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Contaminants Associated with Suspended Sediments in Lakes Erie and Onatario, 1997-2000

By:

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Christopher H. Marvin, Ed Sverko, Murray N. Charlton, P.A. Lina Thiessen, and Scott Painter

ABSTRACT

Sediment traps were installed at individual index stations in the western basin of Lake Erie and the Mississauga (central) basin of Lake Ontario, and refurbished seasonally during the period 1997 – 2000. In Lake Ontario, sediment down flux rates and corresponding contaminant down flux rates were highest in winter and increased with depth due to the influence of resuspended bottom sediments. Sediment down flux rates in western Lake Erie (22 to 160 g m^{-2} d^{-1}) were far greater than in Lake Ontario (0.19 – 3.0 g m^{-2} d^{-1}). Suspended material in western Lake Erie was characterized as predominately resuspended bottom sediments; down flux rates were roughly 5- to 10-fold higher in spring and fall, compared to summer. Suspended sediment concentrations of PCBs and other organochlorine contaminants, represented by both annual means and individual seasonal values, were higher in Lake Ontario throughout the duration of the study, compared to Lake Erie. The mean annual concentration of PCBs in suspended sediments over the period 1997 – 2000 was 330 ng/g in western Lake Erie and 530 ng/g in Lake Ontario. Based on a comparison with historical data from Lake Ontario, mean contaminant concentrations over the period 1997 – 2000 for PCBs, hexachlorobenzene and mirex corresponded to decreases of 38%, 74% and 40%, respectively, since the mid-1980s. Corresponding down flux rates for PCBs, hexachlorobenzene and mirex decreased by approximately 70%, 90% and 80%, respectively, since the 1980s.

NWRI RESEARCH SUMMARY

Plain language title

Contaminants Associated with Suspended Sediments in Lakes Erie and Ontario, 1997 - 2000.

What is the problem and what do sicentists already know about it?

Presence of contaminants in suspended sediments can be a primary source to other media (e.g., bottom sediments) and to higher trophic levels potentially resulting in deleterious health impacts on fish and wildlife.

Why did NWRI do this study?

Research on suspended sediment quality in Lakes Erie and Ontario is complementary to the Great Lakes Sediment Assessment Program, which is currently assessing changes in sediment quality since earlier Departmental surveys conducted in the late 1960s and early 1970s. Information from these programmes is important to the understanding of the anthropogenic activities on open lake environments, and allows assessment of changes in contaminant concentrations since the advent of measures to reduce sources and loadings.

What were the results?

Sediment traps were installed at individual index stations in the western basin of Lake Erie and the central basin of Lake Ontario during 1997 – 2000. In Lake Ontario, sediment down flux rates and corresponding contaminant down flux rates were highest in winter and increased with depth due to the influence of resuspended bottom sediments. Sediment down flux rates in western Lake Erie were far greater than in Lake Ontario. Suspended material in western Lake Erie was characterized as predominately resuspended bottom sediments; down flux rates were roughly 5- to 10-fold higher in spring and fall, compared to summer. Suspended sediment concentrations of PCBs and other organochlorine contaminants, represented by both annual means and individual seasonal values, were higher in Lake Ontario throughout the duration of the study, compared to Lake Erie. Based on a comparison with historical data from Lake Ontario, mean contaminant concentrations over the period 1997 – 2000 for PCBs, hexachlorobenzene and mirex corresponded to decreases of 38%, 74% and 40%, respectively, since the mid-1980s. Corresponding down flux rates for PCBs, hexachlorobenzene and mirex decreased by approximately 70%, 90% and 80%, respectively, since the 1980s.

How will these results be used?

These results are in agreement with studies on bottom sediment contamination, and clearly show the success of initiatives to reduce toxics in the Great Lakes, e.g., GLBTS, GLWQA. As a result of these studies, collaboration between State, Provincial and Federal agencies has been initiated to further study sources and loadings of contaminants that may be associated with local sources. These efforts are critical as elimination of sources is the only feasible management option for reducing deep water open-lake sediment contamination.

Who were our main partners in the study?

Ontario Region

Contaminants associés aux sédiments en suspension dans les lacs Érié et Ontario, de 1997 à 2000

Christopher H. Marvin, Ed Sverko, Murray, N., Charlton, P.A., Lina Thiessen et Scott Painter

RÉSUMÉ

Des pièges à sédiments ont été installées dans certaines stations de référence du bassin ouest du lac Érié et du bassin central (Mississauga) du lac Ontario. Ces pièges ont été renouvelés à chaque saison de 1997 à 2000. Dans le lac Ontario, c'est pendant l'hiver que les taux de sédimentation des particules ainsi que les taux de sédimentation correspondants des contaminants étaient les plus élevés. Ces taux augmentaient avec la profondeur, en raison de l'effet des sédiments de fond remis en suspension. Les taux de sédimentation mesurés dans la partie ouest du lac Érié (22 à 160 g m^{-2} d^{-1}) étaient beaucoup plus élevés que ceux mesurés dans le lac Ontario (0,19 à 3,0 g m^{-2} d^{-1}). Dans la partie ouest du lac Érié, le matériel en suspension était constitué principalement de sédiments de fond remis en suspension; les taux de sédimentation étaient approximativement 5 à 10 fois plus élevés au printemps et en automne, par rapport à l'été. Les concentrations de BPC et d'autres contaminants organochlorés dans les sédiments en suspension, qu'elles soient exprimées en termes de moyenne annuelle ou de valeurs saisonnières individuelles, étaient plus élevées dans le lac Ontario que dans le lac Érié tout au long de la durée de l'étude. Pendant la période 1997 à 2000, la concentration annuelle moyenne de BPC dans les sédiments en suspension était de 330 ng/g dans la partie ouest du lac Érié et de 530 ng/g dans le lac Ontario. Selon une analyse comparative effectuée à partir d'échantillons archivés provenant du lac Ontario, les concentrations

moyennes de BPC, d'hexachlorobenzène et de mirex ont diminué de 38 %, 74 % et 40 % respectivement entre le milieu des années 80 et la période 1997 à 2000. De même, durant ce même intervalle, les taux de sédimentation correspondants de BPC, d'hexachlorobenzène et de mirex ont diminué d'environ 70 %, 90 % et 80 %.

Sommaire des recherches de l'INRE

Titre en langage clair
Contaminants associés aux sédiments en suspension dans les lacs Érié et Ontario, de 1997 à 2000.

Quel est le problème et que savent les chercheurs à ce sujet?
Les contaminants présents dans les sédiments en suspension peuvent être une source primaire pour d'autres milieux (par exemple, les sédiments de fond) ou pour des niveaux trophiques supérieurs et mener éventuellement à des problèmes de santé chez les poissons et les autres espèces sauvages.

Pourquoi l'INRE a-t-il effectué cette étude?
La recherche sur la qualité des sédiments en suspension dans les lacs Érié et Ontario est complémentaire au Programme d'évaluation des sédiments des Grands Lacs, qui évalue actuellement les changements survenus dans la qualité des sédiments depuis les relevés effectués par le Ministère à la fin des années 60 et au début des années 70. Ces programmes fourniront des informations importantes pour la compréhension de l'effet des activités humaines sur le milieu pélagique lacustre et permettront d'évaluer les changements survenus dans la concentration des contaminants depuis l'établissement de mesures visant à réduire les sources et les charges.

Quels sont les résultats?
Des pièges à sédiments ont été installées dans certaines stations de référence du bassin ouest du lac Érié et du bassin central du lac Ontario pendant la période 1997 à 2000. Dans le lac Ontario, c'est pendant l'hiver que les taux de sédimentation des particules ainsi que les taux de sédimentation correspondants des contaminants étaient les plus élevés. Ces taux augmentaient avec la profondeur en raison de l'effet des sédiments de fond remis en suspension. Les taux de sédimentation étaient beaucoup plus élevés dans la partie ouest du lac Érié que dans le lac Ontario. Dans la partie ouest du lac Érié, le matériel en suspension était constitué principalement de sédiments de fond remis en suspension; les taux de sédimentation étaient approximativement 5 à 10 fois plus élevés au printemps et en automne, par rapport à l'été. Les concentrations de BPC et d'autres contaminants organochlorés dans les sédiments en suspension, exprimées en termes de moyenne annuelle ou de valeurs individuelles saisonnières, étaient plus élevées dans le lac Ontario que dans le lac Érié tout au long de la durée de l'étude. Selon une analyse comparative effectuée à partir d'échantillons archivés provenant du lac Ontario, les concentrations moyennes de BPC, d'hexachlorobenzène et de mirex ont diminué de 38 %, 74 % et 40 % respectivement entre le milieu des années 80 et la période 1997 à 2000. De même, durant cet intervalle, les taux de sédimentation correspondants de PCB, d'hexachlorobenzène et de mirex ont diminué approximativement de 70 %, 90 % et 80 %.

Comment ces résultats seront-ils utilisés?
Ces résultats sont en accord avec ceux d'études portant sur la contamination des sédiments de fond et montrent clairement le succès des initiatives visant à réduire les substances toxiques dans les Grands Lacs (notamment la Stratégie nationale sur les produits toxiques dans les Grands Lacs et l'Accord sur la qualité de l'eau dans les Grands Lacs). Ces études ont favorisé une collaboration entre les agences fédérales et les

agences de chaque État ou province pour une étude plus approfondie des sources et charges de contaminants pouvant être associées à des sources locales. Ces efforts sont très importants, puisque l'élimination des sources s'avère la seule façon pratique de réduire la contamination des sédiments de profondeur des milieux pélagiques lacustres.

Quels étaient nos principaux partenaires dans cette étude?
Région de l'Ontario

Contaminants Associated with Suspended Sediments in Lakes Erie and Ontario, 1997-2000

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ABSTRACT

Sediment traps were installed at individual index stations in the western basin of Lake Erie and the Mississauga (central) basin of Lake Ontario, and refurbished seasonally during the period 1997 – 2000. In Lake Ontario, sediment down flux rates and corresponding contaminant down flux rates were highest in winter and increased with depth due to the influence of resuspended bottom sediments. Sediment down flux rates in western Lake Erie (22 to 160 g m^{-2} d^{-1}) were far greater than in Lake Ontario (0.19 – 3.0 g m^{-2} d^{-1}). Suspended material in western Lake Erie was characterized as predominately resuspended bottom sediments; down flux rates were roughly 5- to 10-fold higher in spring and fall, compared to summer. Suspended sediment concentrations of PCBs and other organochlorine contaminants, represented by both annual means and individual seasonal values, were higher in Lake Ontario throughout the duration of the study, compared to Lake Erie. The mean annual concentration of PCBs in suspended sediments over the period 1997 – 2000 was 330 ng/g in western Lake Erie and 530 ng/g in Lake Ontario.

Based on a comparison with historical data from Lake Ontario, mean contaminant concentrations over the period 1997 – 2000 for PCBs, hexachlorobenzene and mirex corresponded to decreases of 38%, 74% and 40%, respectively, since the mid-1980s. Corresponding down flux rates for PCBs, hexachlorobenzene and mirex decreased by approximately 70%, 90% and 80%, respectively, since the 1980s.

INDEX WORDS: Lake Ontario, Lake Erie, suspended sediments, polychlorinated biphenyls, organochlorines

INTRODUCTION

Suspended sediments are an important vector for contaminant transport in the lower Great Lakes. Contaminants originating from a variety of sources can enter the lakes adsorbed on particulate material, or can be partitioned onto suspended sediments from the dissolved phase. Contaminated suspended sediments are then subject to the prevailing lake circulation patterns before ultimately settling in the depositional basins. Common methods for sampling of suspended sediments include centrifugation and sediment traps. Sediment traps offer the advantage of time-integrated sampling over a period of weeks or months, thereby enabling estimates of contaminant down fluxes that are useful in investigating pathways and assessing loading patterns and inventories. Sediment traps deployed in areas of relatively high sedimentation will collect material that reflects current loadings that may not be manifest in bottom sediments until a substantially later point in time. Therefore, sediment traps are useful when changes in contaminant loadings are expected in localized areas over short periods of time, such as in the case of remediation of areas of contaminated sediments. Sediment trap studies of contaminants, nutrients and sedimentation rates have been carried out in several areas of the Great Lakes (Charlton 1983, Chambers and Eadie 1981, Oliver et al. 1989, Oliver and Charlton 1984, Baker et al. 1991, Eadie et al. 1984).

Some of the previous studies of contaminants associated with suspended sediments using sediment traps were conducted in the early 1980s to investigate the changes in loadings as a result of measures to reduce discharges from areas within the Niagara River area of western Lake Ontario during the 1960s and 1970s (Oliver and Charlton 1984, Oliver et al. 1989). These studies provided information on contaminant transport that was used to assist in the interpretation of spatial trends in data from studies of contaminants in lake bottom sediments. We recently reported the results of studies on spatial and temporal trends in surficial bottom sediments in Lakes Erie (Painter et al. 2001) and Ontario (Marvin et al. 2002b). These recent reports also included a comparison of data with those of previous studies conducted in the late 1960s and 1970s. In this paper, we report the results of the analysis of suspended sediments collected at individual stations in the western basin of Lake Erie and in the Mississauga (central) basin of Lake Ontario. Concentrations and down fluxes for a variety of contaminants including polychlorinated biphenyls (PCBs) and organochlorine pesticides were calculated, and compared with earlier studies in Lake Ontario.

METHODS

Sediment Traps

Suspended sediments were collected over various time and depth intervals (Table 1) at individual stations in the western basin of Lake Erie (Station 357, 41°49'13" N

82° 59'59") and the Mississauga basin (Station 403, central basin, 43° 35'50" N 78° 13'48" W) of Lake Ontario during 1997, 1998, 1999 and 2000. Sediment trap assemblies consisted of five lengths of core tubing positioned in triangular racks (Figure 1). These traps were modified from a design used by Charlton (1983). A tailfin attached to the triangular rack enabled the assembly to swivel about the axis of the suspension cable and thereby orienting the core tubes to the prevailing currents in a uniform manner. A removable cup of high-density polypropylene was fitted to the bottom of each tube to provide a receptacle for suspended sediment accumulation. Individual sediment trap assemblies were deployed at 20-m intervals on a cable held taut by a 500-Kg sub-surface float; the complete mooring assembly was anchored using a railway wheel to maintain stability. A second railway wheel with a marker float was connected to the first by a 200-m rope to enable retrieval by dragging if the marker float was dislodged. A typical time to retrieve, refurbish and redeploy moorings was approximately 1 hr. After retrieval, excess water was removed from the tube by removing a plug placed in a hole at the base of the tube immediately above the top of the cup. The contents of cups that had accumulated suspended sediments at discreet depths were combined and allowed to settle overnight prior to a second decanting. Samples were then frozen, freeze-dried and weighed. Loss on ignition (LOI) was determined by combustion in a muffle furnace at 500°C for 2 hrs.

Chemical Analyses

Freeze-dried suspended sediment samples were ultrasonically extracted using a 1:1 mixture of acetone and hexane. The concentrated extract was partitioned with water and back-extracted with dichloromethane. The combined extract was concentrated, and then fractionated on a 3% (w/w) deactivated silica gel column. Mercury was added to extracts to remove sulphur. Extracts were then concentrated to a final volume of 1 mL prior to analysis. Analyses were performed using split/splitless injection with dual column capillary gas liquid chromatography using electron capture detection. Columns were a 30 m x 0.25 mm i.d. 0.25 μm film thickness fused silica DB-1 (confirmation column) and DB-5 (primary column) with hydrogen as a carrier gas. The field surrogate standard contained 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and δ-HCH; laboratory surrogates were 1,3-dibromobenzene and endrin ketone.

Total PCBs were expressed as the sum of 132 individual congeners quantitated by external calibration using a standard solution prepared by the National Laboratory for Environmental Testing (NLET, 1997). Total DDT is expressed as the total of p,p-DDE, p,p-DDD and p,p-DDT. Method blanks and spiked method blanks were run with each set of six samples. The method detection limit (MDL) for total PCBs was approximately 20 ng/g, and for the organochlorine compounds ranged from roughly 0.5 ng/g to 2 ng/g.

RESULTS AND DISCUSSION

Sediment Trap Deployments and Suspended Sediment Fluxes

The sediment trap assemblies shown in Figure 1 were based on a design previously used for the study of the down flux and composition of particulate matter in areas of the Great Lakes (Charlton et al. 1981, Charlton 1983). The key parameter in the design of the traps is the aspect ratio, which is defined as the ratio of the internal diameter of the trap tube to the length. This aspect ratio determines the degree to which material collected passively in the tubes can be resuspended and flushed from the collection cups by *in situ* currents. This design has proven to be a simple and robust method for field applications, and provides stability and ease of retrieval. Samples were subjected to physical measurements including loss on ignition (LOI), and analyzed for a variety of persistent organic pollutants (POPs) including PCBs and organochlorine pesticides. The Lake Ontario sediment trap mooring consisted of a vertical array to enable sampling of suspended sediments at various discrete depths; the Lake Erie mooring was deployed at only one depth (roughly 9 m) due to the shallowness of water in this area. A listing of deployment dates for the Lake Ontario and Lake Erie sediment trap moorings is shown in Table 1. For each period of deployment, dry suspended sediment down flux rates and corresponding percent LOI are also shown.

For some deployments at station 403 in the Mississauga basin, suspended sediment samples from different depths were pooled to afford sample weights sufficient for accurate chemical analyses. This site has been designated as an Environment Canada index station, due to its location in the central area of the middle of three major lake depositional basins, and the availability of historical data. Bottom sediments within the three major Lake Ontario basins are comprised of fine-grained material classified as mixtures of glacio-lacustrine clay, sand, silt and mud (Thomas et al. 1972). A predominant counter-clockwise circulation pattern in Lake Ontario (Pickett and Bermick 1977) can result in distribution of suspended sediment across the entire lake area. Therefore, the physico-chemical characteristics of sediments at station 403 are generally representative of sediments across the entire area comprising the major lake basins (Marvin et al. 2002b, Mudroch 1993). Estimated dry suspended sediment down fluxes in Lake Ontario over the period 1997 – 2000 ranged from 0.19 – 3.0 g m^{-2} d^{-1}. This range was similar to that reported for suspended sediments collected offshore of the mouth of the Niagara River in 1980 (0.8 –

4.2 g m^{-2} d^{-1}, Charlton 1983). In addition, the majority of Lake Ontario percent LOI values (range of percent LOI from 19% – 48%) fell within the range reported in the previous study (16% – 33%).

Typically, greater amounts of sediment were collected in the Lake Ontario traps at greater depths (Table 1). Greater accumulation with increased depth in Lake Ontario was potentially the result of trapping of resuspended surficial bottom sediment (Charlton 1975, Charlton 1983, Gasith 1975, Oliver et al. 1989), and material originating within the nepheloid layer, which is a turbid layer characterized by high suspended solids and light attenuation that is present at depths greater than 60 m across the entire lake (Sandilands and Mudroch 1983). The higher suspended sediment fluxes close to the lake bottom results in a "foot-like" profile of particle mass flux versus depth (Eadie et al. 1984, Chambers and Eadie 1981) that can exhibit seasonal variations, with the greatest fluxes occurring during unstratified periods. While resuspended bottom sediments represented a significant contribution to material collected in the bottom traps, traps nearer the surface may have accumulated more recent material comprised of sediment originating in tributaries, and material autochthonously generated by plankton (Oliver et al. 1989). The contribution of resuspended bottom sediments with low organic content to material accumulated in the sediment traps was also evidenced by a trend toward decreased percent LOI with increased sampling depth (Table 1). Percent LOI throughout the entire study period (1997 – 2000) for Lake Ontario suspended sediments ranged from 16% to 48%; typical total organic carbon (TOC) values in Lake Ontario surficial bottom sediments are on the order of 3%. The 2000 sample year samples for Lake Ontario represented a winter sampling interval (28 Oct 1999 – 7 Apr 2000, Table 1), which enabled a comparison with winter suspended sediment data from station 403 for the period 1982 – 1986 reported by Oliver et al. (1989). As expected, accumulation rates during winter 1999 – 2000 increased over a depth range of 20 – 165 m (Table 1). The range of suspended sediment down flux rates at station 403 (0.61 – 3.0 g m^{-2} d^{-1}) was similar to that reported by Oliver et al. (1983) for the same depth range (1.2 – 3.6 g m^{-2} d^{-1}). Oliver et al. (1983) also observed higher down flux rates in the winter samples, compared to summer samples, which was attributed to increased lake mixing and resuspension during the period of unstratified conditions. In addition, storms can influence physical processes at greater depths during periods of isothermal conditions, resulting in an increased contribution of resuspended bottom sediments to material accumulated in sediment traps over the entire range of depths sampled. Intense winter storms in southern Lake Michigan in 1998 resulted in large-scale resuspension of bottom sediments and correspondingly large fluxes of contaminants (Bogdan et al. 2002); the March 1998 storm was estimated to have resulted in roughly 400 kg of PCBs being resuspended into the water column.

Station 357 represents the primary Environment Canada index station in the western basin of Lake Erie. Sediment traps were typically deployed in all three major Lake Erie basins, but the western basin receives the greatest tributary discharges and exhibits the highest degree of sediment contamination, compared to the central and eastern offshore basin areas (Painter et al. 2001). Therefore, suspended sediments from the western basin index site were selected for chemical characterization. Annual mean suspended sediment down flux rates at station 357 for the period 1997 – 2000 ranged from 22 to 160 g m^{-2} d^{-1}, compared to 0.92 – 1.5 g m^{-2} d^{-1} for the same time period at station 403 in Lake Ontario (Table 1). The relatively high-suspended sediment loadings in the western basin of Lake

Erie were presumably the result of loadings from tributaries, including the Detroit and Maumee Rivers, and the shallow depth (9 m) that results in increased resuspension of bottom sediments. Resuspension was also evidenced by the range of percent LOI, which was substantially lower in western Lake Erie, compared to Lake Ontario due to dilution by bottom sediments with relatively lower organic content (Table 1). In addition, down flux rates during the spring and fall collection periods were typically greater than the summer periods. In 1997, there was a definitive trend in the Lake Erie down flux rates, with rates in the spring and fall (320 and 330 g m^{-2} d^{-1}, respectively) roughly 5- to 10-fold higher than during the summer collection periods. This trend was likely due to a combination of factors, including increased tributary discharges as a result of greater rates of precipitation and runoff during the spring and fall periods, compared to summer, and increased resuspension of bottom sediment during periods when the water column was unstratified. In addition, the bathymetry and high particle residence times within the western basin of Lake Erie result in prolonged periods of high-suspended sediment loadings in the water column.

Suspended Sediment Contaminant Fluxes

Annual mean suspended sediment contaminant concentrations and corresponding down flux rates are shown in Table 2 for PCBs, DDT, dieldrin, hexachlorobenzene (HCB) and mirex over the period 1997 – 2000. These contaminants include designated critical pollutants in Lakes Erie and Ontario, with the exception of mirex, which is relevant to Lake Ontario only (LOTMP 1989). Comparisons of annual mean suspended sediment contaminant concentrations for Lakes Erie and Ontario over the period 1997 – 2000 for PCBs, DDT and dieldrin are shown in Figures 2 – 4. Suspended sediment concentrations, represented by both annual means and seasonal values, were higher in Lake Ontario throughout the duration of the study, compared to Lake Erie. The higher contaminant concentrations in Lake Ontario compared Lake Erie are also reflected in the relative degree of bottom sediment contamination (Marvin et al. 2002a). Estimates of contaminant down flux rates were typically 10- to 100-fold higher for Lake Erie than Lake Ontario (Table 2). In considering the magnitude of the western Lake Erie suspended sediment and contaminant down flux rates, it is evident that the majority of sediment collected in the traps represented resuspended bottom material. Therefore, the Lake Erie estimates are of very limited value in assessing true down flux rates and associated chemical loadings. Table 2 also shows the contaminant data for suspended sediments collected at different depths in Lake Ontario during winter 1999 – 2000, and data for seasonal samples collected in Lake Erie in 1997. There were no apparent trends in suspended sediment contaminant concentrations based on sampling period in either lake, or with depth in Lake Ontario over the entire period of the study. However, the established trends in sediment down flux rates resulted in correspondingly greater contaminant down fluxes with depth in the Lake Ontario samples collected during winter 1999 – 2000, and greater contaminant down fluxes in Lake Erie during spring and fall, compared to summer (Table 2). Similarly, sediment down flux rates at station 403 in Lake Ontario at depths ranging from 20 m to 175 m were higher in spring and fall, compared to summer (Table 1). Although contaminant down flux rates in both Lakes Erie and Ontario were generally higher in spring and fall, compared to summer, the summer season represents the period of greatest mass flux of contaminants out of the lakes. As a result of decreased loadings, both Lakes Erie and Ontario in 1994 were net sources of PCBs, dieldrin, HCB, and DDE to the atmosphere while p,p'-DDT continued to exhibit a net loading (Hoff et al. 1996). Hoff et al. (1996) estimated that as of 1994, 190 kg yr^{-1} of PCBs enters Lake Ontario from the atmosphere, while 440 kg yr^{-1} is volatilised out of the lake. Volatilisation rates during summer in Lake Ontario were roughly double the winter and spring rates, and 20% higher than the fall rate. A very similar trend was observed for Lake Erie.

Since material collected in the winter 1999 – 2000 in Lake Ontario, and all Lake Erie sediment traps over the period 1997 – 2000, was postulated to reflect a significant contribution from resuspended bottom sediments, comparisons were made with data from recent surficial sediment surveys. The mean annual concentration of PCBs in suspended sediments over the period 1997 – 2000 in both Lake Erie (330 ng/g) and Lake Ontario (530 ng/g) were higher than concentrations determined in surficial bottom sediment surveys in 1997 (western basin of Lake Erie, 160 ng/g) and 1998 (Lake Ontario, 100 ng/g). Meanwhile, concentrations of other organochlorine contaminants were more similar in suspended sediments, compared to bottom sediments. In Lake Erie, mean annual concentrations of HCB and dieldrin in suspended sediments from the western basin over the period 1997 – 2000 were 2.8 ng/g and 0.82 ng/g, respectively, while corresponding bottom sediment values in 1997 were 4.0 ng/g and 0.82 ng/g, respectively. In Lake Ontario, mean annual concentrations of HCB and mirex in suspended sediments over the period 1997 – 2000 were 9.3 ng/g and 10.3 ng/g, respectively, while corresponding bottom sediment values in 1997 were 23 ng/g and 6.6 ng/g, respectively. In the case of mirex in Lake Ontario, most known sources in the Niagara River watershed have been significantly reduced (Durham and Oliver 1983, Marvin et al. 2002b), indicating that burdens in suspended sediments primarily originate within the surficial sediment pool. For PCBs in western Lake Erie, the relatively higher PCB levels in suspended sediments, compared to bottom sediments, may have been influenced by contaminants associated with material discharged from the Detroit River. The Detroit River continues to be a vector for active loadings of contaminants, including PCBs and dioxins and furans, which may originate from areas within the river or from other sources in the upstream lakes and connecting channels (Marvin et al. 2002c).

The loss on ignition data (Table 1) indicates that suspended sediments in both Lakes Ontario and Erie contain significantly greater levels of organic carbon, compared to typical bottom sediments. Fine-grained bottom sediments representative of the depositional basins of both lakes typically exhibit total organic carbon (TOC) levels of 0.5% to 3%. The LOI data indicates that suspended sediments in Lakes Erie and Ontario contain roughly 3- to 4-fold and 3- to 15-fold higher levels, respectively, of organic carbon, compared to bottom sediments. Assuming that LOI on a percentage basis is similar to TOC, the lake wide average PCB concentration in Lake Ontario in 1998 for total PCBs (100 ng/g, Marvin et al. 2002a) translates to a TOC normalized value of 3,330 ng/g TOC, based on 3% sediment TOC. The mean 1998 Lake Ontario suspended sediment LOI value of 31%, calculated using the values shown in Table 1, and the mean total PCB concentration of 490 ng/g, results in a value of 1,600 ng/g TOC. This comparison indicates that the relatively high organic carbon in suspended sediments significantly influences contaminant concentrations. We have not determined the degree of correlation of percent LOI with TOC in suspended and bottom sediments from Lakes Erie and Ontario. Some studies have shown good correlation between the two techniques for some soils and sediments (Dean 1974, Ball 1964); however, clay content and carbonate carbon can significantly influence

LOI resulting in an overestimation of TOC (Dean 1974).

Relatively high PCB concentrations in suspended sediments, compared to bottom sediments, have also been observed in Lake Superior. Baker et al. (1991) observed higher concentrations of PCBs and polycyclic aromatic hydrocarbons (PAHs) on suspended sediments collected in sediment traps during both stratified and unstratified conditions, compared to surficial bottom sediments and suspended solids collected by filtration. The higher concentrations during stratification were attributed to higher loadings from atmospheric deposition, and increased sorptive capacity and scavenging efficiency of suspended sediments. Unlike the Lake Superior study, we were unable to establish a trend toward decreasing suspended sediment PCB concentrations with depth. Congener profiles of Lake Ontario surface water, suspended sediments and surficial bottom sediments were somewhat different (Figure 5). The PCB congener profiles of surface water and suspended sediments were more similar; there was a predominance of lesser-chlorinated PCB congeners (di-, tri, tetra- and penta-substituted) in the water and suspended sediment profiles while the congener profile for bottom sediments was more evenly distributed across the entire range of chlorination. The bottom sediment congener profile also exhibited generally higher relative levels of higher-chlorinated PCB congeners, compared to surface water and suspended sediments. The predominance of lesser-chlorinated congeners with correspondingly lower Log K_{ow}s in suspended sediments and surface water indicated adsorption of more soluble PCBs onto suspended sediments directly from the water column. Enrichment of the lesser-chlorinated PCBs on suspended sediments, compared to surficial bottom sediments, was also observed by Eadie et al. (1991) in samples from Lake Superior.

Temporal Trends in Suspended Sediment Contaminant Fluxes

Oliver et al. (1989) reported contaminant concentration and flux data for winter sediment traps deployed at station 403 in Lake Ontario over a 4-year period from 1982 – 1986. Trends in some contaminants, particularly PCBs, were apparent but the authors were unable to determine any significant changes in loadings over the 4-year study period. As with the earlier study, any temporal trends in suspended sediment contaminant concentrations over the period 1997 – 2000 were difficult to assess. However, a comparison of mean contaminant concentrations over the period 1982 – 1986 and 1997 – 2000 resulted in percent reduction estimates for PCBs (860 ng/g vs 530 ng/g), HCB (36 ng/g vs 9.3 ng/g) and mirex (17 ng/g vs 10 ng/g) of 38%, 74% and 40%, respectively (Figure 6). Data from the current study (Table 2) were mostly determined from samples collected year-round, while data from Oliver et al. were based on winter samples when contaminant levels were typically highest; therefore, it is possible that our calculated percent reductions represent best-case estimates. Corresponding estimates of reductions in bottom sediment contamination on a lake-wide basis in Lake Ontario over the period 1968 – 1997 were 40% for mirex, 40% for PCBs and 80% for HCB (Marvin et al. 2002a, 2002b). Estimated reductions in loadings, as determined through a comparison of contaminant down flux rates in 1982 – 1986 and 1997 – 2000 were even more dramatic. Down flux rates for PCBs (1,700 ng m^{-2} d^{-1} vs 520 ng m^{-2} d^{-1}), HCB (94 ng m^{-2} d^{-1} vs 11 ng m^{-2} d^{-1}) and mirex (43 ng m^{-2} d^{-1} vs 7.6 ng m^{-2} d^{-1}) decreased over the period of the mid-1980s to the late-1990s by approximately 70%, 90% and 80%, respectively.

CONCLUSIONS

The evaluation of sediment down flux rates and corresponding contaminant down flux rates in both western Lake Erie and Lake Ontario on a seasonal basis indicated that the bottom sediments represent a major contribution to contaminant cycling in the water column. Based on a comparison with historical data from Lake Ontario, mean contaminant concentrations over the period 1997 – 2000 for PCBs, hexachlorobenzene and mirex decreased by 38%, 74% and 40%, respectively, since the mid-1980s. Corresponding down flux rates for PCBs, hexachlorobenzene and mirex decreased by approximately 70%, 90% and 80%, respectively, since the mid-1980s. These trends in suspended sediments indicate progress toward reduction and subsequent virtual elimination of persistent toxics in the Great Lakes basin. We have observed similar decreases in concentrations of other persistent pollutants in Great Lakes bottom sediments and surface waters (Marvin et al. 2002d).

The mean annual concentration of PCBs in suspended sediments over the period 1997 – 2000 was 330 ng/g in western Lake Erie and 530 ng/g in Lake Ontario. The relatively higher suspended sediment PCB concentrations in both lakes, compared to bottom sediments, indicated ongoing sources. These sources may be related to industrial activities in the watersheds and along major tributaries; contaminants originating within tributary watersheds or derived through atmospheric deposition can ultimately be deposited in open lake areas. Management actions such as bans on PCBs and mirex have undoubtedly been primary contributors to the observed declines in contamination. Other actions have presumably contributed to the declines in suspended sediment contaminant concentrations, including remediation of sites of contaminated sediments, reduction and/or elimination of discharges from hazardous waste facilities, reduction of open-lake disposal of contaminated sediments, and reductions in loadings from atmospheric sources.

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Table 1. Suspended sediment collection intervals, depths of sediment trap deployment, suspended sediment downflux rates (g m^{-2} day^{-1}) and available data for percent loss on ignition (bracketed values) for Lakes Erie and Ontario over the period 1997 – 2000.

Station	Time Interval	Depth	Down flux (g m^{-2} d^{-1})
Lake Erie 357	9 May – 4 Jun 1997	10 m	320 (8.8)
Lake Erie 357	4 Jun – 7 Jul 1997	10 m	30 (9.1)
Lake Erie 357	2 Jul – 1 Aug 1997	10 m	42 (9.4)
Lake Erie 357	1 Aug – 19 Aug 1997	10 m	64 (9.3)
Lake Erie 357	19 Aug – 8 Oct 1997	10 m	330 (8.6)
Lake Ontario 403	23 Apr – 10 Jun 1997	20 m	1.9 (19)
Lake Ontario 403	23 Apr – 10 Jun 1997	140 m	1.6 (17)
Lake Ontario 403	10 Jun – 23 Jul 1997	20 m	0.44 (39)
Lake Ontario 403	10 Jun – 23 Jul 1997	140 m	0.93 (16)
Lake Ontario 403	23 Jul – 31 Oct 1997	20 m	0.20 (48)
Lake Ontario 403	23 Jul – 31 Oct 1997	140 m	0.43 (31)
Lake Erie 357	12 Jun – 1 July 1998	9.3 m	52 (11)
Lake Erie 357	1 Jul – 6 Aug 1998	9.3 m	51 (12)
Lake Erie 357	6 Aug – 9 Sep 1998	9.3 m	31 (15)
Lake Erie 357	9 Sep – 20 Oct 1998	9.3 m	170 (12)
Lake Ontario 403	8 Apr – 22 Jun 1998	19 m + 59 m	0.83 (20)
Lake Ontario 403	22 Jun – 18 Aug 1998	19 m + 59 m	0.24 (39)
Lake Ontario 403	18 Aug – 26 Oct 1998	20 m + 60 m	1.4 (39)
Lake Ontario 403	8 Apr – 22 Jun 1998	164 m + 172 m	1.2 (19)
Lake Ontario 403	22 Jun – 18 Aug 1998	165 m + 173 m	0.86 (36)

Lake Ontario 403	18 Aug – 26 Oct 1998	166 m + 174 m	2.0 (36)
Lake Erie 357	30 Jun – 27 Jul 1999	9.0 m	14 (12)
Lake Erie 357	1 Sep – 4 Oct 1999	9.0 m	29 (15)
Lake Ontario 403	13 Apr – 1 Jun 1999	19 m + 99 m	0.43 (27)
Lake Ontario 403	13 Apr – 1 Jun 1999	165 m + 173 m	0.64 (24)
Lake Ontario 403	1 Jun – 28 Oct 1999	60 m + 100 m	0.19 (31)
Lake Ontario 403	1 Jun – 28 Oct 1999	167 m + 175 m	0.84 (23)
Lake Erie 357	26 Apr – 16 May 2000	8.8 m	28 (9.8)
Lake Ontario 403	28 Oct 1999 – 7 Apr 2000	20 m	0.61 (19)
Lake Ontario 403	28 Oct 1999 – 7 Apr 2000	60 m	0.73 (21)
Lake Ontario 403	28 Oct 1999 – 7 Apr 2000	140 m	1.5 (19)
Lake Ontario 403	28 Oct 1999 – 7 Apr 2000	165 m	3.0 (19)

Table 2. Suspended sediment annual mean contaminant concentrations (ng/g) and daily contaminant down flux rates (bracketed values expressed in ng m^{-2} day^{-1}) for Lakes Erie and Ontario over the period 1997 – 2000. ND under mirex denotes not detected at MDL of 1.0 ng/g. Daily contaminant down fluxes were calculated using the mean daily sediment down flux rates from the values shown in Table 1. [a]Individual depth samples for Lake Ontario winter 2000. [b]Individual monthly samples with contaminant concentrations and down flux rates based on down flux of suspended sediment for individual monthly samples.

	PCBs	**DDT**	**Dieldrin**	**HCB**	**Mirex**
Erie 1997	620 (97,000)	25 (3,900)	1.1 (170)	4.0 (630)	ND
Ontario 1997	820 (750)	35 (32)	3.2 (2.9)	8.1 (7.5)	13 (12)
Erie 1998	250 (19,000)	14 (1,060)	0.67 (51)	4.1 (310)	3.5 (265)
Ontario 1998	490 (530)	37 (40)	6.4 (7.0)	7.8 (8.5)	13 (14)
Erie 1999	150 (3,300)	16 (350)	0.58 (13)	3.9 (86)	ND
Ontario 1999	440 (230)	23 (12)	2.2 (1.2)	4.2 (2.2)	1.2 (.64)
Erie 2000	290 (8,100)	12 (340)	0.92 (26)	4.1 (120)	ND
Ontario 2000	380 (560)	43 (63)	2.6 (3.8)	17 (25)	2.6 (3.8)
Ontario 2000 20 m[a]	390 (240)	37 (23)	1.4 (0.85)	14 (8.5)	11 (6.7)
Ontario 2000 60 m	430 (310)	38 (28)	2.9 (2.1)	17 (12)	15 (11)
Ontario 2000 140 m	350 (525)	43 (65)	3.3 (5.0)	18 (27)	13 (20)
Ontario 2000 165 m	370 (1,100)	52 (160)	3.0 (9.0)	21 (63)	17 (51)
Erie May 1997[b]	660 (210,000)	25 (8,000)	1.3 (420)	4.9 (1,570)	
Erie June 1997	89 (2,700)	19 (570)	ND	3.2 (1,000)	

Erie July 1997	810 (34,000)	27 (1,100)	1.6 (67)	4.2 (180)
Erie August 1997	720 (46,000)	35 (2,200)	1.7 (110)	3.9 (250)
Erie October 1997	830 (270,000)	18 (5,900)	1.0 (330)	4.1 (1,400)

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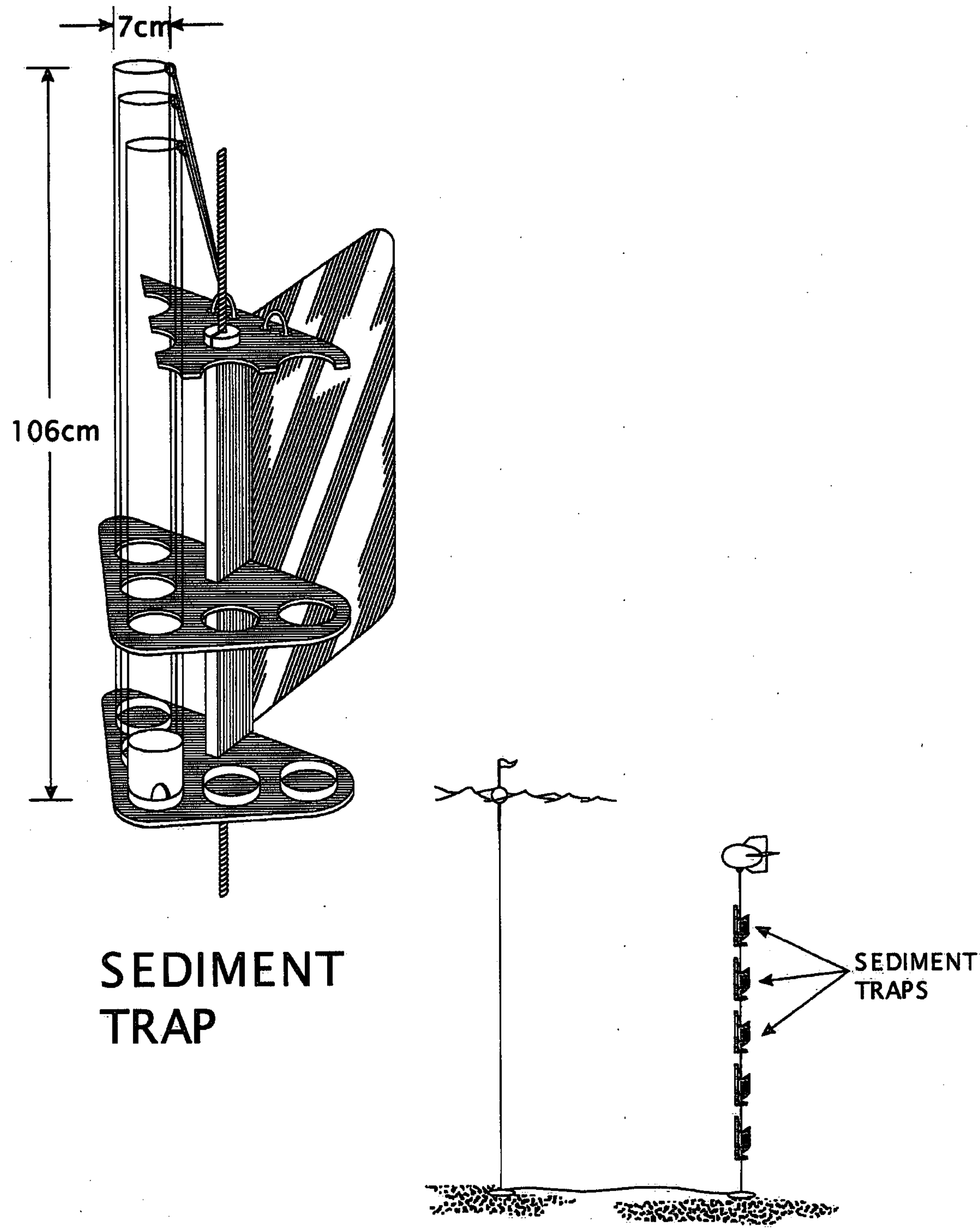
1986 and 1997 – 2000. The 1982 – 1986 data set was taken from Oliver et al. (1989).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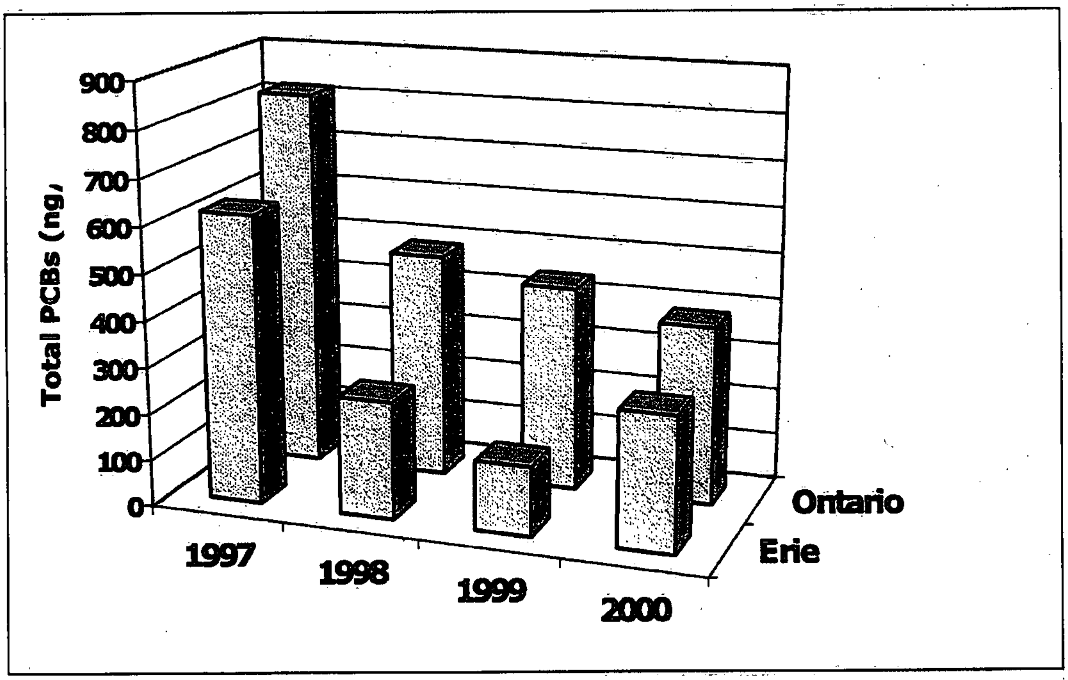
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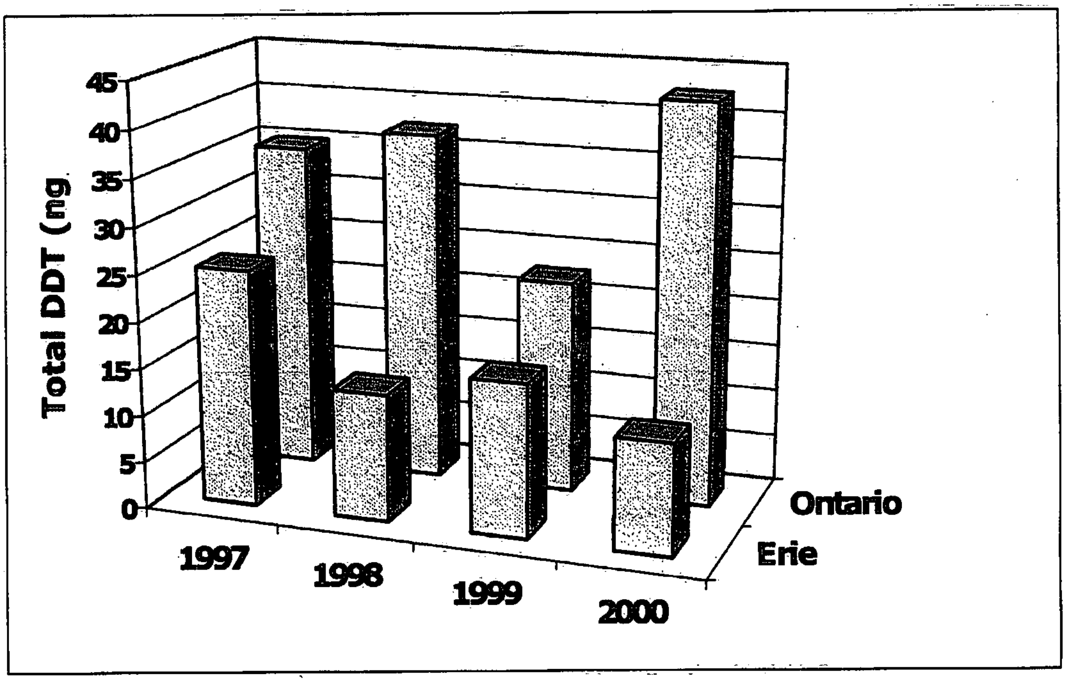
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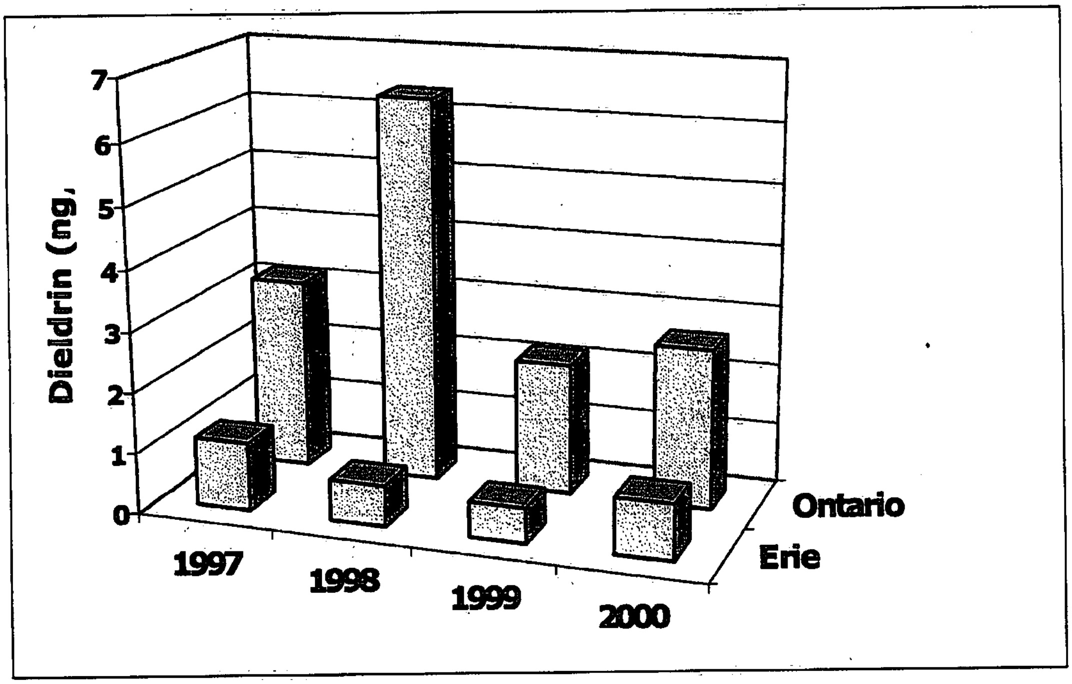
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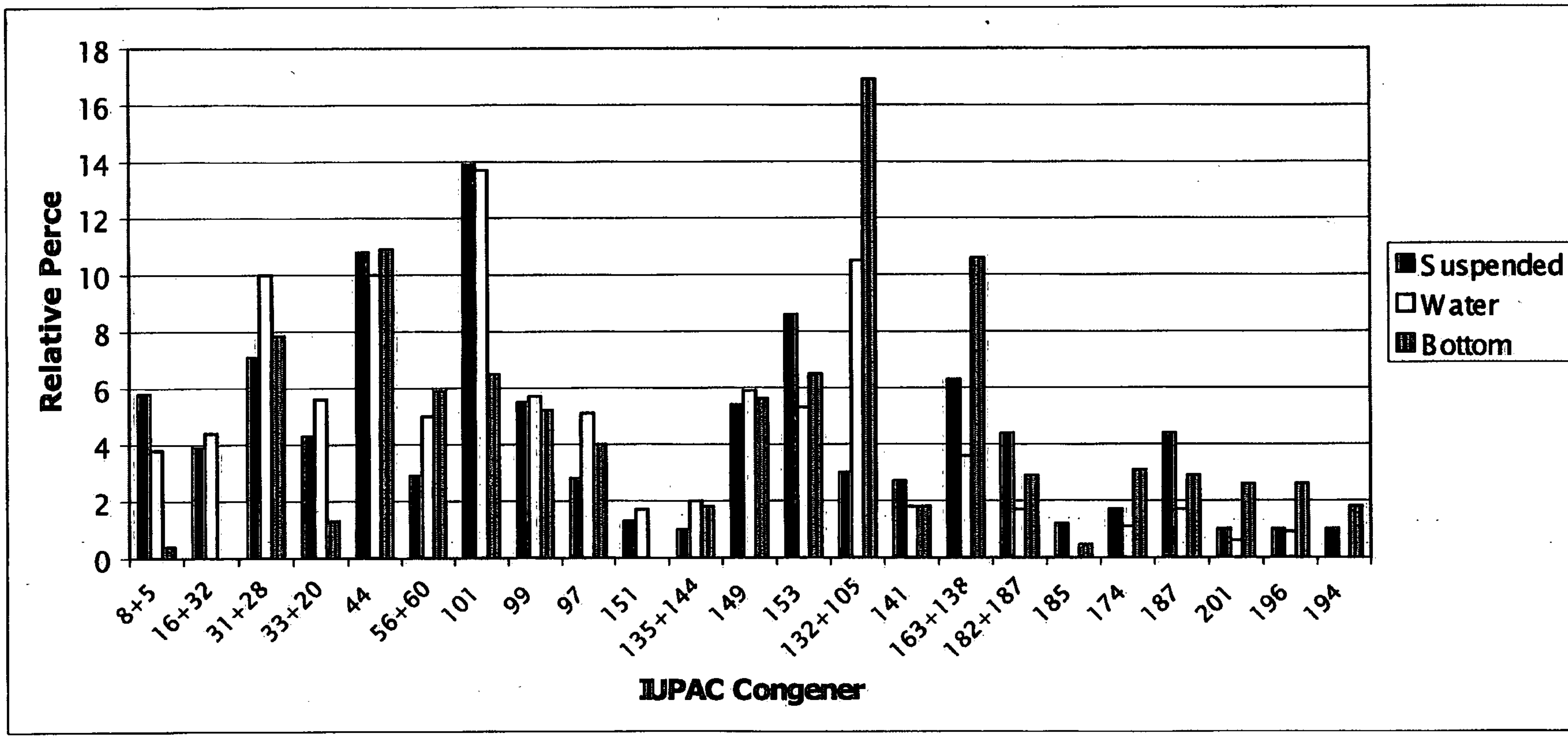
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182+187
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194
IUPAC Congener
Suspended
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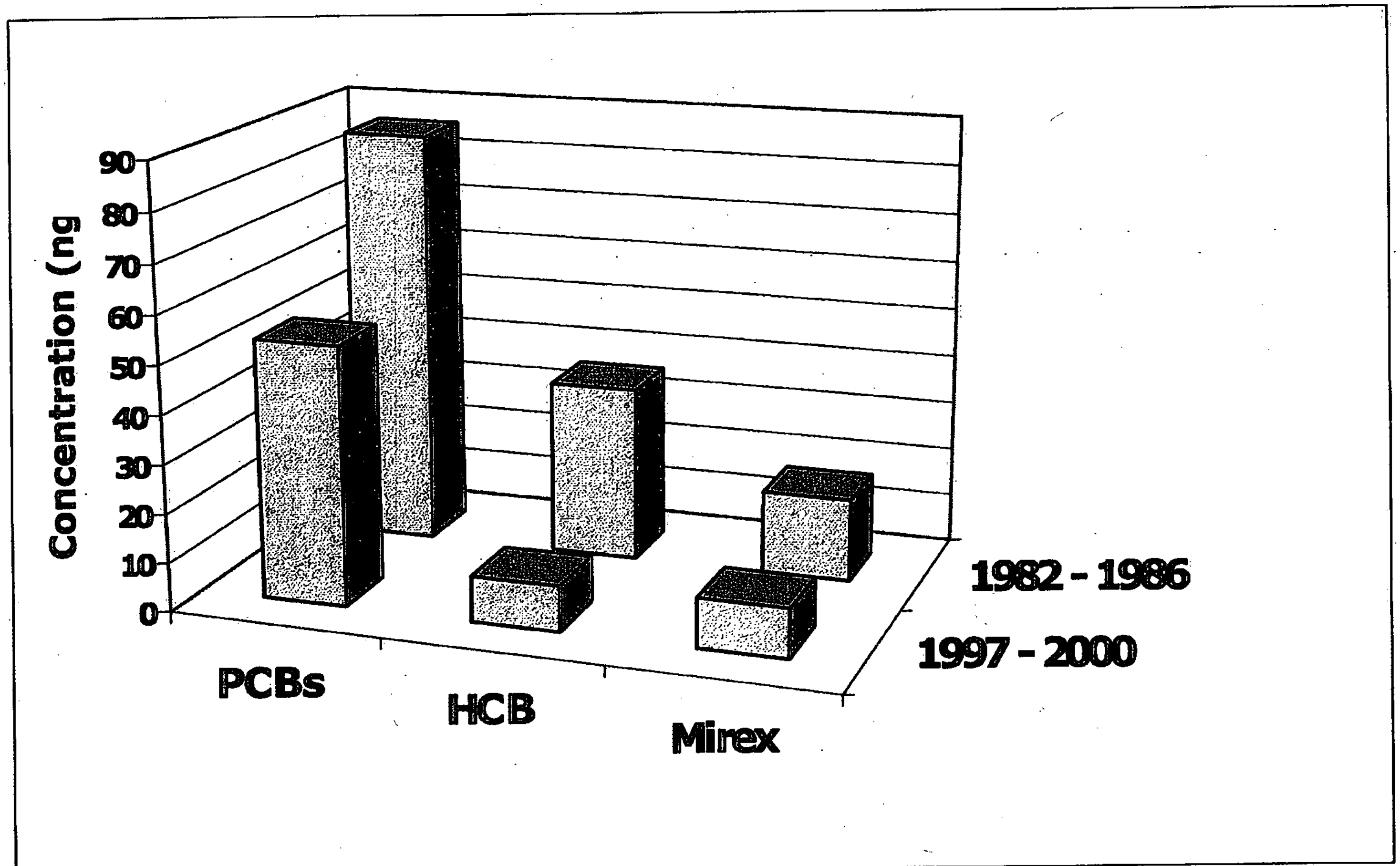
Bottom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PCBs
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1982 - 1986
1997 - 2000

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