

Brominated and Mixed Halogenated Dioxin and Furan Profiles in a Radiometrically-dated Fresh Water Sediment Core from the United Kingdom

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1. Introduction:

Dioxins and furans are classes of toxic, persistent environmental contaminants. These compounds, despite never being deliberately synthesized in any great quantity are present in detectable concentrations in almost every environmental matrix. Their ubiquity, persistence and toxicity have warranted their listing as Persistent Organic Pollutants (POPs) under the Stockholm Convention. Brominated and mixed halogenated dioxins and furans (PBDD/Fs and PXDD/Fs), unlike their comparatively well studied chlorinated analogues have received minimal scientific attention. Despite having comparable physico-chemical and toxicological properties neither PBDD/Fs or PXDD/Fs are listed as POPs. The lack of available scientific data pertaining to these contaminants is due principally to the almost prohibitive expense and analytical difficulty of their analysis. Isobaric interferences with PBDEs, PCBs and PBBs (among others) require extensive clean-up procedures, analysis exclusively by high resolution mass spectrometry, judicious selection of quantification ions and meticulous data interpretation (Fernandes *et al.* 2011). Also, only recently have ¹³C labelled PBDD/Fs and PXDD/Fs internal standards become commercially available.

Hypotheses concerning the sources of these compounds in the environment centre on their formation by high temperature thermolysis in the presence of PBDEs or other potential halogenated phenolic precursors like TBBP-A (D'Silva *et al.* 2004). As such, congener profiles of 'pre-cursor' PBDEs contrasted and compared with those of PBDD/Fs and PXDD/Fs may provide insights into the formation of the latter compounds.

Accordingly, the aims of this study were to: 1. Establish and validate PBDD/F and PXDD/F extraction, clean-up and chemical analysis procedures using a novel high resolution mass analyzer, the Thermo Scientific Q Exactive GC Orbitrap GC-MS system. 2. To elucidate temporal trends in brominated and mixed halogenated dioxin and furan congener profiles in a radiometrically dated fresh water sediment core; and 3. To contrast these profiles against those previously established for PBDEs in the same lake.

2. Materials and Methods

2.1 Sampling and Radiometric dating

Sediment core samples were taken from Edgbaston Pool, a fresh water lake located in the city of Birmingham, UK. This shallow lake has been previously investigated for the presence of PBDEs, PCBs and other BFRs (Yang *et al.* 2016). A single core sample was collected in August 2015 to a depth of 1 m from un-vegetated lake bed towards the centre of the water body. The sediment core was sliced into separate 10 mm sections for radiometric dating, physical and chemical analysis. Physical assessment including TOC was conducted and a ²¹⁰Pb based chronology established with respect to depth and calculated sedimentation rate at the Environmental Radiometric Facility UCL, UK.

2.2 Sample Preparation and Clean-up

Extraction of sediments was conducted on 3 g (dry wt) freeze dried sediment taken from core slices ranging in depth from the surface (0-1 cm) to 49-50 cm depth. Prior to extraction, sediments were spiked with known concentrations of 11 $^{13}\text{C}_{12}$ labeled internal standards (CIL- EDF-5408; Cambridge Isotope Laboratories, www.isotope.com) before Accelerated Solvent Extraction (ASE, Thermo Fisher Scientific, Dreieich, Germany). Extracts were subsequently treated with copper for sulfur removal and a tandem acid silica-carbon column for the removal of lipid and non-planar interfering compounds respectively (Cape-Tech, Maine, USA). Extracts were then reduced to dryness and reconstituted in syringe standards (5 μL) for analysis.

2.3 Chemical Analysis

Post clean-up, planar fraction extracts were analysed for the presence of PBDD/Fs and PXDD/Fs on the Thermo Scientific Q Exactive GC Orbitrap GC-MS. Sample aliquots (2 μL) were introduced to the column via a PTV injector operating in splitless mode. A programmed temperature profile from 150 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ at 14.5 $^{\circ}\text{C}/\text{sec}$ was employed to ensure minimal degradation of thermally liable, higher brominated congeners. Separation was conducted on a Thermo Fisher Scientific Trace Gold Dioxin capillary column (12 m x 0.25 mm x 0.1 μm) with a constant He flow of 1.3 mL/min and an initial temperature of 120 $^{\circ}\text{C}$ held for 3 min before ramping to 250 $^{\circ}\text{C}$ at 6.5 $^{\circ}\text{C}/\text{min}$. A second ramp from 250 $^{\circ}\text{C}$ to 305 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$ held for 7 min was used to ensure elution of all target compounds.

Analysis was performed in positive polarity full scan mode scanning from 150 m/z to 900 m/z before switching to full scan 400 m/z to 900 m/z at RT = 26.5 min to reduce ion suppression of low abundance, higher brominated target species eluting towards the end of the analysis time. All injections were carried out at a resolution of 60000 FWHM with 2 Microscans, a $1\text{e}6$ AGC target with an auto ion injection time, 70 eV (50 μA) electron ionization energy and a source temperature of 280 $^{\circ}\text{C}$.

PXDD/Fs were semi-quantitatively analysed against a 7 point external calibration (0.05 pg – 25 pg) due to the lack of suitable internal standards. Linear correlations for individual congeners yielded R^2 values > 0.999 in all cases except for 2-Br-6,7,8-CDF and 3-Br-2,7,8-CDF for which $R^2 = 0.998$. Peak quantification was performed using the Thermo Fisher Scientific Target Quan (v3) quantification software. Peak quantification was conducted at ± 10 ppm mass deviation from the accurate (5 decimal) masses of the most abundant ion fragment peaks of respective target compounds and confirmed with ratio ion abundance within a 10% deviation from the theoretical.

3 Results and Discussion

In total 11 samples were extracted and purified consisting of core slices ranging in depth from the surface (0-1 cm; dated to 2015) to 49-50 cm depth (dated to 1935). All were analyzed for PBDD/Fs, with 5 for PXDD/Fs. PXDD/F analysis was conducted on sediments corresponding to the following dates: 2012, 2009, 2004, 1999 and 1935. In addition, a procedural blank (where sodium sulfate replaced the sediment sample) was analysed for both PBDD/Fs and PXDD/Fs.

3.1 PBDD/Fs

Sediments were analysed for a total of 14 different congeners (Figure 1) Concentrations ranged from below the sample detection limit (0.05 - 10 pg g^{-1} OC) to 16.04 pg g^{-1} OC for 1,2,3,4,6,7,8 HpBDF obtained from the sample 2004 (14.0 – 15.0 cm depth). Congener profiles (Figure 1) show a strong dominance of furans with virtually no dioxins detected throughout all depths. The furan profile showed a strong association with bromination order with concentrations by the following order HpBDF > HxBDF > PeBDF > TBDF > OBDF for those congeners determined. OBDF was least prevalent, due possibly to its high detection limit (5 pg g^{-1} OC). This profile is in contrast with others found in the literature; for example marine sediments in Osaka Bay, Japan, where PeBDD was the dominant congener observed (Ohta *et al.* 2002) and in flue gas emissions which typically show higher concentrations of lower brominated species (D'Silva *et al.* 2004 and Fernandes *et al.* 2008).

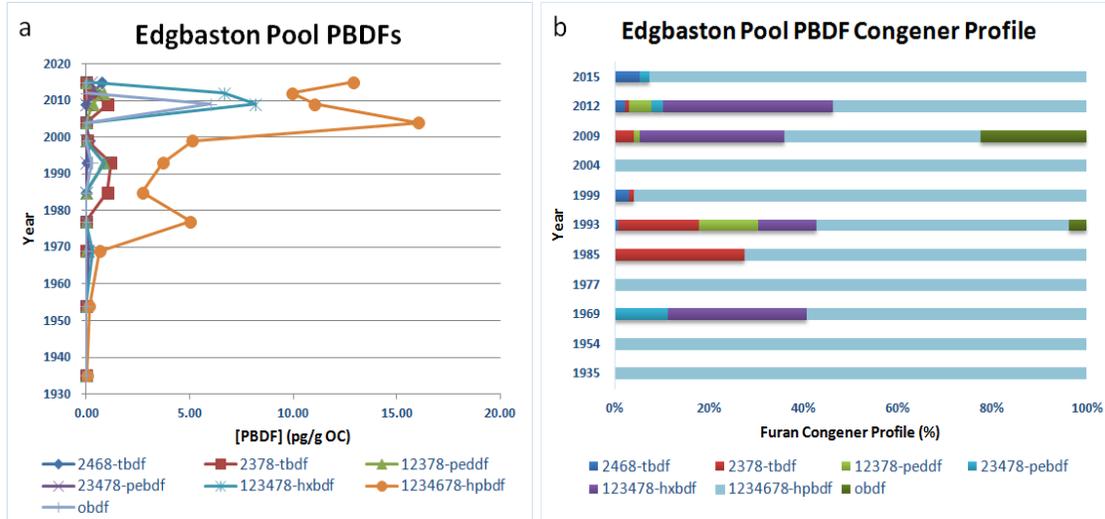


Figure 1(a). Edgbaston Pool sediment PBDF congener concentrations by year and (b) congener relative contribution profiles.

3.2 PXDD/Fs

Sediment slices (n=5) were analysed for a range of mixed halogenated dioxins and furans (Figure 2). Sum concentrations ranged from the lowest limit of detection (0.05 pg g⁻¹ OC) for Σ 2-Br-3,7,8-CDDs to 5.56 pg g⁻¹ OC for Σ 2,3-Br-7,8-CDDs recorded in the 2004 sample, which was removed from figure 2 for scaling purposes. Sample congener composition was dominated by dioxin congeners (Figure 2) which is in contrast to previous results obtained in other studies of food items (Fernandes *et. al.* 2011) and from combustion sources (Söderström *et. al.* 2004). Most notably, the bromo-chloro species 2,3-Br-7,8-CDD was detected in all samples analysed with the exception of one, that pertaining to the year 2012.

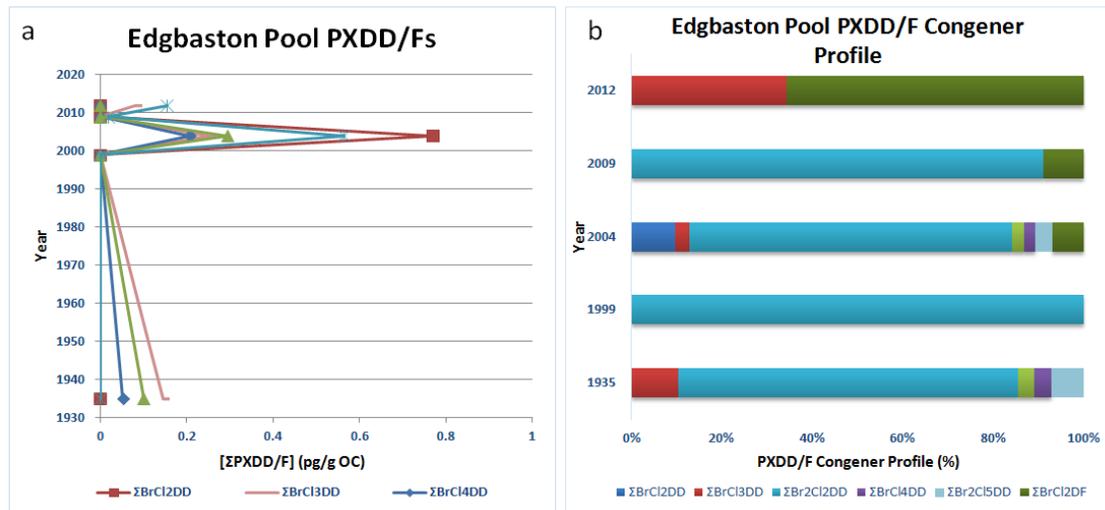


Figure 2(a). Edgbaston Pool sediment PXDD/F congener concentrations by year and (b) congener relative contribution profiles.

3.3 PBDEs

Previously reported PBDE concentrations in a separate dated sediment core from Edgbaston Pool (Yang *et. al.* 2016) are shown in Figure 3. Concentrations of PBDEs show a distinct overall increasing concentration trend post-1970 that is not inconsistent with a similar temporal trend for the PBDD/Fs.

Sediment cores from other UK freshwater lakes are currently being analysed and will shed further light on the existence of any relationship between PBDE and PBDD/F concentration trends. PXDD/Fs showed no systematic relationship when compared to the PBDE temporal profile.

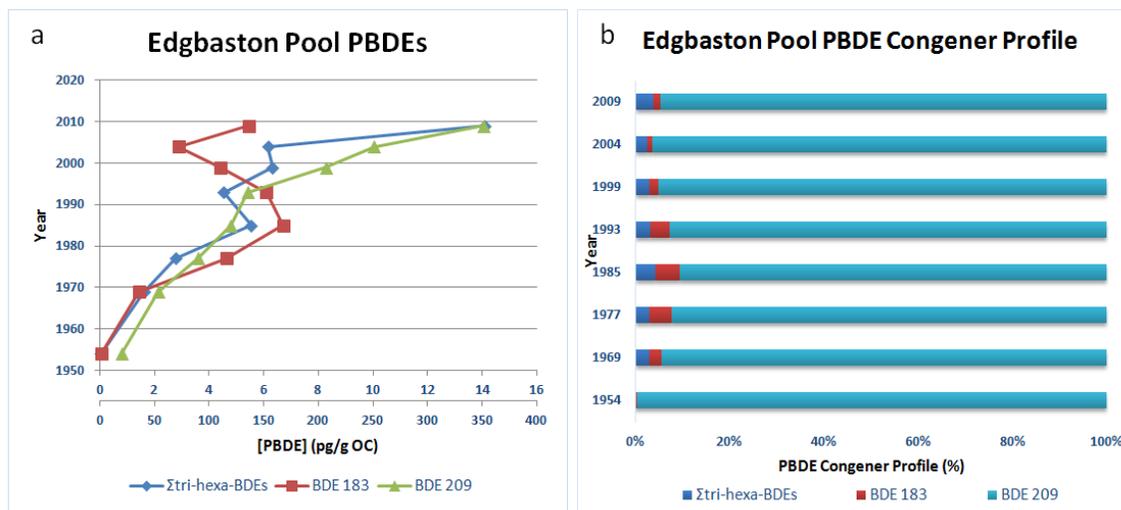


Figure 3(a). Edgbaston Pool sediment PBDE congener concentrations by year, secondary x-axis refers to BDE-209 only. And (b) congener relative contribution profiles. Data adapted from Yang *et. al.* 2016.

4 Conclusions

This study provides the most comprehensive data to date for PBDD/Fs and PXDD/Fs in freshwater sediments. Novel clean up and analysis procedures utilising the Thermo Scientific Q Exactive GC Orbitrap GC-MS instrumentation have been developed. The authors believe this to be the first reported data for these compound groups utilizing this analysis platform. The congener profiles observed in our samples for PBDD/Fs and PXDD/Fs differed substantially from those previously described for other matrices. The post-1970 increasing trend previously reported for PBDEs in our study lake is broadly replicated for the PBDD/Fs, but analysis of sediment cores from other lakes is needed to confirm whether such behavior is replicated elsewhere. PXDD/Fs trends showed no systematic correlation to the PBDE profiles reported.

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