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DISTRIBUTION, REDISTRIBUTION AND GEOCHRONOLOGY  
OF PCB CONGENERS AND OTHER CHLORINATED  
HYDROCARBONS IN LAKE ONTARIO SEDIMENTS

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## ABSTRACT

The concentrations of PCB congeners and several other chlorinated hydrocarbons such as chlorobenzenes, chlorotoluenes, lindane, mirex, DDT, etc. have been determined in Lake Ontario sediments. Surficial sediments show a reasonably uniform contaminant distribution throughout the sedimentation basins (SBs) with no strong plumes to sources. Sediment samples outside the SBs displayed very low contaminant concentrations indicating that over the long term sediment-associated contaminants wind up in the SBs. Sediment trap studies showed that a considerable amount of sediment resuspension occurs in the lake especially when it is unstratified during the winter. This observation helps to explain the fairly uniform concentrations found in the SBs. Sediment core studies showed peak discharges of the contaminants occurred in the late 1950s (DDT) and the mid 1960s (PCBs, mirex and chlorobenzene) in good agreement with production and usage history. Changes in PCB and DDT composition in the cores are discussed.

## RÉSUMÉ

La concentration des congénères de PCB et de plusieurs autres hydrocarbures chlorés comme les chlorobenzènes, les chlorotoluènes, le lindane, le mirex, le DDT, etc. a été déterminée dans les sédiments du lac Ontario. Dans les sédiments superficiels, les contaminants sont assez uniformément distribués dans tous les bassins de sédimentation et ne s'accompagnent pas de panaches importants provenant des sources. Les échantillons de sédiments à l'extérieur des bassins de sédimentation présentent de très faibles concentrations de contaminants, ce qui indique qu'à long terme les contaminants associés aux sédiments se retrouvent dans les bassins de sédimentation. Les études à l'aide de pièges à sédiment ont montré que des quantités considérables de sédiments sont remis en suspension dans le lac, surtout lorsque celui-ci est non stratifié durant l'hiver. Cette observation contribue à expliquer les concentrations assez uniformes retrouvées dans les bassins de sédimentation. L'étude des carottes de sédiments montre que les contaminants se sont surtout accumulés à la fin des années 50 (DDT) et au milieu des années 60 (PCB, mirex et chlorobenzène), ce qui correspond tout à fait aux données historiques concernant la production et l'usage de ces produits. On discute des variations de la composition en PCB et en DDT dans les carottes.

## MANAGEMENT PERSPECTIVE AND EXECUTIVE SUMMARY

PCBs, chlorobenzenes, pesticides and many other chlorinated chemicals were found to be fairly evenly distributed in surficial sediments in the sedimentation basins of Lake Ontario. This result is different from previous studies where contaminated sediment plumes were apparent near the Niagara River. Our data shows that in the long term contaminated sediments are fairly equally distributed throughout the lake in the sedimentation basins by lake currents. The quantities of sediment and associated contaminants in suspension in the lake were measured using sediment traps. It was found that a considerable amount of sediment is resuspended particularly in winter months when the lake is unstratified. This result further illustrates the dynamic nature of the bottom sediments in the lake.

Three sediment cores were finely sectioned and analyzed in detail to obtain an historical record of lake contamination. Peak discharges of DDT and of PCBs, mirex and chlorobenzenes occurred in the late 1950s and in the mid 1960s, respectively, in good agreement with production and usage patterns. For the cores and surficial sediment samples, we were able to estimate the approximate total quantities of the contaminants in the lake's bottom sediments. The quantities were large and ranged from about 1 metric ton for octachlorostyrene to about 50 metric tons for PCBs. These results show that these contaminated sediments will pose a significant problem to the lake for many years to come, even after chemical loadings are reduced or eliminated.

DISTRIBUTION, REDISTRIBUTION ET GÉOCHRONOLOGIE DES CONGÉNÈRES DE  
PCB ET D'AUTRES HYDROCARBURES CHLORÉS DANS LES SÉDIMENTS DU LAC ONTARIO  
Barry G. Oliver, Murray N. Charlton et Raymond W. Durham

PERSPECTIVES DE GESTION ET RÉSUMÉ

Les PCB, les chlorobenzènes, les pesticides et de nombreux autres composés chimiques chlorés sont assez uniformément distribués dans les sédiments superficiels des bassins de sédimentation du lac Ontario. Ces résultats diffèrent des études précédentes qui ont montré que des panaches de sédiments contaminés étaient visibles près de la rivière Niagara. Nos données montrent qu'à long terme les sédiments contaminés sont assez uniformément distribués dans les bassins de sédimentation du lac grâce aux courants. Les quantités de sédiments et les contaminants qui s'y trouvent et qui sont en suspension dans le lac ont été mesurés à l'aide de pièges à sédiment. On a observé que des quantités considérables de sédiments sont remis en suspension, particulièrement au cours des mois d'hiver lorsque le lac est non stratifié. Ces résultats illustrent davantage la nature dynamique des sédiments de fond dans le lac.

Trois carottes de sédiments ont été divisées finement et analysées en détail pour obtenir des données historiques sur la contamination du lac. Les accumulations les plus importantes ont eu lieu à la fin des années 50 dans le cas du DDT et au milieu des années 60 dans le cas des PCB, du mirex et des chlorobenzènes, ce qui concorde avec les modes de production et les usages de ces produits. Dans le cas des carottes et des échantillons de sédiments superficiels, nous avons pu calculer la quantité totale approximative

de contaminants dans les sédiments de fond du lac. Les quantités sont importantes et varient d'environ une tonne métrique dans le cas de l'octachlorostyrène à environ 50 tonnes métriques dans le cas des PCB. Ces résultats montrent que ces sédiments contaminés vont présenter un problème de taille dans le lac pour de nombreuses années à venir, même après diminution ou élimination de la pollution chimique.

## INTRODUCTION

The bottom sediments of Lake Ontario are known to be contaminated with a variety of halogenated organics (1-5). Surficial sediments collected in an 8 km grid in 1968 showed an apparent PCB source to the lake from the Niagara River (1), and sources of mirex to the lake from the Niagara and Oswego Rivers (2). Other contaminants that have been shown to be present at elevated concentrations in the sediments are chlorobenzenes (3), octachlorostyrene (4), DDT (1) and 2,3,7,8-tetrachlorodibenzo-p-dioxin (6). More recent sediment studies on a group of fluorinated aromatic compounds that originate from the Hyde Park dumpsite on the Niagara River, showed that these chemicals were distributed over the entire lake, including the Kingston Basin, a distance of over 200 km from the source (5).

Earlier studies on the physical characteristics of bottom sediments in the lake showed that there were four major lake basins in which sediments were accumulating (7). These basins called the Niagara, Mississauga, Rochester and Kingston, are shown in Fig. 1. Over the rest of the main lake net sediment erosion occurs over the course of the year. Even in the sedimentation basins the rate of sediment accumulation is extremely low ranging from 0.3 to 4 mm per year (8, 9). Because of these slow burial rates, the sediments can act as an important source of contaminants to the lake water and biota for many years.

Previously we analyzed a single sediment core near the mouth of the Niagara River that showed the loading of mirex and chlorobenzenes from the river had decreased in recent years (10). In this paper we report the detailed analysis of three sediment cores, one from each major basin, for a wider variety of chemicals including PCB congeners. In addition, the surficial sediment (0-3 cm) from 38 locations in the sedimentation basins and samples of the mobile particle pool collected using sediment traps in each basin were also analyzed. The data provide new information on the movement and entrainment of sediments and sediment-associated contaminants in Lake Ontario.

#### EXPERIMENTAL

Surficial sediments (0-3 cm) were collected using a 0.5 m<sup>2</sup> box corer from the sedimentation basins in May, 1981 (Fig. 1) as part of a Great Lakes sediment banking network (11). The samples were placed in solvent-cleaned glass jars and frozen until analysis. Three sediment cores (10 cm in diameter) were obtained in July, 1982 from 0.5 m<sup>2</sup> box cores from the Niagara (station 14, 43°23'36"N, 79°24'12"W), Mississauga (station 403, 43°35'50"N, 78°13'48"W) and Rochester (station 64, 43°31'30"N, 76°55'42"W) basins of the lake. The cores were refrigerated upright at 4°C on the ship and then returned to the laboratory where they were sectioned in 0.5 cm intervals. The sections were frozen in glass jars until analysis. Samples of settling resuspended sediments and detritus were obtained from the three major



basins very close to the locations where the cores were recovered at six month intervals from 1982 to 1986 using sediment traps (12). Several traps were deployed at each site at the depths #14-20, 40, 60, 80, 90 and 98 m, #403 - 20, 60, 100, 140, 166 and 174 m, #64 - 20, 60, 100, 140, 180, 204, 211 m. The traps were deployed from May to November and from November to May each year.

The samples were soxhlet extracted with acetone/hexane for 16 hr, back extracted with water to remove the acetone, then the extract was concentrated using Snyder and Kuderna-Danish condenser to the appropriate volume (13). Extract clean-up consisted of passage through an 8 mm I.D. column packed with 1 cm  $\text{Na}_2\text{SO}_4$ , 4 cm 40%  $\text{H}_2\text{SO}_4$  on silica and 2 cm of Florisil (deactivated with 5% water). The extracts were vortexed with mercury to remove sulfur interferences. Recoveries and reproducibilities ( $\pm 10\%$ ) of the procedures have been shown to be good (13). The determinations were carried out using dual capillary columns (30 m, DB5 and DB17) with electron capture detectors ( $350^\circ\text{C}$ ). The carrier gas was helium (linear velocity 20 cm/s) and an extremely slow program rate  $50^\circ$  to  $250^\circ\text{C}$  at  $1^\circ\text{C}/\text{min}$  was used to optimize separations of the PCB congeners. For the PCBs the instrument was calibrated using the Aroclor mixture 1221, 1016, 1254, 1262 in the ratio 10:5:3.5:3 as a secondary standard using the Aroclor composition data of Mullin (14, 15). Commercially available congeners were used to confirm many of the peak assignments and amounts. The PCB numbering system of Ballschmiter and Zell (16) is employed for simplicity. The chlorobenzenes (di-throughhexa), the chlorotoluenes (2,4,5; 2,3,6; and 2,3,4,5,6), hexachlorobutadiene, hexachloroethane, octachlorostyrne,  $\alpha$  and

$\gamma$ -benzenehexachloride,  $\gamma$ -chlorodane, pp-DDT, pp-DDD, pp-DDE, mirex and photomirex have been analyzed as well as the PCB congeners.

Most of the samples were also analyzed using a 30 m, DB5 capillary column coupled to a Hewlett Packard 5970 mass selective detector (MSD) employing single ion monitoring for quantitative confirmation. Agreement between the two detection systems was excellent for all chemicals except the dichlorobenzenes (DCBs). The DCBs were much lower (1/2 to 1/3) on the MSD indicating probable interferences with the ECD determinations of these chemicals which occur near the beginning of the gas chromatographic scan. DCB data from the MSD are used here. For brevity only the behaviour of some typical compounds are discussed in the paper, but the full data set is available as supplementary tables.

## RESULTS AND DISCUSSION

Concentration maps are shown for three representative chlorinated organics: mirex, PCBs and hexachlorobenzene (HCB) in Figs. 1, 2 and 3. The maps indicate that these chemicals are distributed fairly uniformly over the three main sedimentation basins with lower concentrations in the Kingston Basin. The mean concentrations in the Niagara, Mississauga, Rochester and Kingston Basins are: mirex  $30 \pm 20$ ,  $38 \pm 9$ ,  $33 \pm 17$  and  $6.4 \pm 4.3$ ; PCBs  $510 \pm 160$ ,  $690 \pm 220$ ,  $630 \pm 340$  and  $200 \pm 150$ ; and HCB  $110 \pm 84$ ,  $130 \pm 58$ ,  $100 \pm 49$  and  $14 \pm 6.5$ , respectively. Several samples collected near the edge or out of the sedimentation basins contained at least an order-of-magnitude lower contaminant concentrations. This confirms that little net accumulation of sediment was occurring in

these areas. For example HCB concentrations averaged 4 ppb in samples outside the basins compared to 100 ppb within the basins. Thus our data clearly shows that over the long term contaminants entering the lake on suspended sediment eventually make their way to the sedimentation basins of the lake. Pickett and Dossett (17) have described the circulation pattern of Lake Ontario as a counterclockwise gyre moving eastward from the Niagara River along the south shore then westward along the north shore. The three main basins of the lake fall within this circulation regime which undoubtedly transports water and associated resuspended sediments over the entire lake. The Kingston Basin which is outside this circulation pattern was found to have much lower sediment contaminant concentrations. The presence of a nepheloid layer of high turbidity has been observed in the lake (18). Sediment trap studies in the next section will further demonstrate the importance of redistribution of sediments throughout the lake.

This contaminant distribution pattern is different to that reported by Frank et al. (1) for PCBs and Van Hove Holdrinet et al. (2) for mirex in 1968 surficial sediments. In the earlier studies a strong PCB plume emanated from the Niagara River and along the south shore of the lake, and mirex plumes for both the Niagara and Oswego Rivers were observed. Since the loadings of these contaminants to the lake were much greater in the 1960's than currently (10), it is possible that the nearshore sediments were contaminated for the short term with these heavy loadings. Interestingly, Frank et al. (1) observed that the mean PCB concentrations in the lake's three main sedimentation basins were very similar in agreement with the current study.

There are also significant differences in the absolute concentrations of contaminants observed in this and the earlier studies (1, 2). Theoretically, the earlier concentrations should be higher since the samples were collected at a time when loadings to the lake were greater (10). The mean concentrations were, in fact, much lower in the earlier studies - PCBs 85, mirex 7.5 and EDDT 60 compared to current mean values of PCBs 570, mirex 31 and EDDT 140. These differences are probably due to different sampling and analytical methods used in the two studies. The earlier samples were collected with a Shipek dredge from which some of the surface sediment could have been lost during recovery from the great depths of Lake Ontario. With the loss of this surface material, more of the less contaminated deeper sediments may have been analyzed. The newer box core sampler, employed in this study, is largely free of this problem; the surface sediments complete with worm borrows and mounds seems to reach the surface relatively undisturbed. The extraction procedure in the earlier study was direct wet sediment extraction with hexane/acetone for two hours. The current more exhaustive soxhlet extraction for 16 hours may have increased contaminant recoveries. For PCBs, use of packed columns versus the current capillary columns could have contributed to the observed differences. Three sediment samples, archived from the 1968 sampling and taken from locations close to current sediment coring sites, were analyzed by current methodology. Concentration values obtained were close to what would be predicted for the period around 1968 based on our current analysis of sediment cores. This suggests

the analytical procedure differences may be the largest contributor to the discrepancies between the studies.

Congener specific PCB analysis showed that the PCB composition in sediments was fairly uniform throughout the lake. The percentage chlorine of the PCBs averaged 54.3, 54.2, 54.0 and 53.8 for the four basins with an overall mean of  $54.1 \pm 0.6$ . No mono- or dichlorobiphenyls were found in the samples but the detection limit for these chemicals, 30 ppb mono, 3 ppb di, is much higher than for the other PCBs. The mean concentrations of the other isomeric groups were: tri,  $22 \pm 11$ ; tetra,  $200 \pm 77$ ; penta,  $180 \pm 76$ , hexa,  $93 \pm 41$ ; hepta,  $48 \pm 20$ ; octa,  $22 \pm 11$ ; nona,  $5.7 \pm 2.4$ ; deca,  $9.4 \pm 5.3$ , which represented 4, 34, 31, 17, 8, 4, 1, 2 percent of the total PCBs, respectively. The most predominant congeners which comprised over 2% of the total PCBs were: #66(7.9%), #110(6.4); #56+60 (5.7), #101(4.7), #52(4.3), #153(4.3), #70+76(4.0), #44(4.0), #84(3.6), #49(3.4), #87+97(3.4), #28+31(2.9), #118(2.6), #138(2.6), #95(2.4), #180(2.2) and #47+48(2.1).

The chlorobenzenes (CBs) are found in significant concentrations in all the samples. The total di through hexa CBs were 370 ppb with 12% di, 31% tri, 21% tetra, 9% penta and 27% hexa. This order of predominance is quite different from that found in the Niagara River the major source of these chemicals to the lake (68% di, 21% tri, 8% tetra, 2% penta, 1% hexa) (19). This shows that increasing the chlorine content on the benzene ring leads to higher relative accumulation of the chemicals in sediments. In the DDT family pp-DDD and pp-DDE are present in much higher concentrations than parent pp-DDT, showing the gradual degradation of DDT to its major anaerobic

and aerobic degradation products. Photomirex was present in the samples at about 13% of the mirex concentration.

A plot of the log (chemical concentration in bottom sediments/chemical concentration in Niagara River water) versus log  $K_{ow}$  is shown in Fig. 4. As expected, the plot shows that there is an increasing tendency of chemicals to partition to sediments as their octanol-water partition coefficient ( $K_{ow}$ ) increases (20). A similar graph would be generated if this ratio were plotted versus the inverse of the water solubility of the chemicals (20). Lindane and  $\alpha$  BHC, cyclic but non-aromatic pesticides, fall below most points in the graph indicating that they have a much lower tendency to partition to sediments than would be predicted from their  $K_{ow}$ . The very low concentration of these chemicals in sediments was previously noted in samples from Lakes Huron, St. Clair and Erie (21). Lindane and  $\alpha$  BHC were observed to have among the highest concentrations of chlorinated chemicals in offshore Great Lakes water samples (22, 23).

#### Settling Sediments

Samples of sediments and detritus in the watercolumn were collected from 1982 to 1986 using sediment traps. Details of the design and deployment of the traps have been previously reported (12, 24). Figure 5 shows a typical plot found for the total catches as a function of depth for the summer and winter traps. It can be seen that there is a significantly higher catch in the bottom traps as compared to the traps nearer the lake surface for both seasons, showing clearly

that resuspension of bottom sediments is occurring. Also catches are observed to be much higher in the winter than in the summer indicating that more lake mixing and resuspension occurs when the lake is unstratified. The winter also brings more violent storms which can penetrate deeply when the lake is isothermal. Thus, hypothetically in the winter, the material in suspension at all lake depths should be largely resuspended bottom sediments. However, in the summer, material caught in the traps nearer the lake surface should contain a significant portion of material autochthonously generated by plankton in the system and new sediment inputs from tributaries. Traps near the bottom in the summer probably still contain a significant fraction of resuspended bottom sediments.

These hypotheses can be tested by studying the behaviour of several halogenated chemicals entering the lake. For example,  $\alpha$  BHC, as seen previously, is present at very low concentrations in bottom sediments. This chemical is present in the parts-per-trillion range in water (22, 23) and is bioconcentrated by biota to the parts-per-billion range (25). A comparison of  $\alpha$  BHC in winter and summer traps shows higher average  $\alpha$  BHC concentrations in trapped material from the summer months compared to winter ( $2.8 \pm 2.7$  versus  $1.6 \pm 0.8$ ). Some of the summer, near-surface traps had  $\alpha$  BHC values up to 11 ppb showing the significant impact of biota. Conversely mirex shows the completely reverse phenomena with higher concentrations in the winter than in the summer trap material ( $15 \pm 4.4$  versus  $9.4 \pm 1.7$ ). Most mirex sources to the lake have been reduced (10) so the bottom sediments,

contaminated with historical discharges, appear to be the major source of mirex to the watercolumn.

The ratio of photomirex to mirex also displays interesting behaviour in the trap material. Mudambi and Hassett (26) have reported that mirex is converted to photomirex with the loss of one chlorine atom by sunlight photolysis in Lake Ontario water. The ratio of photomirex to mirex in winter traps averaged 0.24, higher than the ratio for bottom sediments (0.13) showing that some of the mirex had reached the photic zone of the lake. The summer photomirex/mirex ratio was even higher (0.27) indicating even longer sunlight exposure of mirex in the summer months. This ratio may prove useful for tracing the recycling of mirex and similar contaminants when more information becomes available on quantum yields of the photolysis reaction.

Table I shows concentration and downflux data for selected contaminants for the winter traps. There does not seem to be any significant change in the concentrations or downfluxes of the contaminants at the individual stations over the four year study. Although there is an apparent decline in PCB's from 82/83 to 85/86 there are too few data to conclude that a trend has developed. Since the traps at this time of the year catch mainly very recently deposited resuspended sediments, these results may indicate that there has been little change in the loadings of these contaminants to the lake over the last four years. It is evident from the table that there is a consistent difference in dry mass and, in most cases, contaminant downflux between the stations. Catches decrease in the order 14 > 403



> 64 in the inverse order of the water depths at the three sites: 100 m, 176 m and 213 m, respectively. Thus, less resuspension appears to occur in deeper water. Comparing the concentration on suspended material to bottom sediments shows that HCB and mirex are lower in the suspended material than the bottom sediments but PCBs are similar in both compartments. The data for the summer traps are less consistent likely due to variable contributions of resuspended sediments to the sediment trap catches.

In an earlier sediment trap study on Lake Ontario by Rosa (27), sediment traps were retrieved at much more frequent, weekly, intervals. Suspended sediment concentrations at various depths were measured at both the time of deployment and the time of retrieval. Rosa found that there was an excellent linear correlation ( $r^2=0.88$ ) between sediment trap catches (STC) and suspended sediment (SS) concentration and proposed the following equation:

$$STC = 0.76 (SS) - 0.3$$

(1) from reference (27).

Using this equation it is possible to approximate the long-term suspended sediment concentration at various depths for the trap sites (Table II). This data can then be used to estimate the total mass of suspended sediments and, thus, the total mass of contaminants in suspension in Lake Ontario. Estimates were made for each basin by using a depth-integrated average suspended sediment concentration and adding 10% for the unknown Kingston Basin. Roughly a total of 5.4

million metric tons of material was suspended in the winter, 3.4 million metric tons in the summer with an overall mean of 4.4 million metric tons. this translates to approximately 100 kg of HCB, 54 kg of mirex and 1500 kg of PCBs suspended in the watercolumn on particulates. These quantities are only a small fraction of the total contaminant storage in bottom sediments (see next section).

### Sediment Cores

The sediment cores were dated using excess  $^{210}\text{Pb}$  profiles and applying Appleby and Oldfield's constant rate-of-supply (CRS) model (28,29). This application of the CRS model, which is similar to Robbins (30) constant flux, variable sedimentation rate method, has been described previously (10). The highest sedimentation rate was observed at station 14 (4 mm/y) followed by station 64 (3 mm/y) and station 403 (2 mm/y). The  $^{137}\text{Cs}$  activity and the concentrations of several of the chlorinated hydrocarbons are plotted versus sediment depth and age in Fig. 6. The production or usage patterns for the chemicals and the fallout pattern for  $^{137}\text{Cs}$  is shown in Fig. 7. The  $^{137}\text{Cs}$  discharge to the atmosphere began with large scale nuclear weapons testing in 1953 and peaked in 1963. The  $^{137}\text{Cs}$  peak, which is visible in all three sediment cores, occurs in 1962 at sites 403 and 64 in excellent agreement with the fallout pattern, but in 1968 in core 14. The deviation in the maximum from predicted at site 14 may be due to interference from a point source for  $^{137}\text{Cs}$  on the Niagara River as

observed by Joshi (31). The appearance of  $^{137}\text{Cs}$  in the core, at a concentration above 5% of the maximum concentration, was observed at approximately the correct time at stations 14 and 64 (1953 and 1952, respectively) but in 1929 for core 403. This may indicate downward mixing of the sediments in this area, which had the lowest sedimentation rate and the least distinct maxima for the chlorinated organics.

Table III shows the observed approximate date of the peak concentration and the compound appearance for the three cores and similar dates for production, usage or fallout of the chemicals. The peak concentrations for mirex, PCBs and HCB occurred in the mid 1960s and there is good agreement between the core record and the production or usage history. This is somewhat later than observed earlier for a single core near the mouth of the Niagara River, where these chemicals appeared to peak between 1959 and 1962 (10). The EDDT peak occurs in the late fifties to early sixties in good agreement with usage patterns. Interestingly, the three DDT pulses in the usage profile appear in cores 14 and 64 but not in the more smeared core 403. The appearance of the chemicals in the cores is reasonably consistent with the production history except in case 403 where the appearance predates the start of production. A downward smearing appears to occur for the organics as well as  $^{137}\text{Cs}$ .

The typical behaviour of pp-DDT and its aerobic metabolite pp-DDE and its anaerobic breakdown product pp-DDD is shown for core 64 in Fig. 8. DDT comprises only about 25% of the total DDT near the core

surface. This observation is not surprising since DDT use was banned in 1972 and its reported half-life in soils is of the order of 3-5 years (40, 41). The DDT abundance drops gradually to less than 2% at the bottom of the core and a large relative concentration increase for DDD is observed. Similar trends were found in the other cores. The half-life of the first-order conversion of pp-DDT to pp-DDD in the sediments can be derived by plotting  $\ln (DDT/DTT+DDD)$  versus time (Fig. 9). The ratio must be used instead of the absolute DDT concentration because of the changing amount of total DDT in the various core segments. The linear correlation coefficients ( $r^2$ ) for the plots are 0.81, 0.88 and 0.74, respectively, for cores 14, 403 and 64 with resulting half-lives of 14, 21 and 15 years. The DDT half-life for sites 14 and 64 are in excellent agreement but site 403, with the lowest sedimentation rate, appears to have a significantly longer DDT half-life. Also, for stations 14 and 64, the plots are linear over the whole core but for 403 the plot appears to plateau in the deeper core layers. The longer DDT half-life and plateauing at this site may indicate lower populations of anaerobic bacteria in the uppermost part of the core compared to the other sites and a low or negligible anaerobe population below about 5 cm. Although the conversion of DDT to DDD in sediments has been observed (42, 43), to our knowledge, this is the first study to estimate the time course of the reaction for in-situ sediments.

Congener specific PCB analyses of the sediment core sections showed that not only does the total PCB concentration change with

sediment depth, but PCB composition also changes. The percentage chlorine of the PCBs increased significantly from about 55% near the top of the cores to 58 to 60% at the bottom of the cores. Changes in the isomeric composition with depth are shown for core 64 in Fig. 10. The percentage composition of the lower chlorinated isomers decreases with depth, whereas, the more highly chlorinated isomers increase with depth. These observations are consistent with the changes in percentage chlorine of the PCBs.

Typical changes in the percentage of various individual congeners in the cores is shown for representative tri-through decachlorobiphenyl in Fig. 11. PCBs 28+31, 52 and 110 gradually decrease in relative concentration going down the cores. The exception to this behaviour is core 403 where there appears to be little change in these constituents. For PCB 153, a hexachlorobiphenyl, a slight increase in abundance is observed in all cores. For the more highly chlorinated PCBs - 180, 201, 206 and 209 fairly dramatic increases in abundances with depth occur in the cores. At first glance this appears to show that anaerobic dehalogenation of the PCBs is occurring. Some investigators have postulated that this reaction occurs in Hudson River sediment (44) but other have had difficulty demonstrating its occurrence (45). If anaerobic degradation were occurring one would expect to see increases in the chlorine content of the PCBs at about the same depth in all cores, i.e. below the oxic zone of 1 to 2 cm. However, the change in composition toward more heavily chlorinated PCBs seems to occur at approximately the same date in all cores and thus at

different depths. Thus, a feasible explanation for the change in PCB composition could be simply a shift in usage pattern from more heavily chlorinated PCBs to less chlorinated PCBs in more recent years. After recognition that PCBs were highly persistent in the environment (46), a shift to formulations containing less of the highly chlorinated isomers, like Aroclor 1016, did occur just prior to implementation of use restrictions (34).

From the core data it is difficult to dismiss entirely the possibility that PCBs may be partially degraded in the sediment. Dechlorobiphenyl (209) should be the most stable, least mobile and most highly sediment partitioned PCB. The only Aroclor which contains a significant amount of 209 (~5 wt %) is Aroclor 1268 (14) which represented much less than 1% of USA produced PCBs (34). Aroclor 1268 was not produced after 1970 so the presence of ~2% decachlorobiphenyl in surficial sediments must indicate a strong preferential adsorption compared to other PCBs unless there are other sources. Thus the increase in percentage of 209 and the other highly chlorinated PCBs like 201 and 206 in the bottom of the cores, is likely due to strong preferential partitioning processes and possibly to higher mobility and loss of the lower chlorinated congeners from the sediments. But, anaerobic degradation cannot be completely ruled out, but the detection of sulfur containing PCB metabolites would probably be required to prove that this phenomena was important.

It is possible to make a crude estimate of total mass of the various chemicals in the bottom sediments by using both the sediment

core and surficial analyses. The total chemical flux is first calculated for each core by summing the masses of chemicals in each segment. Since the chemical concentrations in the cores may not be representative of the entire basin, the concentrations are crudely normalized by using the ratio of mean chemical in surficial sediments of the basin (0-3 cm) divided by the mean chemical concentration in the 0-3 cm interval of the core. This ratio is then multiplied by the flux and the area of the sedimentation basin to obtain the total contaminant mass. The area for the sedimentation basins used in the calculation were 1600, 2700 and 3800 km<sup>2</sup> for the Niagara, Mississauga and Rochester Basins, respectively (47). The contaminant masses for the selected chemicals were substantial (Table IV) ranging from about 1 metric ton for octachlorostyrene (OCS) to about 50 metric tons for PCBs. To improve these estimates an extensive and expensive field coring program would be required. The rough estimates made here show that there is sufficient contamination in the sediments to impact the lake for many years to come. Recent studies have shown that PCB concentrations in fish, after many years of decline following PCB banning, have plateaued or increased slightly in last few years (48). This observation may indicate that internal sediment cycling is keeping the contaminant concentrations elevated despite probable decreases in loadings. With the very low sedimentation rates in the lake, sediments remain in the biologically active zone (5-8 cm for oligochaete worms (48)) for many years.

#### ACKNOWLEDGEMENTS

The authors would like to thank K. Nicol, L. Durham, W. Booth and S. Thompson for their able technical assistance, and R. Bourbonniere for supplying the surficial sediment samples. We also thank the Technical Operations Division for help in collecting the samples.



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## FIGURE CAPTIONS

- Fig. 1 Concentration of mirex (ng/g) in surficial Lake Ontario sediments. Locations of sediment cores (#14, Niagara Basin, #403 Mississauga Basin, #64 Rochester Basin) and of sediment traps marked as Xs.
- Fig. 2 Concentration of PCBs (ng/g) in surficial sediments.
- Fig. 3 Concentration of HCB (ng/g) in surficial sediments.
- Fig. 4 Plot of log chemical concentration in bottom sediment/chemical concentration in Niagara River water versus log octanol-water partition coefficient ( $K_{ow}$ ).
- Fig. 5 Sediment catches (g/m<sup>2</sup>d) for winter (Nov. 82- May 83) and for summer (May 83 - Nov. 83) sediment traps at various depth at station #14.
- Fig. 6 <sup>137</sup>Cs (Bg/g), EDDT, mirex, EPCBs and HCB concentrations (ng/g) versus sediment depth and age for the three cores.
- Fig. 7 Production, usage or fallout profiles for chlorobenzenes (32, 33), PCBs (34), EDDT (35), mirex (36) and <sup>137</sup>Cs (37, 38, 39).
- Fig. 8 Total DDT , pp-DDT , pp-DDE and pp-DDD concentrations in core #64 as a function of depth.
- Fig. 9 First order plots for the anaerobic conversion of pp-DDT to pp-DDD.
- Fig. 10 PCB homologue groups as a percentage of total PCBs for core #64.
- Fig. 11 The behaviour of individual PCB congeners (expressed as a percentage of total PCBs) in the three sediment cores.

**Table I** Concentration (ng/g) and Downflux (ng/m<sup>2</sup>d) in Brackets for HCB, Mirex and PCBs in Winter Sediment Traps

Compound	82/83			83/84			84/85		
	#14	#403	#64	#14	#403	#64	#14	#403	#64
HCB	48(170)	34(39)	NS	38(170)	35(85)	21(43)	48(170)	48(160)	28(48)
Mirex	18(62)	20(23)	NS	12(53)	14(34)	7(14)	17(61)	22(72)	14(24)
PCBs	1300(4500)	1900(2200)	NS	500(2200)	570(1400)	350(720)	470(1700)	680(2200)	410(700) 2
Mass (g/m <sup>3</sup> d)	3.43	1.14	NS	4.42	2.44	2.06	3.61	3.28	1.71

Compound	85/86			Bottom Sediment (1981)		
	#14	#403	#64	Niagara Basin	Mississauga Basin	Rochester Basin
HCB	32(170)	27(91)	NS	110	130	100
Mirex	12(62)	13(44)	NS	33	38	33
PCBs	80(1400)	290(970)	NS	510	690	630
Mass (g/m <sup>2</sup> d)	5.16	3.36	NS			

NS = no sample

Table II Mean Sediment Trap Catches (g/m<sup>2</sup>/d) and Estimated\* Suspended Sediment Concentrations (mg/L) for the Period Nov. 1982 to Nov. 1986.

Trap Depth (m)	Winter		Summer	
	Catch	SS Concentration	Catch	SS Concentration
<u>Station 14</u>				
20	2.5±0.4	3.6	1.2±0.1	1.9
40	3.2±0.9	4.6	1.1±0.2	1.8
60	3.3±0.4	4.8	1.3±0.1	2.0
80	4.0±0.8	5.7	1.5±0.2	2.3
90	5.0±1.1	7.0	1.9±0.3	2.9
98	6.9±1.5	9.6	3.2±1.7	4.6
Mean**		5.0±1.6		2.2±0.6
<u>Station 403</u>				
20	1.2±0.4	2.0	1.1±0.3	1.9
60	1.6±0.4	2.4	1.1±0.4	1.9
100	1.9±0.4	3.0	1.3±0.3	2.0
140	2.5±0.4	3.6	1.5±0.5	2.3
166	3.6±0.4	5.1	1.6±0.4	2.5
174	4.7±0.4	6.6	1.9±0.5	2.9
Mean**		3.1±1.2		2.1±0.3
<u>Station 64</u>				
20	1.2±0.2	1.9	1.1±0.1	1.8
60	1.8±0.4	2.7	1.2±0.1	2.0
100	1.9±0.6	3.0	1.2±0.3	2.0
140	2.2±0.7	3.2	1.4±0.1	2.3
180	2.2±0.7	3.3	1.5±0.2	2.4
202	3.0±0.8	4.4	1.7±0.3	2.7
210	3.4±1.2	4.8	1.8±0.5	2.8
Mean**		3.1±0.8		2.1±0.3

\* Estimated using equation 1 which is from reference 27.  
 \*\* Depth integrated mean.

Table III Year of Peak Concentration and Appearance\* of Chemicals in Lake Ontario Sediment Cores.

Station	Peak Concentration or Appearance*	DDT	Mirex	PCBs	HCB	<sup>137</sup> Cs
14	P	1967	1967	1971	1967	1968
	A	1945	1961	1950	1942	1953
403	P	1953	1962	1962	1965	1962
	A	1920	1942	1929	1920	1929
64	P	1959	1967	1967	1964	1962
	A	1935	1959	1935	1935	1952
Peak Production/Usage		1959	1965	1970	1969**	1963
Start of Production		1944	1959	1929	1915**	1953

\* Appearance at concentrations greater than 5% of maximum.

\*\* Total chlorobenzene production (HCB byproduct).

Table IV Estimated Masses of Some Chlorinated Hydrocarbons in Lake Ontario Sediments.

Parameter	1,2,4-TCB	1,2,3,4-TeCB	QCB	HCB	OCS	EDDT	Mirex	PCBs
<u>Niagara Basin</u>								
Flux (mg/m <sup>2</sup> )	0.69	0.29	0.22	0.58	0.071	1.6	0.19	4.4
Mean Conc. (0-3 cm) in Core (ng/g)	40	17	15	42	4.3	79	18	360
Mean Basin Conc. (ng/g)	75	31	34	110	10	150	30	510
Normalized * Mass (metric tons)	2	0.9	0.8	2	0.3	5	0.5	10
<u>Mississauga Basin</u>								
Flux (mg/m <sup>2</sup> )	0.37	0.13	0.12	0.32	0.042	0.98	0.12	2.2
Mean Conc. (0-3 cm) in Core (ng/g)	41	20	18	51	6.5	100	25	430
Mean Basin Conc. (ng/g)	90	39	40	130	14	190	38	690
Normalized* Mass (metric tons)	2	0.7	0.7	2	0.2	5	0.5	10
<u>Rochester Basin</u>								
Flux (mg/m <sup>2</sup> )	0.62	0.22	0.25	0.74	0.093	1.5	0.22	3.9
Mean Conc. (0-3 cm) in Core (ng/g)	43	20	20	64	6.0	61	23	400
Mean Basin Conc. (ng/g)	76	32	33	100	11	130	33	630
Normalized* Mass (metric tons)	4	1	2	4	0.7	10	1	20
<u>Whole Lake **</u>								
Mass (metric tons)	9	3	3	10	1	30	2	50

\* Data from core normalized to whole basin by multiplying the flux by the ratio (mean chemical concentration in basin (0-3 cm) / mean chemical concentration in 0-3 cm interval of core).

\*\*Calculated by summing the three basins and adding 10% for the small Kingston Basin and the non-depositional zones.



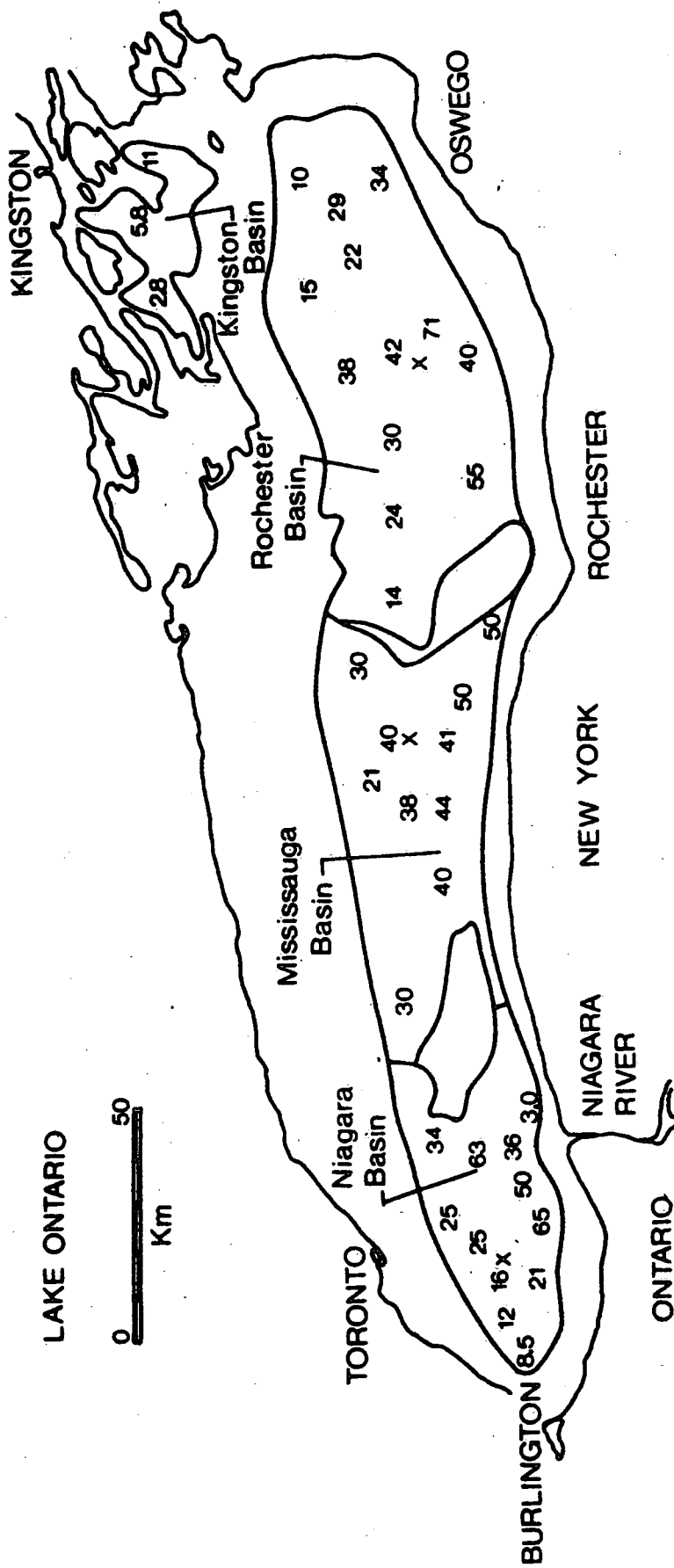


FIGURE 1



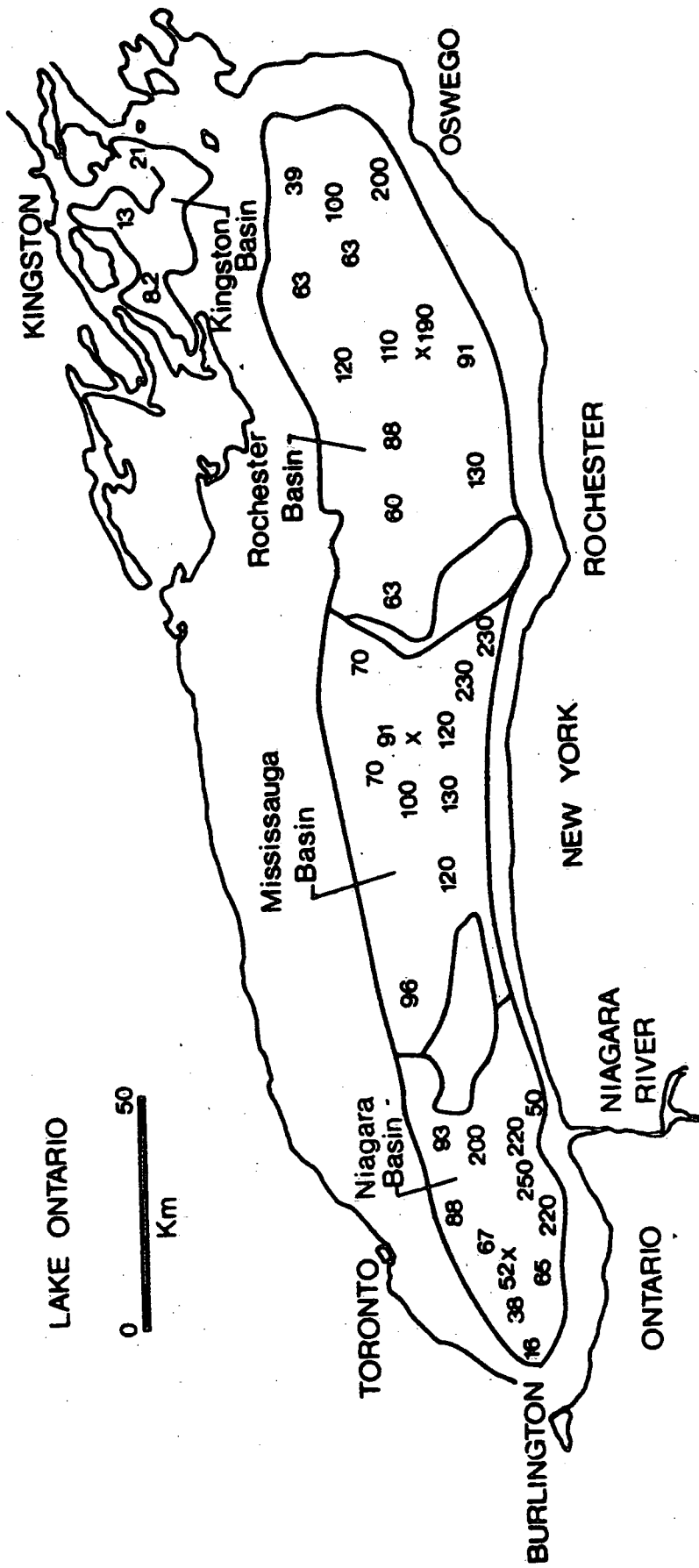


FIGURE 3

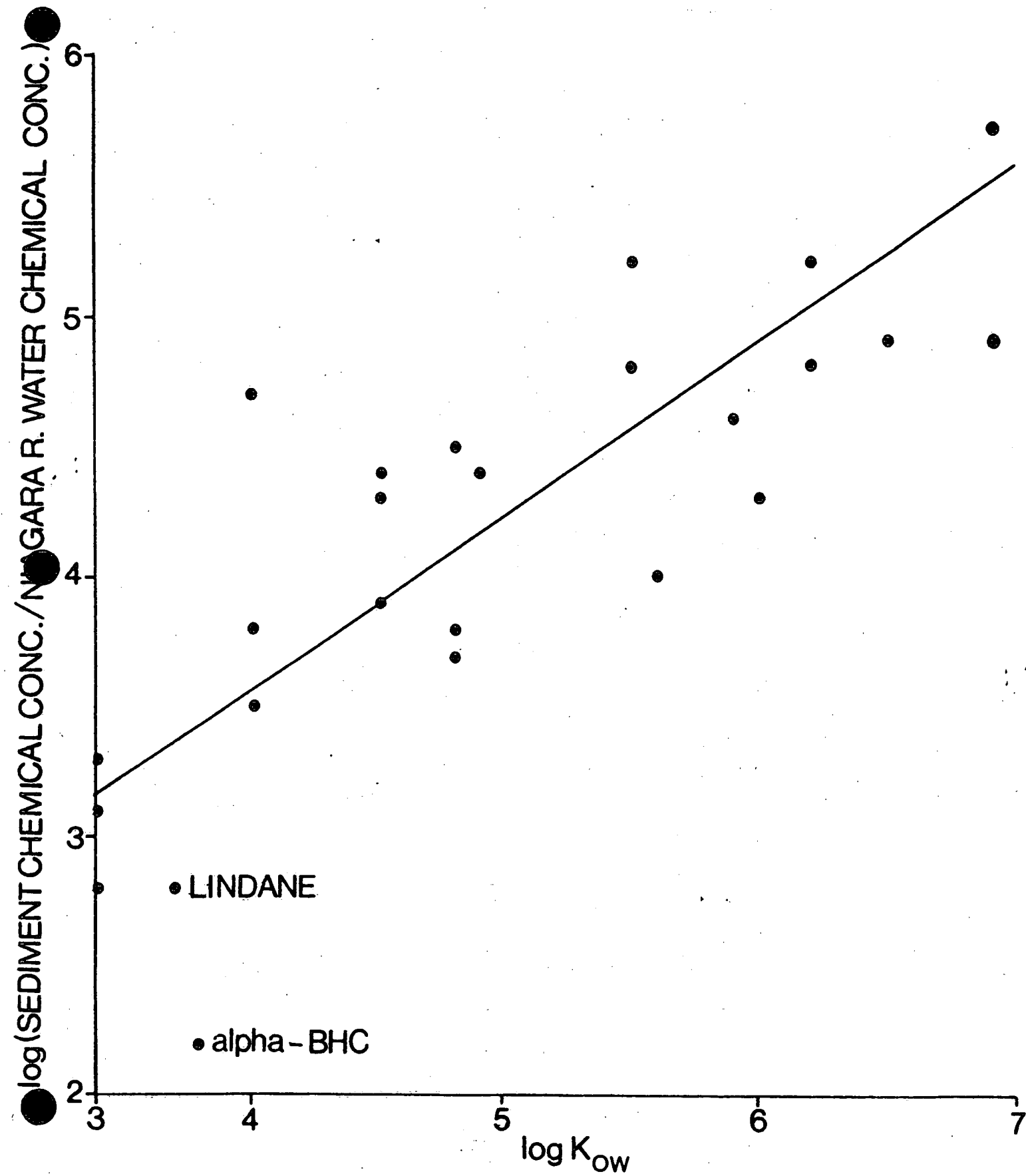


FIGURE 4

FIGURE 5

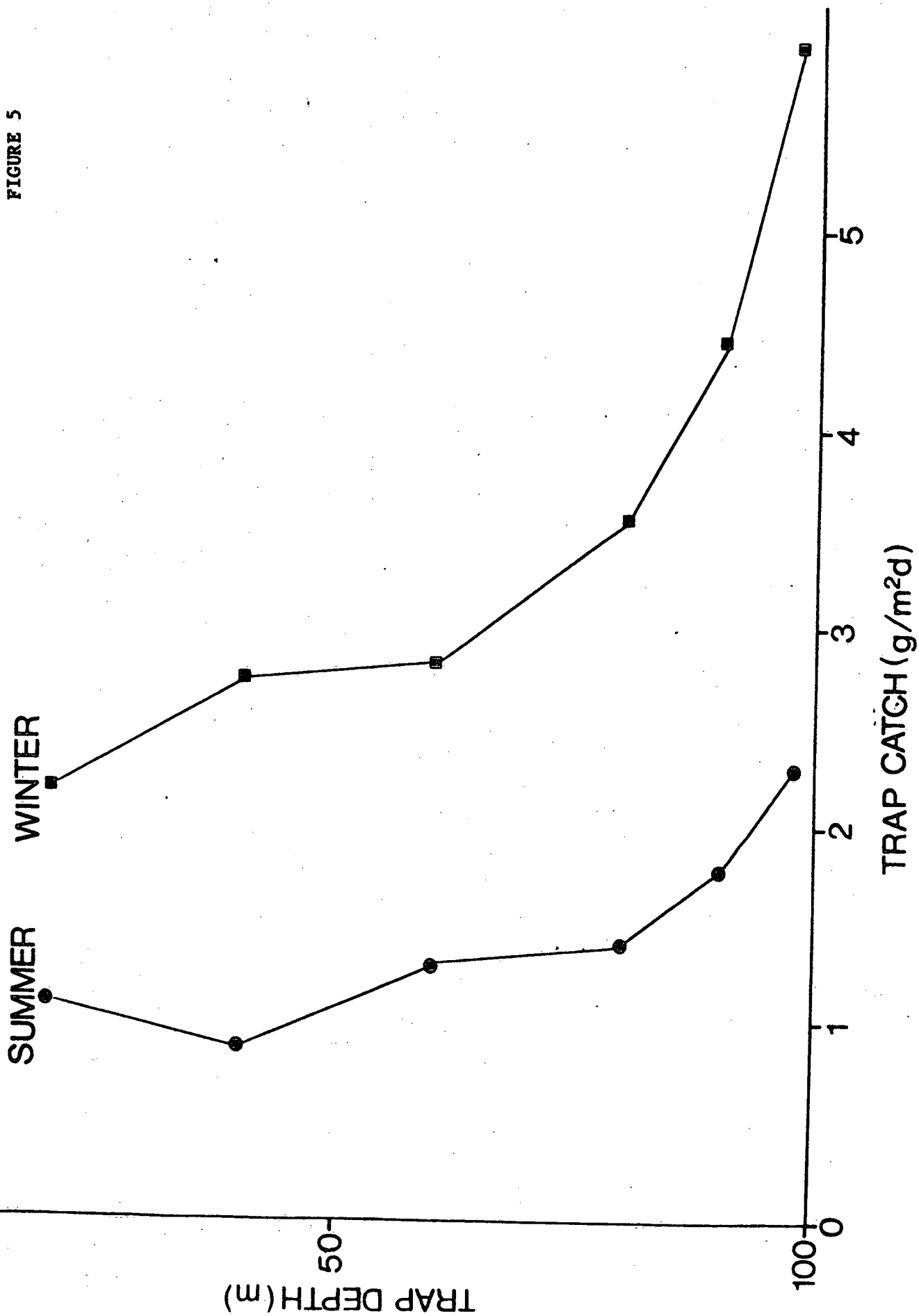


FIGURE 6

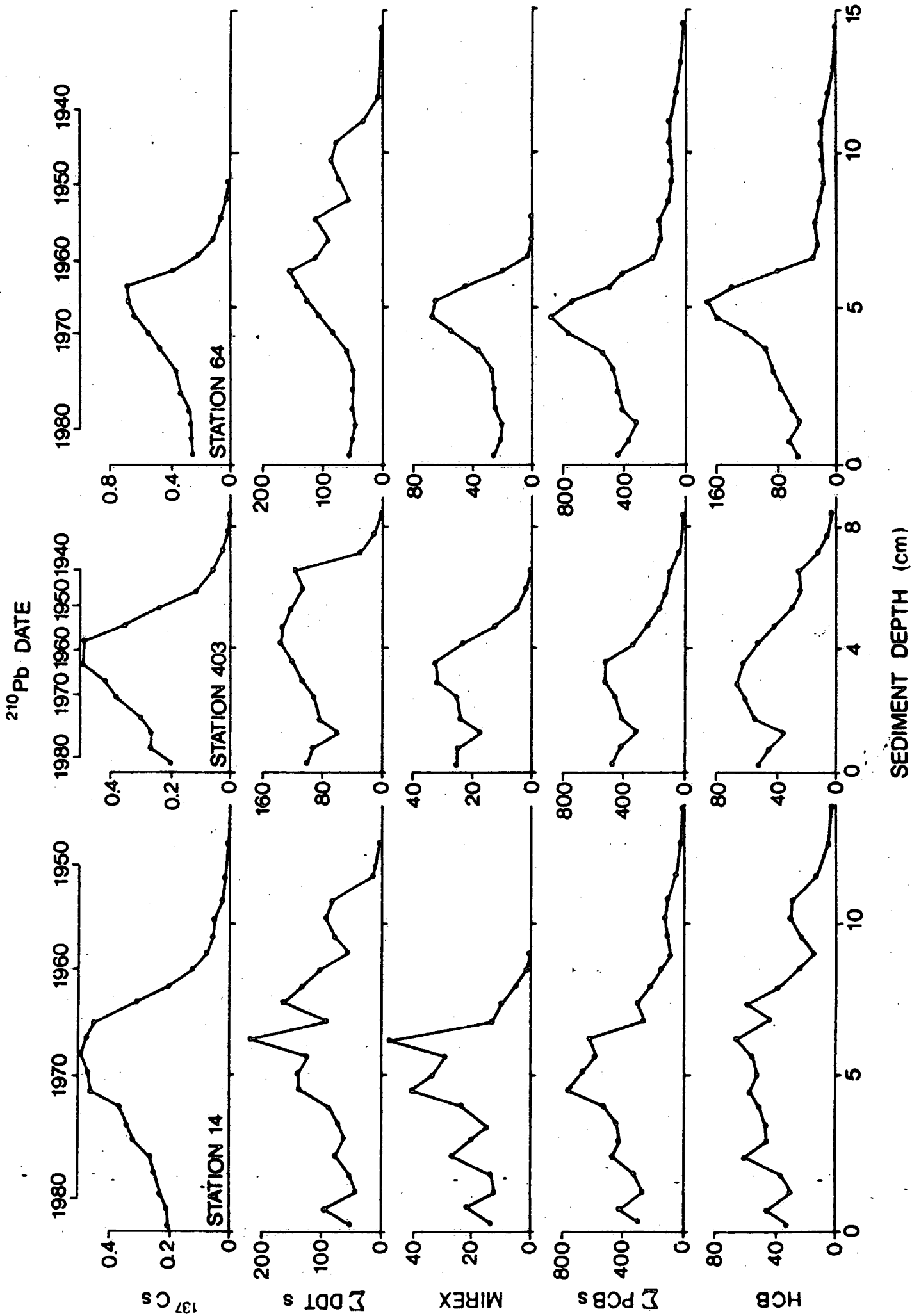


FIGURE 7

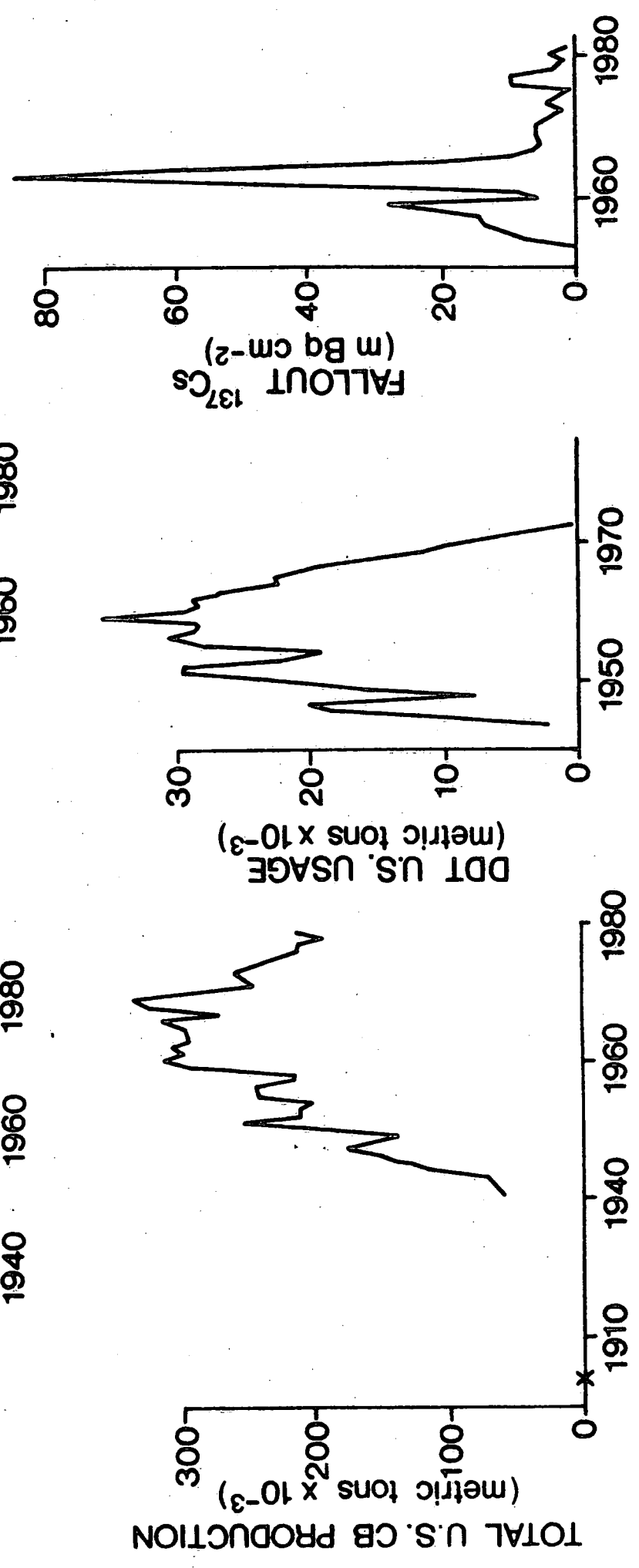
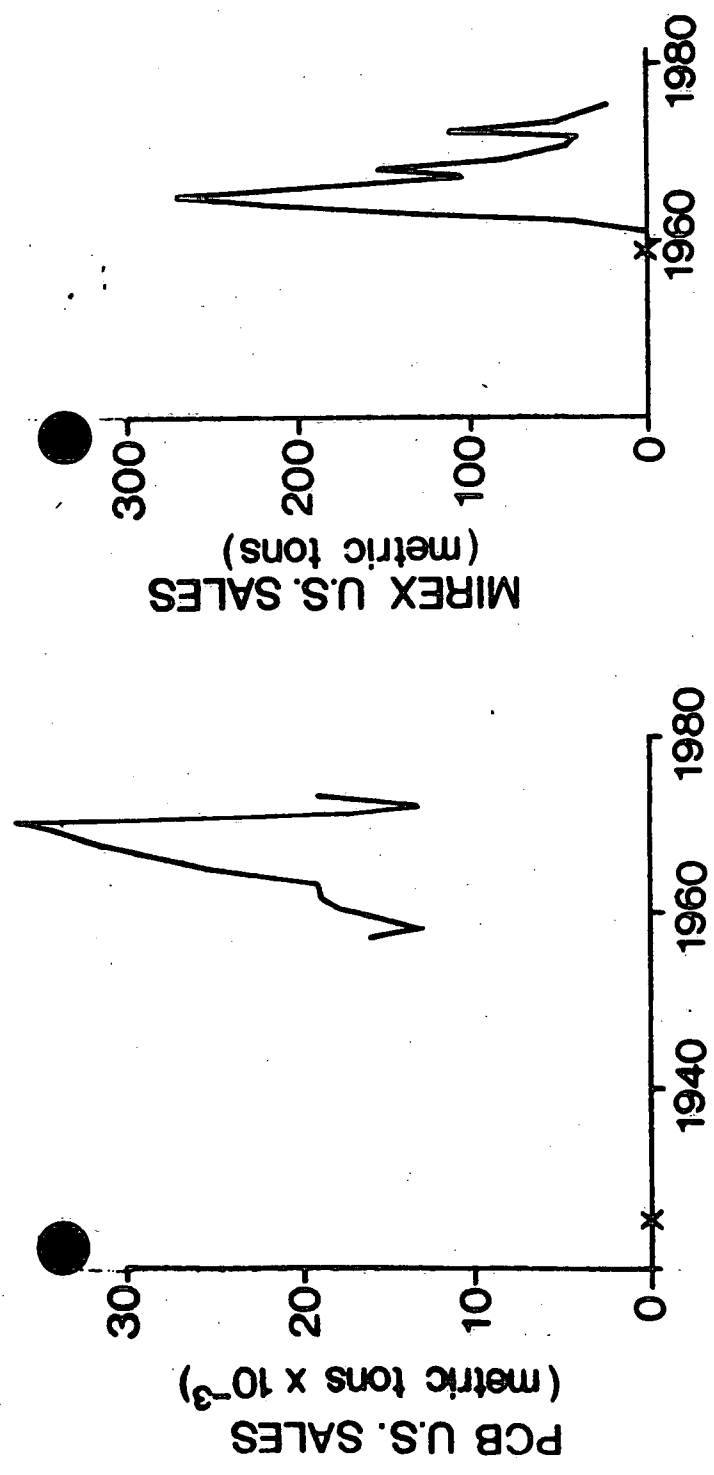
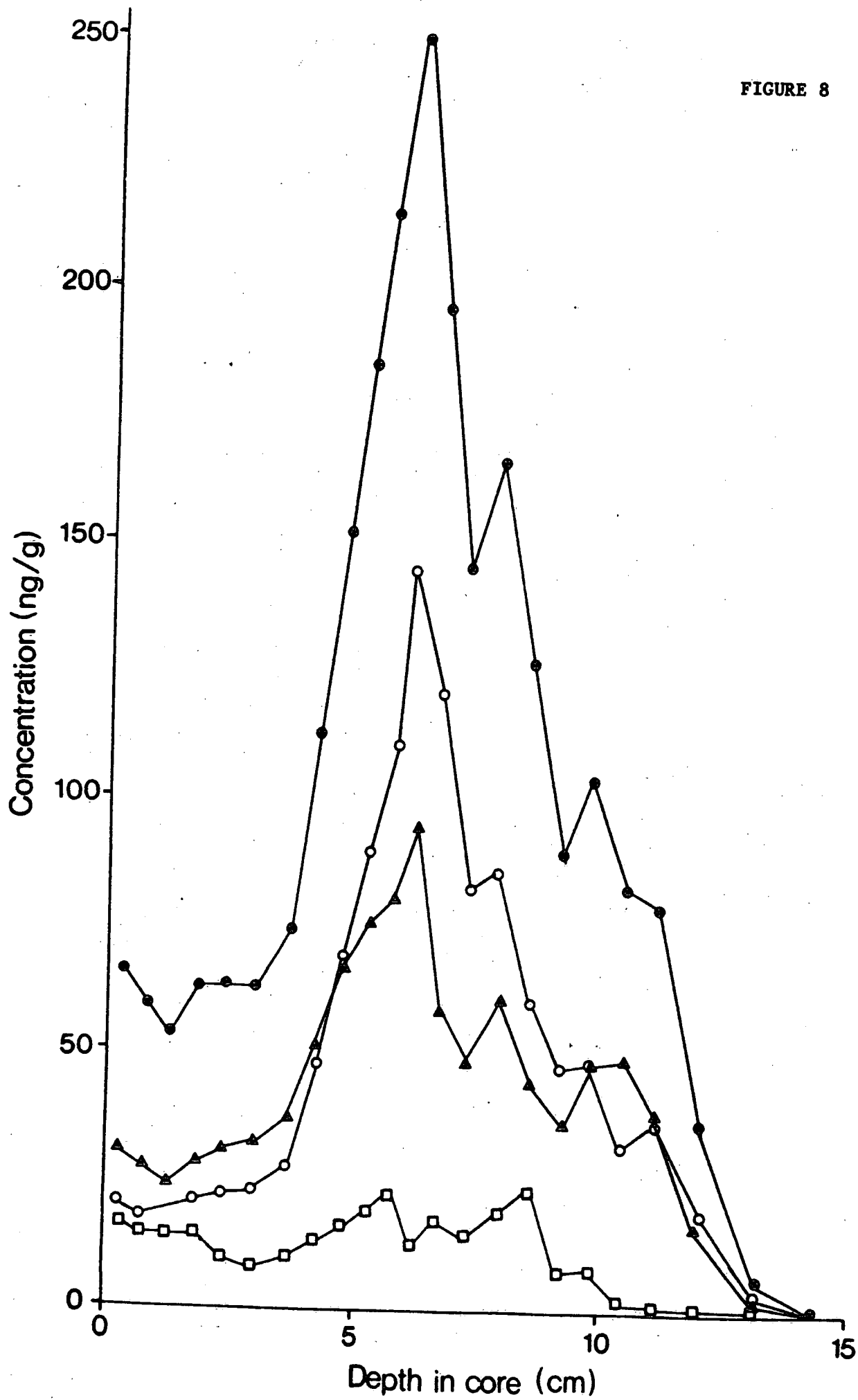


FIGURE 8





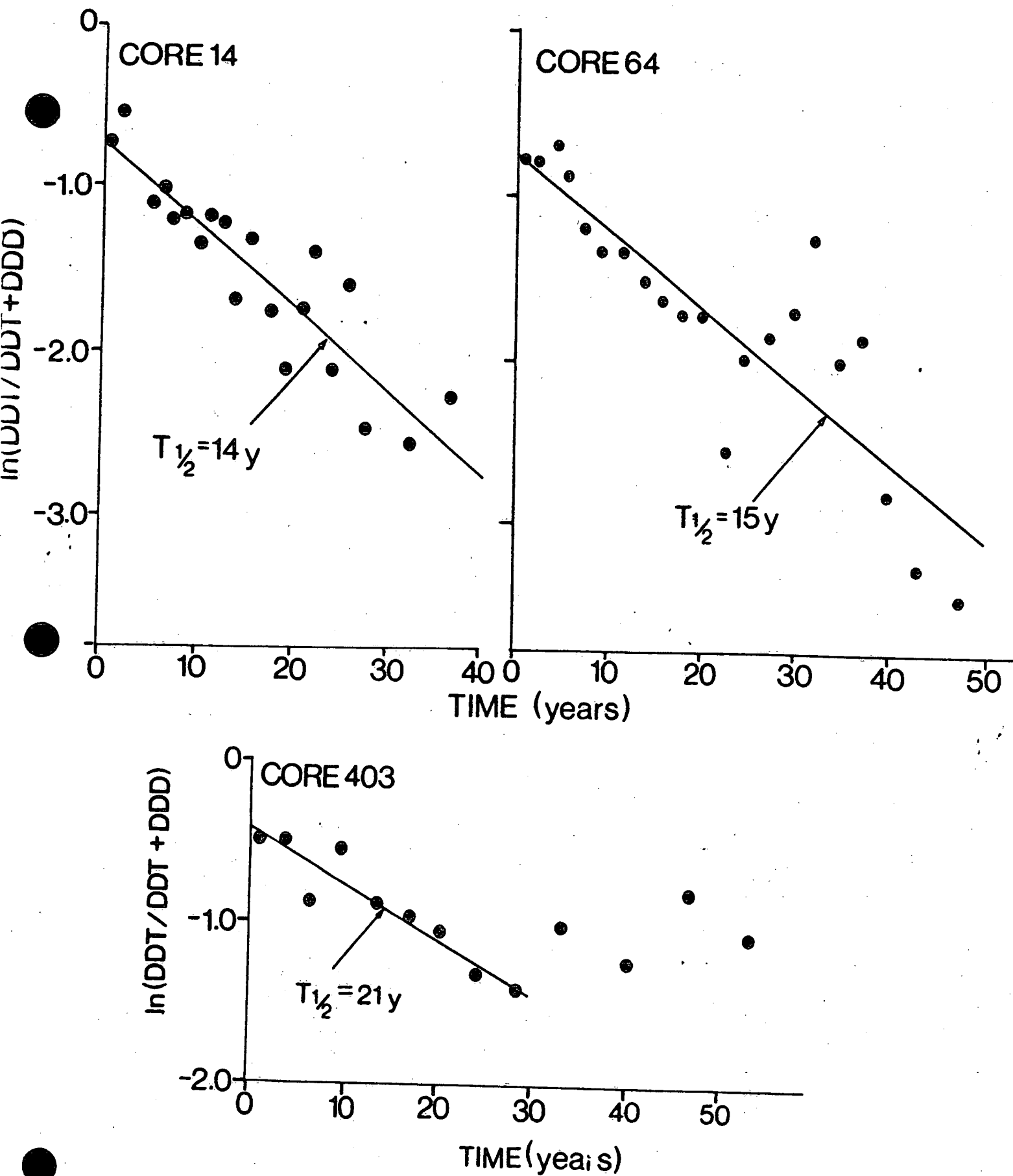


FIGURE 9

CORE 64

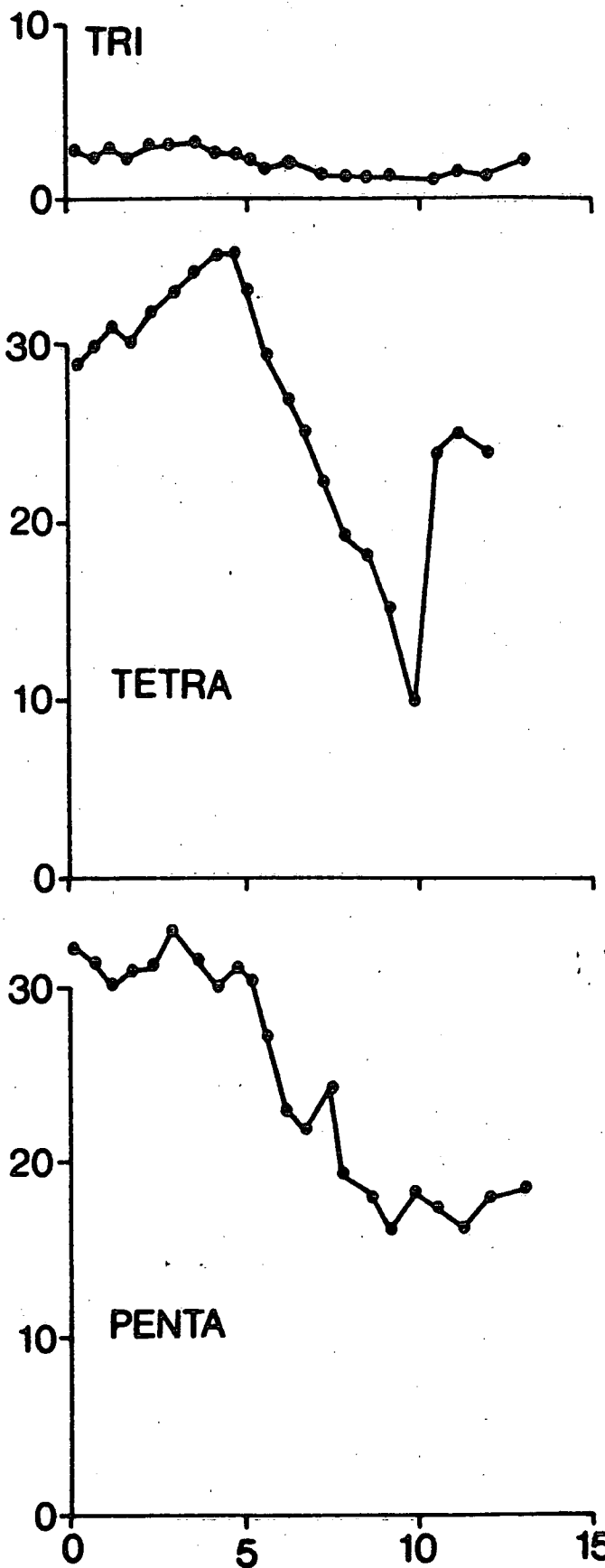
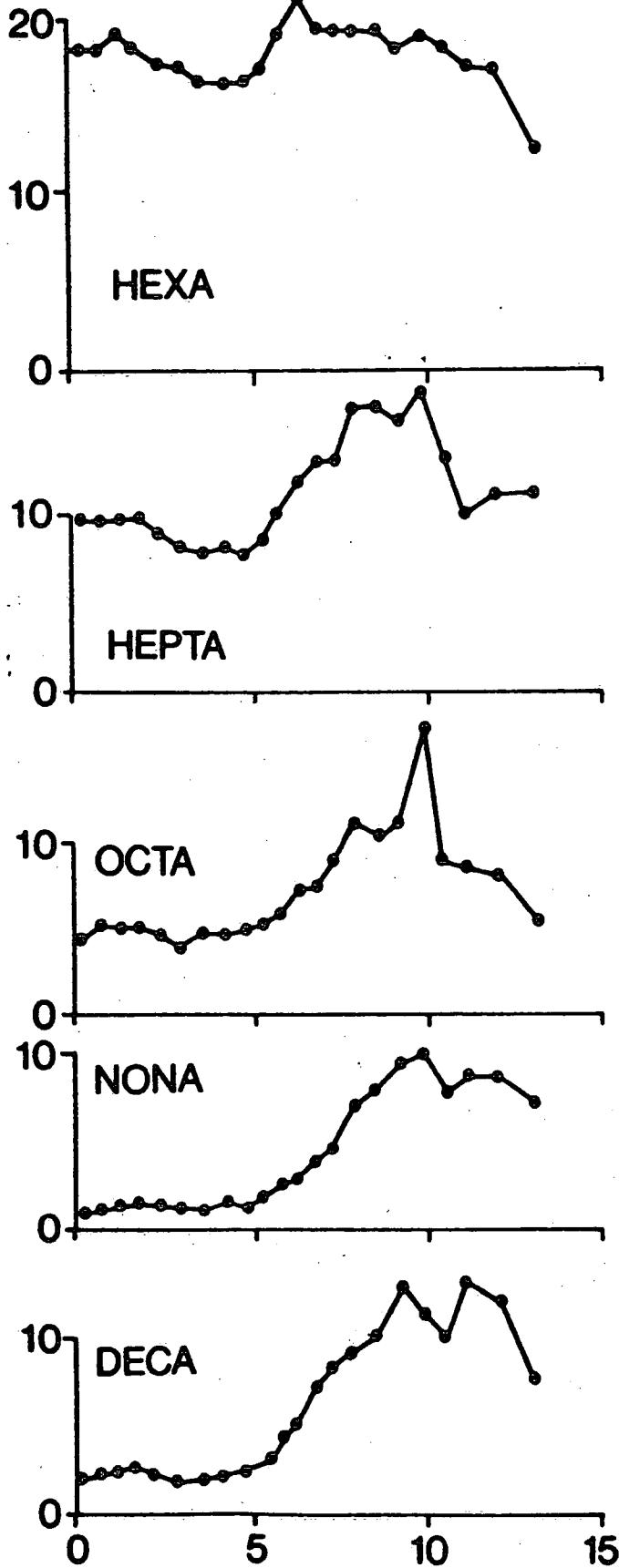


FIGURE 10

CONGENER AS PERCENTAGE OF TOTAL PCBs

FIGURE 11

