

93-12

Environment Canada

Water Science and
Technology Directorate

Direction générale des sciences
et de la technologie, eau

Environnement Canada

Transport and Cycling of PCB in Lake Ontario

By:

A. Mudroch, K. Kaiser, M. Comba, M. Neilson

NWRI Contribution # 93-12

TD
226
N87
No. 93-
12

TRANSPORT AND CYCLING OF PCB IN LAKE ONTARIO

**A. Mudroch, K.L.E. Kaiser, M.E. Comba
Lakes Research Branch
National Water Research Institute
Burlington, Ontario L7R 4A6**

and

**M. Neilson
Water Quality Branch
Inland Waters Directorate, Ontario Region
Canada Centre for Inland Waters
Burlington, Ontario L7R 4A6**

MANAGEMENT PERSPECTIVE

In preparing a management plan for Lake Ontario, knowledge of the processes which control the transport of persistent, toxic contaminants is equally important to information on quantities of the contaminants entering the lake from different external sources. In the early 1980's, the presence of a nepheloid layer in Lake Ontario was reported, and it was suggested that the nepheloid layer may be important in the transport of different contaminants across the lake. A comprehensive study was carried out from 1987 to 1989 to investigate the origin and character of the nepheloid layer in Lake Ontario, and to evaluate its role in the transport of contaminants in the lake. A follow-up study was carried out in 1991, focussing mainly on the transport of polychlorinated biphenyls (PCB) in the suspended matter and water in the nepheloid layer in Lake Ontario.

The results of the study confirm those obtained in 1987 to 1989, showing that the concentrations of total PCB (t-PCB) in the suspended matter in the nepheloid layer were greater than those in the fine-grained recent bottom sediments. The suspended matter in the nepheloid layer contained more lower chlorinated biphenyls, particularly tetra- and pentachlorobiphenyls, than the bottom sediments suggesting the loss of lower chlorinated PCB congeners from the sediments with subsequent accumulation in the suspended matter in the nepheloid layer. Hexa
? HM

About 33% of the total PCB in the bottom and surface water collected in the central basin of the lake in 1991 consisted of 36 chlorinated biphenyl congeners identified as priority PCB by their potential toxicity, frequency and occurrence in environmental samples by the U.S. Army Corps of Engineers, Waterways Experiment Station, Mississippi. The contribution of priority PCB congeners to the total PCB concentration in the suspended matter collected at the same location and time as the water in the lake ranged from 33.7 to 42.5%. Using the results of the 1987 to 1989 and 1991 studies, the calculated quantity of t-PCB residing in Lake Ontario in the aqueous and suspended matter phase is about ~~9,200 kg~~. Considering the quantities of t-PCB in the inputs and outflows from the lake, the calculations indicate that PCB may reside in the Lake Ontario water column between one or two decades after all inputs of these contaminants to the lake become eliminated.

This mols sure no permit

could may not be eliminated from the water column

9 tonnes

INTRODUCTION

The global cycling and deposition of toxic organic chemicals is well recognized as a major source of such compounds to the environment. Deposition of many chemicals from the atmosphere has been established as a major route for the contamination of marine and freshwater ecosystems. With their large surface area, the Laurentian Great Lakes are recipients of many atmospherically transported contaminants. Hydrophobic organic contaminants, such as PCB, deposited from the atmosphere to the Great Lakes become associated with suspended particles in the lake water. After these particles have settled, the contaminants become incorporated into lake bottom sediments. During the settling of the particles and by resuspension of the bottom sediments, particle-associated contaminants are transported across the lakes and may become solubilized under different limnological conditions within the lakes. The behaviour and transport of contaminants in the Great Lakes can be further affected by the existence of the nepheloid layer which has been observed in three of the five lakes: Superior, Michigan and Ontario (Chambers and Eadie 1981; Baker *et al.* 1985; Sandilands and Mudroch 1983). In Lake Ontario, it was shown that the nepheloid layer existed over the entire lake bottom at water depths greater than 60 m from August to November 1981 (Sandilands and Mudroch 1983). The thickness of the layer averaged 22 m in August but extended up to 45 m in October. The suspended matter in the nepheloid layer consisted of diatoms, calcite particles, organic matter and aluminosilicates (Mudroch and Mudroch 1992). Further, it was suggested that the nepheloid layer may be an important medium for lake-wide transport of contaminants originating from atmospheric deposition and inputs from the lake's drainage basin. The objective of this study was to evaluate the role of the nepheloid layer in the transport and cycling of PCB in Lake Ontario. The study is relevant to the long-term management plans for the clean-up of the Great Lakes, and to the assessment of Lake Ontario bottom sediments as an in-situ source of contaminants after all other sources of contaminants to the lake become eliminated.

MATERIALS AND METHODS

Study Area

Lake Ontario is the last downstream lake in the chain of the five Great Lakes. Its surface area is 19,190 km², a maximum length 306 km, width 84 km and depth 245 m. A major tributary of Lake Ontario is the Niagara River with an average annual discharge of 5,712 m³/sec which drains the upstream Lake Erie. The St. Lawrence River with an average annual inflow of 7,400 m³/sec drains Lake Ontario into the Gulf of St. Lawrence of the Atlantic Ocean. Lake Ontario becomes stratified during the summer months with well-

oxygenated hypolimnetic waters and is isothermal after a turnover in the fall. The nepheloid layer starts to develop in late July and becomes mixed throughout the water column during the lake's turnover in the fall.

Nepheloid layer and sediment sampling

Suspended matter in the nepheloid layer was collected at eleven stations in Lake Ontario (Figure 1). The sampling was carried out at stations NL1, NL2, 206 and 210 in August 1987, at stations 623, 624, 625 and 626 in August 1988, and at stations 974, 976 and 999 in August 1989. At station 976, the suspended matter was also collected at 3 m below the water surface in August 1989. In 1991, suspended matter and lake water were collected monthly from April to September, 3 m below the water surface and 15 m above the bottom at station 623. Selection of the sampling stations was based on the occurrence of the nepheloid layer as measured by the light transmission profiles during the past nine years (Mudroch and Mudroch 1992). A horizontal beam transmissometer with a 25-cm path length and Wratten 45 filter was used to obtain light transmission profiles of the water column immediately prior to sampling to select the proper water depth for collection of the suspended matter from the nepheloid layer.

About 6,000 l of water was collected by means of pumps from the surface and the nepheloid layer at eleven stations in the lake (Figure 1) in order to collect a sufficient quantity of material for analyses. Suspended solids were recovered using a pair of continuous-flow Westfalia separators. The flow rate for each centrifuge was maintained at 6 l/min during the 1987-89 sampling, and at 3 l/min during the 1991 sampling. The change in the flow rate was based on the assumption that more colloidal particles can be recovered at a lower centrifuge flow rate. By subsampling the water exiting from the centrifuge, 200 l of water was processed using a large volume continuous liquid-liquid all-glass extractor (Goulden and Anthony 1985) using methylene chloride for the extraction of PCBs from the water at station 623 in 1991.

The particulate residue collected by the separators was freeze-dried, weighed, and homogenized by grinding in an automatic power grinder equipped with an agate grinding dish, and used in subsequent analysis. At each sampling station, bottom sediments were obtained by a box corer. From each box corer, several sediment cores were collected using the procedures described by Mudroch and MacKnight (1991). The cores were subsampled vertically into 3-cm sections, freeze-dried and homogenized by grinding prior to analyses.

Analytical Methods

Concentrations of major elements (Si, Al, Fe, Mg, Ca, K, Na, Ti, P, Mn and P) in suspended material and bottom sediments were determined by x-ray fluorescence spectrometry (Mudroch 1985). The precision of the analysis was determined by analyzing five pellets made from a homogenized sediment sample. Relative deviations for the major elements in analyzed samples can be expected at the following levels: SiO_2 , Fe_2O_3 and CaO - 2%, K_2O and Al_2O_3 - 4%, MgO and Na_2O - 10%. Absolute deviations of 0.1 to 0.2% were found for MnO , TiO_2 , and P_2O_5 . The accuracy of the analyses was verified by running Canadian reference standards Syenite SY-2 and soils SO-2 and SO-4 and comparing the analytical results with the stated reference values for major elements. The concentrations of inorganic and organic carbon were determined with a Leco carbon analyzer. Concentrations of PCBs in the suspended matter and sediment samples collected in 1987-89 were determined by the dual column capillary gas chromatography method using 30-m-long DB1 and SE54 columns with electron capture detectors. Soxhlet extraction of samples by dichloromethane was followed by a fractionation and pre-cleaning by column chromatography as described by Carey and Hart (1986) prior to analysis. The National Research Council, Canada, standard material CLB-1A,B,C and D, a mixture of 51 PCB congeners, obtained from the Atlantic Research Laboratory, National Research Council, Halifax, Nova Scotia, was used as the standard in the analyses. The accuracy of the determination of PCB congeners was confirmed by analysis of sediment reference material HS-1 and HS-2 obtained from the National Research Council, Canada, Halifax, N.S. Reproducibility of the analysis on replicate samples was $\pm 10\%$. The concentrations of total PCBs in the samples collected in 1987-89 are reported as the sum of determined 51 PCB congeners.

In the suspended particles collected in 1991, PCB were determined after mechanical extraction by dichloromethane using a Polytron homogenizer. The extracts were cleaned by column chromatography similar to that used in analysis of suspended particles collected in 1987-89. PCB congeners were determined by dual capillary column gas chromatography using OV1 and OV5 capillary columns. Quantification of PCB congeners was carried out using standards prepared from a mixture of Aroclors and the Green Bay Mass Balance Standard (Swackhamer 1988) obtained through the University of Minnesota. Specific details of the analytical method were described by Backus *et al.* (1992), and are similar to those developed by Comba *et al.* (1989, 1990). PCB congeners in water samples extracted by dichloromethane using the liquid-liquid extractor were quantified using the same methods for cleaning the extracts and capillary chromatography as those used for the suspended particles collected in 1991.

RESULTS AND DISCUSSION

1987 to 1989 Study

During the 1987 to 1989 study, the lake-wide formation of the nepheloid layer commenced in July, and its thickness increased gradually until October, particularly following the primary production peak in surface waters in August. Following the lake's turnover in November, the suspended matter in the nepheloid layer became mixed throughout the water column. The concentration of the suspended matter in the nepheloid layer was only slightly greater than that in the rest of the water column (Table 1). The examination of suspended particles collected from the nepheloid layer by electron microscopy suggested that different physical properties of the suspended particles, such as size, shape, and colour, rather than their quantity were responsible for the reduction of the light transmission in the nepheloid layer. Silica, calcite, and organic matter were the major components of the suspended matter in the nepheloid layer (Table 2). The results indicated that the nepheloid layer originated mainly from the primary production in surface waters and calcite precipitation associated with the photosynthesis during the summer.

In the 1987 to 1989 study, the concentrations of total PCB (t-PCB) in the suspended matter in the nepheloid layer ranged from 151 to 728 ng/g. These concentrations were greater than those in most of the 3 cm surface sediments collected at the same stations (Table 3). Further, the suspended matter in the nepheloid layer contained more lower chlorinated biphenyls, particularly tetra- and pentachlorobiphenyls, than the sediments (Figure 2). This was ascribed to the changes in usage pattern of PCB or to preferential partitioning processes, particularly the loss of lower chlorinated congeners from the sediments with subsequent accumulation in the suspended matter in the nepheloid layer. The concentrations of t-PCB in the suspended matter in the nepheloid layer was greater (543 ng/g) than that in the suspended matter collected at 3 m below the water surface (148 ng/g) at station 976 in August 1989. Differences in the geochemical composition of the suspended matter collected at the 3-m water depth and from the nepheloid layer (Table 2) as well as biological and physico-chemical processes, particularly sorption, during its residence time in the water column could account for the differences in the concentration of particle-associated PCB in surface and bottom waters.

1991 Study

The study concentrated mainly on the partitioning of t-PCB between water and suspended matter sampled monthly from April to September, at 3 m below the water surface and 15 m above the lake bottom at station 623. Selection of the sampling at 15 m above the lake

bottom was based on the past observations of the development of the nepheloid layer, and assuming that 15 m above the lake bottom was approximately the middle of the nepheloid layer at this station. The nepheloid layer at station 623 started to develop in August. The weight of the suspended matter during the sampling period is shown in Table 4. The quantity of the suspended matter at 15 m above the lake bottom increased very slightly only after the development of the nepheloid layer.

Distribution of chlorinated biphenyl congeners in the water and suspended matter - 1991 study

The distribution of the chlorinated biphenyl congeners in the water and the suspended matter phase indicated no apparent difference within each phase at both sampling depths (i.e., 3 m below the water surface and 15 m above the lake bottom) during the study period. The content of chlorine atoms in PCB in the water collected from the centrifuge outflow was $47.3 \pm 1.5\%$ and $45.0 \pm 2.1\%$ in the surface and bottom water, respectively. The content of chlorine atoms in the PCB in the suspended matter collected at 3 m below the water surface and 15 m above the lake bottom, was $51.6 \pm 0.5\%$ and $51.8 \pm 2.0\%$, respectively. These results most likely reflect a greater solubility of PCB congeners with lower chlorine content (Table 5).

No major differences were observed in PCB homologue distribution in the suspended matter samples collected at the 3-m water depth and at 15 m above the lake bottom from April to September. Minor differences were observed at both sampling depths for specific congener composition, particularly increasing quantities of tetrachloro homologues in the April and July samples collected at the 3 m below the water surface, and in the April and September samples collected 15 m above the lake bottom. These increases were accompanied by corresponding decreases in higher chlorinated homologues (Figures 3 and 4).

Homologue distribution in water samples collected from the centrifuge outlet at the 3-m water depth and 15 m above the lake bottom was different, particularly in April. A greater amount of lower chlorinated PCB homologues occurred in the water in April and September relative to the other months (Figures 5 to 9). The contribution of higher chlorinated PCB congeners to bottom waters appeared to be minimal and did not exhibit remarkable difference between sampling at different months. However, increases in the contribution of di-chloro congeners, particularly congener 8(5), to the total PCB concentrations, were observed. Increases in congener 8(5) have been observed for the anaerobic dechlorination of congener 105 with bacteria from Hudson River sediments (Abramowicz 1990). The increase of congener 8(5) in the bottom water may be related to sediment resuspension in Lake Ontario with subsequent partitioning of this congener into the water phase, since the

concentrations in the bottom suspended matter phase showed little variation over the study period.

Following a comprehensive literature survey of the effects of PCB on the environment, Clarke *et al.* (1989) identified chlorinated biphenyl congeners by their potential toxicity, frequency and occurrence in environmental samples and relative abundance in animal tissues. The potential for toxicity of individual congeners was related mainly to their molecular structure, and from the total of 209 congeners 36 were identified as priority PCB. These were further divided by their potential toxicity into the following five groups: group 1A containing congeners 77, 126 and 169, and group 1B containing congeners 118, 128 and 138 (both groups having enzyme-inducing potential and therefore high-concern toxicity); group 2 containing congeners 87, 101, 153 and 183 (less potent as inducers and toxins than the previous group. As a group they contribute 26 to 41% of t-PCB in the bird and animal samples and 7 to 25% of t-PCB in fish and invertebrates); group 3 containing congeners 18, 44, 49, 52 and 151 (weak or non-inducers but have numerous reported environmental occurrences or represent at least 10% composition of t-PCB in tissue samples); and group 4 containing congeners 37, 81, 105, 114, 119, 123, 157, 158, 167, 168 and 189 (mixed-type inducers with lower accumulation in animal tissue). These five groups of congeners were recommended for use in the regulatory evaluation of PCB-contaminated dredged material.

The contribution of the five groups of priority chlorinated biphenyl congeners identified by Clarke *et al.* (1989) to the total concentrations of PCB in the water and the suspended matter sampled at station 623 from April to September 1991, is shown in Tables 6 and 7, respectively. The contribution to the total PCB concentrations in the water was relatively uniform around 33% with the exception of 22.9% in the bottom water collected in September and 38.6% in the surface water collected in August. Changes in the concentrations of congeners in groups 2 and 3 were mainly responsible for the exception. The contribution of priority PCB congeners to the total PCB concentration in the suspended matter ranged from 33.7 to 42.5% with the lowest value in the suspended matter in September at 15 m above the lake bottom, and with the greatest value in June in the suspended matter collected 3 m below the water surface. Fluctuations in the concentrations of congeners 128 and 156(171) belonging to the 1B congeners group were mainly responsible for these changes. In both the water and the suspended matter congeners group 3 represented the largest portion of the five congener groups identified by Clarke *et al.* (1989) followed by groups 2, 1B, 4 and 1A.

A study of the distribution of specific PCB congeners in water, suspended matter and aquatic organisms (Gagnon *et al.* 1990) indicated that chlorine substitution in positions 2, 4 and 5 on the biphenyl ring determined the accumulation of PCB in zooplankton, smelt, tomcod and capelin at the St. Lawrence River estuary. The

following congeners, characterized by chlorine substitution in positions 2, 4 and 5 on at least one biphenyl ring were among the most abundant throughout the food chain: 153, 138, 118(149), 101, 180, 182, 183, 187, 137 and 203. An additional three congeners which were not substituted at positions 2, 4 and 5 (44, 49 and 87) were among the 13 most abundant PCB congeners monitored by Gagnon et al. (1990) in the St. Lawrence River estuary. Contribution to the t-PCB concentrations in water and suspended matter was 28.6% and 41.2%, respectively, during the summer of 1987 in the St. Lawrence River estuary (Gagnon et al. 1990). The contribution of these 13 congeners in our study was 15.9% in the water collected 3 m below the water surface and 17.4% in the water at 15 m above the lake bottom at station 623 in Lake Ontario in June and July 1991. At the same time, the congeners contributed 23.9% and 23.1% to the t-PCB concentration in the suspended matter collected 3 m below the water surface and 15 m above the lake bottom, respectively. Although the contribution of the 13 congeners to the t-PCB concentrations was lower in Lake Ontario than in the St. Lawrence River estuary, the ratio of the contribution in the suspended matter/water was similar: 1.44 in the St. Lawrence River estuary, and 1.50 and 1.35 at 3 m below the water surface and 15 m above the lake bottom, respectively. The abundance and the ratio of the 13 congeners in the suspended matter indicate the importance of the food chain and the partitioning between the solid and aqueous phase in Lake Ontario and the St. Lawrence River estuary. However, we would like to point out that the sampling area in the estuary is in the maximum turbidity zone (MTZ) of the estuary, with average suspended sediment concentrations of 70 mg/l (Comba and Kaiser, submitted for publication in Environmental Science and Technology). Water temperatures in the summer months are around 16 to 19°C and the water depth averages 18 m. The area is subject to large tidal forces, which constantly mix and recirculate the system. Also the estuary has very distinct seasonal carbon cycles, performs selective sorting of the particulate matter and on a seasonal basis acts as a reservoir for pollutants. These factors very strongly influence PCB partitioning and amounts. Therefore it is interesting to note that the absolute ratios of materials remained similar between the two water bodies, i.e., Lake Ontario and the St. Lawrence River estuary.

The relatively high quantity (up to 42.5% of the t-PCB) of those PCB congeners identified as priority PCB by Clarke et al. (1989) and those found accumulating in the food chain in the St. Lawrence River estuary by Gagnon et al. (1990) compared to those in Lake Ontario water and suspended matter suggest a potential for the bioaccumulation and toxic effects of PCB residing in Lake Ontario.

Distribution of t-PCB in the suspended matter and water

The concentrations of t-PCB were between 340 and 1,600 ng/g with mean concentration of 668 ± 530 ng/g in the suspended matter collected at 3 m below the water surface, and between 1,200 to 4,100 ng/g with mean concentration of $1,980 \pm 1,229$ ng/g in the suspended matter collected at 15 m above the lake bottom from April to September 1991 at station 623. The greatest concentrations (4,100 ng/g) existed in the suspended matter at 15 m above the bottom after the development of the nepheloid layer in September (Table 8). These values are greater than those obtained for suspended matter in the nepheloid layer in the 1987 to 1989 study which may be the result of the difference in analytical methods used to determine total PCB.

The concentrations of t-PCB in water collected from the centrifuge outflow were between 1.8 and 14 ng/L with mean concentration 3.9 ± 2.8 ng/L at 3 m below the water surface, and between 3.5 and 11 ng/L with a mean concentration of 6.4 ± 3.6 ng/L at 15 m above the lake bottom (Table 8). These results indicate enrichment of the bottom waters with PCB. The t-PCB concentrations are substantially greater than the previously reported concentrations which were between 0.484 and 2.614 ng/L with a mean of 1.41 ng/L ($n = 31$) in Lake Ontario (Stevens and Neilson 1989) which resulted in somewhat lower K_{ow} values than reported in the literature.

The quantities of t-PCB in the suspended matter in the nepheloid layer calculated from the 1987 to 1989 study ranged from 145 to 1,400 ng/m³. The quantities of t-PCB at station 623 calculated from the 1991 study indicated a difference in the distribution of PCB in the suspended matter at 3 m below the water surface and 15 m above the lake bottom: between 370 and 970 ng/m³ and between 430 and 1,900 ng/m³, respectively (Table 9). The quantities of t-PCB in the water collected from the centrifuge outflow were between 1,800 and 14,000 ng/m³ for 3 m below the water surface and between 4,100 and 11,000 ng/m³ for 15 m above the lake bottom samples (Table 9).

The ratio of t-PCB between the aqueous and suspended matter phase was greatest with a value of 26 in April at 3 m below the water surface. The ratio continuously decreased at both sampling depths at station 623 from April to September with the lowest value of 2.2 at 15 m above the lake bottom in September after the development of the nepheloid layer (Table 9). A decrease in the ratio was most significant from June to July following the commencement of the primary production peak with a subsequent precipitation of CaCO₃. These results confirm our observation from the 1987 to 1989 study on the association of t-PCB with the allochthonous particles generated mainly during the summer months in the surface waters with their subsequent sinking through the water column and accumulation in the nepheloid layer in late August and September. The ratio of t-PCB in the aqueous and suspended matter phase

measured at 3 m below the water surface at the Lake Ontario outflow into the St. Lawrence River was 1.8 and 1.2 during June of 1986 and 1987, respectively (Kaiser *et al.* 1990; Comba *et al.* 1989 and 1990). This ratio was similar to that obtained at 15 m above the lake bottom at station 623 in September 1991. However, the ratio was 13 and 21 at 3 m below the water surface and 15 m above the lake bottom, respectively, at station 623 in June 1991. The station was located at the most westerly end of the lake's central basin, approximately 200 km from the lake's outflow into the St. Lawrence River (Figure 1). Further, the water at the eastern part of the lake close to the outflow may contain more suspended matter than that at the centre of the lake, particularly suspended matter from the first diatom bloom and precipitated CaCO_3 , both occurring in the warmer, shallow nearshore water in June.

Estimated quantities of t-PCB in Lake Ontario

The total concentrations of t-PCB in both the aqueous and suspended matter phases exiting Lake Ontario via the St. Lawrence River were $1,200 \text{ ng/m}^3$ and $2,348 \text{ ng/m}^3$ in 1986 and 1987, respectively (Comba *et al.* 1989 and 1990). These levels were approximately four times lower than the seasonal distribution of t-PCB of $7,200 \text{ ng/m}^3$ in the water and suspended matter measured at station 623. Similar to the observation in the 1987 to 1989 study, no correlation existed between the major elements and t-PCB concentrations in the suspended matter. It appeared that the amount of t-PCB partitioned to particles was a function of the concentration of particles with an active surface area for adsorption of the PCB. Small freshly precipitated particles with a large surface area may concentrate greater amounts of PCB than particles residing in the water column for a longer time during which they can become coated with metals or other elements and compounds.

Calculations showed approximately 118 kg of t-PCB in the suspended matter in the 20-m-thick nepheloid layer during August in the 1987 to 1989 study. The calculated atmospheric input of t-PCB to Lake Ontario using a suggested deposition rate of $8.5 \times 10^{-3} \text{ kg/m}^2$ per year (Strachan and Eisenreich 1988) is around 163 kg annually. The estimated input of t-PCB in water and suspended matter from the Niagara River into Lake Ontario was about 670 kg in 1987 (Comba *et al.* 1993). Using the data of Comba *et al.* (1989 and 1990) about 590 kg of t-PCB exited Lake Ontario annually via the St. Lawrence River. Using the ratio 7.9 for the aqueous/suspended matter, t-PCB (i.e., the average for the surface and bottom samples collected in August 1991, Table 9) and the calculated 118 kg of t-PCB in the suspended matter in the nepheloid layer in August during the 1987 to 1989 study, the quantity of t-PCB residing in Lake Ontario in the aqueous and suspended matter phase is about 9,182 kg. This value is in good agreement with the 9,280 kg of t-PCB calculated from the data obtained for August by the 1991 study.

Using the data obtained at station 623, the calculated quantities of t-PCB were between 6,200 and 21,000 kg in Lake Ontario water and suspended matter from April to September 1991 with an average of 11,500 kg. Further studies are necessary to determine the rate of losses of PCB from the lake water to the atmosphere and the release of PCB by resuspension of bottom sediments to estimate the time required for the natural cleansing of the lake. However, results of our studies indicated that PCB may reside in the Lake Ontario water column between one and two decades after all inputs of these contaminants to the lake become eliminated.

ACKNOWLEDGEMENT

We would like to thank staff members of the Research Support Division, National Water Research Institute, Burlington, Ontario, for their invaluable help in collecting the suspended matter and water samples. Mr. Gary Bruce and Mr. Bruce Harrison, Water Quality Branch, Inland Waters Directorate, Ontario Region, Burlington, Ontario, carried out the extraction of the water samples on board the research vessel Limnos in 1991. Mr. Paulos Youakim, Research Support Branch, National Water Research Institute, Burlington, Ontario, provided invaluable assistance with the determination of PCB in all samples collected in 1991.

REFERENCES

- Abramowicz, D.A. 1990. Aerobic and anaerobic biodegradation of PCB's. A Review. *Critical Reviews in Biotechnology* 10(3):241-249.
- Backus, S.M., Comba, M.E. and Kaiser, K.L.E. 1992. Lake Ontario nepheloid layer. Project LRB 2014-91 and WQB-101-91. Lakes Research Branch Technical Note, National Water Research Institute, Burlington, Ontario.
- Baker, J.E., Eisenreich, S.J., Johnson, T.C. and Halfman, B.M. 1985. Chlorinated hydrocarbon cycling in the benthic nepheloid layer of Lake Superior. *Environ. Sci. Technol.* 19:854-861.
- Carey, J.H. and Hart, J.H. 1986. Gas chromatographic/mass spectrometric (GC/MS) identification of the major components of non-aqueous material from the St. Clair River. *Water Poll. Res. J. Can.* 21:309-322.
- Chambers, R.L. and Eadie, B.J. 1981. Nepheloid and suspended particulate matter in south-eastern Lake Michigan. *Sedimentology* 28:439-447.
- Clarke, J.U., McFarland, V.A. and Pierce, B.D. 1989. Preliminary recommendation for a congener-specific PCB analysis in regulatory evaluation of dredged material. Miscellaneous Paper D-89-2, Department of the Army, Waterways Experiment Station, Vicksburg, Mississippi, 32 p.
- Comba, M.E., Palabrica, V.S., Wasslen, J., Bengert, G.A. and Kaiser, K.L.E. 1989. St. Lawrence River trace organic contaminants study (Part II), 1986. National Water Research Institute Contribution No. 89-51, Burlington, Ontario, 94 p.
- Comba, M.E., Palabrica, V.S., Wasslen, J. and Kaiser, K.L.E. 1990. St. Lawrence River trace organic contaminants study (Part III), 1987. National Water Research Institute Contribution No. 90-01, Burlington, Ontario, 38 p.
- Comba, M.E., Palabrica, V.S., Backus, S.M. and Kaiser, K.L.E. 1993. St. Lawrence River trace organic contaminants study (Part IV), 1989-90. National Water Research Institute Contribution No. 93-xx, in preparation.
- Gagnon, M.M., Dodson, J.J., Comba, M.E. and Kaiser, K.L.E. 1990. Congener-specific analysis of the accumulation of polychlorinated biphenyls (PCBs) by aquatic organisms in the maximum turbidity zone of the St. Lawrence estuary, Quebec, Canada. *Sci. Total Environ.* 97/98:739-759.

Goulden, P.D. and Anthony, D.H.J. 1985. Design of a large sample extractor for the determination of organics in the water. National Water Research Institute Contribution No. 85-121, National Water Research Institute, Burlington, Ontario, Canada.

Kaiser, K.L.E., Lum, K.R., Comba, M.E. and Palabrica, V.S. 1990. Organic trace contaminants in St. Lawrence River water and suspended sediments, 1985 - 1987. *Sci. Total Environ.* 97/98:23-40.

Mudroch, A. 1985. Geochemistry of the Detroit River sediments. *J. Great Lakes Res.* 11:193-200.

Mudroch, A. and MacKnight, S.D. 1991. Bottom sediments sampling. In *Handbook of Techniques for Aquatic Sediments Sampling*, Mudroch, A. and MacKnight, S.D., eds. CRC Press Inc., Boca Raton, Florida.

Mudroch, A. and Mudroch, P. 1992. Geochemical composition of the nepheloid layer in Lake Ontario. *J. Great Lakes Res.* 18:132-153.

Sandilands, R.G. and Mudroch, A. 1983. Nepheloid layer in Lake Ontario. *J. Great Lakes Res.* 9:190-200.

Stevens, R.J.J. and Neilson, M.A. 1989. Inter- and intralake distribution of trace organic contaminants in surface waters of the Great Lakes. *J. Great Lakes Res.* 15: 377-393.

Strachan, W.M.J. and Eisenreich, 1988. Mass balancing of toxic chemicals in the Great Lakes: the role of atmospheric deposition. International Joint Commission, Science Advisory Board/International Air Quality Advisory Board, Windsor, Ontario, pp. 113.

Swackhamer, D.L. 1988. Quality Assurance Plan, Green Bay Mass Balance Study. I. PCBs and Dieldrin. University of Minnesota, March 11, 1988.

TABLE 1. Concentration of suspended matter in the nepheloid layer during the 1987-89 study.

| Station | Concentration of suspended matter in the nepheloid layer* (mg/l) |
|--|--|
| <i>Western Basin</i> August 1987 | |
| NL-1 | 0.97 |
| NI-2 | 1.38 |
| 206 | 1.92 |
| 210 | 1.91 |
| <i>Central Basin</i> August 1988 | |
| 623 | 0.96 |
| 624 | 2.23 |
| 625 | 0.60 |
| 626 | 0.50 |
| <i>Eastern Basin</i> August 1989 | |
| 974 | 2.12 |
| 999 | 0.71 |
| 976 | 2.10 |
| 976, 3 m surface water | 1.83 |

* at the midpoint of the nepheloid layer.

TABLE 2. Geochemical composition of the suspended matter in the nepheloid layer in 87-89 study (in %, dry weight).

| Sample Number | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | CaO | Na ₂ O | K ₂ O | TiO ₂ | MnO | P ₂ O ₅ | C ² |
|------------------|------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|------------------|------|-------------------------------|----------------|
| NL1 | 15.6 | 2.6 | 1.31 | 1.34 | 28.3 | 0.83 | 0.99 | 0.13 | 0.08 | 0.68 | 11.9 |
| NL2 | 52.8 | 6.3 | 2.60 | 1.36 | 18.5 | 1.16 | 1.34 | 0.26 | 0.19 | 0.29 | 6.5 |
| 206 | 53.2 | 8.3 | 3.82 | 1.45 | 14.6 | 0.95 | 1.58 | 0.36 | 0.25 | 0.24 | 6.0 |
| 210 | 52.9 | 9.8 | 4.85 | 1.75 | 14.1 | 0.88 | 1.95 | 0.53 | 0.24 | 0.27 | 5.5 |
| 623 | 66.6 | 2.8 | 1.16 | 1.18 | 21.3 | 1.58 | 0.97 | 0.11 | 0.04 | 0.44 | 7.4 |
| 624 | 65.1 | 4.3 | 2.23 | 1.22 | 15.2 | 1.19 | 1.52 | 0.23 | 0.06 | 0.48 | 12.9 |
| 625 | 66.9 | 2.7 | 1.13 | 1.39 | 19.3 | 0.92 | 1.13 | 0.11 | 0.04 | 0.53 | 8.7 |
| 626 | 57.9 | 2.7 | 1.15 | 1.45 | 16.9 | 1.98 | 0.91 | 0.11 | 0.04 | 0.50 | 9.2 |
| 974 | 51.9 | 8.3 | 4.10 | 1.73 | 15.8 | 1.09 | 2.33 | 0.51 | 0.13 | 0.32 | 6.6 |
| 976 | 47.5 | 7.4 | 3.23 | 1.59 | 20.7 | 0.93 | 2.13 | 0.35 | 0.09 | 0.33 | 5.6 |
| 999 | 54.0 | 4.2 | 2.47 | 1.96 | 18.4 | 1.83 | 1.25 | 0.48 | 0.11 | 0.50 | 12.5 |
| 976 ¹ | 4.9 | 0.7 | 0.40 | 1.35 | 50.7 | 0.71 | 0.60 | 0.05 | 0.04 | 0.85 | 9.8 |

¹ suspended matter from surface water at 3m depth.

² organic carbon.

TABLE 3. Concentrations of PCBs (in ng/g dry weight) in the suspended matter in the nepheloid layer and surficial sediments during August. (87-89 study)

| Station Number | Nepheloid Layer | Sediments (0-3 cm) |
|----------------|-----------------|--------------------|
| NL1 | 208 | 247 |
| NL2 | 584 | 50 |
| 206 | 728 | 405 |
| 210 | 384 | 95 |
| 623 | 151 | <1 |
| 624 | 351 | <1 |
| 625 | 411 | 346 |
| 626 | 491 | <1 |
| 974 | 594 | 125 |
| 976 | 543 | 74 |
| 976* | 148 | |
| 999 | 550 | 180 |

*sampled at 3 m below surface.

TABLE 4. Concentration of suspended matter 3 m below the water surface and 15m above the lake bottom at station 623 in 1991.

| Sampling Time | Sampling Depth | Concentration of suspended matter (mg/L) |
|---------------|-----------------------|--|
| April | 3 m below surface | 0.34 |
| April | 15 m above the bottom | 0.38 |
| June | 3 m below surface | 0.96 |
| June | 15 m above the bottom | 0.31 |
| July | 3 m below surface | 2.2 |
| July | 15 m above the bottom | 0.45 |
| August | 3 m below surface | 0.99 |
| August | 15 m above the bottom | 0.42 |
| September | 3 m below surface | 1.4 |
| September | 15 m above the bottom | 0.46 |

TABLE 5. Mean chlorine content of t-PCB in water and suspended matter at station 623 in 1991 (in %).

| SAMPLING TIME | WATER | | SUSPENDED MATTER | |
|------------------|---------|--------|------------------|--------|
| | SURFACE | BOTTOM | SURFACE | BOTTOM |
| April | 49 | 46 | 51 | 54 |
| June | 46 | 47 | 52 | 51 |
| July | 49 | 47 | 51 | 50 |
| August | 47 | 45 | 52 | 54 |
| September | 45 | 44 | 52 | 50 |

TABLE 6. Contribution of priority congeners to the t-PCB concentrations in centrifuged water (in % of t-PCB).

| CONGENER GROUPS ¹ | | | | | | |
|------------------------------|-----|-----|------|------|-----|-------|
| Month/depth | 1A | 1B | 2 | 3 | 4 | Total |
| April (3 m) ² | 0.4 | 3.4 | 12.0 | 14.5 | 2.9 | 33.2 |
| April (bottom) ³ | 0.4 | 3.0 | 7.7 | 19.2 | 2.8 | 33.1 |
| June (3 m) | 0.1 | 3.1 | 7.0 | 16.8 | 6.7 | 33.7 |
| June (bottom) | 0.3 | 3.8 | 8.6 | 17.2 | 3.3 | 33.2 |
| July (3 m) | 0.2 | 3.9 | 8.9 | 19.0 | 0.6 | 32.6 |
| July (bottom) | 0.3 | 2.8 | 6.6 | 22.3 | 1.1 | 33.1 |
| August (3 m) | 0.2 | 4.4 | 9.2 | 22.1 | 2.7 | 38.6 |
| August (bottom) | 0.2 | 3.9 | 8.2 | 17.5 | 3.2 | 33.0 |
| September (3 m) | 0.2 | 6.3 | 11.0 | 17.3 | 2.9 | 37.7 |
| September (bottom) | 0.1 | 2.7 | 5.6 | 12.4 | 2.1 | 22.9 |

¹ after Clarke et al. (1989).

² sampled 3 m below the water surface.

³ sampled 15 m above the lake bottom.

TABLE 7. Contribution of priority congeners to the t-PCB concentrations in suspended matter (in % of t-PCB).

CONGENER GROUPS¹

| Month/depth | 1A | 1B | 2 | 3 | 4 | Total |
|-----------------------------|-----|-----|------|------|-----|-------|
| April (3 m) ² | 0.8 | 4.6 | 11.3 | 17.1 | 1.5 | 35.3 |
| April (bottom) ³ | 0.6 | 4.2 | 11.2 | 18.6 | 1.7 | 36.3 |
| June (3 m) | 0.5 | 8.5 | 11.7 | 15.9 | 5.9 | 42.5 |
| June (bottom) | 0.5 | 7.5 | 11.6 | 14.3 | 4.3 | 38.2 |
| July (3 m) | 0.7 | 5.2 | 12.4 | 17.0 | 3.9 | 39.9 |
| July (bottom) | 1.3 | 8.4 | 11.1 | 14.6 | 5.2 | 40.6 |
| August (3 m) | 0.7 | 7.3 | 11.4 | 13.4 | 4.6 | 37.4 |
| August (bottom) | 0.2 | 4.9 | 11.7 | 16.1 | 3.5 | 36.4 |
| September (3 m) | 0.3 | 6.7 | 11.4 | 13.2 | 4.0 | 35.6 |
| September (bottom) | 0.7 | 2.7 | 11.1 | 18.0 | 1.2 | 33.7 |

¹ after Clarke et al. (1989).

² sampled 3 m below the water surface.

³ sampled 15 m above the lake bottom.

TABLE 8. Concentrations of t-PCB in water and suspended matter at station 623 in 1991.

| Sampling Time | Depth | t-PCB in suspended matter (ng/g) | t-PCB in water (ng/g) |
|---------------|---------------------|----------------------------------|-----------------------|
| April | 3 m ¹ | 1,600 | 14.0 |
| April | bottom ² | 2,000 | 11.0 |
| June | 3 m | 590 | 8.2 |
| June | bottom | 1,400 | 9.6 |
| July | 3 m | 440 | 5.3 |
| July | bottom | 1,200 | 3.5 |
| August | 3 m | 370 | 3.0 |
| August | bottom | 1,200 | 4.0 |
| September | 3 m | 340 | 1.8 |
| September | bottom | 4,100 | 4.1 |

¹ sampled 3 m below the water surface.

² sampled 15 m above the lake bottom.

TABLE 9. Monthly quantities of t-PCB (per unit volume) in water and suspended matter and t-PCB water/suspended matter ratio at station 623 in 1991.

| Sampling Time | Depth | t-PCB water (ng/m ³) | t-PCB in suspended matter (ng/m ³) | Ratio t-PCB in water/suspended matter |
|---------------|---------------------|----------------------------------|--|---------------------------------------|
| April | 3 m ¹ | 14,000 | 540 | 26 |
| April | bottom ² | 11,000 | 760 | 14 |
| June | 3 m | 8,200 | 570 | 14 |
| June | bottom | 9,600 | 430 | 22 |
| July | 3 m | 5,300 | 970 | 5.5 |
| July | bottom | 3,500 | 540 | 6.5 |
| August | 3 m | 3,000 | 370 | 8.1 |
| August | bottom | 4,000 | 500 | 8.0 |
| September | 3 m | 1,800 | 480 | 3.8 |
| September | bottom | 4,100 | 1,900 | 2.2 |

¹ sampled 3 m below the water surface.

² sampled 15 m above the lake bottom.

FIGURE CAPTIONS

- Figure 1. Suspended matter, water and sediment sampling stations in Lake Ontario.
- Figure 2. Distribution of PCB homologues in suspended matter in the nepheloid layer and in bottom sediments in 1987 to 1989.
- Figure 3. Distribution of PCB homologues in suspended matter at 3 m below the water surface at station 623 in 1991.
- Figure 4. Distribution of PCB homologues in suspended matter at 15 m above the lake bottom.
- Figure 5. Distribution of PCB homologues in water collected from the centrifuge outlet at station 623 in April 1991.
- Figure 6. Distribution of PCB homologues in water collected from the centrifuge outlet at station 623 in June 1991.
- Figure 7. Distribution of PCB homologues in water collected from the centrifuge outlet at station 623 in July 1991.
- Figure 8. Distribution of PCB homologues in water collected from the centrifuge outlet at station 623 in August 1991.
- Figure 9. Distribution of PCB homologues in water collected from the centrifuge outlet at station 623 in September 1991.

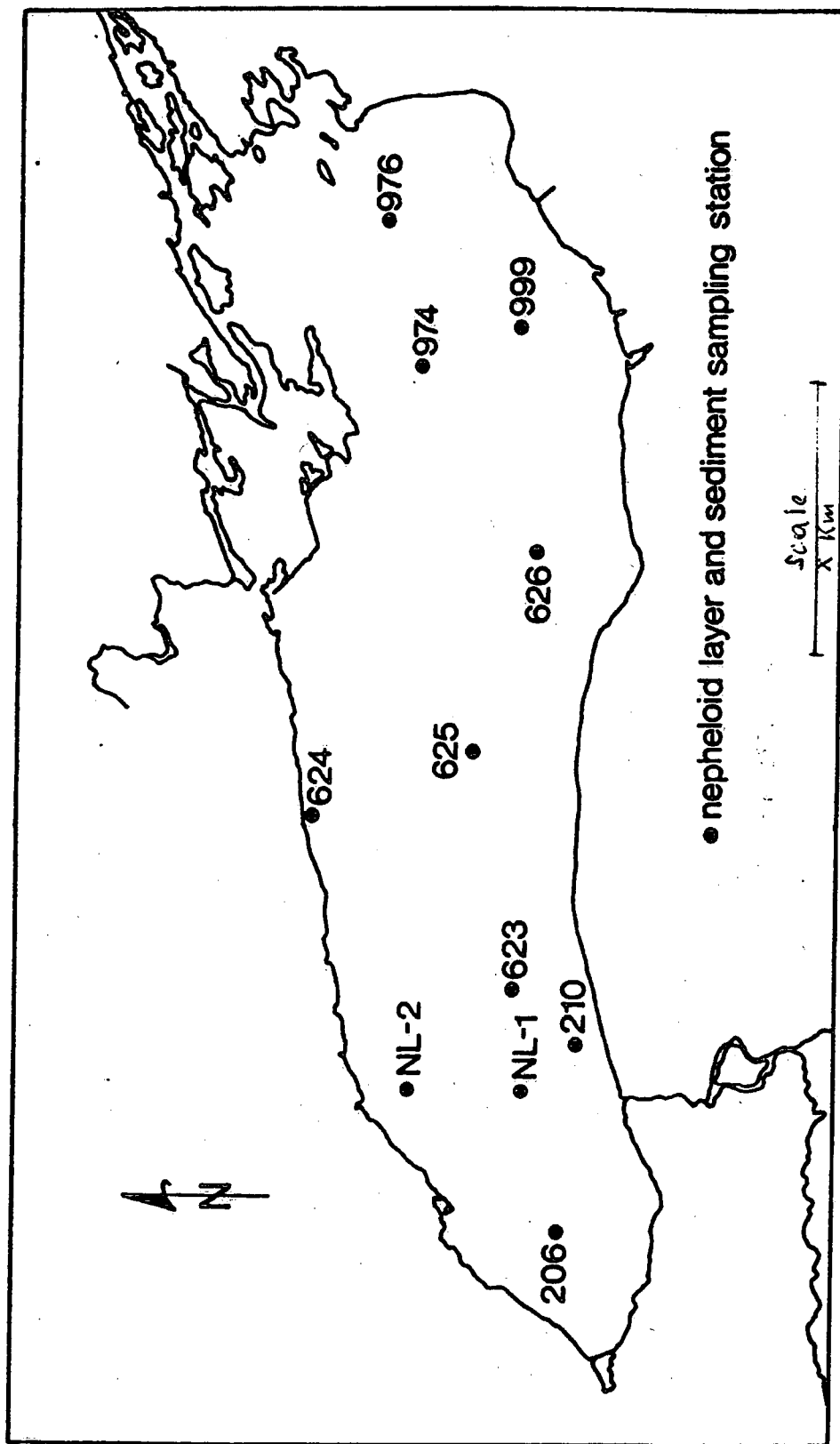


Figure 1

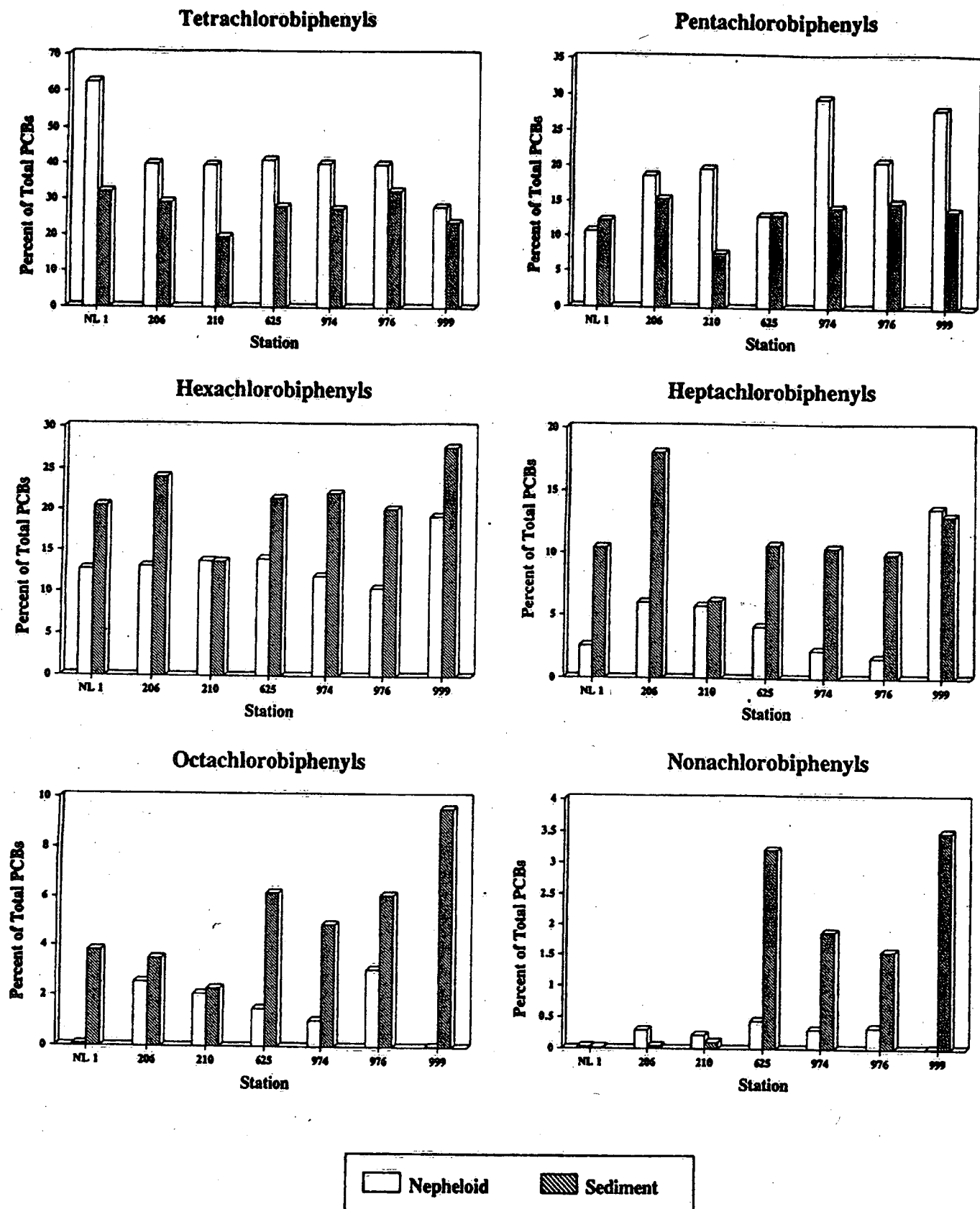
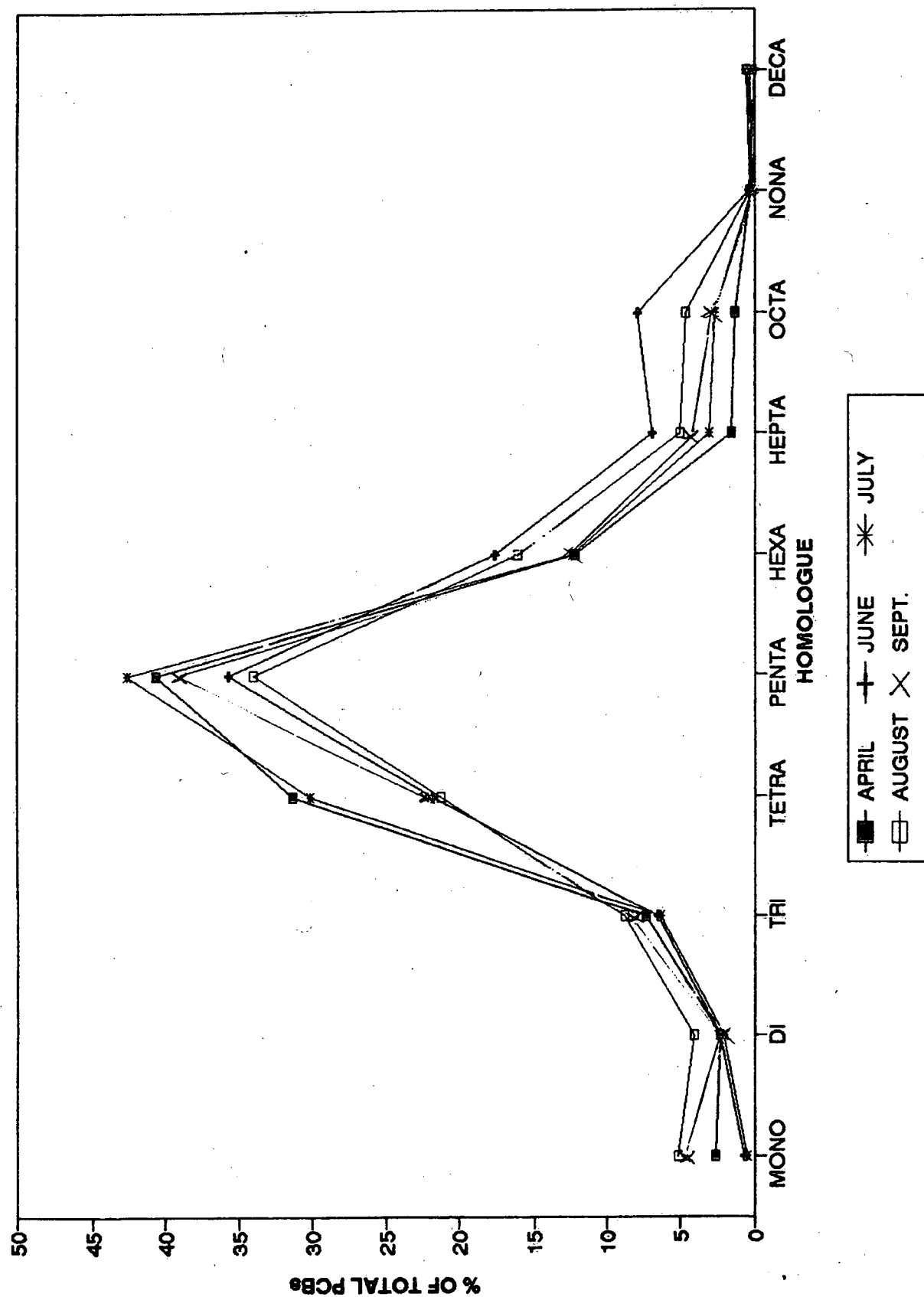
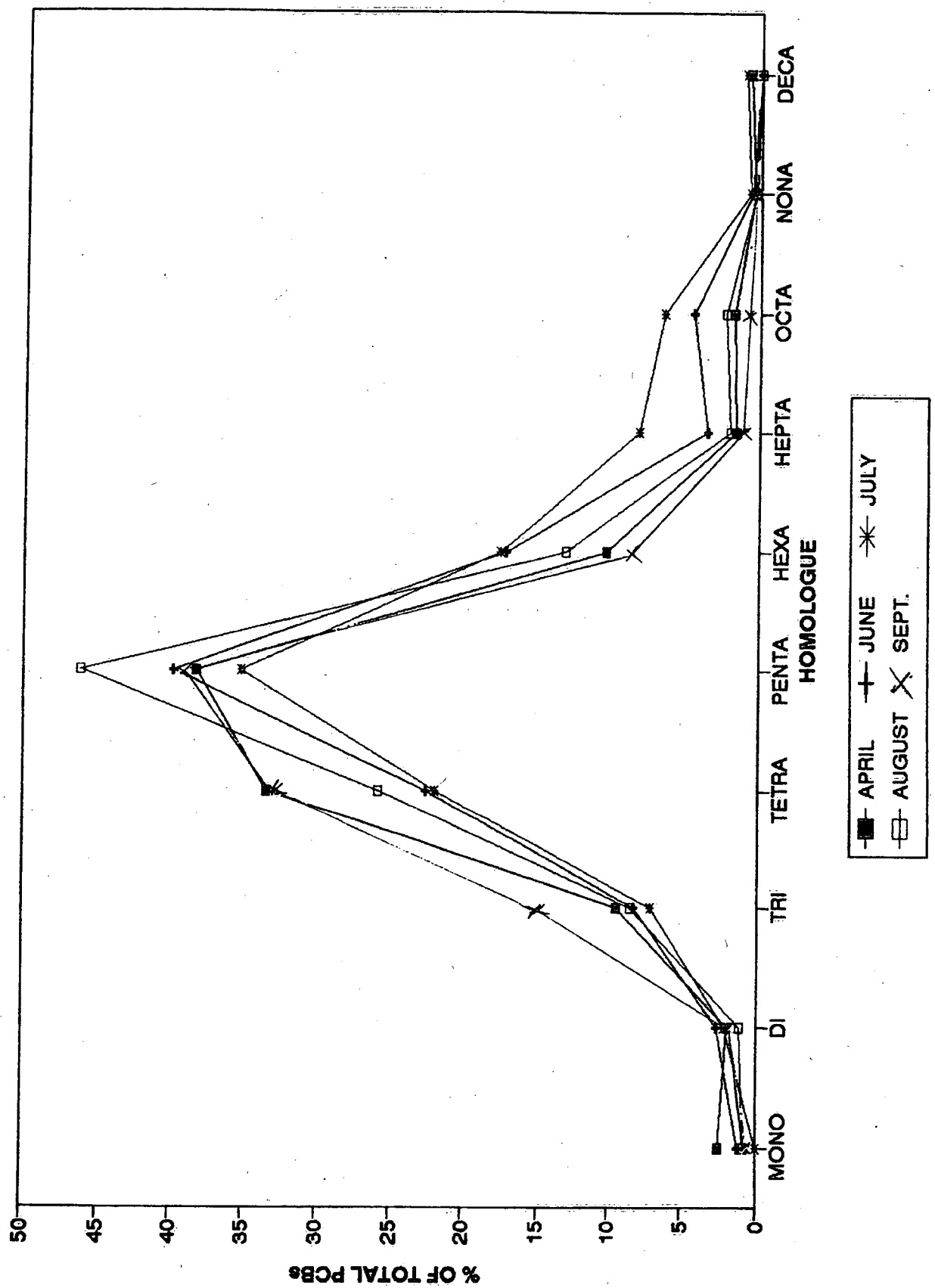


Figure 2.



@ 3m

Figure 3.



@ 15m from bottom

Figure 4.

APRIL

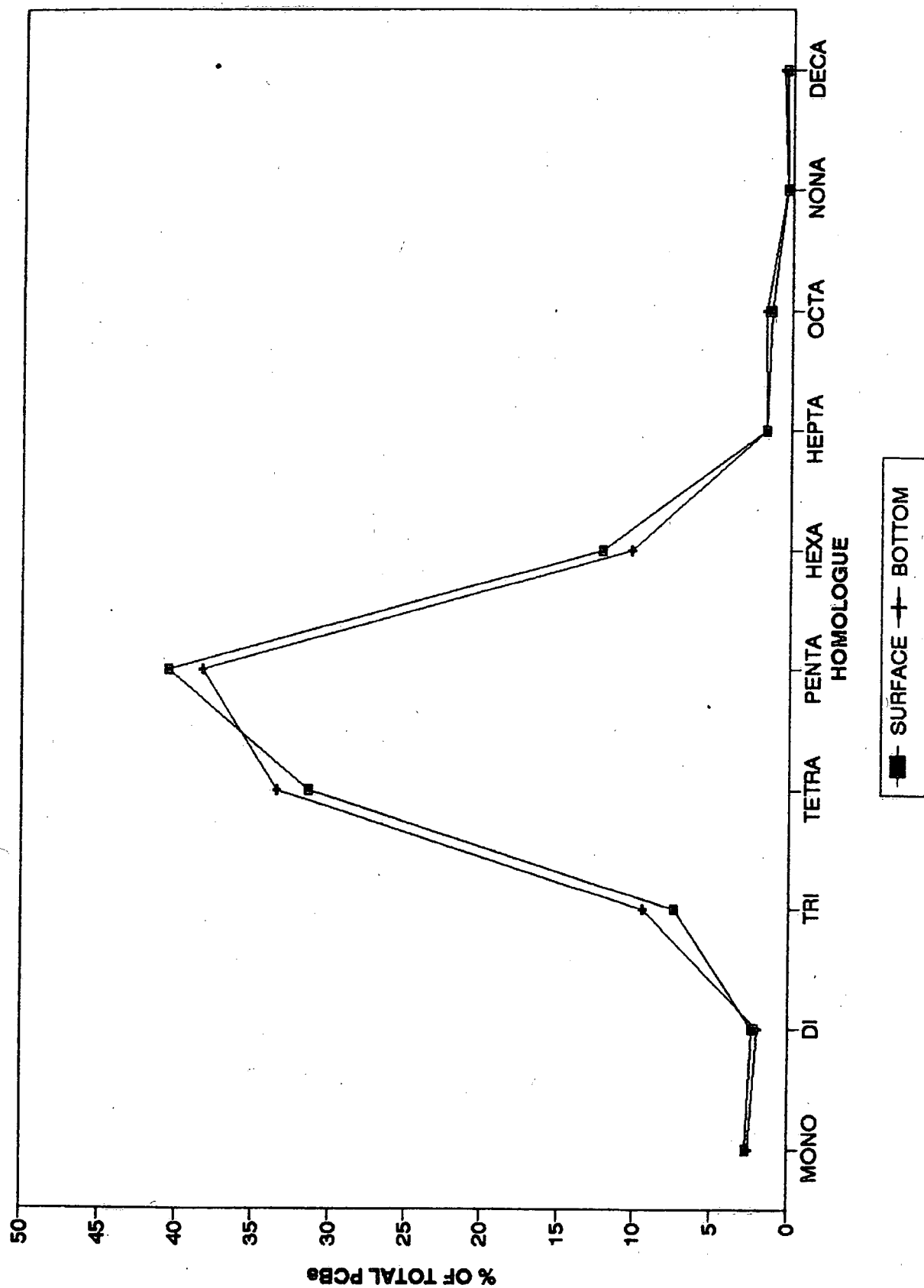


Figure 5

JUNE

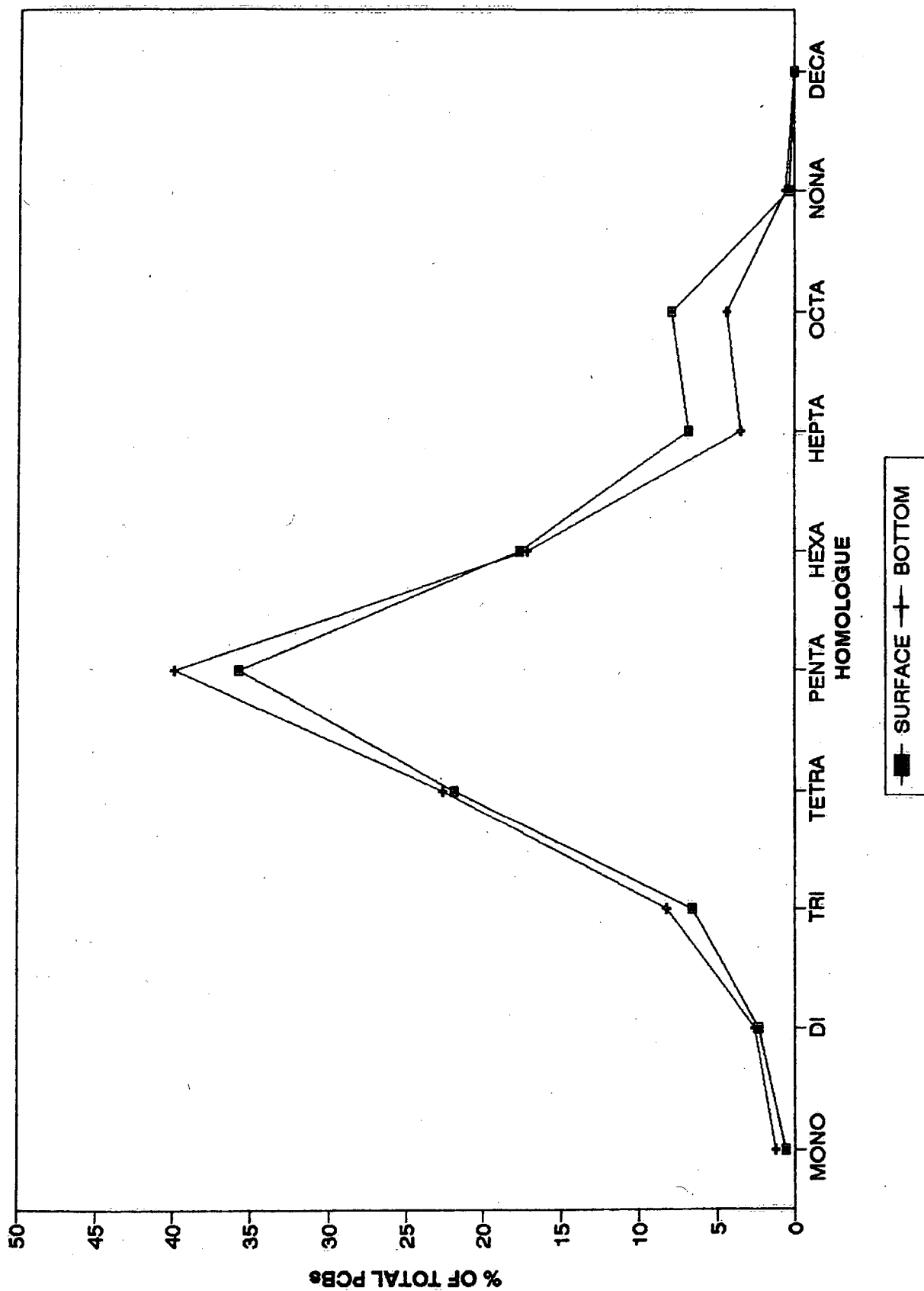


Figure 6

JULY

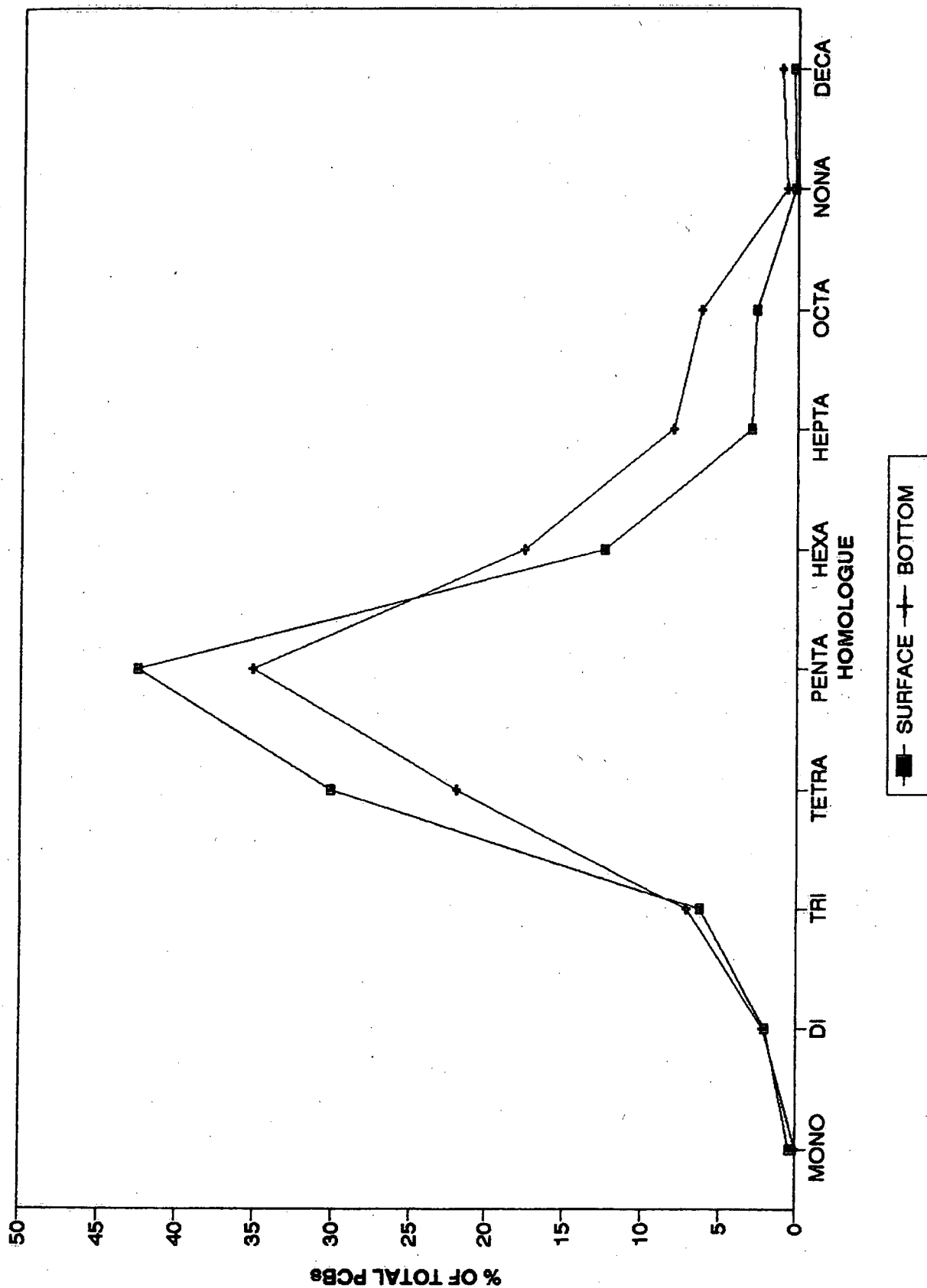


Figure 7

AUGUST

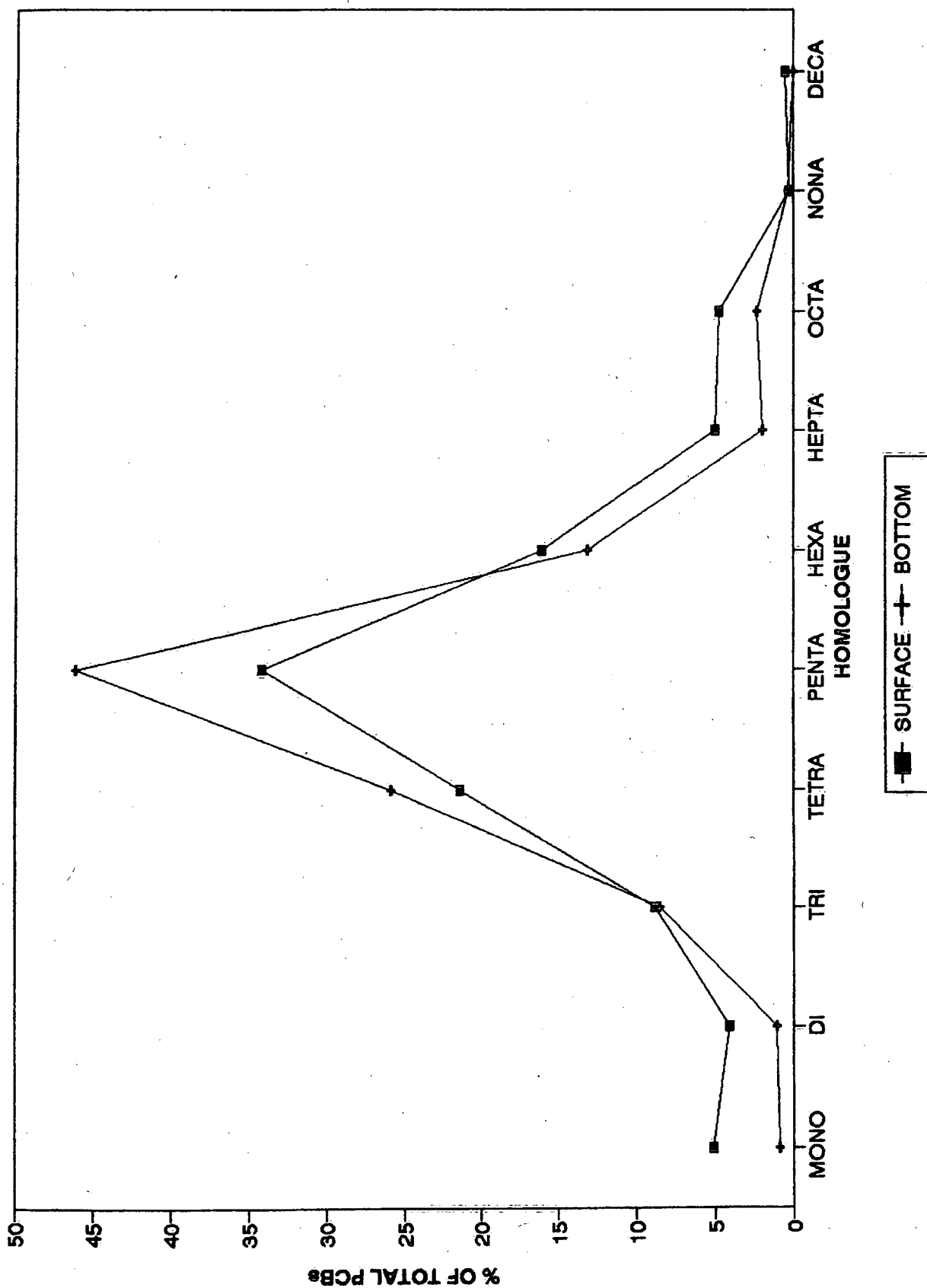


Figure 8.

SEPTEMBER

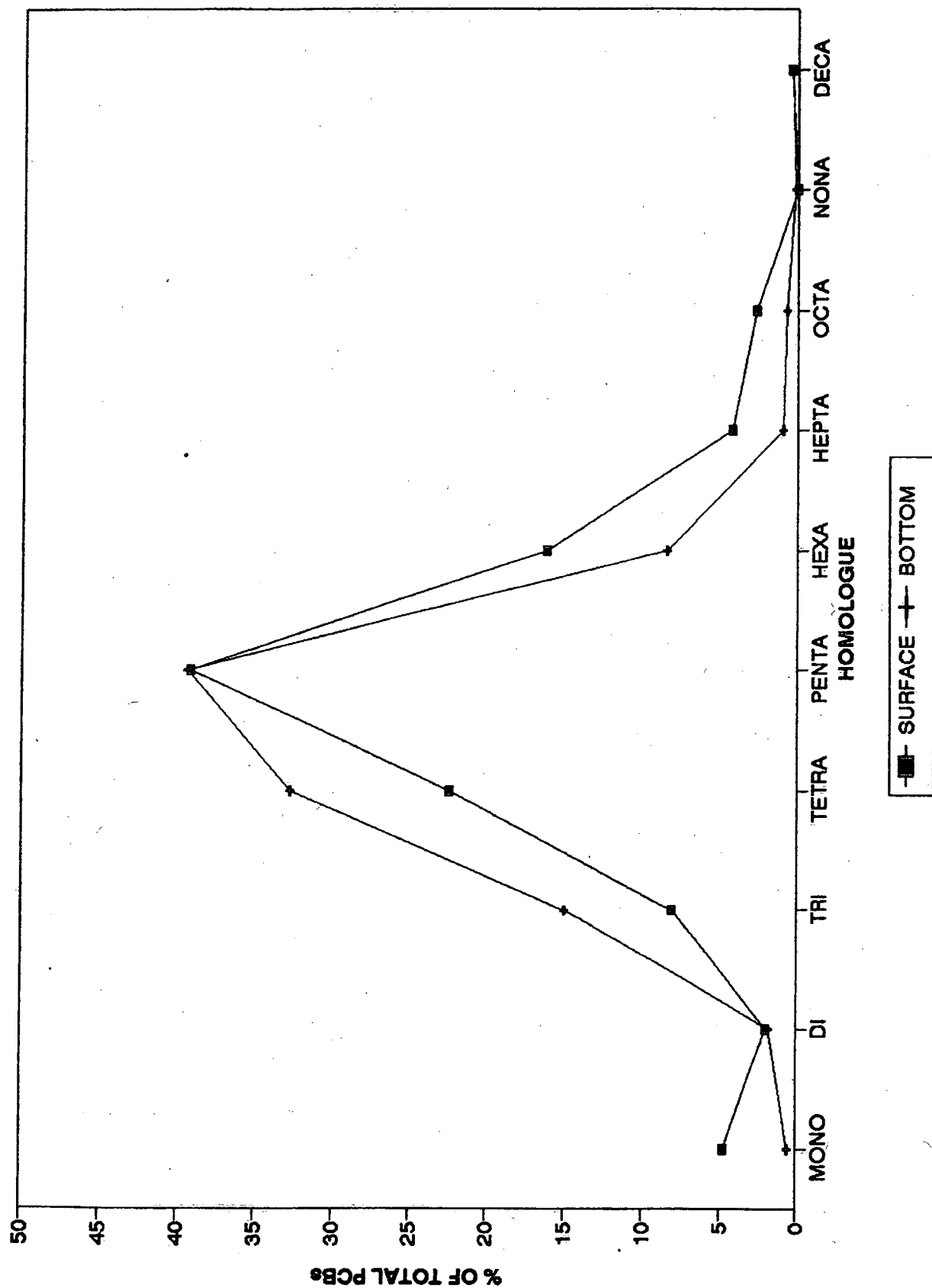


Figure 9.



Environment Canada Library, Burlington
3 9055 1017 7934 5



Environment
Canada

Environnement
Canada

Canada

Canada Centre for Inland Waters

P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre

11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre

105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey

351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures

Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
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