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PCBs in Great Lakes sediments, determined by positive matrix factorization

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A B S T R A C T

Previously determined PCB concentrations in 10 dated sediment cores from Lakes Michigan, Huron, Erie, and Ontario are analyzed by positive matrix factorization in order to find characteristic congener patterns including signs of anaerobic dechlorination. Three or four factors are sufficient to describe the PCB data for each lake. All four lakes are dominated by Aroclors 1248A, 1248G, 1254A, and 1254G. Aroclor 1260 is only a significant factor in Lake Michigan prior to 1975, reflecting in part a usage patterns of heavy chlorinated Aroclors early and less chlorinated Aroclors in the phase-out years in the 1970s. Dated records of factors or sources indicate clear PCB concentration maxima for Lakes Erie (1981) and Ontario(1968), while redistribution of PCBs in the less contaminated Lakes Michigan and Huron has occurred after 1980. Using a single data matrix for all four lakes provides a common basis and possibility to examine low degrees of dechlorination, while individual data matrices for each lake provide more accurate results and better separation of factors. Lakes Ontario, Michigan, and Huron undergo dechlorination via reactions such as 66(24-34) → 25(24-3) and 18(25-2) → 4(2-2) consistent with reactions H' + M, while Lake Erie appears to be dominated by 18(25-2) → 4(2-2) and 53(25-26) → 19(26-2) that are typical for processes M + Q.

Introduction

Polychlorinated biphenyls (PCBs) have been widely investigated due to their detrimental effects on humans and biota of the environment. For the North American Great Lakes, there has also been a large amount of research on PCBs in the atmosphere, water and sediments (Li et al., 2009; Hermanson et al., 1991; Marti and Armstrong, 1990; Marvin et al., 2002). While production of commercial PCB mixtures, sold under the registered trademark Aroclors, was terminated in 1977, PCBs continue to present a threat due to their presence in water and aquatic sediments.

The study of PCB transport in aquatic systems is often carried out by examining source strengths and dispersion patterns, for example, for input to lakes from rivers and the atmosphere. Net release of PCBs from water to the atmosphere can also take place, as observed for Lake Michigan (Hornbuckle et al., 2006). An alternative way of apportioning sources and their contributions is to apply receptor modeling in which the fate of pollutants is determined from measured concentrations of PCB congeners at a given site.

Receptor modeling was developed initially in air pollution studies but has recently been successfully applied to aquatic systems. In chemical mass balance (CMB) modeling the source profiles must be known (Christensen et al., 1997) while in factor analysis both source profiles and contributions can be determined, as long as minimal information about sources is available (Rachdawong and Christensen, 1997; Henry, 2003; Magar et al., 2005; Bzdusek et al., 2006a,b; Du et al., 2008). This information can be that certain compound values in sources are zero or near zero or that there are several measurements that contain zero contribution for at least one source. In positive matrix factorization (PMF) (Bzdusek et al., 2006a,b; Du et al., 2008) or eigenvalue based factor analysis (Rachdawong and Christensen, 1997), the first condition is required, while in polytopic vector analysis (PVA) (Magar et al., 2005) or principal component based Unmix (Henry, 2003) the second must be fulfilled.

PMF has shown to be especially well suited to determine factors of low contributions such as the ones from an original Aroclor mix in a strongly dechlorinating environment (Bzdusek and Christensen, 2006). The reason for this may be linked to the weighting of elements of the data matrix in the least squares objective function with the inverse of standard deviations of the values. This gives equal weight to both high and low signals ensuring that weak signals will be adequately represented.

Studies of PCBs based on PMF application have been performed to quantify anaerobic dechlorination in sediments of Lake Hartwell, South Carolina and Sheboygan River, Wisconsin(Bzdusek et al., 2006a,b) and to determine PCB sources and contributions in the Delaware River (Du

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et al., 2008). It has also recently been applied to groundwater, landfills, and wastewater collection systems to identify anaerobic dechlorination through the presence of specific congeners (Rodenburg et al., 2010). PMF should, therefore, be useful to characterize characteristic sources or patterns of PCBs in Great Lakes sediments. This includes congener patterns that may be indicative of in situ anaerobic dechlorination. Dechlorination is a natural detoxification process which can be part of natural recovery (Bzdusek et al., 2006a). Previous attempts to demonstrate dechlorination in sediments of the Great Lakes, and especially Lake Ontario where degradation chances are highest due to high PCB concentrations, have been made (Li et al., 2009; Oliver et al., 1989; Wong et al., 1995; Marvin et al., 2003). However, the dechlorination process has not been satisfactorily demonstrated. The reason is the difficulty in separating variations vs. depth in sediment of fraction of certain homologs or of *para*, *meta*, and *ortho* substitution due to dechlorination in sediments from variations caused by differences in PCB input to the system.

The objectives of this work were to apply PMF modeling to sediment PCB data from the Great Lakes to characterize sources and characteristic congener patterns for Lakes Michigan, Huron, Erie, and Ontario, to determine dated records of these patterns, and to look for signs of anaerobic dechlorination in lake sediments based on the PCB congener patterns. Source profiles generated by PMF modeling were compared with candidate Aroclor profiles by using a cosφ coefficient of proportional similarity where φ is the angle between a congener pattern and the Aroclor.

Materials and methods

Sampling and laboratory analysis

Sediment cores were taken from open water locations in Lakes Michigan, Erie, Huron, and Ontario in summer 2002 onboard of the Research Vessel *Lake Guardian* of the U.S. Environmental Protection Agency (EPA). A total of 10 locations were sampled (Fig. 1 and Table S1 of Supplementary Materials). At each location, four or five subcores were taken from the box corer using pre-cleaned acrylic tubes. Immediately after being collected, individual subcores were extruded and sectioned in 1.0–5.0 cm intervals. Each sediment sample was well characterized by its physical properties (percent solids, wet and dry bulk density, particle density, and porosity) and chemical composition (content of organic matter, organic carbon, soot carbon, nitrogen and oxygen). The year of deposition for each sample was determined from Pb-210 activities, which was measured based on alpha emissions from Po-210 using Po-209 as a yield tracer using a Canberra Alpha Analyst system (Meriden, CT).

Chemical analysis included Soxhlet extraction, Kuderna-Danish concentration, and cleanup using silica gel chromatography. Before extraction, known amounts of 2,3,5,6-tetra chlorobiphenyl (PCB65) was added as analytical surrogates. PCBs were analyzed on a HP 6890 gas chromatograph (GC) coupled with a HP 5973 electron impact mass spectrometer (EI-MS) with selective ion monitoring (SIM). PCB30 and PCB204 were added before GC injection as internal standards for quantification. A total of 39 PCB congeners were quantitatively analyzed, including those with Ballschmiter and Zell (BZ) numbers 1, 2, 3, 4, 6, 8, 9, 16, 18, 19, 22, 25, 28, 52, 44, 56, 66, 67, 71, 74, 82, 87, 99, 110, 138, 146, 147, 153, 173, 174, 177, 179, 187, 180, 194, 195, 199, 203, and 206.

The mean recovery of the analytical surrogate PCB-65 was 87% ranging from 60% to 160% except Lake Ontario, from which the sediment samples generally have higher recoveries than 90% up to 300%. The high recovery is similar to those in a report on the sediments of Lake Ontario (Marvin et al., 2003) where PCB concentrations in the sediments are much higher than in the other lakes. One sample in each core was analyzed in duplicate. The average relative standard deviation (RSD) was in the range of 6.6–40%. Method blanks and matrix blanks (pre-1900 sediment samples) were run for each core to monitor potential laboratory contamination. The averages of chemical concentrations in the matrix blanks of each core were subtracted from the results of chemical analysis. Standard reference material SRM 1939A (river sediment) obtained from the National Institute of Standards and Technology (NIST) was analyzed. The average recovery for 11 PCB congeners was 81% and 79% for two runs, respectively.

More detailed procedures of the sampling, sample characterization and dating, and chemical analysis are given elsewhere (Song et al., 2004, 2005a,b; Buckley et al., 2004; Li et al., 2006a,b). A region-wide analysis on the spatial distribution, time trends, homolog pattern, and the implications with regard to atmospheric deposition and long-range transport was published recently by Li et al. (2009).

Positive matrix factorization

The PMF model used here (Bzdusek, 2005; Bzdusek et al., 2006a) is based on equations described by Paatero (1997). The governing equation of the PMF model is

$$X = GF + E \tag{1}$$

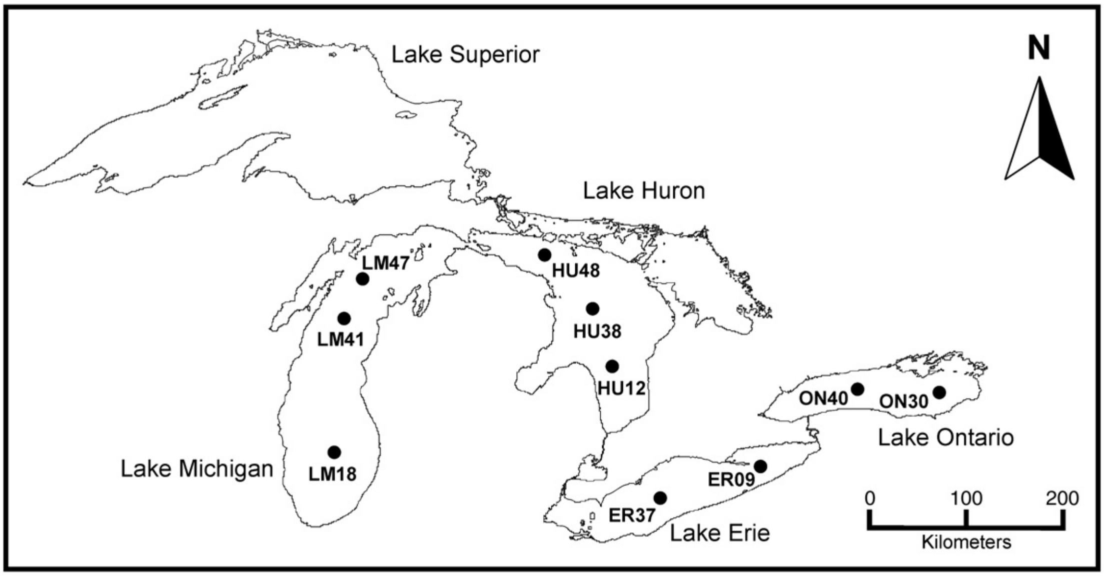

Fig. 1. Sampling locations for the Great Lakes.