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TRACE ORGANIC CONTAMINANTS IN THE DETROIT RIVER

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NWRI CONTRIBUTION No. 85-31

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EXECUTIVE SUMMARY

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Journal: To be submitted to Journal of Great Lakes Research (special issue on Detroit River)

Date: 7 Jan. 1985

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The results indicate continuing inputs of all contaminant groups to the river from a variety of sources, particularly from sewage treatment plant effluents and several tributaries. The contaminant distributions and intercorrelations also indicate that major sources of PCB's, PNA's, OC's and CB's are concentrated on the westerly river shore, while CP's enter the river mainly from the easterly shore.

Trace Organic Contaminants in The Detroit River

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Running Head: Organic Contaminants in the Detroit River

ABSTRACT. Concentrations of polychlorinated biphenyls (FCB's). polynuclear aromatic hydrocarbons (PNA's), chlorobenzenes (CB's), chlorophenols (CP's), and a number of other organochlorine compounds (OC's) have been determined in the surface microlayer, subsurface water, suspended solids, sediments, and in sediment pore water at 20 sampling stations in the Detroit River. data are discussed in terms of contaminant sources, pathways sinks. Spatial trends along and across the river relationships of contaminant groups within and between compartments are investigated.

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ADDITIONAL INDEX WORDS: Lake St. Clair, Lake Erie, chlordane, dieldrin, endosulfan, heptachlor, heptachlor epoxide, hexachlorobutadiene, lindane, octachlorostyrene, contaminant partitioning.

RÉSUMÉ. Des concentrations de biphényles polychlorés (PCB), d'hydrocarbures aromatiques polynucléaires (PNA), de chlorobenzènes (CB), de chlorophénols (CP) et d'un certain nombre d'autres composés organochlorés (COC) ont été décelées dans la micropellicule de surface, dans l'eau, dans les matières en suspension, dans les sédiments et dans les eaux intersticielles des sédiments de 20 points d'échantillonnage de la rivière Détroit. Ces données sont étudiées afin de déterminer la source, les transformations et le dépôt des contaminants. Les tendances spatiales sont analysées aussi bien sur la longueur que sur la largeur de la rivière, ainsi que les rapports des groupes de contaminants à l'intérieur des divers compartiments et entre ces derniers.

Les résultats indiquent des apports continuels de tous ces groupes de contaminants dans les rivières provenant d'une grande variété de sources, particulièrement des effluents des usines de traitement des eaux d'égout et de plusieurs tributaires. Les répartitions et intercorrélations des différents contaminants indiquent également que les principales sources de PCB, PNA, COC et CB sont concentrées sur la rive occidentale de la rivière, tandis que les CP proviennent principalement de la rive orientale. TERMES ADDITIONNELS : lac St.Clair, lac Érié, chlordane, dieldrine, endosulfane, heptachlor, heptachlorépoxyde, hexachlorobutadiène, lindane, octachlorostyrène, séparation des contaminants.

INTRODUCTION

This study is part of a multidisciplinary investigation of environmental aspects of contaminant sources, distribution. partitioning, and their implications for the ecosystem of a large river. As the largest tributary to Lake Erie, the Detroit River has a major impact on the lake, particularly its western basin. Contaminants such as polychlorinated biphenyls (PCB's), pesticides and metals are carried by the river into the lake and result in elevated in the water, sediments and biota. Recent declines in the levels of organic contaminants in certain biota are likely the result of several factors, including the economic recession experienced since 1980, the addition or improvement of industrial municipal effluent treatment plants, and a general environmental consciousness. However, the present conditions could rapidly worsen again if an increase in industrial activity were not to be coupled with an even stronger increase in waste treatment and effluent control. Recent changes in waste disposal practices many industrial sources underline the need for a better understanding of contaminant transport and effects in specific receiving water systems. An example of that knowledge and scientific research addressing it has been shown in previous studies on the Niagara River - Lake Ontario system (Allan et al. 1983). This for location-specific investigations required now because many industrial effluents are now routed through municipal sewage treatment systems or disposed of storm sewers or smaller tributaries, or are entering the river through diffusers installed in the high current zone of the a consequence, previous degradation, adsorption, and transport mechanisms have changed and contaminant loadings are more difficult to ascertain. Until recently, many point sources such as pipes delivering effluents could easily be checked and investigated. When combined with many other waste streams and introduced to the river via diffusers placed in the

high current zones, these effluents and their effects are more difficult to track. Therefore, for the protection of the aquatic resource, an in-depth knowledge of the contaminant transport, removal, bioavailability and other mechanisms is now more necessary than ever before. The highly industrialized area of the Detroit River is of prime concern in this regard and this report addresses some of the outstanding questions on contaminant sources and fates.

EXPERIMENTAL

In May 1983, water, sediment, and suspended sediment samples were collected from twenty stations in the Detroit River. Bulk water samples of 200 L each were extracted on site with an aquatic phase liquid extractor (APLE) as described by McCrea and Fisher (1984) from continously collected 300 L samples after removal of suspended solids by centrifugation with a Westphalia centrifuge. The suspended solids from the centrifugation process were also analyzed. Where possible, surface microlayer samples were collected at the same time according to the procedure outlined by Harvey (1966). Surficial sediment samples (depth 5 to 10 cm) were taken by Shipek sampler or Ekman dredge. A11 samples were analyzed for organochlorine pesticides (OC's). (PCB's), polychlorinated biphenyls polynuclear aromatic (PNA's), chlorobenzenes (CB's) hydrocarbons and toxaphene residues.

The water samples were base/acid extracted and partitioned on 3% de-activated silica gel. The sediment samples were pressed through a 5 methoxychlorm pore size Teflon filter (Millipore 1swp-142-50) with a head pressure of 345 kPa (50 psi) of UHP nitrogen; details are given by Comba et al. (1985). The suspended solids and pressed sediment samples were freeze-dried and extracted under sonification with methylene chloride, then fractionated on 3% de-activated silica gel. The pore water

samples so obtained were treated and processed as noted above for the bulk water samples. Additional water samples of 1 L size were preserved with sodium hydroxide and analyzed for chlorinated phenols as described by Metcalfe et al. (1984).

A1 1 extracts were analyzed by gas chromatography with an electron capture detector on a HP 5880-A instrument. assurance was maintained by using three different stationary phases with narrow bore (0.25 methoxychlorm) fused The following column types were used: a 30 m, DB-5 (SE-54 equivalent) from Chromatographic Specialties Brockville, Ontario; a 30 m, OV-1 (Hewlett-Packard), and a 30 m, OV-17 experimental column (courtesy of Hewlett-Packard Canada Ltd.). Aliquots of 1 methoxychlorL volume were injected with an autosampler and an acceptance window of ±0.03 seconds was used component identification by retention time comparison. Typical chromatographic conditions were: injection port: 250 detector: 350 °C, carrier gas: hydrogen at 1 mL/min. temperature regime was typically 90 °C for 2 min, then programmed at 4 °C/min to a final temperature of 280 °C.

All extracts for polynuclear aromatic hydrocarbons were analyzed on a Varian 3700 gas chromatograph with a flame ionization detector. Injections were made manually onto a conventional 30 m, DB-5 (SE-54 equivalent) fused silica capillary column (Chromatographic Specialties) at 90 °C. After an isothermal period of 2 min, the temperature was programmed at 4 °C/min to a final hold at 310 °C. Carrier gas was hydrogen and a 10:1 injector split ratio was applied.

Further details as to the collection sites, collection and analytical methods employed, and results of individual samples are given in the National Water Research Institute summary report (Comba et al. 1985).

RESULTS

Background

In the Detroit River and the western basin of Lake principal identified organic contaminant burdens reported in the various aquatic system compartments are FCB's. DDT common metabolite (DDE), hexachlorobenzene (HCB), and to a lesser extent the compounds dieldrin, chlordane, endosulfan hexachlorocyclohexanes, primarily lindane. Among these. PCB's are the most predominant organic contaminants found in fish and herring gull eggs. In many samples they still exceed the IJC water quality objectives for the protection of the biota and their consumers (IJC 1983). The current levels of DDT in herring eggs from Fighting Island (Struger et al. 1985) declining and DDT is no longer a major contaminant burden in spottail shiners in the Detroit River (Suns <u>et</u> <u>al.</u> However, DDT levels were not declining in Lake Erie walleye, rainbow trout, rainbow smelt, coho salmon or gull Middle Island. In fact, increasing levels of DDT were observed for these species and locations in 1979 and 1980 surveys This observation coincides with high DDT levels in Detroit River sediments reported for the vicinity of the Chemical Co. at Fort Wayne (Thornley and Hamdy Therefore, it appears likely that the increased concentration of in Lake Erie fish resulted from a spill whose material moved rapidly downstream to end up in the depositional areas of western Lake Erie basin.

There is little information on chlorobenzenes (CB's) in wildlife other than for hexachlorobenzene (HCB) which may not be representative of the entire CB group due to its introduction from different types of sources. Chlorobenzenes other than HCB do not appear to be on the increase as is evident from recent residue data on spottail shiners (Suns et al. 1985). Similarly,

HCB concentrations are relatively low in Lake Erie walleye, rainbow trout and rainbow smelt (IJC 1983), but it is commonly found in Detroit River sediments (Thornley and Hamdy 1984) as well as in herring gull eggs (Struger et al. 1985).

Spottail shiners from the river also had little or no chlorophenol (CP) burdens (Suns et al. 1985), and at present, no PNA burdens are reported for fish in the Detroit River or the western basin of Lake Erie.

Major contaminants

apparent from the PCB and CB distribution patterns shown in Figures 1 and 2, both types of chemicals appear to originate at the same sources. This could possibly be the result of trichloro- and tetrachlorobezenes as FCB O.F the use replacements in electrical transformers (EFS 1984). Currently active sources for these compounds were found to be in the Trenton Channel at the mouth of the Frank and Poet Drain south of the Trenton sewage treatment facility (255) and also at the main outfall of the Detroit sewage treatment plant STP. station 352), as well as the River Rouge Contaminated suspended solids and sediments were found south of Connor's Creek (384), south of Little River (379) and near Ford Canada Ltd (370). Comparatively small FCB loadings were observed to come from Lake St. Clair; however, CB's were present at the upper end of the river near the western shore.

Effluents containing PCB and CB residues usually also carry a variety of other common organochlorine contaminants (Fig. 3). For example, the Detroit STP effluent is a principal source of dieldrin, heptachlor, heptachlor epoxide, chlordane, endosulfan and hexachloroethane. The Rouge River is a major source of heptachlor, heptachlor epoxide, endosulfan and bindane. The Trenton Channnel has active inputs of lindane, dieldrin,

endosulfan, heptachlor and hexachlorobutadiene and to a lesser extent, hexachloroethane and chlordane. The actual locations of these point sources in the Trenton Channel could not be identified in this study; however, their sources are likely to be in the areas previously identified as sources of volatile halocarbon compounds (Comba and Kaiser 1985). In particular, the Frank and Poet Drain and the Trenton sewage treatment plant were observed to be large contributors of such volatile contaminants.

Lake St. Clair contains detectable levels of octachlorostyrene, heptachlor, lindane, and chlordanes. The latter was previously thought not to be contributed by the lake to the river because of its absence from the sediments (Ho)drinet et al. 1977). The data given here, however, would suggest a preferential partitioning of chlordanes into the water column and some loadings to the Detroit River via this route are evident. Residues of endosulfan, heptachlor, and the only occurrence of methoxychlor were also found downstream of Connor's Creek near the head of the Detroit River. Low level background concentrations of DDT were detected in sediments and suspended solids from Lake St. Clair, River Rouge, Trenton Channel and at the mouth of the Detroit River. No current sources of DDT were found in the river by this survey. These observations are similar to those for residues in spottail shiners (Suns et al. 1985).

Three specific areas in the Detroit River were observed to be sources of polynuclear aromatic hydrocarbons (PNA's), with the most contaminated zones all downstream of major manufacturing plants as shown in Fig. 4. These zones are indicated by the high FNA concentrations at the stations 255 214 in, repectively downstream of the Trenton Channel, station 311 (Ecorse River), and stations 314, 330, and repectively downstream of the River Rouge. The PNA's associated with each location partitioned differently in the river system. Lower molecular weight PNA's (C_{10} to C_{14}) were preferentially

associated with the water column while those of higher molecular weight (C_{14} to C_{20}) adsorb onto suspended solids and surficial sediments. In the Trenton Channel and the Ecorse River, a greater abundance of the higher molecular weight PNA's were observed with the opposite being the case in the Detroit River area. This may result from either different concentrations of individual PNA's in the waste streams from combined industrial and other effluents or from different removal efficiencies for the various constituents by the treatment systems. Furthermore, dredging activities, such as in the Rouge River may also affect the distribution and relative abundance of individual PNA compounds.

Measurements of chlorinated phenols in subsurface water of the Detroit River showed only low levels in the aqueous phase with most concentrations in the ng.L⁻¹ (part per trillion) range. The sources of chlorophenol loadings to the river (Fig.5) originate from sewage treatment plant effluents, from large storm sewers and from some leachates at Fighting Island. Mirex, endosulfan, toxaphene, chlorinated toluenes and chlorinated anisoles were not detected at any of the twenty intensive sampling stations in this study.

Distribution between compartments

Although the prevalent sink for these compounds in the Detroit River system are sediments, such as shown for PCB's and chlorobenzenes (CB's), (Platford et al. 1985), these compounds are also known to readily bioaccumulate in the biotic compartment. In general, compounds which predominate in the biota are also found to partition from the water into the other aquatic compartments including suspended solids and surficial sediments. This is typically the case for PCB's, CB's, DDT and related chemicals. PCB's and CB's were detected in all five of the aquatic compartments studied. In fact, PCB's were present in

96% of all samples analyzed. The insecticide p,p'-DDT and its principal metabolite p,p'-DDE were detected in surficial sediments and suspended solids, while the isomer o,p'-DDE was primarily associated with the surface microlayer.

Residues of dieldrin, hexachloroethane, heptachlor heptachlor epoxide were detected solely in the water phase. Hexachloroethane and dieldrin were exclusively in the microlayer and subsurface waters, respectively, while heptachlor and heptachlor epoxide were present in both phases. isomers and lindane were also associated with the subsurface and pore water phases under turbulent river flow conditions. amounts of chlordane were detected in the sediments depositional zones at the Ecorse and Rouge Rivers and lindane was found in trace levels in one sample of suspended solids. Endosulfan residues were detected in subsurface water, suspended solids and in trace amounts in pore water of one sediment Octachlorostyrene and hexachlorobutadiene were found adsorbed to either suspended solids or surficial sediments were not associated with any of the aqueous phases. None of the compounds mentioned above were found to be concentrated surface microlaver.

DISCUSSION

Eased on volatile halocarbon concentrations in the water column (Comba and Kaiser 1985), major contaminant inputs to the Detroit River originate from a number of point sources including sewage treatment plant discharges, combined overflow and storm sewers and from several tributaries to the river. The processes controlling the pathways of these trace organic contaminants generally depend on the characteristics of both the effluents and the receiving water. For example, for ionizing compounds such as pentachlorophenol, the ambient pH can markedly influence their partitioning, hence adsorption and desorption processes, degradation and bioconcentration (Kaiser and Valdmanis 1982).

Significant amounts of contaminants enter the river system after some treatment at municipal waste treatment plants. In addition, loadings appear to be derived from direct and indirect discharges of untreated wastes to the river. The composition of such waste streams varies widely and the contaminant transport is further influenced by the type and concentration of dissolved organic and inorganic constituents (Landrum et al. 1984), size, type and density of suspended particulates (Mudroch 1985) and other water quality parameters.

PCB's and PNA's

is generally accepted that the contaminant transport in large river systems is predominantly a function of the sediment characteristics (Holdrinet et al. 1977). Table 1 gives the correlation coefficients (r^2) of linear regression analyses of major contaminant groups with the contents in the sediments of organic carbon, clay, silt, and sand for each of the aquatic compartments investigated, namely surficial sediments, water, suspended solids, bulk water and the surface No significant relationships were found to exist between the contaminant groups and the clay, silt and sand fractions of the river sediment. However, PCB's were found to correlate with the organic carbon concentration while PNA's showed a low, significant correlation with the same sediment parameter. oberservation is to be expected from the high coefficients of PCB congeners and earlier results on PCB's in Lakes St. Clair and Erie by Holdrinet et al. (1977).

It appears surprising that both PCB's nor OC's in the suspended solids fraction fail to show any significant correlation with the sediment organic carbon concentration (Table 1). Instead, they appear to be better correlated with the clay, silt and sand portions of the sediments. This absence of a significant correlation of PCB's in suspended solids with the

organic carbon in sediments indicates that PCB's entering the river are associated with the aqueous fraction rather than the suspended solids. Further support for this conclusion is evident from the regression coefficients for the bulk water compartment, as shown in Table 1. However, it is thought that the concentrations of PCB's in the aquatic phase are due to kinetic control of the adsorption processes in the river. The mean of the river is approximately 3 km.hr $^{-1}$, so that its mean residence time is less than one day. Therefore, the relatively high levels of FCB's in the river water when compared to the sediments, for example at stations 346, 255 and 223 Versus station 213, may be a temporary phenomenon resulting from their way of introduction and the short residence time in which a thermodynamically favoured adsorption onto the particulate matter and sediments can not be achieved. Support for this argument is further derived from the [FCE(water)]/[organic carbon(sediment)] ratios, given in Table 2. The data are separated into eastern (Canadian) and western (US) shoreline stations and give the concentrations of PCB's and PNA's in water and sediments, organic in sediments and the above noted ratios. PCB(water)/C ratios show, at least for the eastern river shore, a systematic increase from 50 to 356. This spatial trend interpreted to show the mixing of contaminated river sediment along the entire stretch of the river, thus smoothing spatial differences across the river. In contrast, the FCB(water)/C ratios for stations on the western river shore (Table significantly higher and remain quite constant throughout the river length. With the continued (but incomplete) adsorption and precipitation of PCB's from the bulk water fraction to the sediments, as indicated by the significant correlation of FCB's in water with organic carbon in sediments (Table 1), it concluded that significant FCB loadings enter the river at points along its eastern shore.

The PNA concentrations in the bulk water are highly correlated with PNA levels in each of the four sediment fractions

(Table 1). Compared to PCB's, the PNA's are associated to a higher degree with the suspended solids fraction. This is apparent from the correlation of PNA's in the suspended solids and bulk water fractions of the river water with that of the river sediments. PNA's can be adsorbed onto particulate matter of both inorganic and organic nature and, in contrast to other contaminants, exist also as particles themselves. This fact likely is also the reason for the strong correlations of PNA's in water with all of the four sediment fractions, as shown in Table 1.

The FNA(water)/C ratios vary widely on both river shores (Table 2). Some increasing trend may exist along the river, but the data do not appear to be conclusive. In contrast, the PNA(sediment)/C ratios on the right shore increase by several orders of magnitude, indicating large inputs in that zone. It can be assumed that major portions of such inputs are derived from coal and coking operations associated with the steel industries in that area.

OC's and CB's

As evident from the significant correlation coefficients of OC and CB concentrations in the dissolved aquatic (bulk water) phase with the organic carbon content of sediments, these compounds are either truly dissolved or adsorbed phytoplankton | of <2m size which is, operationally defined, a part of this fraction (Table 1). surficial sediments in the river are steadiliy transported system, these relationships indicate continued additions of such contaminants into the river water. 00 contaminants in the bulk water and surface microlayer compartments of the river (Table 1) are strongly correlated the sediment organic carbon and silt fractions which indicates their major sources to be tributaries and urban runoff, both high

in organic carbon and silt. Similar findings were recently obtained by Oliver and Nicol (1982). OC's are also associated strongly with the surface microlayer. Many of these compounds are quite volatile and known to be present in precipitation from the atmosphere (Swain 1978; Strachan and Huneault 1979). Their input via atmospheric fallout is consistent with their presence in the surface microlayer as also shown by Platford et al. (1985).

Contaminant intercorrelations

It is of interest to compare the concentrations of the major contaminant groups with each other, particularly for the two major compartments, namely water and sediments. Table 3 gives the correlation coefficients for a variety of linear regressions of PCB's, OC's, CB's and FNA's in water and sediments in the two compartments. In addition, coefficients are given on the relationships of the organic compounds with several inorganic and organometallic species, recently investigated by Chau et al. (1985), Lum and Gammon (1985), and Maguire et al. (1985).

Good correlations are found between OC's and CB's in water, and PNA's and Pb in sediments with OC's and CB's in water. Not surprisingly, neither PCB or PNA concentrations in water are significantly correlated with their respective concentrations. As noted above, additions of these compounds to certain stations does not result in higher water at concentrations in sediments of the immediate vicinity manifest themselves only in the depositional areas further downstream. In the sediments, FCB's show a minor relationship with FNA's. OC concentrations are highly correlated with extractable iron. This is consistent with the presence in the aqueous phase and likely indicates a significant degree of coprecipitation with iron hydroxide and phosphate complexes in the alkaline environment of the receiving water.

Conclusions

Although several major contaminant sources and pathways in the Detroit River have been identified, many details as contaminant pathways and effects have yet to be elucidated. dominant factor influencing these is the strong river current. separated into a number of deep channels with large, shallow areas in between. This enables fish and other mobile species to move in and out of contaminated zones. Therefore, relationships of contaminants with biological effects may be difficult to ascertain, at least in terms of specific, small localized areas. For example, areas known to receive industrial effluents were found to have high numbers of tumors in fish (Baumann 1984; Sonstegard 1977). Although elevated levels of PNA's have been in such areas, no specific causes have been determined at this time. Conversely, some effluents were shown to have high acute toxicity to certain bacteria but the particular toxicants are not yet identified (Ribo et al. 1985).

The precise processes controlling contaminant transport and movement between the aqueous compartments are still Recent studies by Oliver and Niimi (1983) indicate a direct uptake of low molecular weight compounds, such as chlorobenzenes, by fish. In contrast, hexachlorobenzene and many chlorobiphenyls take much longer to equilibrate in test are thought to bioaccumulate mainly through the food-chain. Therefore, even small concentrations of certain compounds in some effluents can give rise to visible and toxic concentrations in higher trophic level organisms. An example of that is the presence of chlorostyrenes in waterfowl in this area (Kuehl Reichel <u>et al.</u> 1977). Important factors bearing on these pathways appear to be the complexing effects of natural humic and introduced surface-active ions and non-electrolytes (Landrum et al. 1984). The adsorption characteristics contaminants will also be influenced by seasonal changes in

general water quality parameters of effluents as well as the receiving water. Compounds such as polynuclear aromatic hydrocarbons are likely to enter the river both dissolved and as particles. The relative rates of dispersion and accumulation of these are not known, nor are their relative abundances.

A variety of organochlorine contaminants, including a number of biocides appear to enter the river from urban and rural runoff. The contributions of many of these sources are difficult to measure as their loadings are very dependent on the amount and precipitation events and the atmospheric regime in general. Furthermore, these and the other contaminants may exist in soils and upstream sediments for prolonged periods of before they find their way into the river. For example, FCB's in sediments of Lake St. Clair are known to move slowly downstream (Holdrinet et al. 1977). In order to address these problems effectively, good loading budgets are needed which distinguish between present and past sources. Progress in that direction likely come from detailed investigations of the relative abundance of the various PCB congeners in the different compartments.

ACKNOWLEDGEMENTS

We thank Mr. Larry Benner, Technical Operations Division, National Water Research Institute and the Canadian Coast Guard, Amherstburg for assistance with the sample collections.

REFERENCES

- Allan, R.J., Mudroch, A. and Sudar, A. (Eds.) 1983. The Niagara River/ Lake Ontario pollution problem. Special issue, <u>J. Great Lakes</u> Res. 9: 109-340.
- Baumann, P.C. 1984, Cancer in wild freshwater fish populations with emphasis on the Great Lakes. <u>J. Great Lakes Res.</u> 10: 251-253.
- Chau, Y.K., Wong, P.T.S., Bengert, G.A., Glen, B. and Dunn, J.L. 1985. Occurrence of alkyllead compounds in environmental samples of the Detroit and St. Clair Rivers. <u>J. Great Lakes Res.</u> 11: 000-000.
- Comba, M.E. and Kaiser, K.L.E. 1985. Volatile halocarbons in the Detroit River and their relationship to contaminant sources.

 J. Great Lakes Res. 11: 000-000.
- Chau, Y.K. and Bengert, G.A. 1984. A chemical survey of the Detroit River, 1983. National Water Research Institute, Inland Waters Directorate, Report #, in preparation.
- EPS, 1984. Environmental Protection Service, Environment Canada, 1982. Reviews of substitutes for polychlorinated biphenyls in transformers, EPS 3-EP-84-1.
- Harvey, G.W. 1966. Microlayer collection from the sea surface: A new method and initial results. <u>Limnol</u>. <u>Oceanogr</u>. 11: 608-613.

- Holdrinet, F.R., Braun, H.E., Thomas, R.L., Kemp, A.L.W., and Jaquet, J.M. 1977. Organochlorine insecticides and PCB's in sediments of Lake St. Clair (1970 and 1974) and Lake Erie (1971). Sci. Tot. Environment 8: 205-227.
- IJC 1983. Great Lakes Water Quality Board. Report on Great Lakes

 Water Quality, Appendix, Great Lakes Surveillance. International

 Joint Commission, Windsor, Ontario.
- Kaiser, K.L.E. and Valdmanis, I. 1982. Apparent octanol/water coefficients of pentachlorophenol as a function of pH. Can. J. Chem. 60: 2104-2106.
- Kuehl, D.W., Johnson, K.L., Butterworth, B.C., Leonard, E.N., and Veith, G.D. 1981. Quantification of octachlorostyrene and related compounds in Great Lakes fish by gas chromatographymass spectrometry. <u>J. Great Lakes Res.</u> 7: 330-335.
- Landrum, P.F., Nihart, S.R., Eadle, B.J., and Gardner, W.S. 1784. Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. Environ. Sci. Technol. 18: 187-192.
- Lum, K.R. and Gammon, K.L. 1985. Geochemical availability of some trace and major elements in surficial sediments of the Detroit River and western Lake Erie. <u>J. Great Lakes Res.</u> 11: 000-000.
- Maguire, R.J., Tkacz, R.J. Sartor, D.L. 1985. Butyltin species and inorganic tin in waters and sediments of the Detroit and St. Clair Rivers. J. Great Lakes Res. 11: 000-000.
- McCrea, R.C. and Fisher, J.D. 1984. Design and testing of an aqueous phase liquid-liquid extractor (APLE) for the determination of organochlorine contaminants. Environment Canada, Inland Waters Directorate, Burlington, Ontario, Canada. 18 p.

- Metcalfe, J.L., Fox, M.E. and Carey, J.H. 1984. Aquatic leeches (<u>Hirudinea</u>) as bioindicators of organic chemical contaminants in freshwater ecosystems. <u>Chemosphere</u> 13: 143-150.
- Mudroch, A. 1985. Geochemistry of the Detroit River sediments.

 <u>J. Great Lakes Res.</u> 11: 000-000.
- Oliver, B.G. and Nicol, K.D. 1982. Chlorobenzenes in sediment, water and selected fish from Lakes Superior, Huron, Erie and Ontario. <u>Environ. Sci. Technol.</u> 16: 532-536.
- chlorobenzenes from water by rainbow trout: Correlations with partition coefficients and environmental residues. Environ.

 Sci. Technol. 17: 287-291.
- Platford, R.F., Maguire, R.J., Tkacz, R.J., Comba, M.E. and Kaiser, K.L.E., 1985. The distribution of hydrocarbons and chlorinated hydrocarbons in various phases of the Detroit River. J. Great Lakes Res. 11: 000-000.
- Reichel, W.L., Prouty, R.M., and Gay, M.L. 1977. Identification of polychlorinated styrene compounds in heron tissues by gas-liquid chromatography-mass spectrometry. <u>J. Ass. Off. An. Chem.</u> 60: 60-62.
- Ribo, J.M., Zaruk, B.M., Hunter, H., and Kaiser, K.L.E. 1985.

 Microtox toxicity test results for water samples from the

 Detroit River. <u>J. Great Lakes Res.</u> 11: 000-000.
- Sonstegard, R.A. 1977. Environmental carcinogenesis studies in fishes of the Great Lakes of North America. <u>Ann. New York Acad. Sci.</u> 298: 261-269.

- Strachan, W.M.J. and Huneault, H. 1979. Polychlorinated biphenyls and organochlorine pesticides in Great Lakes precipitation.

 <u>J. Great Lakes Res.</u> 5: 61-68.
- Struger, J., Weseloh, D.V., Hallett, D.J., and Mineau, F. 1985.

 Organochlorine contaminants in herring gull eggs from the Detroit and Niagara Rivers and Saginaw Bay (1978 1982): Contaminant discriminants. J. Great Lakes Res. 11: 000-000.
- Suns, K., Crawford, G. and Russell, D. 1985. Organochlorine and mercury residues in young-of-the-year spottail shiners from Detroit River, Lake St. Clair and Lake Erie. <u>J. Great Lakes Res.</u> 11: 000-000.
- Swain, W.R. 1978. Chlorinated organic residues in fish, water, and precipitation from the vicinity of Isle Royale, Lake Superior.

 J. Great Lakes Res. 4: 398-407.
- Thornley, S. and Hamdy, Y. 1984. Report on an assessment of the bottom fauna and sediments of the Detroit River. <u>Ontario</u>

 <u>Ministry of the Environment.</u> 48 p.

TABLE 1. Linear regression coefficients (r²) of selected contaminant groups with sediment characteristics, including its carbon content and its clay, silt and sand fractions; number of observations in parentheses a,b,c.

Compartment and	Sediment portion										
Contaminant Group		Clay (2-4jum)	Silt (4-63jum)	Sand (>63µm)							
Surficial sed	iments		ren dare dres desp d'est biés agus joue faire aus gans ann	to their free may their their time that their man man man and							
•	.10 (15)	-		Notice							
	.31 (16)**		· 	-							
Pore water, i	ncluding parti	culates of <50,	ım size								
PNA	 .	0.18 (13)	0.20 (12)	0.20 (13)							
PÓB	****	0.22 (14)	0.17 (13)	0.21 (14)							
06		0.21 (14)	0.17 (13)	0.20 (14)							
B	· 	0.22 (14)	0.17 (13)	0.20 (14)							
Suspended sol	ids, excluding	phytoplankton									
FNA O	.42 (9)*	, 44.69	0.28 (8)								
PCB		***	0.10 (9)	-							
00	****	0.16 (8)	0.36 (7)	0.22 (8)							
CB 0	.22 (10)	ania'	0.19 (9)								
Bulk water, i	Bulk water, including phytoplankton										
PNA O	.42 (18)***	0.19 (18)*	0.48 (17)***	0.33 (18)***							
PCB O	.12 (18)	-	***								
00, 0.	.24 (16)*		· ·	. -							
•	.34 (18)***		***	***							
Surface micro	layer, unfilte	red									
	.14 (14)	-									
OC -		0.15 (12)	0.48 (11)***	0.30 (12)*							

Abbreviations: PCB: polychlorinated biphenyls; CB: chlorobenzenes;
OC: organochlorine pesticides; FNA: polynuclear aromatic hydrocarbons.

Dashes (-) indicate correlation coefficients of r² <0.10.</p>
Stars (*) indicate level of significance: *: P<0.05; **: P<0.02;</p>
: P<0.01; *: P<0.001.</p>

TABLE 2. FCB and PNA concentrations in bulk water and sediments and organic carbon (C) concentrations in sediments with FCB/C and PNA/C ratios for selected stations in the Detroit River a,b.

	=======================================		=========				= == == == == == == == == == == == == =		
Station #	PCB		PNA		E	PCB/C		PNA/C	
	Water (ppt)	Sed.		er Sed.	Sed.	Water	Sed.	Water	- Sed.
Western	shore					THE WASHINGTON COMMITTEE THE STATE OF THE ST			
0399	620	36	230	< DL	1.09	569	33	211	9
0384	350		44	*****	5.15	68	-	9	
0352	1400	•	1700		2.18	642	:-	780	
0314	900		5300		***	*****	****	***	
0224	900	170	310	13000	2.69	334	63	115	4830
0214	630	120	290	23000	1.16	543	104	250	19800
Eastern	shore								
0370	200	210	< DL	2800	4.03	50	52	*****	695
0353	350		1600	660	2.15	163		744	307
0330	890	160	6100	550	5.95	150	27	1025	92
0280	420	9	<dl.< td=""><td>< DL</td><td>1.53</td><td>275</td><td>6</td><td></td><td>n-</td></dl.<>	< DL	1.53	275	6		n-
0269	850	93	160	20000	3.92	217	28	41	5102
0212	850	210	3900	2000	2.39	356	88	1632	837

 $^{^{}a}$ DL: detection limit (10 ppb); ppb: parts per 10 9 ; ppt: parts per 10^{12} .

b Dashes (-) indicate absent data.

TABLE 3. Linear regression coefficients (r^2) of selected contaminant groups in water and sediment compartments of the Detroit River; number of data pairs in parentheses a,b,c.

In water Contaminants FCB OC CB In water OC (1.00)0.95 (13)**** Pb (alkyl) 0.36 (12)* Sn (alkyl) 0.11 (12)0.18(12)In sediments **FCB** 0.21 (13) 0.25 (13) 0.20(13)ÒC 0.18(14)PNA 0.56 (13)*** 0.40 (13)** Sn (inorganic) 0.14 (13) b (inorganic) 0.48 (14)*** 0.63 (14)**** 0.67 (13)**** In sediments In sediments FNA 0.30 (14)* (1.00)000.34 (14)** (1.00)Sn (inorganic). 0.17 (14) Pb (extractable) 0.19(14)Fe (extractable) 0.81 (7) ****

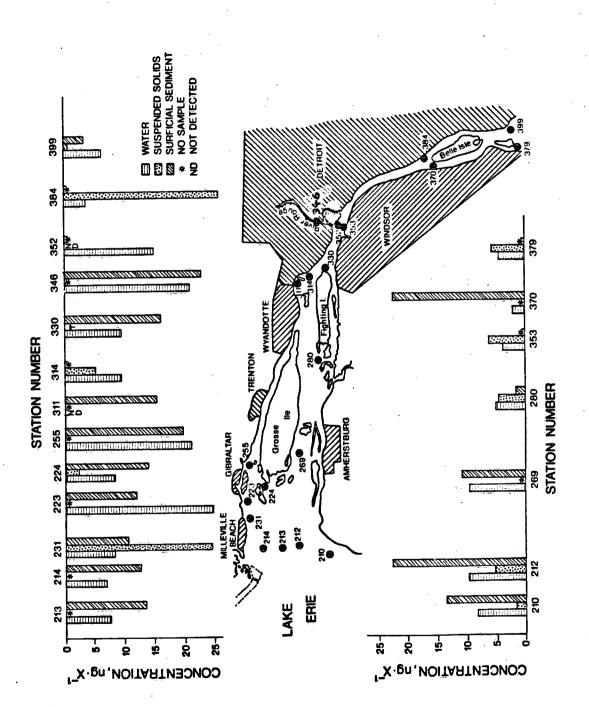
a For abbreviations and levels of significance see Table 1.

^b Fb, Fe and Sn data from Chau <u>et al.</u> (1985), Lum and Gammon (1985), and Maguire <u>et al.</u> (1985).

Dashes (-) indicate correlation coefficients of r^2 <0.10.

List of Figures

- FIG. 1. Polychlorinated biphenyls (PCB's) in water, suspended solids and surficial sediments of the Detroit River. Concentrations in ng.kg⁻¹ (sediments, suspended solids) and ng.L⁻¹ (water), respectively.
- FIG. 2. Clorobenzenes (CB's) in water, suspended solids and surficial sediments of the Detroit River. Concentrations in $\log \log^{-1}$ (sediments, suspended solids) and $\log \log^{-1}$ (water), respectively.
- FIG. 3. Organochlorine contaminants (OC's) in water, suspended solids and surficial sediments of the Detroit River. Concentrations in $ng.kg^{-1}$ (sediments, suspended solids) and $ng.L^{-1}$ (water), respectively.
- FIG. 4. Polynuclear aromatic hydrocarbons (PNA's) in water, suspended solids and surficial sediments of the Detroit River.
- Concentrations $\text{in ng.kg}^{-1} \text{ (sediments, suspended solids) and ng.L}^{-1}$ (water), respectively.
- FIG. 5. Sample stations and concentrations of chlorophenol congeners in water of the Detroit River.



LAKE

CONCENTRATION, ng. X

CONCENTRATION, ng·X·Y

