Concentrations, Inventories, and Accumulations of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Sediments of the Great Lakes

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have never been manufactured intentionally and yet are ubiquitous throughout the environment. They occur as by-products of a wide array of combustion and manufacturing processes. They are chemically stable, bioaccumulate in the food web, and have adverse ecological and human health effects at very low concentrations. Occurrence of PCDD/PCDFs in the Great Lakes is of prime concern because of the huge freshwater storage volumes of the lakes and the large populace surrounding, and served by, the lakes.

Sources of PCDD/PCDFs to the Great Lakes include atmospheric transport and deposition, riverine inputs, and direct and indirect discharges. Some direct measurements of input source concentrations have been made but a complete inventory of all source functions would be impossible.[1] Even so it is necessary to have information on their current and past input rates in order to help assess the effectiveness of past regulatory tools in reducing their concentrations and to help predict the effect of future efforts. PCDD/PCDFs associate strongly with particles in the water column and are delivered efficiently to the sediments. Their concentration profile with sediment depth is thus an indication of the changes in their input rates with time. Some measurements of sediment concentrations have been made, but the data base is small.[2,3] From 1990 - 1994, we have analyzed sediment samples from Lake Superior, two remote lakes near the Apostle Islands of Lake Superior, Lake Michigan, and Lake Ontario for PCDDs and PCDFs.

Objectives

The purpose of the study was to determine the history of sediment accumulations of PCDD/PCDFs from a series of sediment cores from Lakes Superior, Michigan, and Ontario. In addition, cores from "control" inland lakes, assumed to receive their inputs from only the atmosphere, were analyzed. Using these sediment records we had the following as objectives:

1. Determine the changes in concentrations of the PCDD/PCDFs with time in each of the lakes.
2. Determine the accumulation rates and changes in accumulation rates of the PCDD/PCDFs in each of the lakes.
3. Determine the time of onset of accumulation of PCDD/PCDFs in each of the lakes.
4. Determine the current accumulation rates of PCDD/PCDFs in each of the lakes.
5. Determine the total areal sediment inventory of PCDD/PCDFs in each of the lakes.
6. Estimate the minimum atmospheric contribution of total input to each of the lakes by comparison of the areal sediment inventories to the control lakes.

Methodology

Sediment samples from the Great Lakes were obtained by either box corer from the U.S. EPA *R/V Lake Guardian*, box corer from the submersible *Johnson Sea Link* operated from the *R/V Seward Johnson*, or the submersible *Clelia* operated from the *R/V Edwin Link* of Harbor Branch Oceanographic Institute. Remote lake samples were gathered by SCUBA diver courtesy of the U.S. Geological Survey. Two samples were taken from Lake Superior, three from Lake Michigan (two from the north depositional zone and one from the south), and three from Lake Ontario (one each in the west, central, and east depositional basins). The cores were subsectioned into 0.25 - 2.0 cm sections and each section was dated using ^{210}Pb techniques and analyzed by gas chromatography mass spectrometry in electron capture negative ionization mode.[2,4] PCDD/PCDFs were analyzed for tetra- through octa- chlorinated homologs which were summed to calculate total PCDD/PCDF concentrations.

Results

Most of the cores exhibited maximum subsurface concentrations correlating to the early-to-mid 1970s. Peak concentrations were lowest in the remote lakes and Lake Superior (ca. 0.3 ng/g total PCDD and PCDF), greater in Lake Michigan (ca. 2.0 ng/g PCDD and PCDF), and greatest in Lake Ontario (ca. 14 ng/g PCDD and PCDF).

Sedimentation rates were determined from ^{210}Pb activity and sediment depth corrected for compaction. Accumulation (product of concentration times sedimentation rate) onset of PCDD/PCDF occurred in the 1930-1940 horizon for all lakes. Peak accumulations, corrected for depositional focusing, were ca. 5-10 pg/cm^2-yr in the remote lakes and Lake Superior, 25-100 pg/cm^2-yr in Lake Michigan, and 350-575 pg/cm^2-yr in Lake Ontario. Current focus-corrected accumulations in Lake Ontario are about 120-220 pg/cm^2-yr, and in Lake Michigan about 15-60 pg/cm^2-yr. PCDD accumulation in Lake Superior and the "remote" lakes has been unchanged since peaking but PCDF accumulation has declined by about 70% in Lake Superior. (Figure 1, panel a.). This indicates that Lakes Michigan and Ontario are receiving either significant non-atmospheric sources of PCDD/PCDFs or that the atmospheric concentrations of PCDD/PCDF are significantly greater in the air masses over Lakes Michigan and Ontario than the more remote control lakes and Lake Superior.

PCDD and PCDF focus-corrected inventories (ng/cm^2) are ca. 0.5 in Lake Superior and the remote lakes, increase to 0.8 - 2.5 in Lake Michigan, and are highest in Lake Ontario at ca. 14 - 19 (Figure 1,

panel b.). The northern stations of Lake Michigan show higher inventories and accumulations than the southern station. We had hypothesized that the southern, more urbanized area of the lake would have the greater inventories and accumulations. In Lake Ontario, the central station exhibits the highest current accumulation rate while the eastern station has equal or higher inventory. This may indicate that current inputs that can reach the eastern lake have been more effectively reduced than those to the central basin.

Homolog profiles in the remote lakes and Lake Michigan are similar. Lake Ontario cores are similar within the lake but exhibit a different pattern for furans than the remote lakes or Lake Michigan (Figure 2). The similarity in homolog profile between the control lakes and Lake Michigan indicate similar source functions while the difference between Lake Ontario and the others indicate an additional source to Lake Ontario.

Conclusions

The onset of accumulation of PCDD/PCDF to the Great Lakes basin was in the 1930-1940 horizon with peak accumulations occurring in the early-to-mid 1970 time frame. Lake Michigan and Lake Ontario are receiving current inputs of PCDD/PCDF ca. five and twenty times that of the remote "control" lakes and Lake Superior. This could indicate either additional non-atmospheric sources to the two lakes or enhanced atmospheric flux to the lakes. Based on "control" lake current accumulations, the minimum current atmospheric inputs to Lake Michigan and Lake Ontario are ca. 20% and 5% respectively. Similarity in homolog profiles between Lake Michigan and the control lakes suggests that the atmospheric inputs to Lake Michigan may dominate. The altered PCDF homolog profile in Lake Ontario may indicate significant non-atmospheric sources to the lake.

References

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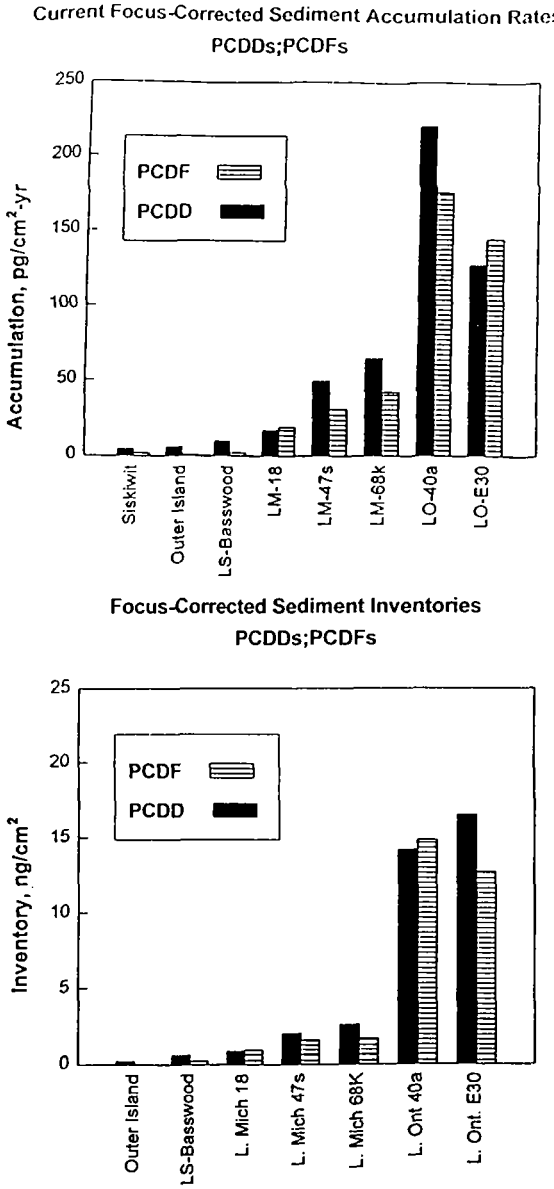

Figure 1. Panel a. Accumulation of PCDD/PCDFs in the surface sediments of cores taken from the Great Lakes and "Remote Lakes". Accumulations are corrected for depositional focusing. Panel b. Areal inventories of PCDD/PCDFs observed in sediment cores of the Great Lakes and "Remote Lakes". The inventories are corrected for depositional focusing.

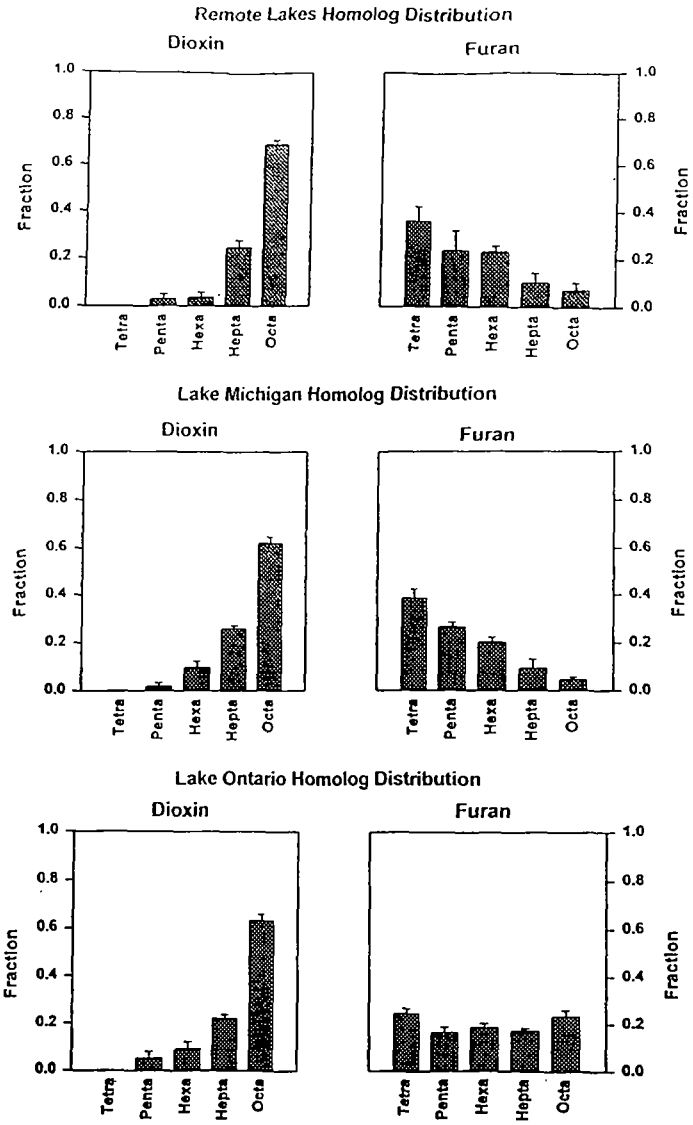

Figure 2. Representative composition of total PCDD and PCDF, by homolog, for sediment cores taken from remote lakes (top plots), Lake Michigan (middle plots), and Lake Ontario (bottom plots). The remote lakes receive inputs of PCDD/PCDF via the atmosphere only.