Brominated flame retardants in products: Results of the Swiss market survey 2008

Eva Bantelmann[1], Albert Ammann[2], Urs Näf[3], Josef Tremp[4]
[1]Canton Aargau, Agency for Consumer Protection, Chemical Safety, Obere Vorstadt 14, CH-5000 Aarau, Switzerland
[2]Canton Berne, Cantonal Laboratory Berne, Environmental Safety, Muesmattstrasse 19, CH-3012 Berne, Switzerland
[3]Canton Zurich, Official Food Control Authority of the Canton of Zurich, Chemicals Department, PO Box 1471, CH-8032 Zurich, Switzerland
[4]Federal Office for the Environment FOEN, Substances, Soil, and Biotechnology Division, CH-3003 Berne, Switzerland

Introduction

While brominated flame retardants (BFRs) have been extensively studied worldwide in different compartements of the environment, wildlife and also in humans (de Wit 2002; Birnbaum & Staskal 2004), there is only very limited information available in the published literature on the uses of individual BFRs in industrial and consumer products. The addition of brominated flame retardants minimizes the flammability and combustibility of polymeric materials. Because fire safety regulations are getting stricter worldwide, the application of flame retardants is indispensable for the industry to meet the safety standards. BFRs belong to the most effective flame retardant systems and can be incorporated in most polymers without altering their favourable technical and visual characteristics. Therefore their use has steadily increased over the years. Housings of electric and electronic appliances and machines, printed circuit boards, lighting, wiring and electric power distribution equipment, expanded and extruded polystyrene foams for insulation of buildings, polymers for use in transportation, and components of textiles, carpets and furniture are commonly made flame retardant with brominated organic substances (Lassen & Løkke, 1999). In most materials the brominated flame retardants are incorporated as additives, leading to a release of these substances during service life and recycling processes of waste, as these BFRs are not chemically bound to the polymer matrix. The permanent surrounding by flame retardant electro- and eletronic consumer products as well as textiles and building materials indoors is an important factor to consider as some studies demonstrate the abundance of brominated flame retardants in interior air samples and dust probably originating from abrasion particles of the household effects (Batterman et al. 2009; Hazrati & Harrad 2006; Abdallah et al. 2008; Zota et al. 2008). Some studies even predict that indoor dust and the uptake of BFRs over the skin and by hand-mouth contact has more influence on the BFR concentration in the blood and breast milk than food (Lorber 2008; Stapleton et al. 2008). Because of their potential hazard for human health and environment, some brominated flame retardants have been restricted in the European Union and Switzerland. In Switzerland, the placing on the market and use of polybrominated biphenyls (PBBs), pentabromodiphenyl ether (pentaBDE), and octabromodiphenyl ether (octaBDE) as substances on its own as well as in preparations with contents of each of these BFRs equal to or exceeding 0.1% by mass is prohibited. Placing on the market – but not the use – of articles that contain these substances in concentrations equal to or exceeding 0.1% by mass is banned as well. Excluded from the ban is only the placing on the market and use of these BFRs (as substance, in preparations and in articles) for analysis and research purposes.

This study gives an overview of a national market survey regarding selected BFRs in polymer parts of a wide range of industrial and consumer products, including electrical devices, building materials and lighting equipment. The aim of the survey was to evaluate the compliance of commercial articles with the provisions of the Swiss restrictions on BFRs described above. As Switzerland is Clearing House Country for the OECD activities on voluntary risk management action on BFRs, the Swiss Federal Office for the Environment was also interested to get information on the current use of tetrabromobisphenol A, decabromodiphenyl ether (decaBDE), and hexabromocyclododecane (HBCD). DecaBDE and HBCD are currently discussed as candidates for future restrictions.

Materials and Methods

The national survey was carried out in 2008 with the participation of authorities of 18 Cantons, charged with the enforcement of the chemicals legislation. The analytical work has been shared by 6 cantonal laboratories supported by the Swiss Federal Laboratories for Materials Testing and Research (Empa) for quality control. Selection of the article categories have been based on fire safety requirements and on data about the importation of selected goods provided by the federal custom authority. Sampling of articles has been carried out by inspectors of the cantonal authorities in manufacturing and importing companies of selected article categories. A semi-quantitative, non-destructive X-ray method (e.g. handheld Niton XLt-797 XRF analyzer, Thermo Scientific) was used on site for selection of articles that contain bromine in at least one component at concentrations above 500 mg/kg. Bromine was used as a screening parameter for BFR. The bromine concentration of 1907 components out of 1359 articles were measured in total. The reliability of the x-ray method was pre-examined by comparing its results with the neutron activation analysis (NAA), based on measurements of 60 polymer containing components from different articles. The comparison of these two independent methods showed an excellent correlation for bromine. Only articles containing more than 500 mg/kg bromine were collected for further analysis of BFRs. The concentration of the target substances PBB, pentaBDE, octaBDE, decaBDE, HBCD and additive TBBPA have been determined by GC/MS, GC/ECD or LC-MS/MS, depending on the substance and the available equipment of the individual laboratories. All data were assigned to the appropriate category of the individual articles, defined by the European WEEE-directive (DIRECTIVE 2002/96/EC), and a few additional categories.

Results and Discussion

25 % of the articles tested by the handheld XRF analyzer contained more than 500 mg/kg of bromine. In particular plastic components of the category "Automatic dispensers" as e.g. professional coffee mashines for gastronomy and "Lighting equipment" contained bromine substances. 214 component samples with bromine concentrations ≥ 500 mg/kg were analysed for the BFR target substances. The relation between the bromine concentration and the analytical confirmation of the target substances is shown in Fig. 1. Samples with bromine concentrations between 15-20 % covered most of the target substances. As illustrated in Figure 2, 28 % of all analyzed 214 samples contained at least one of the BFR target substances. The highest portions of BFR target substances were found in samples belonging to the articles categories "building materials" and "IT and telecommunications". However, the latter category comprises only 7 samples and can therefore not be considered as representative. From all samples containing a target substance, most (each 40 %) contained decaBDE or TBBPA. No pentaBDE and PBB has been detected in all the samples. Two samples belonging to the lighting

equipment had to be classified as “non compliant to legal obligations” by the cantonal authorities, because they contained octaBDE. 17 samples contained decaBDE, which has been banned in the EU but not yet in Switzerland. Only in 7 % of all 1907 components that have been analysed on site by XRF screening within this market survey one or more target BFR were found, whereas 18 % contained other bromine substances as a likely component of other, non-target brominated flame retardants.

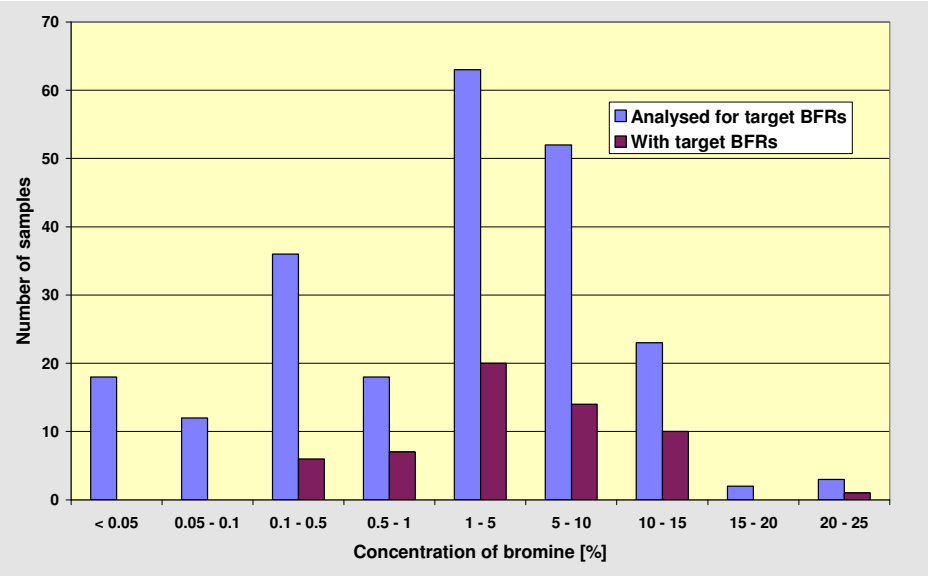

Fig. 1: Bromine concentration distribution of samples analysed for the target brominated flame retardants (BFRs) and their fractions with identified target BFRs.

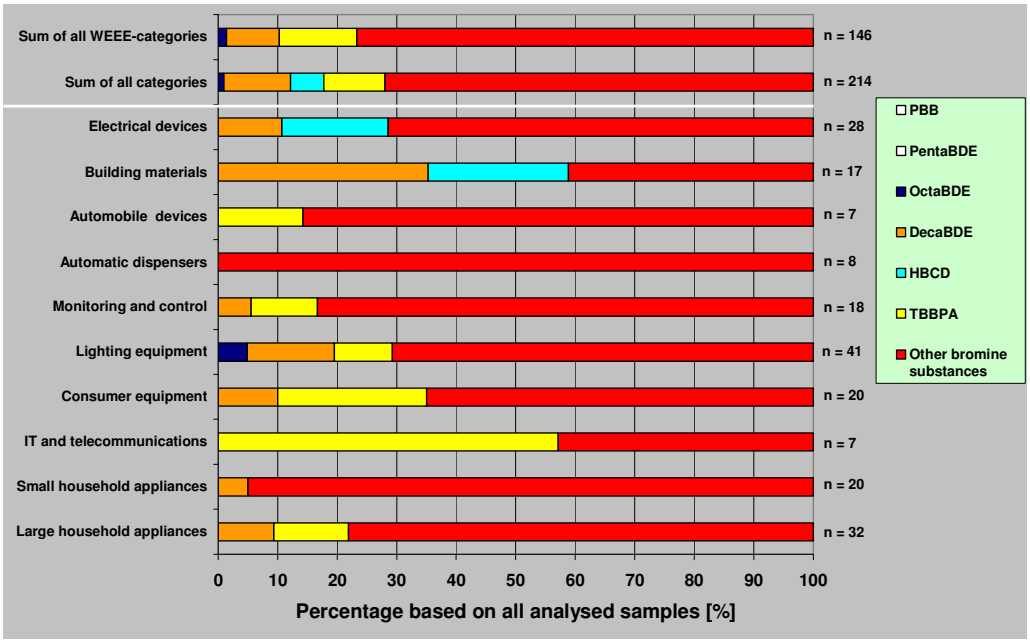

Fig. 2: Percentage of target substances and other brominated substances based on the analysed samples per product category.

The results of this market survey clearly shows that the BFRs which are banned in Switzerland, i. e. PBB, pentaBDE, and octaBDE have been almost completely phased-out in "living products", which are currently on the market. However, decaBDE, TBBPA, and HBCD are still present in many articles. The results of this survey further show that a large portion (72%) of the bromine containing components of the investigated articles could not be attributed to the BFR target substances but likely contain other brominated organic substances as fire retardants. This fact rises questions on the identity of alternative BFRs and its hazard profiles and environmental fate.

It is planned to continue with the analysis of bromine containing samples to determine the structural identity of unknown brominated organic substances.

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