THE SPATIAL DISTRIBUTION OF
CHLORINATED HYDROCARBON RESIDUES IN THE
SEDIMENTS OF INNER LONG POINT BAY, LAKE ERIE

February 1983

The Honourable
Andrew S. Brandt
Minister

Gérard J. M. Raymond
Deputy Minister
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MEMORANDUM

TO: Directors
FROM: D. N. Jeffs, Director
Water Resources Branch

RE: GREAT LAKES REPORT "THE SPATIAL DISTRIBUTION OF CHLORINATED HYDROCARBON RESIDUES IN THE SEDIMENTS OF INNER LONG POINT BAY, LAKE ERIE".

Attached is a copy of the Inner Long Point Bay report which was prepared for release by the Great Lakes Section of this Branch.

A survey was carried out in Inner Long Point Bay during 1979 to determine the distribution of organochlorine contaminants in the sediments within the bay. The levels of these contaminants in the sediments provides valuable information on past and present usage and the effectiveness of past control measures.

Please advise if further copies of the report are required by your staff.

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The Spatial Distribution of Chlorinated Hydrocarbon Residues in the Sediments of Inner Long Point Bay, Lake Erie

February 1983

By

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. A. McLarty of the Ministry of the Environment, West Central Region, Stoney Creek, Ontario who participated in the collection of sediment samples. Staff of the Pesticides and Inorganic Trace Contaminants Sections of the Ministry of the Environment, Main Laboratory in Rexdale, conducted analysis of the sediment samples.

The authors are also indebted to Ms. J. Winiecki and Ms. J. Barnes, who assisted in the finalization of the manuscript.
SUMMARY

The Ministry of the Environment carried out a survey of Inner Long Point Bay on September 5, 1979 and November 18, 1979, to determine the distribution of organochlorine contaminants in the sediments within the bay.

Because of the capacity of organochlorine compounds to bind with fine grained sediments and their persistence in the environment, pesticide use in agricultural areas such as the drainage basin of Inner Long Point Bay is a potential source of contamination of Great Lakes sediments. The determination of the levels of these contaminants in the sediments of Inner Long Point Bay provides valuable information on past and present usage and the effectiveness of control measures.

In general, Inner Long Point Bay sediments exhibited low levels of PCB's and pesticides with the exception of the northwestern portion of the bay where average PCB's levels amounted to 77 µg/kg, in excess of the provincial guideline (50 µg/kg) for open-water disposal of dredged materials. This level is comparable to that found in the Eastern Basin of Lake Erie. Road oiling for dust control and atmospheric fall out of PCB's are probable sources of sediment contamination.

Hexachlorobenzene (HCB), heptachlor epoxide and mirex were not detected above the detection limit of 1 µg/kg.

Total DDT residues indicated high levels in the deeper portions of sediment cores reflecting the heavy use of DDT as an agricultural pesticide in the past. The mean level in surficial sediment amounted to 12 µg/kg which was less than that found in other Lake Erie harbours. This average level was mainly attributed to the presence of the stable compound p,p’-DDD, a metabolite of DDT, which appeared consistently throughout the bay.

The results of this study are being provided to the International Great Lakes scientific community as part of this Ministry's contribution to the two-year intensive study of Lake Erie conducted under the guidelines of the Great Lakes International Surveillance Plan (GLISP).
CONCLUSIONS

1. Surficial sediment distribution within Inner Long Point Bay does not follow the characteristic pattern usually associated with sediment deposition at the deltas of river mouths. Coarse material (sands) is found farthest away from the creek mouths towards the bay mouth and appears to be derived mainly from littoral drift. Fine sediments transported by the tributary creeks appear distributed, likely by waves and currents, towards the northwest portion of the bay (Figure 5). There is an apparent gradient from coarse material at the lakeward end of the bay to fine deposits along the northwestern portion.

2. It has been noted that the configuration of the Inner Bay is constantly changing and since movement of material out of the bay is restricted, it is becoming shallower and marshier and may eventually silt in completely (24). Any remedial measure to prevent the Inner Bay from silting in will require sediment control from both agricultural drainage and littoral drift derived from shoreline erosion.

3. The levels of DOT and its metabolites within Inner Long Point Bay are similar to those found in embayments and harbours on Lake Erie's north shore that receive agricultural drainage. DDT and its metabolites are found to be concentrated within the central, deeper portion of the bay and may be due to some resuspended fines settling in this deeper portion. Localized pockets of DDT contamination also occur along the north shore in the western portion of the Inner Bay and may be due to previous local inputs through storm runoff. Two stations (1279 and 1280) close to the mouths of Big and Dedrick Creeks show levels of p,p'-DDD. This may be due to residues of this compound still in the soils of the drainage basin which are gradually eroded and transported into the bay.

4. PCB distribution within the Inner Bay closely resembles that of the fine sediment i.e. it is concentrated along the northwest portion of the bay and may be due in large part to the affinity of fine sediments for PCB's. Fifteen percent of the stations (six out of thirty-nine) showed levels above that recommended by the Ministry of the Environment for open water spoils disposal. Two stations (1282, 1284) in the Inner Bay and Station 1316 outside the Inner Bay showed elevated levels (240 µg/kg, 160 µg/kg, 200 µg/kg, respectively). The reason for these levels was not apparent.
5. Analyses of cores from selected stations show levels of DDT and its metabolites, alpha-BHC and dieldrin increase with depth in the sediment. This reflects previous heavy use with the decreasing levels in recent sediment reflecting a curtailment of use. This finding also shows that control of these compounds is effective.

6. p,p′-DDD and chlordane appear to be quite stable in sediment and, as shown in other studies (3), are effective geochemical tracers of sediment transport and deposition.
INTRODUCTION

In 1979 the Ontario Ministry of the Environment conducted a sediment survey of Inner Long Point Bay. The primary focus of this study was on the identification of emerging problems, that is, "to determine the presence of new or hitherto undetected problems in the Great Lakes Basin Ecosystem, leading to the development and implementation of appropriate pollution control measures." (Annex 11 of IJC 1978 Agreement) (1).

Studies conducted under the Pollution from Land Use Activities Reference Group (PLUARG, 1978) indicated that sediment runoff from tributary drainage basins constituted a major source of trace contaminants to the coastal zone of the Great Lakes (6, 7).

Inner Long Point Bay and the Big Creek Marsh provide habitat for many internationally important migratory birds and waterfowl as well as unique or endangered species of plants and animals. Protection of this coastal zone is necessary in the form of upstream controls for pesticide use and the reduction of sediment loading from runoff and erosion.

In accordance with the significance placed on toxic and hazardous contaminants assessment and management in the Great Lakes system, the Inner Long Point Bay study concentrated on the familiar persistent toxic substances (1). The distribution of these substances in sediments provides valuable information on the fate of PCB's and pesticides (eg. Aldrin, Dieldrin, DDT and metabolites, Endrin, Heptachlor/Heptachlor Epoxide, Lindane) formerly in use in the drainage basin of Inner Long Point Bay, and the effectiveness of management policies and controls. The transport and accumulation of those compounds presently in use in the basin (eg. Chlordane, Endosulphan) can be assessed and agricultural practices can be modified to reflect new concerns. The DDD metabolite of DDT and Chlordane are especially useful tracers because they are quite stable in anoxic sediments and they can be determined, analytically, at low levels (ppb) (3).

The 1979 study of Inner Lang Point Bay did not address heavy metals in the sediments because an earlier study of Big Creek, which provides the major drainage into Long Point Bay, and Big Creek Marsh showed very low levels of heavy metals in the sediment (4).

This study was part of Ontario's overall contribution to the two-year intensive study of Lake Erie organized under the Great Lakes International Surveillance Plan (GLISP).
Background Studies

Investigations of water quality characteristics of Inner Long Point Bay conducted by J. H. Leach in 1978 and 1979 (5) have indicated that the Inner Bay is eutrophic and more productive than the nearshore areas of eastern Lake Erie. Loadings of both nutrients and suspended materials from Big Creek have contributed to the eutrophic status of the bay. The only significant changes in water quality of the Inner Bay since 1962 have been the increasing levels of nitrate. This upward trend in nitrate levels can be attributed to the increase in corn acreage (about seven fold in Norfolk county since 1950) since corn requires fertilizer with a high nitrogen ratio (5).

Description of the Study Area

Inner Long Point Bay is located on the northern shore of the eastern basin of Lake Erie (Figure 1). Long Point, a sand spit formed by alongshore drift of sediment from shoreline erosion along the central basin, forms the southern boundary of the bay. The Norfolk sand plain, which covers approximately 310 ha, forms the boundary along the northwest periphery of the bay. At the interface between the Inner Bay and Long Point Bay is a submerged sand bar (baymouth bar) running from Deep Hole Point to Potohawk Point (Figure 2). The present morphology of the bay is the result of both natural and man-induced alterations. Historical geomorphology and changes to the aquatic habitat have been described by Whillans (3, 9).

The Inner Bay (Figure 2) has a shoreline of 40.7 km, and a surface area of 7,300 ha. Approximate water volume within the bay is 77.7 x 10^6 m^3, with a mean depth of 1 m and a maximum depth of 3.05 m (to International Great Lakes Datum IGLD (10)). The lakeward extent of the bay is defined by a line extending from Deep Hole Point to Potohawk Point (5). The bay receives drainage from Big Creek and Dedrick Creek, which encompass drainage areas of 72,228 ha and 8,287 ha, respectively.

Intensive agriculture, primarily cash crops such as tobacco, corn and wheat, forms the major land use in the Big Creek drainage basin.

Pesticides and nutrients used in agricultural practices such as spraying crops in the drainage basin, are transported by water in association with suspended and bottom sediment in Big
Creek into Inner Long Point Bay (4). Geology, hydrology and land use characteristics of the Big Creek drainage basin have been described by Yakutchik and Lammers (12), Hardy (13) and the Big Creek Conservation Authority (14-19).

Big Creek constitutes the major source of fine grain sediment input to the bay. Sediment loading is a function of the hydrologic characteristics of the basin with more than 50% of the annual suspended solids loading occurring during spring flows (Figure 4). Suspended sediment loading for the upper Big Creek drainage basin (above Walsingham) ranged from 35,199 tonnes per annum during 1969, to 12,971 tonnes per annum during 1970 with a mean of 25,500 tonnes per annum over the period from 1967 to 1976 (11).

Inner Long Point Bay provides habitat for many species of warm water fish, furbearing mammals and migratory waterfowl (8, 20, 21). Because of these abundant biological resources, the area is used extensively for outdoor recreation which includes wildlife observation, sport fishing, hunting, and trapping.
FIELD METHODS

Sediment Collection

Figure 3 shows the location of the forty-two sediment sampling stations in Inner Long Point Bay.

The surficial sediments at thirty-nine stations were sampled during September and November, 1979. Multiple grabs of the surficial sediments were taken with an Eckman dredge type sampler (152 mm x 152 mm x 152 rim) and composites of the grabs were taken at each station. Core samples (150 mm in length) were obtained at six stations (1280, 1287, 1296, 1300, 1311, and 1315) using a Phlegar gravity core sampler with an internal diameter of 38 mm.

Sample Processing

The sediment from each core was extruded and sectioned into 30-mm segments and submitted for analysis of organochlorine residues.

Extensive growth of rooted aquatic macrophytes in the bay necessitated careful removal of fresh plant debris from all surface grab sediment samples. Samples were then placed in jars and submitted for analysis.

Analysis

Physical analyses included the determination of grain size and percent loss on ignition (22, 23). Chemical analyses included organochlorine residues: DDT and its metabolites (p,p’-DDE, p,p’-DDD, o,p’ and p,p’-DDT), lindane, alpha and beta benzene hexachloride (BHC) isomers, mirex, hexachlorobenzene (HCB), polychlorinated biphenyls (PCB’s), dieldrin, endrin, thiodan (alpha and beta endosulphan), alpha and gamma chlordane, heptachlor and heptachlor epoxide. Analyses were performed on homogeneous extracts of samples according to standard MOE analytical methods (22, 23).
RESULTS AND DISCUSSION

Physical Composition and Distribution of Bay Sediments

Figure 4 shows the seasonal distribution of suspended solid loadings from Big Creek at the upstream Water Survey of Canada stream gauge at Walsingham, Ontario. The distribution is characteristic of tributary discharges to Lake Erie with a spring maximum snowmelt runoff during March.

The spatial distribution of sediment according to grain size composition is shown in Figures 5 and 6. The sediments grade from sand at the lakeward extent of the Inner Bay to fine silt at the western end of the bay. This distribution of surficial sediment is not characteristic of the normal sediment distribution pattern at river mouths (i.e. coarser material close to the river mouth grading outwards to fines). It appears that circulation in the bay is influenced by main lake currents (24) to such an extent that fresh material brought down by the creeks draining into the bay are redistributed through current and wave action. Some of the littoral drift material moving eastwards that enters Long Point Bay (25) possibly ends up in the Inner Bay. It has also been noted that this net drift of material derived through bluff erosion of the northwestern shore of Long Point Bay is towards the bayhead (20).

In light of the previous studies (24, 25) and the distribution pattern of sediments noted in the current study, most of the coarse grain sediment seems to enter the Inner Bay from main lake sources. The surficial sediment in Big Creek Marsh is typical of material brought down by Big Creek and consists primarily of silt (57 to 76% silt)(4). The Big Creek deposits are distributed by waves and currents, with the fines being carried towards the western shore of the Inner Bay.

Sediment Chemistry

Figure 7 shows the distribution of sediments based on loss on ignition (expressed in percent) contoured at 1% intervals. This measurement gives an indication of the organic content of sediment. Levels ranged from less than 1% to 7% with a gradient of decreasing concentrations from the creek discharge northwards along the western edge of the bay. As noted earlier, fresh plant material was removed from samples thereby leaving only detrital organic matter. Based on the samples collected, plant debris from the macrophytes appears
to be well degraded.

The analytical results for PCB's and eighteen organochlorine pesticides for the thirty-nine stations sampled in Inner Long Point Bay are listed in Table 1. These results are discussed below.

**DDT and Metabolites**

More than half (59%) of the stations sampled in the Inner Bay showed detectable levels of DDT and its metabolites (p,p’-DDE + o,p’-DDT + p,p’-DDD + p,p’-DDT). The stability of p,p’-DDD in sediment is shown by the presence of this metabolite in most of these samples (3). The mean value of DDT was 12 µg/kg and ranged from 5-27 µg/kg. This average level was less than those found in other Lake Erie harbours such as Port Rowan (26 µg/kg), Port Burwell (25 µg/kg), Port Dover (24 µg/kg) and Wheatley (116 µg/kg) (26).

The distribution of DDT and its metabolites in surficial sediment (Figure 8) suggests recent fluvial input only at stations 1279 and 1280, located approximately 1 km from the discharge of Big and Dedrick Creeks. The levels of DDT found at these stations reflect the persistence of DDT in the soils of the drainage basin. Its use in tobacco production was curtailed in 1970-1972 (5).

Analysis of a core sample from station 1280 indicated that the surface layer (0 to 30 mm) accounted for 7.4% of the total DDT residues in the 150 mm core sample (Figure 9). Total DDT residues increased with core depth to a maximum of 31.4% over the 90 to 120 mm interval. Heavy use of DDT as an agricultural pesticide in the past was clearly reflected by the higher values in the deeper portion of the core, as was the curtailment of use in more recent core layers.

Several stations in the central portion of the Inner Bay which corresponds to the deepest portion of the bay showed detectable level of DDT and its metabolites. This seems to be a reflection of material trapped in this area as a result of resuspension and translocation towards the deeper portion in the centre of the bay.
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Detection Limit: 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 5 5 5 5 1 1 1 5

NOTE: 0 = none detected.

Samples composited from multiple Eckman grabs.
**Other Organochlorine Compounds**

The pesticides aldrin, dieldrin and endrin (use discontinued in 1969) were detected at low levels (1 µg/kg) in surficial sediment at a few stations only (Table 1). The record of past dieldrin use was well demonstrated in a 150 mm core from station 1296 where almost 60% of the dieldrin was found in the core section from 90 to 150 mm (Figure 10). Comparison with the DDT residues discussed above illustrates the degree of persistence in soil of the two families of insecticides, since their use was curtailed at about the same time (dieldrin 1969, and DDT 1970-1972).

**Polychlorinated Biphenyls (PCB's)**

Approximately one third (33%) of the stations sampled in the Inner Bay showed detectable levels of PCB's with a mean value of 77 µg/kg and a range of 24-240 µg/kg. This mean value is comparable to that found in the Eastern Basin of Lake Erie (86 µg/kg) (26). It is greater than those found in sediments of Port Rowan harbour (53 µg/kg), Port Burwell (17 µg/kg) and Port Dover (30 µg/kg), but less than that found in Wheatley Harbour (285 µg/kg) (26). It also exceeds the Ontario Ministry of the Environment guideline for open-water disposal of dredged materials for PCB's (50 µg/kg).

The distribution of PCB's in the Inner Bay surficial sediment (Figure 11, detected residues are shown in stippled zones) follows a pattern very similar to that of fine grained sediments i.e. PCB's were detected mainly in the western portion of the bay. This pattern also reflects the strong affinity between PCB's and fine grained sediment. The use of PCB contaminated oils in road oiling for dust control (27) and atmospheric fall out of PCB's as noted under PLUARG (7) are the probable sources of PCB's in the bay. Although 15% of the stations (6 out of 39) showed levels above that recommended by the Ministry of the Environment for open water disposal of dredged spoils, stations 1282 and 1284 showed high levels of PCB's (240 µg/kg, 160 µg/kg, respectively) relative to those found in the bay. This may require future resampling. Station 1316, outside the Inner Bay, also showed high levels of PCB's (200 µg/kg) which is likely due to sources not related to Inner Long Point Bay.
Chlordane

Almost half (44%) of the 39 stations sampled for surficial sediments showed detectable levels of the cis isomer of chlordane (alpha-chlordane) with a mean of 2 µg/kg and a range of 1-5 µg/kg. The spatial distribution of alpha-chlordane in recent sediment is similar to that noted for DDT (Figure 12). In the main body of the bay the distribution suggests past fluvial input and some translocation of material to the deeper portion of the bay. Recent deposition is noted in the immediate vicinity of the outlet of Big and Dedrick Creeks (Station 1280) and the western portion of the bay.

Chlordane consists of approximately 25 to 30% cis and trans-chlordane isomers, 10 to 11% heptachlor, and the remainder of chlordene and nonachlor (28). Heptachlor itself has not been widely used in Ontario (use discontinued in 1969) and the presence of heptachlor and its metabolite heptachlor epoxide in the environment likely results from its presence in chlordane (7). This class of organochlorine insecticides is similar in persistence and activity to DDT (29).

Benzene Hexachloride (BHC)

More than half (64%) of the stations sampled in the Inner Bay showed detectable levels of benzene hexachloride with a mean value of 2 µg/kg and a range of 1-8 µg/kg. Figure 13 shows the distribution of the three isomers of benzene hexachloride (alpha, beta and gamma) in the surficial sediments of the Inner Bay. Lindane is the common name for the gamma-BHC isomer, with the commercial organochlorine insecticide consisting primarily of gamma isomers and sane alpha and beta isomers. The spatial distribution shown in Figure 13 suggests recent deposition.

Core analysis of alpha-BHC at station 1300 indicated that the surface layer (0-30 mm) accounted for 8.5% of the total residue in the 150 mm core. Total BHC increased with depth to a maximum of 44.1%, over the 120 to 150 mm depth interval (Figure 15). Core results at this site suggest a higher rate of use in the past with a decline in recent years. As for DDT, the bulk of BHC associated with suspended particulate matter from tributary input is incorporated into sediments with little exchange of particulate-associated contaminants outside of the bay.
Endosulphan

Eighteen percent (18%) of the stations sampled showed detectable levels of cis-endosulphan (trade name Thiodan I) with a mean of 2 µg/kg. Figure 14 shows the distribution of cis-endosulphan in recent sediments. With use restrictions on DDT in the early 1970's, endosulphan (an organochlorine pesticide) was substituted for the control of foliar insects on tobacco. Later, because of unacceptable high residue levels in cured tobacco leaf, it was removed from the 1975 Tobacco Production recommendations of OMAF (30). The presence of endosulphan in sediments, therefore, is a result of only a short period of use.

Beta endosulphan (Thiodan II), hexachlorobenzene (HCB), heptachlor epoxide, p,p’- DDE and Mirex were not detected above the MOE laboratory sediment detection limit of 1 µg/kg.
LIST OF REFERENCES


10. Canadian Hydrographic Service, "Lake Erie-Long Point Bay", Chart No. 2110, Department of Fisheries and Oceans, Ottawa, Canada.


FIGURE 1. Location Map of the Study Area - Inner Long Point Bay, Lake Erie.
FIGURE 2. Inner Long Point Bay Bathymetry, Contour Interval 1.0 m to IGLD (5).
FIGURE 3. Station Locations.
FIGURE 4. Seasonal Sediment Loading Characteristics, Big Creek Near Walsingham, Ontario - Stn. 02 GC007. CWS Sediment Survey Data (11).
FIGURE 5. Distribution Of Grain Size (Mean Values) In Surficial Sediment (0-30 mm), Contour Interval 0.5 PHI Units (φ).
FIGURE 7. Distribution Of Surficial Sediment (0-30mm) Based On Loss On Ignition (%), Contour Interval 1%.
FIGURE 8. Stations At Which Levels Of PCB's, DDD, DDT And Chlordane Were Detected In Surficial Sediment.
FIGURE 9. Distribution Of DDT And Its Metabolites in Surficial Sediment (0-30mm), Contour Interval 5 µg/kg.
FIGURE 10. Core Analysis, \( \Sigma \) DDT, Dieldrin And Lindane At Three Selected Stations.
FIGURE 11. Distribution Of Polychlorinated Biphenyls (PCB'S) In Surficial Sediment (0-30mm), Contour Interval 20 µg/kg.
FIGURE 12. Distribution of cis-Chlordane In Surficial Sediment (0-30 mm), Contour Interval 1 µg/kg.
FIGURE 13. Distribution Of Benzene Hexachloride (BHC) In Surficial Sediment (0-30mm), Contour Interval 1 µg/kg.
FIGURE 14.  Distribution of cis- Endosulphan in Surficial Sediment (0-30 mm), Contour Interval 1 µg/kg.