frozen on dry ice, and weighed. (Due to the method of field processing, only average and not individual wet weights were obtained for clams from each station in 1982). Tissues were kept frozen (-20°C) until analyzed.

#### **Laboratory Methods**

A brief description of the methods of analysis for water and clam samples is given here. Detailed analytical methods are described in the Ontario Ministry of the Environment "Handbook of Analytical Methods for Environmental Samples" (Ontario Ministry of the Environment 1983).

The soft tissues of three clams from each station were analyzed on a wet weight basis for contaminants. For PCBs, OCS, and organochlorine pesticides, tissues were first digested in concentrated HCl and then extracted with 25% dichloromethane in hexane (v/v). Powdered NaHCO<sub>3</sub> was added to the extract to neutralize the sample. The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and volumetrically diluted to 100 mL with hexane. A suitable aliquot was submitted for cleanup using Florisil 100–200 mesh (dry pack).

Extracts were analyzed by electron capture (Ni<sup>63</sup>)—gas chromatography using the following instruments, columns, and conditions for the compounds indicated (detection limits, in ng/g, in brackets):

- (i) Hewlett Packard 5710 gas chromatograph equipped with a 4 m x 2 mm ID glass packed-column with 3% Dexil 300 on Chromosorb W HP; isothermal at 240°C; 5% methane in argon carrier gas.
  - total PCBs (20);
  - aldrin, p,p-DDE, heptachlor, HCB, and OCS (1);
  - mirex (5).
- (ii) Hewlett Packard 5880 gas chromatograph equipped with simultaneous dual capillary columns, 30 m SE54 and 30 m DB 1701; temperature-programmed from 110 to 250°C at 4°C/min.; helium carrier gas.
  - alpha-, beta-, and gamma-BHC (1);
  - alpha- and gamma-chlordane (2);
  - o,p-DDT, p,p-DDT, and p,p-DDD (5).

Data capture and quantitation were performed using the HP 3353 data system for (i) and the HP 5880 GC intrinsics for (ii).

Extraction of clams for chlorinated aliphatics and aromatics analysis was as described above; however, to prevent evaporative losses, extracts were not taken to dryness during rotary evaporation. Columns are as described above in (ii). Compounds included in this analysis and their detection limits (ng/g, in brackets) were:

- 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene (2):
- 1,2,3,4- and 1,2,4,5-tetrachlorobenzene (0.5);
- hexachloroethane, hexachlorobutadiene, pentachlorobenzene, 2,3,6- and 2,4,5-trichlorotoluene (1).

Lipid content of samples was determined gravimetrically on an aliquot after evaporation of the solvent.

Water samples to be analyzed for PCBs, OCS, and organochlorine pesticides were extracted with dichloromethane, dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated by rotary evaporation. Florisil (PR) 60-100 mesh (wet pack) was used for cleanup, and the samples were taken up in iso-octane after vortex/vacuum evaporation. Conditions for elec-

tron-capture gas chromatographic analysis were as outlined above for clam tissue extracts. Compounds and their detection limits (ng/L, in brackets) were:

- total PCBs (20);
- aldrin, alpha-, beta-, and gamma-BHC, p,p-DDE, heptachlor, HCB, and OCS (1);
- alpha- and gamma-chlordane (2);
- o,p-DDT, p,p-DDT, p,p-DDD, and mirex (5).

Lack of analytical capability at the time precluded analysis for chlorinated aliphatics and aromatics in water samples.

Calcium and magnesium in water samples were analyzed by automated AAS in the presence of LaCl. Hardness of water was determined by a semi-automated titrimetric procedure utilizing EDTA and Erichrome Black T indicator. Suspended solids concentration was determined gravimetrically.

# RESULTS AND DISCUSSION

# Water Quality

Table 1 summarizes physico-chemical data obtained at each biological monitoring station during the 1982 and 1983 studies. Although these physical and chemical measurements were restricted to the beginning and end of the 3-week exposure periods, it is evident from the range of values observed that parameters such as magnesium (6.2-7.6 mg/L in 1982, 6.4-7.6 mg/L in 1983), pH (7.2-8.6 in 1982, 7.2-8.1 in 1983), temperature (19.0-25.0°C in 1982, 16.0 to 22.0°C in 1983), and dissolved oxygen (8.1 to 10.1 mg/L in 1982, 8.5 to 10.5 mg/L in 1983) did not vary greatly either temporally or spatially, and were within applicable Provincial (Ontario Ministry of the Environment 1978) and/or Agreement (International Joint Commission 1978a) objectives for the protection of aquatic life. In contrast, hardness (90-120 mg/L in 1982, 90-157 mg/L in 1983), calcium (25.0-37.0 mg/L in 1982, 24.3-50.4 mg/L in 1983), suspended solids (1.06-25.20 mg/L in 1982, 4.02-25.70 mg/L in 1983), conductivity (230-400 us/cm in 1982, 220-520 us/cm in 1983) and bottom current speed (0.00-0.19 m/sec in 1982, 0.05-0.33 m/sec in 1983) exhibited somewhat greater temporal and spatial variability and are more reflective of the dynamic nature of the nearshore environment with its associated inputs. Concentrations or rates of some of these parameters (e.g., calcium, magnesium, hardness, sus-

TABLE 1. Physico-chemical characteristics of St. Clair River and Detroit River waters.

Station	Vane	Calcium mg/L	Magnesium mg/L	Hardness mg/L	Suspended Solids mg/L	Conductivity us/cm @ 25°C	рН	Temperature °C	Oxygen mg/L	Current Speed m/sec
		. IIIg/L	mg/ L	mg/ L	mg/ L	457 CHI (@ 25 C	Pri		***D'	
St. Clair				0.1.00.1	1.04/1.10	260/220	77/73	10.0/10.0	0.2/0.2	0.05/0.04
72	82	26.5/27.0	6.8/6.4	94/94	1.96/4.19	260/230	7.7/7.2	19.0/19.0 20.0/19.0	9.3/9.2 9.2/9.3	0.05/0.04
73	82	27.0/27.5	7.0/6.4	95/96	3.00/5.48	260/250	7.8/7.3		9.4/9.3 8.6/8.8	0.00/-
74	82	28.0/29.0	7.0/6.4	98/99	2.26/2.27	320/390	7.0/7.6	21.0/21.0	9.0/9.1	0.15/-
76	82	26.5/28.5	7.0/6.2	95/96	2.41/2.99	400/340	7.7/6.8	20.5/20.0	9.0/9.1	0.137-
77	82	26.5/27.5	7.0/6.2	95/94	5.47/8.96	270/250	7.7/8.1	20.0/19.0	9.2/9.4 9.0/9.2	0.05/-
78	82	25.5/27.5	6.8/6.4	92/94	4.95/9.01	320/270	8.2/6.9	25.0/23.0		0.13/-
79	82	26.5/27.5	7.0/6.2	95/94	6.78/5.85	310/280	8.1/7.3	23.0/21.0	8.7/9.0	0.07/~
82	82	26.5/27.5	7.0/6.6	95/96	4.71/6.74	330/240	8.1/8.3	20.0/18.5	9.1/9.5	
83	82	26.5/27.0	7.0/6.6	94/94	7.77/6.36	270/240	8.0/8.2	22.5/20.5	9.0/9.2	0.05/-
85	82	25.5/26.5	6.8/6.4	92/92	4.94/1.06	270/240	8.5/8.4	22.0/22.0	10.1/9.3	0.05/-
86	82	26.5/27.0	7.0/6.4	94/94	6.94/4.14	260/230	8.2/8.1	20.5/20.0	8.8/9.1	0.05/-
88	82	26.5/26.5	7.0/6.2	96/92	4.10/7.50	260/230	7.8/8.4	20.0/21.0	8.9/8.9	0.05/-
89	82	25.0/26.0	6.8/6.2	91/90	7.02/4.43	270/230	8.3/8.6	21.5/21.0	10.0/9.6	0.19/-
Detroit	River									
51	82	-/28.0	-/6.8	-/97	10.20/7.61	300/250	8.5/8.4	21.5/21.0	8.9/9.2	0.05/-
53	82	26.0/27.5	7.4/6.4	95/95	7.80/9.77	270/250	8.2/8.4	22.0/21.5	8.8/8.9	0.14/-
54	82	27.0/27.5	7.4/6.4	98/96	18.50/22.30	280/270	8.4/8.4	21.0/21.5	9.0/8.8	0.00/-
55	82	27.5/28.5	7.6/6.6	99/97	3.22/14.80	280/250	8.2/8.4	21.0/21.0	8.9/8.7	0.02/-
56	82	26.5/28.5	7.2/6.6	95/98	8.51/12.20	280/250	8.2/8.3	22.0/20.5	8.6/9.5	0.15/-
57	82	26.5/27.5	7.4/6.4	97/95	16.80/13.90	290/250	8.1/8.4	22.0/20.5	8.8/9.1	0.08/-
	83	24.3/25.4	6.4/6.5	87/90	4.02/ 9.19	220/240	8.0/8.1	19.0/20.6	9.4/8.5	0.05/0.23
58	82	28.0/28.5	7.6/6.6	102/98	18.30/17.10	310/260	8.2/8.1	22.0/21.5	8.8/8.8	0.04/-
60	83	26.3/25.8	6.9/6.7	94/92	9.29/11.60	240/250	8.0/7.7	19.5/21.0	9.3/8.6	0.31/0.33
61	83		********				-/7.7	-/21.0	-/8.8	0.20/-
62	82	29.5/28.0	7.4/6.6	104/97	15.50/12.00	310/250	8.2/8.3	22.5/21.5	8.0/8.1	0.06/-
	83	26.9/27.6	7.6/6.8	98/97	25.70/10.80	260/300	7.9/7.8	18.0/20.9	9.5/8.5	0.15/0.12
63	82	26.5/27.5	6.4/6.6	93/96	10.00/9.83	280/240	8.4/8.5	22.0/21.0	8.8/9.0	0.14/-
	83	25.8/24.7	7.0/6.6	93/89	7.08/9.86	230/240	8.1/7.4	16.0/20.2	10.0/9.2	0.25/0.27
64	82	28.0/27.5	6.8/6.6	98/96	12.10/7.86	360/290	8.4/8.4	22.0/21.0	9.0/9.1	0.02/-
	83	25.8/26.9	7.0/6.7	93/95	9.92/17.30	420/320	8.0/7.2	18.0/21.0	9.5/9.0	0.15/-
65	82	30.0/29.0	7.2/6.6	104/99	14.60/6.65	300/250	8.4/8.5	22.0/21.0	8.6/	0.02/-
	83	28.2/28.4	6.9/6.8	99/99	8.09/8.03	250/280	8.0/7.6	16.0/21.0	10.1/9.0	0.09/0.16
66	82	31.5/30.0	7.0/6.6	107/102	10.40/8.87	320/270	8.4/8.5	21.5/21.0	8.8/8.5	0.04/-
	83	32.4/33.4	7.0/7.0	110/112	16.90/13.50	300/300	7.9/8.0	17.5/21.0	9.6/10.1	0.15/0.16
67	82	27.5/27.5	6.8/6.6	97/96	10.90/9.16	310/280	8.1/8.3	22.5/22.0	9.0/9.0	0.06/-
68	82	33.5/36.0	7.2/6.8	114/117	25.20/19.50	400/390	8.3/8.5	21.0/21.5	8.5/8.5	0.09/-
69	82	29.5/37.0	6.8/6.6	101/120	22.00/14.80	330/270	8.1/8.1	22.0/22.0	8.8/8.7	0.05/-
70	82	29.5/28.5	7.0/6.6	102/97	22.80/13.40	300/380	8.2/8.5	22.0/21.5	8.3/8.2	0.06/-
73	82	27.5/28.0	6.4/6.6	95/97	11.20/7.04	320/270	8.2/7.9	21.0/21.0	8.6/8.7	0.04/-
77	83	50.4/25.5	7.5/6.4	157/90	11.80/9.24	240/520	7.7/8.1	18.0/20.0	9.5/9.2	0.15/0.23
78	83	26.2/25.4	6.5/6.6	92/90	20.00/15.30	230/240	7.6/7.6	18.0/22.0	9.6/10.5	0.09/0.06
Balsam	Lake									
01	82				< 0.64/-	180/-	8.1/-	22.0/-	8.8/-	0.00/-
~-	83	15.7/25.5	2.1/6.5	48/90	< 0.47/9.20	120/-	8.2/-	25.0/-	11.2/-	0.00/-

Notes: 1) Station numbers correspond to locations on Figure 1.

pended solids, and current speed) were generally somewhat higher in St. Clair River and Detroit Rivers waters than in Balsam Lake (Table 1).

The effect of inputs on local water quality is further demonstrated by the data on the six organochlorines detected in surface samples (Table 2). For example, elevated (up to 33 ng/L) concentrations of HCB at and downstream of station 74 indicate inputs in the Sarnia area of the St. Clair

River. Furthermore, these detections were restricted to the Ontario side of the river as far as the outlet to Lake St. Clair. A similar trend was evident for OCS although levels (1 to 2 ng/L) were barely above the detection limit. This spatial trend is similar to the findings of a dispersion study carried out on the river, which entailed the development of a numerical model as well as field monitoring for verification (McCorquodale et al. 1983,

<sup>2)</sup> Sample dates: 16 August/9 September 1982; 17 June/8 July 1983.

<sup>3) &</sup>quot;-" indicates no sample or no analytical result.

TABLE 2. Organochlorine concentrations (ng/L) in St. Clair River and Detroit River waters.

Station	Year	PCBs	α-BHC	$\beta$ -BHC	γ-ВНС	HCB	OCS
St. Clair							
72	82	ND	4/5	ND	ND/I	ND	ND
73	82	ND	6/5	ND	ND/1	ND	ND
74	82	ND	5/5	15/ND	ND/1	2/1	1/2
76	82	ND	5/4	ND	ND	6/2	1/1
77	82	ND	5/2	ND	ND	ND	ND
78	82	ND	7/4	ND	ND/7	33/5	1/1
79	82	ND	6/3	ND	ND/3	12/3	2/NE
82	82	ND	6/2	ND	ND	ND	ND
83	82	ND	4/3	ND	ND	ND	ND
85	82	ND	4/ND	ND	ND	ND/11	ND/2
86	82	ND	4/5	ND	4/ND	ND	ND
88	82	ND	6/5	ND	ND/1	ND	ND
89	82	ND	5/5	ND	ND	1/ND	ND
				J. 1.300-	112	1/142	141,5
Detroit R							
51	82	ND	3/5	ND	ND/1	ND	ND
53	82	60/40 (60/54)	ND/5	ND	ND/1	ND	ND
54	82	ND/65 (60)	4/6	ND	ND/3	ND/2	ND
55	82	ND/40 (60)	3/1	ND/2	ND	1/ND	ND
56	82	ND	6/5	ND	ND/2	ND	ND
57	82	45/ND (54)	7/5	ND	ND	ND	ND
	83	ND/-	ND/4	ND	ND	ND	ND
58	82	ND	7/6	ND	ND/1	ND	ND
60	83	ND/-	ND/3	ND	ND	ND	ND
61	83	···	annual .			-	
62	82	55/40 (54)	8/5	7/ND	6/2	1/1	ND
	83	ND/-	3/3	ND	ND	ND	ND
63	82	ND	6/7	5/ND	ND/4	ND	ND
	83	ND	4/4	ND	ND	ND	ND
64	82	ND	6/5	ND	ND	ND	ND
	83	ND	3/4	ND	ND	ND	ND
65	82	ND	5/6	ND	ND/I	ND	ND
	83	ND	3/4	ND	ND	ND	ND
66	82	ND	ND/5	ND	ND	ND	ND
	83	ND	3/4	ND	ND	ND	ND
67	82	ND	6/5	ND	ND	ND	ND
68	82	ND	5/5	ND	ND/4	ND	ND
69	82	ND	6/3	ND	ND/4	ND	ND
70	82	20/ND (54)	7/5	ND ND	ND/2	I/ND	ND
73	82	220/ND (60)	7/4	ND	ND/3	1/ND	ND
77	83	ND	4/2	ND	ND	ND	ND
78	83	-/ND	-/3	-/ND	-/ND	-/ND	-/ND
					, 1 112	7112	, 1 4 11.
Balsam L							
01	82	ND/-	5/-	ND/-	ND/-	ND/-	ND/-
	83	ND/-	2/3	ND	ND	ND	ND

Notes: 1. Station numbers correspond to locations on Figure 1.

<sup>2.</sup> Sample dates: 16 August/9 Sept. 1982; 17 June/8 July 1983.

<sup>3. &</sup>quot;-" indicates no sample or no analytical result; ND = not detected at applicable detection limit (unless otherwise indicated, a single "ND" indicates lack of detection in both samples).

<sup>4.</sup> For PCBs: numbers in brackets refer to Aroclor type in samples, e.g., (60/54) = resembled Aroclors 1260 and 1254 on first and second sample dates, respectively.

Hamdy and Kinkead 1979). This study indicated that plumes from the multiple sources in the Sarnia area were mainly confined to a narrow band along the Ontario shoreline of the river. While no provincial or Agreement objective is available for OCS at present, maximum concentrations of HCB found at stations 78 (33 ng/L), 79 (12 ng/L), and 85 (11 ng/L) were above a proposed objective level of 6.5 ng/L for the protection of aquatic life (Ontario Ministry of the Environment unpublished report).

In the Detroit River, OCS was not detected (ND) and HCB was only found at low levels in water samples from five stations (range: ND-2 ng/L). In contrast, inputs of PCBs were indicated at or upstream of stations 53 and 57 (ND-60 ng/L) at Detroit, station 62 (40-55 ng/L) at Ecorse, stations 73 and 70 (ND-220 ng/L) in the Trenton Channel and stations 54 and 55 in the Windsor area (ND-65 ng/L). The above (detected) values exceeded the Provincial objective (Ontario Ministry of the Environment 1978) for the protection of aquatic life (1 ng/L).

Of the three hexachlorocyclohexanes (BHCs), the alpha isomer was detected most frequently, with a similar range of concentrations detected in both rivers as well as in Balsam Lake (1 to 7 ng/L). This indicates that this organochlorine is relatively ubiquitous. Other organochlorine pesticides were not detected in water samples.

#### Organochlorine Contaminants in Clams

The following discussion of results is based on contaminant concentrations on a wet weight basis. Mean water content of the clams, as determined by drying to a constant weight at 100°C, was 84%; therefore, conversion of concentrations to a dry weight basis can be made using a multiplication factor of 6.25. Also, the fresh weight concentrations can be converted to a lipid basis by dividing by the lipid contents expressed as a decimal fraction (overall mean: 1.0%).

The influence of water quality variation or of tissue contaminant burdens on the biochemical or physiological condition and behavior of *E. complanatus* at the different stations was not the primary objective of this work, and more specific tests would be necessary to address these aspects (see, for example, Bayne 1976). However, the clams do not appear to have encountered acutely toxic conditions since no mortality occurred during the 1982 or 1983 studies. Furthermore, the expo-

sure period in cages did not have an adverse impact on the clams' average wet weight, as shown by a comparison of the values prior to exposure in 1982 (7.2 g) and 1983 (6.8 g) and weights 3 weeks later (7.0 to 9.5 g and 6.9 to 8.2 g, respectively). With one exception (station 88 in the St. Clair River), lipid contents (range of means: 0.4 to 1.4%) also did not vary significantly between stations or as a function of exposure. Therefore, normalization of contaminants data to a standard weight or lipid content was not felt necessary.

Mean concentrations of contaminants in clam tissues were calculated using all available data. In cases where ≤2 of 3 replicates had no detectable levels, these "ND" values were assigned a value of one half the detection limit for calculations of mean and standard deviation. Means calculated in this manner are flagged by an asterisk in Table 3.

Of the 25 organochlorine contaminants looked for, 14 were detected in clam tissues from one or more stations (see Table 3). Their presence represents accumulation over the 3-week exposure period, since (with the exception of 2 ng/g p,p-DDE in 1983) no detectable levels of these contaminants were found in a representative subsample of clams shucked and frozen immediately after their removal from the Balsam Lake collection site in 1982 or 1983 (station 01 in Table 3). These "pre-exposure" residue data for Balsam Lake clams correlate with the absence of measurable quantities of most organochlorines in Balsam Lake water samples (Table 2, Ontario Ministry of the Environment unpublished data).

The following discussion of results focuses mainly on hexachlorobenzene (HCB), octachlorostyrene (OCS), pentachlorobenzene (QCB), hexachlorobutadiene (HCBD), 2,3,6-trichlorotoluene (TCT), and polychlorinated biphenyls (PCBs), since they were either most frequently detected or their distribution and levels in clam tissues were markedly different between the St. Clair and Detroit rivers.

For each of these contaminants and each year, only data from those stations having detectable concentrations in clams were used in a one-way ANOVA. The data were transformed prior to the analysis to equalize variances (Box and Cox 1964). If the F-test was significant (p<0.05), a Student-Newman-Keuls Test (Sokal and Rohlf 1969) was used to determine groups of stations with similar contaminant levels. Overlapping groups detected by the SNK test were combined. The results are shown in Figures 2-5.

TABLE 3. Organochlorine concentrations (ng/g, wet weight) in clams exposed to St. Clair River and Detroit River waters.

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Station Year	ar PCBs	Aldrin	α-BHC	α-Chlordane	y-Chlordane	DDT.	דממיה מ	חחקים מ	DDF	H/B	daon	300	Ę	2,3,6-	9/6	Wet
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	~ 1 }-1	2	Z	Q N	Tr.	2	Ţ.	S	*3+1	Tr.	S	1+0			12402	
		2	2	*2±2	Tr.	2	Ţ.	2	4	1	ŀ	É			44.00	ς c - τ
7.0		ä	*4±3	S	*2+2	2	S	S	1	24.43	83 ± 13	\$5 × 10			7.0H+.1	1
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	QN ?	Н	<u>-</u>	S	S		2 2	3	e e	: 5	: E	2			1.0 ± 0.3	9.5
79 82		<u>-</u>	1+0	9 5	3 5	ב ב	2 5	<u> </u>	2 !	2	4 4 4	$21 \pm 2$			$0.8 \pm 0.3$	7.3
		Ž	) -  <sub>[</sub> -]	į	3 5	2 !	2 !	2	2	Ï.	6	22±6			$0.6\pm 0.1$	7.3
		2 5	11.	2 ;	2	2	S	2	2	2	2	+			$0.7 \pm 0.3$	7.3
		2	o ∓-	2	2	2	2	2	2	S	Ž	- + +			0 0 7 0 0	. 0
20 00		2	0 ∓ 0	S	S	S	Ê	Ş	Ę	* T 7*	2 + 0	20.46			0 H 0 A	5.0
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		į	9 9	9 1	3	2	Š			Ir.					1.2 + 0.2	7.4
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3 6																

Station numbers correspond to locations on Figure 1. Contaminant concentrations in clams from station 0! (Balsam Lake) represent stating (background) levels for 3-week exposure.
 Replicate(s) with no detectable concentration assigned value of half the detection limit.
 ND - not detected in any replicates at applicable detection limit.
 T - trace; mean calculated concentration less than detection limit.
 "" - no sample or no analytical result.
 Por PCBs: numbers in brackets refer to Atoclor type, e.g., (54.66) = resembled mixture of Arochor; 1254 and 1260.

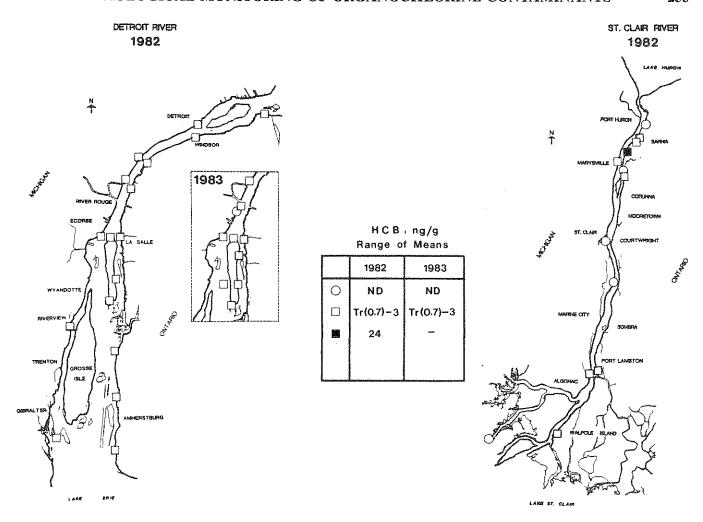


FIG. 2. Distribution of Hexachlorobenzene in clams exposed in the St. Clair River (1982) and the Detroit River (1982 and 1983). Symbols delineate groups of stations derived as described in text (ND = not detected; TR = trace).

#### a) Hexachlorobenzene (HCB)

HCB was detected in clams from 60% of the stations in the St. Clair River (Table 3). At many of these stations, mean levels were relatively low. ranging from trace (<1 ng/g) to 4 ng/g. However, the mean concentration in clams from station 76 (24 ng/g) was significantly (p<0.05) higher than at all other locations, indicating a source in the Sarnia area (Fig. 2). Based on previous studies (Hamdy and Kinkead 1979), contaminant levels in clams at this station reflect the combined effect of a number of upstream (Sarnia) discharges. While HCB in water samples also indicated inputs in the Sarnia area, the highest concentrations were found at stations 78 and 79, downstream of Talfourd Creek and station 76. This difference may be partially attributable to the fact that water samples were obtained just below the surface, while clams were

situated on the bottom. Since the discharge plume of Talfourd Creek is often thermally buoyant, any additional inputs from this stream may have been missed by the biomonitor. This interpretation is supported by the somewhat higher temperatures recorded at stations 78 and 79 (Table 1).

HCB was detected at the majority ( $\geq 90\%$ ) of the stations monitored in the Detroit River during 1982 and 1983. These low mean levels (trace to 3 ng/g) did not differ significantly ( $p \geq 0.05$ ) from those found at stations 85, 86, and 89 situated at the outlet of the St. Clair River. HCB concentrations were also near the detection limit (1 ng/g) in young-of-the-year spottail shiners collected from the river in 1982 and 1983 (Suns et al. 1985). These results indicate the absence of discrete sources in the Detroit River. Although analysis of surficial sediments collected in 1980 (Thornley and Hamdy

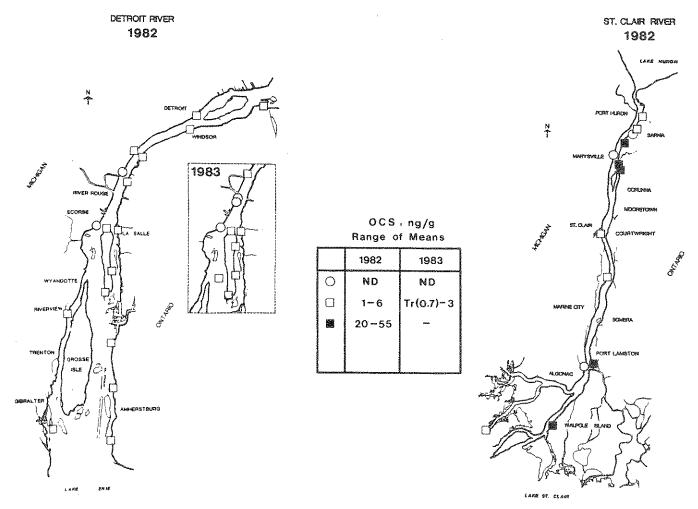


FIG. 3. Distribution of Octachlorostyrene in clams exposed in the St. Clair River (1982) and the Detroit River (1982 and 1983). Symbols delineate groups of stations derived as described in text (ND = not detected; TR = trace).

1984) found elevated levels of HCB at locations close to our stations 58 and 62, these were not reflected by clam or spottail shiner tissue levels, suggesting that the sediment-associated HCB was not biologically available to these organisms.

# b) Octachlorostyrene (OCS)

Although occurrence of OCS was restricted to the Ontario side of the St. Clair River, it was somewhat more frequently detected in clams (77% of locations) than was HCB (Table 3). As with HCB, the mean concentration of OCS (55 ng/g) was highest at station 76. This, as well as detectable levels (1-6 ng/g) at stations 72 and 73, indicates upstream source(s) along the Sarnia waterfront and possibly in Lake Huron as well. OCS was found in fish collected in Saginaw Bay, on Lake

Huron, in 1980 (Kuehl et al. 1981) and in the early 1970s (Kuehl et al. 1976). Although concentrations in clams located below Talfourd Creek at stations 78 and 79 (21–22 ng/g) were lower than at station 76, this difference was not significant ( $p \ge 0.05$ ) (Fig. 3). No further decreases were observed with increasing distance: concentrations in clams from Port Lambton near the mouth of Chenal Ecarte (29 ng/g) and the South Channel (20 ng/g) were not significantly lower than those some 30 km upstream at Talfourd Creek.

OCS was detected in clams from most ( $\geq 70\%$ ) stations in the Detroit River in 1982 and 1983, but at significantly lower (p<0.05) concentrations (trace-4 ng/g) than at the South Channel outlet of the St. Clair River. This indicates an absence of additional inputs of this contaminant in the Detroit River.

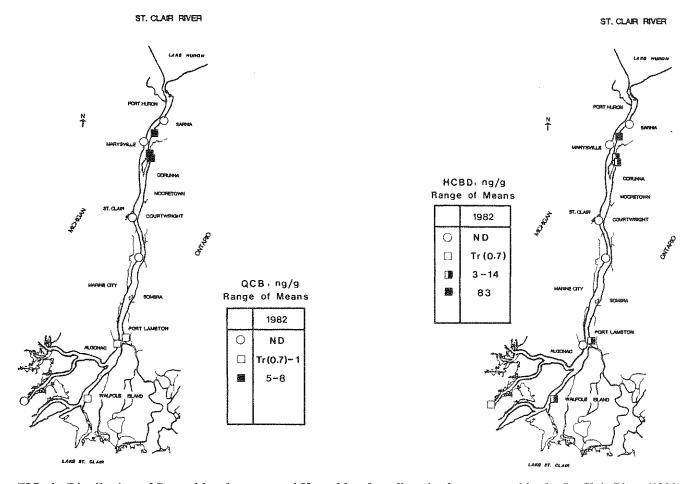


FIG. 4. Distribution of Pentachlorobenzene and Hexachlorobutadiene in clams exposed in the St. Clair River (1982). Symbols delineate groups of stations derived as described in text (ND = not detected; TR = trace).

# c) Pentachlorobenzene (QCB) and Hexachlorobutadiene (HCBD)

The distribution of QCB and HCBD was essentially restricted to the St. Clair River, with levels above detection being found at about 55% of the stations in 1982 (Table 3). The highest mean concentration of HCBD (83 ng/g) was considerably greater than that of QCB (8 ng/g). Although data were not available for all stations, the significantly (p<0.05) higher concentrations of these contaminants at stations 76, 78, and 79 indicated upstream sources in the Sarnia area (Fig. 4). Previous work (Bonner and Meresz 1981) also detected HCBD in industrial effluents and sediments in this portion of the river.

# d) 2,3,6-Trichlorotoluene (TCT)

This chlorinated aromatic was also mainly restricted to the St. Clair River (Table 3). However,

unlike HCB, OCS, QCB, and HCBD, TCT was found downstream of both Port Huron and Sarnia, with mean levels near the detection limit (trace-3 ng/g), and with no obvious cross-channel gradient. This suggests low-level inputs on both sides of the river.

With the exception of OCS, the above compounds have commercial as well as industrial applications (Hawley 1981, Kirk et al. 1980, Ware and West 1977). However, the presence of HCB, OCS, QCB, and HCBD at detectable levels in the St. Clair River is probably related to industrial processes. OCS and HCB are by-products of the electrolytic production of chlorine (Kaminsky and Hites 1984, United States Environmental Protection Agency 1980a). Kaminsky and Hites correlated the geographic occurrence of OCS in sediments and fish in the Great Lakes to a number of nearby chlorine producers. These included the Sarnia, Ontario, Dow Chemical Plant and the Wyan-

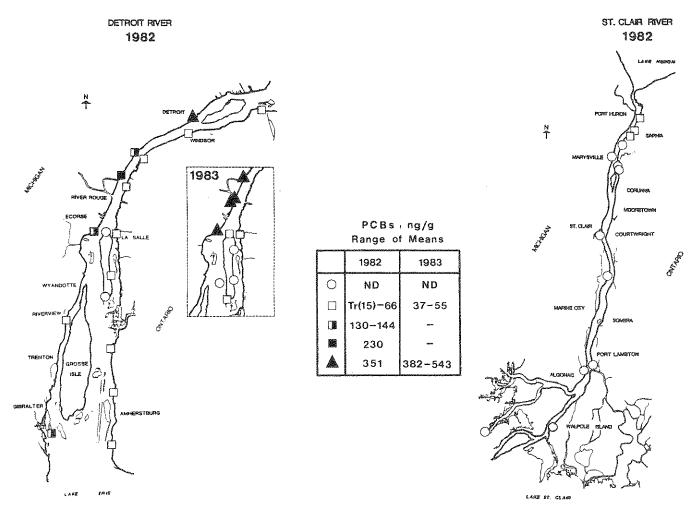


FIG. 5. Distribution of Polychlorinated Biphenyls in clams exposed in the St. Clair River (1982) and the Detroit River (1982 and 1983). Symbols delineate groups of stations derived as described in text (ND = not detected; TR = trace).

dotte, Michigan, Pennwalt Corporation facility. HCB and HCBD are also by-products generated during the manufacture of a number of chlorinated hydrocarbon solvents (Mumma and Lawless 1975, United States Environmental Protection Agency 1980b) and QCB is co-produced during the formation of HCB (Ware and West 1977).

# e) Polychlorinated Biphenyls (PCBs)

PCBs were only detected in clams from three locations (stations 72, 73, and 74) in the St. Clair River, all within a 3.5 km section of the Sarnia waterfront (Table 3 and Fig. 5). Bottom sediments sampled here in 1977 and 1978 revealed that the highest concentrations of PCBs generally coincided with point-source (industrial) discharges and extended from Polysar to Suncor. Concentrations in this sec-

tion of the nearshore averaged over 3 ppm, with a maximum of 10 ppm, and sediments also contained high levels of oils and greases. Sport fish collected from the St. Clair River and Lake St. Clair also contained elevated levels of PCBs (Ontario Ministry of the Environment 1979). However, mean concentrations in clams exposed on the bottom in 1982 were relatively low, ranging from just above detection (26 ng/g) upstream of Imperial Oil to 44 ng/g below Polysar. This suggests either small, localized inputs or only limited bioavailability of PCBs from the historically contaminated sediments. The availability of organochlorine contaminants (such as PCBs) from sediments, to water or benthic organisms is affected by factors such as waves, currents, bioturbation, sediment particle size, and organic matter content (Lynch and Johnson 1980) as well as the organism's life habit (Fox et al. 1983). With respect to organic matter, Meier and Rediske (1984) have shown that while oily sediments will accumulate high levels of nonpolar contaminants such as PCBs, those contaminants will be less available to benthic organisms such as midges.

In contrast to the St. Clair River, detectable concentrations of PCBs were found in clams from the majority ( $\geq$  70%) of stations in the Detroit River and mean concentrations were generally higher. Concentrations at some locations along the Ontario shoreline (up to 66 ng/g) were higher than at the St. Clair River outlet (ND) or at station 51 (20 ng/g) near the inlet to the Detroit River, indicating sources or bioavailability along the Windsor to Amherstburg shoreline. However, in both 1982 and 1983, the highest concentrations were found in clams exposed along the Michigan shoreline. The significantly (p<0.05) higher levels in clams from the Detroit, River Rouge, Ecorse, and Trenton areas (130-543 ng/g) indicate sources of biologically available material. This cross-river gradient in PCBs is particularly evident if one compares levels in clams from Ecorse to LaSalle (135-ND-66 ng/g in 1982, 382-55-37 ng/g in 1983) and from Gibralter to Amherstburg (130-46 ng/g in 1982). These results correlate with the findings of Walters et al. (1972), which indicated that the outflow of the Detroit River to the western basin of Lake Erie was composed of three main water masses: two contaminated edge flows separated by a cleaner mid-channel flow. The two edge flows each comprise about 25% of the total river flow (International Joint Commission 1978b). Similar PCB gradients (inlet vs. outlet as well as cross-channel) have been observed for 1980 samples of surficial sediments (Thornley and Hamdy 1984) and in 1982 and 1983 collections of spottail shiners (Suns et al. 1985).

Concentrations of PCBs in clams from stations 57, 62, and 63 were about two to three times higher in 1983 than in 1982, suggesting an increase in inputs along the River Rouge-Ecorse waterfront. However, this may be related to other variables such as river flow, storm events, or rainfall, making it difficult to infer any trend without further (long-term) monitoring data.

Although the above discussion of station-tostation differences is based on *total* PCB concentrations, the predominant mixtures present in water samples and clam tissues usually resembled Aroclors 1254 or 1260, or mixtures of the two (see Tables 2 and 3).

# f) Organochlorine Pesticides

Organochlorine pesticides, including aldrin, chlordane, and DDT, were for the most part only detected in clams at a few urbanized locations and then at levels at or near the respective analytical detection limits (Table 3).

The DDT metabolite, p,p-DDE, was only detected in the Sarnia area of the St. Clair River (1-4 ng/g), whereas it was found on both sides of the Detroit River in the Windsor (<1-1 ng/g), LaSalle (1-3 ng/g) and the Detroit to Ecorse (1-12 ng/g) areas as well as the lower river (<1-4 ng/g). While no similar trends were observed in water samples, the detections in tissues suggest relatively localized availability or input.

Although alpha-BHC was detected in water at relatively uniform levels at all stations (Table 2) it was only found at concentrations near the detection limit (<1-4 ng/g) in clams from the St. Clair River, downstream of Port Huron and Sarnia. This distribution was similar to that of TCT.

Although water quality data were not available for chlorinated aliphatic and aromatic compounds, the data for E. complanatus show it to be an effective accumulator and indicator of the presence of a range of higher molecular weight organochlorine contaminants including PCBs, HCB, OCS, HCBD, QCB, TCT, and some of the pesticides such as chlordane and the DDT metabolite, p,p-DDE. BHCs, however, were not accumulated as well, which correlates with their low bioconcentration potential in other bivalves (Ernst 1977). The degree of bioaccumulation by an organism is determined by a variety of factors, biological as well as physical and chemical. An example of the latter may be the generally higher concentration and more frequent detection of OCS than of HCB in clam tissues, which was the opposite of the trend observed for water samples (cf. Tables 2 and 3). This could be due to the lower water solubility and greater n-octanol/water partition coefficient and bioconcentration factor of OCS relative to HCB (Veith et al. 1979).

Comparison of tissue and water data also reveals that much more frequent sampling as well as lower detection limits for some contaminants (e.g., PCBs) would be necessary to address the high temporal variability in concentrations and to generate the spatial resolution afforded by the biological monitor. This reults from the fact that, due to their relatively continuous exposure and tendency to accumulate lipophilic contaminants in their tisporal variability in concentrations and to generate

the spatial resolution afforded by the biological monitor. This reults from the fact that, due to their relatively continuous exposure and tendency to accumulate lipophilic contaminants in their tissues, biota will reflect even sporadic inputs or peaks which may be missed by routine water sampling.

Unionid clams, because of their relatively sedentary habit, filter feeding activity, and low position in the food chain, provide an important indication of biologically available contaminants in a relatively restricted area. Therefore, the presence of the more frequently detected chlorinated organics in the introduced (caged) clams after 3 weeks' exposure is important, since these compounds have relatively high bioconcentration factors in other biota, including fish (Oliver and Niimi 1983, Veith et al. 1979, Goldbach et al. 1976). Clams are also potentially important in the flux of energy and contaminants between the pelagic and benthic environments, since their food consists of plankton and organic detritus (Pennak 1978), and in some areas they may comprise the major portion of the benthic biomass (Negus 1966). Finally, since resident unionids are infaunal to semi-infaunal, high densities can alter physical and chemical properties of sediments (and the availability of contaminants in them) by their burrowing, feeding, and respiratory activities (McCall et al. 1979).

#### SUMMARY AND CONCLUSIONS

Results of 1982 and 1983 monitoring studies utilizing caged clams and concurrent water sampling indicated the presence of biologically available sources or active inputs of a number of chlorinated organics in the nearshore environment of the St. Clair and Detroit rivers.

As indicated by significantly higher concentrations in clams and by detections of some of the same contaminants in water samples, there were industrially-related sources of HCB, OCS, QCB, and HCBD along the Sarnia, Ontario, section of the St. Clair River in 1982. The impact of these sources appeared to be mainly restricted to the eastern (Ontario) shoreline, extending downstream into the delta. Consequently, the bulk of these contaminants seems to be entering Lake St. Clair via the South Channel and Chenal Ecarte, which carry 42% and 5%, respectively, of the river's flow (U.S. Army Corps of Engineers, Detroit Office, personal communication).

In contrast to the St. Clair River, QCB, HCBD, and TCT were essentially absent from clams

exposed in the Detroit River. Furthermore, while HCB and OCS were generally ubiquitous in clams, concentrations were at or near the analytical detection limits, suggesting an absence of specific source areas in the Detroit River and the possible influence of upstream (St. Clair River) sources during 1982 and 1983.

At present, there is insufficient information to determine the magnitude of loadings of these organochlorines to downstream waters by the St. Clair River. However, relative to other Great Lakes such as Lakes Huron and Erie, concentrations of QCB and HCB were highest in water, sediments, and fish from Lake Ontario (Oliver and Nicol 1982), suggesting that the relative magnitude of sources in the Niagara River is greater than those in the St. Clair River. Indeed, levels of these and other chlorinated aromatics were generally higher in E. complanatus exposed in selected source areas of the Niagara River in 1983 (Ontario Ministry of the Environment unpublished data) than in the St. Clair River in 1982.

Although PCBs were detected in clams exposed along the Sarnia, Ontario, section of the St. Clair River, the low tissue concentrations indicated relatively small inputs or limited bioavailability from historically contaminated sediments in this area. The absence of detectable levels in clams from downriver locations indicates that there was little or no transport of this material to Lake St. Clair, or if there was, it was not in a biologically available form. This reflects the cessation of discharges of PCBs in the Sarnia area during 1975 (Ontario Ministry of the Environment 1979) and the restriction of their use mainly to closed-system electrical and heat transfer operations in Ontario (Health and Welfare Canada 1980).

Sources of PCBs were evident along the Michigan shoreline of the Detroit River, with the major inputs originating in the Detroit and River Rouge areas. Although detections of PCBs in clams from the Windsor and Amherstburg areas also indicate the presence of Ontario sources, these appear to be relatively small compared to those along the Michigan shoreline, since tissue levels along the latter were up to 16-fold higher. These results coincide with previous findings that the Detroit River is a primary source of PCBs to the western basin of Lake Erie, with sources along the western shoreline being most important (Suns et al. 1985, Ontario Ministry of the Environment 1981, Frank et al. 1977).

Additional studies to further delineate the sources of the above contaminants, their magni-

tude, and impact were initiated in 1984. These included biological monitoring, ambient river and tributary water monitoring, and sampling of selected Ontario dischargers.

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