

EMISSION TEST CHAMBER STUDY: SPECIFIC EMISSION RATES OF PBDE FROM SELECTED MATERIALS UNDER VARIOUS CONDITIONS

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Introduction

In recent years the interest has been focussed on possible sources of PBDE contamination occurring in various environmental compartments.^{1,2,3} Levels of PBDE in total in human blood, milk, and tissues have increased exponentially by a factor of 100 during the last 30 years where significant differences in concentrations between peoples from Europe and the US could be observed.⁴ Levels in mothers milk from the US also indicate that the PBDE concentrations were found to be higher than the levels of PCB in 30% of the test women. However, a strong correlation is given between PCB and PBDE concentrations in environmental samples, no correlation could be observed between PCB and PBDE levels in mothers milk.⁵ The mechanisms that lead to this ubiquitous distribution are much less clear. Possibilities include the uptake via the food chain, ingestion of particles of flame retardant-treated products, inhalation of contaminated indoor air⁶ and house dust⁷, or dermal resorption via the direct contact of PBDE containing materials. To make statements on the emission behaviour in order to expand the existing knowledge of possible routes of PBDE exposure the emission of several PBDE was tested in 0.02 m³ emission test chambers⁸ and in a purge-and-trap experiment from various materials at standard environmental conditions (23°C, 50% R.H., controlled area und unit specific air flow rates q_a and q_u) and also at elevated temperature. Unit and area specific emission rates (SER_u and SER_A) obtained from the emission data were determined and were extrapolated to estimate indoor exposure to selected materials protected by PBDE.

Materials and Methods

Dessicators with a volume of 0.02 m³ were used for the emission tests.⁹ Fundamentals and performance of emission measurements are prescribed by several International Standards.^{10,11} The measurements were performed at standard climatic conditions (23°C and 50% R.H.) and at 60°C. Active air sampling was done using glass tubes (25 cm x 12 mm i.d. x 14 mm o.d.) with one or two polyurethane foam (PUF) plugs (12 mm diameter x 5 cm long). Sample volumes drawn through the plugs varied between 10-30 m³ for all samples. The PUF plugs were extracted using a soxhlet extractor in toluene followed by analysis with GC/MS (Agilent GC 6890/Kodiak 1200 MS). After the end of the test selected dessicators were rinsed with toluene and acetone followed by analysis. Samples: printed circuit board plus protective case with unknown contents of PBDEs ($t_{total} = 2640$ h), a piece of an old, stored TV Set housing containing techn. OctaBDE (bromine: 7.3 % by mass), reference polyurethane rigid foam (PUR, $Area_{sample} = 0.013$ m²) with 1 % and 2 % by mass of the technical PentaBDE formulation, ABS material containing technical OctaBDE at 2 % by mass.¹² The accelerated emission of PentaBDE components from PUR (2% by mass) was investigated in a purge and trap experiment simulating working conditions at various temperatures (23°C, 40°C, 60°C). At this a cut piece of material (0.003 m²) was placed in a 500 mL round bottom flask using a heating mantle for preliminary heating and PUF plugs for air sampling.^{13,14} For all samples PBDEs 3, 8, 17, 28, 47, 66, 100, 99, 85, 153, 154, 138, 183, 196, 197, 209 were monitored.

Results and Discussion

Over the 33-d test at standard conditions the printed circuit board showed emissions of BDE28 and BDE47 in the range 1 to 3 ng m⁻³. The increase of temperature to 60°C showed a clear rise in concentration of the PBDE congeners already detected at 23°C. BDE47 emission increases to maximum of 500 ng m⁻³ compared with an average of 1 ng m⁻³ obtained at 23°C. This corresponds to an increase in the emission by about a factor of 500 while the temperature increases. BDE99 likewise a main compound of the technical PentaBDE could not be detected at 23°C, however shows a clear increase to about 60 to 70 ng m⁻³ when the temperature is elevated to 60°C. In addition further PBDE (17, 66, 99, 100, 85, 154) could be identified. Figure 1 illustrates the percentage of selected components in the technical pentaBDE product and PBDE emission results. The diagram shows that the emission decreases markedly with an increasing degree of bromination and decreasing vapour pressures. This reduction is particularly obvious in the transition from BDE47 to BDE99.

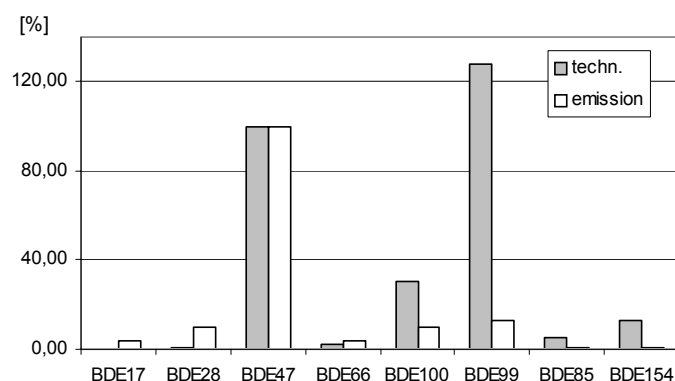


Figure 1. Comparison of the percentage of PBDEs in the emission samples (60°C) with the components in technical PentaBDE. BDE 47 is set as 100%.

Unit specific emission rates SER_u at 60°C were calculated from the data obtained considering the sum mass $m_{emission}$ determined by emission and the mass m_{sink} determined by rinsing the emission test chamber walls ($m_{emission} + m_{sink} = m_{total}$) and varied between 0.04 and 14.19 $ng\ unit^{-1}\ h^{-1}$, with BDE47 showing the highest SER_u . The 83-d and 126-d test of both PUR with varying concentrations of the technical PentaBDE formulation (1% and 2% by mass, respectively) show similar emission levels. BDE47 and BDE99 were identified as the main emittents in this experiment. Beside this PBDE 66, 85, 100, 17 and 28 could be determined with trace levels in the range 2 to 2.5 $ng\ m^{-3}$. Figure 2 demonstrates the concentration profile of BDE47 and BDE99 over the test period.

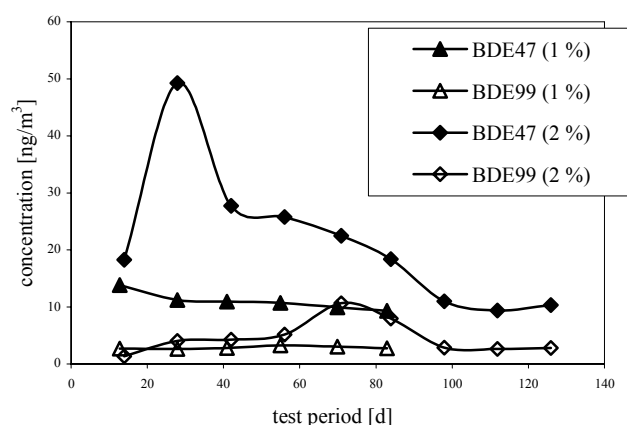


Figure 2. Concentration profile of BDE47 and BDE99 from polyurethane foam with varying concentration of the technical PentaBDE formulation (1% and 2% by mass) as a function of time.

Independent from the slight variation in concentration the emission of BDE99 show qualitative agreements for both samples. A more significant difference can be observed for BDE47. The emission of BDE47 (PUR/PentaBDE 2%) reaches a maximum after about 20-30 days, then the concentration drop to a value around 10 $ng\ m^{-3}$ within the investigation period. No such a maximum can be observed for BDE47 in the sample PUR/PentaBDE 1%. Sink effects (adsorption the chamber walls), migration, surface characteristics and the varying vapour pressures of the PBDE has to taken into account for a more comprehensive evaluation of these

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findings. However on the basis of the measurements it has to be assumed that the value of the equilibrium concentration c_{eq} of BDE47 and BDE99 is 10 ng m^{-3} and 3 ng m^{-3} , respectively. Under these conditions $SER_A (= c_{eq} * q_A = c_{eq} * 9.23 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1})$ were calculated with $SER_{A,BDE47} = 92 \text{ ng m}^{-2} \text{ h}^{-1}$ and $SER_{A,BDE99} = 28 \text{ ng m}^{-2} \text{ h}^{-1}$. Over the 105-d test no emission of the octaBDE formulation was proved from the piece of an old television set housing. BDE28, BDE47, BDE66, BDE99 and BDE100, which are generally not found in the octaBDE formulation, were detected in the chamber air. However, several PBDE were detected in the rinsing fraction of the chamber walls. SER_A may be estimated from the total mass of the emitted PBDE congeners ($m_t = m_{sink}$) taking account of the total test time t_t . m_{sink} derived from the mass of PBDE found on the chamber walls (Table 1). Likewise the second experiment (ABS/OctaBDE tech. 2%) confirmed the emission behaviour of OctaBDE components. The sample in the 0.02 m^3 emission test chamber showed trace concentrations of up to a maximum of 0.8 ng m^{-3} for PBDE 153, 154 and 183 from a test period of 100 days. Table 1 displays the SER_A of detected PBDE congeners obtained from the rinsing fractions m_{sink} and/or $m_{emission}$.

Table 1. Area specific emission rates SER_A of PBDE from ABS/OctaBDE 2% tech. and a TV Set Housing/OctaBDE tech. (old, stored).

Samples	BDE												
	17	28	47	66	100	99	85	154	153	183	197	Nona ¹	209
TV Set housing													
m_{sink} [ng]	-	37 ²	1159*	26	90*	293*	-	39*	171	790	259	147	49
SER_A [ng m ⁻² h ⁻¹]	-	0.2	6.6	0.5	0.5	1.7	-	0.2	1	4.5	1.5	0.8	0.3
ABS/OctaBDE													
m_{sink} [ng]	-	-	-	-	-	-	-	51.3	66.7	107	19.8	-	-
SER_A [ng m ⁻² h ⁻¹]	-	-	-	-	-	-	-	0.19	0.25	0.4	0.07	-	-

$SER_A = m_{sink} \text{ Area}_{sample}^{-1} t_t^{-1}$; Area_{sample} : 0.07 m^2 (old TV Set housing/OctaBDE), 0.08 m^2 (ABS/OctaBDE); total test period t_t : 2520 h (old TV Set housing/OctaBDE), 3360 h (ABS/OctaBDE). ¹ unknown NonaBDE congener; * based on the sum of m_{sink} and $m_{emission}$; ² based on $m_{emission}$.

The SER_A of BDE47 and BDE99 from the purge and trap experiment at varying temperatures are displayed in Figure 2. As a result of extending the temperature an exponential rise of emission can be observed.

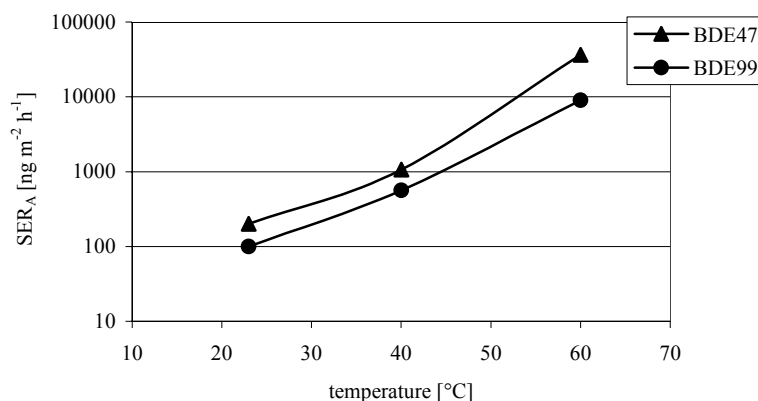


Figure 2. Area specific emission rates SER_A [ng m⁻² h⁻¹] obtained from the purge and trap experiment for BDE47 and BDE99 from polyurethane foam with 2% by mass of the PentaBDE technical formulation as a function of temperature.

Table 2 shows the tolerable concentration TC estimated for selected groups of PBDE congeners.¹⁵ To estimate the indoor exposure, emission levels of PentaBDE congeners obtained from polyurethane were compared with these values: considering a model room of 17 m^3 , with an air exchange rate of 0.5 h^{-1} , a sample size of 0.95 m^2 (e.g. two office chairs) and using the SER_A of $42 \text{ ng m}^{-2} \text{ h}^{-1}$ (sum of BDE99 and BDE100) sumPentaBDE

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concentrations of 4.5 ng m^{-3} were estimated. This experimental value is much smaller than the calculated TC. Under these conditions the exposure via inhalation of OctaBDE to DecaBDE congeners seems to be negligible as these PBDE exhibit a more or less low vapour pressure which suggests that a considerable part is adsorbed to surfaces.

Table 2. NOAELs of PBDE congeners, estimated TDI-values (Uncertainty: 1000) and TC-values (Resorption: 100 %, time of exposure: 24 h, Body weight: 70 kg, RV: $20 \text{ m}^3 \text{ d}^{-1}$)

	NOAEL [$\text{mg kg}^{-1} \text{ d}^{-1}$] ¹⁶	TDI [$\text{mg kg}^{-1} \text{ d}^{-1}$]	TC ¹ [$\mu\text{g m}^{-3}$]
PentaBDE-congeners	1.77	0.002	7
OctaBDE-congeners	2.51	0.003	11
DecaBDE	1.0	0.001	4

¹Calculated from $\text{TC} = \text{TDI} \cdot \text{MM} \cdot \text{AI} \cdot \text{AR} / \text{RV}$; TC = tolerable concentration, TDI: tolerable daily intake = $[\text{NOAEL} / \text{UF}]$ with NOAEL (no observed adverse effect level) and UF (Uncertainty factor); MM: mean mass index [kg], AI: dose by this route [%], AR: exposure time [h], RV: daily respired volume by an adult person [m^3/d].

Results obtained so far show that the analysis and emission test chambers are well suited to be applied to BFR with up to six bromine atoms. With decreasing volatility the influence of sink effects comes stronger. Thus PBDE >6 bromine were detected on the wall surfaces of emission test chambers, but apart from traces, not in emission test chamber air. This result, in addition to the physicochemical characteristics of PBDE (> 6 bromine), confirms that these congeners are mainly present in particle bound form in the environment. Since high brominated diphenylethers are mainly present in a particle-bound form, an additional inhalation and oral intake route is possible through house dust and other sorts of dust in general.

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