

## **Chronology of PBDE Air Deposition in the Great Lakes from Sedimentary Records**

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### **1. Relevance to Great Lakes Atmospheric Deposition Priorities:**

We propose to investigate the history of air deposition of polybrominated diphenyl ethers (PBDEs) in the Great Lakes by retrieving sedimentary records. The project falls into the EPA's priority area of "air deposition and source characterization monitoring". The significance of this work stems from the following considerations.

Although not a group of persistent bioaccumulative toxics (PBTs) particularly specified in EPA's RFP, PBDEs are more environmentally persistent than PCBs due to their higher resistance to various degradations (de Boer et al., 1998). Their high lipophilicity ( $\log K_{ow} = 4.3$  to 9.9, compared with 4.5 to 8.0 for PCBs) indicates a strong bioaccumulation potential. Evidence of their toxic, carcinogenic, and hormone-disrupting effects is also mounting rapidly. A review of the current state of knowledge on PBDEs is given by Darnerud, et al. (2001). The Abstracts of the Second International Workshop on Brominated Flame Retardants (BFR, 2001; Betts, 2001) compile the most up-to-date research achievements.

While many chlorinated pesticides and PCBs are legacies of the past, PBDEs are currently being produced at a rate of 50,000 tones a year worldwide (Darnerud et al., 2001). The widespread uses of PBDE as flame retardants in electronic devices, textiles, furniture, plastics, and vehicles, has made them globally ubiquitous. They have been found in measurable amounts in literally everywhere scientists looked (Renner, 2001). For example, PBDEs were found in deep ocean whales (de Boer et al., 1998), giving evidence of their long-range transport via the atmosphere. The sum concentration of eight PBDEs in Swedish mother's milk increased exponentially from the early 1970s to the late 1990s (Meironyte et al., 1999). The concentrations of PBDEs were found 70 times higher than normal in the blood of occupationally exposed workers (Sjodin, 1999). All of these foreshadows that a potentially severe environmental problem related to PBDEs may be on its way (de Boer et al., 1998).

There should be no doubt about the presence of PBDEs in the Great Lakes. About 40% of the world total consumption of PBDEs occurs in North America (Manchester et al., 2001). The concentration of PBDEs in the air of four land locations near the Great Lakes ranged from 140 to 3,100  $\text{pg m}^{-3}$ , and did not show significant variations from 1997 to 1999 (Strandberg et al., 2001). PBDEs were found in the fish of all the five lakes (Luross et al., 2000), and Lake Michigan fish contained six times more PBDEs than the Baltic salmon (Asplund et al., 1999). The correlation of PBDE tissue concentration with age in Lake Michigan salmon implies that PBDEs have been in the lake for many years (Manchester et al., 2001).

Air deposition has proved to be the major source of many PBTs, including PCBs and dioxins, to the Great Lakes. This has been particularly true in the last decade when emissions from most known point sources have been greatly reduced (Delta Institute, 2001). For PBDEs, the major point sources are thought to be the incineration of disposed commercial products, as well as sewage and sludge releases (Darnerud et al., 2001). Due to their widespread use, volatilization from various products can be a source of PBDEs in the air with even more significant amounts than from the point sources. In addition, because PBDEs are mostly found in the technosphere

and ready-made plastic products, their uncontrolled release into the environment will continue for years to come (Darnerud et al., 2001).

Sedimentary records have been used to reconstruct historical input of persistent pollutants. At locations where air deposition is the major pathway of input, chronology of air deposition can be directly revealed from data obtained from laminated sediment cores. Two such studies on PBDEs have been published in Europe (Nylund et al., 1992; Sellstrom et al., 1989). In contrast to PCBs and DDT, PBDE concentrations in the sediment core collected south of Baltic Proper near Sweden showed an exponential increase after the late 1970s, more than doubling from 1986 to 1987 (Darnerud et al., 2001; Nylund et al., 1992).

## **2. Problem Statement:**

To our best knowledge, no information is available on the inventory, spatial distributions, and temporal trends of PBDE concentration and flux in the water and sediments of the Great Lakes. This lack of information hinders the assessment of the fate and transport of PBDEs and their impact on the ecosystem and human health in the region.

Our research plan is based on the following hypotheses:

*Hypothesis-1: Air deposition is the major source of PBDEs to the sediments of the Great Lakes.* The vapor pressure of PBDEs ranges from  $10^{-5}$  to  $10^{-12}$  Pa at 25°C (Wong et al, 2001; Tittlmier and Tomy, 2001). Nevertheless, 80% of BDE-47, 55-65% of BDE-100 and BDE-99, and 30% of BDE-153 in the air were found in the gas phase while the rest were associated with air-borne particulates (Strandberg et al., 2001). Considering the relatively rapid equilibrium between air and water phases of similar organic pollutants such as PCBs (Mackay and Bentzen, 1997), the strong affinity of PCB-like compounds for particulates in the water column, and their high resistance to degradation, it is expected that the sedimentary record will provide an accurate record of air deposition of PBDEs in the Great Lakes region.

*Hypothesis-2: In contrast to recent trends in PCB deposition rates, the sedimentary record of PBDEs will show an increase in recent years.* Although there have been reports of a strong correlation between PBDEs and PCBs concentrations in both air (Strandberg, et al, 2001) and fish (Manchester et al., 2001) collected in the Great Lakes, such a correlation may not exist in an chronological order in the sediment column. The concentration of PCBs in the Great Lakes has declined during the last decades, as reflected by the sediment core and fish data (Hillery et al., 1997; Smith, 1995). Given the increasing uses of PBDE in the past decades, and the direct evidence of steady air concentration in the Great Lake region in recent years (Strandberg et al., 2001), we expect the chronology of PBDEs air deposition to be significantly different from that of PCBs in the same sedimentary record.

*Hypothesis-3: The spatial distribution of PBDEs in Great Lakes sediment will indicate that PBDEs are predominantly from anthropogenic sources.* For PCBs, higher concentrations are often found in air and sediments closer to urban centers and industrial areas. Although natural synthesis of brominated aromatics have been reported (Renner, 2001), the finding that Chicago air contains as high as 10 times the PBDEs concentrations of non-urban areas in the Great Lakes region (Strandberg et al., 2001) underscores the anthropogenic origin of PBDE.

*Hypothesis-4: The sediment will have a different PBDE congener pattern than those found in air and fish.* The relative abundance of congeners is an important tool for tracking pollution sources and risk assessment. Despite the fact that 75% of the commercial PBDEs are deca-BDE (Manchester et al., 2001), those found in environmental samples, including air and fish samples

collected in the Great Lakes region, mostly resemble the composition of commercial penta-BDE. Disagreement exists on whether deca-BDE undergoes debromination in the environment (Renner, 2001). From a limited number of European and Japanese studies, deca-BDE was found in sediments, ranging from < 25 to > 11,600 ppb (dry weight). With the Great Lakes sediments, we will investigate PBDEs with 3 to 10 bromines to gain more insight into this issue.

### **3. Proposed Work and Outcomes:**

#### Sampling Locations

Sampling locations in the Great Lakes will be selected from the pre-established stations. Three or four points in Lake Michigan and one or two in each of the other lakes will be sampled. A few cores will be collected at locations near the sampling points where air concentrations were previously measured (Strandberg, et al, 2001).

We will also sample two or three inland seepage lakes within the Great Lakes basin. The only source of PBDEs to these lakes is atmospheric deposition. Therefore, comparison between the chronology of PBDE accumulation in these lakes and in the Great Lakes will provide additional information, which enables the assessment of the contribution from air deposition to total burden of PBDEs in the sediment of the Great Lakes.

The potential sites for inland seepage lake sampling include Isle Royale National Park in Lake Superior and the North Temperate Lakes Long Term Ecological Research (NTL-LTER) area in northern Wisconsin. Both of these sites contain seepage lakes with a large body of data from long term ecological studies, including studies of air deposition to the Great Lakes basin. Isle Royale is ideal for air deposition research due to its location and pristine nature. The predominant wind direction at Isle Royale is from the upper Midwestern United States (Thurman and Corwell, 2000), the air plume from urban Thunder Bay, Ontario, 52 km northwest, may also bring pollutant chemicals to the island. A number of studies have been done on Isle Royale for the time trends of air deposition of PCBs (Swackhamer et al., 1988; Strachan, 1985), dioxins (Baker and Hites, 2000; Astle et al., 1987; Czuczwa and Hites, 1986a, 1986b), PAHs (McVeety and Hites, 1988), and pesticides (Thurman and Cromwell, 2000; Sergeant et al., 1993; Strachan, 1985; Swain, 1978). The NTL-LTER site is in northern Wisconsin near the Michigan border. It is close to three of the Great Lakes and approximately 300 miles northwest of Chicago. The LTER program is funded by the National Science Foundation and run by the University of Wisconsin-Madison. We also propose to select a seepage lake in a region closer to a major urban center (Chicago) than Isle Royale and northern Wisconsin. Effort is being made to identify a suitable lake in upper Illinois to lower Wisconsin or in western central Michigan. Sediment cores in a carefully chosen lake closer to urban sources will be compared with those obtained from the remote sites and the Great Lakes. This comparison should provide evidence on the atmospheric transport and the anthropogenic origin of PBDEs.

Specific lakes will be identified from these sites according to the following criteria: (1) they are seepage or recharge lakes with no significant surface inflow; (2) the ecosystem is not significantly altered by human activities (e.g. acidified lakes are not suitable); (3) levels of biological activities is close to that of the Great Lakes (e.g. eutrophic lakes will not be selected due to potentially extensive biodegradations); (4) sediment characteristics (e.g. organic carbon content and nature, grain size distribution, etc.) are not significantly different from those of the Great Lakes; and (5) lake bottom topographic feature have prevented extensive sediment movement and mixing. The information needed for selecting the lakes will be collected from various sources including the databases of NTL-LTER and State Department of Natural

Resources. Discussion with our project consultants and other researchers in the field will also be held. The final decision will be made with consultation of the Air Deposition team at EPA. Exact sampling locations will be referenced to latitude and longitude using GPS.

### Sampling

Sediment sampling in the Great Lakes will take place onboard the EPA *R/V Lake Guardian* during its regular biannual monitoring survey trips. The box corer on the *R/V Lake Guardian* is capable of reaching 3-feet deep into the sediment and taking a cube cleanly (Ison, personal communication). Given the known sediment deposition rates for the sampling locations, this depth is sufficient to cover the deposition periods for PBDEs. Subsamples (cores) will be taken from this cube using a polycarbonate cylindrical corer tube. Multiple cores may be taken, each core will be sliced at 0.5 to 5 cm intervals, and corresponding intervals will be combined to ensure sufficient amounts of each sample for sediment characterization, dating, and chemical analysis (detailed below). For each slice, about 2 mm sediment in contact with the wall of the cylindrical corer will be discarded to minimize the smearing effects which may occur during subsampling the cube and extruding the corer. The slices will be placed into solvent-washed glass jars with aluminum foil lined lids, and kept frozen until use.

In selected inland lakes, particular spots of sampling will be chosen in a deep and flat location where the effects of light penetration and sediment movement are minimal. The spots will be found using a depth finder and topographic maps. A push corer will be used on board of a rowboat or motorboat, as we did four year ago on the Lake Calumet, Chicago. The corer equipment and accessories are available from the Center for Great Lakes Studies of the University of Wisconsin-Milwaukee. Multiple cores will be taken and sectioned in a similar manner as described above.

The total number of sediment samples will be 250 to 350 with 10 to 15 cores.

### Sediment Characterization and Dating

Sediment samples will be characterized for water content, specific gravity, and porosity according to the standard methods (ASTM 1998a, 1998b). In addition, particle size, surface area, and pore structure, as well as natural organic matter (NOM) content will be determined. We will first fractionate the sediment based on size using wet sieves and x-ray sedimentography. For each size fraction of selected samples, we will conduct elemental analysis (C, N, O, and H using a Carlo Erba Flash EA1112 elemental analyzer), and analyze organic matter (mass loss of dry sediment after combustion at 375° C), and soot carbon (organic carbon after combustion at 375° C; Gustafsson et al. 1997). The physical structure of the bulk sediment will be characterized by mercury porosimetry (Micromeritics 9320 porosimeter; Micromeritics 1996c), nitrogen gas adsorption/BET surface area (Micromeritics ASAP 2010 surface area/porosimeter; Micromeritics 1996a,b), and particle size by x-ray sedimentography (Micromeritics 5100 particle size analyzer). All of these techniques are in routine use in our laboratories (Rockne et al. 2000, Rockne et al. 1999). Such a detailed characterization of sediment samples will allow us to compare the sorption/sequestration behavior of PBDEs with other PBT chemicals being investigated in our lab, such as PCBs and PAHs, and to better understand the mechanism of phase transfer process between water and sediments.

Sediment dating will be done at the Center for Great Lakes Studies in Milwaukee, using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  techniques. The sedimentation rate will be calculated from the dating results. The flux of PBDEs into the sediment will be determined from the measured chemical concentration, the

*in-situ* density, the sedimentation rate, and a focusing factor, as we have done previously for PAHs and PCBs (Jang and Li, 2001; Ab Razak et al., 1996). The *in-situ* sediment density will be calculated from the measured porosity and specific gravity. The estimation of the focusing factor, which is the ratio between actual inventory of  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  in the sediments and that expected from the atmospheric input, is described in Zhang et al. (1993) and Christensen et al. (1997).

### Chemical Analyses of PBDEs and PCBs

Procedures of sample treatment and instrumental analysis for PBDEs will be developed based on our extensive experience with PCBs as well as previously published work on PBDEs. Briefly, the samples will be mixed thoroughly after being warmed to room temperature. An aliquot will be weighted and mixed with sufficient amount of precleaned anhydrous  $\text{Na}_2\text{SO}_4$  to make a friable mixture. This mixture will be Soxhlet-extracted using hexane:acetone (1:1) for 24 hours. The volume of the extract will be reduced on a Kuderna-Danish concentrator for cleanup. Various operational parameters in silica gel fractionation and cleanup have been intensively investigated in our lab (Jang and Li, 2001; Li et al., 1998). In this work, the parameters, including the silica gel activation level, eluting solvent, and fraction volumes, etc., will be optimized for PBDE analyses. Concentrations of selected PCB congeners will also be measured in order to compare with PBDEs. All concentrations will be reported on dry weight basis.

PBDE congeners will be purchased from Cambridge Isotope Laboratories (Andover, MA). All of the equipment for the analyses outlined in this proposal are available in either the PI's, co-PI's, or cooperating laboratories. Our Environmental Chemistry lab is equipped with Hewlett-Packard Model 6890+/5973 GC/MS (EI/NCI/PCI) and Model 5890 II GC/ECD/FID. The GC/MS has a special inlet for large volume injection using the programmable temperature vaporization (PTV) technique, which allows 60  $\mu\text{L}$  injection (compared with only 1 or 2  $\mu\text{L}$  with traditional splitless inlet) for each run in our routine analysis. This has significantly lowered the detection limits in our current project with PAHs (Norlock et al., 2001). This feature is particularly important for our proposed work, because environmental PBDEs levels reported in the literature are significantly lower than those of PCBs. There is a possibility that this advanced technique could allow us to detect PBDEs in natural waters, on which no successful monitoring has been done to date (Darnerud et al., 2001).

QA/QC protocols will be submitted for approval before field sampling and lab work begin. Standard operation procedures (SOPs) will be developed. Commercially available  $^{13}\text{C}$  labeled PDPEs and PCBs (CIL, Andover, MA) will be used as analytical surrogates and internal standards. Standard reference material (SRM) with certified PBDE concentrations will be used to check the overall performance, when it becomes available (National Institute of Standard and Technology, Gaithersburg, MD). The analytical difficulty for deca-BDE reported by Standberg, et al. (2001) will be carefully dealt with.

### Outcomes

The following will be project deliverables:

- (1) The spatial distribution and temporal variation of PBDEs concentration in the sediment for each of the Great Lakes and the selected inland lakes.
- (2) Comparison between the chronology of PBDE fluxes in the Great Lakes and the selected inland lakes, and a reconstructed history of PBDE air deposition fluxes into the Great Lakes sediment.

- (3) A comparison between PBDE and PCB concentrations and time trend of air deposition fluxes to the Great Lakes watershed.
- (4) Comparisons between PBDE concentrations in the sediment and fish (Manchester, et al., 2001; Luross et al., 2000; Asplund et al., 1999), and between sediment and air (Strandberg et al., 2001).
- (5) Comparisons between PDBE levels in the Great Lakes and in other regions of the US and of the world.
- (6) Dependence of PBDE concentrations on the physicochemical characteristics of the sediments.
- (7) A comparison among different PBDE congeners in their concentrations and fluxes, as well as dependence of the variations on the chemical structure and physicochemical properties (vapor pressure, Kow, water solubility) of the congeners.

Results of this research will be disseminated through the publication in high-quality peer-reviewed scientific journals such as *Environmental Science and Technology*. We will work with EPA to respond to any information request regarding the results of this study, and to design the most effective way to disseminate the results to various clients.

#### Tentative Schedule

10/01 – 12/01	01/02 - 07/02	08/02 – 06/03	07/03 – 09/03
Sampling			
Analytical method development			
	Sediment characterization		
	Sediment dating		
	Chemical analysis		
			Data analysis
			Final reporting

#### **4. Budget:**

	Personnel	Fringe	Travel	Supplies	Contract	Tuition	Indirect	Total
Year-1	38,484	3,310	6,700	6,000	3,000	8,006	32,122	97,623
Year-2	40,409	3,476	2,810	3,000	2,500	8,407	29,161	89,762
<b>Total</b>	<b>78,893</b>	<b>6,786</b>	<b>9,510</b>	<b>9,000</b>	<b>5,500</b>	<b>16,413</b>	<b>61,283</b>	<b>187,385</b>

#### Brief Justifications:

##### Salary and Fringe Benefit:

Dr. Li: one summer month per year, fringe benefit rate 25.61%.

Dr. Rockne: 0.5 summer month per year, fringe benefit rate 25.61%.

Dr. Mills: one summer month per year, fringe benefit rate 13.42%.

1 PhD student (50%): sampling, chemical analysis, laboratory maintenance.

1 MS student (25%): sampling, sediment characterization and dating.

##### Travel:

Sampling trips: include car rental (\$15/day, university rate) and mile charges (\$0.39/mile), lodging, and per diem; based on 3 people, 10 trips, and an estimated \$250 miles per trip.

Conferences: include registration, airfare, hotel, and per diem; based on 1 person-conference in the first year, and 2 person-conferences in the second year.

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**Supplies:**

Consumables: include chemicals, standards, glassware, instrument consumables, etc.

Sampling supplies: include sampling boat and equipment rentals for inland lake sampling.

Note: There is no cost for using *R/V Lake Guardian* for sampling the Great Lakes during its the regular survey trips (personal communication with Georgy Ison, EPA5)

**Contract:** (estimated costs)

Sediment dating using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  at the Center for Great Lakes Studies, Milwaukee.

**Tuition:** 34.5% of student salary.

**Indirect:** 55.87% of total direct cost.

**5. Key Personnel:**

The curriculum vitae of all key personnel listed below are attached as appendices.

**Principal Investigator:** An Li, Ph.D., Assistant Professor in Environmental chemistry, School of Public Health, The University of Illinois at Chicago. 2121 West Taylor St. (M/C 922), Chicago, Illinois 60612, Tel: (312)996-9597; Fax: (312)423-9898; E-Mail: anli@uic.edu; Webpage: <http://www.uic.edu/~anli>.

Dr. Li started her environmental research career in 1979 with sampling sediments of the Bohai Sea and analyzing petroleum fractions in sediment and water samples. She was the key personnel in the projects on PAHs, PCBs, and pesticides in the sediments of the Milwaukee Harbor, and participated in Great Lake sediment sampling in 1995-6. Recently, one of her major projects at UIC, "Spatial and temporal distribution and source apportionment of priority organic pollutants in the sediments of Lake Calumet, Chicago", was accomplished with four journal publications. Dr. Li will take the overall responsibility for this project, including overseeing the directions and progress, ensuring data quality, student assistants hiring and training, coordinating among participating parties, and budget management.

**Co-Investigator:** Karl J. Rockne, Ph.D. Assistant Professor of Environmental Engineering, Department of Civil and Materials Engineering, University of Illinois at Chicago. 3077 ERF, 842 W. Taylor Street (M/C 246), Chicago, Illinois 60607-7023. Tel: (312)413-0391; Fax: (312)996-2426; Email: krockne@uic.edu; Webpage: [www.uic.edu/~krockne/](http://www.uic.edu/~krockne/)

Dr. Rockne's research focuses on applied and fundamental studies of environmental biogeochemical processes. He has systematically studied microbial transformations and the fate of contaminants in sediment and has demonstrated proof-of-concept for anaerobic PAH biodegradation through coupled electron donor and electron acceptor transformations. He has extensive experience working with hydrophobic organic contaminants in sediments during his time at the University of Minnesota, the University of Washington, Rutgers University, and the University of Illinois-Chicago. Dr. Rockne will assist the PI in project oversight and will be responsible for the sediment characterization phase of the study.

**Co-Investigator:** Bill Mills, Ph. D. Research Assistant, Air Pollution Training Institute, School of Public Health, University of Illinois at Chicago. 2121 West Taylor St. (M/C 922), Chicago, Illinois 60612, Tel: (312)996-2094; Fax: (312)423-9898; E-Mail: [wmills1@icarus.uic.edu](mailto:wmills1@icarus.uic.edu).

Dr. Mills' research encompasses the development of new analytical methods and study of the environmental fate and transport of chemicals. His first work in this field was as a member of prestigious team of scientists at the Experimental Lakes Area in Canada looking at the changes

in lake water and sediments from acid deposition.. Dr. Mills has over 18 years experience on the occurrence and chemical fate of numerous classes of organic pollutants including the chlorinated and polybrominated diphenylethers. Dr. Mills will assist the PI with i) analytical methodology, ii) Quality Assurance/Quality Control issues, iii) assistance on the statistical data analysis including geostatistical methods, iv) data interpretation on atmospheric deposition related matters.

Consultant: William C. Sonzogni, Ph. D., Professor, Environmental Chemistry and Technology, College of Engineering, University of Wisconsin-Madison. Director, Water Science and Engineering Laboratory, 660 North Park Street, Madison, WI 53706. Tel: 608/262-4554, Fax: 608/262-0454, Email: sonzogni@facstaff.wisc.edu.

Research Interests: Common theme is interdisciplinary environmental research that can be applied to better manage our resources. Topics include trace toxic contamination of the aquatic environment, quantification of pollutant loads, and the chemical limnology of the Great Lakes and other water bodies. Some specific problems addressed include the biological degradation of contaminants and the relative risks of various pollutants. The analytical chemistry of detecting pollutants (as well as biological-based techniques such as bioassays) has been an important component of the research. In recent years, Dr. Sonzogni has directed research projects on PBDEs in the Great Lakes (Sonzogni and Manchester, 2001; Manchester et al., 2001)

## **6. Great Lakes Region Collaboration:**

The proposed research is a collaborative effort between the School of Public Health and the College of Engineering at the University of Illinois at Chicago. Information exchange and technical discussions will be held with the researchers at the Water Chemistry Program, University of Wisconsin-Madison, and Civil Engineering, University of Wisconsin-Milwaukee. The Great Lakes Center (GLC) for Occupational and Environmental Safety and Health at University of Illinois at Chicago is currently conducting a comprehensive assessment of policies and practice on PCBs in the Great Lakes region, with the support from the Joyce Foundation (Chicago, IL) and in collaboration with the Canadian Environmental Law Association. We will collaborate with GLC to develop exposure and risk assessment programs on PBDEs.

## **7. Other Funding Sources:**

Matching funds will include faculty salary during the school year and equipment (computers and software) costs to be provided by the University of Illinois at Chicago. Laboratory management funds (up to \$15,000 per year) are available from the UIC School of Public Health. This fund can be used for analytical instrument maintenance if necessary.

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