

CURRENT DEPOSITION AND HISTORICAL PROFILES OF DECABROMODIPHENYL ETHER IN SEDIMENT CORES

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Introduction

The determination of historical profiles and concentrations of pollutants in dated sediment cores has provided valuable information on sources, time trends and current inputs of many persistent organic pollutants (POPs) including polyaromatic hydrocarbons^{1,2}, PCBs^{3,4}, toxaphene⁵ and chlorinated dioxins/furans^{6,7}. Results from a north-south mid-continental transect of Canadian lakes showed declining deposition rates of POPs in surficial sediments with increasing north latitude^{8,9}. For PCBs and Σ DDT, the declining rates with latitude parallel the decline in average annual air concentrations measured at several mid-latitude sites and Arctic locations in the mid-1990's¹⁰. Taken together, these results suggest that lake sediment cores can provide data on atmospherically derived inputs of hydrophobic POPs to lakes and terrestrial surfaces over a range of temperature and geological conditions.

Polybrominated diphenyl ethers (PBDEs) have been shown to be increasing in herring gull eggs and lake trout in the Great Lakes^{11,12} and in the Arctic ringed seals¹³. The source of PBDEs to the Arctic environment is presumably via long range transport from urban areas in North America which is the major use area for PBDEs globally¹⁴. However, the spatial extent of PBDE contamination is not known. Our objective was to examine the fluxes and geographical extent of PBDEs along a latitudinal and a longitudinal gradient and to compare this with known priority POPs and heavy metals (e.g. lead) in the same samples. We were particularly interested in the determination of decabromodiphenyl ether (BDE 209), because it is the most widely used PBDE mixture, is extremely hydrophobic, has low vapor pressure¹⁵ and octanol-air partition coefficient and therefore is likely to be transported on particles¹⁶. Thus it provided an interesting contrast to more volatile, gas phase contaminants such as PCBs

Materials and Methods

Sediment collection: We selected lakes along a north-south transect from southern Ontario and upper New York state to Ellesmere Island. Except for Lake Ontario, all lakes were uninhabited or had a history of very limited human disturbance. Sediment cores from remote lakes were collected through holes drilled into the ice or from a small boat between August 1998 and May 2001. A core was collected in western Lake Ontario core (station 1007, 43°26'01"N; 79°24'00"W) from the CCGS Limnos in June 1998 using a box corer. Cores were extruded on site and slices placed in plastic "WhirlPak" polyethylene (PE) bags or glass "ointment" jars with aluminium foil lined caps. PE bags were used for cores collected in 1998-2000 and glass jars for all other cores. The cores were sliced to achieve maximum temporal resolution while obtaining sufficient mass for ²¹⁰Pb dating and contaminant analysis. All cores from the Arctic were collected with a 6.5 cm diameter corer and sliced at 0.5 cm intervals while most of cores from south of 55°N were

collected with the 10 cm KB core and sliced at 1 cm intervals. Sediments were maintained in a cool dark storage site during the field work and then shipped by air freight to the laboratory where they were stored in the dark at 4°C. Sediment slices were dated using ^{210}Pb and ^{137}Cs and sedimentation rates and dates were estimated using CRS and CIC models¹⁷.

Analysis of sediment samples: Sub-samples from cores with interpretable ^{210}Pb profiles were analysed for a suite of halogenated organics following methods of Muir et al.^{8,9} with minor modifications to allow for isolation of PBDEs. Sub-samples of some cores were also analysed for mercury and lead. All sediment sample extraction and cleanup steps were conducted in a certified clean room at NWRI (positively pressured, HEPA/carbon filtered air) to limit contamination. In brief: Wet sediments were centrifuged to remove excess water. Moisture content was determined on a subsample prior to centrifugation. The wet sediment was mixed with a drying agent and extracted on an accelerated solvent extractor (ASE) or in a Soxhlet apparatus using dichloromethane (DCM). PCB 30 and octachloronaphthalene (OCN) were added to all sediments prior to extraction and used as internal standards. Combined DCM extracts were mixed with mercury to remove sulfur. Extracts were then chromatographed on an activated silica column. PCBs and p,p'-DDE were eluted with hexane while PBDEs were eluted with (1:1) hexane:DCM. Extracts were then carefully reduced in volume and taken up in isooctane for gas chromatographic analysis.

PBDEs were determined by GC-high resolution MS¹⁸ using an Micromass Instruments Autospec Ultima. The GC injection port was configured for a 1 mL volume on-column injection, with an initial temperature of 160°C, held for 1 min, and ramped at 100°C/min to 280°C for 55 min. Gas chromatographic separation prior to MS was achieved using a 60 m x 0.25 mm x 0.25 mm Restek Rtx5 capillary column. Sample ionization was performed in electron ionization (EI) mode at an electron voltage ranging between 35 to 40 eV depending on the optimization parameters of the instrument. The source temperature was 270°C and the resolving power of the analyzer was 10 000.

Results and Discussion

Tetrabromo- to decabromo BDEs were detectable in recent sediments from all lakes investigated in Ontario and Québec and in northern New York State, but were near or at detection limits in cores collected north of 55°N (Table 1). However, blanks for BDE congeners 47 and 99 were

Table 1. Sediment core locations, sedimentation rates and concentrations of BDE209

Location	Lake	Date	Latitude	Longitude	Sedimentation $\text{g m}^{-2} \text{yr}^{-1}$	BDE 209 (pg/g dw)
Nunavut (Arctic)	AX-AJ	1998	80°00'N	87°00'W	110	75
Nunavut (Arctic)	Romulus	2000	79°54'N	85°06'W	780	<100
Nunavut (Arctic)	Char	1997	74°40'N	94°50'W	100	42
Northern Québec	B2-1	2000	57°45'N	76°10'W	150	<100
Western Québec	Dasserat	2000	48°16'N	79°26'W	120	561
Eastern Ontario	Opeongo	1998	45°22'N	78°22'W	120	8180
Upper NY State	Connery Pond	2001	44°20'N	73°45'W	150	1147
Ontario/NY State	Lake Ontario	1998	43°26'N	79°24'W	500	112,000

significant in cores collected and stored in plastic bags and thus we have concluded that results for those congeners need further study. These bags were rinsed with DCM and found to contain nanogram amounts of BDE 47 and 99. Although this level of contamination is low it could have contributed to the PBDE levels in the samples. Fewer blank problems were encountered with sediment stored in glass jars.

In contrast to the lower brominated PBDEs, there were essentially no blank problems with deca- and nonabromo congeners. The depositional fluxes of BDE 209 were determined in 8 cores are shown in Figure 1. BDE 209 was not detected in sediments from two of the lakes. BDE 209 was detected only in recent slices of all cores including Lake Ontario which, unlike the other lakes,

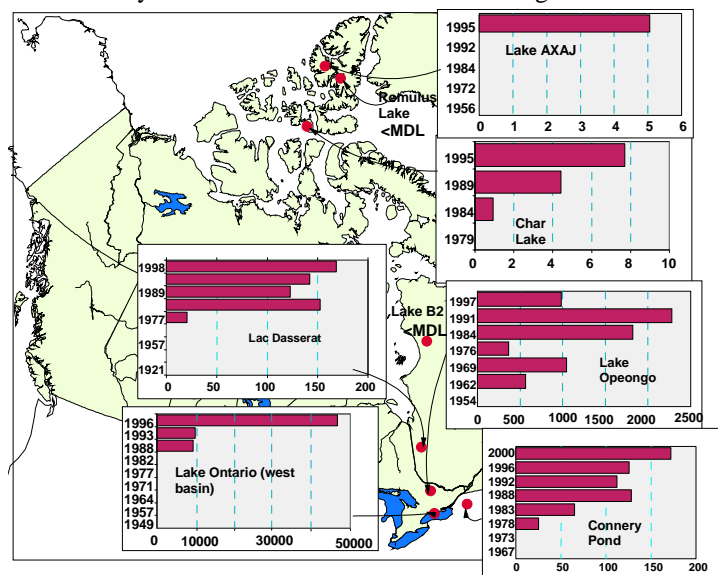


Figure 1. Profiles of BDE 209 in dated lake sediment cores.

likely receives direct inputs of BDE 209 from municipal waste treatment effluents and other urban sources. Lake Opeongo is located in Algonquin Park while Connery Pond is in Adirondack Park and both would likely have received BDE 209 inputs only from atmospheric deposition although inputs from use of boats and other equipment on the lake cannot be ruled out. BDE 209 was found in deeper slices in Opeongo than in the other lakes. The reason for this is unclear – there may be much more bioturbation in this core than in the others. BDE 209 is highly sorbed to particles and thus susceptible to particle mixing.

The three high Arctic lakes have much lower fluxes consistent with their remote locations. However, Char Lake is located near the Resolute airport and inputs of PBDEs cannot be ruled out entirely. AX-AJ, on the other hand is completely isolated and was visited only for sediment core sampling. Romulus Lake had a very high sedimentation rate compared to the other Arctic lakes (Table 1) which may explain the non-detectable levels of PBDEs in this core.

BDE 209 fluxes differ by 125-fold between Opeongo and Char Lake and 34-fold between Connery Pond and Lake AX-AJ. This is a larger difference than seen for Σ DDT and Σ PCB in the same cores where the difference was 29-fold and 5-fold, respectively¹⁹. The difference is consistent with the much lower mobility of BDE 209 that would be predicted from its physical

properties. Wania and Dugani¹⁶ have predicted a CTD of 480 km for BDE 209 compared to 1113 km for BDE 47 and 2843 km for PCB153. BDE 209 has very low vapor pressure and is anticipated to be mainly particle sorbed in the atmosphere^{15,16}. Thus the rapid apparent decline is entirely consistent with its transport mainly on particles.

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