

IDENTIFICATION OF A NOVEL BROMINATED FLAME RETARDANT IN DUST

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Introduction

In 2006, a fate study on selected brominated flame retardants (BFR) was conducted under outdoor conditions in the Artificial Stream and Pond System (FSA) of the Federal Environment Agency. Decabromodiphenyl ether (BDE-209) and 1,2-bis(pentabromophenyl)ethane (DBDPE) were dosed once resulting in an initial concentration of approximately 100 ng/L in two ponds and one stream mesocosm^{1,2}. One pond and one stream mesocosm served as control systems. BDE-209 and DBDPE were analysed in water samples over a period of 52 days and quantified by use of short column GC/ECNI-MS. On day five a massive increase of the water concentrations was observed for BDE-209 and DBDPE, exceeding the starting concentration by a factor of more than five. This phenomenon was also observed in the controls. As analytical errors and faults in sampling and sample preparation could be excluded, it was suspected that the enormous increase in concentrations was due to atmospheric deposition after heavy rainfall. This incident prompted the present study focusing on the identification and quantification of brominated flame retardants (BFRs) in dust collected close to the FSA. Here we report on the identification of tetrabromobisphenol-A-bis-(2,3-dibromopropylether) (TBBPA-DBPE), a BFR, which to our knowledge has only once be suspected to be present in environmental samples³. Moreover, concentrations of 19 BDE congeners, and several non-BDE based BFRs are given.

Materials and Methods

Dust Sample Extraction and Cleanup

The dust sample was manually collected from a metal surface close to the pond system. It was dried, the total amount of 0.71g was spiked with internal standards (IS) (Table 1) and extracted with toluene at 14 MPa and 125°C by using an ASE 200 accelerated solvent extractor (DIONEX GmbH, Idstein, Germany). Sulfur was removed using copper granules placed in the ASE extraction cell together with the sample. The obtained extract was cleaned-up by gel permeation chromatography and multi-layer column chromatography (silica gel, and acid-impregnated silica gel).

Gas Chromatography/Mass Spectrometry (GC/MS)

Quantification of BFRs was performed by capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC/ECNI-MS) in the selected ion monitoring mode (SIM) under the following conditions: GC 6890+/MSD 5973 (AGILENT, Palo Alto, CA, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Switzerland) and PTV injector CIS 4 plus (GERSTEL, Muelheim/Ruhr, Germany); splitless injection with an initial temperature of 125°C and programmed with 12°C/sec to a final injector temperature of 325°C. Used capillary columns from (RESTEK, Bellefonte, PA, USA): a) 20 m RTX-CLPI[®] column with (0.18 mm ID, df = 0.18 µm), b) 5 m RTX-CLP[®] column with (0.1 mm ID, df = 0.1 µm). Further GC/MS conditions: a) column flow of 0.9 ml/min; GC temperature program: 80°C (hold 2 min) – 25°C/min to 200°C – 10°C/min to 300°C (hold 30 min) b) column flow of 1.2 ml/min; GC temperature program: 80°C (hold 2 min) – 16°C/min to 300°C (hold 10 min). Injection volume for both columns: 1 µl; carrier gas: helium; CI ion source; reagent gas: methane; ion source temperatures: 200 °C (ECNI), 230 °C (EI). Full scan ECNI and electron ionisation (EI) mass spectra were recorded in the mass range of 50 to 800 amu. BFRs elute from column a) between 10 and 45 minutes and from column b) between 4 and 16 minutes. The most prominent ions (Table 1) were recorded in SIM mode. Fluorinated BDEs (F-BDE-28, FF-BDE-47, F-BDE-100, FF-BDE-201 and F-BDE-208), and ¹³C-labelled BDE-209 were used as internal standards. Standards were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, U.S.A.), CHIRON (Trondheim, Norway) and Wellington Laboratories Inc. (Guelph, Ontario, Canada.).

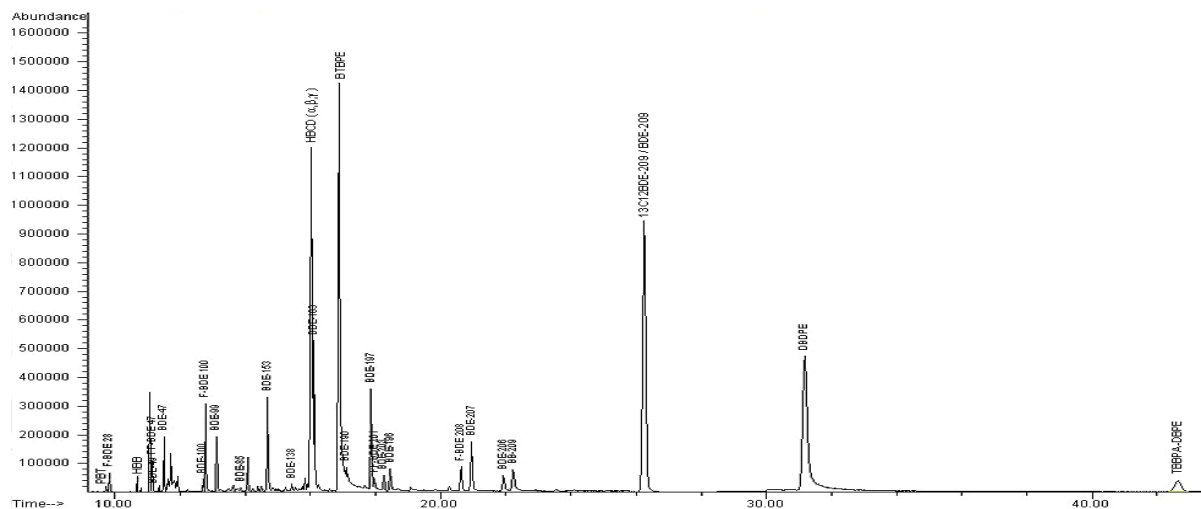


Figure 1: Total ion chromatogram of the dust sample taken close to an artificial pond of the FSA. Column: RESTEK 20 m RTX-CLP I[®] with (0.18 mm ID, df = 0.18 μ m); ECNI-MS (SIM)

Results and Discussion

Identification of Tetrabromobisphenol-A-bis-(2,3-dibromopropylether)

A total of 16 BDE congeners, six non-BDE based BFRs and an unknown compound eluting after DBDPE from the GC column were detected in the studied dust sample. The unknown peak was identified as TBBPA-DBPE by comparing its retention time with that of a pure standard analysed under identical GC conditions and ECNI and EI mass spectrometry. When analysing the dust extract by short column GC/ECNI-MS in the full scan mode a complete mass spectrum could be recorded, this was in line with ECNI mass spectrum of the TBBPA-DBPE standard. Due to the preferential cleavage of bromine under ECNI conditions m/z 79/81 and m/z 160 were the ion clusters with the highest abundances, but diagnostic fragments in the mass range 250 to 800 amu were also observed (Fig.2). These fragments indicate successive loss of bromine, cleavage of the ether bond, which results in the loss of the dibromopropyl group and cleavage of the C-C between the aromatic ring and the tertiary carbon of the TBBPA under formation of the 2,6-dibromo-4-isopropyliden-phenyloxonium-ion at m/z 292. The molecular mass of TBBPA-DBPE of 936 exceeds the mass range of the mass spectrometer and could thus not be seen in the spectrum. The obtained ECNI mass spectrum showed some differences compared to that obtained by Karlsson³ who suspected the presence of TBBPA-DBPE in a dust sample collected in Sweden. This may be explained by the strong dependency of ECNI mass spectra on experimental conditions (e.g. ion source temperature) and the type of instrument used⁴. The EI full scan mass spectrum of a standard solution is shown in Figure 3. The mass spectrum is quite complex and resembles that reported by Köppen et al.⁵ who analysed TBBPA-DBPE by atmospheric pressure chemical ionisation (APCI) mass spectrometry. Major fragments in the EI-spectrum result from successive loss of bromine, cleavage of the ether bond, and loss of a methyl group from the tertiary carbon atom of the TBBPA moiety. Recording of a full scan spectrum of the suspected TBBPA-DBPE in the dust sample was not possible due to the low concentration present. Hence, the most prominent masses identified in the EI mass spectrum of the standard were recorded in the SIM mode after GC analysis of the dust extract on a 5 m capillary column. The resulting mass chromatograms showed small peaks at the expected retention time, which could be clearly discriminated from noise. To summarise, the obtained chromatographic and mass spectrometric information provides sufficient evidence to attribute the unknown peak to TBBPA-DBPE. There is only one report on the suspected occurrence of TBBPA-TBPE in a dust sample from Sweden³, however, no concentration was given. An attempt to detect this compound in river sediment and sewage sludge samples from Germany using high-performance liquid chromatography and diode array detection failed⁵. TBBPA-DBPE is manufactured e.g. by Great Lakes Chemical Corporation and Albemarle Corporation and is marketed under the trade names PE-68 and Saytex HP-800 AGC, respectively. It is used as additive BFR in polypropylene and high impact polystyrene resins⁶. The extent of application in Western Europe in 1998 was estimated to 1500 metric tons⁶.

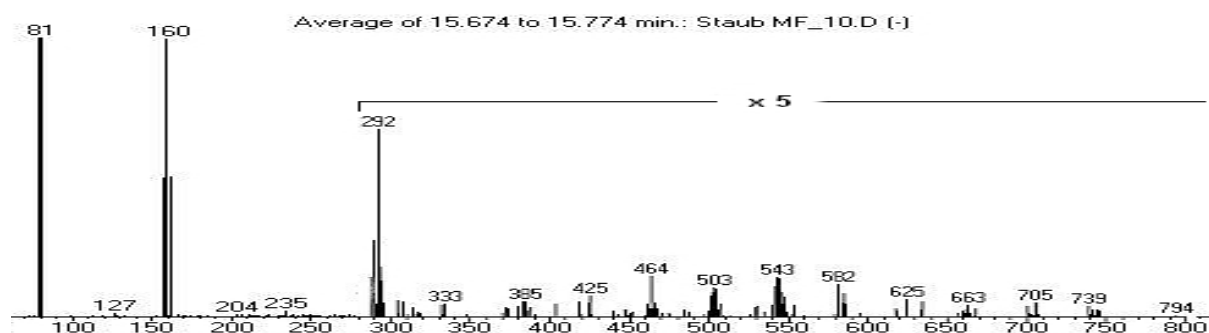


Figure 2: Full scan ECNI mass spectrum of the suspected TBBPA-DBPE peak in the dust extract

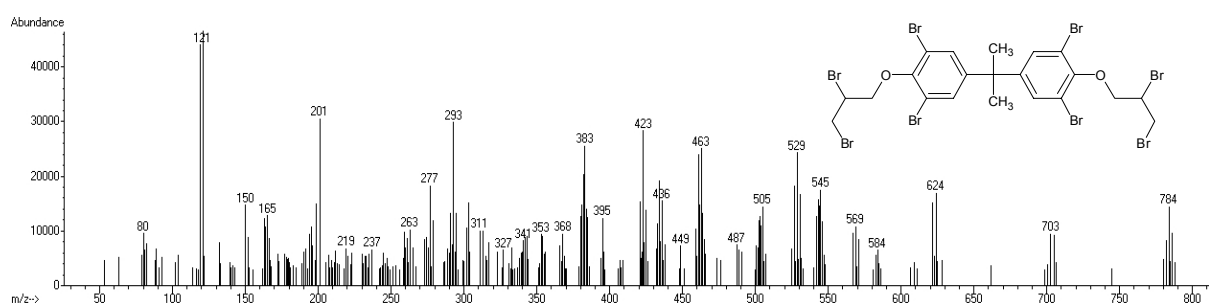


Figure 3: Full scan EI mass spectrum of TBBPA-DBPE standard, 200 ng/μl in toluene

BFR content and composition

The non-BDE based BFRs hexabromocyclododecane (HBCD), 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), DBDPE and TBBPA-DBPE constituted the major components found in the dust sample. Moreover, decabromodiphenyl (BB-209), pentabromotoluene (PBT), and hexabromobenzene (HBB) were detected at low concentrations. In total, these brominated flame retardants contributed approximately 77% (3,550 ng/g dw) to the total BFR content. The sum of tri- to decabrominated BDEs was 1,080 ng/g dw of which 68% could be attributed to BDE-209. The predominance of non-BDE based BFRs in the examined dust sample indicates that other BFRs play an increasing role as substitutes for technical PBDE formulations in different polymers. HBCD, DBDPE and BTBPE are known to be potential replacement products of decaBDE and octaBDE, respectively, and should therefore be included in future monitoring programmes.

Acknowledgements

We gratefully acknowledge Brian Yeo, Wellington Laboratories Inc., for the kind gift of a small amount of crystalline TBBPA-DBPE and Lydia Windmüller for her valuable technical assistance with sample analysis.

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Table 1: Concentration of BFRs in a dust sample collected close to an artificial pond of the FSA, LOQ = limit of quantification

BFR Compound	Target mass m/z	Qualifier mass m/z	Related internal standards (target mass)	Conc. [ng/g dw]	LOQ [ng/g dw]
BDE-17	79	81, 161	F-BDE-28 (79)	<LOQ	0.01
BDE-28	79	81, 161	F-BDE-28 (79)	<LOQ	0.03
BDE-47	79	81, 161	FF-BDE-47 (79)	25.4	0.03
BDE-49	79	81, 161	FF-BDE-47 (79)	0.40	0.07
BDE-66	79	81, 161	FF-BDE-47 (79)	<LOQ	0.07
BDE-77	79	81	FF-BDE-47 (79)	0.06	0.03
BDE-85	79	81, 161	F-BDE-100 (79)	0.10	0.02
BDE-99	79	81, 161	F-BDE-100 (79)	19.3	0.04
BDE-100	79	81, 161	F-BDE-100 (79)	3.31	0.01
BDE-138	79	81, 161	F-BDE-100 (79)	2.83	0.02
BDE-153	79	81, 161	F-BDE-100 (79)	50.0	0.03
BDE-154	79	81, 161	F-BDE-100 (79)	12.0	0.03
BDE-183	79	81, 161	FF-BDE-201 (426.6)	116	0.11
BDE-196	79	81, 408.6	FF-BDE-201 (426.6)	27.6	0.18
BDE-197	408.6	79, 81	FF-BDE-201 (426.6)	50.0	0.02
BDE-203	79	81, 161	FF-BDE-201 (426.6)	17.9	0.08
BDE-206	79	81, 486.5	F-BDE-208 (486.6)	11.4	0.12
BDE-207	486.6	79, 81, 408.6	F-BDE-208 (486.6)	13.0	0.04
BDE-209	486.6	484.6	13C12BDE-209 (494.6)	729	0.04
Σ PBDE				1079	
PBT	79	81, 485.6	F-BDE-28 (79)	0.97	0.01
PBEB	79	81, 501.6	F-BDE-28 (79)	<LOQ	0.01
HBB	551.4	79, 81	FF-BDE-47 (79)	0.48	0.01
BB-153	79	81	F-BDE-100 (79)	<LOQ	0.08
HBCD	79	81, 159.8	FF-BDE-201 (426.6)	2093	0.18
BTBPE	79	81	FF-BDE-201 (426.6)	1060	0.03
BB-209	79	81, 785.4	F-BDE-208 (486.6)	37.9	0.47
DBDPE	79	81	13C12BDE-209 (494.6)	353	0.29
<i>TBBPA-dbpe</i>	79	81	<i>13C12BDE-209 (494.6)</i>	<i>1300</i>	<i>61.3</i>
Σ Non-BDE based BFR				3546	
Σ Total BFR				4625	