IDENTIFICATION OF "NOVEL" BROMINATED FLAME RETARDANTS IN NEW PRODUCTS OF THE SWISS MARKET

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Introduction

Due to their toxicity and persistence in the environment the former widely used bromianted flame retardants (BFR) penta- and octabromodiphenyl ether (penta-BDE and Octa-BDE) were banned by the European Union in 2004 and several states of the USA[1, 2]. Since 2009 penta-BDE and Octa-BDE are also listed as persistent organic pollutants (POP) under the Stockholm Convention and parties must take measures to eliminate the production and use of the chemicals[3]. In Switzerland, products containing polybrominated biphenyls (PBB), penta-BDE, octa-BDE, and decabromodiphenyl ether (deca-BDE) are not allowed to be placed on the market when their concentration is above 0.1% by mass. According to the Swiss legislation deca-BDE might be used in some special products when, after considering best technologies, no alternative for deca-BDE is available. In 2008 a national market survey was carried in Switzerland with the main objective to control if the Swiss legislation for BFR in products placed on the market is fulfilled. Different product categories were selected on the basis of fire safety requirements and on data about the importation, which were provided by the Swiss federal custom authority. About 25% of approximately 2000 products contained bromine above 500 mg/kg. Although only 25% out of 250 closer analyzed products contained the selected target BFR (PBB, penta-BDE, octa-BDE, deca-BDE, HBCD and TBBPA)[4]. The result of the market survey clearly showed that a large quantity of approximately 75% of the bromine, detected in products available on the Swiss market, belong to structurally unknown or "novel" brominated compounds. Based on this surprising high number of "novel" brominated flame retardants (NBFR) used in new consumer products 36 samples were analyzed by GC/MS in the full scan mode to identify the chemical structure of the unknown compounds and to get by this way a first small overview on the presence of NBFR used as alternatives for banned BFR.

Materials and methods

The materials to be analyzed by full scan GC/MS were selected on the basis of their bromine content, determined semi quantitative by XRF (handheld Niton XLt-797 XRF analyzer, Thermo Scientific), and the results from the quantitative target BFR determination carried out with GC/ECD, GC/MS or LC/MS-MS, which confirmed the absence of target BFR above 0.1% by mass. The XRF bromine content of the selected materials was in the range of 1'000 to 182'000 ppm (0.1 to 18.2%). Solvent extracts of 36 selected polymer products were analyzed by GC/MS in the magnetic full scan mode. The material intake for the solvent extraction was in the range of 100 to 500 mg resulting in a final material equivalent in the extract of 1 to 5 mg/mL. Most of the extractions were carried out with toluene, but tetrahydrofuran (THF) and dichloro methane were also used to extract or dissolve some polymer materials. From the solvent extract one micro liter was injected split less in the GC/MS (MAT95 mass spectrometer, thermo Finnigan MAT, Bremen, Germany), which was operated at a mass resolution of 1'000 in the magnetic full scan mode to detect m/z values between 45 and 1000. The scan speed was set between 0.5 to 1 s/scan. The gas chromatographic separation was carried out on a Restek RTX5-Sil MS column (30 m x 0.25 mm, 0.10 µm film thickness). Unknown compounds were identified by the comparison of the acquired mass spectra with the NIST/EPA/NIH mass spectral library (NIST05, 190'000 spectra) or the evaluation of the mass spectra and later comparison with mass spectra of reference materials.

Results and discussion

In most of the analyzed materials the unknown bromine source could be identified by full scan GC/MS analysis. Eleven out of the 36 analyzed products contained decabromodiphenyl ethane (DBDPE) as flame retardant, which is more than 30%. In six samples (17%) tribromophenol (TBP) was detected and seven samples (19%) showed the presence of an unknown tetra-, hexa- or octabromo compound, which unfortunately could not be identified properly on the basis of the mass spectra. Very possibly it's a derivative of TBBPA with different bromine containing substituents like TBBPA bis(2,3-dibromopropyl ether) (TBBPA-DBPE). The samples containing DBDPE generally also showed smaller signals of the three possible nonabromodihphenyl ethane congeners. In

four samples (11%) pentabromotoluene (PBT) could be detected in small amounts and therefore it's probably more a degradation- or byproduct of DBDPE which was simultaneously present in two out of the four samples. Tribromostyrene (TBS) was also present in four samples (11%) but the signals were quite small in three out of the four samples. Three samples (8%) showed mass spectra of the NBFR 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE). Generally samples with this flame retardant also show signals of tribromophenol which is probably formed by the decomposition of BTBPE in the GC-injector, or is present in the flame retarded material as a byproduct of the mother compound or as an impurity formed under thermal stress during the extrusion of the polymer material. Hexabromobenzene (HBB) could be detected in three samples (8%), also present in three samples (8%) was tris(2,3-dibromopropyl)isocyanurate (TBC, see Figure 2). This brominated compound is as far as known not mentioned in the scientific literature as NBFR. Tetrabromobenzene (TeBBz) was present in two samples (5.6%). Some NBFR could be detected only in one out of the 36 samples included in this study; they are displayed together with the other NBFR in Figure 1. The five major NBFR found were DBDPE, TBBPA-DBPE, TBP, BTBPE, and TBC. Although the frequency of occurrence was higher for some brominated monoaromatic compounds like pentabromotoluene (PBT), the signal intensity of these compounds in the total ion chromatogram was generally not very strong. The results are in good agreement with a recently published review on NBFR, where DBDPE, TBBPA-DBPE, and BTBPE are mentioned as important representatives of a group of NBFR used as replacements for banned formulations[5]. The results show clearly that many different BFR are used in new products entering the Swiss market. The structures and physico-chemical properties of these "novel" brominated flame retardants are often very similar to already banned BFR, and therefore their toxicological and ecotoxicological impact on humans and the environment might also be comparable. Unfortunately little information exists on these important characteristics and properties of NBFR, therefore further research is needed to define the sources, sinks, and the fate of "novel" brominated flame retardants in our environment, including the formation of possibly toxic metabolites or degradation products.

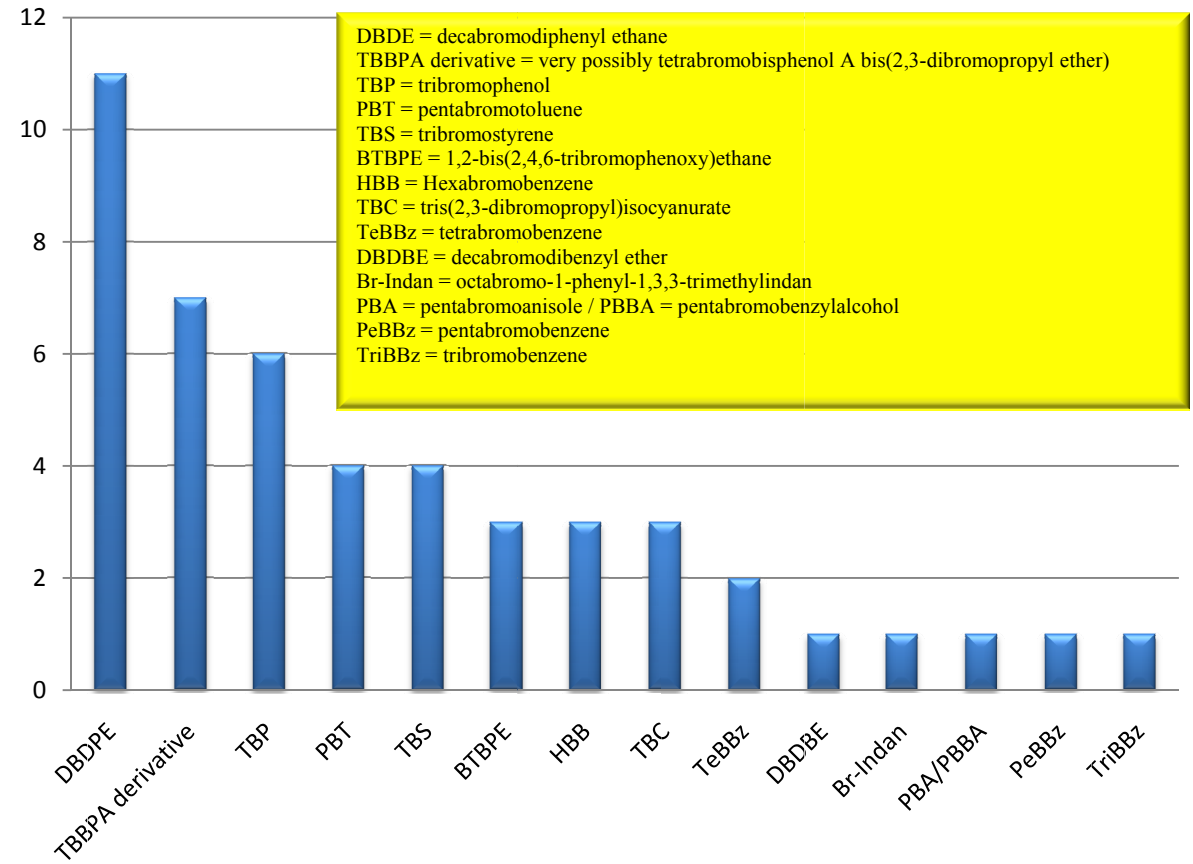

Figure 1: Frequency of NBFR in 36 analyzed new consumer products available on the Swiss market. One product can contain more than just one NBFR.

Additionally the end of life, including waste- and recycling streams, of BFR and NBFR treated materials should be observed carefully in order to avoid the release of toxic and persistent compounds into our environment, as well as the production of cross contaminated recycling products.

Recently various publications reported the occurrence of NBFR in our environment e.g. in indoor dust[6], air, water, soil, sediments and wildlife. The above mentioned review article includes the most recent studies[5]. The presence of NBFR in our environment is not very surprising. Probably the so called "novel" BFR were used for several decades as alternatives to other brominated flame retardants. This assumption is supported by the IPCS monograph on flame retardants published in 1997 by the WHO, which already at that time included most of today's more than 75 known brominated flame retardants, including the so called "novel" ones[7]. The analysis of several rather old polymer products in our laboratory by GC/MS revealed that even in these samples the "novel" BFR were present. A surface wipe sample, taken with a toluene moistened piece of cotton, from a 30 year old integrator (HP 3390A; XRF determined bromine content of 16%) and analyzed by GC/MS showed that BTPE was used as FR. Two more then 15 year old computer monitors (HP Ultra VGA 1280 and Sony Trinitron Multiscan 17sf II), with bromine contents of 8 and 9% respectively, were both flame retarded with TBBPA and TBBPA derivatives. Additionally two composite samples, one composed by ten old computer monitor housings and the other composed by ten old TV cabinets, from a WEEE recycling plant outside of Zürich, almost exclusively contained "novel" BFR. The computer housings showed signals of BTBPE, TBBPA, and TBBPA derivatives. The TV cabinets showed main signals for TBBPA, BTBPE, as well as some minor signals of HBCD, and hepta- to deca-BDE. TV cabinets and computer monitors are generally more than ten years old when they end up in a recycling process. A substance flow analysis carried out at the above mentioned recycling plant a few years ago indicated that WEEE fractions sampled in 2003 contained only 34 mg/kg penta-BDE, 530 mg/kg octa-BDE, 510 mg/kg deca-BDE, 1420 mg/kg TBBPA, and 17 mg/kg HBCD. On the other side the fractions showed average bromine concentrations of 5500 mg/kg. Therefore the authors concluded that roughly 60% of the bromine present in the WEEE fractions must be attributed to other brominated substances used as PBDE substitutes[8]. This result is in perfect agreement with the result from the Swiss market survey carried out in 2008, where approximately 75% of the bromine content could not be assigned to known BFR. The slightly higher fraction of unknown or "novel" brominated flame retardants found in the recently carried out market survey might also represent a continuous shift away from banned and "old" BFR to "novel" BFR. That substances like BTBPE were used as flame retardants for decades was also confirmed by the analysis of sediment cores from Lake Michigan. Hoh et al reported an increase of BTPE in the sediments of Lake Michigan by almost two orders of magnitude beginning in the early 1970s until the early 1990s[9]. Concentrations of deca-BDE were approximately one order of magnitude higher in the same sediment core. Unfortunately no concentrations were reported for the top layer of the sediment core representing the years 1993 to 2004. In Switzerland BTPE was found in sewage sludge samples from eight WWTP close to Zürich, sampled in the years 1993, 2002, and 2007 at average concentrations of 8.8, 22, and 14 ng/kg dw, respectively (unpublished data). The concentration of deca-BDE in those samples was with 180, 830, and 260 ng/kg dw approximately 20 to 40 times higher. Nevertheless the presence of BTBPE in 18 year old sewage sludge samples confirms the assumption that "novel" BFR were in use for many years. "Novel" are many NBFR only in term of the attention they received by the scientific community during the last few years and the recent detection in different environmental compartments. Unfortunately many years the attention was only paid to a few single classes of brominated flame retardants e.g. PBDEs, TBBPA, and HBCDs, meanwhile many other brominated flame retardants with similar physico-chemical characteristics were used in a variety of products. The scientific focus should therefore be opened further, before other replacement chemicals with harmful properties find their way into consumer products and finally via different pathways into our environment. Up to now little attention has been paid to phosphorous and nitrogen based flame retardants. Many organophosphates are high production volume chemicals, which also can possess harmful characteristics (e.g. tris(2-chloroethyl)phosphate). With possible future bans on NBFR organophosphates and nitrogen based FR might be produced and used in even larger quantities. From the 36 analyzed samples included in the presented study 20 (56%) showed signals of one or more organophosphates, which in most cases probably were added as polymer refiner (plasticizer, antioxidant e.g. Irgafos 168), with the additional benefit of acting under thermal stress as a flame retardant. Sixteen samples (50%) contained significant amounts of tris(2,4-ditertbutylphenyl)phosphate. The WHO monograph on flame retardants mentions that structurally similar phosphorous based chemicals are used as flame retardants[7]. Further research is needed to evaluate the use of NBFR and other chemicals used in consumer products as replacements for banned BFR.

Additionally the fate of this chemicals and their impact on humans and the environment must be urgently studied.

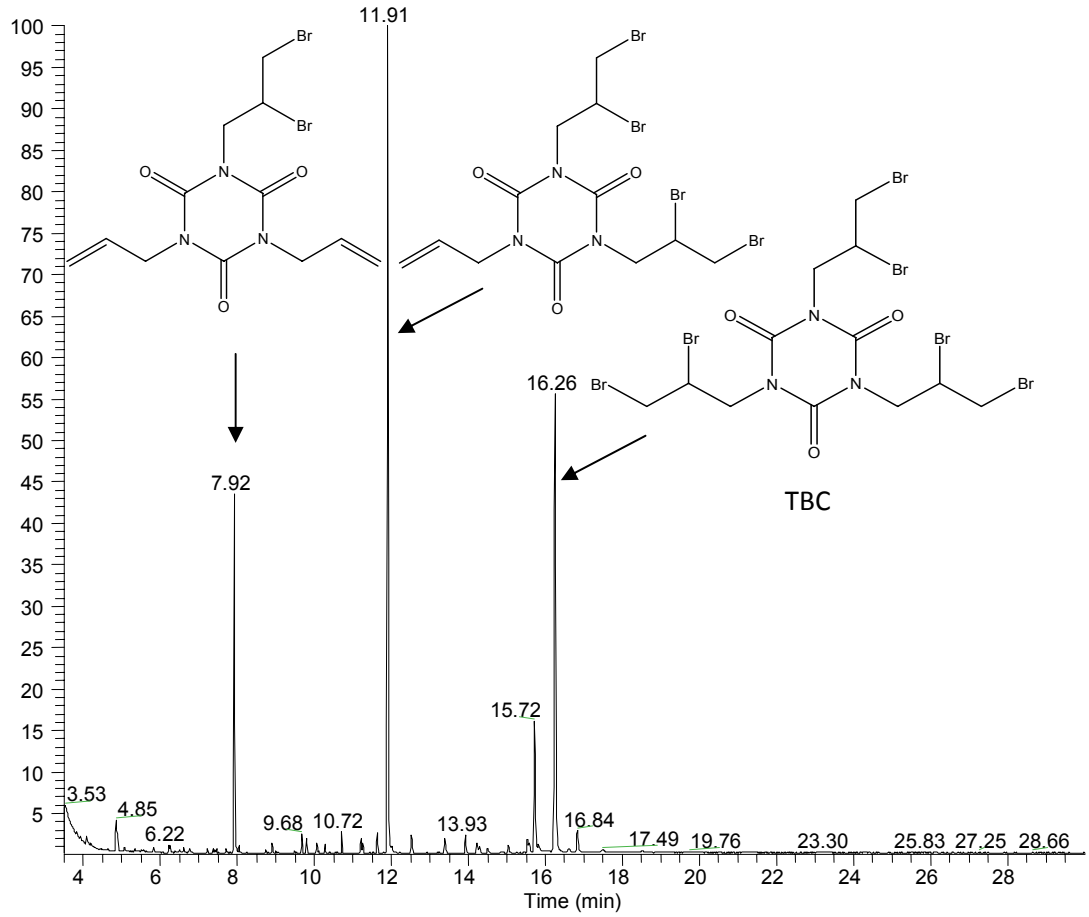

Figure 2: GC/MS total ion chromatogram of a polymer sample with an XRF determined bromine content of 3.3%. The sample was taken from the switch box of a new table lamp. The main product is with a retention time (RT) of 16.26 minutes tris(2,3-dibromopropyl)isocyanurate (TBC, CAS 52434-90-9). The signals with the RT of 7.92 and 11.91 minutes belong to by- or degradation products of the mother compound. The chemical structures are shown.

Acknowledgments

The Swiss Federal Office for the Environment (FOEN) is acknowledged for financial support of this study. Special thanks go to the participating cantonal authorities for providing sample materials.

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