

# Emission of phosphorus organic and polybrominated flame retardants from consumer products and building materials

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## ABSTRACT

The emission behaviour of flame retardants from different materials was examined. The tests were done in different emission test chambers and cells under standard conditions (23°C, 50% RH, fixed area ( $q_a$ ) and product ( $q_u$ ) specific air flow rates). Selected products were investigated under working conditions or at elevated temperature (e.g. 60°C). The results indicate that emissions of several phosphorus organic and brominated flame retardants (up to hexabrominated compounds) are quantifiable using this technique. There is a limited applicability regarding adsorption effects on chamber materials for flame retardants with a low volatility (e.g. hexabromocyclododecane). The low volatile decabromodiphenylether was not detectable from insulating rubber. As a result of the investigations TCPP was found to be one of the most dominant flame retardant. The calculated area specific emission rates for TCPP, e.g., ranged from 20 up to 140  $\mu\text{g m}^{-2} \text{h}^{-1}$  depending on the sample type.

## INDEX TERMS

Flame retardants; SVOC/POM; Material emission

## INTRODUCTION

Many plastics in consumer products and building materials contain flame retardants (FR) for fire safety reasons. The most frequently used organic FRs are brominated FRs (BFR) and organophosphoric compounds (POC). Due to their worldwide output selected FR are now ubiquitous and can be found in sediments and biota (de Wit, 1999). Very little is still known about the human and environmental exposure via the use of flame retarded goods and the possible contribution to indoor air pollution (Pardemann *et al.*, 2000; Hansen *et al.*, 2001; Salthammer and Wensing, 2002). Hence, the aim of the present study is the investigation of the emission behaviour of polybrominated diphenylethers (PBDE), (polybrominated biphenyls) (PBB), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), hexabromobenzene (HB), halogenated alkyl phosphate esters (e.g. tris(chloropropyl)-phosphate (TCPP)), aryl phosphate esters (e.g. triphenylphosphate (TPP) and diphenylcresylphosphate (DPK)), resorcinol-bis-diphenylphosphate (RDP), and bisphenol A-bis-diphenylphosphate (BDP) in different materials and products. The results presented in this paper are a continuation of the project whose first results have been published recently (Kemmlein *et al.*, 2002).

## METHODS

### Materials

The following samples were investigated: expandable polystyrene (EPS), extruded polystyrene (XPS), polyisocyanurate (PIR) and rubber insulating boards ( $q_a = 1.24 \text{ m}^3 \text{m}^{-2} \text{h}^{-1}$ ), different polyurethane (PU) assembly foams ( $q_a = 5.12 \text{ m}^3 \text{m}^{-2} \text{h}^{-1}$ ), upholstery foam, upholstery stool, mattresses ( $q_a = 1.41 \text{ m}^3 \text{m}^{-2} \text{h}^{-1}$ ), personal computer systems, printed circuit board, TV and PC housing ( $q_u = 0.128 \text{ m}^3 \text{piece}^{-1} \text{h}^{-1}$ ).

### Emission Test Chambers and Cells

Glass cells (0.001  $\text{m}^3$ ) and emission test chambers (0.02 and 1  $\text{m}^3$ ) were used to perform the examinations (Kemmlein *et al.*, 2002). The chamber and the cells were operated at a temperature

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of  $23 \pm 0.1^\circ\text{C}$  and a RH of  $50 \pm 3\%$ . For simulation of working conditions (printed circuit board) the  $0.02\text{ m}^3$ -emission test chamber was heated to  $60 \pm 0.1^\circ\text{C}$  (RH of  $8 \pm 3\%$ ).

### Sampling and Sample Preparation

Air sampling using PUF-plugs and sample preparation for the determination of BFRs and POCs are described elsewhere and are used with some minor modifications (Kemmlin *et al.*, 2002). TBBPA was analysed after derivatization with acetic anhydride. Acetone is used instead of cyclohexane for the extraction of POCs. For the analysis of BDP the acetone was evaporated and acetonitrile was added for analysis with HPLC.

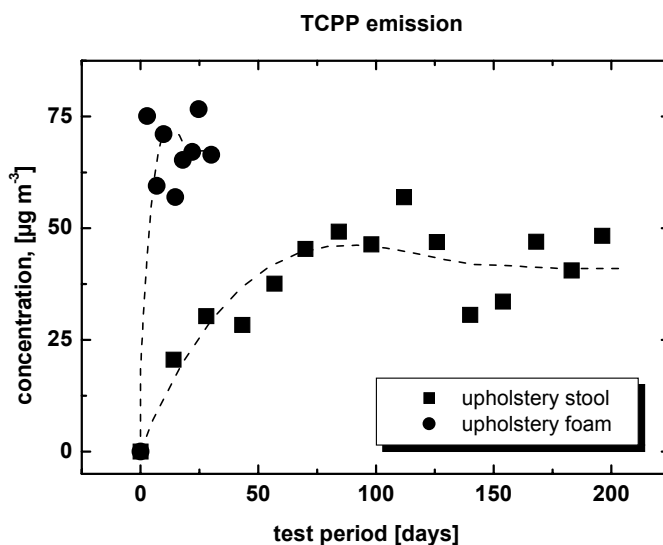
### Gas Chromatography-Mass Spectrometry

The analyses of the BFRs were performed on an Agilent gas chromatograph 6890 Series and a Kodiak 1200 mass spectrometer (max. 1500 amu, Bear Instruments Inc., USA). The POCs were analysed on an HP gas chromatograph 5890 Series 2 and a HP MSD 5971 (max. 600 amu, HP, USA). The analyses of BDP were performed on a HP1100 liquid chromatograph equipped with a diode array detector (210 nm, reference 360 nm) (Kemmlin *et al.*, 2003).

## RESULTS AND DISCUSSION

Figure 1 shows the concentration profile of TCPP emitted from an upholstery stool (PU-foam covered with textile) as a function of time ( $q_u = 1\text{ m}^3\text{ piece}^{-1}\text{ h}^{-1}$ ;  $0.001\text{ m}^3$  emission test cell). Up to a testing period of 100 days the determined levels increase slowly to a value of about  $45\text{ }\mu\text{g m}^{-3}$ . After 160 days, the system is situated in a steady state. Based on the assumption that equilibrium conditions exist the concentration level was determined to a value of  $41\text{ }\mu\text{g m}^{-3}$ . The textile contains HBCD and decabromo diphenylether as flame retardant. No emission could be detected over the testing period of 170 days.

In addition, the concentration profile of TCPP emitted from an upholstery foam ( $q_a = 1.10\text{ m}^3\text{ m}^{-2}\text{ h}^{-1}$ ) without covering is also shown in Figure 1. In contrast to the furniture, the concentration profile shows a sharp increase with a maximum of  $75\text{ }\mu\text{g m}^{-3}$  at the beginning of measurement. This confirms the assumption that the emission of TCPP from the investigated upholstery stool is determined by a diffusion process through the covering matter and resulting sink effects. Table 1 shows the area specific emission rates of TCPP ( $SE_{a,TCPP}$ ).  $SE_{a,TCPP}$  of assembly foams (AF), insulating boards (IB) and a mattress are also included.



**Figure 1** Concentration of TCPP emitted from an upholstery stool in comparison with a pure upholstery foam as a function of time.

**Table 1** Area specific emission rates ( $SER_a$ ) of TCPP ( $\mu\text{g m}^{-2} \text{h}^{-1}$ ) from different products

Product	$SER_{a,\text{sum}}^a$ ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	$SER_{a,\text{eq}}^b$ ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	Product	$SER_{a,\text{sum}}^a$ ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	$SER_{a,\text{eq}}^b$ ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )
Upholstery stool	28	36	AF (smooth, new)	–	50
Upholstery foam	–	77	AF (rough, stored)	130	140
Mattress	–	0.012	AF (smooth, stored)	70	50
AF ( $\delta = 0.02 \text{ g cm}^{-3}$ )	40	16	IB ( $\delta = 0.03 \text{ g cm}^{-3}$ )	0.70	0.60
AF (rough., new)	–	70	IB ( $\delta = 0.08 \text{ g cm}^{-3}$ )	0.35	0.21

<sup>a</sup> Calculated from:  $m_{\text{tot}} / (t_{\text{tot}} \times A)$ ;  $m_{\text{tot}}$  ( $\mu\text{g}$ ): total sum concentration (integrated emission) + total content (chamber walls);  $t$  (h): test period;  $A$  ( $\text{m}^2$ ): sample area.

<sup>b</sup> Calculated from:  $c_{\text{eq}} \times q$ ;  $c_{\text{eq}}$  ( $\mu\text{g m}^{-3}$ ): postulated equilibrium concentration;  $q$  ( $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$ ): area specific air flow rate.

The good correlation between both independent methods makes it evident that the investigated systems were situated in equilibrium states at the end of the experiments. Concerning the interpretation of the results, it has to be taken into account that the various materials contain different amounts of TCPP.

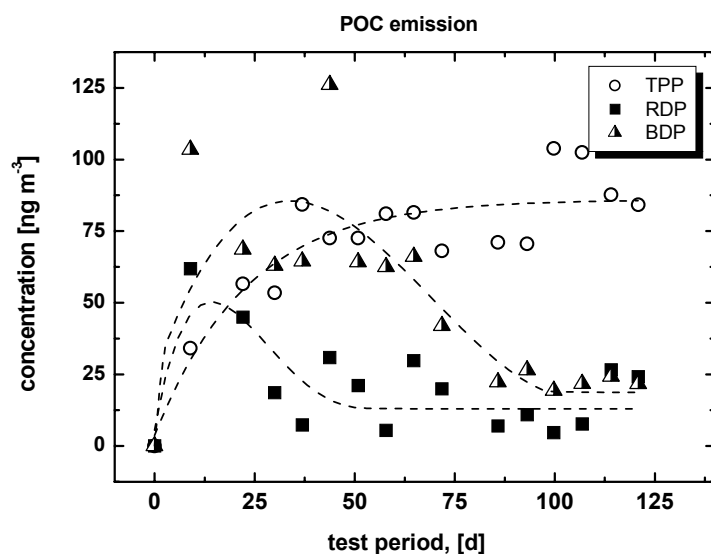
EPS- (HBCD content 1–2%) and XPS- (HBCD content <1%) insulating boards have been tested in a  $0.02 \text{ m}^3$  emission test chamber and  $0.001 \text{ m}^3$  cell, respectively. No emission could be detected up to 120 days for both materials. Using the  $0.001 \text{ m}^3$  emission test cell measurable concentrations about  $1.8 \text{ ng m}^{-3}$  were found for XPS. Rinsing the chamber walls with toluene resulted in  $1.2 \mu\text{g m}^{-2}$  ( $0.001 \text{ m}^3$ ) and  $3.3 \mu\text{g m}^{-2}$  ( $0.02 \text{ m}^3$ ) for EPS and  $0.33 \mu\text{g m}^{-2}$  ( $0.001 \text{ m}^3$ ) and  $21 \mu\text{g m}^{-2}$  ( $0.02 \text{ m}^3$ ) for XPS. Based on the contents obtained from rinsing following area-specific emission rates were calculated:  $4 \text{ ng m}^{-2} \text{h}^{-1}$  ( $0.02 \text{ m}^3$ ) and  $1 \text{ ng m}^{-2} \text{h}^{-1}$  ( $0.001 \text{ m}^3$ ) for EPS and  $29 \text{ ng m}^{-2} \text{h}^{-1}$  ( $0.02 \text{ m}^3$ ) and  $0.1 \text{ ng m}^{-2} \text{h}^{-1}$  ( $0.001 \text{ m}^3$ ) for XPS.

The molecular weight of decabromodiphenylether (DecaBDE) amounts to  $959 \text{ g mol}^{-1}$  and one vapour pressure found in literature is  $4.63 \times 10^{-6} \text{ Pa}$  ( $20^\circ\text{C}$ ) (NICNAS, 2001). In order to get information about the emission behaviour of this extremely low volatile compound synthetic vulcanized rubber has been examined ( $0.02 \text{ m}^3$  emission test chamber). Up to test period of 277 days no emission of DecaBDE could be determined. After discontinuing the experiment no DecaBDE could be found on the chamber walls. Lower brominated PBDE formed by possible decomposition of DecaBDE were not found in the air samples and only with trace amounts on the chamber walls.

Two PC system units (System A: PC, monitor, mouse, keyboard, printer; system B: PC, monitor, mouse, keyboard;  $1 \text{ m}^3$  emission test chambers;  $23^\circ\text{C}$ , 50% RH) were analysed for possible emissions of BFR and POC ( $q_u = 1 \text{ m}^3 \text{piece}^{-1} \text{h}^{-1}$ ). The measurements were performed under working conditions of the PC. With the aim to study possible adsorption vaulted glass bowls ( $\varnothing$ : 22 cm) were placed in the emission test chamber before starting and were analysed after discontinuing the experiment. Additionally, the emission test chamber B was heated up to  $80^\circ\text{C}$  for 6 h at the end of the testing period and air sampling was done at the same time.

Up to a test period of 90 days no significant emissions of the specified BFR could be detected from system A. Trace amounts of TetraBDE (BDE47) and PentaBDE (BDE100, BDE99, BDE85) were found with levels less than  $0.3 \text{ ng m}^{-3}$ . HB was found with an average concentration of about  $1 \text{ ng m}^{-3}$ . Figure 2 shows the concentration of the identified POCs TPP, RDP and BDP. Both RDP and BDP obtain a maximal concentration about 20–40 days, after that the concentrations decrease and about 100 days, the system is situated in a kind of a steady state. Based on the assumption that equilibrium conditions exist the concentration levels  $c_{\text{eq}}$  were determined to be  $13 \text{ ng m}^{-3}$  (RDP)

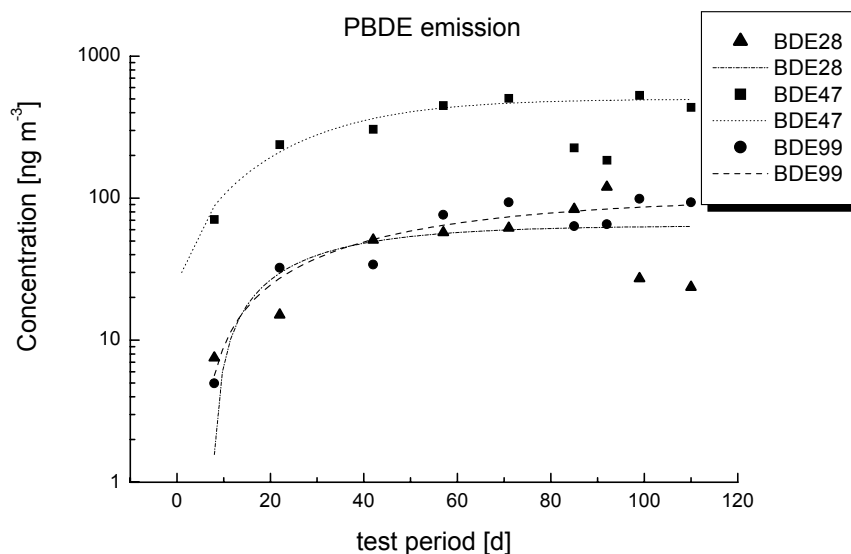
and  $20 \text{ ng m}^{-3}$  (BDP). In contrast, the concentration profile of TPP increases continuously. After 100 days the value of the equilibrium concentration is about  $85 \text{ ng m}^{-3}$ .



**Figure 2** Concentration of TPP, RDP and BDP emitted from a PC (A) as a function of time.

Based on the postulated equilibrium concentrations  $c_{eq}$  and analogous criteria used for calculation of emission rates in Table 1 product-specific emission rates ( $SE_{u,POC} = c_{eq} \times q_u$ ) were calculated and show levels of  $13 \text{ ng piece}^{-1} \text{ h}^{-1}$  for RDP,  $20 \text{ ng piece}^{-1} \text{ h}^{-1}$  for BDP and  $85 \text{ ng piece}^{-1} \text{ h}^{-1}$  for TPP. The PC system B showed no emission of BFRs up to 152 days. HB could also be determined with  $1 \text{ ng m}^{-3}$ . The POCs showed concentration profiles up to  $200 \text{ ng m}^{-3}$ . Based on  $m_{tot}$  (see also Table 1) the resulting  $SE_{u,POC}$  ( $m_{tot} / (t_{tot} \times A)$ ) for RDP ( $2 \text{ ng piece}^{-1} \text{ h}^{-1}$ ), BDP ( $44 \text{ ng piece}^{-1} \text{ h}^{-1}$ ), TCPP ( $24 \text{ ng piece}^{-1} \text{ h}^{-1}$ ) and TPP ( $25 \text{ ng piece}^{-1} \text{ h}^{-1}$ ) were calculated. Sampling at elevated temperature (system B) showed levels of one TetraBDE isomer (BDE47) with a concentration of about  $150 \text{ ng m}^{-3}$  and two PentaBDE isomers (BDE100, BDE99) with concentrations ranging between  $28$  and  $61 \text{ ng m}^{-3}$  due to re-adsorption from chamber walls acting as sinks. For both systems no BFRs were found in the extract of the vaulted glass bowls except TBBPA (A:  $116 \text{ ng m}^{-2}$ ; B:  $64 \text{ ng m}^{-2}$ ).

The emission of FR from a printed circuit board equipped with a housing was examined at  $60^\circ\text{C}$  ( $0.02 \text{ m}^3$  emission test chamber,  $q_u = 0.128 \text{ m}^3 \text{ piece}^{-1} \text{ h}^{-1}$ ). Several PBDE (BDE28, BDE47, BDE99, BDE17, BDE66, BDE100, BDE85, BDE154, BDE153, BDE138) and POC (TPP, RDP, BDP) were found. Figure 3 shows the emission of selected PBDE (BDE28, BDE47, BDE99) over a test period of 120 days.



**Figure 3** Emission of PBDE from a printed circuit board (60°C), simulated working conditions as a function of time.

Based on the sum concentration  $m_{\text{tot}}$  (see Table 1) the  $\text{SER}_{\text{u,BFR}}$  for PBDEs were calculated (Table 2).

**Table 2** Product specific emission rates ( $\text{SER}_{\text{u,BFR}}$ ) of PBDE ( $\text{ng piece}^{-1} \text{h}^{-1}$ ) from a printed circuit board (60°C).

	TriBDE		TetraBDE		PentaBDE		HexaBDE		
Ballschmitter-No.	17	28	47	66	100	99	85	154	153
$\text{ng piece}^{-1} \text{h}^{-1}$	0.6	1.9	14.2	0.4	1.3	2.6	0.1	0.1	0.04

Concerning the POCs,  $\text{SER}_{\text{u,POC}}$  of  $18 \text{ ng piece}^{-1} \text{h}^{-1}$  (RDP),  $182 \text{ ng piece}^{-1} \text{h}^{-1}$  (BDP), and  $496 \text{ ng piece}^{-1} \text{h}^{-1}$  (TPP) were determined.

In default of new materials flame retarded with TBBPA a part of an old PC housing was examined for TBBPA emissions ( $0.02 \text{ m}^3$  emission test chamber). Up to 150 days no emission could be detected, but rinsing the chamber walls resulted in  $356 \text{ ng m}^{-2}$ . The resulting  $\text{SER}_{\text{a}}$  was  $0.4 \text{ ng m}^{-2} \text{h}^{-1}$ . In addition, a part of an old television set housing flame retarded with technical OctaBDE was investigated. Technical OctaBDE contains different hexa-, hepta-, octa- and nonabrominated PBDE. No emission could be detected, but the extract of the chamber walls contained different HeptaBDE-, OctaBDE-, NonaBDE-congeners and DecaBDE. The resulting  $\text{SER}_{\text{a,BFR}}$  were calculated for one HeptaBDE isomer ( $4.5 \text{ ng m}^{-2} \text{h}^{-1}$ ), one OctaBDE isomer ( $1.5 \text{ ng m}^{-2} \text{h}^{-1}$ ), one NonaBDE isomer ( $0.8 \text{ ng m}^{-2} \text{h}^{-1}$ ), and DecaBDE ( $0.3 \text{ ng m}^{-2} \text{h}^{-1}$ ), all identified as main compounds in technical OctaBDE. TriBDE (BDE28), TetraBDE (BDE47, BDE66), and PentaBDE (BDE99, BDE100) were also found ( $\text{SER}_{\text{a,BFR}}$ :  $0.2\text{--}6.6 \text{ ng m}^{-2} \text{h}^{-1}$ ).

## CONCLUSION AND IMPLICATIONS

Based on the results presented it could be concluded that the use of flame retarded products may affect the indoor air quality and could be a possible route of exposure for humans and the environment in general. Temperature factors have to be considered, because higher temperature

increases the emission. Non-volatile compounds mainly occur as particle bonded in indoor air and there they could be concentrated, that implies acting concentrations could possibly be higher under real conditions. For a comprehensive evaluation of possible risks the different physical, chemical and toxicological properties of the different FR types should bear in mind. More data about the emission behaviour of FRs in different materials are required with special regard to material migration, ageing and long-term emission in particular.

## ACKNOWLEDGEMENT

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

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