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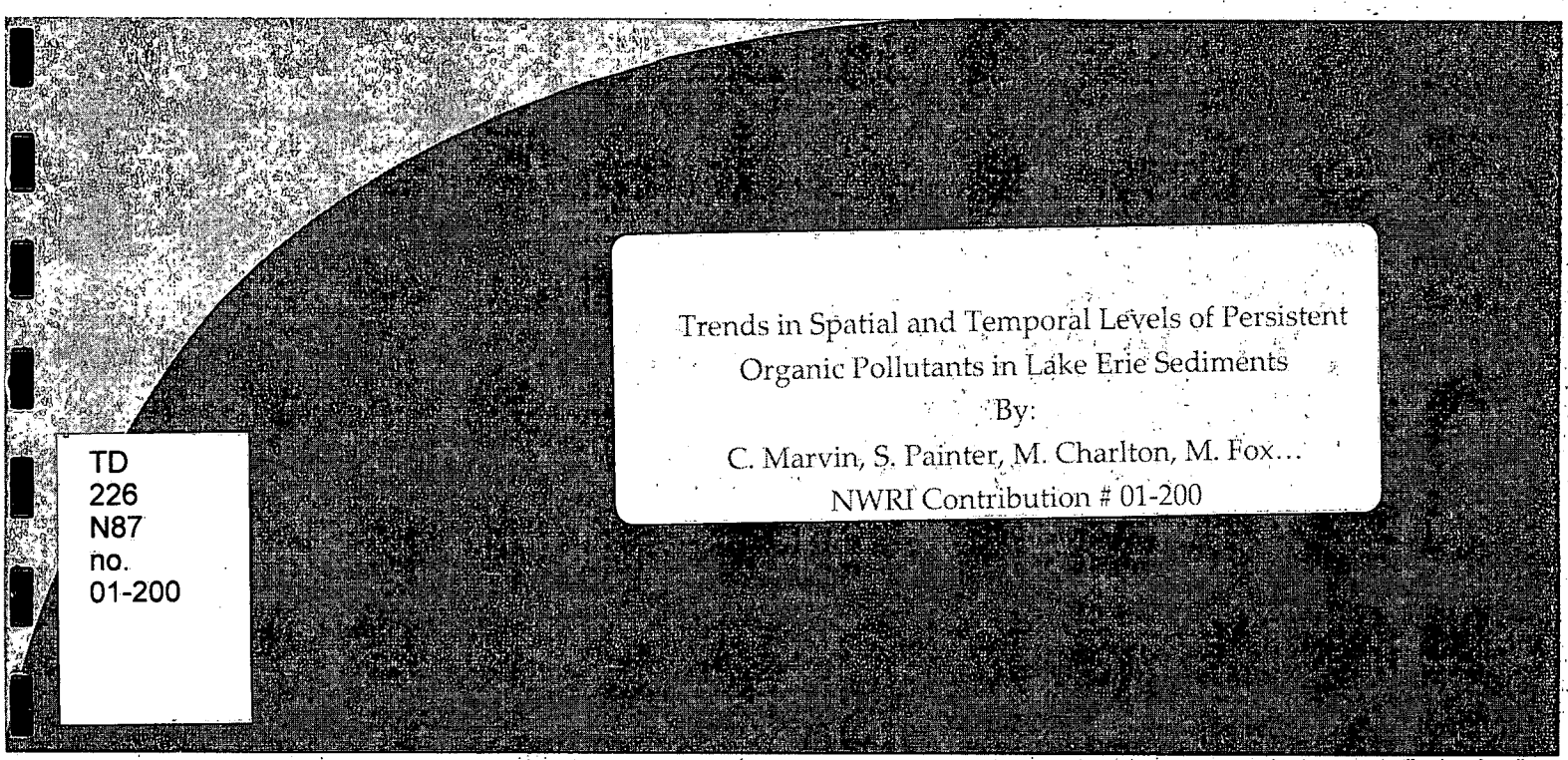

Trends in Spatial and Temporal Levels of Persistent Organic Pollutants in Lake Erie Sediments

By:

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NWRI Contribution # 01-200

01-200

## MANAGEMENT PERSPECTIVE

- **Title:** Trends in Spatial and Temporal Levels of Persistent Organic Pollutants in Lake Erie Sediments.

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- **NWRI Publication #:** 01-200
- **Citation:**

- **EC Priority/Issue:** This work was done under Great Lakes 2000 in collaboration with Ontario Region as part of the Environment Canada Lower Lakes Sediment Monitoring Programme. This work supports the NWRI Nature Business Line result of understanding and reducing human impacts on the health of ecosystems.

- **Current Status:** Lake Erie sediment surveys were conducted in 1997 and 1998 to characterize spatial and temporal trends in contamination and for comparison with historical levels to assess the degree of improvement in environmental quality since the advent of measures to reduce sources. These surveys were also designed to assist in the identification of possible sources of contamination and areas where contamination exceeded Canadian sediment quality guidelines for the protection of aquatic biota. Lakewide sediment contaminant concentrations were found to have significantly decreased from levels observed in samples collected in 1971 in previous Environment Canada surveys. This trend was also evidenced by contaminant profiles of core samples from all three major basins. There was a lakewide spatial trend in increasing sediment contamination from the eastern basin to the western basin, and from the north-central basin to the south-central basin. Sediments in many areas of Lake Erie still exceeded Canadian Federal and Provincial guidelines. However, exceedances of sediment guidelines describing contaminated environments in

1997/98 were largely restricted to the western basin and the southern portion of the central basin. Exceedances of Canadian Sediment Quality probable effects guidelines were most numerous for dioxins and furans followed by mercury. The Canadian threshold effects guideline for polychlorinated biphenyls (PCBs) and the Provincial lowest effect guideline were exceeded at 50% and 21% of the sites, respectively.

- Next Steps: Publish in a scientific journal and communicate to Lake Erie LaMP process.

**Tendances spatiales et temporelles dans les teneurs en polluants organiques persistants des sédiments du lac Érié**

C.H. Marvin, S. Painter, M. Charlton, M. Fox (ret) et L. Thiessen

## SOMMAIRE À L'INTENTION DE LA DIRECTION

On a réalisé cette étude dans le cadre du Programme de surveillance des sédiments des Grands Lacs inférieurs d'Environnement Canada (Grands Lacs 2000), en collaboration avec la Région de l'Ontario. Cette étude, qui doit faciliter la compréhension des répercussions sur l'état des écosystèmes et leur réduction, répond aux objectifs du secteur d'activité Nature de l'INRE.

Les relevés des sédiments du lac Érié effectués en 1997 et en 1998 ont permis de caractériser les tendances spatiales et temporelles de la contamination et d'effectuer des comparaisons avec des valeurs historiques afin d'évaluer le degré d'amélioration de la qualité de l'environnement depuis qu'on a pris des mesures visant à réduire les sources de cette contamination. On a également conçu ces relevés afin de faciliter l'identification des sources possibles de contamination et des points où la contamination dépassait les limites des Recommandations canadiennes pour la qualité des sédiments, destinées à protéger le biote aquatique. On a constaté que les concentrations panlacustres de contaminants des sédiments présentent des baisses significatives par rapport aux teneurs mesurées dans des échantillons prélevés en 1971, lors de relevés antérieurs d'Environnement Canada. On a également mis en évidence une tendance semblable dans les profils des contaminants des carottes prélevées dans les trois principaux bassins. On observait une autre tendance spatiale panlacustre : une augmentation de la contamination des sédiments d'est en ouest et du centre-nord au centre-sud du bassin. Dans de nombreux secteurs du lac Érié, les teneurs des sédiments dépassaient encore les limites fédérales et provinciales canadiennes. Toutefois, ces dépassements correspondant aux milieux contaminés en 1997-1998 se limitaient principalement aux portions ouest et sud du centre du bassin. Par rapport aux limites des Recommandations canadiennes pour la qualité des sédiments, les dépassements des dioxines et des furanes étaient les plus nombreux, et ceux du mercure venaient en deuxième place. Les limites des recommandations canadiennes pour les effets de seuil des polychlorobiphényles (PCB) et les limites provinciales (plus faible concentration avec effet) étaient dépassées à 50 et à 21 % des sites, respectivement.

On doit publier ces résultats dans une publication scientifique et les communiquer au programme du Plan d'aménagement panlacustre du lac Érié.

**Résumé**

En 1997, on a effectué un relevé des sédiments du lac Érié afin de caractériser les tendances spatiales de la contamination et de comparer les valeurs historiques, afin d'évaluer le degré d'amélioration de la qualité de l'environnement depuis qu'on a qu'on a pris des mesures visant à réduire les sources de contaminants. On a également conçu ce relevé de façon à faciliter l'identification des sources possibles de contamination et des points où la contamination dépassait les limites des Recommandations canadiennes pour la qualité des sédiments, destinées à protéger le biote aquatique. On a noté une baisse significative des concentrations panlacustres de contaminants comme les polychlorobiphényles (PCB) et divers composés organochlorés, notamment les métabolites de l'hexachlorobenzène, de l'á-HCH et du DDT, par rapport aux valeurs des échantillons prélevés en 1971. On a constaté que les teneurs panlacustres moyennes en PCB des sédiments avaient chuté de 136 à 43 ng/g de 1971 à 1997. On observait également une autre tendance spatiale panlacustre, l'augmentation de la contamination des sédiments d'est en ouest et du centre-nord au centre-sud dans le bassin. Dans certains secteurs du lac Érié, les teneurs en contaminants organiques des sédiments dépassaient encore les limites du gouvernement fédéral du Canada et les limites provinciales de l'Ontario. Toutefois, les dépassements des limites des sédiments correspondant à des milieux contaminés en 1997 se limitaient en grande partie aux portions ouest et sud du centre du bassin. Les limites des recommandations canadiennes pour les effets de seuil des PCB (34,1 ng/g) et les limites de l'Ontario (plus faible concentration avec effet – 70 ng/g) étaient dépassées à 50 et à 21 % des sites, respectivement.

# Trends in Spatial and Temporal Levels of Persistent Organic Pollutants in Lake Erie Sediments

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**Abstract**

A Lake Erie sediment survey was conducted in 1997 to characterize spatial trends in contamination and for comparison with historical levels to assess the degree of improvement in environmental quality since the advent of measures to reduce contaminant sources. This survey was also designed to assist in the identification of possible sources of contamination and areas where contamination exceeded Canadian sediment quality guidelines for the protection of aquatic biota. Lake-wide contaminant concentrations of polychlorinated biphenyls (PCBs) and a variety of organochlorine compounds including hexachlorobenzene, α-HCH and the DDT metabolites were found to have significantly decreased from levels in samples collected in 1971. Lakewide average sediment PCB levels were found to have decreased from 136 ng/g in 1971 to 43 ng/g in 1997. There was a lake-wide spatial trend in increasing sediment contamination from the eastern basin to the western basin, and from the north-central basin to the south-central basin. Levels of organic contaminants in sediments in some areas of Lake Erie still exceeded Canadian Federal and Ontario Provincial guidelines. However, exceedances of guidelines describing contaminated environments in 1997 were predominately restricted to the western basin and the southern portion of the central

basin. The Canadian threshold effects level guideline for PCBs (34.1 ng/g) and the Ontario Provincial lowest effect guideline (70 ng/g) were exceeded at 50% and 21% of the sites, respectively.

**INDEX WORDS**: Lake Erie, polychlorinated biphenyls, organochlorines, pesticides, sediment, polycyclic aromatic hydrocarbons

## INTRODUCTION

The presence of persistent and bioaccumulative pollutants can adversely impact Great Lakes ecosystems, wildlife, and biodiversity. Knowledge of occurrence and spatial distribution of toxic substances can further understanding of the role anthropogenic activities in releasing these compounds to the environment, and provide information to assist in devising effective strategies to mitigate potential health effects. Environment Canada conducted a survey in Lake Erie in 1971 to characterize the spatial extent of sediment contamination by metals and organochlorine contaminants (Frank et al. 1977, Thomas and Jaquet, 1976, Thomas et al., 1976). Sediment levels of metals including total mercury, lead, zinc, cadmium and copper were compared to pre-colonial concentrations. Levels of contaminants including mercury, PCBs and DDT were elevated in the western basin adjacent to the outflow of the Detroit River. Sources of PCBs were also apparent along the southern shore of Lake Erie while dieldrin appeared to have sources along both the southern and northern shores. A core sample from the western basin showed that PCBs and other organochlorine contaminants began to significantly accumulate in Lake Erie sediments during the mid-1950s. In general, sediments in the western basin of Lake Erie exhibited high levels of contamination while sediments in the central and eastern basins exhibited levels intermediate between those in the western basin and lower levels

in Lake St. Clair sediments.

In 1995, Environment Canada revisited 50 of the original 259 sites from the 1971 survey. The 1995 sediment samples, as well as archived 1971 samples, were analyzed for PCBs and other organochlorines. The PCB and organochlorine pesticide concentrations had decreased considerably from those reported in 1971. Environment Canada conducted an additional Lake Erie survey in 1997 to enable a broader range of analyses for the assessment of current sediment contamination relative to sediment quality guidelines, and to further assess the improvement in sediment contaminant conditions from the original 1971 survey (Painter et al. 2001). This paper presents an overview of the spatial distribution of sediment contamination by persistent organic pollutants in Lake Erie, and a temporal characterization for selected compounds through a comparison of data from the 1971 and 1997 surveys.

## METHODS

### *Sample collection*

Surficial sediment samples were collected aboard the CCGS Limnos in 1997 from sixty-three locations using a mini box core sampling procedure (Figure 1). The top 3 cm of the sediment were sub-sampled for the analyses of chlorinated organic contaminants, total metals, grain size, and nutrients. At three index stations, one in each of the western, central, and eastern basins, both mini box core and benthos gravity core samples were obtained for sub-sampling for surficial sampling and sampling with sediment depth. Mini box cores were sub-sampled every 1 cm from 0 to 15 cm, every 2 cm from 16 to 30 cm and every 5 cm to 40 cm. Samples for organic contaminant analyses were collected in pre-washed glass jars. Samples for other characterizations were collected in either

polypropylene or teflon jars. All samples were frozen immediately for transport to the laboratory.

*Analyses*

Frozen sediment samples were thawed, followed by air-drying of 5-gram subsamples. Dry sediment samples were extracted in dichloromethane at 100°C and 2,000 psi using an Accelerated Solvent Extractor (ASE, Dionex Inc.). Solvent extracts were gently reduced in volume under nitrogen to a final volume of 1 mL in iso-octane. Extracts were then subjected to an open-column deactivated Florosil [2g] cleanup procedure. Elution of the column with 10 mL 50% pentane in dichloromethane [fraction A] followed by 10 mL dichloromethane [fraction B] afforded two fractions for analysis. Fraction A was treated with mercury to remove sulphur.

Analyses for PCBs and other organochlorine compounds were carried out on a Hewlett-Packard Model 5890 gas chromatograph equipped with dual columns (0.25 mm i.d. 0.25 μm thickness DB-5 and a 0.25 mm i.d. 0.25 μm thickness HP-50) and dual electron capture detectors. Method blanks and standard reference materials (SRMs) were processed with each set of 10 field samples. Surrogate standards applied to sediment prior to extraction included PCB #30, PCB #204, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and δ-BHC. An external calibration method was employed for quantitation using individual organochlorine standards and a 132-congener PCB standard from the National Laboratory for Environmental Testing, Environment Canada. Total PCB values were expressed as the sum of the following congeners, numbered according to the method of Ballschmiter and Zell (B/Z #): B/Z# 16, 24, 28, 31, 32, 44, 52, 74, 87, 99, 101, 110, 118, 138, 149, 163, 174, 180, 182, 187, 194, 195, 201 and 206.

Polycyclic aromatic hydrocarbons (PAHs) were analyzed on a 0.25 mm i.d. 0.25 μm thickness DB-5 column using a Hewlett Packard Model 5890 Series II gas chromatograph equipped with a Model 5971A mass selective detector. The instrument was operated in selective ion monitoring (SIM) mode with a 1μL on-column injection. Sediment samples were spiked with a laboratory standard containing four polycyclic aromatic hydrocarbons including naphthalene-$d_8$, fluorene-$d_{10}$, pyrene-$d_{10}$ and benzo[a]pyrene-$d_{12}$. Spike recoveries, exclusive of naphthalene-$d_8$, were typically greater than 80%. Method blanks were carried through the complete sample preparation and analysis procedures. Between-run reproducibilities were typically 10%. Total PAH values were calculated based on the sum total of the individual concentrations of the following compounds: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]pyrene, perylene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene.

## RESULTS AND DISCUSSION

### *Polychlorinated Biphenyls*

Total polychlorinated biphenyl (PCB) concentrations in 1997 showed a lake-wide decrease since 1971 (Figure 2). This decreasing temporal trend was common among a number of contaminant classes including polychlorinated dibenzo-p-dioxins and dibenzofurans, and trace metals including mercury (Painter et al. 2001). Levels of PCBs reported for the 1971 survey resulted from analysis of frozen sediment archived by Frank et al. (1977), therefore, the data for both 1997 and 1971 were generated using the same protocol thereby enabling a direct comparison that was not influenced by differences in

analytical methodology. Total PCB values were calculated as the sum total concentrations of the 24 most predominant congeners in Lake Erie sediment. Analysis of a subset of samples (N=6) showed that the total PCB values based on the sum of the24 individual congeners reported in this study represented 54 ± 2.7% of the total PCB value based on the sum of 131 individual congeners, quantitated using a dual-column method and a mixed congener analytical standard obtained from the National Laboratory for Environmental Testing (Environment Canada).

Levels of sediment PCB contamination decreased roughly three-fold from a lake-wide average value of 136 ng/g in 1971 to 43 ng/g in 1997. The spatial trend in PCB contamination for the 1997 data set was toward increasing values from the eastern basin to the western basin, and from the northern area to the southern area of the central basin. The spatial trend for the 1971 data exhibited higher relative PCB levels in some deeper water areas of the eastern basin, compared to the 1997 data set. Frank et al. (1977) did not observe a significant decrease in PCB contamination from the central to the eastern basins in their 1971 survey. The processes through which PCB contamination declined over the period 1971 to 1997 did not influence the profiles of the predominant congeners, which were observed to remain quite consistent (Figure 3). However, in general the individual percentage contributions of the lower molecular weight congeners (B/Z numbers less than 118) to the total PCB burden was greater for the 1971 samples, compared to those collected in 1997.

None of the stations surveyed in 1997 exceeded the Canadian Sediment Quality proposed probable effect level (PEL, 277 ng/g dry wt) guideline for the protection of aquatic biota for total PCBs, compared to 3 sites in proximity to the mouth of the Detroit

River that exceeded this guideline value in 1971. In 1997, 29 sites (51% of stations) exceeded the Canadian threshold effect level (TEL, 34.1 ng/g) and 12 sites (21% of stations) exceeded the Ontario Provincial lowest effect level (LEL, 70 ng/g). The sites exceeding the Ontario Provincial LEL were in the western basin and southern portion of the central basin.

Temporal trends in total PCB contamination were further defined through analyses of core samples (Figure 4). The western basin (station 1085) core profile was the most distinct; there was a marked increase in contamination from the bottom of the core (30 cm depth) to a depth of approximately 20 cm. This interval represented a period of time ranging mid-1950s through the 1960s, based on $^{210}Pb$ dating. Relatively consistent total PCB levels were detected to a depth of approximately 6 cm where concentrations began a trend toward decreasing levels to the top of the core. The horizon for total PCB contamination in the central basin (Station 1098) core occurred at the 17-18 cm interval. There was a bimodal distribution in the central basin core profile, and a trend towards decreasing total PCB contamination in the top 6 cm of the core similar to the profile in the western basin core. The eastern basin (Station 1040) core profile was more difficult to interpret; levels of total PCBs in this core were relatively consistent with depth at a level we have judged to be representative of ambient background levels.

The overall temporal decrease in PCB contamination of Lake Erie sediments was consistent with reports that the number and magnitude of PCB sources to the Great Lakes has decreased 20-fold since the 1970s (Froese et al. 1997), and that sources of contamination have become limited primarily to atmospheric deposition and localized point-source emissions. The Integrated Atmospheric Deposition Network (IADN)

estimated a decrease in wet and dry atmospheric PCB loadings to Lake Erie from 180 Kg in 1988 to 34 Kg in 1996 (United States Environmental Protection Agency, 2000 and Hoff et al., 1996). The high number of exceedances of sediment guideline values in the western basin indicated that the Detroit River continues to be a primary vector for PCB contamination in this area of Lake Erie (Stevens and Neilson, 1989). Froese et al. (1997) estimated that 600 Kg PCBs/year were transported through the Trenton Channel in the Detroit River into the western basin, of which greater than 98% originated from upstream sources. This loading represented a potential decrease from 1,500 Kg/year in 1988.

The Detroit River may also have influenced the trend toward higher PCB levels in the southern area of the central basin, compared to the northern area. Frank et al. (1977) reported that sediment-bound contaminants, including PCBs, tended to move south from the Detroit River in a counter-clockwise pattern across the Sandusky Basin in the area south of Pelee Island. Elevated PCB levels along the southern shore of the central basin may also have been influenced by inputs from heavily industrialized areas including Cleveland and Ashtabula. In contrast to the 1971 survey, we found no evidence that PCBs transported from the western basin and southern areas of the central basin are ultimately deposited in significant amounts in the eastern basin. All sediments collected in 1997 from stations east of a boundary running south from Long Point to Presque Isle Bay exhibited low PCB levels (Figure 2). Concentrations of total PCBs in recently deposited lakebed and streambed sediments within the Lake Erie – Lake St. Clair drainages are highest in heavily urbanized and industrialized watersheds including those of the Detroit River, the Clinton River, the Maumee River, and the Cuyahoga River

(Myers et al. 2000). These major tributaries heavily influence the western basin and south-central basin areas of Lake Erie, where sediment PCB values are highest.

***Hexachlorobenzene and Hexachlorocyclohexanes***

Spatial trends in organochlorine contamination in Lake Erie sediments were generally similar to those observed for PCBs, with the highest levels confined to stations in the western basin and the southern area of the central basin. Figures 5 and 6 show the comparisons of levels of alpha-hexachlorocyclohexane (α-HCH) and hexachlorobenzene (HCB) between 1971 and 1997; surficial sediment concentrations of both these compounds were found to have decreased substantially. In the case of both α-HCH and HCB, the data presented reflect a comparison between samples collected in 1997 and frozen archived samples from the 1971 survey analyzed using the same methodology. All stations sampled in 1997 exhibited lower levels of HCB, compared to 1971. The highest HCB concentration determined in the 1997 survey was 12 ng/g at a station near the outflow of the Detroit River. Two stations in this same area sampled in 1971 exhibited concentrations of 31 ng/g and 60 ng/g (Figure 6). The majority of HCB entering Lake Erie has been attributed to waterborne inputs (Cohen et al. 1985). Oliver and Bourbonniere (1985) found HCB levels in western Lake Erie basin sediments collected in 1982 to range from 4.6 ng/g to 17 ng/g. The authors also identified the St. Clair River as a major vector for HCB contamination. In general, levels of α-HCH in Lake Erie surficial sediment also decreased over the period 1971 to 1997. As with HCB, the highest individual sediment concentrations were detected in samples from stations influenced by discharges from the Detroit River. According to air monitoring data, atmospheric deposition continues to result in a net loading of both α-HCH and γ-HCH to

Lake Erie, however, deposition estimates have shown a temporal trend toward decreasing values (Hoff et al., 1996).

The spatial distribution of gamma-hexachlorocyclohexane (γ-HCH, lindane) in Lake Erie sediments in 1997 is shown in Figure 7. γ-HCH concentrations were higher than α-HCH concentrations at almost all stations. The lake-wide average sediment concentration for α-HCH was 0.75 ng/g, compared to an average for γ-HCH of 2.1 ng/g, resulting in a ratio of the alpha to gamma isomers of 0.36. These data provided no evidence of significant bio-isomerization of γ-HCH to α-HCH. McConnell et al. (1992) estimated that annual air deposition for γ-HCH was roughly 10-fold higher than for α-HCH. Ridal et al. (1996) estimated net loadings of γ-HCH to the Great Lakes over the period May to October, in contrast to a net volatilization of α-HCH for the same time period. In addition, γ-HCH is currently registered and widely used in agricultural applications in both Canada and the United States, primarily as a seed treatment. Annual usage of lindane in the United States was reported to decrease from 268 tonnes to 114 tonnes over the period 1980 to 1990, while usage in Canada increased from 200 tonnes to 284 tonnes over the same period (Li et al. 1996). Waite et al. (2001) estimated that 510,000 kg of lindane was applied in the Canadian prairies during 1998. The Environment Canada Open Lakes Surveillance Program has determined that lindane deposition from precipitation decreased from 1984 to 1990 but has remained unchanged since 1990. In addition, lindane concentrations in Great Lakes surface water in 1995 were highest in the western basin of Lake Erie, compared to Lakes Superior and Ontario (Williams et al. 1998). Figure 7 shows γ-HCH sediment concentrations in relation to Canadian Federal and Ontario Provincial sediment guideline values. Over 50% of the

stations exceeded the Canadian PEL for γ-HCH (1.38 ng/g); this percentage represented the highest value calculated for any contaminant in Lake Erie sediments. The accumulation of γ-HCH was further studied through analysis of a box core from a site in the western basin (Figure 8). The core profile lacked a distinct trend and sediment concentrations were fairly consistent from the surface to a depth of roughly 20 cm. Levels of γ-HCH below 25 cm were roughly 3-fold less than the surficial concentrations.

*Dieldrin*

Dieldrin is one of the most frequently detected contaminants in fish collected from areas of the Lake Erie – Lake St. Clair drainages within the United States (Myers et al. 2000). The distribution of dieldrin in Lake Erie sediments was similar to that of other organochlorine contaminants (Figure 9). However, the lake-wide average of 3.7 ng/g was approximately 3-fold higher than the value determined by Frank et al. (1997) for the 1971 survey in which dieldrin was analyzed using a packed-column GC method. Roughly 50% of the stations in the 1997 survey exceeded the Canadian TEL (2.85 ng/g) for dieldrin while 14% exceeded the PEL (6.67 ng/g). Exceedances of the PEL were restricted to sites in the western basin in proximity to the Detroit River, a site in the Sandusky Basin, and some near-shore stations along the southern shoreline of the central basin. Air monitoring data from IADN showed precipitation concentrations of dieldrin at the Lake Erie site were three-to-four-fold higher compared to other Great Lakes sites (Hoff et al. 1996). This observation has been attributed to historically high usage rates of dieldrin in agricultural areas of the Lake Erie watershed (USEPA, 2000). The Environment Canada Open Lakes Surveillance Program determined surface water concentrations of dieldrin in the western basin of Lake Erie in 1994 to be clearly

elevated, compared to Lakes Superior and Ontario; dieldrin concentrations ranged from 0.18 ng/L to 0.76 ng/L (Williams et al. 1998). The highest concentration (0.76 ng/L) was detected near the outflow of the Maumee River. The accumulation of dieldrin determined from analysis of a box core from the western basin is shown in Figure 10. There was a distinct trend toward increasing concentrations of dieldrin with decreasing depth. A similar profile for dieldrin was also observed in a core from southern Lake Michigan (Golden, 1994). As a result of this observation, we are further investigating spatial and temporal trends in dieldrin accumulation in Lake Erie sediments using box cores from a series of index stations.

***DDT***

The DDT compounds are prevalent in sediments in the Lake Erie – Lake St. Clair drainages (Myers et al. 2000). These compounds have also been found to bioaccumulate in fish, but tissue guideline level exceedances (according to New York State Department of Environmental Conservation values) were fewer than for PCBs. The highest levels of DDT were detected in fish in areas characterized by urban and mixed land use patterns, including the Cuyahoga River at Cleveland, Ohio (Myers et al. 2000). The spatial distributions of p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE in Lake Erie sediments are shown in Figures 11, 12 and 13, respectively. Data presented for the 1971 survey were taken from Frank et al. (1977), and do not enable a direct comparison of values generated using the same analytical methodology. The parent p,p'-DDT was detected at lower concentrations than the metabolites in both 1971 (lake-wide average of 1.6 ng/g) and 1997 (lake-wide average of 1.8 ng/g). There was also an absence of any definitive spatial trend in DDT contamination. Spatial trends in p,p'-DDD and p,p'-DDE

in 1971 were similar to that of PCBs, including some relatively high levels in deep-water areas of the eastern basin. Lake-wide average concentrations p,p'-DDD (11.5 ng/g) and p,p'-DDE (8.8 ng/g) in 1971 were substantially higher than corresponding averages in 1997 which were 2.2 ng/g and 4.0 ng/g, respectively. As with PCBs, a trend toward increased levels contamination from the eastern basin to the western basin was evident for p,p'-DDE, however, this trend was not apparent for p,p'-DDD. Figure 14 shows the cumulative concentration of total DDT with depth in a box core from a station in the western basin. The core profile and relative amounts of p,p'-DDT, p,p'-DDE and p,p'-DDD were similar to those reported by Oliver et al. (1989) for a core from the Rochester basin of Lake Ontario. As was observed in the surficial sediment samples, the anaerobic metabolite p,p'-DDD was most predominant, followed by the aerobic metabolite p,p'-DDE. Concentrations of the parent DDT in the core were very low compared to the metabolites. Peak concentrations of total DDT were observed at a depth of 24 cm that corresponded to an approximate date of 1955 to 1960, based on $^{210}Pb$ dating methods.

***Polycyclic Aromatic Hydrocarbons***

Polycyclic aromatic hydrocarbons (PAHs) are among the most prevalent contaminants in stream bed and river sediments in the Lake Erie – Lake St. Clair drainages (Myers et al. 2000), being detected in roughly 55% of all samples collected in the drainages by the United States Geological Survey over the period 1990 – 1997. Figure 15 shows the spatial distribution of total PAHs in Lake Erie sediments. Spatial trends for PAHs were not as apparent as for organochlorine contaminants, presumably due to the multitude of rural and urban sources of these ubiquitous compounds. However, the highest concentrations were observed at sites in the western basin and

along the southern shoreline. Two sites near the outflow of the Cuyahoga River at Cleveland, Ohio exhibited total PAH values that exceeded the Ontario Provincial LEL. Figure 16 shows the distribution of benzo[a]pyrene, which is among the most biologically active PAHs. One site on the southern shoreline exhibited a concentration of benzo[a]pyrene that exceeded the Canadian Federal PEL (782 ng/g). Accumulation of PAHs in Lake Erie sediments was further studied through analysis of core samples from each of the major lake basins (Figure 17). Trends in the core profiles were generally similar for all three basins. The western basin box core (station 1085) profile exhibited a trend toward increasing concentrations from the bottom of the core to maximum concentrations at a depth range of 15 cm to 20 cm followed by a trend toward decreasing concentrations to the surface. The central basin benthos core (station 1098) profile exhibited a dramatic increase in PAH contamination over a depth interval of 35 cm to 45 cm, relatively constant levels to approximately 15 cm, and then a trend toward decreasing levels to the surface. The profile for the eastern basin box core (station 1040) was less distinct, but exhibited a general trend toward decreasing PAH contamination from the bottom of the core to the surface.

***Other Contaminants***

Chlordane is frequently detected in fish within the Lake Erie – Lake St. Clair drainages (Myers et al. 2000). The spatial distribution of total chlordane in Lake Erie surficial sediments is shown in Figure 18. With only one exception offshore of the western Ohio shoreline, exceedances of the Canadian TEL of 4.50 ng/g were restricted to four stations in the western basin. There were no apparent spatial trends in chlordane in the central and eastern basins. The distribution of total endosulfan, a current-use

insecticide, was similar to that of most organochlorine pesticides and exhibited a trend toward elevated levels in the western basin and along the southern shoreline (Figure 19). Myers et al. (2000) estimated that roughly 2,000 pounds of endosulfan was applied in the Lake Erie – Lake St. Clair drainages during 1994 – 1995.

## SUMMARY

Spatial trends in sediment contamination in Lake Erie were generally similar for most compound classes, including total PCBs. In general, there was a trend toward decreasing contamination from the western basin to the eastern basin, and from the northern area of the central basin to the southern area of the central basin. The spatial data when considered in its entirety provides compelling evidence that the Detroit River continues to be a primary vector for contamination in Lake Erie, and particularly the western basin. In the case of the Detroit River, sources of these contaminants may lie both with the river proper and the upper Great Lakes and connecting channels. In addition, the observed lake-wide trends were presumably influenced by industrial activities in the watersheds along other major tributaries, and areas along the southern shoreline. Other major influences in the observed trends may have included atmospheric deposition, prevailing currents, sediment transport and deposition processes, open-lake disposal of dredged material, and remediation of contaminated areas. Frank et al. (1977) reported that trends in total PCB and total mercury contamination in the western basin were attributable to the outflow from the Detroit River in west bank, center bank and east bank water masses. We were unable to infer any such source information in this study due to the decreased sampling intensity, compared to the 1971 study. However, Environment Canada monitoring of suspended sediment quality in Lake Erie has shown

that the western basin continues to be subjected to active loadings of several classes of contaminants, including PCBs and dioxins and furans. The Detroit River has been identified as a primary source of these contaminants, but significant loadings from other tributaries cannot be discounted.

Levels of most contaminants in Lake Erie sediments were found to have decreased significantly over the period 1971 to 1997. Levels of sediment PCB contamination were found to have decreased roughly three-fold from a lakewide average value of 136 ng/g in 1971 to 43 ng/g in 1997. This temporal trend was also evidenced by profiles of core samples from the three major basins. Core profiles of dieldrin and lindane did not indicate a trend toward decreasing temporal values which made these contaminants unique among the organochlorines, however, these observations were similar to those reported in studies of other Great Lakes. Sediments in many areas of Lake Erie still exceeded the strictest Canadian and Province of Ontario Sediment Quality Guideline as defined by the threshold effect level (TEL) and lowest effect level (LEL), respectively. However, exceedances of Canadian and Ontario Provincial sediment guidelines describing contaminated environments in 1997 were largely restricted to the western basin, and the southern area of the central basin. The Canadian TEL for PCBs and the Province of Ontario LEL were exceeded at 50% and 21% of the sites, respectively. PCBs are among the contaminants primarily responsible for the fish consumption advisories in Lake Erie.

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## LIST OF FIGURES

**Figure 9.** Lake Erie surficial sediment dieldrin concentrations (ng/g dry wt.) in samples collected in 1997. Canadian Sediment Quality threshold effect level (TEL) = 2.85 ng/g, probable effect level (PEL) = 6.67 ng/g, Ontario Provincial Sediment Quality lowest effect level (LEL) = 2.00 ng/g.

**Figure 10.** Profile of dieldrin in a sediment box-core sample collected in the western basin of Lake Erie. All concentrations expressed in ng/g dry weight.

**Figure 11.** Lake Erie surficial sediment total p,p'-DDE concentrations (ng/g dry wt.) in samples collected in 1971 and 1997. Canadian Sediment Quality threshold effect level (TEL) = 1.42 ng/g, probable effect level (PEL) = 6.75 ng/g.

**Figure 12.** Lake Erie surficial sediment total p,p'-DDD concentrations (ng/g dry wt.) in samples collected in 1971 and 1997. Canadian Sediment Quality threshold effect level (TEL) = 3.54 ng/g, probable effect level (PEL) = 8.51 ng/g.

**Figure 13.** Lake Erie surficial sediment total p,p'-DDT concentrations (ng/g dry wt.) in samples collected in 1971 and 1997. Canadian Sediment Quality threshold effect level (TEL) = 1.19 ng/g, probable effect level (PEL) = 4.77 ng/g.

**Figure 14.** Cumulative concentrations of DDT representing the sum totals of o,p'-DDT, p,p'-DDT, p,p'-DDE and p,p'-DDD in a sediment box-core sample collected in the western basin of Lake Erie. All concentrations are expressed in ng/g dry weight.

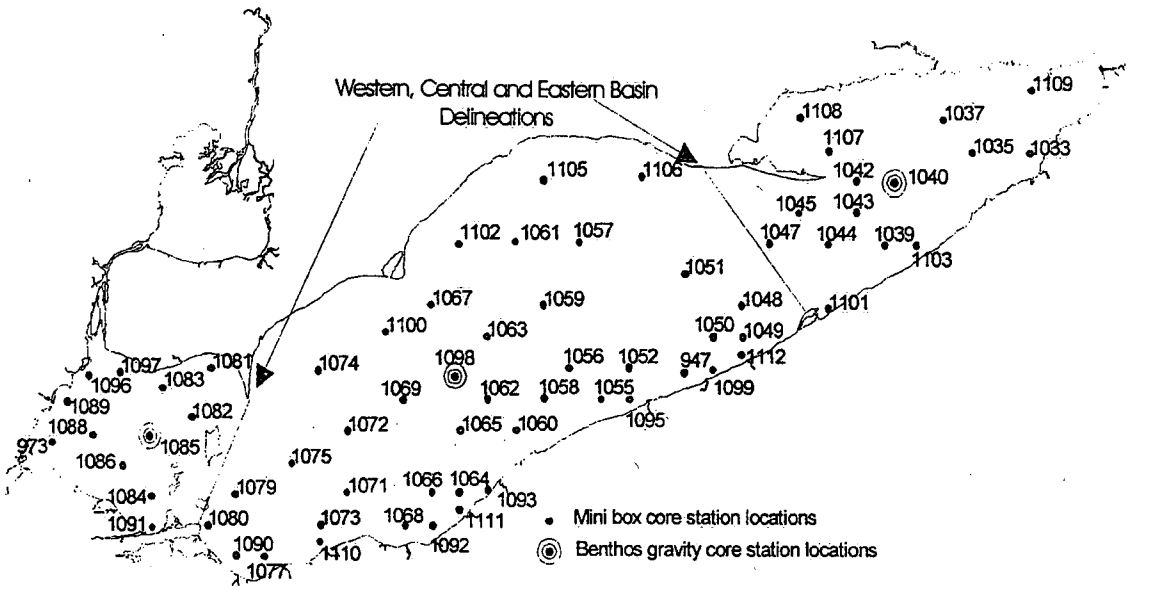
**Figure 15.** Lake Erie sediment total PAH concentrations (ng/g dry wt.) in samples collected in 1997. Ontario Provincial lowest effect level (LEL) = 4,000 ng/g.

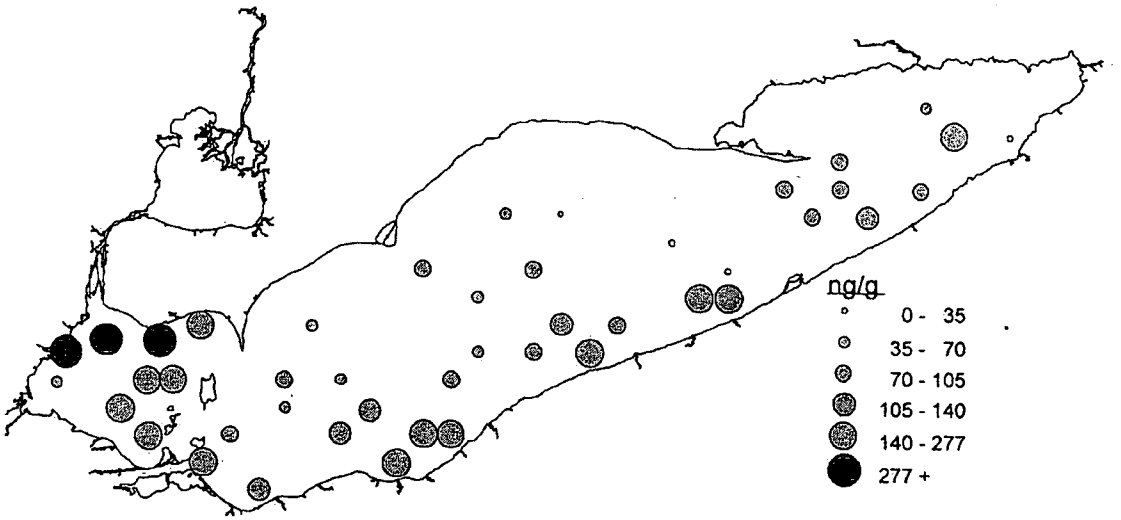
**Figure 16.** Lake Erie sediment benzo[a]pyrene concentrations (ng/g dry wt.) in samples collected in 1997. Canadian Sediment Quality threshold effect level (TEL) = 31.9 ng/g, probable effect level (PEL) = 782 ng/g, Ontario Provincial lowest effect level (LEL) = 370 ng/g.

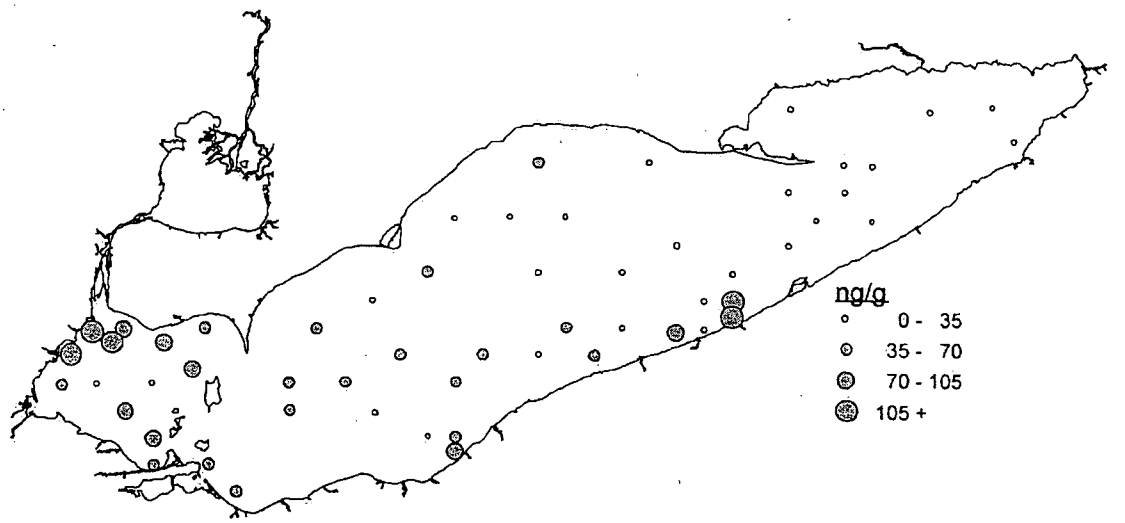
**Figure 17.** Profiles of polycyclic aromatic hydrocarbons in Lake Erie sediment box-core samples (western basin station 1085 and eastern basin station 1040) and benthos core samples (central basin station 1098). All concentrations expressed in ng/g dry weight.

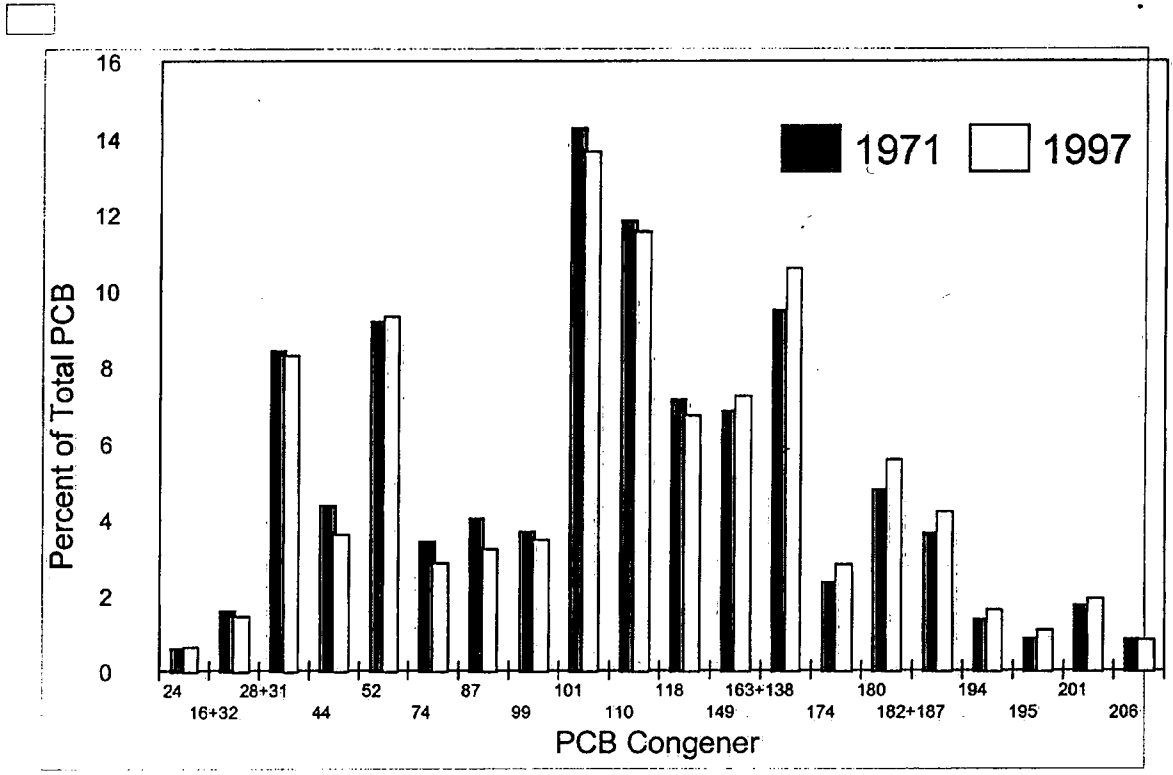
**Figure 18.** Lake Erie surficial sediment total chlordane concentrations (ng/g dry wt.) in samples collected in 1997. Canadian Sediment Quality threshold effect level (TEL) = 4.50 ng/g, probable effect level (PEL) = 8.87 ng/g.

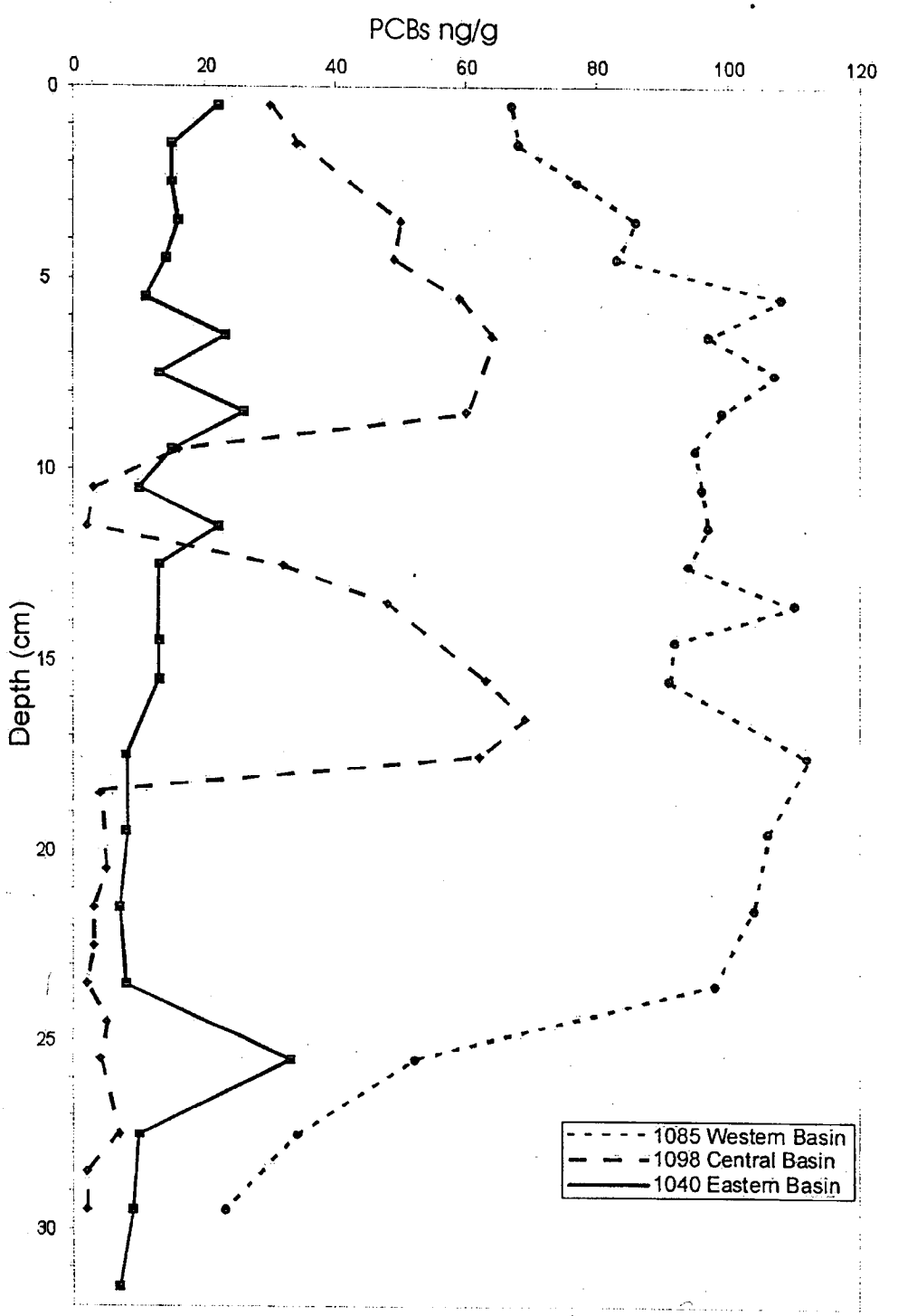
**Figure 19.** Lake Erie surficial sediment total endosulfan concentrations (ng/g dry wt.) in samples collected in 1997.


Western, Central and Eastern Basin Delineations
1109
1108
1037
1107
1035
1033
1105
1106
1042
1040
1045
1043
1102
1061
1057
1047
1044
1039
1103
1051
1067
1059
1048
1101
1100
1063
1050
1049
1097
1081
1074
1098
1056
1052
947
1112
1096
1083
1069
1062
1058
1055
1099
1089
1082
1088
1072
1065
1060
1095
973
1085
1086
1075
1084
1079
1071
1066
1064
1093
1091
1080
1073
1068
1111
1090
1110
1092
1077
Mini box core station locations
Benthos gravity core station locations


ng/g
0 - 35
35 - 70
70 - 105
105 - 140
140 - 277
277 +


ng/g
0 - 35
35 - 70
70 - 105
105 +


1971
1997
Percent of Total PCB
0
2
4
6
8
10
12
14
16
24
16+32
28+31
44
52
74
87
99
101
110
118
149
163+138
174
180
182+187
194
195
201
206
PCB Congener


PCBs ng/g
0
20
40
60
80
100
120
Depth (cm)
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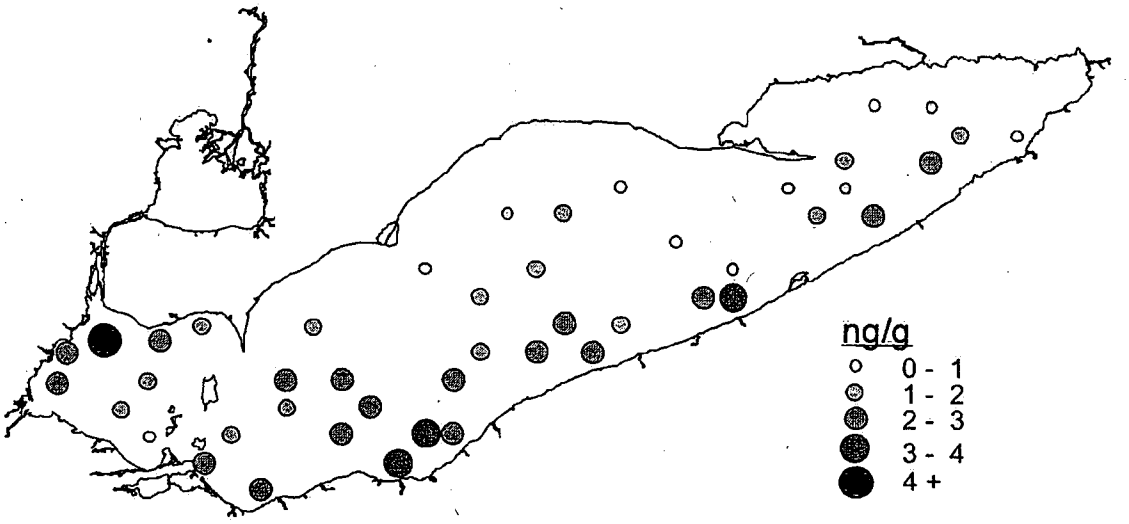
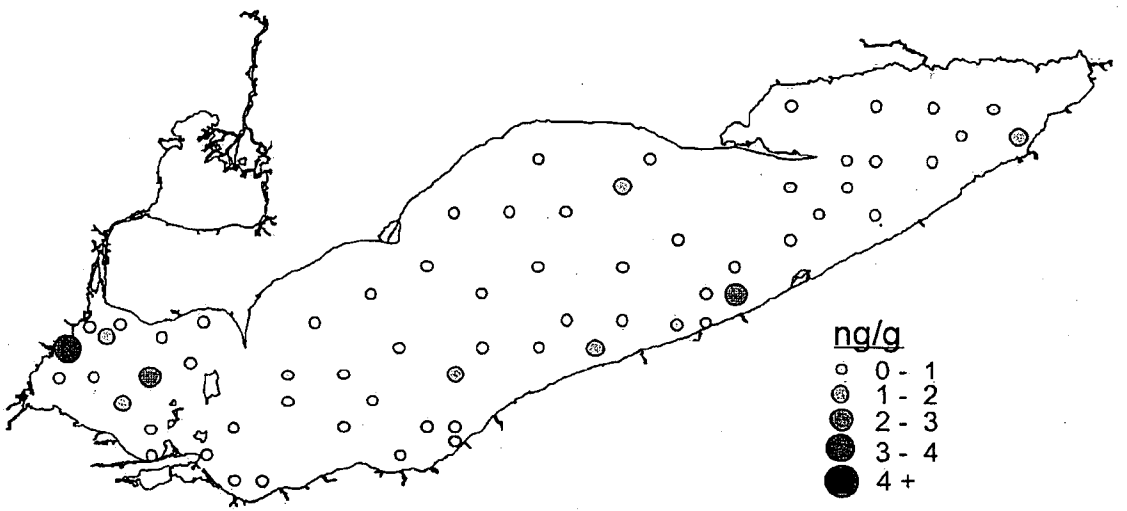
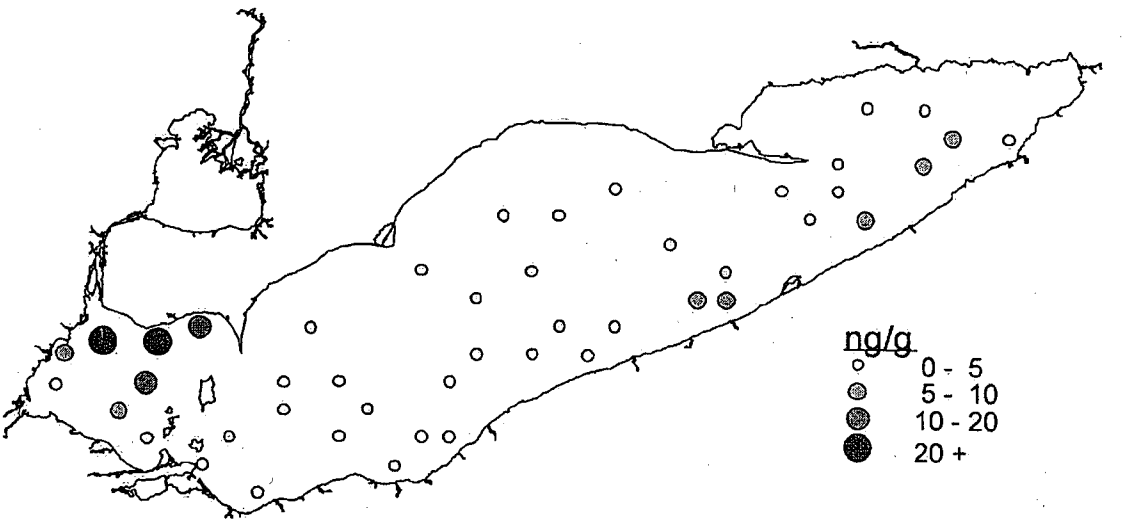
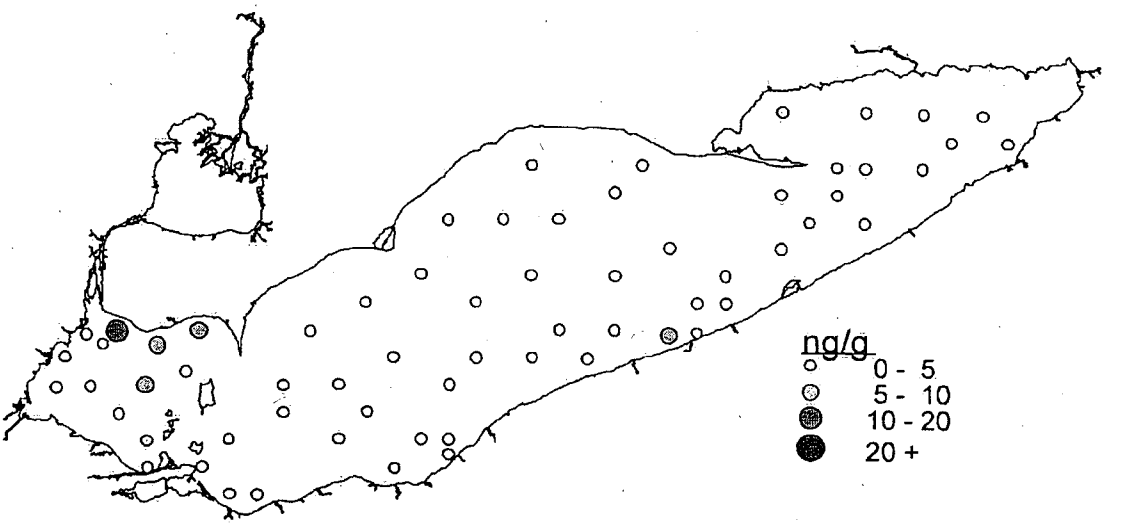
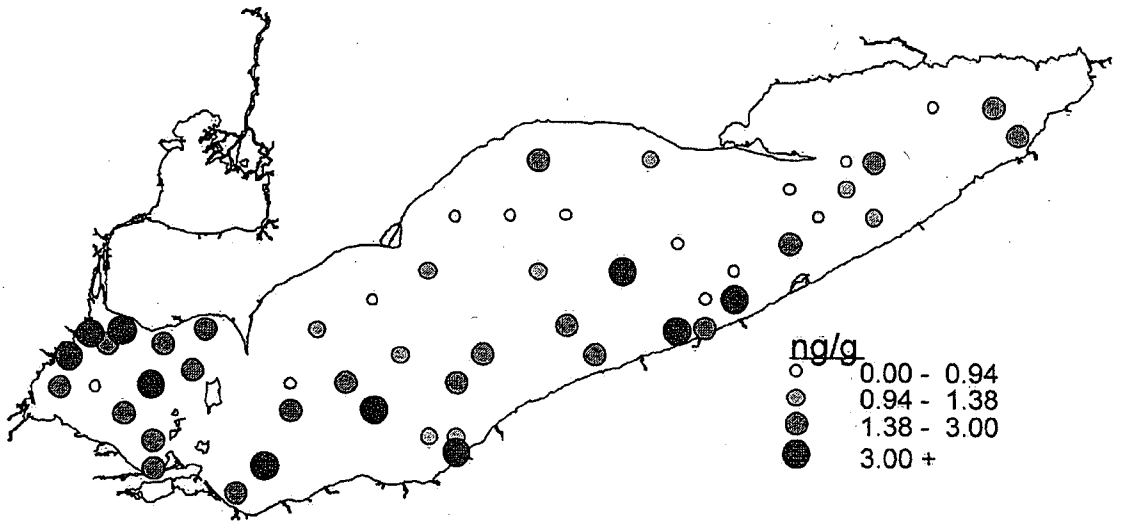
5
10
15
20
25
30
1085 Western Basin
1098 Central Basin
1040 Eastern Basin

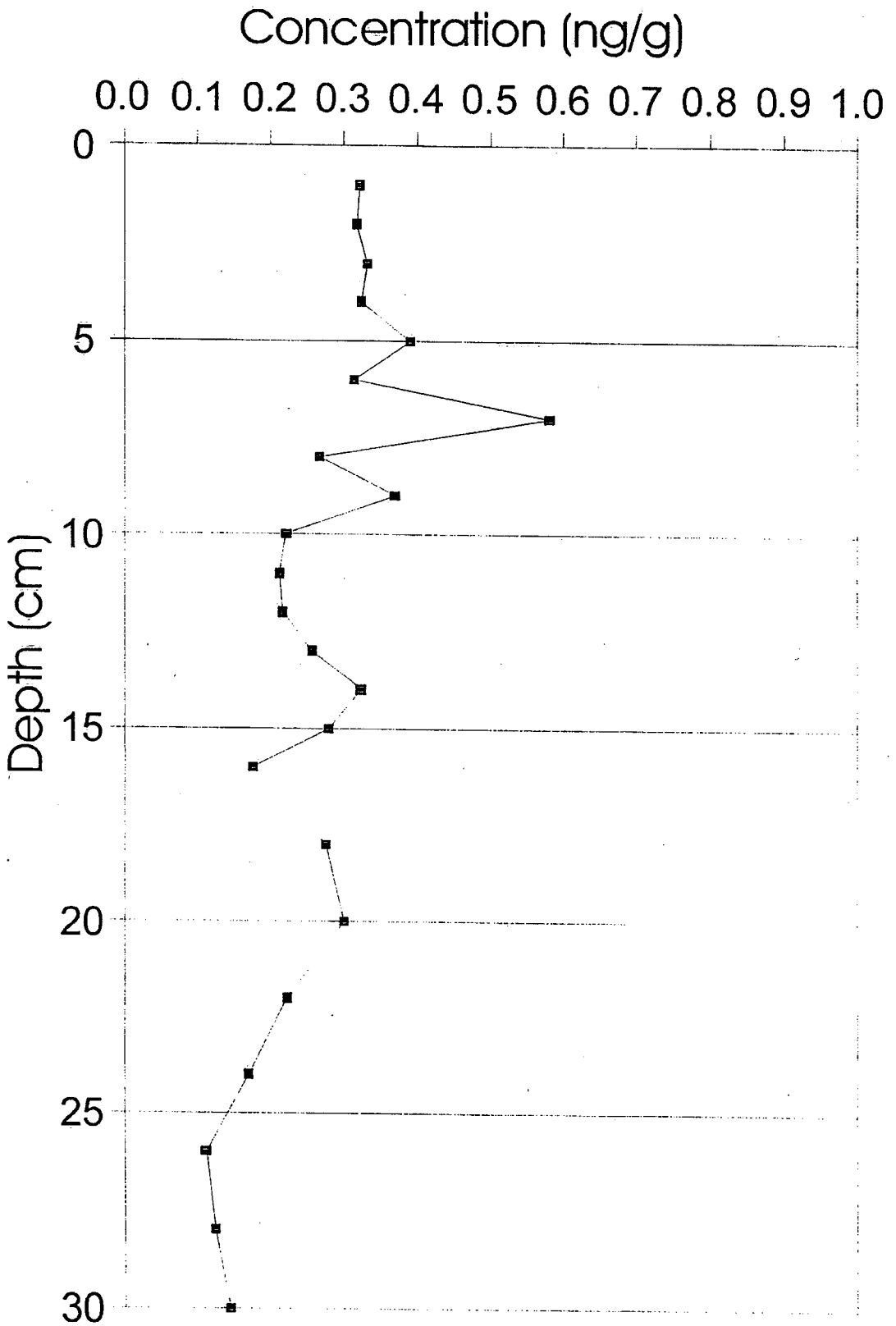

ng/g
0 - 1
1 - 2
2 - 3
3 - 4
4 +


ng/g
0 - 1
1 - 2
2 - 3
3 - 4
4 +


ng/g
0 - 5
5 - 10
10 - 20
20 +


ng/g
0 - 5
5 - 10
10 - 20
20 +


ng/g
0.00 - 0.94
0.94 - 1.38
1.38 - 3.00
3.00 +


Concentration (ng/g)
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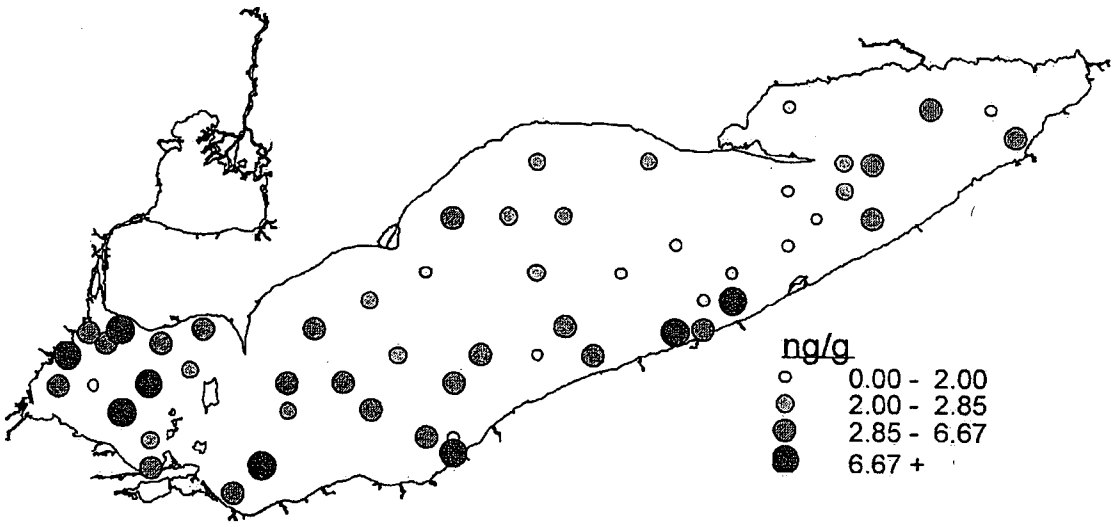
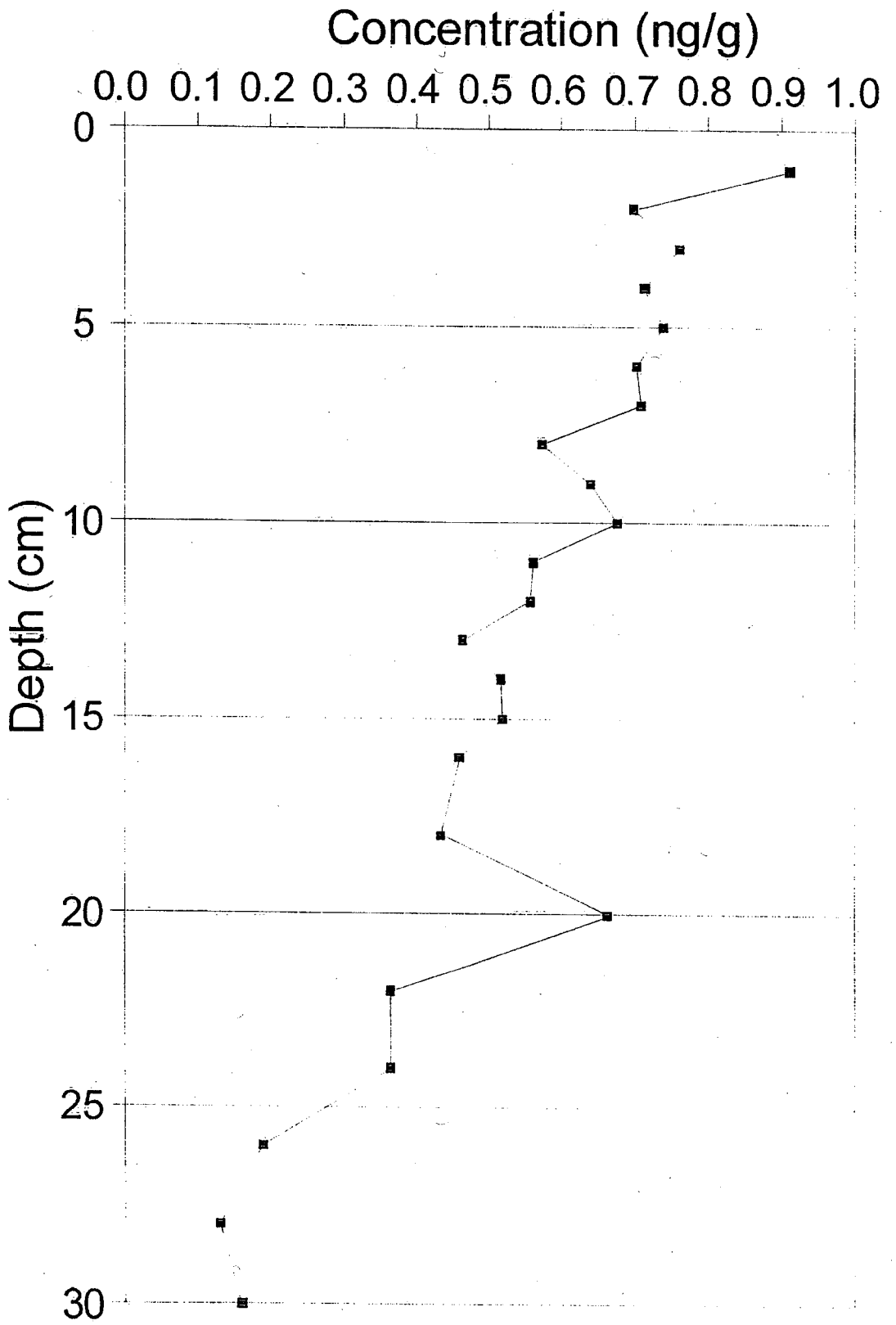
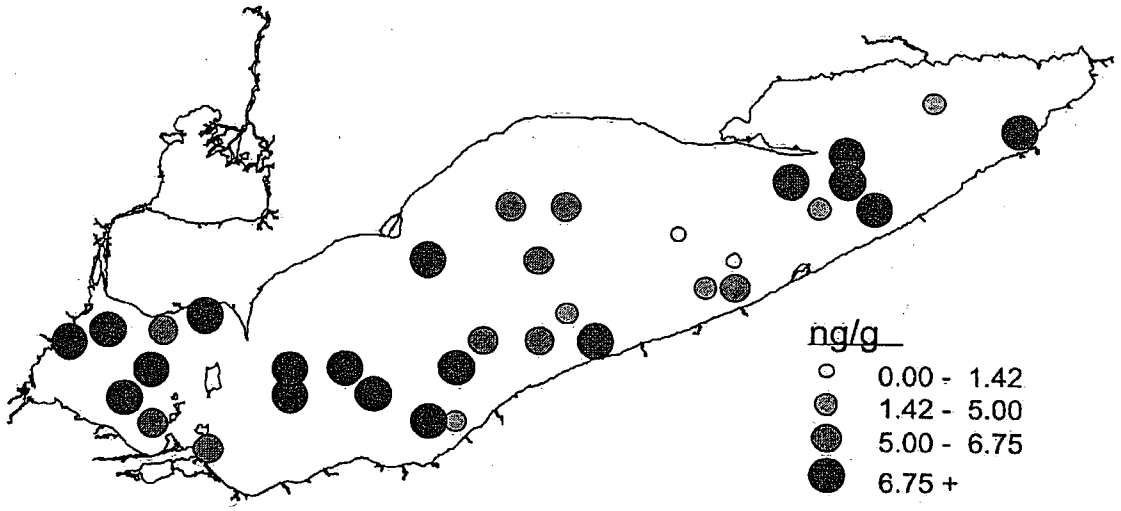
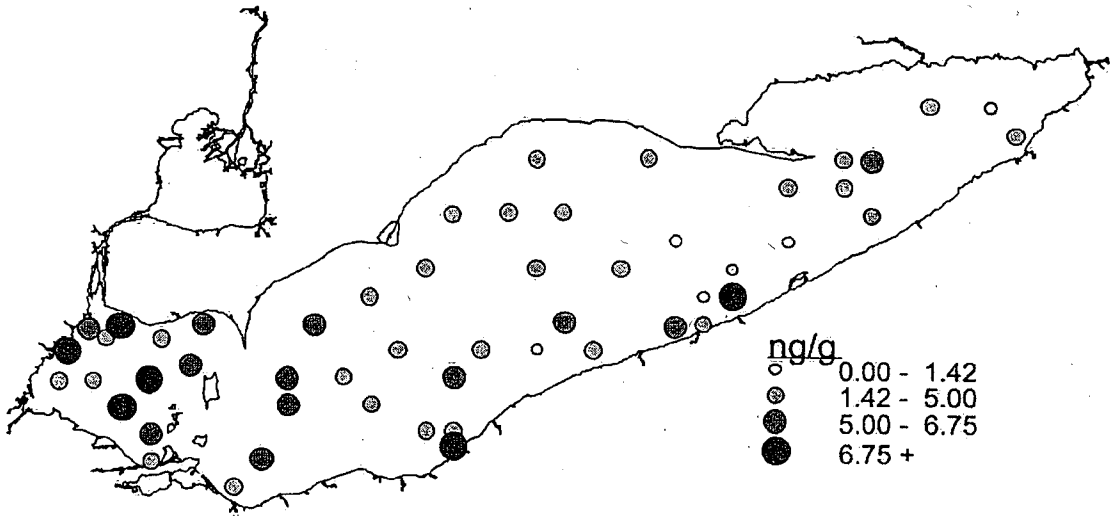
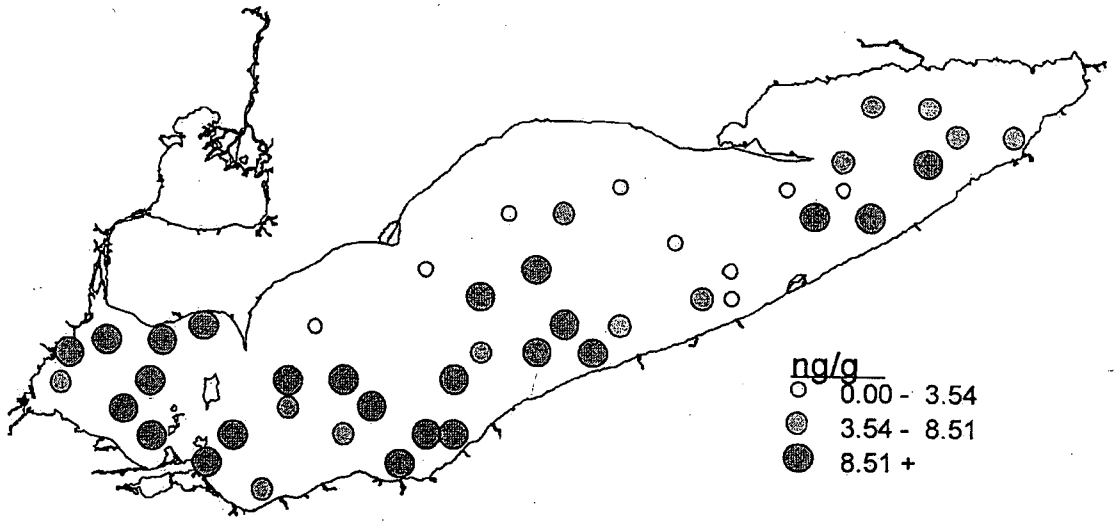
Depth (cm)
0
5
10
15
20
25
30

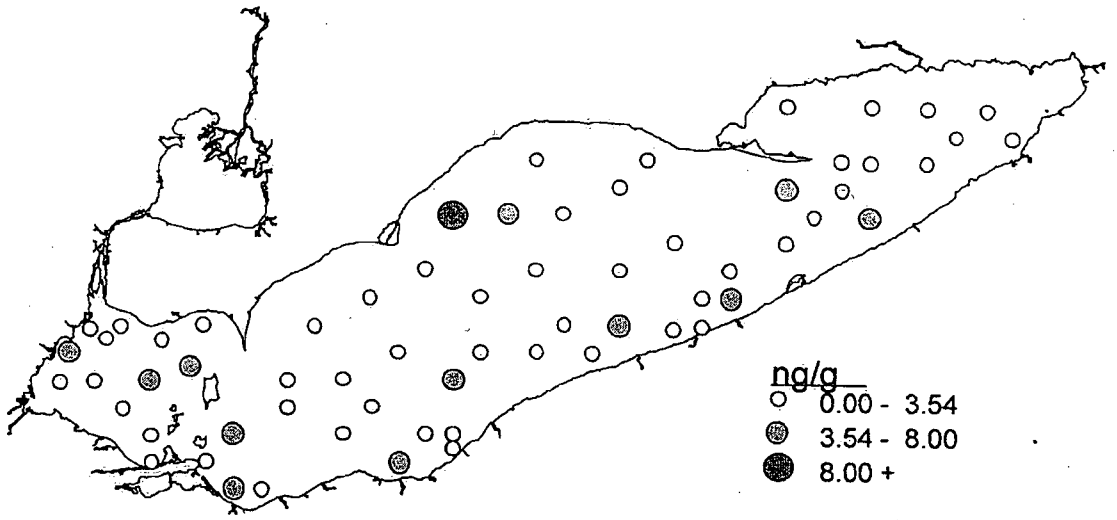

ng/g
0.00 - 2.00
2.00 - 2.85
2.85 - 6.67
6.67 +

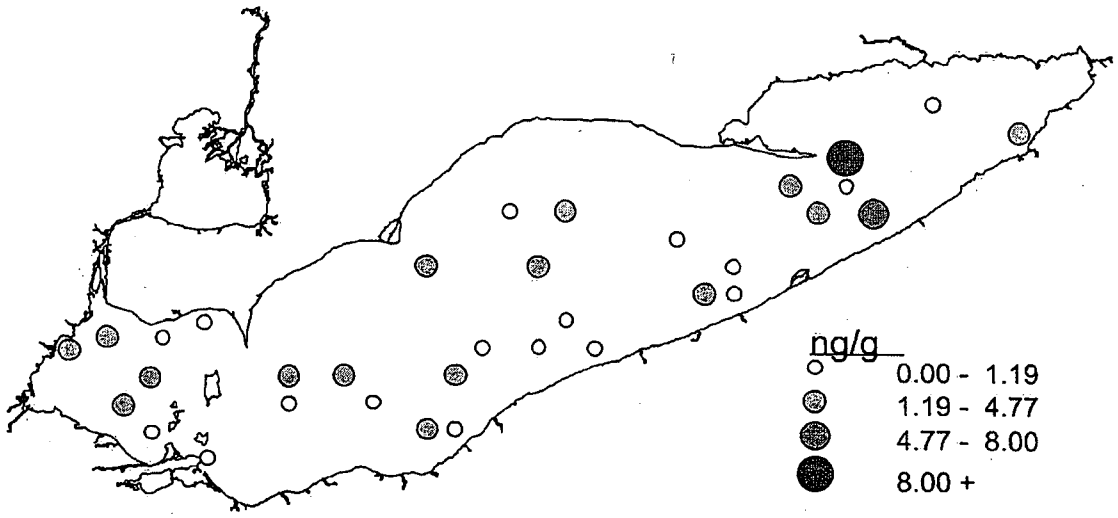

Concentration (ng/g)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Depth (cm)
0
5
10
15
20
25
30

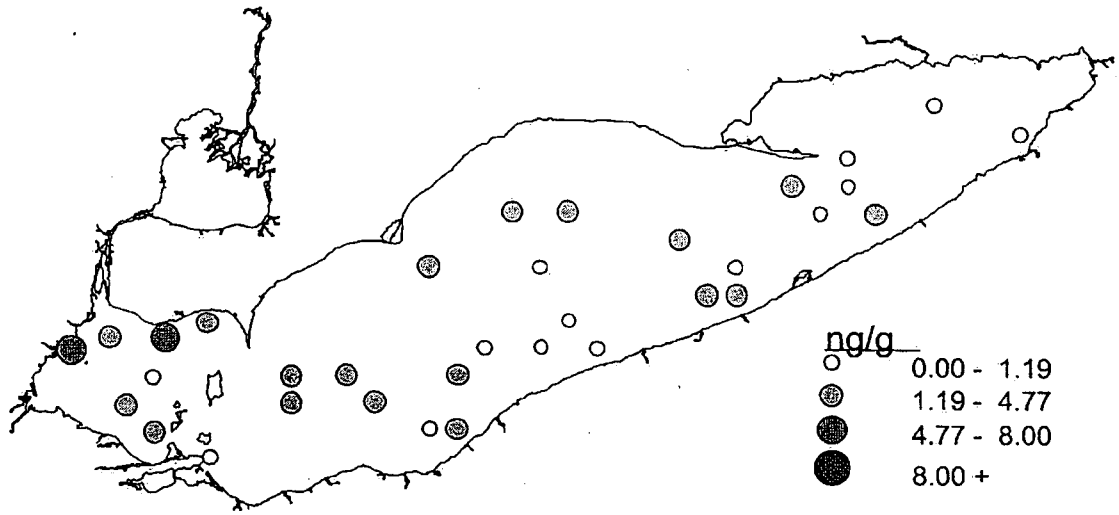

ng/g
0.00 - 1.42
1.42 - 5.00
5.00 - 6.75
6.75 +


ng/g
0.00 - 1.42
1.42 - 5.00
5.00 - 6.75
6.75 +


ng/g
0.00 - 3.54
3.54 - 8.51
8.51 +


ng/g
0.00 - 3.54
3.54 - 8.00
8.00 +


ng/g
0.00 - 1.19
1.19 - 4.77
4.77 - 8.00
8.00 +


ng/g
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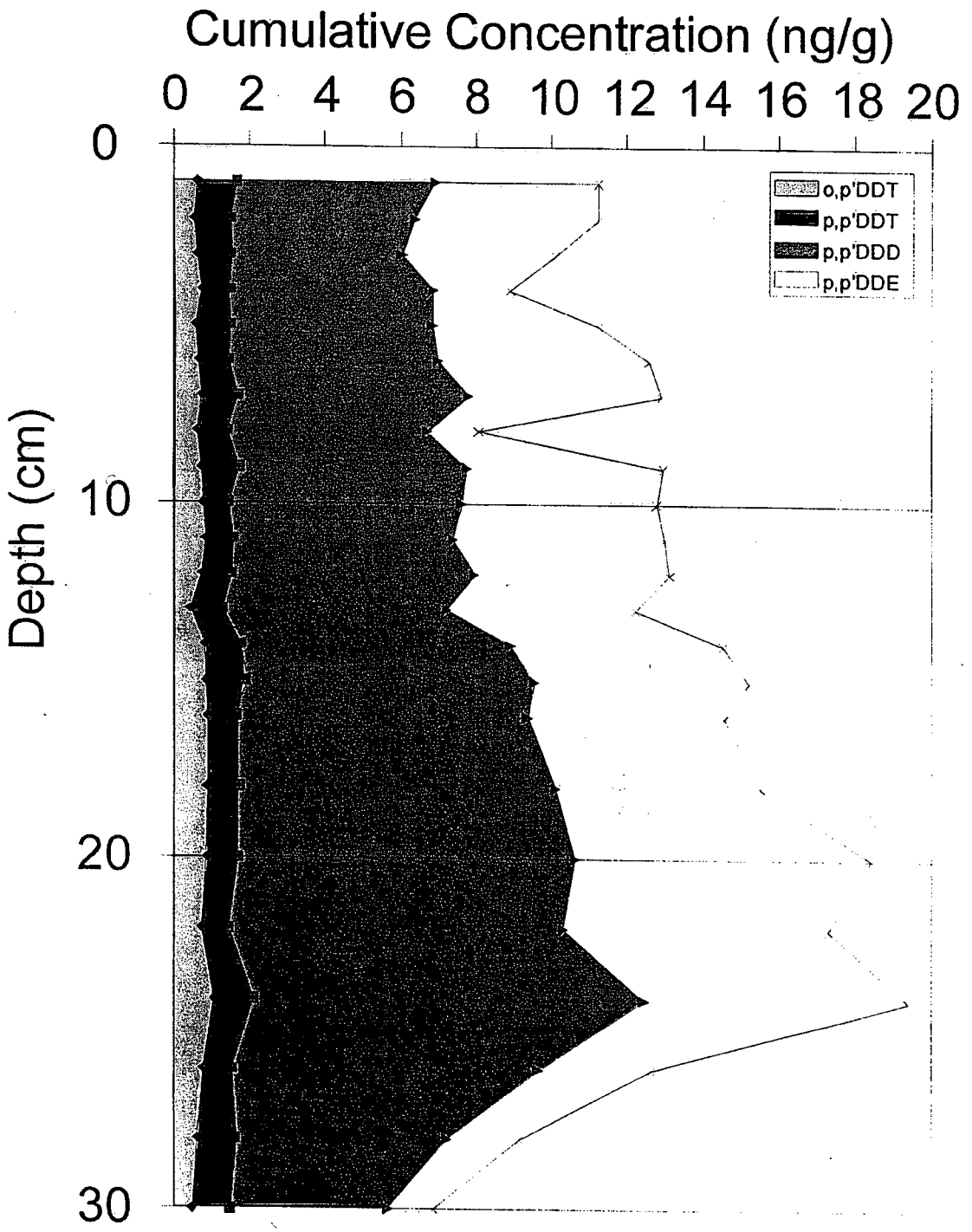
1.19 - 4.77
4.77 - 8.00
8.00 +


Cumulative Concentration (ng/g)
0 2 4 6 8 10 12 14 16 18 20
Depth (cm)
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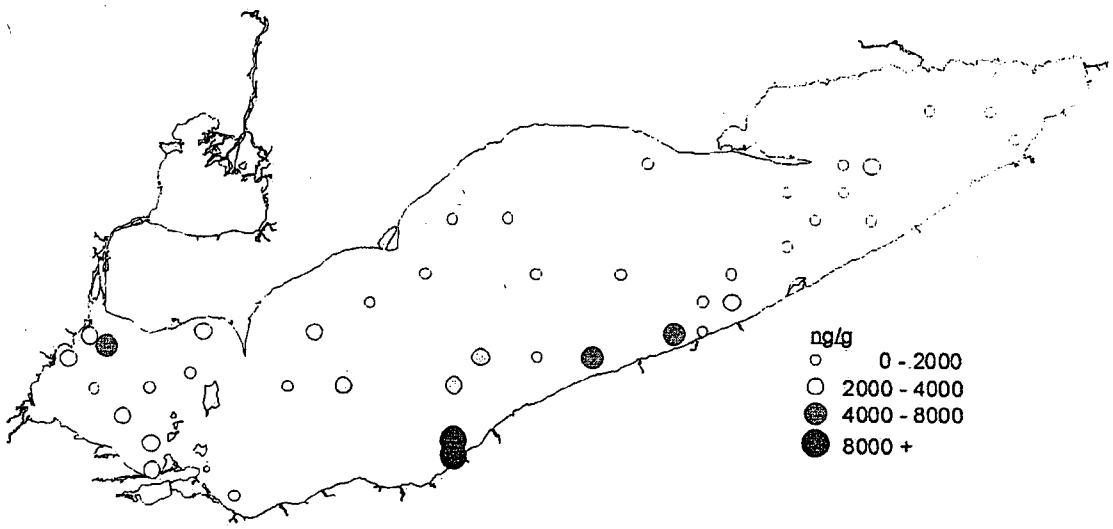
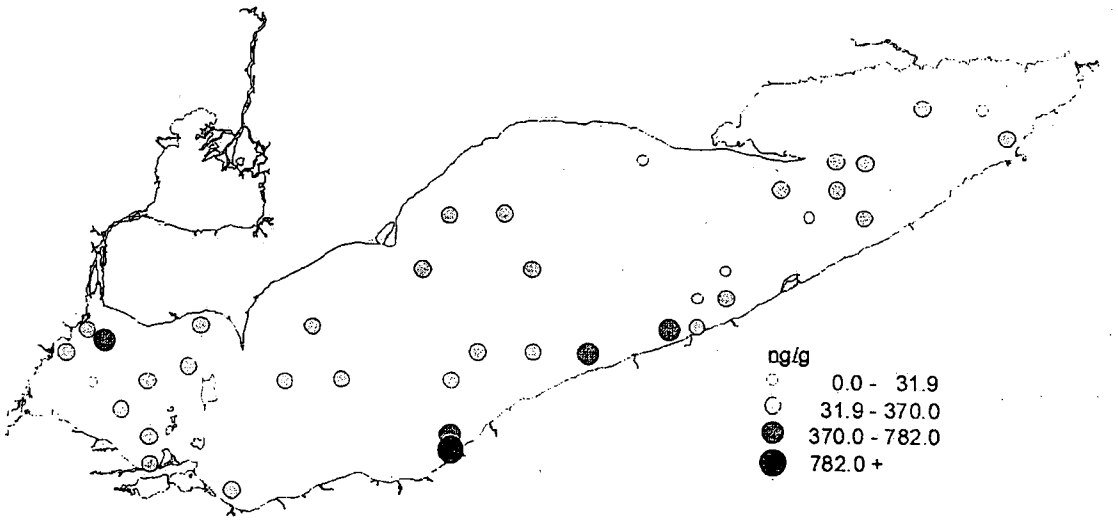
10
20
30
o,p'DDT
p,p'DDT
p,p'DDD
p,p'DDE


ng/g
0 - 2000
2000 - 4000
4000 - 8000
8000 +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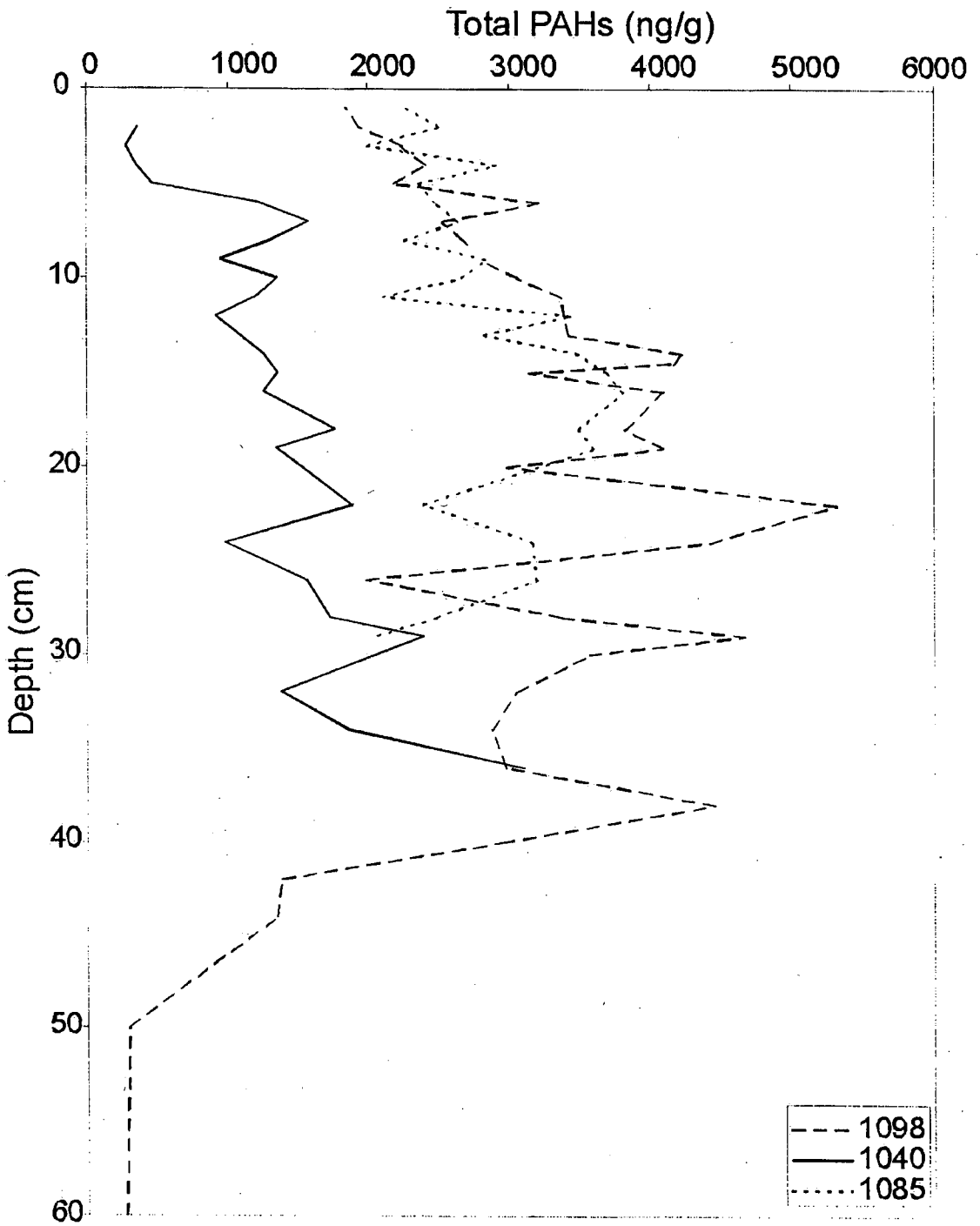
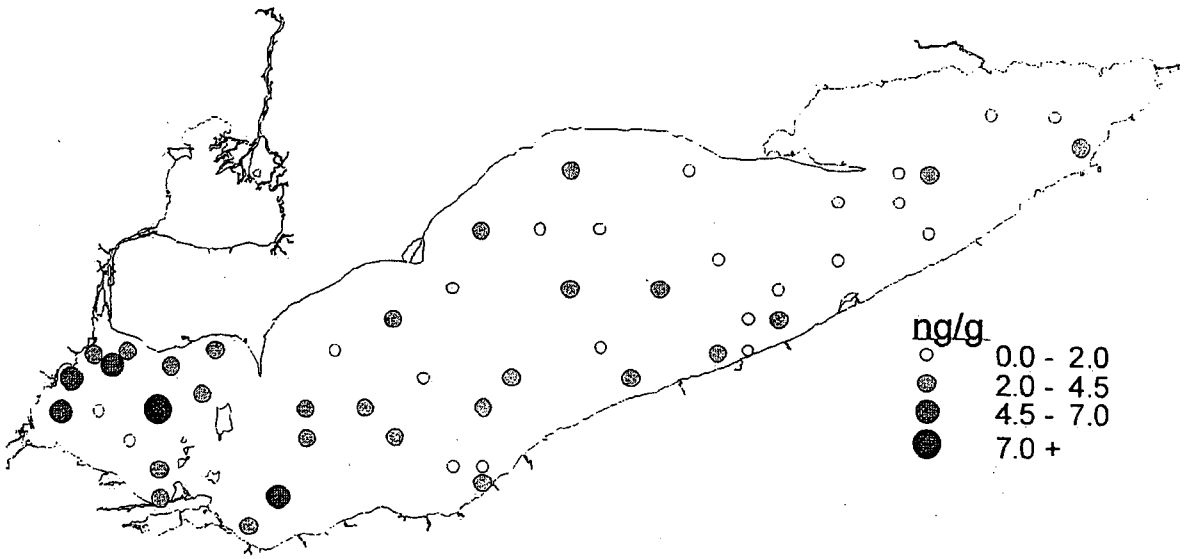
31.9 - 370.0
370.0 - 782.0
782.0 +


Total PAHs (ng/g)
0
1000
2000
3000
4000
5000
6000
Depth (cm)
0
10
20
30
40
50
60
1098
1040
1085


ng/g
0.0 - 2.0
2.0 - 4.5
4.5 - 7.0
7.0 +


ng/g
0 - 5
5 - 10
10 - 20
20 +

Environment Canada Environnement Canada

Canada

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Montreal, Quebec
H2Y 2E7 Canada

**Place Vincent Massey**
351 St. Joseph Boulevard
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K1A 0H3 Canada

**Centre canadien des eaux intérieures**
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867, chemin Lakeshore
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L7R 4A6 Canada

**Centre national de recherche en hydrologie**
11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

**Centre Saint-Laurent**
105, rue McGill
Montréal (Québec)
H2Y 2E7 Canada

**Place Vincent-Massey**
351 boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada