

REGIONAL ANALYSIS OF TEMPORAL TRENDS OF CONCENTRATIONS OF POLYCHLORINATED BIPHENYL IN LAKE SEDIMENTS

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EXTENDED ABSTRACT

Polychlorinated biphenyls (PCBs) consist of 209 possible congeners, which were used primarily as dielectric and coolant fluids in closed systems, but also as plasticisers in many products. They were widely used in the United States from 1929-1979 and after which they were banned because of wide-spread occurrence in the environment and potential effects on wildlife and humans. In the Great Lakes region of the U.S.A., it has been shown that atmospheric transport is the dominant pathway for PCB loadings to the environment and that urban areas are major sources. Understanding of the specific spatial pattern of PCB loadings to the Great Lakes is limited because of the coarse spatial distribution of existing sampling sites. However, in general, loadings have been reported to be greater in the southern area of the region and lesser in the north, possibly related to urbanization and industrialization in the south. Although now banned, PCBs are still present in the Great Lakes environment and thus there is interest in the dynamics of movement among compartments in and rates of changes in concentrations in the environment. It is hypothesized that since the ban on PCBs, the previously observed spatial gradient loadings is lessening. In order to test this hypothesis, chronological records in sediments from 34 inland lakes that are widely distributed across the State of Michigan, U.S.A., which itself occupies a significant footprint in the Great Lakes region, were examined to determine: 1) the history of PCB loadings; 2) the spatial distribution of those loadings and inventories; and 3) how loadings have changed over time. These data also afforded the study of the temporal and spatial changes in patterns of relative abundances (fingerprints) of PCB congeners. Changes in patterns can give insight into: 1) the importance of local versus larger regional inputs for PCBs and 2) how well mixed the atmosphere is. One might hypothesize that local sources have unique congener fingerprints and that the fingerprints of regional sources would reflect a more well mixed system. This hypothesis was tested by use of cluster analysis of concentrations PCB congeners from 1970 and 2000. Selected results are that larger inventories (total mass of PCBs in sediment) are found in the southern area and lesser masses in the northern areas. The larger inventories in the south are mainly near urban areas. More remote from urban areas, inventories are similar for both southern and northern areas. The spatial pattern of relative concentrations of congeners deposited in 1970 is different between north and south and unique near urban areas. In 2000 patterns more unique to urban areas have lessened and patterns in the north and south become more similar. The results of this study are consistent with both hypotheses and show the increasing influence of regional PCB loadings since banning PCBs.

Keywords: PCBs, atmospheric deposition, sediment chronologies, cluster analysis

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of synthetic organochlorides comprised of up to 209 possible congeners, which were used as dielectric and coolant fluids as well as plasticizers and became an environmental concern in the State of Michigan, the Great Lakes Region of North America as well as Globally (Golden et al, 1993; Auman et al., 1997; Henry et al., 1998; Kannan et al., 2000; Funga et al., 2005). They were widely used in the United States from 1929 to 1979, when they were banned because of wide-spread occurrence and potential risks to health of wildlife and humans. Patterns of spatial and temporal distribution of PCBs have been studied for decades to understand their sources, transport and fate in the environment (Eisenreich et al, 1979; Gioia et al, 2011). Previous studies have shown that the pattern of distribution of PCBs in the Great Lakes region is influenced by long-range atmospheric transport and localized atmospheric inputs, particularly from urban areas (e.g., Eisenreich et al. 1981; Offenberg et al. 2005). Understanding of specific patterns of spatial distribution and loadings of PCB loadings to the Great Lakes is limited because of the coarse spatial distribution of existing sampling sites (Golden et al, 1993; Sun et al. 2007). However, in general, on a regional scale, atmospheric PCB concentrations near Lake Michigan, Erie and Ontario were found to be greater than those near Lake Superior and Huron and are attributed to the higher population density in the southern part of Great Lakes region (Shen et al, 2009).

Although now banned, PCBs are still present in the Great Lakes environment and thus there is interest in how the environment is recovering from historical loadings of PCBs. It is hypothesized that since the ban on PCBs, the previously observed spatial gradient of loadings is lessening. More specifically, during the time of larger loadings of PCBs such as the 1970s, the regional gradient of loadings of PCBs and currently urban centers will be larger sources of PCBs, than more remote regions and or general fallout from the atmosphere. In order to test this hypothesis, chronological records in sediments from 34 inland lakes that are widely distributed across the State of Michigan, U.S.A., which itself occupies a significant footprint in the Great Lakes region. Sediment cores were studied to examine the spatial and temporal distribution of loadings and current inventories. These data also allowed study of changes in temporal and spatial distributions of relative abundances (fingerprints) of PCB congeners. Changes in patterns of relative abundances can give insight into: importance of local versus larger regional inputs for PCBs; and mixing in the atmosphere. It is hypothesized that local sources have unique fingerprints and that fingerprints of the larger regional sources would have a different pattern due to mixing of patterns from multiple sources. This hypothesis was tested using cluster analysis, of relative concentrations of PCB congeners from 1970 and 2000.

Cluster analysis is often used to identify sources and to examine spatial patterns of PCB congeners (Howel, 2007). For example, the fingerprints of PCB congeners in outer Green Bay, Wisconsin, USA is more similar to the fingerprint of inner Green Bay than that of Lake Michigan (Cacela et al, 2002) giving insight into transport processes. Cluster analysis of PCB congeners across Europe showed that there were clear differences in the fingerprints between rural and urban areas and that that geographically related locations have similar congener patterns (Howel, 2007).

2. MATERIAL AND METHODS

Cores of sediment were collected from the deepest portion of 34 Michigan inland lakes (Fig. 1) from 2002 to 2008 by use of a MC-400 Lake/Shelf Multi-corer deployed from the monitoring vessel Nibi. Cores were extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core. ^{210}Pb was measured on one sub-core from each lake to determine porosity, accumulated dry mass, rates of

sedimentation, time of deposition and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Dating models were verified by use of ^{137}Cs , stable Pb peak and presence of excess ^{210}Pb . Another sub-core was sectioned and used for quantification of PCBs. Unlike the ^{210}Pb sub-core, it was sectioned at one cm increments for the entire core length. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fourth sections were combined.

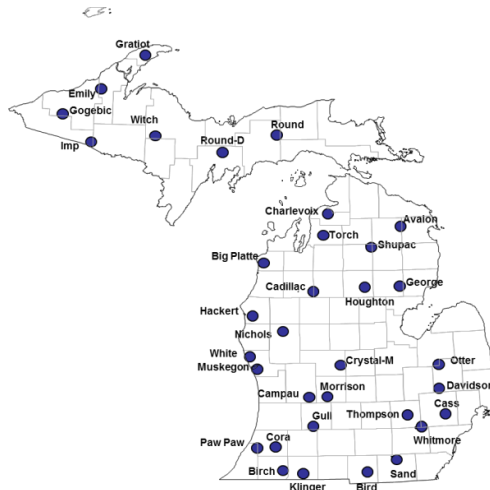


Fig. 1. Lake sampling locations, State of Michigan, USA.

Rates of accumulation of PCBs and concentrations in a year of high PCB emission (1970) and a recent year (2000) were compared. Rates of accumulation of PCBs in the sediment cores were calculated (Equation 1).

$$Accum (ng/cm^2/yr) = C_{sed} (ng/g) \times W (g/cm^2/yr) \dots\dots\dots(1)$$

Where: Accum=PCB accumulation rate (ng/cm²/yr), C_{sed}=concentration of PCB in surficial sediment (ng/g dry wt), and W=mass sedimentation rate (ng/cm²/yr).

Focusing-corrected sediment accumulation rates, calculated as Accum/FF, are a function of the rate of accumulation from atmospheric input (Golden et al, 1993). Inventories (total mass) of PCBs in sediment cores were calculated as (Equation 2):

$$Inv (ng/cm^2) = \sum_i [C_{sed}(ng/g) \times (1-\phi) \times \rho(g/cm^2) \times d(cm)] \dots\dots\dots(2)$$

Where: Inv = total PCB dry mass in a core (ng/cm²), C_{sed} = sediment concentration, ϕ = porosity, ρ =bulk density, d=thickness of sediment increment. Focusing-corrected inventories were calculated as Inv/FF to yield PCB burdens which may reflect basin or lake-wide inventories, where FF=focusing factor. This calculation technique has been often used in studies of organochlorine inventories in sediments of the Great Lakes (Golden et al., 1993).

Cluster analysis was performed on the PCB congener data using JMP 5.0 for Windows. Twenty PCB congeners were measured and analyzed in this study. The values that are below the detection limit were assigned the half detectable value for that particular congener before analysis. Relative proportions of congeners were expressed as the proportion of total PCB mass (by wt), where total PCB mass is defined as the sum of congeners. This is termed percentage standardization, which was used by Stern et al. (1997). These data are often described as “compositional data” as they have the feature that the proportions of pollutants in a sample sum to 1. Since compositional data have

been known problems with correlation coefficients and standard multivariate techniques (Pearson, 1897) which leads to problems with the interpretation of simple summary statistics, log-ratio transformation of the compositional data was also used as proposed by some (Aitchison, 1982; Howel, 2007). The log-ratios are calculated by dividing the compositional data of each PCB congener in each lake by the geometric mean of the twenty PCB congeners of that lake (Equation 3).

$$\text{Log-ratio} = \log(p_{ij}/g(p_j)) \dots\dots\dots (3)$$

Where: p_{ij} =the proportion of PCB congener i in Lake j , $g(p_j) = (p_{1j}p_{2j} \dots p_{dj})^{1/20}$ (Howel, 2007). The congener compositional data and log ratio transformed data of two particular time horizons: 1970 (high PCB emission) and 2000 (current year) were studied by cluster analysis. Three, four, five and six clusters were studied for both data sets. The same conclusions about trends can be reached from all of these studies and only the four cluster analysis is presented (Figure 5).

3. RESULTS

3.1 Accumulation rates and surface sediment concentrations

Focusing corrected accumulation rates in 1970, which was the year of peak production of PCBs, vary from 0-25 (ng/cm²/yr) and in 2000 vary from 0-6 (ng/cm²/yr) (Figure 2A and 2B). Total concentrations of PCBs among lakes vary significantly, from 0 to 3000ng/g (Figures 2C and D). However, in recent years, such as 2000,

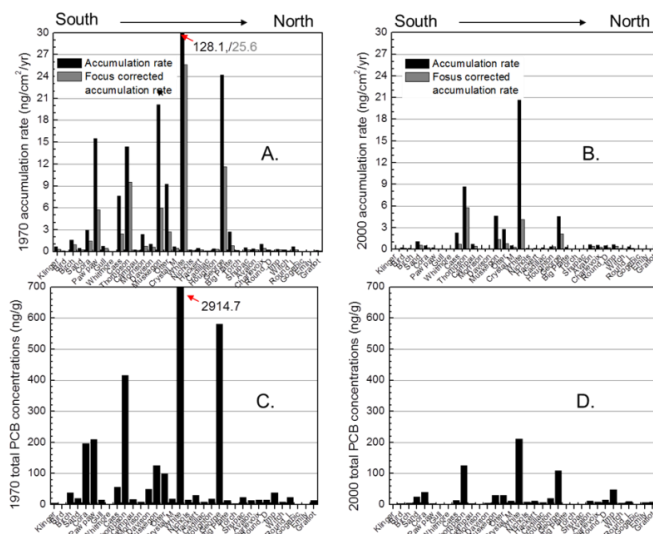


Fig. 2. PCB accumulation rates and surface sediment concentrations. A. 1970 accumulation rate, b. 2000 accumulation rates, D. 1790 surface concentrations, D. 2000 surface sediment concentrations.

concentrations are less and the difference in concentrations among the lakes is less (0-200 ng/g). The above results indicate that the atmospheric input in 2000 is less than it was in 1970. In the year of peak production, patterns of loading of PCBs were more influenced by local sources while in more recent years it is more influenced by regional atmospheric deposition, which is consistent with the hypothesis. However, there are a few lakes where concentrations of PCB surface sediments remain elevated (e.g., Thompson and White lakes) most likely due to the legacy of larger loadings of PCB in

their watersheds.

3.2 Inventories

Inventories of PCBs in sediments of inland lakes in Michigan were calculated. The sedimentary records of Lakes George, Otter, Muskegon, and Morrison only date back to 1932, 1948, 1964 and 1973, respectively, thus, actual inventories of those four lakes would be greater than those reported. However, this should not affect interpretation of the data since the record does include most of the years after production of PCBs started, and because the inventories of those four lakes are already greater than those of most

other lakes Inventories of PCBs in sediments in the Lower Peninsula are greater than those in the Upper Peninsula. There is no apparent south to north decreasing gradient as hypothesized. Total inventories of PCBs in sediments of most lakes are between the average inventories of PCBs in Lakes Superior (4 ng/cm^2) and Michigan (125 ng/cm^2) (Golden et al, 1993). These values represent the regional PCB background, indicating that the regional loadings of PCBs from the atmosphere, which are similar across Michigan. Some lakes, such as White, Thompson, and Muskegon, have greater inventories ($1000, 700, 200 \text{ ng/cm}^2$) related to localized deposition from the atmosphere near the industrialized urban area.

3.3 Congener patterns

The results of the multivariate statistical analysis, cluster analysis of patterns of relative proportions of PCB congeners measured at various locations indicate which lakes are similar in the relative abundances or “fingerprint” of congeners by the same shading. The cluster analysis was stratified by time period, 1970 or 2000. Thus, lakes can only be compared within the time period and not between time periods. Lakes with the same shading between time periods are not from the same cluster (Figure 4).

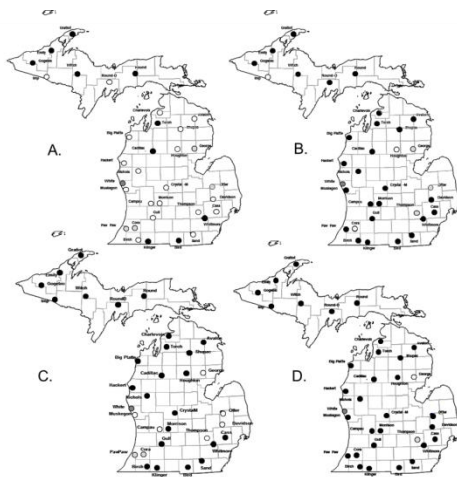


Fig. 5. Results of cluster analysis. In each figure, PCB fingerprints are the same for like colors. Similar colors between figures do not imply similar fingerprints. A. 1970 compositional, b. 2000 compositional D. 1970 log ratio, D. 2000 log ratio.

In 1970, the congener cluster pattern of compositional data shows two major clusters (Fig. 4A). The Upper Peninsula is dominated by one cluster and the Lower Peninsula is dominated by another cluster. In 2000, one major cluster dominates (Fig.

4B) from south to north. It indicates that in 1970, the sources for PCBs in the south and the north regions are apparently different. But in 2000, PCBs in the atmosphere appears more well mixed and representing more of a regional source. The cluster analysis of the log ratio transformed data (Fig. 4C, Fig. 4D) showed similar patterns. In 1970, White, Muskegon, Thompson and six other lakes stand out (Fig. 4C), and those lakes happened to have elevated PCB concentrations and inventories (e.g., Fig. 2).

4. CONCLUSIONS

The hypotheses driving this study are that (1) during the time of high PCB production the influence of population centers on loadings cause a spatial gradient in PCB loadings and that in recent times because of environmental legislation banning the use of PCBs loadings and spatial gradients would be lessened and 2) in recent times PCB loadings reflect more of a regional signal. The results of this research show changes over time in sediment concentrations, accumulation rates, and congener patterns that are consistent with both hypotheses. The results also show the effectiveness of environmental legislation and that more recent loadings are less and demonstrate recovery of the environment from historical loadings.

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