

Detection of Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) in Abiotic Samples from Southern Ontario, Canada

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Introduction

Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) are of great interest environmentally because of their potential thyroidogenic effects. OH-PBDEs can compete with thyroxine for binding sites on transthyretin¹, one of the three main thyroid hormone transport proteins in mammals. OH-PBDEs are being identified in the tissues, mainly blood, of humans and aquatic wildlife species²⁻⁴. OH-PBDEs in wildlife can be metabolically derived in an organism from bioaccumulated precursor PBDEs, and/or possibly from anthropogenic and natural sources⁵. It has been suggested that OH-PBDEs could also exist in the abiotic environment, and there is currently only one known report of OH-PBDEs in an abiotic compartments. Hua et al. (2005)⁶ reported two unidentified tribromo-OH-PBDE congeners in surface waters and wastewater treatment plant effluent from the Detroit River.

There are 837 possible mono-OH-PBDE congeners compared to 209 PBDE congeners, but only 18 OH-PBDEs standards are currently available. Identification of specific OH-PBDEs in environmental samples is challenging. Thus we have found Gas chromatography high resolution mass spectrometry (GC-HRMS) provides a clearer and more complete characterization of all OH-PBDE homolog groups and congeners. Accordingly, this study describes our attempts to detect OH-PBDEs in the abiotic environment such as water, rain, snow samples collected from several regions of southern Ontario, Canada.

Materials and Methods

Precipitation samples were collected monthly at 3 locations, using an automated wet only collector, in southern Ontario (Canada) from April to June 2004. Precipitation was extracted directly onto a XAD2 resin column. Large volume water samples (~100L) were collected from various sites in southern Ontario, including the Detroit River, Hamilton Harbour, and Toronto Harbour near the Ashbridges Bay municipal waste treatment plant with a Westfalia Field Centrifuge System. Large volume snow samples (1-2 m³) were collected at various locations across southern Ontario in February 2002 using pre-cleaned aluminum boxes. Snow meltwater and centrifuged lake waters were pumped through XAD2 resin. Water samples from Hamilton Harbour were collected directly by pumping through 0.7 µm glass fiber filter into an XAD2 column.

Extraction and Cleanup of OH-PBDEs and PBDEs was based on a method previously reported³. The internal standards were spiked onto XAD2, and eluted with methanol and dichloromethane. Elution was washed with NaCl solution, and the pH was raised using KOH solution to force the OH-PBDEs into an aqueous fraction (phenolic fraction), and the PBDEs into the organic fraction (neutral fraction). Concentrated sulfuric acid was added to the phenolic fraction, and this solution was then extracted with MTBE:hexane. This extract was derivatized using diazomethane. The derivatized fraction containing methoxylated PBDEs (MeO-PBDEs) was cleaned up using an acidified silica gel column. The neutral fraction contained PBDEs was also cleaned using an acidified silica gel, and then put through a non-acidified silica gel column for separation. The ¹³C-BDE138 was added to final solution as performance standard.

GC-HRMS in electron ionization (EI) mode was selected for quantification of the MeO-PBDE derivatives. GC-HRMS was carried out on a Micromass Ultima HRMS in selected ion mode (SIM) at mass resolution of 10,000, following separation on a Agilent 6890 GC using a 60 m DB5-MS column. These compounds were quantified by an isotope dilution method. The higher selectivity of the HRMS (10,000 mass resolution) allows unknown peaks to be labelled as MeO-PBDEs.

Results and Discussion

OH-PBDEs were detected in almost all the samples analyzed (rain, snow and water samples). The presence of these compounds in

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various environmental water compartments from areas of the Great Lakes indicates that OH-PBDEs are biotically and/or abiotically derived and released into the environment. The representative GC-HRMS chromatograms of OH-PBDEs (derivatized to MeO-PBDEs) detected in water and rain samples are illustrated in Figure 1. These samples contained di- to pentabromo-OH-PBDEs, most of which could not be structurally identified with the standards available. The 11 congeners could be identified using the 18

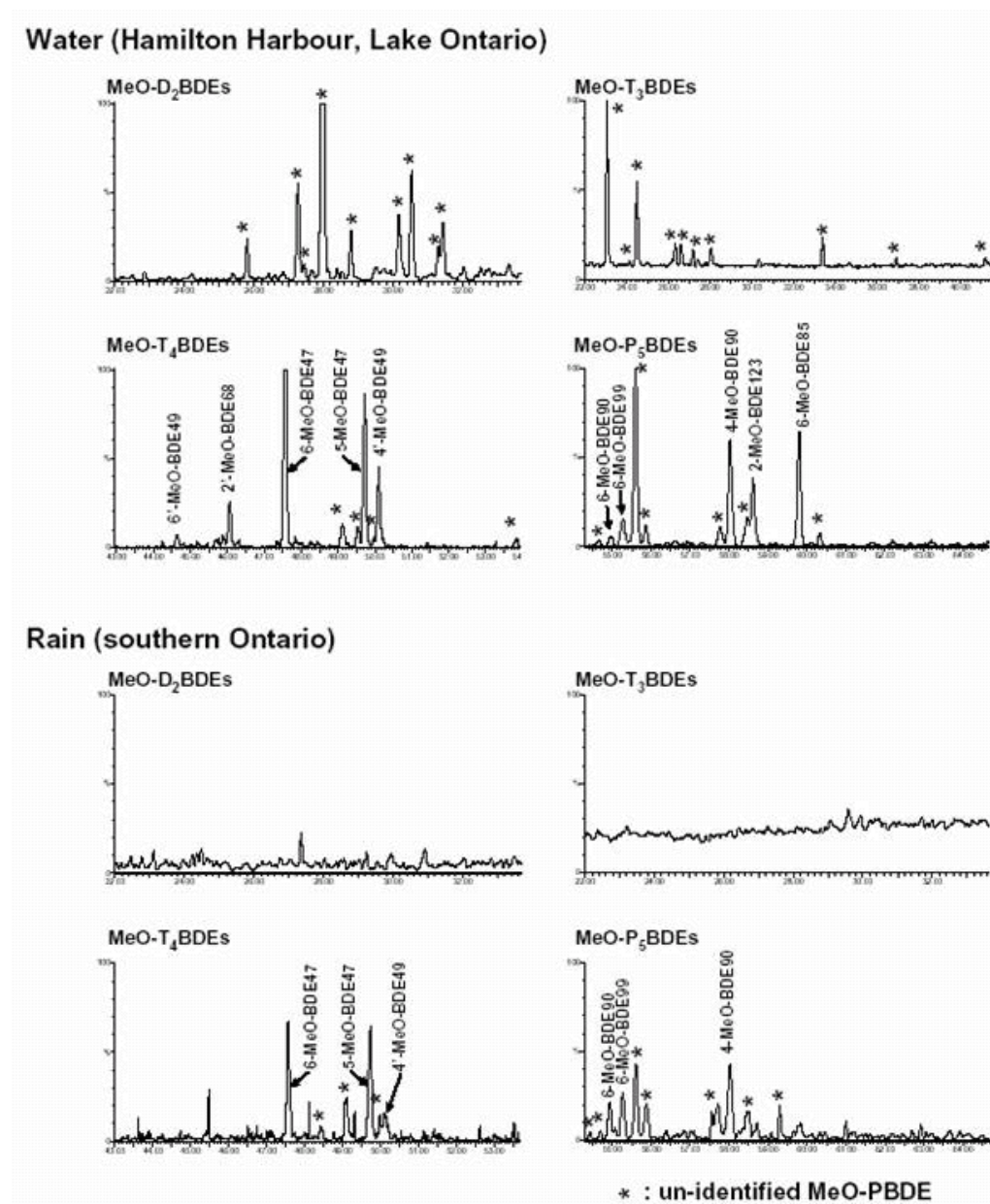


Figure 1. GC-HRMS (EI, 10,000 mass resolution) combined selected ion chromatograms of OH-PBDEs (derivatized to MeO-PBDEs) in surface water and rain from southern Ontario, Canada. Un-identified peaks were confirmed using isotopic ratio.

available congeners of MeO-PBDEs standards available which ranged from di- to hexabromo-substitution, while as many as 42 congeners were detected but not identifiable (Figure 1). Blanks contained small amounts of un-identified MeO-PBDEs (di- to hexabromo).

In general, a larger number of OH-PBDE peaks were detected in surface water samples than rain and

snow samples from several southern Ontario locations (Figure 1). A similar trend was also found in OH-PCBs⁷, but the ratio of OH-PBDEs in surface waters to rain was higher than observed for OH-PCBs. PBDEs, which are the precursor compounds of OH-PBDEs, have lower vapor pressures than PCBs and are much less prominent in air in the Great Lakes basin⁸. In addition, surface water samples from Toronto harbour and Hamilton harbour near municipal waste treatment outfalls showed much larger number of OH-PBDE peaks than other samples, and it is consistent with a recent finding of OH-PBDEs in wastewater treatment plant effluent from the Detroit River⁶. OH-PBDEs could be formed from microbial oxidation of PBDEs entering the plants or from reactions with OH radical if ozone is used to treat the final effluent. This could possibly be a significant source of OH-PBDEs to the aquatic environment.

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