Abstracts
BFR 2001

Part 2

Analysis and Fate, Products, Standards and Uses

Analysis and Fate

Products, Standards and Uses

Analysis of Brominated Flame Retardants – Methodological Issues

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Summary

The analysis of brominated flame retardants has shown a rapid development over the last five years. Various GC/MS methods for a congener-specific analysis of PBDEs and PBBs are now available. Methods for HBCD, TBBP-A and decaBDE are being developed. The use of large volume injection and multi-dimensional GC techniques may be helpful to enhance the sensitivity and selectivity of the methods.

Introduction

Brominated flame retardants (BFRs) are being analysed in a growing number of environmental laboratories. The three most frequently analysed BFRs are polybrominated diphenylethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A). In addition, polybrominated biphenyls (PBBs) are often analysed along with the PBDEs, but their concentrations in environmental samples are generally low. The number of PBDE and PBB congeners found in environmental samples is lower than for PCBs[1], because the three technical PBDE mixtures, Penta-mix, Octa-mix and Deca-mix, consist of a limited number of congeners. The main PBDEs reported in environmental samples are 2,4,2',4'-tetraBDE (47), 2,4,5,2',4'-pentaBDE (99), 2,4,6,2',4'-PeBDE (100), 2,4,5,2',4',5'-hexaBDE (153), 2,4,5,2',4',6'-hexaBDE (154), and 2,3,4,5,6, 2',3',4',5',6'-decaBDE (209). Possibly, 2,3,4,6,2',4',5'-hepta BDE (183) may also be of importance, as this is one of the main compounds in the technical Octa-mix, but until now only a limited number of data on this congener is available. Other BDE congeners have been reported as well, but only in low concentrations. HBCD consists of three isomers: α, β and γ. These three isomers are very difficult to separate by normal gas chromatographic (GC) techniques. A separation of these three isomers could give information on selective degradation routes of HBCD. TBBP-A is one compound, but its dimethylated version, presumably a metabolite, also occurs in environmental samples.

Extraction

Extraction techniques used for the determination of BFRs are generally comparable to those used for PCBs. Soxhlet extraction is one of the most frequently used techniques. During the first international interlaboratory study on PBDEs[2], with a participation of 18 laboratories, solvent combinations used included: toluene, toluene/acetone (8:2, v/v), hexane/acetone (1:1, v/v), hexane/acetone (3:1, v/v) and acetone/dichloromethane (1:1, v/v). Other techniques used were ultra turrax extraction with acetone/pentane/water, acetone/hexane/diethylether, or acetone/hexane mixtures, ultrasonic extraction with acetone/hexane, column extraction with dichloromethane or dichloromethane/hexane (1:1, v/v), accelerated solvent extraction (ASE) with dichloromethane, hexane/ dichloromethane or ethyl acetate, and supercritical fluid extraction (SFE). None of the techniques showed a significantly higher or lower recovery of the BDEs than one of the others. Allchin[3] carried out a comparative study of Soxhlet extraction with four different solvent combinations and SFE. He reported that SFE showed higher recoveries than the Soxhlet extraction methods, but also that the SFE results showed a much higher variation coefficient. The four solvent combinations in Soxhlet extraction showed little difference in the recovery. HBCD and TBBP-A are extracted with identical techniques, but a treatment of the extract with basic water may be needed for the separation of TBBP-A from the other compounds[4,5].

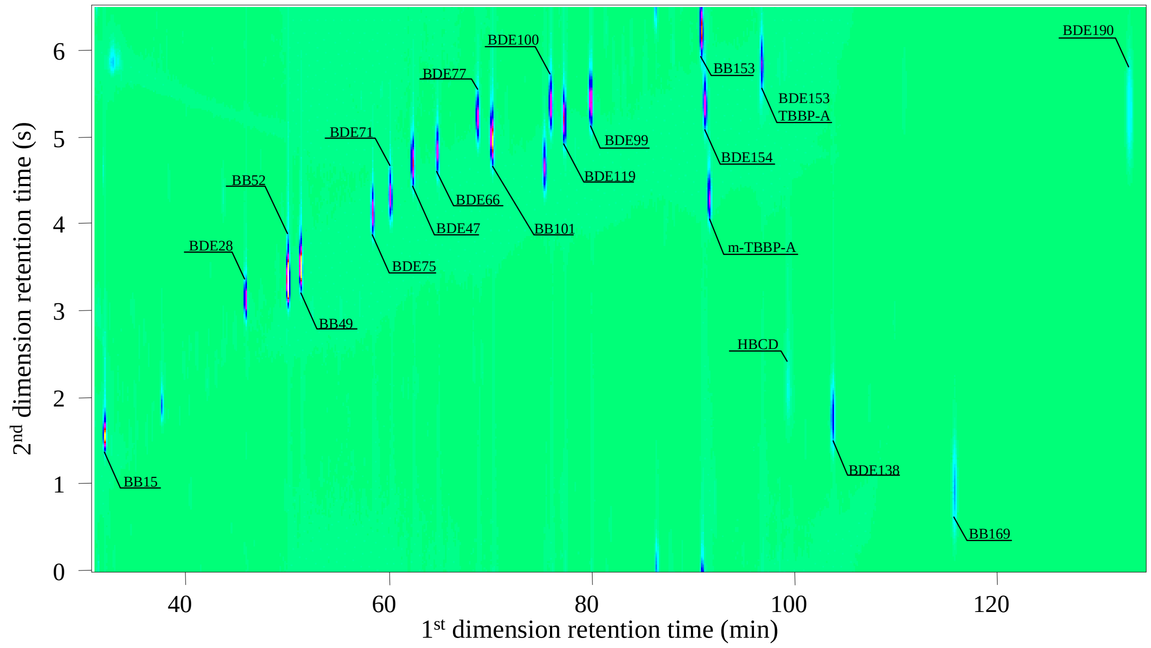
Clean-up

The clean-up techniques currently used include gel permeation chromatography (GPC), column chromatography (alumina, silica, florisil), and sulphuric acid[2]. Combinations of these techniques occur, e.g. first one technique for fat separation, followed by a second one for fractionation. Various methods are being used for the removal of sulphur from sediment samples: copper or mercury treatment, extraction with a tetrabutylammonium solution[6], silica/silvernitrate columns and GPC.

Final determination

The final determination of BFRs is normally carried out by GC coupled with MS detection. Electron capture detection (ECD) may also be used, but the selectivity is obviously less good as this detector also responds to chlorine. MS techniques used include both high resolution (HR) and low resolution (LR)MS. Until now it could not be shown that HRMS detection was superior to LRMS[2]. The LRMS techniques used are most often based on negative chemical ionisation (NCI), which offers a higher sensitivity than electron impact (EI). The drawback of the NCI technique is that for most PBDEs only the bromine can be monitored (m/z 79 and 81). Occasionally, some higher mass fragments can be used for quantification, such as the m/z 486.7 and 488.7 for decaBDE. EI would offer more selectivity, but that is combined with a lower sensitivity. Covaci et al. showed that by combining GC/EI-MS with large volume injection and narrow bore columns (0.1 mm internal diameter), a sensitivity can be obtained which is comparable to that of NCI-MS, but now combined with the selectivity of EI-MS[7]. Most laboratories used splitless injection although on-column injection may be safer as regards possible degradation of higher brominated compounds such as decaBDE. However, when using on-column injection, contamination of the first part of the column by dirty sample extracts could possibly lead to more dramatic effects than with splitless injection. The use of a splitless pulse-pressure injection technique may be a good solution. The analysis of decaBDE is considerably more difficult than those of most other BFRs. DecaBDE is sensitive for (UV) light in the laboratory and for higher temperatures. The use of amber glassware is therefore recommended for decaBDE analysis. In addition, decaBDE should not be exposed to too high temperatures for too long periods. Consequently, the use of short GC columns (<20m) is recommended for the determination of decaBDE. As the determination of the other BDEs requires a good resolution, it is recommended to separate that analysis from that of decaBDE. Also, the end temperature of the oven programme used should not be too high (<290 °C) for a too long period (few minutes).

Non-polar columns are normally used for a congener-specific determination of BDEs and BBs. A good separation can be obtained for most congeners at 50m columns, but the pairs BB 153 and BDE 154, and TBBP-A and BDE 153 co-elute in many cases. The use of multi-dimensional (MD)GC offers a solution for this problem. Comprehensive MDGC (GCxGC) in particular now offers the possibility of separation BB 153 and BDE 154 in one GC run (Figure 1). TBBP-A and BDE 153 can be distinguished by using GC/MS.



Sample:	Analytes concentration ca 5 pg/µl; Injection volume 1.5 µl
Columns:	30m × 0.25mm × 0.25µm HP-1, 9cm × 0.1mm × 3.5µm 007-1, 100cm × 0.1mm × 0.1µm HT-8
1st oven:	90°C (2 min), 5°C/min → 170°C, 1°C/min → 250°C (15 min)
2nd oven:	110°C (2 min), 5°C/min → 190°C, 1°C/min → 270°C (15 min)
µ-ECD:	Temperature 300°C, Data acquisition rate 50 Hz, Make up gas flow 60 ml/min
Injector:	Splitless, Temperature 300°C, He inlet pressure 55 psi, Purge time 1 min, Total flow 80 ml/min
Sweeper:	Modulation period 6.5 s, Stroke velocity 0.15 revs/s, Pause before return 0.4 s

Figure 1. Two-dimensional chromatogram of a GCxGC-ECD analysis of a PBB/PBDE/HBCD/TBBP-A standard solution.

This GCxGC technique is now developing towards a robust technique which is very helpful for the analysis of complex mixtures, including BFRs[8,9]. It can easily be coupled to a micro-ECD. Coupling with LRMS is more difficult as the response speed of the MS detectors is normally too slow to allow a good integration of the peaks. However, as such a good selectivity is already obtained in the GC part of the analysis, MS detection may not be necessary at all. Alternatively, coupling with a Time-of-Flight (ToF)MS may offer the ultimate solution.

For the separation of the three isomers of HBCD a combination of liquid chromatography (LC) with MS may be very useful. However, until now it has not been tried to use GCxGC to solve this problem. TBBP-A and dimethylated TBBP-A may be analysed with GC/MS without derivatisation. Particular problems are not expected with the GC analysis of these compounds.

Quality assurance

Analytical standards of most BFRs including most congeners are now available. Most laboratories still have difficulties to decide upon a proper internal standard to be used for the BFR analysis[2]. ^{13}C labelled standards have been made available, but when using NCI-MS, these are of little value, as only the bromine ion is being monitored. Obviously, the decaBDE analysis will require a different, higher boiling compound as internal standard than most of the other BDEs, which are primarily in the tetra-hexa region. Until now one international interlaboratory study has been organised[2]. The results showed a good comparability of the 18 participating laboratories for BDE 47, but less good comparability for the other BDEs, in particular for decaBDE. A second interlaboratory study, possibly including the analysis of HBCD and TBBP-A, is in preparation. Until now no certified reference materials have been made available. A European research project, entitled BROC: Biological Reference materials for Organic Contaminants, will start in June 2001, aiming at the production of two CRMs for BDEs, one fish material and one sediment.

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Abiotic transformation of polybrominated diphenylethers (PBDEs): Photolytic debromination of decabromo diphenyl ether.

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Summary

Photolytic debromination of DeBDE was investigated on different environmentally relevant matrices, viz. sand, soil and sediment. Debromination was found and debromination products identified as lower brominated PBDEs.

Introduction

Polybrominated diphenyl ethers (PBDE) are additive flame retardants used in plastics, textiles and electronic equipment. Some tetra- and pentaBDEs have been found to bioaccumulate and biomagnify in biota and concentrations have increased during the 1970s and 80s (1,2). Te- and PeBDEs have been shown to be biologically active and potentially toxic (3). The most commonly used PBDE products contain mainly decabromodiphenyl ether (DeBDE), but in environmental samples lower brominated PBDEs dominate (1). However, in sediments taken near user sites DeBDE has been found (4-7). Previous studies show that PBDE and other brominated organic compounds in solvents undergo rapid photolytic debromination in the presence of UV-light under laboratory conditions (8). Photolytic debromination could be one reason for the relative dominance of lower brominated PBDE in the environment. The aim of this study was to investigate the debromination process of DeBDE on different matrices (both dissolved in toluene and layed on natural matrices such as sand, soil and sediment) and exposed to sunlight or artificial ultraviolet (UV) light and to characterize and possibly identify the degradation products (9). The results of these experiments will increase the understanding of the possible transformation and fate of DeBDE in the environment.

Materials and Methods

Five different matrices were used in the experiments, viz. toluene, silica gel, sand, soil and sediment. The toluene was a glasdistilled quality from Fluka (Burdick and Jackson). The silica gel (Merck) and the lake-sand (Kebo) were thoroughly washed with toluene to remove any organic matter. The soil was an agricultural soil from Jyndevad, Denmark, selected as a typical Nordic soil (10) and the sediment was from Dättern, a bay on Lake Vänern, Sweden, with low contaminant levels (11). The matrices were portioned into Pyrex-tubes and DeBDE, dissolved in toluene, was added. The toluene was then allowed to evaporate while the samples were kept in the dark.

UV-exposure experiments were performed both in the laboratory with artificial UV-light and under natural conditions with outdoor sunlight (sand, soil, sediment). The laboratory exposure light-source consisted of four mercury UV-lamps, Philips TLK 40W/09N, equipped with filters to give a spectra as close as possible to sunlight in the UV-range. The irradiance intensity from the UV-lamps at the exposure spot was 1.6 mW/cm^2. Sunlight exposures were performed in July 1997 in Umeå, Sweden (63^o 51' N, 20^o 17'E, 20 m altitude above sea level). The weather conditions were excellent with clear skies. Maximum UV-irradiance from the sun at mid-day was 2.3 mW/cm^2. Subsamples of each matrix were exposed to artificial UV-light in the laboratory. Subsamples of sand, soil and sediment were exposed to outdoor sunlight. Irradiance from 24 hours of sunlight corresponds to approximatly 9 hours of artificial UV-light in this experiment. Each series consisted of blanks, dark controls and the samples to be exposed and the experiments were performed in triplicates. Sediment samples were reconstituted in water before exposure. The Pyrex tubes with DeBDE adsorbed to the matrices were placed on a "rocking/rolling action" apparatus. For the indoor experiments the setup was placed under mercury UV-lamps in a hood and samples were taken from 0 to 32 hours. For the outdoor experiments the set-up was placed on a shadowless roof adjacent to the laboratory and samples were taken from 0 to 96 hours.

All samples were extracted in the Pyrex tubes used for UV exposure. The method used was a scaled down version of the method described by Nylund et al. (2). Sulphur was removed from the sediment and soil samples (2). The silica gel, sand, soil and sediment samples were then treated with concentrated sulphuric acid to remove less persistent substances. The analyses were done by GC-MS measuring the negative ions formed at chemical ionisation (m/z -79 and -81 for the brominated compounds) (7). Extraction and work-up were performed avoiding exposure of samples to light.

Results

In all matrices studied, debromination of DeBDE and the formation/debromination of lower brominated PBDE (nona- to hexaBDEs) could be found. Among the congeners formed in toluene, all correspond to components found in technical PBDE flame retardant products. The increase and decrease of nona- to hexaBDEs shows that the process is mainly a step-wise debromination process. The time course in toluene is rapid, with a half-life for DeBDE of less than 15 minutes. On sand, soil and sediment the time course for this debromination process is considerably slower. The half-life for the DeBDE on sand is about 14 hours in the indoor experiments and approx. 35 for outdoor experiments. Exposure of the sand indoors and outdoors results in similar half-lives for the DeBDE when compared to the total irradiance since 35 hours sunlight outdoors corresponds to approx. 13 hours of artificial UV-light

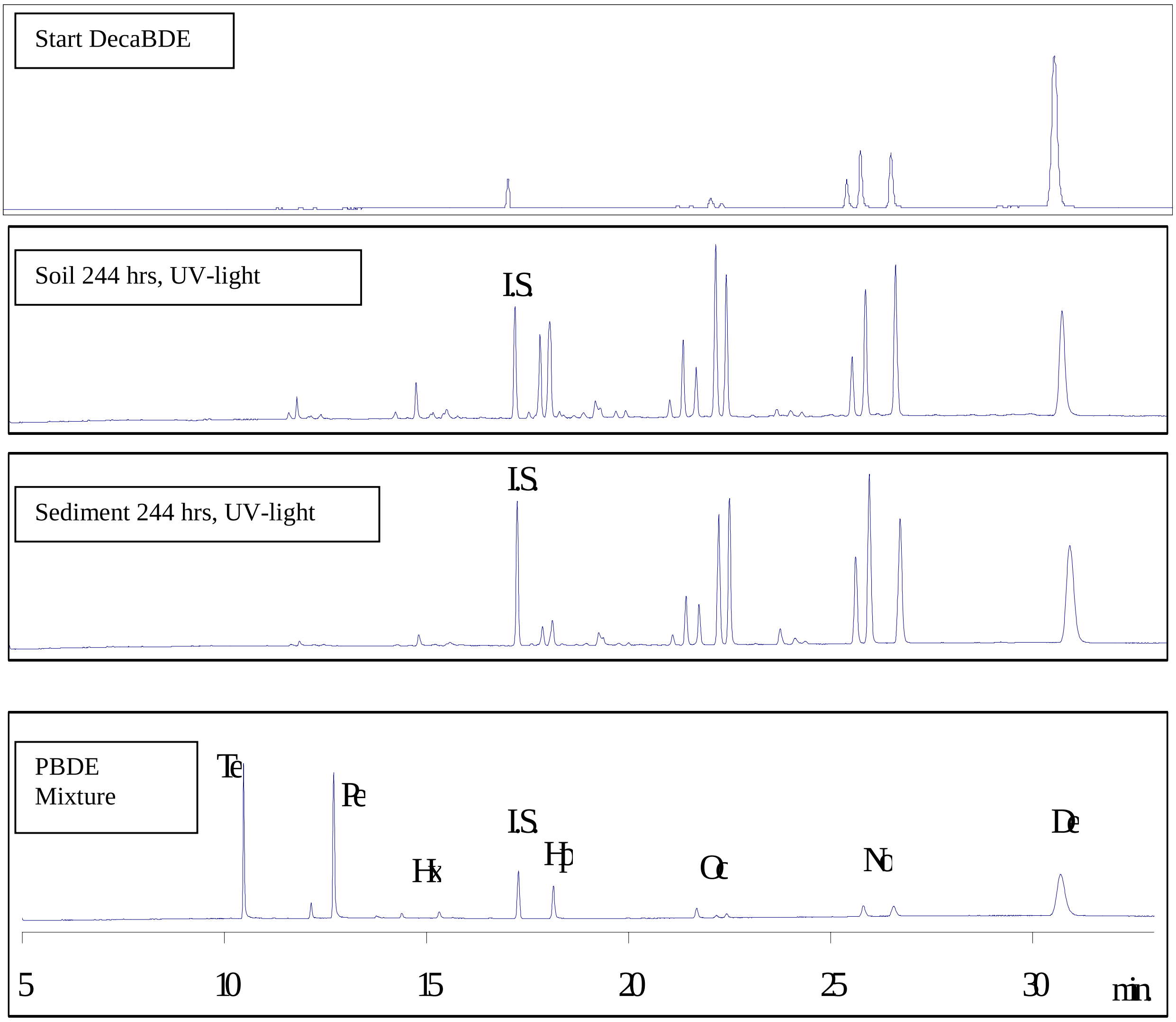

Figure 1. Photolytc debromination of DeBDE on soil and sediment after 244 hours of UV-light exposure.

indoors. In sunlight, the sediment and soil the half-lives were estimated to approx. 100 and 200 hours, respectively.

In Figure 1, the chromatograms of long time UV-light exposure of DeBDE on soil and sediment are shown. The DeBDE product added to the samples is shown as time zero for toluene. The PBDE mixture is a mixture of penta-, octa- and decabromodiphenyl ether products As can be seen in the figure, the chromatograms for sediment and soil after 244 hours exposure are nearly identical. Thedebromination of DeBDE leads to formation of lower brominated PBDEs but other products are also possible. Watanabe et al. (12) showed the formation of PBDFs as photolytic productsfrom DeBDE dissolved in hexane. The search for these and other transformation products will be included in future work.

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Measurements of Octanol-Air Partition Coefficients (K_{OA}) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment

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Summary

Octanol-air partition coefficients (K_{OA}) are reported for thirteen polybrominated diphenyl ethers (PBDEs) over the temperature range (15 – 45) °C. K_{OA} exhibits a log – linearly relationship with inverse absolute temperature and values at 25 °C range from 9.3 (PBDE-17) to 12.0 (PBDE-126). These are approximately an order of magnitude greater than observed for the counterpart polychlorinated biphenyls (PCBs). Examples are shown of how K_{OA} can be used to describe the partitioning of PBDEs between air and environmental organic phases such as aerosols and soil.

Introduction

PBDEs are ubiquitous environmental pollutants that have exhibited increasing levels in human milk over the last 25 years.[1] They have been detected in various biotic and abiotic matrices and their presence in remote regions, such as the arctic [2], indicates that they are susceptible to long-range atmospheric transport. It is important therefore to assess the volatility of PBDEs and to describe their partitioning to terrestrial organic phases including aerosols.

K_{OA} is thought to be the key descriptor of the absorptive partitioning of semi-volatile compounds between the atmosphere and terrestrial organic phases found in soil, vegetation and on aerosols.[3] Measurements of K_{OA} and its temperature dependence have been made for a range of semi-volatile organic chemicals (SOCs) including chlorobenzenes, PCBs, PAHs, PCNs, organochlorine pesticides, and now PBDEs. K_{OA}-based models have been developed for describing aerosol-air [4] and soil-air [5] partitioning.

Results

The octanol-air partition coefficient K_{OA} was correlated against 1/T (1/K) over the temperature range (15-45) ^{o}C and showed a $\log_{10}$-linear relationship according to the equation,

$$\text{Log } K_{OA} = A + B/T \qquad \text{Eq. 1}$$

Regression parameters for Eq. 1 are listed in Table 1, along with K_{OA} and p^{o}_{L} values for selected congeners at 25 ^{o}C. The temperature coefficient for octanol-air transfer ΔH_{OA} (ΔH_{OA} = B* 2.3* R, where R =8.314) is also listed in Table 1. In general K_{OA} values for PBDEs were an order of magnitude greater than previously observed for the counterpart PCBs. This has important implications on how PBDEs are distributed in the environment, especially for their partitioning into organic phases such as soil, vegetation and aerosols.

Recently, Tittlemier and Tomy [4] and Wong et al.[5] reported sub-cooled liquid vapour pressures for PBDE congeners that were determined by the GC-retention method. However, the results from these two studies were not consistent and in some cases discrepancies were more than an order of magnitude. Figure 1 is a plot of log K_{OA} versus log p^{o}_{L}, comparing the results of this study against the two published data sets for p^{o}_{L}. In both cases there appears to be a near 1:1 relationship between K_{OA} and p^{o}_{L}. This comparison does not allow us to determine which p^{o}_{L} data are more correct. However, when results from other SOC classes (PCBs, PCNs, PCDD/Fs) are added (Figure 1) it appears that the data from Wong et al.[6] are more consistent.

Partitioning to aerosols and soils

Expression have been developed that can relate concentrations of SOCs in air to their respective equilibrium values on aerosols [6] and soil [7]. For aerosols,

$$\text{Log } K_P = \log K_{OA} + \log f_{om} - 11.91 \qquad \text{Eq. 2}$$

where K_P = is the particle gas partition coefficient (μg m^{-3}) which relates the portion of chemical on particles to its gas-phase concentration and f_{om} is the fraction of organic matter on the aerosol that is free to exchange chemical. The fraction on particles, ϕ, is calculated as,

$$\phi = K_P\, TSP / (K_P\, TSP + 1) \qquad \text{Eq. 3}$$

TSP (μg m^{-3}) is the concentration of suspended particulate matter in air. Typical values for f_{om} and TSP are 0.2 and 25 respectively. Based on equation 2 and 3, predicted percentages on aerosols were determined at 25 ^{o}C for all PBDE congeners (Table 1) with the following approximate ranges: tetra-PBDEs, 20-30%; penta-PBDEs, 40-70%; hexa-PBDEs, 80%+.

These results agree well with recent measurements by Strandberg et al.[8] at (20 +/- 3) °C of gaseous and particulate PBDEs in the Great Lakes atmosphere.

For soil, Hippelein and McLachlan [7] related the dimensionless soil-air partition coefficient (K_{SA}) for SOCs to the octanol-air partition coefficient using the relationship,

$$K_{SA} = 2\ f_{oc}\ K_{OA}, \qquad \text{Eq. 4}$$

where f_{oc} is the fraction of organic carbon in the soil. Based on this expression and mean total air concentration for congeners – 47, 99, 100, 153, 154 reported by Strandberg et al.[8] for the period 1997-1999 (3 background sites, 1 urban site, see Table 1 footnote), the equilibrium soil concentrations were calculated and are listed in Table 1. Calculations were based on a typical soil having a soil solids density of 2500 kg m^{-3} and f_{oc} =0.02. Predicted soil concentrations (ng g^{-1} dry wt.) ranged from 0.32 (PBDE-154) to 7.8 (PBDE-99).

In conclusion, the availability of physical chemical data for PBDEs puts us in a unique and interesting position where we can model the partitioning and predict concentrations of PBDEs in various compartments in-step with or ahead of actual measurements. Our predictions based on measured K_{OA} values suggest that PBDEs will be strongly partitioned to soil and that particle-gas partitioning will play a key role in the transport and fate of PBDEs.

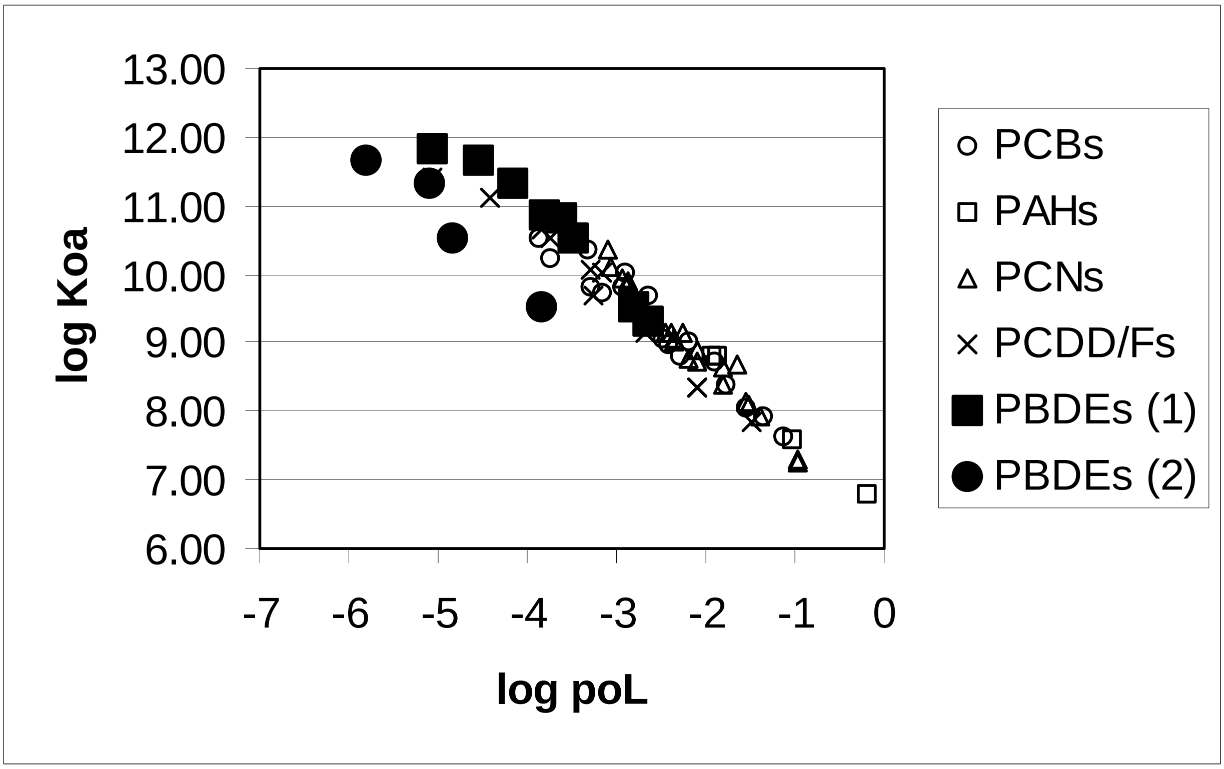

Figure 1. Log K_{OA} versus log p^o_L (Pa) at 25 °C for selected SOCs. PBDE (1) = p^o_L data from Wong et al.[5] PBDE (2) = p^o_L data from Tittlemier and Tomy [4].

	Log K_{OA} (25 °C)	**A**	**B**	**ΔH_{OA} ($kJmol^{-1}$)**	**Aerosol % (predicted)**	**C_{soil} (ng g^{-1},dw) (predicted)**
PBDE-17	**9.30**	**-3.45**	**3803**	**72.8**	**1.2**	
PBDE-28	**9.50**	**-3.54**	**3889**	**74.5**	**1.9**	
PBDE-47	**10.53**	**-6.47**	**5068**	**97**	**17**	**4.2**
PBDE-66	**10.82**	**-7.88**	**5576**	**107**	**29**	
PBDE-77	**10.87**	**-5.69**	**4936**	**94.5**	**32**	
PBDE-100	**11.13**	**-7.18**	**5459**	**105**	**45**	**0.85**
PBDE-99	**11.31**	**-4.64**	**4757**	**91.1**	**56**	**7.76**
PBDE-85	**11.66**	**-6.22**	**5331**	**102**	**74**	
PBDE-126	**11.97**	**-8.41**	**6077**	**116**	**85**	
PBDE-154	**11.92**	**-4.62**	**4931**	**94.4**	**84**	**0.32**
PBDE-153	**11.82**	**-5.39**	**5131**	**98.2**	**80**	**0.45**
PBDE-156	**11.97**	**-5.80**	**5298**	**101**	**85**	
PBDE-183	**11.96**	**-3.71**	**4672**	**89.5**	**85**	

Table 1. K_{OA} values for PBDEs over the temperature range (15-45) °C. Regression coefficients (A and B) are for Eq. 1 (i.e. log Koa = A +B/T). Percentage on aerosols and equilibrium soil concentrations predicted at 25 °C using Eq.2,3 and 4 respectively and parameters listed in the text. Mean air concentrations (pg m^{-3}) at (20 +/- 3) °C from Strandberg et al.[8] – PBDE-47, 10.8; PBDE-100, 0.87; PBDE-99, 6.6; PBDE-154, 0.19; PBDE-153, 0.28 – note: these total air concentrations were corrected using Eq. 1 to determine gas-phase concentrations that were used in the calculation.

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Presence of PBDDs/DFs in Flame Retardant Materials and their Behavior in High-Temperature Melting Processes

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Summary

Brominated compounds in flame retardants were examined. PBDDs/DFs at ppm levels were detected in waste TV casing, waste PC casing and printed circuit boards. High concentrations PBDDs/DFs input were decomposed to more than 99% in a melting system in which mixtures of incineration residues and polymer resin were melted at approximately 1300 C. Also in gasification melting furnaces in which only domestic waste were melted, the decomposition rate of PBDDs/DFs were more than 99%.

Introduction

Recently, the detection of polybrominated diphenyl ether (PBDEs) in the environment has been reported. PBDEs have been widely used as brominated flame retardants and enhance the flame retardation quality of consumer products through the addition to or reaction with plastics and synthetic fiber. Their effects on the environment and human health have been a cause of concern1). Furthermore, it has beenn reported that PBDDs/DFs form via thermolysis of brominated flame retardants. The behavior of PBDDs/DFs in the process of manufacturing brominated flame retardants and during the combustion of products containing brominated flame retardants in municipal solid waste (MSW) incinerator has recently attracted attention2). This study examined concentrations of organic brominated compounds (PBDDs/DFs, PBDEs) in flame retardant plastic materials and also investigated PBDDs/DFs emission factor during the process of melting treatment at high-temperature. Melting recycling has become a major focus as a decomposition technology for waste containing chemicals.

Methods

Brominated compounds in flame retardant resin and waste electrical appliances were chemically analyzed. Three kinds of flame retardants resin were used as samples. PBDEs/PE resin were made by adding PBDEs to PE resin, TBBP-A/ABS resin were made by adding TBBP-A to ABS resin and BPs/PS resin were made by adding BPs to PS resin. Waste TV (mixture of 40 television manufactured in 1987-1995), Waste PC (mixture of personal computer manufactured in 19**-19**) and cellular phones were used as samples of waste electric appliances.

Emission factor of PBDDs/DFs in the process of melting were investigated at two full-scale test plants as following: one was an ash melting furnace (capacity approx. 2.5ton/day) 3), in which incineration residues and plastic (ABC resin +PVC) were melted and the other was a gasification melting furnace (capacity approx.10ton/day) 4) in which only domestic household waste was melted. Both furnaces are in test plants having flue gas treatment facilities. Melting treatment were performed at approx.1300 C. The experiment was conducted under two conditions in the ash melting furnace. The oxidizing condition was set to supply all of the combustion air into the primary chamber of the melting furnace. The reducing conditions were set to supply the primary combustion air with 80% of stoichiometric air into melting furnace and post combustion chamber with 20%.

Results and Discussion

Table 1 shows concentrations of brominated compounds in flame retardant resin and waste electric appliances. The concentrations of PBDEs/PE were detected with 3,100ng/g as the highest value in three resin samples. In the TV casing materials and printed circuit boards, more PBDEs were present than TBBP-A. The PBDEs homologue distribution profiles in the TV casing showed that the levels of NoBDEs-DeBDE were high. In printed circuit boards showed that TeBDEs-PeBDEs were relatively common. This tendency was also seen in PC casing and circuit boards. In PC casing, NoBDE were dominant but the PBDEs homologue distribution profiles shifted towards the low brominated PBDEs when PC casing materials were mixed with printed circuit boards. PBDDs/DFs in waste TV and waste PC values were very high at ppm levels even compared to other studies5). Further studies to see if this trend is usual have been conducted considering uneven concentrations and numbers of samples.

Table 1 Concentrations of PBDEs and PBDDs/DFs in flame retardant products and their wastes

	Flame retardant resins			Waste TV		Waste PC		Waste cellular phone
	PBDEs/PE	TBBP-A/ABS	BPs/PS	Casing (n=2)	Circuit board (n=2)	Casing	Casing+circuit board	
PBDEs [ug/g]	20000	-	-	2,100~6,300	4,100~11,000	7,600	2,900	12
TBBP-A [ug/g]	-	420	-	2.4~1,300	500~520	2,900	3,400	28
PBDD/DFs [ng/g]	3,100	0.62	45	3,000~66,000	38,000~130,000	160,000	30,000	370

Table 2 shows the concentrations of PBDDs/DFs and PCDDs/DFs in the processes of ash melting furnace. Concentrations of PBDDs/DFs and PCDDs/DFs in the experimental samples were 650~760ng/g and 750~1,600ng/g 5.6~7.7ng-TEQ/g respectively. The material input was a mixture with 93.8% incineration ash of MSW and 2.4% PBDEs/ABS resin. PBDDs/DFs contribution of PBDEs/ABS resin was 85% in the reducing test, and 99.9% in the oxidizing test as PBDDs/DFs concentration was 27,000ng/g at the maximum. Concentrations of PBDDs/DFs in melting slag were significantly lower than those in the experimental samples. For the oxidizing test, PBDDs/DF increased in in bag filter of the flue gas path. Further investigation is necessary because it is thought that the increase of PBDDs/DFs was caused by *de novo* synthesis.

Table 3 shows concentrations of PBDDs/DFs and PCDDs/DFs in the gasification melting furnace. In the materials input, the concentrations of PBDDs/DFs and PCDDs/DFs were 4.0ng/g and 1.8ng/g 0.016ng-TEQ/g respectively. The concentration of PBDDs/DFs was low at the background level.

Table 2 Behavior of PBDDs/DFs and PCDDs/DFs in the melting system

		Experimental samples [ng/g]([ng-TEQ/g])			Flue gas [ng/Nm^3]([ng-TEQ/Nm^3])			Melting residues [ng/g]([ng-TEQ/g])	
		PBDEs/ABSresin	Incineration residues of MSW	Input samples	Exit of chamber	Inlet of B.F.	Outlet of B.F.	Melting slag	Melting fly ash
PBDDs/DFs	Reducing test	27000	120	762	3.4	3.2	1.6	0.24	2.0
	Oxidizing test		0.18	649	3.4	0.73	3.4	0.014	0.044
PCDDs/DFs[*1]	Reducing test	ND (0)	1700 (8.2)	1597 (7.7)	19 (0.22)	48 (1.2)	90 (1.6)	0.27 (0.0033)	2.8 (0.031)
	Oxidizing test		802 (6.0)	752 (5.6)	27 (0.21)	26 (0.49)	67 (0.90)	0.38 (0.0055)	0.88 (0.0097)

[*1] Values in parentheses are 2,3,7,8-TCDD toxicity-equivalent.

Although the samples were mostly domestic household waste, they contained small amount of brominated compounds such as PBDEs and TBBP-A used as flame retardant. Concentrations of PBDEs and TBBP-A were 230ng/g and 4,400ng/g respectively. In the materials output, PBDDs/DFs were detected in the nonflammable fraction which included recovered metal. They were not detected in the other by-products of melting process and flue gas. Melting fly ash contributed largely to PCDDs/DFs in the by-products of melting process but concentrations of melting fly ash were lower than those of incineration fly ash.

Table 3 Concentrations of PBDDs/DFs and PCDDs/DFs in gasification melting system

	Input samples [ng/g]?ng-TEQ/g?	Flue gas [ng/Nm^3]?ng-TEQ/Nm^3?			Residues [ng/g]?ng-TEQ/g?			
		Outlet of cooling duct	Outlet of bag filter	Outlet of catalyst tower	Nonflammables	Melting slag	Dust in cooling zone	Melting fly ash
PBDDs/DFs	4,0	ND<10	ND<10	ND<10	2,4	ND<1.0	ND<1.0	ND<1.0
PCDDs/DFs[*]	1,8 (0.016)	88 (0.62)	2,0 (0.026)	1,7 (0.018)	0,11 (0.00068)	0,032 (0.00053)	4,5 (0.033)	51 (0.44)

[*] Values in parentheses are 2,3,7,8-TCDD toxcity-equivalaent.

Output and input amount per 1ton waste were calculated by substance flow analysis of PBDDs/DFs in the melting furnace. Amount of incineration residues was calculated as 180kg/ton waste in ash melting furnace in which a mixture of incineration residues and waste plastics was melted. The ratio of ABS resin in fly ash was equivalent to approx. 0.5% in original domestic waste. To compare these results with a usual MSW incineration treatment, we analyzed at full-scale incineration plants A6) and B7), which have stocker type incinerators. Incineration capacity was 200t/day and 85ton/day, respectively. The PBDDs/DFs concentrations in MSW were not measured in Plant A; therefore, they were estimated from the data of Plant B. In Plant B, PBDDs/DFs concentrations in domestic household waste and shredded bulky waste were 0.53-1.4ng/g, average 0.97ng/g and 2.9ng/g respectively. In Table1, PBDDs/DFs in waste TV casing were 3,000-66,000ng/g, average 34,500ng/g. PBDDs/DFs were almost completely decomposed by the melting treatment at approx. 1300C. In the ash melting furnace, in particularly, although input amounts were high due to the addition of PBDEs/ABS resin, PBDDs/DFs were decomposed to more than 99% in the melting process. In gasification melting furnace, PBDDs/DDFs in melting fly ash, slag and flue gas were scarce. Considering that output amounts of PBDDs/DF increased when MSW was incinerated with shredded bulky waste containing flame retardant in such a full-scale incineration facility A, melting treatment is one of the more effective measures for emission control of chemicals such as PBDDs/DFs.

Table 4 Output/ input amount of PBDDs/DFs in melting and incineration of MSW

			Input amount	Output amout					Decomposition rate
				Total	Flue gas	Bottom ash	Slag	Fly ash	
Melting	Ash melting furnace	Reducing test	140,000	81	3.0	-	37	41	99.94%
		Oxidizing test	130,000	8.4	5.4	-	2.2	0.77	99.99%
	Gasfication melting furnace	Domestic household waste	2,300	19	0	19*	0	0	99.17%
Incineration of MSW	Plant A	Domestic household waste	550**	64	21	28	-	15	-
		Mixture with 25% large size crushed bulky waste	1,000**	993-1,439	17	952-1,197	-	22-225	-
		Mixture with 50% crushed electric appliances	1,700,000***	3,935	129	269	-	3,537	-
	Plant B	Domestic household waste	240-850	12	2.8	0.53	-	9.1	95-99%

Unit is [ug/ton waste]. Amount of incineration residues were calculated as 180kg/ton waste in ash melting furnace.

*Nonflammables were in gasification melting furnace

**Values estimated from data of plant B

***Mixing ratio of waste casing estimated 10% of crushed electric appliances.

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Combustion of brominated flame retardants

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Summary: Three different brominated flame retardants were co-incinerated with MSW imitating pellets. Target compounds in analysis were bromo flame retardents and bromo/chloro dibenzo-p-dioxins and dibenzofurans. Results show an increase in total formation of halogenated dioxins. No bromo flame retardents remained after combustion.

Most brominated flame retarded products sooner or later end up as waste were a big part is combusted. Combustion of municipal solid waste (MSW) is common in many countries either for energy recovery, or simply for minimizing waste volumes. It is also common that electronic scrap undergoes combustion in the metal recovery process. It is since long known that chlorine forms chlorinated dibenzo-p-dioxins (PCDD) and chlorinated dibenzofurans (PCDF) during most types of combustion. It is also known that combustion of brominated flame retardants can give rise to brominated dibenzo-p-dioxins (PBDD) and brominated dibenzofurans (PBDF), and hence, bromine and chlorine will together give bromochloro dibenzo-p-dioxins (PBCDD) and bromo-chloro dibenzofurans (PBCDF). In this investigation we have studied formation of PBCDD/F's from co-combustion of decabromodiphenyl ether (DeBDE), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A respectively with MSW. The aim was to compare bromine and chlorine in their ability to form halogenated dioxins and dibenzofurans in a combustion process. Chlorine and bromine have some different physico-chemical properties which affect their combustion behaviour. These differences make brominated compounds more effective flame retaders than chlorinated compounds. Ingrid Fängmark [1] postulated in 1993 that formation of PCDD/F is strongly linked to temperature and residence time in the post-combustion zone. In 1999 Evalena Wikström [2] postulated that the formation is a two step reaction; First formation of unchlorinated dioxin precursors as well as dibenzofurans and also other PAH's at high temperature. Secondly, chlorination of these carbon skeletons. Chlorine is only active as a chlorination agent in the Cl_2 form, HCl is mainly inert and needs a catalyst like Cu to become the chlorinating Cl_2. In the case of bromination, it is likely that the pathway is similar to the ones of chlorination. A difference between chlorine and bromine is their equilibriums in high temperatures. Br_2 exist to larger extent than Cl_2 in the flue gas temperatures were halogenation takes place. It is also likely that BrCl is formed, BrCl is known to be a strong halogenation agent.

The results show that more brominated dibenzofurans are formed than chlorinated ones under equal combustion. A noteworthy effect of co-combustion of bromine and chlorine containing waste is the formation of mixed chloro-bromo dibenzofurans. This formation of TBCDF is aprox. 50 times larger compared to combustion of only chlorine containing waste. The increase can be explained by the changed composition of halogenation species in the flue gas.

The results also indicate that the flame retardants are fully degradated at normal combustion conditions. No rests of the flame retardants could be seen in the flue gas. Decabromodiphenylether is often considered to be a good precursor for formation of PBDF's due to their similar structures. In these experiments, no difference could be seen though in the formation of PBCDD/F between the flame retardants, even though their structures are quite different.

Another investigation[3] has shown a small increase of dioxin formation when small amounts of bromine are co-incinerated with MSW. Our results confirms those findings and show that it is unfavourable to co-combust large amounts of bromine (batch-wise) with MSW due to the immense dioxin increase.

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BROMINE RECOVERY IN INCINERATORS AND ALTERNATIVE THERMAL PROCESSES FROM PLASTICS OF E&E EQUIPMENT CONTAINING BROMINATED FLAME RETARDANTS AS SUSTAINABLE SOLUTION.

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Abstract:

With waste disposal costs increasing and public and regulatory concern to maximise waste recovery, innovative ways in which to identify and develop technically and economically feasible methods of recovering Waste from Electrical and Electronic Equipment (WEEE) need to be developed. Since 1998, the Bromine Science and Environmental Forum (BSEF) has sponsored the development of pilot trials for the recycling of bromine and the recovery of energy from WEEE plastics. Plans are now underway to build a plant to recycle bromine and recovery energy.

The objective is to recover the 10,000 tons [1] of bromine from WEEE generated in Europe annually. To maximise the economic efficiency of the operation, additional feed streams, such as plastics from automotive shredder residues (ASR), packaging material for brominated products and other bromine containing wastes could be considered.

The recovery potential of the project was first analysed in a thermal process study [2] followed by thermal pilot trials to produce the bromine products. The effect of increasing the bromine concentration up to 100 times via addition of 20-25% WEEE plastics in the feed of a standard modern Municipal Solid Waste Incinerator (MSW) was investigated at the Forschungszentrum Karlsruhe (TAMARA incinerator) in Germany in cooperation with APME. The following observations were made:

- Addition of artificially high levels of bromine in the feed resulted in improved burnout in the combustion process; Elementary bromine could not be detected up to a load of 300 mg HBr/Nm3 in the air;
- There was no increase of brominated and chlorinated dioxin/furans;

- There was a distinct decrease in heavy metals in the grate ash due to volatilization with bromine;
- The bromine components in the flue gas can be recovered as HBr or bromine salts and used in the bromine industry as raw material;
- The emissions of hydrogen halides and dioxins could easily be controlled even at high plastic WEEE input (up to 25% of the feed).

Introduction

Every year, about 3,500 people die in fires in the European Union [3]. According to the European Commission the use of flame retardants (FRs) accounts for a 20% reduction in fire fatalities. Further by introducing in 1988, FRs in furniture in the UK, 1,860 people are alive today [4].

Brominated flame retardants (BFR)s represent the major flame retardant group in electrical and electronic equipment (EEE). Some 75 different BFRs exist on the market today. BFRs are used for protection against the risk of accidental fires in a wide range of EEE and act to decrease the risk of fire by increasing the fire resistance of the materials in which they are applied.

After EEE has outlived its use, it is discarded and becomes waste. Recovery of the bromine from WEEE plastics is an option in parallel to mechanical recycling [5]. Various plastics containing brominated flame retardants have been tested and have been found to be fully recyclable meeting all legislative and market requirements.

Modern incineration techniques or pyrolysis/ gasification are the most technically advanced solutions to recover bromine. A program has been developed to find a sustainable solution for the bromine found in WEEE. Firstly, the consultancy firm Kennedy & Donkin carried out a study to investigate the amounts of WEEE containing BFRs in Europe [1].

Second, a thermal process study [2] followed by thermal pilot trials for production of bromine products were undertaken in order to evaluate the recovery potential.

Two pilot trials were set up using WEEE in the feed stream at the following pilot plants:

- the TAMARA pilot plant in Germany, a scaled down model of a grate combustion furnace,.
- the Gibros pilot plant, a small pyrolysis-gasification facility at ECN in Holland (study not finalised at the time of writing)

The materials tested in the TAMARA pilot trial were printed wiring board mixtures, TV backplates and other mixed electronic waste typically found at the outlet of dismantlers.

WEEE was artificially increased up to 20-25% of the total feed along with a standard fuel representing today's typical municipal solid waste in Europe. During the test, the bromine concentration was increased from the typical level in waste of 30 – 100 up to 2,750 mg/kg

The role of Bromine (Br) in the formation of halogenated dioxins and furans

The typical Br content in municipal solid waste is very low (30 - 100 mg/kg) compared to Chlorine (Cl) (5000 – 8000 mg/kg). Hence Br containing dibenzo-p-dioxins and dibenzofurans are present in the flue gas of waste combustion plants at very low concentrations.

With raising Br input by the co-feeding of flame retarded plastics the formation of Br containing dioxins and especially furans increased and seemed to fall into a constant range at Br loads of approx. 500 – 1000 mg/kg. The prevailing homologues analysed were those containing one Br atom. It could be demonstrated that the total load of halogenated dioxins and furans stayed almost constant in spite of the increased load of brominated and chlorinated materials. The results from these tests underline the fact that the formation of halogenated dioxins and furans is dependent on the availability of products of incomplete combustion and that, if the burnout is optimised, the amount of halogens in the fuel has no significant influence on the amount of dioxins and furans formed.

During the tests on WEEE samples taken after the flue gas had passed a charcoal filter resulted in residual PCDD/F concentrations of <0.001 ng(TE)/m^3 which is a factor of 100 lower than the internationally accepted emission standard of 0.1 ng(TE)/m^3. Bromine containing homologues could not be detected. This supports the conclusion that the contribution of Br containing species is of no concern to the emission of Municipal Solid Waste (MSW) incineration plants with a modern air pollution control system.

Bromine recovery as a sustainable solution

During the pilot trial the flue gases were quenched in water. The HBr was collected in a bypass system as HBr solution for further evaluation of recovery by the bromine industry.

The main flue gas stream was quenched in a caustic solution for recovery of the HBr as sodium bromide for further evaluation of the bromine recovery. For these streams a program was set up for testing the produced bromine products for technical and economical evaluation of bromine recovery.

These experimental results were partly verified by experiences gained from full-scale experiments and are in line with results reported in the relevant scientific literature. This means that combustion combined with bromine recovery is an ecologically acceptable and economically sound disposal route for halogen-containing plastic waste at least up to levels of 10% of municipal solid waste.

Conclusions:

- It can be concluded that bromine recovery from WEEE plastics and ASR is technically, economically and ecologically feasible.
- Elementary bromine could not be found in the flue gas up to a total Br concentration of about 300 mg/Nm^3 (depending on SO_2 content).
- WEEE plastics in modern incinerators can have a positive effect on the burnout
- No increase of dioxins/furan occurs when WEEE is added to the feed [6].
- Besides mechanical recycling [7] and energy recovery [1], this feedstock recycling method could play an important role in an integrated waste management concept for plastics containing brominated flame retardants [5].

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P1

Automated Rotary Valve On-Column Injection for Determination of Polybrominated Diphenyl Ethers by Gas Chromatography

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Sample injection is a critical factor when analyzing high boiling compounds such as polybrominated diphenyl ethers (PBDE) with gas chromatography (GC). Discrimination of high boiling compounds is a common problem associated with the split/splitless injector. The traditional on-column injector and the septum equipped temperature programmable injector (SPI) are on-column type of injectors that has been used successfully to introduce PBDE with little or no discrimination and high reproducibility. The SPI may however suffer from leaks and septum contamination. A drawback of all the injectors described above is that none of them is easily coupled on-line to a liquid chromatograph (LC) in order to obtain a hyphenated LC-GC analytical system. An easy automated, non-discriminating, versatile and robust injector is preferred.

We have constructed and evaluated an automated rotary valve on-column injector. It has been mounted on a GC-ECD and a GC-MS system and applied to analysis of PBDE. This injection technique benefits from injection volumes up to 50 µl which facilitates injection of PBDE samples with low concentration. The rotary valve injector also enables convenient on-line coupling possibilities to various clean-up systems in order to obtain hyphenated analytical systems. Further advantages are absence of septum peaks, leaking septa and reduced manual handling. The injector has been evaluated using a PBDE standard solution. When connected to a GC-ECD system, the repeatability of the absolute peak area for an injection volume of 15 µl was < 2.7 % RSD for all analytes (except one, BDE-154, 5.9 % RSD) and the carry over was less than 1 %.

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Determination of PBDEs in human adipose tissue by large volume injection narrow bore (0.1 mm id) capillary gas chromatography-electron impact low resolution mass spectrometry

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Summary. Human adipose tissue (n=20) from Belgium was analysed for PBDEs using large volume injection narrow-bore (0.1 mm id) capillary gas chromatography-electron impact low resolution mass spectrometry. Concentrations of PBDEs (sum of BDE 28, 47, 99, 100 and 153) range between 1.7 and 10.1 ng/g fat and are similar to reported values from Spain and Sweden.

Introduction. Due to their persistance and bioaccumulation potential, polybrominated diphenyl ethers (PBDEs) are found in the environment and in humans[1]. They have been measured in adipose tissue samples from Spain[2], Sweden[3] and Finland[4]. Because concentrations of PBDEs in humans are in the order of ng/g lipid weight, most of the analytical work has been carried out by highly sensitive systems as gas chromatography-high resolution mass spectrometry[5] (GC/HRMS) or gas chromatography-negative chemical ionization low resolution mass spectrometry[6] (GC/NCI-LRMS).

Electron impact low resolution mass spectrometry (EI-LRMS) was used mostly for the determination of PBDEs in samples with relatively high concentrations[7], but its use for humans was limited due to lower sensitivity. Here we show that a combination of large volume injection (LVI), narrow-bore (0.1 mm id) capillary column and EI-LRMS can be used for the determination of PBDEs in human adipose tissue. This is the first report on PBDE levels in Belgian population.

Methods and instrumentation. Human adipose samples (n=20) were obtained by autopsy from the Universitary Hospital of Antwerp, Belgium. One gram of each sample was accurately weighted and mixed with anhydrous Na_2SO_4 till a fine floating powder was obtained. After addition of 100 µl of internal standards (13.06 pg/µl in iso-octane from a mixture of ^{13}C-BDE 47, 99 and 153), the powder was extracted by automated hot Soxhlet for 2 hours with 75 ml of hexane : acetone : dichlormethane = 3:1:1 (v/v). After concentration and determination of lipid content, the extract was subjected to clean-up on 2 successive solid phase cartridges containing acid silica and acid silica : neutral silica : deactivated basic alumina (from top to bottom), respectively. PBDEs (and PCBs) were eluted with 50 ml hexane. The eluate was concentrated to almost dryness and 100 µl of the recovery standard (bromobiphenyl (PBB) 80 – 18pg/µl in iso-octane) was added, after which it was reconcentrated to approximately 60 µl.

A Hewlett Packard 6890 GC was connected via a direct interface with a HP 5973 mass spectrometer. A 10m x 0.10mm x 0.10µm AT-5 (5% phenyl polydimethyl siloxane) capillary column (Alltech) was used with helium as carrier gas at constant flow of 0.4 ml/min. Twenty µl (4x5 µl) were injected in a Gerstel (CIS 4) PTV in solvent vent mode (vent flow 100 ml/min for 1 min, injector at 70°C for 1.1 min and then heated with 700°C/min to 270°C) with the split outlet opened after 2.1 min. The interface temperature was set at 300°C. The temperature program of the AT-5 column was 2.2 min at 70°C, 40°C/min to 230°C, 25°C/min to 280°C, 5 min at 280°C. The LRMS was operated at 70 eV in selected ion monitoring (SIM) mode. Dwell times were set at 10 msec. Two most abundant ions were monitored for each level of bromination for native and labeled PBDE. Retention times, ion chromatograms and ratio of the monitored ions were used as identification criteria. A deviation of ion ratios of less than ±20% from the theoretical value was considered acceptable.

Results and discussion. The targeted compounds eluted from the GC column between 6.1 and 9.2 min. The short retention times are due to the use of a narrow-bore capillary column (id=0.1mm), which offers the resolution power of conventional column (id=0.25mm), but decreases the analysis time with more than 50% (Figure 1). Furthermore, the smaller id results in a smaller peak width and an increased mass sensitivity (higher S/N ratios for the same amount injected). Thus, for human samples with relatively high concentrations of PBDEs (adipose tissue), it is possible to use EI-LRMS with sufficient accuracy. Moreover, with the introduction of extract volumes up to 20 µl, low detection limits (DL) can be achieved (Table 1). A good linearity ($r^2>0.995$) was achieved for each compounds between 2 x DL (calculated for a S/N=3) and 10 ng/g fat. Recoveries of internal standards, ^{13}C-labeled BDEs (calculated based on PBB 80 added prior to injection) were between 81 and 103% with a standard deviation of less than 21% (Table 1). Analysis of two samples of biota (eel and porpoise liver) used for the first interlaboratory test on PBDE[8], showed a variation of 10-15% from mean values.

Concentrations of PBDEs in Belgian adipose tissue were ranging between 1.70 and 10.13 ng/g fat. This is in concordance with concentrations reported in other countries[2-4]. Interestingly, BDE 47 was not always the most abundant congener. Higher values of BDE 153 were obtained in some samples. Blanks were run to check for interferences, but no significant contribution to these high values was observed. Similar trends were seen in some samples (n=13) from Spain[2] (Table1). Following the addition of appropriate internal standards, the extraction and clean-up procedure allowed also the determination of PCBs and DDTs on the same sample aliquot. Low correlation coefficients were obtained between PBDEs and PCBs (r^2=0,34) or PBDE and age (r^2=0.07). Meneses[2] has observed in 13 samples that the highest as well as the lowest levels of PBDEs correspond to elder men, while for other persistent organohalogenated contaminants (PCBs, DDTs) older persons were found to have higher levels due to bioaccumulation and long-half lives of the compounds.

Table 1. Acquisition parameters and concentrations of targeted compounds in Belgian human adipose tissue samples (n=20).

Target compounds	RT (min)	Ions	Recovery (%)	DL (ng/g fat)	Mean ± SD (ng/g fat)	Range (ng/g fat)	Spain[2] (ng/g fat)
BDE 28	6.18	406, 408		0.05	0.11 ± 0.07	nd – 0.26	
^{13}C-BDE 47*	7.03	496, 498	81 ± 12				
BDE 47	7.03	484, 486		0.1	1.45 ± 1.01	0.54 – 4.71	1.36
^{13}C-BDE 99*	7.94	576, 578	84 ± 17				
BDE 99	7.95	564, 566		0.15	0.29 ± 0.38	nd – 1.61	0.42
BDE 100	7.72	564, 566		0.15	0.48 ± 0.34	nd – 1.50	0.51
^{13}C-BDE 153*	9.16	496, 498	103 ± 21				
BDE 154	8.92	484, 486		0.25	nd	nd	nr
BDE 153	9.17	484, 486		0.25	1.47 ± 0.70	nd – 2.79	1.83
Sum BDE					3.73 ± 2.11	1.70 – 10.13	
Sum PCBs					830.8 ± 428.5	263.4 – 1757.4	

nd-not detected, nr-not recorded

When compared with HRMS, EI-LRMS are instruments easy to maintain and operate. It also allows the use of 13C-labeled standards as internal standards (this procedure is not possible when using NCI-LRMS). Moreover, the higher selectivity of EI is important compared to NCI where often only Br ions can be measured. However, the response factors in EI are very different for congeners with different degree of bromination. Thus, detection of highly brominated congeners is problematic in EI-LRMS, due to low concentrations to be measured and poor sensitivity. It is possible to tune manually the MS to obtain increased sensitivity for higher masses. The problem can be overcome by using large volume injection which allows the introduction of a larger amount of extract, thus increased sensitivity. However, the clean-up procedure should be very efficient as interferences may easily disturb the chromatogram.

Conclusions. GC/EI-LRMS in combination with LVI and narrow bore capillary column was found suitable for the determination of major PBDE congeners in 20 human adipose tissue samples from Belgium and may serve as an alternative for GC/NCI-MS and GC/HRMS.

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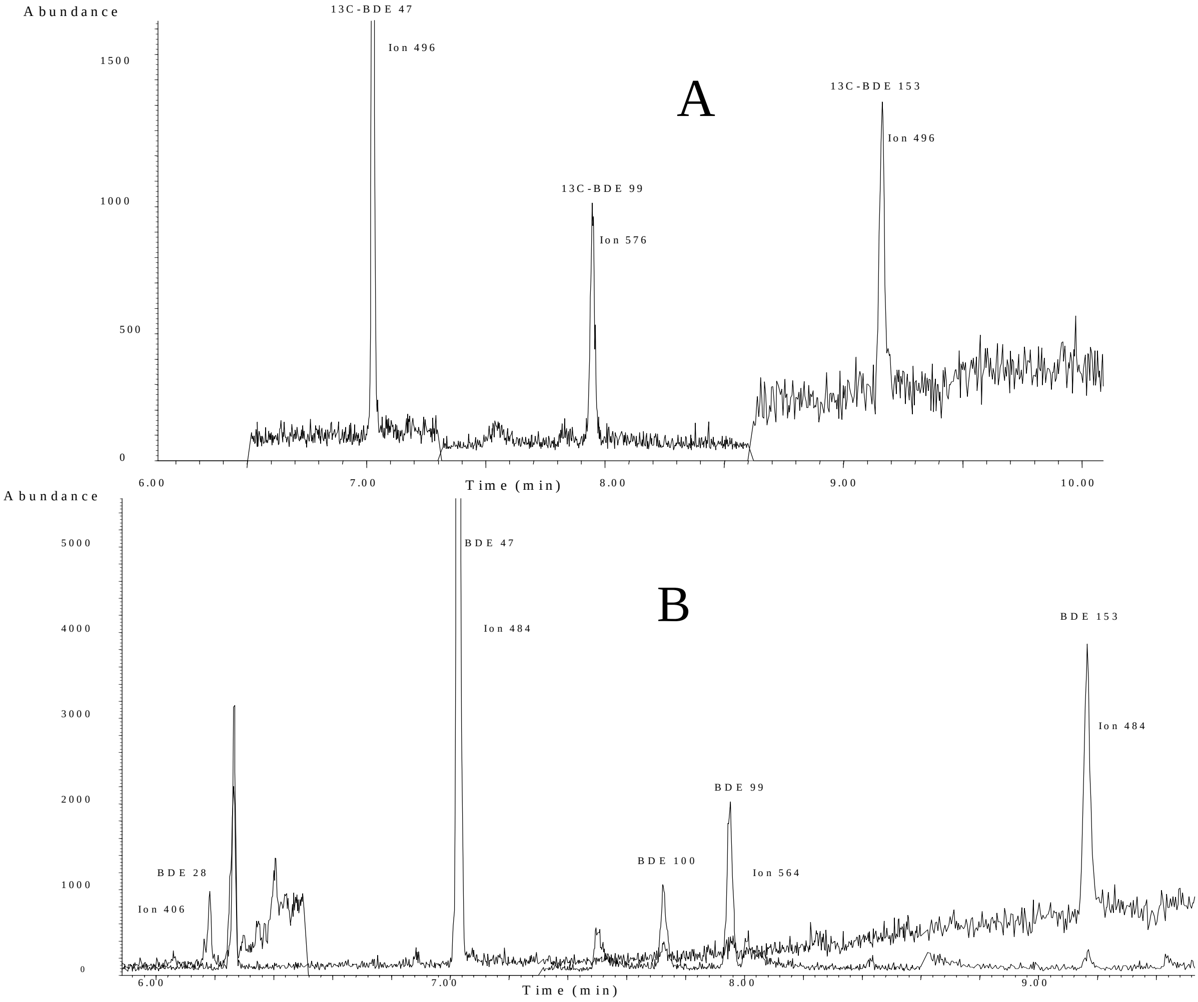
Figure 1. Selected ion chromatograms of a human adipose tissue extract: ^{13}C-labeled BDEs (chromatogram A) and target PBDEs (chromatogram B).



Two approaches for extraction and analysis of Brominated Flame Retardants (BFR) and their degradation products in recycled polymers and BFR containing water

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In a first step we were able to develop a fast method (microwave assisted extraction combined with liquid chromatography) for identifying and quantifying TBBPA, oligomeric epoxy with TBBPA, DBDPE, DBB and Brominated trimethylphenyl Indan in recycled ABS and PS.

In a second step the influence of water and pH on the degradation products of TBBPA, DBB and DBDPE was followed by solid phase microextraction/gas chromatography-mass spectrometry. TBBPA was the most sensitive flame retardant towards ageing. 5 degradation products including Bromophenol, 2,4 dibromophenol and 2,4,6 tribromophenol were successfully identified.

Extraction of BFR from ABS and PS

Microwave assisted extraction (MAE)

All extractions were performed with an MSP-1000 microwave from CEM corporation.

The procedure was as follow: 0,5 g of sample was cooled with liquid nitrogen. It was then ground to a size of 1 mm by using a centrifugal mill from Retsch (type ZM1). The sample was mixed with 15 mL isopropanol and 15 mL methanol in a microwave extraction vessel. All solvents used were Lichrosolv (HPLC) grade from Supelco. The sample was heated in the extraction chamber to 130ºC: 10 minutes from 0ºC to 130ºC, 20 minutes at 130ºC.

Liquid chromatography (HPLC)

The separations were performed with an HPLC Series II 1090 from Hewlett Packard. Usually 10 µl of the sample was injected. The column was a 250 mm LC-18 reverse-phase from Supelco with 4,6 mm ID and a particle size of 5 µm. 100 % methanol was used as mobile phase at a flow-rate of 1 mL/min. Detection wavelengths were 206 and 291 nm.

TBBPA, oligomeric epoxy with TBBPA, DBDPE, DBB and Brominated trimethylphenyl Indan were successfully extracted from recycled ABS and PS, quantified and identified. The new method consisting of MAE combined with HPLC save a lot of time and solvent when compared to Soxhlet extraction. Furthermore, MAE provides a very good control over the temperature of extraction as well as an environmentally friendly closed environment. This method can be applied for extraction of all kind of additives present in plastic materials[1].

Degradation study of TBBPA, DBB and DBDPE in water at 100°C and pH 7 (resp. 5)

5 mg of TBBPA (resp. DBB and DBDPE) were placed in sealed vials with 15 mL water at 100°C during 6 weeks. Sampling was performed every week. The mixture BFR/water was extracted by 5 mL chloroform. The solvent is then evaporated and the remaining solid extract analysed by solid phase microextraction/gas chromatography-mass spectrometry. Solid phase extraction is of particular interest when performing ageing studies and extracting low molecular weight compounds coming from degradation mechanisms[2,3].

Solid phase microextraction

The flame retardant degradation products were extracted with fibers coated with carbowax/divinylbenzene (CB/DVB). The thickness of the coating material was 65 μm. The fiber was exposed to the headspace over the solid extract for 30 min at 80°C. The thermal desorption time of the fiber in the GC injector was 5 min.

Empty bottles and water were tested to give the impurities from the background.

Gas Chromatography-Mass Spectrometry (GC-MS)

The samples were analysed by a Finnigan polaris GCQ-Plus^{TM} mass spectrometer. A Cp-Sil 8CB (5% phenyl / 95% polydimethylsiloxane) capillary column from Chrompack (30 m * 0,250 mm) was used. The column temperature was held at 40°C for 1 min and then programmed to 250°C at 10°/min. The injector temperature was 220°C. Helium was used as a carrier gas.

The relative concentrations of Bromophenol, 2,4 dibromophenol and 2,4,6 tribromophenol as well as 2 other molecules coming from the degradation of TBBPA (not yet fully characterised) were followed during the 6 weeks of ageing. Of all these degradation products, 2,4 dibromophenol (main peak in the chromatograms) is the molecule that shows the fastest increase in concentration. It is interesting to note that at pH 7 the degradation of TBBPA seems to occur faster than at pH 5. It is due to the fact that TBBPA is more soluble at pH 7 than pH 5 in water at 100°C.

Both DBB and DBDE are not soluble in water. We do not see either any major release of degradation products during the ageing period of 6 weeks.

Acknowledgements:

The Brite-Euram Sure-Plast european project is gratefully acknowledged for financial support. Indumetal Recycling S.A. (Asua-Erandio, Spain) and Gaiker (Zamudio, Spain) are thanked for providing reference samples and BFR.

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P8

Vapor Pressures of the Polybrominated Diphenylethers

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Summary:

The supercooled liquid vapor pressures P_L of 23 polybrominated diphenylether congeners were determined as a function of temperature with a gas chromatographic retention time technique. P_L at 298.15 K ranged from 0.1 Pa for monobrominated diphenylethers to 10^{-6} Pa for hepta-brominated diphenylethers. The halogen substitution pattern was found to influence PBDE vapor pressure, indicating that congeners with bromine substitutions in the ortho positions to the ether-link have higher vapor pressures.

Introduction:

Despite the recent interest in polybrominated diphenylethers (PBDEs), basic physical-chemical property data are sparse, in particular on a congener-specific basis. Here we report the supercooled liquid vapor pressures P_L and the enthalpies of vaporization $\Delta_{VAP}H$ for 23 PBDE congeners, determined with the gas chromatographic (GC) retention time technique by Bidleman[1]. The method is particularly suited to substances of low polarity, because the interactions of an apolar molecule with an apolar stationary GC phase such as polydimethyl-siloxane resemble the interactions between that molecule and its own pure liquid phase[2]. It is the only feasible method, if only very small quantities of a compound are available, as is presently the case for individual PBDE congeners. The investigated set of chemicals includes the congeners most prevalent in environmental samples, most notably PBDE-47 and PBDE-99.

Data Analysis:

The procedure for deriving P_L of the PBDEs from GC retention times followed the method developed and described by Bidleman[1]. Briefly, for each analyte a vapor pressure P_{GC} was calculated using:

$$\ln (P_{GC}/Pa) = (\Delta_{VAP}H / \Delta_{VAP}H_{ref}) \cdot \ln (P_{Lref}/Pa) + C \qquad (1)$$

where P_{Lref} and $\Delta_{VAP}H_{ref}$ refer to the well-established vapor pressure and enthalpy of vaporization of a standard reference compound. In this case, this compound was p,p'-DDT with a vapor pressure of $\log (P_L/Pa) = 12.48 – 4699.5 (T/K)^{-1}$. The ratio of the enthalpies and the constant C in equation 1 were obtained by plotting and linearly regressing the ratios of the measured isothermal GC retention times t_R/t_{Rref} at each temperature against the vapor pressure of the reference compound at that temperature using[1]:

$$\ln (t_R/t_{Rref}) = [1-(\Delta_{VAP}H / \Delta_{VAP}H_{ref})] \ln (P_{Lref}/Pa) – C \qquad (2)$$

Equation 2 assumes that the infinite dilution activity coefficients in the stationary phase are the same for the analyte and the reference compound[9] . As this is an approximation, P_{GC} is not always identical to the vapor pressure of the (super-cooled) liquid P_L, and a calibration of the method with closely related compounds is advisable[7]. This calibration involved eight PCB congeners for which vapor pressure is well known from measurements based on the effusion and gas saturation techniques. The calibration equation was:

$$\log (P_{GC} / Pa) = 1.0368 \cdot \log (P_L / Pa) - 0.0239 \qquad r^2 = 0.9718 \qquad (3)$$

Because the enthalpy of vaporization of the reference compound $\Delta_{VAP}H_{ref}/kJ \cdot mol^{-1}$ is known, $\Delta_{VAP}H$ of the analytes can easily be derived from the enthalpy ratio obtained in the regression of equation 2.

Results:

Table 1 lists the measured vapor pressures P_{GC} and P_L of the 23 PBDE congeners at 298.15 K, as well as the intercepts b_L and slopes m_L of the temperature regressions:

$$\log (P_L / Pa) = m_L / (T / K) + b_L \qquad (4)$$

Enthalpies of vaporization $\Delta_{VAP}H$ are also listed. The values for P_{GC} were highly reproducible as is evident from the small standard deviations derived from three independent determinations.

Discussion:

Clearly, the vapor pressure decreases linearly with increasing size of the molecule. Each additional bromine substitution causes a drop in vapor pressure of the PBDEs by a factor of six to nine. However, the measured vapor pressures within a homologue group, such as the tri- and tetra-bromo diphenylethers, can range over half an order of magnitude. Closer examination of the data revealed that within a homologue group the vapor pressure increases with the number of bromine substitutions in the ortho-positions to the ether-link (2, 2’, 6, 6’). A similar dependence of vapor pressure on the halogen substitution pattern has been noted for the PCBs[3] and was explained by the distortion from planarity between the two aromatic rings caused by multiple halogen substitutions in the ortho-positions. The data presented here suggested that a similar effect may be occurring for the brominated diphenylethers. On average, the addition of a bromine in one of the ortho-positions increased vapor pressure by approximately 0.2 log units. A similar analysis using data reported by Kurz and Ballschmiter[4] indicated that the chlorine substitution pattern has a similar effect on the vapor pressure of polychlorinated diphenylethers (PCDEs), although it was less pronounced than for the PBDEs. In contrast to the PCBs, this effect can not be explained by a lack of planarity, because even in the absence of halogen substitutions the diphenylether structure is non-planar. The bulky halogens in the 2,2’,6,6’ positions obviously cause subtle differences in three dimensional molecular structure or polarity that result in weaker intermolecular interactions in the pure substance and thus slightly higher vapor pressure.

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Table 1. GC Determined Vapor Pressures P_{GC} with Standard Deviations from Three Independent Determinations, Supercooled Liquid Vapor Pressure P_L at 298.15 K, Enthalpies of Vaporization $\Delta_{vap}H$, and Slopes m_L and Intercepts b_L of Equation 4 for 23 PBDE Congeners.

ID	**Br – substitution**	**P_{GC} / Pa**	**P_L / Pa**	**$\Delta_{vap}H$ / kJ·mol^{-1}**	**m_L**	**b_L**
BDE-1	2-	0.160 ± 0.003	0.163	-63.7	-3327	10.37
BDE-2	3-	0.125 ± 0.002	0.128	-65.4	-3416	10.56
BDE-7	2,4-	0.0153 ± 0.0004	0.0168	-75.4	-3941	11.34
BDE-8	2,4’-	0.0124 ± 0.0002	0.0137	-76.4	-3991	11.42
BDE-10	2,6-	0.0256 ± 0.0005	0.0277	-73.1	-3818	11.25
BDE-12	3,4-	0.0107 ± 0.0003	0.0119	-77.4	-4020	11.56
BDE-13	3,4’-	0.0101 ± 0.0001	0.0113	-77.0	-4044	11.62
BDE-15	4,4’-	0.0088 ± 0.0001	0.00984	-78.0	-4071	11.65
BDE-30	2,4,6-	0.00396 ± 0.00005	0.00456	-85.1	-4232	11.85
BDE-32	2,4’,6-	0.0019 ± 0.0008	0.00225	-83.3	-4352	11.94
BDE-33	2’,3,4-	0.00149 ± 0.00003	0.00178	-81.0	-4443	12.15
BDE-35	3,3’,4-	0.00115 ± 0.00001	0.00139	-86.4	-4512	12.28
BDE-37	3,4,4’	0.0008 ± 0.0003	0.00102	-86.7	-4528	12.20
BDE-47	2,2’,4,4’-	0.00025 ± 0.00001	0.000319	-92.0	-4805	12.62
BDE-66	2,3’,4,4’-	0.00019 ± 0.00001	0.000238	-93.5	-4882	12.75
BDE-69	2,3’,4,6-	0.00032 ± 0.00001	0.000400	-91.1	-4757	12.56
BDE-75	2,4,4’,6-	0.00039 ± 0.00001	0.000492	-90.1	-4706	12.48
BDE-77	3,3,4,4’-	0.000120 ± 0.000004	0.000156	-95.3	-4977	12.89
BDE-82	2,2’,3,3’,4-	0.000048 ± 0.000001	0.0000647	-99.1	-5175	13.17
BDE-99	2,2’,4,4’,5-	0.00005 ± 0.00003	0.0000682	-100.3	-5241	13.41
BDE-115	2,3’,4,4’,6-	0.000022 ± 0.000001	0.0000302	-101.8	-5319	13.32
BDE-153	2,2’,4,4’,5,5’-	0.0000058 ± 0.0000003	0.00000843	-107.6	-5620	13.78
BDE-190	2’,3,3’,4,4’,5,6-	0.00000057 ± 0.00000008	0.000000905	-115.8	-6048	14.24

P9

Estimation of Soot-Water Distribution Coefficients for PBDE by means of HPLC-DAD

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Summary

The soot carbon-water partition coefficient, K_{sc}, for 2,2',4,4'-tetrabromodiphenylether is presented and compared to values from representatives of other compound classes and to published parameters accounting for hydrophobicity. The K_{sc} values are calculated statistically from HPLC chromatograms, using column-packing material of standardized diesel soot.

Introduction

When studying the fate of, e.g., polybrominated diphenylethers (PBDEs), it is important to identify relevant environmental sorbents. The sorbent traditionally considered to determine solid water distribution is organic matter. However, it appears necessary to split general organic matter (TOC) into sub components for better understanding of PBDEs fate, bioavailability and partitioning in e.g., sediment and soil. One such important sub component is soot carbon. It has been shown that soot carbon makes up a small (2 – 15 % of TOC) but important fraction of total particulate matter in aquatic systems.[1,2] In addition, field observed organic matter normalized distribution coefficients (K_{oc}^{obs}) not accounting for soot carbon appear to be elevated compared to predictions.[3] It has therefore been hypothesized that better distribution predictions can be achieved by introducing soot as a major sorbent for organic pollutants such as PBDEs. Hence, the general model for solid-water partitioning is extended with an additive soot term, attributing the influence of soot. [4]

$$K_d = f_{oc}K_{oc} + f_{sc}K_{sc} \qquad (1)$$

where f_{oc} and f_{sc} is fraction organic and soot carbon, respectively, in sorbent, K_{oc} and K_{sc} are organic and soot carbon distribution coefficients. The role of soot for estimating bioavailability for polycyclic hydrophobic compounds has been elaborated in previous papers [4,5]. However, for most of the PBDEs the general lack of literature values calls for initial partitioning studies, resulting in better understanding of their possible fate in natural systems. The aim of this study is to introduce the role of soot in estimating the partitioning of PBDEs in the environment and compare experimentally derived soot partition coefficients from single compounds of the general classes of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins.

Experimental

Experiments have been conducted exploring the partitioning to soot in a HPLC column by water-methanol cosolvency elution for 2,2',4,4'-tetrabromodiphenylether (BDE 47), biphenyl, 2,2',6,6'-tetrachlorobiphenyl (CB 54), and dibenzo-p-dioxin. The detector used was of type diode array, allowing wavelength selection. The column experiments have been conducted in triplicates by injecting 100 µmol of each compound into a column with a solid phase consisting of a mixture of soot (diesel particulate matter, National Institute of Standards and Technology SRM 1650) and porous coarse silica. The soot content was 0.2 % (w/w). Due to the relationship between retardation and partitioning it is possible to calculate partition coefficients from column experiments. Distribution coefficients of the solutes at different water-methanol ratios can be derived from chromatograms using first moment statistics.[6] Variation of the methanol-to-water ratio enables K_d to be $\log_{10}$-linearily extrapolated into pure aqueous conditions.[7] All extrapolated $logK_d$ values is corrected by silica and organic carbon sorption to obtain the final expression describing the sorption to soot:

$$K_{sc} = \frac{K_d - f_{oc}K_{oc} - f_{si}K_{si}}{f_{sc}} \tag{2}$$

where f_{si} is silica fraction in sorbent and K_{si} is pure silica distribution coefficient. All programs for calculating distribution coefficients from HPLC-DAD chromatograms were written in MATLAB © (The Mathworks Inc.).

Results and discussion

In Table 1 $logK_{ow}$, $logK_{oc}$ and $logK_{sc}$ are shown for biphenyl, PBDE congener 47, dibenzo-p-dioxin and PCB congener 54. The estimates of the standard error in the $logK_{ow}$ values are obtained from given references. The $logK_{oc}$ values were calculated using a linear free energy relationship (LFER) between $logK_{oc}$ and $logK_{ow}$, originally established for PCBs.[11] It is clear that using LFER for other compound classes than PCBs is *not* optimal. However, these approximations were done due to the lack of data. The standard error estimation in $logK_{oc}$ were derived using LFER, hence σ_{oc} may be regarded as a crude estimate of the true standard error. The experimental error, σ_{sc}, based on error propagation in experimentally determined soot partition coefficient is small, considering errors introduced by uncertainties in older literature values and the limited applicability of the LFER. However, from equation (2) the contribution of errors in $logK_{oc}$ is scaled down by f_{oc}, a factor much smaller than unity.

Table 1. Summary of soot partitioning studies.

Compound	$logK_{ow} \pm \sigma_{ow}$	$logK_{oc} \pm \sigma_{oc}$	$logK_{sc} \pm \sigma_{sc}$
Biphenyl	4.09 ± 0.3 [8]	3.22 ± 0.27	5.09 ± 0.05
BDE 47 (2,2',4,4')	6.0 ± 0.15 [9]	4.95 ± 0.14	7.44 ± 0.08
Dibenzo-p-dioxin	4.2 ± 0.5 [10]	3.58 ± 0.45	6.13 ± 0.05
PCB 54 (2,2',6,6')	5.21 ± 0.3 [8]	4.23 ± 0.27	6.35 ± 0.08

In Table 1 the soot distribution coefficient varies significantly between the different compound classes here represented. An increase in halogenation and hydrophobicity corresponds to an increase in soot binding affinity. The truly planar dibenzo-p-dioxin as well as the non-planar ortho substituted PCB 54 have different hydrophobicity but tend to bind to soot more similarly than the non planar “ortho substituted” BDE 47. The role of soot for PBDEs has been elucidated and soot’s significant role as an important sorbent for similar compounds is indicated.

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P10

Photo decomposition of brominated diphenylethers in methanol/water

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Summary

The present study indicates that the photo decomposition rate of polybrominated diphenyl ethers (PBDEs) is dependent on the degree of bromination. Further, it confirms the results of previous studies that decaBDE is decomposed to brominated diphenyl ethers with lower degree of bromination and to polybrominated dibensofurans (PBDFs).

Introduction

Since PBDEs are showing increasing levels in the environment[1] there have become an increasing interest in the fate of these substances. One of the questions is whether or not these substances react in the environment, and if they do, how fast and into what. There are few data published on the reactivity of PBDEs. Photochemical reactions are of interests since these types of aromatic substances absorb natural solar light.

Previously mostly the photochemical reactions of decaBDE have been investigated[2, 3]. The photolysis of decaBDE has previously been shown to decompose into PBDE congeners containing 3-9 bromine atoms and PBDFs containing 1-6 bromine atoms[2].

The aim of the present study is to investigate the photo reactivity of PBDE congeners related to degree of bromination of the PBDEs.

Materials and Methods

Chemicals: BDE-138 (2,2',3,4,4',5'-hexaBDE) was synthesized as described by Örn et al.[4] BDE-47 (2,2',4,4'-tetraBDE) and BDE-77 (3,3',4,4'-tetraBDE) were preformed according to Marsh et al.[5] Other PBDE congeners were synthesized as described below. DecaBDE was purchased from Fluka Chemie AG.

Instruments: Gas chromatography-mass spectrometry (GC-MS) was performed on an ion trap GCQ-instrument from Thermoquest. The gas chromatograph was equipped with a fused silica capillary column (DB-5.15 m×0.25 mm, 0.025 mm film thickness, J&W Scientific, Folsom, CA). The temperature program was: 80°C for 5 min, 20°/min to 280°C, the final temperature was held for 20 min. High-performance liquid chromatography was performed on a Shimadzu (LC-4A) equipped with a UV detector (Shimadzu SPD-2AS) and a C18 reversed-phase column (Supelcosil LC-18, 250×4.6 mm, 5μm particles) from Supelco. The detection wavelength was set at 240 nm and the mobile phase 5% water in acetonitril for deca and nona-BDE and 10% water in acetonitril for the other BDEs. The flow rate was 1mL/min. The fluorescent tube was a Philips TL 20W/09N. The fluorescent tube does not emit light with wavelengths below 290 nm.

Synthesis: BDE-99 (2,2',4,4',5-pentaBDE), BDE-183 (2,2',3,4,4',5',6-heptaBDE) and BDE-203 (2,2',3,4,4',5,5',6-octaBDE) were synthesized by the reaction of 2,2',4,4',5,5'-hexabromodiphenyliodonium chloride and 2,4-dibromophenol (Aldrich-Chemie), 2,3,4,6-tetrabromophenol and pentabromophenol (Aldrich-Chemie) respectively, in an aqueous solution in the presence of a bas. 2,2',4,4',5,5'-Hexabromodiphenyliodonium chloride was obtained by modifications of the method described by Marsh et al.[5] for other bromodiphenyliodonium chlorides using 1,3,4-tribromobenzene (Aldrich-Chemie) and iodylsulfate as starting materials. 2,3,4,6-Tetrabromophenol was obtained by treating 3-bromophenol (Aldrich-Chemie) with bromine in acetic acid.

Photochemical reactions: The photochemical experiments where performed in a cylindrical vessel with a height of 480 mm, an outer diameter of 85 mm and a volume of 1.6 L. The fluorescent tube was placed in the middle to ensure uniform illumination. All of these experiments where performed in a mixture of methanol:water (80:20). The initial concentrations where 1 µM, except for decaBDE where the initial concentration was 0.4 µM. All calculations have been made on the assumption of first order reaction.

Results and Discussion:

The reaction rate seems to be almost totally dependent on the degree of bromination (table 1). The low brominated PBDE congeners decompose slowly while octa- and decaBDE decompose quite rapidly. The assumption of first order reaction seems to be relevant since there are constant half-lives (figure 1) of about 30 minutes.

Table 1.

BDE nr.	Number of bromine	Rateconst.(min^{-1})	Half lives
47	4	$4*10^{-5}$	12 d
77	4	$3*10^{-5}$	16 d
99	5	$2*10^{-4}$	2.4 d
138	6	$4*10^{-4}$	1.2 d
183	7	$4*10^{-4}$	1.2 d
203	8	0.0023	5 h
209	10	0.024	30 min

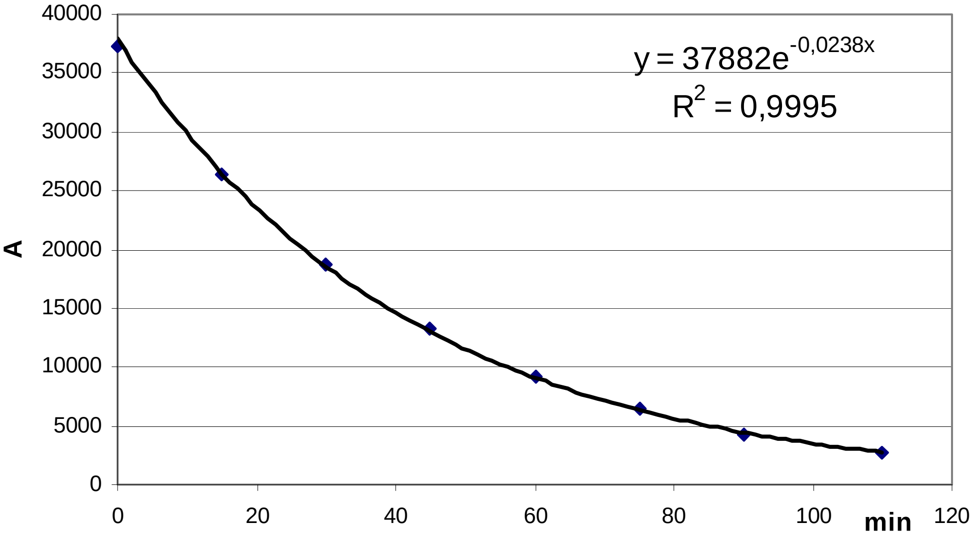

Figure 1. Photo decomposition of decaBDE. Y-axes represents the integrated area under the peak in the HPLC chromatogram.

The decomposition of decaBDE generates a number of decomposition products with lower degree of bromination (figure 2). All compounds containing more than six bromine atoms are PBDEs. Very small amounts of compounds containing six bromine atoms may have been found as well. Compounds with less then six bromine atoms all seem to be PBDFs. These findings are in accordance with those of Watanabe and Tatsukawa[2] except that they found PBDEs with less than six bromine atoms and PBDFs with more than five bromine atoms. This can be due to the use of different emission sources and different solvents in the photochemical reactions. Since decaBDE is decomposed quite rapidly and the reaction rate decreases with decreasing number of bromine (table 1) the levels of the low brominated diphenyl ethers increases quite rapidly in the solution. The total area under the peaks in the HPLC chromatogram has only decreased by approximately 10% when almost all decaBDE has been decomposed. This indicates that almost all of the original substance has decomposed to PBDEs with lower degree of bromination and PBDF congeners. The decrease in the total area can be explained by the decreasing response at 240 nm with decreasing bromination.

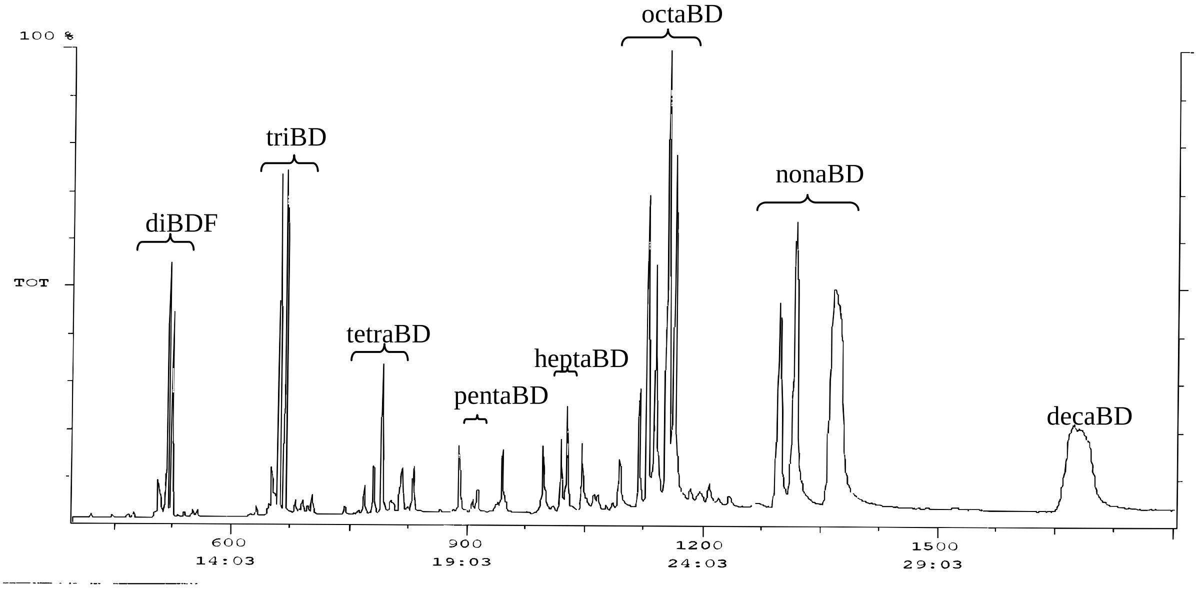

Figure 2. GC-MS chromatogram of decaBDE illuminated 90 minutes.

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Testing Concept for Comparable Evaluation of Emissions of Brominated Flame Retardants and Thermal Degradation Products: Comparison of Halogenated and Halogen-free Flame Retarded Printed Wiring Boards

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Summary

A testing concept including a standardised combustion unit, a sampling device allowing a broad spectrum of analysis and a scheme for comparable evaluation using a natural polymer as reference material is presented. The procedure allows simulation and comparable evaluation of possible emissions of halogenated flame retardants and thermal degradation products during combustion, accidential fires, thermal recycling etc. A comparison of three halogen-free printed wiring boards to a standard FR4 board and a reference is presented to illustrate usefulness of the procedure.

Introduction

Presence of halogens (Br, Cl) in various products such as electronic devices or plastics are well known to be able to form toxicologically relevant thermal degradation products under thermal stress conditions (combustion, accidental fires, thermal recycling processes). Polyhalogenated dioxins and furans (PXDD/PXDF) are examples of such degradation products and have been identified e.g. in emissions from waste incineration[1, 2] or ambient air of recycling plants[3].

Presence of polybrominated dioxins and furans (PBDD/PBDF) are often connected with presence of brominated flame retardants, both as impuritiy or by-product of the corresponding flame retardant itself or in emissions formed during thermal stress from the flame retardant [2,4]. Considering formation or by-products of PXDD/PXDF and considering toxicological relevance of brominated flame retardants itself [5] these compounds are under increased scrutiny in Europe. Furthermore, considering product safety and environmental properties of products, manufactures and distributors of flame retarded products are focusing on replacement of halogenated flame retardants by halogen-free materials.

Consequently, there is a need for product testing both, for evaluation of potential hazardous emissions through thermal stress of flame retarded products and evaluating improvements by halogen-free substitutes. Oekometric has developed a testing concept, allowing comparable evaluation of emissions of brominated flame retardants or thermal degradation products under standardised conditions. This procedure has been used for example to comparably evaluate potential emissions of halogen-free flame retarded printed wiring boards from different suppliers as well as in comparison to halogenated flame retarded standard board.

Methods and Materials

The testing concept (Figure 1) is based on a standardised combustion unit coupled with a sampling device allowing simulation of a wide spread of thermal stress conditions and efficient sampling of emissions. Comparable evaluation of emission data of individual products are done by using comparable products (standard materials, materials from other suppliers etc.) and a reference material. The natural polymer beech wood is used as reference material. Smoke from beech wood is an officially accepted additive in food (German Ordinance on Admission of Additives in Food) and represents therefore an officially tolerated input of thermal degradation products into food chain. Emissions from consumer products as determined by the procedure described below are relatively compared other products and the reference material.

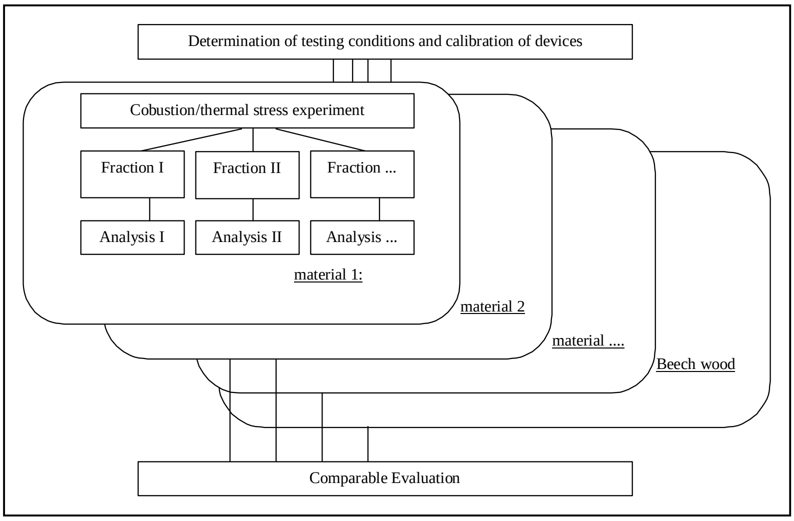

Figure 1: General testing concept

The testing procedure uses a standardised combustion unit according to DIN 53426 and ISO/TR 9122 (Figure 2). This unit is suited for the simulation of most classes of fire-stages such as non-flaming decomposition, flaming developing fires and flaming combustion.

Emission samples were taken by passing effluent fume gases over corresponding adsorbent materials or through absorption solutions (depending on analytical parameters). Figure 2 shows an example of such a sampling device as used in the experiments for printed wiring boards described below.

The sampling device allows analysis of a variety of toxicologically relevant compounds. Usual analysis spectrum for product testing in connection with materials suspected to contain halogenated compounds includes PCDD/PCDF, Chlorinated Phenols (CP), PBDD/PBDF, Polybrominated Diphenylethers (PBDE), Polybrominated Biphenyls (PBB), Brominated Phenols (BP), Polycyclic Aromatic Hydrocarbons (PAH), GC-MS-Screening of high volatile and semi volatile compounds as well as selected inorganic compounds. Further chemical analytical parameters as well as biological parameters (toxicity assays) are possible.

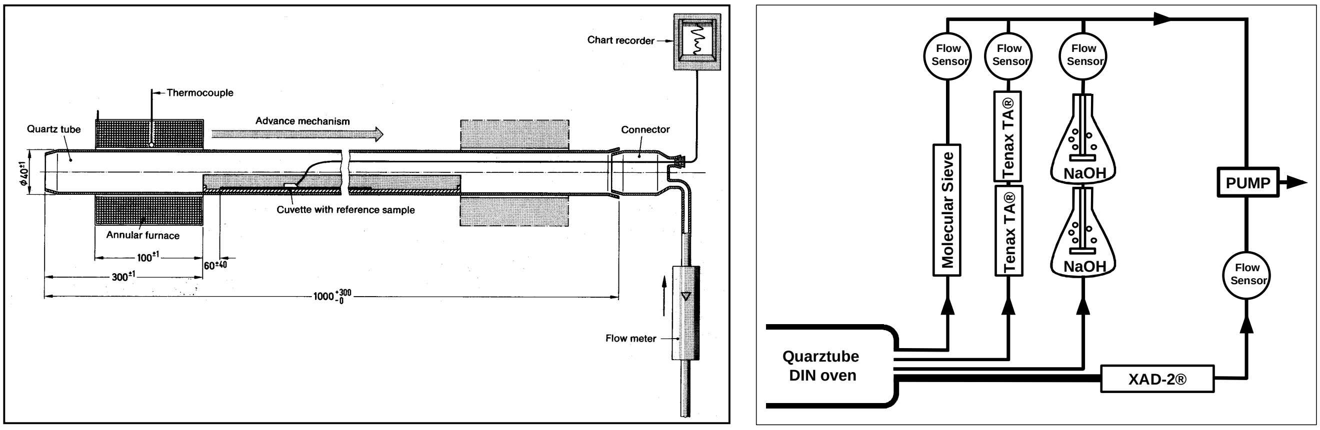

Figure 2: Combustion unit according to DIN 53436 [6] and example of a sampling device

Results: Comparison of halogented flame retarded and halogen free printed wiring boards

With the procedure illustrated above, Oekometric has e.g. comparably evaluated printed wiring boards (PWB) made using “halogen-free” laminates from three different suppliers. A standard FR4-PWB was used as a control and beech wood – as illustrated above – as reference. A combustion at 600°C were investigated [7]. Table 2 list results for PCDD/PCDF and PBDD/PBDF. Supplier 3 could be identified to have a material with relevant chlorine levels to form 2,3,7,8-substituted PCDD/PCDFs under the given conditions. This findings were confirmed by chlorophenol results [7]. Considering PBDD/PBDF only formation of monobrominated congeners could be identified from the “halogen-free” boards, again with supplier 3 providing the highest levels. As expected, high levels could be detected in the FR4 sample. PBB could only be detected from the FR4 board (mono – tri) at levels of 1- 9 mg/kg combusted material. No PBDE could be detected in any sample.

Conclusion

Using the described testing procedure it was possible to control improvement of emission behaviour of “halogen-free” flame retarded printed wiring boards in comparison to standard brominated flame retarded FR4 board. Furthermore, differences in remaining halogen levels or in the ability to form PXDD/PXDF could be identified between different suppliers of “halogen-free” boards. This example illustrates usefulness of the testing procedure in product development and product testing concerning reduction of hazardous emissions during combustion, accidential fires or thermal recycling processes of products.

Table 2: Results PCDD/PCDF and PBDD/PBDF [7]

	Unit	**Supplier 1 600 °C**	**Supplier 2 600 °C**	**Supplier 3 600 °C**	**FR4 600 °C**	**Beech wood 600 °C**
Total amount of TCDD	µg/kg c. m.1)	< 0.10	< 0.10	1.05	< 0.10	< 0.10
Total amount of PeCDD	µg/kg c. m.	< 0.10	< 0.10	0.47	< 0.10	< 0.10
Total amount of HxCDD	µg/kg c. m.	< 0.10	< 0.10	0.26	< 0.17	< 0.10
Total amount of HpCDD	µg/kg c. m.	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Total amount of TCDF	µg/kg c. m.	0.93	< 0.10	5.85	< 0.10	< 0.10
Total amount of PeCDF	µg/kg c. m.	0.47	< 0.10	2.46	< 0.39	< 0.10
Total amount of HxCDF	µg/kg c. m.	< 0.10	< 0.10	0.64	< 0.18	< 0.10
Total amount of HpCDF	µg/kg c. m.	< 0.10	< 0.10	0.21	< 0.26	< 0.10
2,3,7,8-TCDD	µg/kg c. m.	< 0.01	< 0.01	0.01	< 0.01	< 0.01
1,2,3,7,8-PeCDD	µg/kg c. m.	< 0.01	< 0.01	0.04	< 0.01	< 0.01
1,2,3,4,7,8-HxCDD	µg/kg c. m.	< 0.01	< 0.01	0.02	< 0.01	< 0.01
1,2,3,6,7,8-HxCDD	µg/kg c. m.	< 0.01	< 0.01	0.03	< 0.10	< 0.01
1,2,3,7,8,9-HxCDD	µg/kg c. m.	< 0.01	< 0.01	0.02	< 0.05	< 0.01
1,2,3,4,6,7,8-HpCDD	µg/kg c. m.	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
OCDD	µg/kg c. m.	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
2,3,7,8-TCDF	µg/kg c. m.	< 0.01	< 0.01	0.07	< 0.01	< 0.01
1,2,3,7,8-PeCDF	µg/kg c. m.	< 0.01	< 0.01	0.12	< 0.18	< 0.01
2,3,4,7,8-PeCDF	µg/kg c. m.	< 0.01	< 0.01	0.13	< 0.01	< 0.01
1,2,3,4,7,8-HxCDF	µg/kg c. m.	< 0.01	< 0.01	0.08	0.03	< 0.01
1,2,3,6,7,8-HxCDF	µg/kg c. m.	< 0.01	< 0.01	0.07	0.03	< 0.01
1,2,3,7,8,9-HxCDF	µg/kg c. m.	< 0.01	< 0.01	0.01	< 0.01	< 0.01
2,3,4,6,7,8-HxCDF	µg/kg c. m.	< 0.01	< 0.01	0.10	< 0.08	< 0.01
1,2,3,4,6,7,8-HpCDF	µg/kg c. m.	< 0.03	< 0.03	0.13	0.30	< 0.03
1,2,3,4,7,8,9-HpCDF	µg/kg c. m.	< 0.03	< 0.03	< 0.03	0.07	< 0.03
OCDF	µg/kg c. m.	< 0.10	< 0.10	0.19	0.84	< 0.10
I-TEQ (includ. detection limit):	µg/kg c. m.	0.03	0.03	0.14	0.07	0.03
I-TEQ (exclud. detection limit):	**µg/kg c. m.**	**0.00**	**0.00**	**0.14**	**0.01**	**0.00**

	Unit	**Supplier 1 600 °C**	**Supplier 2 600 °C**	**Supplier 3 600 °C**	**FR4 600 °C**	**Beech wood 600 °C**
Total amount MBDD	µg/kg c. m.1)	< 1.0	< 1.0	< 1.0	10381.0	< 1.0
Total amount DBDD	µg/kg c. m.	< 1.0	< 1.0	< 1.0	8872.0	< 1.0
Total amount TrBDD	µg/kg c. m.	< 1.0	< 1.0	< 1.0	2599.0	< 1.0
Total amount TeBDD	µg/kg c. m.	< 1.0	< 1.0	< 1.0	975.0	< 1.0
Total amount PeBDD	µg/kg c. m.	< 1.0	< 1.0	< 1.0	340.0	< 1.0
Total amount HxBDD	µg/kg c. m.	< 5.0	< 5.0	< 5.0	129.0	< 5.0
Total amount MBDF	µg/kg c. m.	1.3	6.3	189.0	23536.0	< 1.0
Total amount DBDF	µg/kg c. m.	< 1.0	< 1.0	< 1.1	11748.0	< 1.0
Total amount TrBDF	µg/kg c. m.	< 1.0	< 1.0	< 1.0	1770.0	< 1.0
Total amount TeBDF	µg/kg c. m.	< 1.0	< 1.0	< 1.0	593.0	< 1.0
Total amount PeBDF	µg/kg c. m.	< 1.0	< 1.0	< 1.0	232.0	< 1.0
Total amount HxBDF	µg/kg c. m.	< 5.0	< 5.0	< 5.0	107.0	< 5.0
2,3,7,8-TBDD	µg/kg c. m.	< 0.1	< 0.1	< 0.1	1.1	< 0.1
1,2,3,7,8-PBDD	µg/kg c. m.	< 0.1	< 0.1	< 0.1	4.5	< 0.1
1,2,3,4,7,8-/ 1,2,3,6,7,8-HxBDD	µg/kg c. m.	< 0.5	< 0.5	< 0.5	5.0	< 0.5
1,2,3,7,8,9-HxBDD	µg/kg c. m.	< 0.5	< 0.5	< 0.5	3.1	< 0.5
2,3,7,8-TBDF	µg/kg c. m.	< 0.1	< 0.1	< 0.1	1.4	< 0.1
1,2,3,7,8-PBDF	µg/kg c. m.	< 0.1	< 0.1	< 0.1	3.6	< 0.1
2,3,4,7,8-PBDF	µg/kg c. m.	< 0.1	< 0.1	< 0.1	5.6	< 0.1
1,2,3,4,7,8-/1,2,3,6,7,8-HxBDF	µg/kg c. m.	< 0.5	< 0.5	< 0.5	26.7	< 0.5
2,3,4,6,7,8-HxBDF	µg/kg c. m.	< 0.5	< 0.5	< 0.5	6.2	< 0.5
1.2.3.7.8.9-HxBDD	µg/kg c. m.	< 0.5	< 0.5	< 0.5	0.7	< 0.5

1) c. m. = combusted material

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Investigations on Emissions Of Flame Retardants from Consumer Products and Building Materials

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Summary

The objective is the investigation of the emission of flame retardants from different building materials and consumer products and to get information about their emission behavior and contribution to the contamination of the indoor environment.

Special emission test chambers will be used as a reference method for the emission tests. The advantage of emission test chambers is the faultless assignment of emitted substances to the material under standardized conditions in comparison to real indoor measurements. In addition, it is possible to determine the time-dependence of emissions as an important parameter for emission test duration.

Conception

There are five product groups of interest:

- upholstered furniture
- mattresses
- personal computers (monitor, computer, printer)
- PU insulating boards and other comparable materials (PS insulating boards e.g.)
- PU assembly foam

In this project, halogenated and non-halogenated organic flame retardants will be investigated. Mainly, the following substances are of interest: polybrominated diphenylethers, polybrominated biphenyls, hexabromocyclododecane, tetrabromobisphenol A, decabromodiphenylethane, chlorinated paraffines, and aryl/alkyl phosphoric esters.

All relevant information on flame retardants from a recent research project of the German Federal Environmental Office dealing with the assessment of environmentally significant flame retardants will be taken into consideration. Up to 50 measurements of different materials or material combinations of the mentioned product groups are planned. Their emission behavior will be tested over a period of at least 28 days under standard conditions (temperature: 23°C, relative humidity: 50%, area specific air flow rate: $1m^3/m^2h$ or other product specific air flow rates, air velocity: 0.1 - 0.3m/s). Additionally, measurements under special conditions, e.g. at elevated temperature or working conditions (PC) are variations. The test program includes 5 emission measurements per product group. The 25 measurements left may be used for an additional testing of several products or for testing by accelerated aging or long-time testing. Important parameters are time-dependence of emission, time lag between manufacturing and measuring, procedure of sampling, and the influence of storage and aging. Most of the tests will be done in special $1m^3$ and 20 l emission chambers and emission test cells. The known larger chambers are unsuitable for substances with a boiling point higher than 200°C because of sink effects.

Simultaneously, a direct analysis of the flame retardant content of the products or parts of it will be carried out. Applied techniques are classical soxhlet extraction and additionally, direct thermal desorption. This dynamic head space technique has to be investigated for qualitative/quantitative propositions to assess the emission capability of materials. A screening method also needs to be tested. Comparison measurements are planned.

Basically, all sampling and testing methods will be optimized for the selected flame retardants and their volatility. Reference measurements with several institutes as a requirement for an accepted test method for e.g. an eco-label will take place.

Exchange of know-how with national and international institutes and manufacturers of flame retardants and flameproof products are planned. It is part of the project to present results at related symposia.

Equipment

The Federal Institute for Material Research and Testing (BAM) provides a variety of emission test chambers and cells, respectively, as listed below. These test chambers and cells meet the requirements for emission measurements according to the European Prestandards ENV 13419-1 and ENV 13491-2.

- standard-VOC-emission test chambers, $1m^3$
- 20 l glass emission test chambers
- different emission test cells
- $20m^3$ emission test chamber,
- clean air supply
- humidification system

- different techniques for a reduction of chamber sink and memory effects for very low volatile/high boiling substances
- equipment for measurements of air mixing

The laboratory IV.22 of BAM is also well equipped for sample preparation described in prENV 13491-3, and Tenax sampling/thermal desorption/analysis by GC-MS according to the soon expected draft of the European Prestandard ENV 13491-4. Additionally, there are several methods of air sampling on a wide range of sorbent materials like special polyurethane foam (PUF) for instance. PUF is tested for several substances like dioxins, furans, PCB's, PAH, and some modern biocides like pyrethroids and triazoles, all of them having an extreme low volatility. For analytical techniques, different gas chromatography systems coupled with mass spectrometry are available.

Acknowledgements

The German Federal Environmental Office (Umweltbundesamt) is gratefully acknowledged for the financial contribution to the project under no. 299 65 321.

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MOBILITY, SORPTION AND FATE OF TETRABROMOBISPHENOL A (TBBPA) IN LOAM SOIL AND SAND.

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Summary

In this study [^{14}C] TBBPA was applied to the soil at the upper concentrations found in contaminated Swedish sediment (500ppb).[1] For the duration of the experiment there was significant redistribution of [^{14}C] through the soil to a depth of 15cm; however, TBBPA was not present in the effluent. TBBPA appeared to be strongly sorbed to the soil and, under these anaerobic conditions, did not appear to be degraded. Approximately 4% of the [^{14}C] TBBPA was eluted from the sand column, which indicated that TBBPA was more mobile in sand than in the loam.

Introduction

It has been established that tetrabromobisphenyl A (TBBPA) is metabolized in the rat to the glucuronic acid and sulphate ester conjugates in the liver, and excreted into the GI tract via the bile. Subsequent deconjugation in the GI tract results in excretion of 92% of the dose in the feces as unchanged TBBPA.[2] In an effort to determine the fate of TBBPA after excretion in feces, we studied TBBPA mobility, sorption, and fate in soil.

Materials and Methods

A Glyndon silt loam (coarse silty, mixed, superactive, frigid, aeric calciaquoll) obtained from Galesburg, ND, USA was dried at 85^{o} C for 24h, and 1126g was evenly packed in a glass column (8.4cm x 15.2cm; 842ml) with a stainless steel end cap. The pore volume, the space inside the packed soil column occupied by liquid was calculated to be 417ml assuming saturation. Sandwiched between the soil and the end cap were a 40 mesh stainless steel screen and six layers of cheesecloth. The soil was wetted with 455ml of 0.01M $CaCl_2$ solution from the bottom over a 24h period. This was done to maintain soil structure and reduce the amount of entrapped air. A steady-state flow velocity of 4.1mm min^{-1} was then established with 0.01M $CaCl_2$ from the top of the column. After steady-state flow velocity was achieved, a pulse of [^{14}C] TBBPA (0.39μCi, 563μg) was applied to the soil surface in a volume of 135ml, and eluted with 4.6L of 0.01M $CaCl_2$ (approximately 11 pore volumes) at the same steady-state flow velocity. The effluent flowing out of the column was fraction collected and each fraction (ca. 20ml) analyzed for ^{14}C. The soil column was extruded from the column and cut into one cm sections. During the extrusion process the soil column was compressed approximately one centimeter. The sections were dried and assayed for ^{14}C by combustion analysis on a Packard Model 307 Oxidizer. Selected sections [14 (top), 12, 10, 5, 3, and 1cm from column bottom; 10g] were individually extracted sequentially with toluene, ethyl acetate, and methanol in an Accelerated Solvent Extractor (Model 200; ASE; Dionex, Sunnyvale, CA, USA). Thin-layer Chromatography (TLC) analysis on these fractions was conducted using silica gel plates (250 m; Whatman Lab. Div., Clinton, NJ, USA) with the following solvent systems: a) methylene chloride:hexane (1:1) and b) tetrahydrofuran:ethyl acetate:hexane (12.5:12.5:25).

As a comparison, standard, washed laboratory sand (Catalog No. 3382-5, J. T. Baker Chem. Co., Phillipsburg, NJ, USA) was packed in the same size column as the soil, and the pore volume was calculated to be 303ml, assuming saturation. The sand was saturated with a solution of 268ml of 0.01M $CaCl_2$ from the bottom over a 24h period, again to maintain structure and reduce the amount of entrapped air. A steady-state flow velocity of 4.8mm min^{-1} was then established with 0.01M $CaCl_2$ from the top of the column. After steady-state flow velocity was achieved a pulse of [^{14}C] TBBPA (0.34μCi, 490μg) was applied to the sand surface in volume of 135ml and eluted with 4.4L of 0.01M $CaCl_2$ (approximately 14 pore volumes) at the same steady-state flow velocity. The effluent flowing out of the column was fraction collected and each fraction collection volume (ca. 20ml) analyzed for ^{14}C. The sand column was then eluted with methanol, and extruded in four sections and analyzed for ^{14}C by LSC.

TBBPA sorption was done using a batch equilibration technique. The soil used was the Galesburg loam described above. Soil to water ratio used was 1.6g to 8ml, respectively. Then ^{14}C- spiked TBBPA was added so that the solution concentrations were 2.5, 0.25, and 0.025 g/ml in 0.01M $CaCl_2$ in separate vials. Each of the concentrations were run in triplicate. The slurries were agitated by rotation of the vial top to bottom (360^{o}/5 sec). At 48, 96 and 168h, the bottles were centrifuged at 1,700 rpm, triplicate 100µl samples removed, and radioactivity analyzed by liquid scintillation counting (LCS).

Results and Discussion

No radioactivity from [^{14}C] TBBPA was eluted from the soil column with 0.01M $CaCl_2$ even after 11 pore volumes were displaced. Combustion analysis of the soil sections showed 16.2% of the ^{14}C from TBBPA remained in the first centimeter of soil with six to seven percent in each of the next four sections. Generally, radioactivity in the remaining sections of the column appeared to taper off from four to two percent, except for a slight raise in activity (five percent) three to five centimeters from the bottom (Figure 1). In the ASE extraction, only the toluene extract of each section contained ^{14}C, which was shown to be TBBPA by chromatography in both TLC systems. Although it appeared that TBBPA was strongly sorbed to the soil because there was no radioactivity in the column effluent, there was significant redistribution of the TBBPA to a depth of 15 cm.

A small amount of ^{14}C (4.5%) was found in the effluent of the sand column in the fractions from between 0.86 to 1.4 pore volumes (260 to 430ml). Nearly 73% of the TBBPA, as determined by two TLC systems, was recovered when the column was eluted with methanol. Virtually no ^{14}C was detected in sand from any of the four methanol rinsed sections.

Batch studies at 48h showed that 97.9, 92.6, and 93.6% of the 0.025, 0.25, 2.5µg/ml [^{14}C] TBBPA, respectively, were bound to the soil. Sorption of [^{14}C] TBBPA to the soil at the later timepoints were the same.

These results show that TBBPA is sorbed extensively by loam soil and sand. This is consistent with an earlier report indicating that because of TBBPA's high partition coefficient (K_{ow} = 4.3 - 5.3) and low water solubility. Therefore, TBBPA, in the environment, would be expected to sorb largely to sediment and organic matter in the soil.[3]

Acknowledgments

The technical assistance of Barbara K. Magelky and Colleen M. Pfaff are gratefully acknowledged. Financial support was obtained from MISTRA for synthesis of the radiolabelled TBBPA.

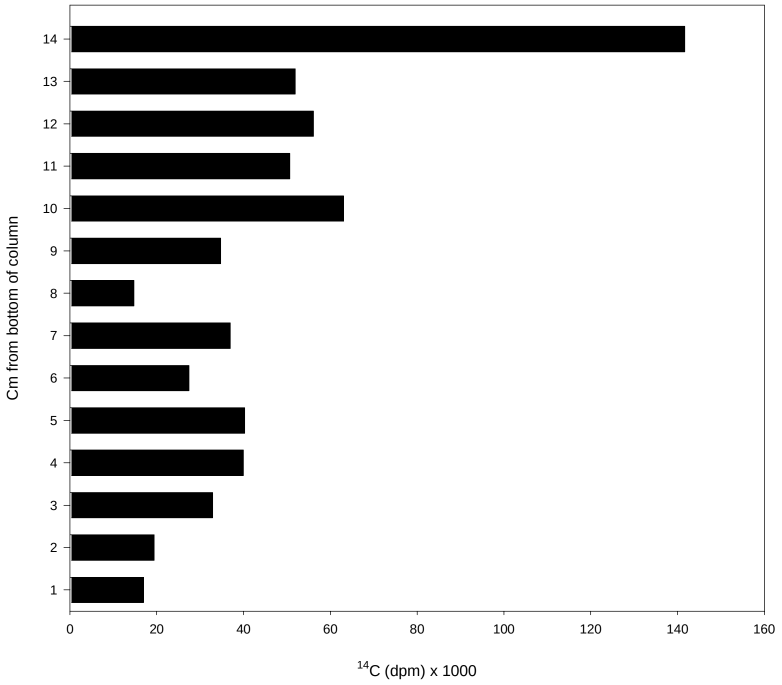

Figure 1. [^{14}C] TBBPA at various soil column depths following elution with 11 column volumes of 0.01M $CaCl_2$

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Assessment of the environmental fate of emerging concern: a case study of the polybrominated diphenyl ethers, including a local-scale assessment with a new developed urban model

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Summary

The environmental behavior of a selection of PBDE congeners has been studied, according to the five-stage strategy described by Mackay et al.[1] and the sixth stage of risk assessment by MacLeod and Mackay[2]. A site-specific fugacity model for the centre of Stockholm has been developed in order to estimate the local fate of these compounds in an urban area. Key data gaps and research needs are identified. The local-scale fate assessment shows that urban areas like Stockholm may act as sources of PBDEs.

Introduction

A five-stage process for assessing the fate of new and existing chemicals has been illustrated by Mackay et al.[1]. MacLeod and Mackay[2] added a sixth stage of risk assessment to the process. This strategy is believed to provide a full understanding of the fate and effects of a chemical, when satisfactorily accomplished. However, for chemicals of emerging concern, there is normally a lack of the data that is needed to accomplish this goal. The strategy can nevertheless be implemented, in order to identify key data gaps, and to provide a first understanding of the likely fate of the chemicals, which can help focussing further research.

The polybrominated diphenyl ethers belong to one class of chemicals suffering from this lack of data. We here demonstrate the six-stage strategy for this group of compounds by compiling available data on physical-chemical properties, environmental occurrence, emissions and toxicity and evaluating the results and the likely fate of these compounds.

Stage 1. Chemical classification and properties

Twenty representative congeners were selected as suggested by Harju and Tysklind[3], as well as the diphenyl ether. Experimental data on physical-chemical properties of individual PBDE congeners were compiled. Where data were lacking, properties were estimated with EPIWIN estimation software. To enhance the interpretation and correlation of the physical-chemical properties, the “three solubility” approach[4] was implemented. Solubilities in air, water and octanol were calculated and plotted against Le Bas Molar Volume. The equations derived for the solubilities of PBDEs were as follows:

$\log (S_A) = 3.73 - 0.036 \times V$ $r^2 = 0.81$ SE: 0.72

$\log (S_W) = 7.70 - 0.043 \times V$ $r^2 = 0.96$ SE: 0.45

$\log (S_O) = 5.58 - 0.013 \times V$ $r^2 = 0.48$ SE: 0.70

The standard errors (SE) of the regression lines are less than one log unit and the r^2 for air and water are higher than 0.8. For octanol, the r^2 is lower, which can be explained by the fact that S_O contains the cumulative error in S_W and K_{OW}, since $S_O = K_{OW} \times S_W$. On the whole, the regression lines correlate the physical-chemical properties quite well and can thus be used to derive properties for screening-level modeling purposes. For a full understanding of the fate these compounds, the standard errors of the correlation equations are still unacceptably high, which is mostly due to the discrepancy between estimated and experimental values. As more experimental data on individual congeners emerge, the equations can be further improved until they have reached a satisfactorily level.

Stage 2. Monitoring data and environmental emissions

In a number of investigations, polybrominated diphenyl ethers have been detected in biological samples. Occurrence in samples from Arctic air[5] and sperm whales[6], indicate that PBDEs are indeed global contaminants. No actual emission measurements have been performed on individual congeners of this group of chemicals, but an extensive study has been undertaken in Denmark using a Substance Flow Analysis approach to estimate emissions of total BFRs in the Danish environment. These estimates can be extrapolated to other European countries, yielding the following emissions, given certain assumptions:

BDE 47: Air: 2.38 mg/(person.year); Water: 0.10 mg/(person.year); Soil: 0.45 mg/(person.year)
BDE 99: Air: 3.76 mg/(person.year); Water: 0.16 mg/(person.year); Soil: 0.71 mg/(person.year)
BDE 209: Air: 46.1 mg/(person.year); Water: 2.02 mg/(person.year), Soil: 8.64 mg/(person.year)

Stage 3. Evaluative assessment of fate

An evaluative assessment was performed using the EQC model[7] assuming emissions of 1000 kg/h to each compartment. The solubility equations obtained in stage 1 were used to derive physical-chemical properties for three selected congeners representing different degrees of bromination, as input data to the EQC model. Level I, II and III modeling were performed at this stage. The level I results indicate that the majority of the PBDEs tend to partition to soil (97.7-97.8%), with sediment being the second largest sink (2%). At level II, the major environmental loss processes were identified. The dominant loss process for all the modeled congeners is reaction in soil, which becomes increasingly important with increasing degree of bromination. Removal processes in air and water become less important with increasing bromination. The environmental persistence for all the congeners is estimated to be around 220 days. A small percentage of the tetrabrominated congener is lost by advection in air (0.47 %). Despite their low mobility, the fraction partitioning to air is enough for these chemicals to undergo long-range transport, as evidenced by their detection in Arctic samples[9]. At level III, chemical was emitted to air, water and soil individually, and then to all three compartments simultaneously. The results show that when emitted to air a large proportion is transported to soil and sediment, with the fraction partitioning to sediments decreasing with increasing bromination. Emission to water results in a large fraction being transported to sediments, which increases with degree of bromination. When emitted to soil, the majority of the chemical stays there. When emitted to all compartments simultaneously, the chemicals will be transported from air to soil and water and from water to sediment. As degree of bromination increases water-sediment and air-soil intermedia transport processes become dominant and removal by soil reaction becomes the dominant loss process from the environment.

Stage 4 + 5. Regional and local-scale assessment using the ”CeStoc” Model

A regional model was used to evaluate the fate of PBDEs in an industrialized area, showing reasonable agreement with observed data. For the local assessment, a site-specific urban model was developed and parameterized to the centre of Stockholm (the “CeStoc” model). The model was calibrated with the PAH fluoranthene, for which more monitoring data exist and for which emission data are more reliable. The model was then run for three PBDE congeners with the Danish emission estimates as input data and environmental concentrations, transport processes and distribution patterns were predicted. The results show that for a small urban area such as Stockholm, the majority of the chemical is transported out of the region through air advection, rather than being deposited to soil. This is mostly due to the short residence time of air in small areas, and the fact that these compounds are mainly emitted to the air compartment. The model predictions were compared to observed levels showing reasonable agreement with observed levels. Fig 1 shows the results for the sediment compartment.

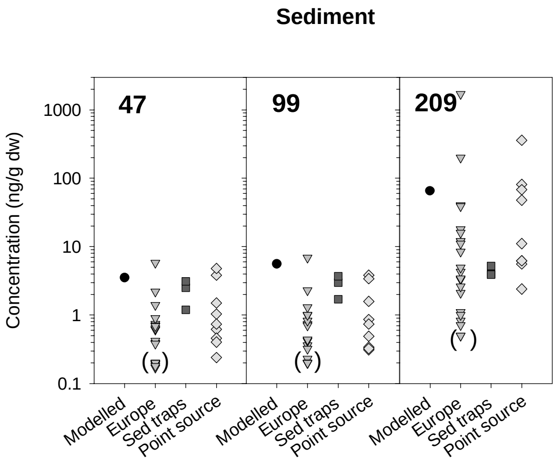

Figure 1. Comparison between predicted concentration and observed levels of different PBDE congeners in sediment.

Conclusions

This study represents an initial screening-level approach to estimate the environmental behavior of the PBDEs. The study confirms that PBDEs are of environmental concern due to their hydrophobicity and long residence times, and that tetra- and penta-brominated congeners might be of most concern. The local-scale fugacity model has been shown to predict environmental levels quite well, given reliable input values on emission and degradation rates. The local assessment indicates that urban areas may act as sources of these compounds and that the impact of degree of bromination is low in a small area such as Stockholm. The present understanding of the behavior of PBDEs is far from complete, and further research should be focused on measuring physical-chemical properties of individual PBDE congeners, on obtaining monitoring data of environmental concentrations and to obtain emission data. As new data become available, the mass balance can be continously improved using the framework outlined here.

Acknowledgements

We are grateful for funding from NSERC and the consortium of chemical companies, which support the Canadian Environmental Modelling Centre. We would also like to thank Miljöförvaltningen in Stockholm for the funding of the local-scale part of this project.

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Concentrations in air and dust of polybrominated diphenyl ethers and tetrabromobisphenol A

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Summary

Two air samples and two samples of sedimentary dust were collected daily during a two week period at an electronic dismantling plant in Örebro, Sweden. For the air samples the total concentrations of PBDEs were 11 and 21 ng/m^3. The corresponding values for the sedimentary dust samples were 30600 and 14900 ng/g. Of the eight PBDE congeners determined, decaBDE, pentaBDE and tetraBDE dominated. Similar levels were found for tetrabromobisphenol A (TBBPA).

Introduction

Brominated flame retardants (BFRs) are used extensively in different materials to prevent or retard the initial stages of fire development[1-3]. Air concentrations of these chemicals have been investigated in occupational settings, e.g. in an electronic dismantling plant, both indoor and ambient air were investigated[4]. Recycling of electronic goods is a rapidly growing industry. A study by Sjödin *et al.* has shown that BFRs are released into air during recycling of electronic goods[4]. For workers in these settings occupational uptake of polybrominated diphenyl ethers (PBDEs) has been demonstrated by blood analysis[5]. Concerns have been risen lately about the uptake and accumulation of certain congeners in humans. Furthermore, PBDEs have continuously increased in human milk since 1972 to 1997 in Sweden[6], increasing two-fold every fifth year[7]. It is important to identify potential sources of exposure and exposure patterns as a basis for uptake studies and further risk assessments. The aim of this study was to provide preliminary information, preceding further studies of occupational exposure at an electronic dismantling plant in Örebro.

Material and Methods

Air samples were collected daily during a two-week period in August 2000. The stationary sampling was performed with a high flow sampling pump at fixed sampling sites, however well reflecting the true exposure (breathing zone) of the workers[8-9]. The airflow varied between 10 to 20 l/min for the different units. The adsorbing equipment consisted of a 37mm filter cassette containing a mixed cellulose filter and XAD-2 adsorbent. The sedimentary dust samples were collected at two different locations within the factory. They were kept in pre-washed glass vials until analysis. The analysis was performed with HR-GC/MS according to methods previously described[10].

Results and Discussion

The air concentration of total PBDE was 11ng/m^3 and 21 ng/m^3 respectively, and for tetrabromobisphenol A (TBBPA) 12ng/m^3 and 37ng/m^3, at the two locations. The congeners were dominated by decaBDE followed by 2,2’,4,4’,5-pentaBDE and 2,2’,4,4’-tetraBDE (table 1).

Table 1. Total concentrations (ng/m^3) of brominated flame retardants, in air from the electronic dismantling plant.

Compound (BDE no.)	Dust removal area	Dismantling hall
2,2’,4,4’-tetrabromodiphenyl ether (#47)	0.70	2.4
2,2’,4,4’,6-pentabromodiphenyl ether (#100)	0.13	0.44
2,2’,4,4’,5-pentabromodiphenyl ether (#99)	1.1	4.0
2,2’,3,4,4’-pentabromodiphenyl ether (#85)	0.05	0.17
2,2’,4,4’,5,6’-hexabromodiphenyl ether (#154)	0.12	0.30
2,2’,4,4’,5,5’-hexabromodiphenyl ether (#153)	0.46	1.2
2,2’,3,4,4’,5’-hexabromodiphenyl ether (#138)	<0.02	0.047
2,2’,3,3’,4,4’,5,5’,6,6’-decabromodiphenyl ether (#209)	7.9	12
Total amount of PBDE	11	21
Tetrabromobisphenol A (TBBPA)	12	37

The same pattern was found for the sedimentary dust samples (table 2). As expected, the levels of all PBDE congeners were higher in the dismantling hall area. However, the air and the sedimentary dust samples from the dust removal area and the dismantling hall area showed similar patterns of the congeners. Comparing the two locations within the plant on a percentage basis, there was a clear difference in the composition of the congeners in air and dust. DecaBDE was higher in the dust removal area, whereas the other congeners were lower in this area compared to the dismantling hall area; (figure 1). The concentrations of the PBDEs and of TBBPA in our study were within the same order of magnitude as in the Sjödin study[4], but we detected slightly higher levels of TBBPA and much lower levels of decaBDE in our study. Levels of PBDEs in outdoor air and in air from a teaching hall were 0,22 ng/m^3 and 1,4 ng/m^3 respectively[4].

Table 2. Total concentration (ng/g) of brominated flame retardants in sedimentary dust from the electronic dismantling plant.

Compound	Dust removal area	Dismantling hall
2,2’,4,4’-tetrabromodiphenyl ether	1700	1900
2,2’,4,4’,6-pentabromodiphenyl ether	290	380
2,2’,4,4’,5-pentabromodiphenyl ether	2800	3400
2,2’,3,4,4’-pentabromodiphenyl ether	140	150
2,2’,4,4’,5,6’-hexabromodiphenyl ether	280	250
2,2’,4,4’,5,5’-hexabromodiphenyl ether	1300	750
2,2’,3,4,4’,5’-hexabromodiphenyl ether	73	41
2,2’,3,3’,4,4’,5,5’,6,6’-decabromodiphenyl ether	24000	8100
Total amount of PBDE	31000	15000
Tetrabromobisphenol A	31000	4100

Conclusions

We found that air concentrations at the electronic dismantling plant were within the same order of magnitude and displayed the same patterns, as previously reported in similar occupational settings in Sweden. Compared to levels in indoor air and air from a teaching hall our results at an electronic dismantling plant were elevated, approximately 100 respectively 10 times. This justifies further assessments of workers’ occupational exposure, including uptake and elimination kinetics and metabolic pathways.

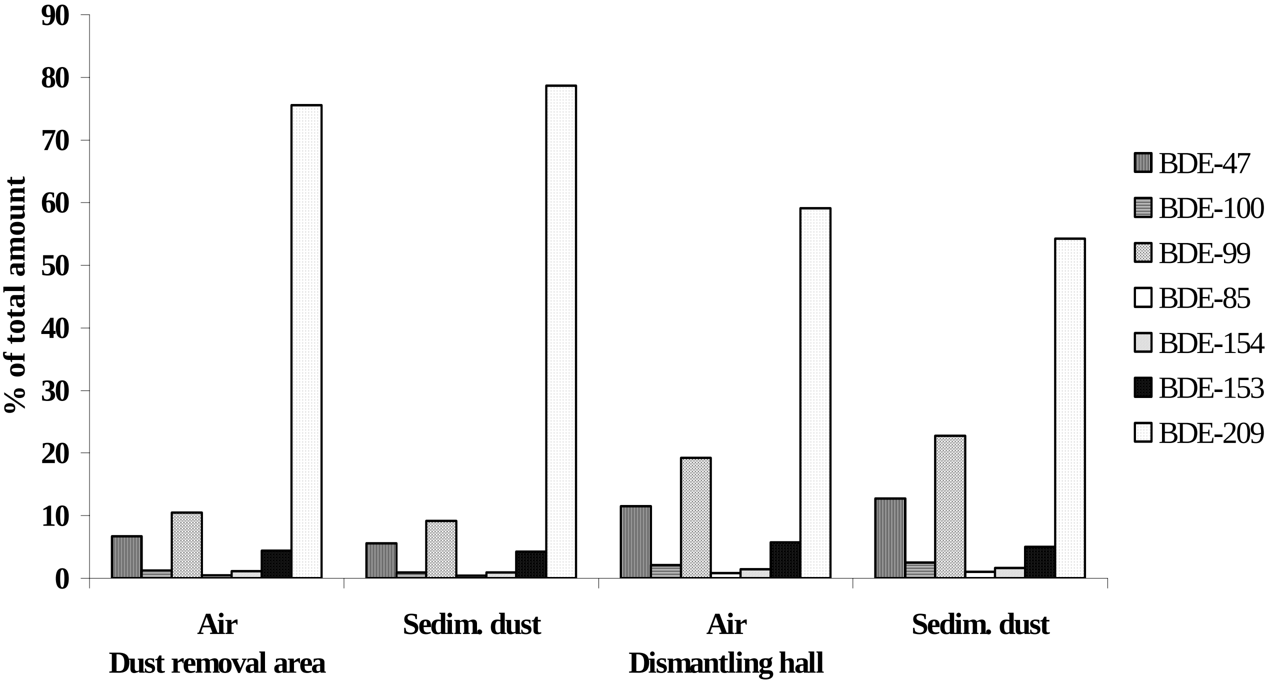

Figure 1. Percentage composition of air and sedimentary dust concentrations within the different locations at the electronic dismantling plant.

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P15

Reactivity of brominated diphenyl ethers vs. methane thiolate

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Summary

Polybrominated diphenyl ethers (PBDEs) are used as additive flame retardant in e.g. computers, TV-sets and textiles [1]. Today, the PBDEs are widespread in the environment and present also in humans [2]. The aim of the present study was to study the reactivity of some of the major PBDEs in the environment towards nucleophilic displacement of bromine substituents by methanethiolate. Decabromodiphenyl ether (BDE-209), 2,2’,3,4,4’,5’,6-heptabromo- diphenyl ether (BDE-183), 2,2’,4,4’,5-pentabromodiphenyl ether (BDE-99) and 2,2’,4,4’-tetrabromodiphenyl ether (BDE-47) were treated with sodium methanethiolate for 88 h at room temperature. Aliqouts were collected after 80 and 160 min, 24 h and analysed by gas chromatography.

Materials and methods

Chemicals: BDE-47 was synthesised as described by Norström et. al (1976) [3] and recrystallised in hexane. BDE-99 and BDE-183 were synthesised as described by Eriksson et. al (2001)[4] BDE-209 and methanethiol were obtained from Fluka Chemie AG (Buchs, Switzerland). Pyridine was obtained from Labscan (Dublin, Ireland), tetrahydrofuran (THF), dichloromethane and hydrochloric acid from Sigma-Aldrich, , sodium sulphate from Merck, and potassium hydroxide and sodium from Kebolab (Stockholm, Sweden).

Instruments: gas chromatography (GC) was performed using a Varian 3400 instrument. The oven was programmed as follows: 80 °C for 1 minute, 80- 290 °C 20 °C/min, and finally 290 °C, for 14 min. The injection temperature was 290 °C.

Synthesis of sodium methanethiolate: sodium (0,42 g, 18,3 mmol) was added to freshly distilled THF (30 ml) [5]. The mixture were cooled on an ice-bath and condensed methanethiol (1 ml, 17 mmol) was added at. The reaction was stirred on an ice-bath over night the product precipitated. The product was filtered off and dried in vacuum.

General procedure for the nucleophilic displacement reactions: The BDE (23 μmol) was dissolved in freshly distilled pyridine (100 ml) [5] and sodium methanethiolate (11,3 mmol) was added. The reaction mixture was stirred for 88 h at room temperature. Samples were taken after 80, 160 minutes and 24 h. Water were immediately added to the samples and the products were extracted with dichloromethane. The organic layer was washed with water several times, dried over sodium sulphate, and finally analysed by GC.

Result and discussion.

The reactivity of the PBDEs were found to be BDE-209> BDE-183>BDE-99> BDE-47, i.e the reactivity was correlated to the bromination degree of the compounds. BDE-209 was remarkably reactive, being completely transformed already after 80 minutes. After the same time there was only small amounts of BDE-183 left while BDE-99 and BDE-47 remained intact. Similar findings from comparable studies on methanethiolate reactions on chlorobiphenyls have been reported by others[6]. Chlorobiphenyls with two or less chlorine substituents in each phenyl ring did not react with methanethiolate in methanol while chlorobiphenyls substituted with three chlorine atoms in one of the phenyl rings formed methanethiolated products [6]. Hexachlorobenzene has also been shown to form methylthiolated chlorobenzenes when treated with methanethiolate in methanol [7].In conclusion, decaBDE is infact a rather reactive compound. This is in accordance with the observed short half- life in e.g. humans of this compound ($T_{1/2}$ ≈7 days)[8]

Acknowledgement

Financial support for the present work was obtained from MISTRA, Sweden.

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P16

The Physico-Chemical Properties of some Brominated Flame Retardants

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The physico-chemical properties [aqueous solubilities (S_w), sub-cooled liquid vapour pressures (P^o_L), Henry's law constants (H) and octanol-water partition coefficients (K_{ow})] of a number of brominated flame-retardants (BFRs) are reported.

Introduction

The physico-chemical properties of a compound govern its transport and fate and can be used to predict its behaviour in the environment. The fundamental physico-chemical properties described in this study are aqueous solubility, sub-cooled liquid vapour pressure, Henry's Law constant, and the octanol-water partition coefficient. There is a paucity of physico-chemical data for organobromine compounds such as BFRs. Existing studies generally involve the use of commercial mixtures, which may contain many unique compounds.[1,2] Physico-chemical data generated by such studies reflect the properties of the bulk mixture instead of the individual compounds. Our previous study was the first to measure physico-chemical properties (sub-cooled liquid vapour pressures) of individual brominated compounds.[3] The present work is an extension of that initial study, expanding the number of BFRs analyzed and physico-chemical properties examined.

Materials and methods

The BFR compounds examined in this study were hexabromobenzene (HBB) and the following BDE-congeners: BDE-3, BDE-15, BDE-28, BDE-47, BDE-66, BDE-77, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183 and BDE-190.

a). Water Solubility. The generator column technique was used for S_w determination of 5 BDE congeners (BDE-15, BDE-28, BDE-47, BDE-154 and BDE-183).[4] The generator column consisted of a stainless steel 150 mm x 3.9 mm i.d. column maintained at a temperature of 25°C and packed with glass beads that were coated with the test compound. Water (HPLC grade) was then pumped through the column at a flow-rate of 1 mL/min. The water was then extracted and analyzed to determine concentration at saturation.

b). Vapour Pressure. Sub-cooled liquid vapour pressures (P^o_L) at 25°C of all the BFR compounds were determined using the GC retention time technique developed by Hinckley *et al.*[5] This technique relates a compound's P^o_L to its retention time (relative to a reference compound) obtained during an isothermal GC run. P^o_L of a number of PCB congeners (CB-15, CB-28, CB-52, CB-118, CB-153, CB-180, CB-187, CB-194, CB-206 and CB-209) were determined and were in good agreement with literature P^o_L values determined in other GC retention time vapour pressure studies. Details of the instrumentation and methodology used is given in Tittlemier and Tomy.[4] Henry's law constants (H), defined as the ratio of the P^o_L to the compound's S_w, were determined for BDE congeners in which both S_w and P were measured.[6]

c). Octanol Water Partition Coefficient. K_{ow}'s were measured on 8 BFRs (HBB, BDE-47, BDE-85, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183) by the 'slow-stirring' technique.[7] The source of the BDE congeners for our K_{ow} studies were commercial PBDE technical mixtures (Great Lakes Chemical Co., DE-71 and 79); the HBB was an individual standard. In this method, the test compounds in octanol were allowed to equilibrate with an octanol-saturated aqueous phase. The solution was slowly stirred and maintained at a constant temperature (25°C). Sampling of both layers was done periodically. The partition coefficient, K_{ow}, was then measured as the ratio of the concentration of the test compound in the octanol to its concentration in the octanol saturated water phase. K_{ow} of a number of PCB congeners (CB-180, CB-202, CB-206 and CB-209) were determined concurrently and were in fairly good agreement with literature K_{ow} values.

Results and Discussion

The physico-chemical properties of the BFR compounds are shown in Table 1. In general, the degree of bromination on the diphenyl ether ring had notable effects on each of the physico-chemical properties we examined. The log K_{ow} of the PBDE congeners, for example, showed an increase with increasing bromine content (Fig 1 (A), slope = 0.345). There is also a trend of decreasing P^o_L with an increase in bromine content of the diphenyl ether molecule (Fig 1 (B), slope = –0.949). An increase in the bromine content also caused in a reduction in the S_w of BDE's (Fig 1(C)) according to the relation:

$$\log S_w = -0.434\ (\#\text{Br atoms}) - 3.0118,\ r^2 = 0.902 \qquad ...1$$

Table 1. Physico-chemical properties for a series of BFRs.

BFR	S_w (25°C, g/L)	P^o_L (25°C, Pa)	H (Pa m^3/mol)	log K_{ow}
HBB[a]	--	7.5E-04	--	6.09
BDE-3	--	0.76	--	--
BDE-15	1.3E-04	0.030	75	--
BDE-28	7.15E-05	1.7E-04[b]	0.96	--
BDE-47	1.53E-05	2.1E-05[b]	0.67	6.19
BDE-66	--	1.1E-04	--	--
BDE-77	--	8.0E-05	--	--
BDE-85	--	3.6E-06[b]	--	6.57
BDE-99	--	1.2E-05[b]	--	6.53
BDE-100	--	3.6E-05	--	6.30
BDE-138	--	1.9E-06[b]	--	--
BDE-153	--	5.5E-06	--	6.87
BDE-154	8.71E-07	2.9E-06	2.14	6.97
BDE-183	1.98E-06	6.2E-07	0.23	7.14
BDE-190	--	2.3E-07[b]	--	--

[a] hexabromobenzene [b] values taken from Tittlemier and Tomy.[3]

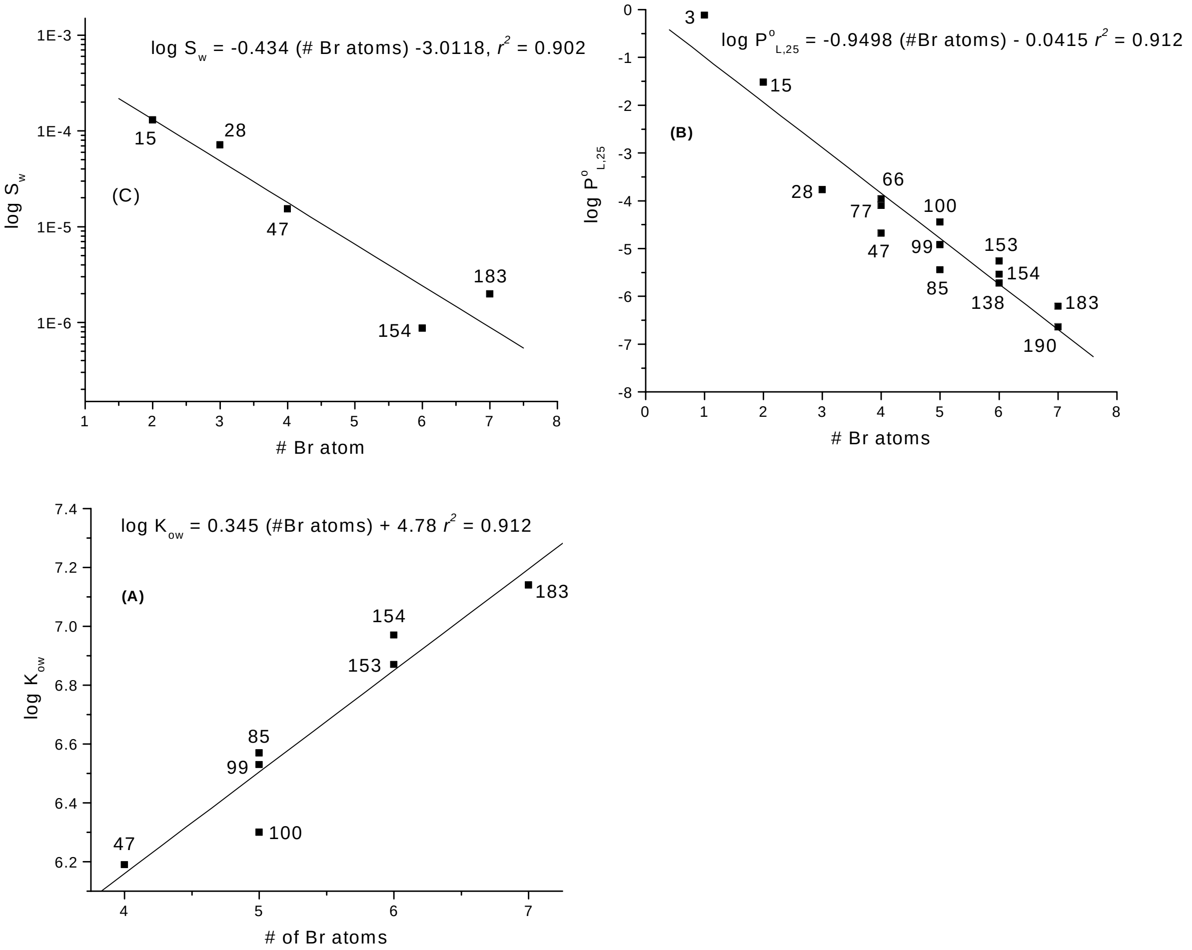

Fig 1. Variation of PBDE (a) log K_{ow}, (b) subcooled liquid vapour pressure ($P^o_{L,25}$), and (c) log S_w, with bromine content.

The Henry's law constants for BDE congeners (determined as the ratio of P^o_L / S_w) ranged from 0.23 Pa m^3/mol for BDE-183 to 75 Pa m^3/mol for BDE-15. These values place these BDEs in the class of volatile to semi-volatile organics, similar to lower chlorinated PCB congeners (PCB 2 and 7; H's = 75.5 and 96.7 Pa m^3/mol, respectively)[8], toxaphene (0.42 Pa m^3/mol)[8] and (–HCH (0.13 Pa m^3/mol).[8]

To our knowledge these are the first physico-chemical properties of individual BFRs. Our efforts to experimentally measure the physico-chemical properties on the remaining congeners (*see* Table 1) is continuing.

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P64

The determination of the partition coefficients of BDE-99, BDE-209 and TBBPA, between plankton, water and glass in a system designed for toxicity testing

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A series of four experiments were run to assess the partitioning coefficient of BDE 99, BDE 209 and TBBPA between plankton, water and glass as a function of different phytoplankton concentrations, glass surface areas and chemical concentrations. The aim was to be able to estimate the dose of the chemical to which the plankton is exposed. The results showed that the partitioning coefficients were the same in all the experiments and that no differences in partitioning could be observed with changed variable values.

The first experiment was performed to assess the time required to reach equilibrium between the phases. The chemicals were C^{14} marked and the test systems (microcosms) were 250 ml glass bottles which were filled with 200 ml of water. The phytoplankton community had a chlorophyll a concentration of 12.5 µg/l and 0.045 µCi of the chemicals were added to each bottle. TBBPA and BDE 99 reached equilibrium after 20 and 80 hours respectively. The experiment was cancelled after 140 hours, after which it still was not clear if BDE 209 had reached equilibrium.

In the second experiment the chlorophyll a concentration ranged between 4 and 18 µg/l, while other variables were held constant. These concentrations represent approximate chlorophyll a concentrations in an oligotroph to an eutroph lake. The log plankton/water coefficients seemed to be independent of the chlorophyll a concentration and were calculated to 6.5, 7.5, 8.0, for TBBPA, BDE 209 and BDE 99 respectively.

In the third experiment the glass content of the bottles ranged between 16100 mm^2 and 26000 mm^2 representing a change in holder volume by a factor 10. This was done by adding glass rods (3 mm thick, and 70 mm long) to the microcosms. The coefficients seemed to be independent of glass content and were the same as in the previous experiment.

In the final experiment chemical concentration ranged between 0.02 and 100% of the solubility of the chemicals in DMSO. The chlorophyll a concentration was 20 µg/l. The coefficients seemed to be the same as in the two previous experiments and seemed to be independent of chemical concentration. The results show that the dose of a compound to an unspecified plankton community can be estimated if the added concentration and partitioning coefficient is known.

P4

STEREOSPECIFIC WAY OF SYNTHESIS OF POLYBROMINATED N-ARYLIMIDES OF ENDO- AND EXO-BICYCLO/2.2.1/-HEPT-5-ENE-2,3-DICARBOXYLIC ACID

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The method of preparation of "hindered" tribromanilines by liquid phase oxidative bromination of metha-substituted anilines has been developed. It was shown that imidation of synthesized tribromoanilines by anhydrides of endo- and exo-bicyclo/2.2.1/-hept-5-ene-2,3-dicarboxylic acid occurs in hard conditions and leads to non-planar N-arylimides stipulated by steric influence of o,o^1-bromine atoms.

We have previously /1,2/ showed that brominated mono- and bis-imides of cyclic dicarboxylic acids are efficient antipyrenes providing incombustibility for polymeric materials.

In this connection the investigation on synthesis of polybrominated imides of endo- and exo-bicyclo/2.2.1/-hept-5-ene-2,3 dicarboxylic acids has been carried out. The symmetric 2,4,6-tribromaniline and its derivatives containing various substitutents in o-, m- and p-position of aromatic ring, which have been synthesized by liquid-phase oxidative bromination of aniline and its derivatives had been used as an initial amine. In this case, the mixture consisting of aqueous solution of potassium or sodium bromide and 20-22% hydrogen peroxide in of 6-8% hydrochloric acid taken in molar ratio of KBr (NaBr) : H_2O_2 : HCl equal 1 : (3-4,5) : (3-6) : (3-8) respectively was used as brominating agent.

It has been established that the reactions of liquid-phase oxidative bromination of o-, m- and p-substituted anilines are differed both on character of bromination and on formation of end products. It has been found that in the case of o- and p-substituted anilines containing substituents of first type (OCH_3, CH_3, Cl, etc) bromination leads to colored solid products with complex composition. It is difficult to isolate the individual products of bromination due to possible transformation of the molecules of o- and p-substituted anilines to quinoid structure with formation of complex mixture similar to "aniline black".

Anilines containing substituents of the second type (NO_2, COOH etc) in o- and p-position being brominated form 2,4- and 2,6-dibromanilines and this witnesses the important role of electron nature of substituents in stabilization of localized and delocalized forms of aromatic ring in the processes of liquid-phase oxidative bromination.

Meta-substituted anilines, independently of electron nature of substituents, being brominated in similar conditions form symmetric 2,4,6-tribromanilines with quantitative yield since m-substituents do not promotes formation of quinoid structure.

A presence of bromine atoms in substituted anilines creates the specific electron-steric effect and as a result low activity of compounds in the reactions of their imidation is observed. Unlike other aromatic amines, 2,4,6-tribromanilines do not interact with anhydrides of cyclic dicarboxylic acids in medium of solvents /3/ with formation of corresponding imides. In this case the more hard conditions of the reaction (e.g.: temperature 170-180^{o}C and duration 36-50 h in hermetically sealed ampule and equmolar ratio of components) are required.

It was shown that the reaction of imidation of 2,4,6-tribromaniline and its o-, m- and p-substituted derivatives of endo- and exo-bicyclo/2.2.1/-hept-5-ene-2,3-dicarboxylic acids proceeds in the conditions indicated above with yield of 53-75% depending on the taken tribromaniline. The rise of the temperature of the reaction over 180^{o}C leads to pitching of the reaction products.

It is assumed that in the prepared N-(2,4,6-tribromphenyl)imides of endo- and exo-bicyclo/2/2.1/-hept-5-ene-2,3-dicarboxylic acids the planes of phenyl and imide rings are in interperpendicular slow down conformation due to steric interaction between atoms of o-substituted bromines of phenyl ring and carbonyls of imide fragment of the molecules.

2,4,6-Tribromaniline and its o-, m-, p-substituted derivatives and also imides prepared on their basis were used as antipyrenes to polyethylene of middle pressure and to epoxide resins. Small quantities of the antipyrenes provide incombustibility of compositions.

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P5

New Synthetic Methods for Polybrominated Diphenyl Ether Congeners

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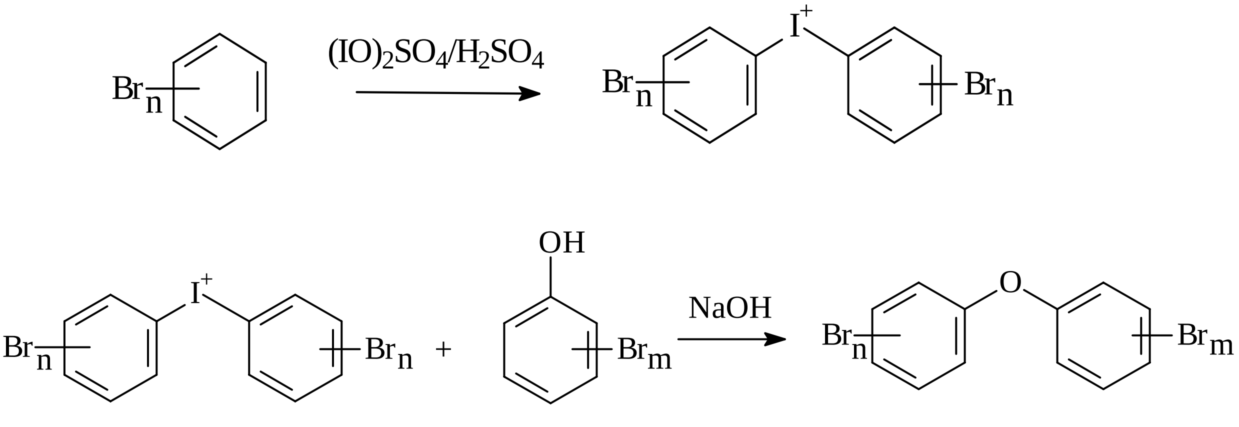
Abstract - We have developed methodology for the synthesis of PBDE congeners that are 2,4,5-tribrominated or higher in each ring. These congeners are inaccessible through the previously developed iodonium salt methodology.

Introduction

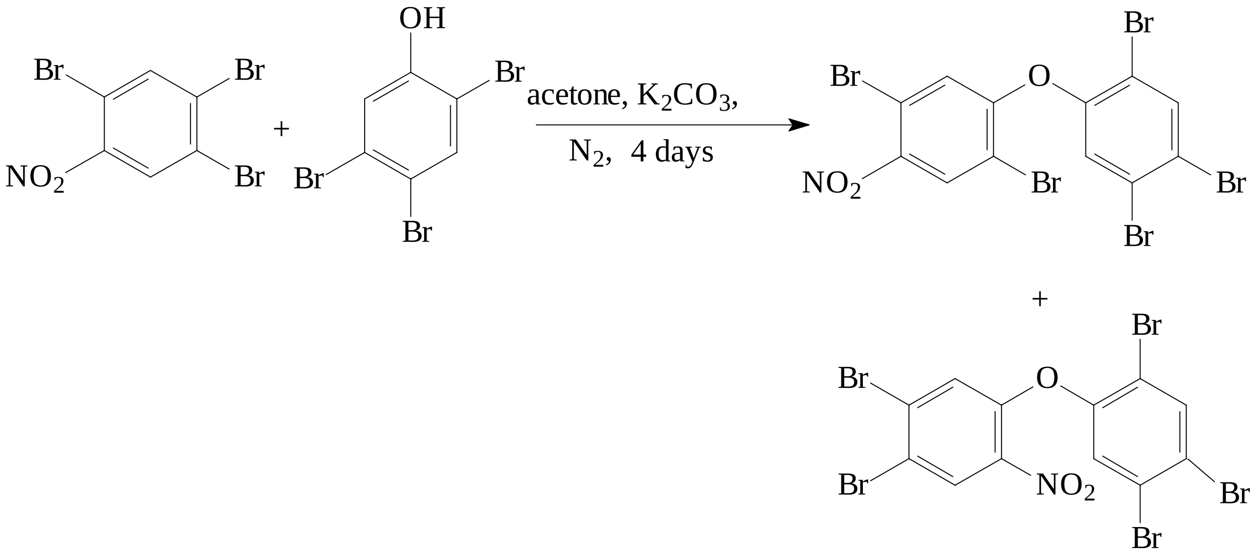
Pure, well-characterized PBDE congeners are needed as standards for analytical work and for investigating the toxicological properties of PBDEs. Previously, Marsh et al. (*1*) described a general synthetic method for both symmetrical and unsymmetrical PBDE congeners, involving conversion of a substituted bromobenzene to an aryliodonium salt, which is then coupled to a bromophenol.



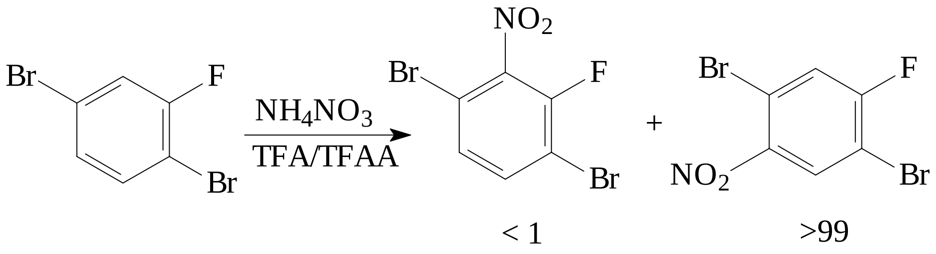
This method was used to synthesize PBDEs having Br_n = unsubstituted, 4-bromo-, 2,4-dibromo-, and 3,4-dibromo- by condensing the appropriate aryliodonium salt with various brominated phenols. However, this approach was unsuccessful for congeners in which Br_n = 2,4,5-tribromo- because the iodonium salt was inaccessible. We have devised new synthetic methodology for congeners that are inaccessible using the previous methodology, mostly based on S_N2Ar displacement of a halide ion activated by an *o*- or *p*-nitro group. Compounds were characterized using ^{1}H NMR at 400 MHz and HRMS, and their purities were assayed by GC; purification always included a final chromatography over Celite/activated carbon to remove possible traces of brominated dibenzofurans or dibenzodioxins.

Results and Discussion

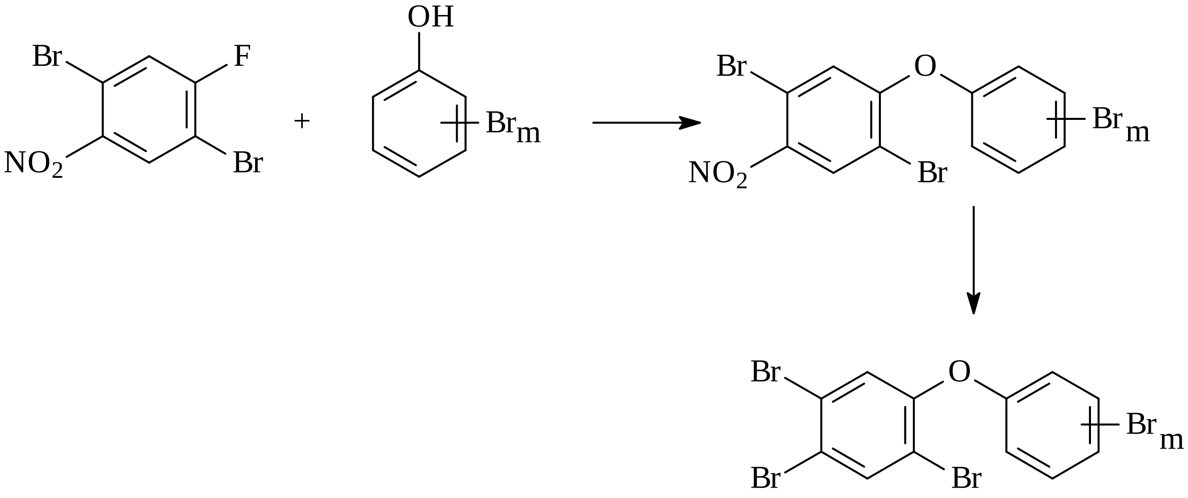
We first attempted to form PBDE 153 by the condensation between 2,4,5-tribromophenol and 1,2,4-tribromo-5-nitrobenzene. This was unsatisfactory on account of excessive reaction times, poor yield (40%), and the formation of an inseparable mixture of two isomers, resulting from equal attack of the phenolate *o*- and *p*- to the nitro group.



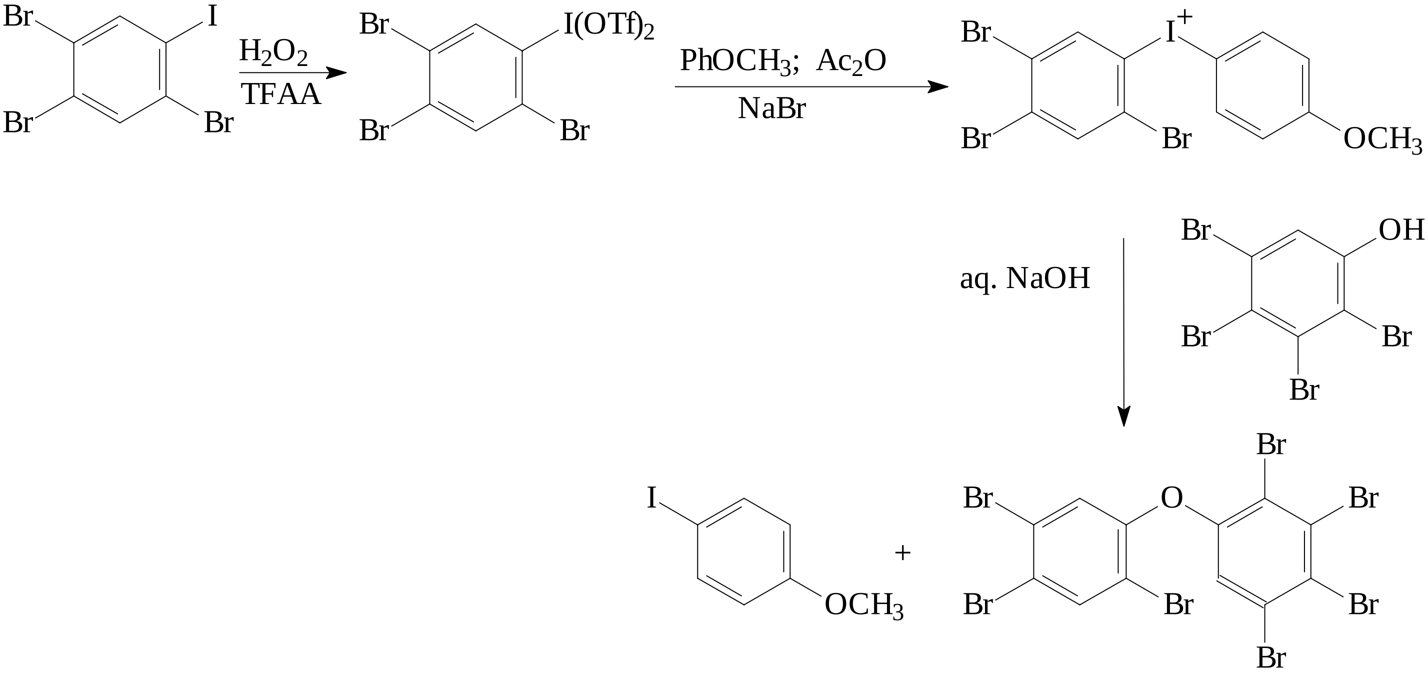
Instead, we synthesized the key precursor 2,5-dibromo-4-fluoronitrobenzene, by nitrating the commercially available 2,5-dibromofluorobenzene, which under our conditions occurred in >90 % yield and with almost complete regiospecificity.



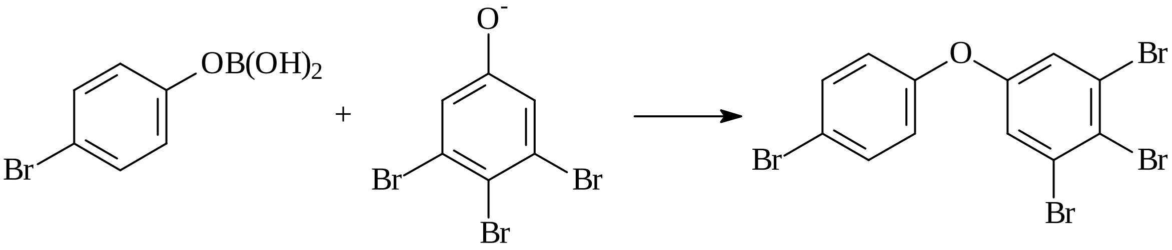
2,5-Dibromo-4-fluoronitrobenzene underwent nucleophilic displacement of the 4-fluoro substituent by a bromophenolate anion (acetone solvent, K_2CO_3 as base, 4 h). The NO_2 group was then converted to Br by reduction (Sn/HCl/HOAc), diazotization, and Sandmeyer reaction with CuBr. This method was used for the synthesis of PBDEs 153 and 154 in acceptable yield (81 and 48%), but yields were unsatisfactory for congener 183 (12%)



Congener 183 was prepared more successfully through an unsymmetrical iodonium salt, which was prepared in 20% yield by condensing the iodosyl triflate with anisole, as shown below (*cf.* Refs *2, 3*). Reaction of the iodonium salt with 2,3,4,5-tetrabromophenol in alkaline solution led exclusively to the displacement of *p*-iodoanisole, affording the desired 2,2′,3,4,4′,5,5′-heptabromodiphenyl ether in 45% isolated yield. This method may have general application, although we have not yet explored this possibility.



Congener 81 (3,4,4′,5-tetrabromodiphenyl ether) was prepared by a modified Suzuki coupling, based on the chemistry of Evans *et al*. (*4*) in 40% yield. This method requires scrupulous care in drying the reagents, because the arylboronic ester is highly moisture sensitive; its hydrolysis gives *p*-bromophenol, which condenses with additional boronic ester to give 4,4′-dibromodiphenyl ether, which must be separated from the desired product.



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Identification of Brominated Flame Retardants in plastics from End Of Life Electric and Electronic Equipments in view of WEEE directive

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Summary: The main objective of the present work is the qualitative and quantitative identification of the most common brominated flame retardants used in some relevant plastics from Electric-Electronic Equipment in order to obtain a reliable recycled material according to the Draft WEEE Directive requirements.

Polymers in electric and electronic applications often have to fulfil flame retardancy requirements and usually, polybrominated compounds are added to the polymers to achieve the required flame retardant behaviour[1]. The brominated flame retardant industry have been producing more than 50 different chemicals of which approximately 30 have been of significant commercial use. Of these 30 substances, Tetrabromobisphenol A and Deca-bromodiphenyl Oxide have been the most used.

There are a few studies of the environmental fate of BFRs. The three most studied BFR classes are polybrominated biphenyls (PBBs), polybrominated diphenyl oxides or ethers (PBDPEs) and tetrabromobisphenol A (TBBPA). One major concern associated with these chemicals is the formation of furans and dioxins as thermal decomposition products. Several studies have been conducted and the results vary according to the products tested, temperatures applied, and other test conditions such as presence of oxygen and catalysts[2]. Some studies reveal that when PBDPE flame retardants containing plastics are recycled, the concentration of dioxins and furans specified by the German legislation are exceed[3]. Other studies indicate that when reprocessing of plastics with DeBDPE no dioxins and furans are found. However, when plastics with OctaBDPE are reprocessed polybrominated dioxins and furans are found[4]. Therefore, further investigations are needed.

On the other hand, TBBPA containing plastics show no significant concentrations of dioxins and furans before and after the recycling process.[3]

Therefore, in view of the Memorandum and the Draft European Directive on WEEE, who proposes separate treatment of plastics containing certain flame retardants, it will be important the detection of these brominated compounds in plastics. Thus, with the intention of obtain a reliable and guaranteed recycled product from End Of Life Electric-Electronic plastics and also to obtain a material that meets the European Directive requirements, it is necessary quantitative and qualitatively identification of the different type of brominated flame retardants used in plastics in the past and today.

Therefore, as a first step, several samples have been prepared with different type and percentage of additives in order to elaborate a spectra reference library for a MIR spectroscopy equipment, PID/22 developed by BRUKER. These reference samples have been prepared according to the most used materials and flame retardants in Electric-Electronic Equipments[5]. The objective is also to determine the detection limit of this equipment and improve the capability of identification.

The polymers used for the preparation of the reference samples are ABS, SB, PC+ABS and PPE+SB and the different flame retardants TBBPA, TBBPA Oligomeric Epoxy, DeBDPE, OcBDPE, HBCD (Hexabromocyclododecane), DeBB and BTMPI (Brominated Trimethylphenyl Indan). The percentage of the additives varies from 1,000 ppm to 200,000 ppm on most of cases and the samples have been prepared both in white colour and in black colour. Prepared samples for the reference library are listed in table 1; samples marked as “In progress” are these samples which are under preparation.

It is also interesting the determination of the detection limit of the Beilstein test, which is commonly used for the detection of halogenated compounds in plastics. If a clean copper wire in contact with a halogen-containing compound is placed in a flame, the presence of halogen is revealed by a green to blue colour. Thus, this study will improve the possibilities of this simple test by means of determining its detection limit.

Beilstein test results obtained with the prepared samples reveal that this test detects presence of halogenated compound normally above 10.000 ppm. In some cases could be lower.

Using the reference library of the IR equipment, quantitative and qualitative identification of different BFRs has been performed in a representative group of 100 TV housings and PCs. The obtained results are summarised in table 2.

The results show that presence of halogenated flame retardants, when the concentration is high (aprox. 5%), is detected by the IR equipment and by the Beilstein test giving a concordant result. However, these are provisional results, which must further analysed with a more complete and representative reference library.

FLAME RETARDANT (FR)			ABS		SB	
Type	ppm	%	White	Black	White	Black
TBBPA	100	0,01	╱	ABS-B-1	╱	╱
	150	0,015	╱	ABS-B-2	╱	╱
	250	0,025	╱	ABS-B-3	╱	╱
	500	0,05	╱	ABS-B-4	╱	╱
	1.000	0,1	In progress	ABS-B-5	In progress	In progress
	2.000	0,2	╱	ABS-B-6	╱	╱
	3.000	0,3	╱	ABS-B-7	╱	╱
	4.000	0,4	╱	ABS-B-8	╱	╱
	5.000	0,5	╱	ABS-B-9	╱	╱
	10.000	1	In progress	ABS-B-10	In progress	In progress
	20.000	2	In progress	ABS-B-11	In progress	In progress
	50.000	5	In progress	ABS-B-12	In progress	In progress
	100.000	10	ABS-W-13	ABS-B-13	In progress	In progress
	200.000	20	ABS-W-14	ABS-B-14	In progress	In progress
TBBPA epoxy oligomer	1.000	0,1	ABS-W-15	In progress	In progress	In progress
	10.000	1	ABS-W-16	In progress	In progress	In progress
	30.000	3	ABS-W-17	In progress	SB-W-17	SB-B-17
	50.000	5	ABS-W-18	In progress	SB-W-18	SB-B-18
	100.000	10	ABS-W-19	ABS-B-19	SB-W-19	SB-B-19
	200.000	20	ABS-W-20	ABS-B-20	SB-W-20	SB-B-20
DeBDPE	1.000	0,1	ABS-W-23	ABS-B-23	SB-W-23	SB-B-23
	10.000	1	ABS-W-24	ABS-B-24	SB-W-24	SB-B-24
	30.000	3	ABS-W-25	ABS-B-25	SB-W-25	SB-B-25
	50.000	5	ABS-W-26	ABS-B-26	SB-W-26	SB-B-26
	100.000	10	ABS-W-27	ABS-B-27	SB-W-27	SB-B-27
	200.000	20	ABS-W-28	ABS-B-28	SB-W-28	SB-B-28
OcBDPE	1.000	0,1	ABS-W-29	ABS-B-29	SB-W-29	SB-B-29
	10.000	1	ABS-W-30	ABS-B-30	SB-W-30	SB-B-30
	30.000	3	ABS-W-31	ABS-B-31	SB-W-31	SB-B-31
	50.000	5	ABS-W-32	ABS-B-32	SB-W-32	SB-B-32
	100.000	10	ABS-W-33	ABS-B-33	SB-W-33	SB-B-33
	200.000	20	ABS-W-34	ABS-B-34	SB-W-34	SB-B-34
HBCD	1.000	0,1	ABS-W-35	ABS-B-35	SB-W-35	SB-B-35
	10.000	1	ABS-W-36	ABS-B-36	SB-W-36	SB-B-36
	30.000	3	ABS-W-37	ABS-B-37	SB-W-37	SB-B-37
	50.000	5	ABS-W-38	ABS-B-38	SB-W-38	SB-B-38
	100.000	10	ABS-W-39	ABS-B-39	SB-W-39	SB-B-39
	200.000	20	ABS-W-40	ABS-B-40	SB-W-40	SB-B-40
DeBB	1.000	0,1	In progress	In progress	SB-W-43	SB-B-43
	10.000	1	In progress	In progress	SB-W-44	SB-B-44
	30.000	3	In progress	In progress	SB-W-45	SB-B-45
	50.000	5	In progress	In progress	SB-W-46	SB-B-46
	100.000	10	ABS-W-47	ABS-B-47	SB-W-47	SB-B-47
	200.000	20	In progress	In progress	SB-W-48	SB-B-48

╱ Not considered samples for the reference library

Table 1. Reference samples for the PID/22 library (only ABS and SB polymers)

Table 2. First approach of identification of BFRs in plastics of a group of 100 TV housings and PCs

Sample	IR equipment result		Belstein Test
	Polymer	Additive	
1	SB	-	NO
2	SB	20% DeBDPE	YES
3	SB	20% DeBDPE	YES
4	ABS	5% HBCD	YES
5	SB	-	NO
6	SB	-	NO
7	SB	20% DeBDPE	YES
8	SB	-	NO
9	SB	20% DeBDPE	YES
10	SB	-	NO
11	SB	-	YES
12	ABS	-	NO
13	SB	-	NO
14	SB	-	NO
15	SB	-	NO
16	SB	-	YES
17	SB	-	YES
18	SB	20% DeBDPE	YES
19	SB	-	NO
20	SB	-	NO
21	SB	-	NO
22	PVC	PVC	YES
23	SB	-	NO
24	ABS	-	NO
25	SB	-	YES
26	SB	-	YES
27	SB	-	NO
28	ABS	10000 ppm TBBPA	NO
29	SB	20% DeBDPE	YES
30	SB	-	NO
31	SB	-	NO
32	SB	20% DeBDPE	YES
33	SB	-	NO
34	SB	-	YES
35	SB	-	NO
36	SB	-	NO
37	ABS	5% HBCD	NO
38	SB	-	NO
39	ABS	-	NO
40	SB	-	NO
41	PVC	PVC	YES
42	SB	-	NO
43	SB	-	NO
44	SB	-	NO
45	SB	-	NO
46	SB	-	NO
47	ABS	-	NO
48	ABS	5% HBCD	NO
49	ABS	5% HBCD	NO
50	SB	-	NO
51	ABS	10% TBBPA	YES
52	PC+ABS	65/35	NO
53	PC+ABS	65/35	NO
54	ABS	10% TBBPA	YES
55	ABS	5% HBCD	YES
56	PVC	PVC	YES
57	ABS	10% TBBPA	YES
58	SB	5%HBCD	YES
59	ABS	5% HBCD	NO
60	SB	-	NO
61	PPE+SB	-	NO
62	ABS	-	NO
63	SB	-	NO
64	ABS	-	NO
65	ABS	-	NO
66	SB	-	NO
67	ABS	10% TBBPA	YES
68	SB	5% HBCD	YES
69	ABS	10% TBBPA	YES
70	PC+ABS	65/35	NO
71	ABS	10% TBBPA	YES
72	ABS	5% HBCD	YES
73	SB	10% DeBDPE	YES
74	ABS	10% TBBPA	YES
75	ABS	10% TBBPA	YES
76	ABS	5% HBCD	YES
77	ABS	10% TBBPA	YES
78	ABS	10% TBBPA	YES
79	SB	-	NO
80	ABS	10% TBBPA	YES
81	PC+ABS	-	NO
82	ABS	10% TBBPA	YES
83	SB	5% HBCD	YES
84	PVC	PVC	YES
85	SB	10% DeBDPE	YES
86	SB	5% HBCD	YES
87	PPE+SB	-	NO
88	ABS	20% TBBPA	YES
89	ABS	10% TBBPA	YES
90	ABS	-	NO
91	ABS	5% HBCD	YES
92	PPE+SB	-	NO
93	SB	5% HBCD	YES
94	ABS	10% TBBPA	YES
95	SB	20% DcBDPE	YES
96	SB	-	NO
97	SB	5% HBCD	YES
98	ABS	10% TBBPA	YES
99	ABS	10% TBBPA	YES
100	PPE+SB	-	NO

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P7

Brominated Flame Retardants: Commercially Available Analytical Standards

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In 1996 Cambridge Isotope Laboratories (CIL) first introduced its line of chlorinated and brominated diphenyl ether analytical standards. In 1997, a standard cocktail containing 23 native BDE congeners, and one ^{13}C-labeled BDE congener (3,3',4,4'-TetraBDE) was produced for breakthrough investigations by Canada's Departments of Environment and Fisheries and Oceans. Because only one ^{13}C-labeled BDE standard was available, labeled C1BDE standards were also included.

In 1999 18 native and several ^{13}C-labeled BDE congeners were added to the product line, including ^{13}C-labeled BDE #'s 47, 99, 100 and 126. Also in 1999, CIL branched out to add standards for other flame-retardant compounds, including native and ^{13}C-labeled Tetrabromobisphenol-A (TBBPA) and native α-, β-, and γ- Hexabromocyclododecane (HBCDD). Then, in early 2000, CIL produced a new Polybrominated Diphenyl Ether Analytical Standard Solution, and Surrogate Spiking Solution to be used in the project being coordinated by Environment Canada. Since then, ^{13}C-labeled BDE congeners 3, 15, 28, 153, 183, and 209 have been added to the expanding product line. Quality Control measurements for these individual compounds will be discussed.

With the continued production of Brominated Diphenyl Ether Flame retardants, further interest must be placed on Brominated Dioxins and Furans. These compounds are likely formed as by-products of PBDE manufacture, and possibly from incineration of PBDEs. As has been noted by other key speakers, while there is a substantial lack of information regarding these compounds in the environment, it is generally considered that they hold relative toxicities close to their Chlorinated counterparts. In an effort to assist laboratories with this research, CIL has produced a series of analytical standards for Bromated Dioxins and Furans, mixed Bromo/Chloro Dioxins and Furans, and cocktails of these compounds, both ^{13}C-labeled and unlabeled.

In the future, CIL will continue to expand its standard offerings for Brominated Flame Retardants. Future projects will be driven largely by discussions with researchers attending this meeting, but will include more ^{13}C-labeled BDE congeners, more analytical mixes, and calibration solutions to further assist analytical laboratories.