Abstract

Introduction

Since the interior atmosphere represents a major part of the built environment, determining emissions from those sources which influence indoor air quality is of great importance. Recently, interest has been focussed on flame retardants (FR) which have been increasingly used in consumer and building products in combination with a rapid increase in the use of plastics. The aim of the research project initiated by the Federal Environmental Agency, Germany is the investigation of the emission behaviour of selected FRs from interior-relevant products.

Flame retardant emission has been tested on a number of consumer goods and building products within this project. The products tested (insulation and assembly foams, IT devices, upholstered furniture, upholstery foams, mattresses and circuit boards) represent a cross-section of products relevant for use indoors.

Analytical methods and materials

The tests were performed in emission test chambers and cells of various sizes in combination with suitable sampling and analysis methods. Emission test chambers with volumes of 0.02 m³ (per DIN 55666) and 1 m³ were used within this project as well as 0.001m³ BAM emission test cells for the investigations and all operated under the same standard climatic conditions at T = 23 °C and R.H. = 50 %. The principle of mantle tempering was used for all emission test chambers and cells. The documents from CEN TC 264, WG 7 (Air properties, emissions from building materials) and CEN TC 112, WG 5 (Wooden materials, formaldehyde) set the relevant technical basis for the execution of emission tests and the design of emission test chambers. The standard DIN V ENV 13419, Part 1 - 3 compiled in connection with CEN TC 264, WG 7 contains the determination of emissions of volatile organic compounds (VOC) by emission test chambers and cells and the production, treatment and preparation of emission samples.

The product loading factor was calculated depending on product type and 17.4 m^3 of model room volume and 7 m^2 of floor area was used (DIN V ENV 13419-1). A unit-specific air flow rate was introduced instead of a surface-specific air flow rate for products with a non-specific surface (for example PC systems). Test parameters (volumetric air flow rate, air flow rate, sampling volume etc.) are adjusted to the product properties accordingly.

The following flame retardants were analysed: polybrominated diphenylethers (PBDE), polybrominated biphenyls (PBB), hexabromocyclododecane (HBCD), tetrabromo-bisphenol A (TBBPA), chloroparaffins, and halogenated and non-halogenated organophosphate compounds (OPC). The physicochemical characteristics of the analysed emitters, which mainly belong to the semivolatile organic compounds (SVOC), require air sampling by adsorption on polyurethane foam (PUR foam). The testing time is usually at least 100 days, in some cases 200 days, in order to ensure development of a steady state which is necessary for the measurement. Sample preparation of the PUR foam takes place by soxhlet or ultrasonic bath extraction using suitable organic solvents. Identification and quantitative determination are performed by gas chromatography/mass spectrometry (GC/MS) or High Performance Liquid Chromatography (HPLC) and following UV detection.

Results

Experiments carried out in emission test chambers of different sizes reflect the substantial problem of OPC analysis: it is to be expected that sink effects would strongly influence the analytical results due the physicochemical properties of the tested organophosphate and bromine containing compounds. Experimental results showing that about 25 % to 100 % of the emitted flame retardants are adsorbed by the chamber walls, confirm this expectation. Qualitative tests are carried out on flame retardants by direct extraction and GC/MS analysis as well as x-ray fluorescence analysis for preparation and check of emission tests.

The results described in the following are summarised according to the individual product groups.

Insulation foams

Chlorinated organophosphates are extensively used in building products. TCPP is especially important in this respect which, as this study shows, is mainly used in insulation foams and also in assembly and upholstery foams.

One group of the insulation foams tested within the project was polyisocyanurate foams (PIR), which was directly delivered by the manufacturer from current production. Two different PIR foams were used for the tests, which differ in their density and accordingly in their flame retardant content. These foams were also tested in different emission chambers and cells (0.02 m^3 / 0.001 m^3) to determine the influence of different test chamber sizes and the resulting sink effects. Area-specific emission rates in the range of 0.3 to 0.7 $\mu g\ m^{-2}\ h^{-1}$ can be estimated from the equilibrium concentrations and total emitted masses during the test period. The comparison of both test chamber systems shows that a more favourable source to sink ratio, as in the 0.001 m^3 emission cell, leads to slightly increased measured values.

HBCD is used almost exclusively for flame retarding purposes in polystyrenes. Expanded polystyrene (EPS) was used for the determination of the HBCD emission - specifically manufactured for the tests' purposes. HBCD content was between 1-2% according to the manufacturers' data. Comparative measurements were also performed in different test chambers in this instant. Apart from traces, no EPS emission could be detected above the detection limit of the procedure of 0.33 $ng\ m^{-3}$ in any of the test chambers under the appropriate test conditions during a testing time of 105 days. Rinsing the chamber and cell walls with organic solvents resulted in a value between 1-3 $\mu g\ m^{-2}$ HBCD at the chamber walls. Comparative emission tests of HBCD were accomplished on extruded polystyrene (XPS). The HBCD content was under 1% according to manufacture data. No emission could be detected under the appropriate test conditions for XPS in the 0.02m^3 emission test chamber. On the other hand the 0.001m^3 emission test cell provided trace concentrations of up to 1.79 $ng\ m^{-3}$ from a testing time of 105 days. However, the values fell again under the detection limit after 150 days and no HBCD could be measured in the later part of the test. The chamber and cell walls were also rinsed with organic solvents after the end of the test. Area-specific emission rates of 1-4 $ng\ m^{-2}\ h^{-1}$ for EPS and 0.1 - 29 $ng\ m^{-2}\ h^{-1}$ for XPS were calculated from the HBCD contents determined at the wall surfaces. It cannot be excluded that the measurement values obtained are too small due to possible decomposition and lack of HBCD solubility.

The determination of decaBDE emission from vulcanised rubber took place in a $0.02m^3$ emission test chamber with a testing time of up to 277 days. Neither air sampling nor chamber wall rinsing was able to reveal any decaBDE emission considering the determination limit of 6 ng m^{-3}. The possibility also exists in this case that the compound cannot be analytically detected due to insolubility, possible decomposition or strong adsorption on the chamber walls. A material analysis accomplished at the end of the test failed to provide any indication on the presence of further PBDEs in the material. In addition to brominated flame retardants the synthetic rubber also contains organophosphorus compounds in a technical mixture of DPC, containing about 20 % TPP. Emission rates of approx. 85 ng m^{-2} h^{-1} were calculated for DPC and about 50 ng m^{-2} h^{-1} for TPP from the equilibrium concentrations using the concentration profiles, which reflect the steady-state conditions of the system after about 100 days.

The determination of chloroparaffin emission (according to the manufacturer's data: 70 % chlorine content, chain length C_{16-20}) from closed-cell polyethylene insulation foam took place in a $0.02m^3$ emission test chamber under standard conditions. No emission was detected during a test period of up to 203 days.

Assembly foams

Assembly foams used in this study were closed-cell polyuretane foams (PUR), which are produced from in situ pressurised vessels. B2 assembly foams manufactured for the tests contained either preparations with a flame retardant content of 14 to 18 % of TCPP or a preparation without additive halogenated flame retardants; a mixture of technical DPC and TEP. No TCEP could be found in any of the tested insulation and assembly foams in view of the detection limits. A multiple of the emission rates is expected due to a strongly increased flame retardant content in assembly foams (compared with insulating materials). The experiments gave emission rates of between 40 and 70 µg m^{-2} h^{-1} for TCPP.

Halogen free OPC from an assembly foam exhibited emission rates of 125 ng m^{-2} h^{-1} for DPC and 130 ng m^{-2} h^{-1} for TPP, which was determined from the equilibrium concentrations. Since the DPC preparation is a technical mixture, which contains up to 20 % of TPP, the almost identical emission rates can be explained by comparable physicochemical data.

IT devices

Two PC workplaces were tested in 1m^3 emission test chambers under operational conditions to investigate the emission behaviour of polybrominated and organophosphate flame retardants from IT devices. Potential sources for flame retardant emission are the plastics used in the cases. Which FR is actually used, depends on the respective polymer type. The printed circuit boards used may represent another source of emission. The base material, component parts and solder stop are sometimes treated with different flame retardants. In addition, there are flame retarded cables and small components. Therefore all guide substances of PBDE, PBB and OPC plus TBBPA and HB were tested in the emission samples.

Workplace A consisted of a monitor, a computer, a keyboard, a mouse and a printer of different manufacturers. The case plastic of the monitor is PC/ABS as per manufacturer data, with a TCO99 conform FR on phosphorus basis. ABS, PC-PS FR 40, HIPS and PC were determined as plastics of the printer case. The computer inclusive mouse and keyboard is a system unit with ABS as the case plastic. Since the model is TCO labelled and no halogen free flame retardant is available for ABS because of material properties, it has to be assumed that no flame retardant was used for this case.

Work place A was tested for 93 days altogether to determine the emission of polybrominated and organophosphate FR. Traces of a tetrabromodiphenylether (BDE47) and three pentabromodiphenylethers (BDE100, BDE99 and BDE85) were detected among polybrominated FRs and the concentrations were below 0.27 ng m^{-3}. These values were below the detection limit at the end of the test. Hexabromobenzene (HB) was found in concentrations of around 1 ng m^{-3}. Due to the physicochemical characteristics of these substances it has to be assumed that a large part of the emitted components are adsorbed on the walls of the 1m^3 emission test chamber. The tested product surfaces themselves make a contribution of their own, which can exert a sink effect on the emitted components. Since polybrominated flame retardants are not contained in the case plastics, the PBDEs trace concentrations are very probably due to small components and flat units. The x-ray fluorescence analysis supports this assumption. The cause behind the occurrence of hexabromobenzene is difficult to explain based on available data.

Work place B consisted of a monitor, a computer, a keyboard and a mouse from the same manufacturer. The plastic case of the monitor is marked with the TCO99 and the German "Blue Angel" environmental label and is treated with halogen free FR based on phosphorus. The computer front panel and the keyboard do not contain any flame retardants according to the manufacturers' data.

Emission tests on polybrominated flame retardants were performed over a period of 152 days. The work place tested exhibited no emission of polybrominated flame retardants. The only exception was hexabromobenzene, which was found here too in trace concentrations around 1 ng m^{-3} which dropped below the detection limit in the following part of the test. In order to achieve a more effective and sensitive sampling of the components adsorbed on the chamber walls, the empty $1m^3$ emission test chamber was fired after the end of the test at 80 °C for 6 hours and a $0.54m^3$-volume sample was taken. 150 ng m^{-3} of a tetraBDE (BDE47) and 28 and 61 ng m^{-3} of two pentaBDEs (BDE100, BDE99) were detected. In addition, traces of an unknown heptaBDE isomer and hexaBDE BDE153 were found. A number of circuit board components, the mainboard and various small components may be considered as possible sources for PBDEs detected. The results of x-ray fluorescence analysis support this theory. The results on the PC work places tested suggest that very low emission of polybrominated flame retardants in particular can be expected.

TPP, RDP and BDP emission was found in both PC work places tested. The printer case tested also showed the same qualitative findings. Therefore the experiments reflect the trend to use triaryl and bisphosphates as flame retardants. The unit-specific emission rate of TPP is common to all three product groups tested and is between 30 and 50 ng $unit^{-1}$ h^{-1}. These calculations were based on equilibrium indoor air concentrations of c_{eq} = 85 ng m^{-3} (PC work place A) and c_{eq} < 50 ng m^{-3} (PC work place B). Emission concentrations under steady-state conditions and a comparison of the unit-specific emission rates for the two other organophosphates reveal significant differences. RDP dominates the emission (SER_{RDP} ~ 13 - 49 ng $unit^{-1}$ h^{-1}) for PC work place A, while BDP with emission rates of SER_{BDP} = 40 - 50 ng $unit^{-1}$ h^{-1} and 12 ng $unit^{-1}$ h^{-1} dominates the measurements for PC work place B and the additional printer case tested. However, further data are missing to interpret the measurements in detail. The clearly positive proof of a halogenated phosphoric acid ester (TCPP), which first contradicted manufacturer data, is possibly due to a unidentified contamination.

As a comparison the emission of polybrominated FR was tested additionally on two old cases. One of them (date of manufacture 1995) was flame retarded with TBBPA. No TBBPA emission was found during a test period of 153 days taking into account a determination limit of 0.3 ng m^{-3} for diacetyl TBBPA. A TBBPA content of 356 ng m^{-2}

was determined on the chamber walls after the end of the test, from which an area-specific emission rate of 369 pg m^{-2} h^{-1} was obtained.

The second old case (manufactured in 1979 or earlier) was a part (0.07 m^{-2}) of a television rear wall which, according to the data of the University of Erlangen-Nuremberg, contains the flame retardant octaBDE. A triBDE (BDE28: max. 0.5 ng m^{-3}), two tetraBDE (BDE47: max. 8 ng m^{-3}; BDE66: max. 0.24 ng m^{-3}) and two pentaBDE isomers (BDE100: max. 0.27 ng m^{-3}, BDE99: max. 0.84 ng m^{-3}) were found in measurable concentrations in the emission samples. After the end of the test the flame retardant contents 568 ng m^{-2} of tetraBDE (BDE47) and 514 ng m^{-2} of pentaBDE (BDE99) were found in the rinsed fractions. In addition, clearly detectable contents of two hexaBDE isomers (BDE154: 95 ng m^{-2} and BDE153: 460 ng m^{-2}) were determined, of which only traces were found in the emission samples. Furthermore the complete octaBDE product was detected on the chamber walls. Since the sample tested was over 20 years old, it cannot be decided any longer whether the PBDEs with moderate degree of bromination resulted from decomposition during the long storage time, or were already present as impurities in the product. The following emission rates were obtained from the FR contents determined at the wall surfaces (in ng m^{-2} h^{-1}): 4.5 (heptaBDE), 1.5 (octaBDE), 0.83 (nonaBDE) and 0.28 (decaBDE).

Circuit boards

Emission of additives from materials is affected considerably by temperature. A flame retarded circuit board was examined in two test periods first at 23 °C and then at 60 °C to investigate the influence of temperature on possible emissions. The circuit board was of type CEM3, whose base material was flame retarded by a reactive organophosphate component. The circuit board is additionally encased by a plastic case and this case contains < 12 % of TPP according to manufacturer data.

The investigations at 23 °C supplied values between 1-3 ng m^{-3} for a triBDE (BDE28) and a tetraBDE (BDE47). The emission chamber test at 60 °C showed a clear concentration increase of the proven PBDE and further PBDEs were identified. Thus an increase of up to 500 ng m^{-3} was found for BDE47. Furthermore three pentaBDE (BDE85, BDE99 and BDE100), another triBDE (BDE17) and a hexaBDE (BDE154) were identified. Unit-specific emission rates were calculated from the data obtained after the analysis of the rinse fraction and the overall emission of the single PBDEs. So an emission rate of 0.6 (BDE17) and 1.9 ng $unit^{-1}$ h^{-1} (BDE28) was calculated for the two tribromodiphenylether. Tetrabromodiphenylether BDE47 supplied the highest value with 14 ng unit^{-1} h^{-1}. Further emission rates obtained were (in ng unit^{-1} h^{-1}): 0.4 (tetraBDE 66); 1.3 (BDE100), 2.6 (BDE99), 0.1 (BDE 85), 0.1 (BDE154) and 0.04 (BDE153). Qualitative analyses on materials, which were accomplished by direct extraction and GC/MS analysis as well as with x-ray fluorescence analysis, confirmed the emission measurements and provided hints on to the sources of emission for the polybrominated components.

The influence of temperature is also clearly visible in connection with organophosphorus compounds. Under normal conditions no RDP and BDP emission can be detected by air sampling. TPP concentration approaches an equilibrium value of approx. 40 ng m^{-3}, which corresponds to an emission rate of 5 ng unit^{-1} h^{-1}. Tempering of the experimental setup at 60 °C results in a clear change of the concentration profiles. Concentration of TPP, determined by air sampling, rises to a maximum; the equilibrium concentration of 2 µg m^{-3} determined from the experiment, leads to an emission rate of 250 ng unit-1 h^{-1}. The two other OPCs also show characteristic concentration profiles at 60 °C, which can be determined by air sampling. Unit-specific emission rates 25 ng unit^{-1} h^{-1} for RDP (c_{eq} = 200 ng m^{-3}) and 250 ng unit^{-1} h^{-1} for BDP (c_{eq} = 2 µg m^{-3}) can be calculated from the steady-state equilibrium concentrations.

Upholstered furniture and mattresses

The products investigated in this study were a mattress (Germany), an upholstery foam (European Market, England) and an upholstered stool (English market). A PUR soft foam was used in all cases as a polymer matrix which was flame retarded by TCPP (3-7 % mattress; 5-10 % upholstery foam). The following emission rates were obtained: 75 µg m^{-2} h^{-1} (upholstery foam), 36 µg m^{-2} h^{-1} (upholstered stool covered with upholstery fabric) and 12 ng m^{-2} h^{-1} (mattress). A emission rate of TCPP from the upholstered stool, decreased by a factor 2 in comparison with the foam, can be explained by the fact that the foam is coated by an upholstery fabric (see also PBFR). The determined room air concentrations and emission rates of TCPP belong to the highest values determined in this study. The reduced emission from the mattress cannot be explained by test results available.

Since according to manufacturer data the upholstery fabric is flame retarded by polybrominated flame retardants in contrast to soft foam, the upholstered stool was also tested for possible PBFR emissions. However no emission of brominated organic compounds could be detected up to a testing time of 168 days. Subsequently, the material was qualitatively tested by direct extraction. This showed the following flame retardants: decabromodiphenylether, various nonabromodiphenylether isomers, hexabromocyclododecane and further moderately brominated cyclododecanes and a row of unidentified brominated compounds. HBCD and decaBDE are used as standard compounds for back finishing of upholstery materials. The results of the emission tests confirm the results of the investigations on HBCD and decaBDE described for insulating materials. Also there is no emission of decaBDE and only a low emission of HBCD could be detected.

Discussion

The procedures used are well suited to detect the emission of organophosphorus compounds both qualitatively and quantitatively, in particular tris(1-chloro-2-propyl) phosphate (TCPP), triphenylphosphate (TPP) and diphenylcresilphosphate (DPC). Exceptions are recorcinol-bis-(diphenylphosphate) (RDP) and bisphenol-A-bis(diphenyl-phosphate) (BDP), for which the emission tests by air sampling are dominated by sink effects. The analysis methods are well suited to be applied for brominated flame retardants with up to six bromine atoms. With decreasing volatility the influence of sink effects becomes stronger and hampers the determination of emission. Thus hexabromocyclododecane (HBCD) was detected on the wall surfaces of emission test chambers, but, apart from traces, not in emission test chamber air. The results are not sufficient for a comprehensive representation of the emission behaviour and exposition assessment of flame retardants. There are further gaps in our knowledge, for example, concerning the explanation of high flame retardant contents in house dust. Nevertheless, the study provides a substantial basis for follow-up investigations. It appears desirable to extend the investigations, for example, to long-term measurements for test periods over 1 year and to determine the influence of material aging and various flame retardant concentrations on the emission.