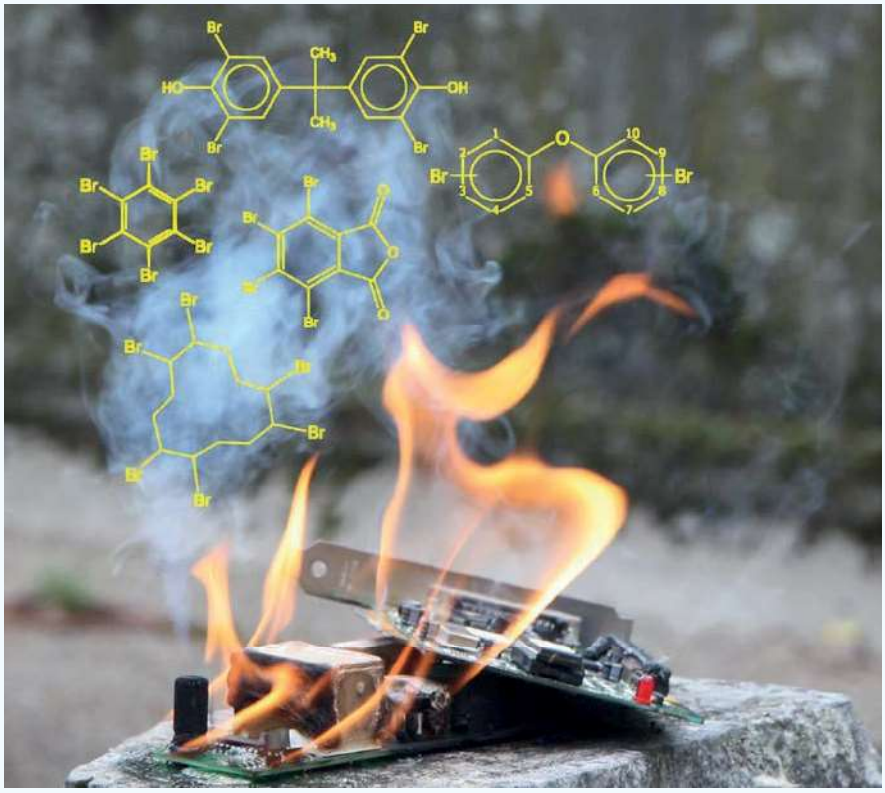
Emerging and Novel Brominated Flame Retardants (BFRs) in food: Current status of the European legislation

Gauthier Eppe, Georges Scholl, Edwin de Pauw and Jean-François Focant
CART University of Liège, Allée de la Chimie 3, B-6c Sart-Tilman, B-4000 Liège, Belgium



Established BFRs

Brominated flame retardants (BFRs) are anthropogenic chemicals that are used with the aim of increasing the fire resistance of materials. These brominated organic compounds started to be industrially produced in the beginning of the 1970s and their cumulative current production volume exceeds 400,000 tons/year [1]. The main usage concerns the electronic industry, principally in the electronic goods in printed circuit boards, connectors and cables or components such as plastic covers (e.g. television, computers) but they are also used in carpets, upholstery, furnishing and paints.

BFRs are incorporated as either additive (blended with polymer), such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and hexabromocyclododecanes (HBCDDs) or reactive ingredients (covalently bonded to polymer), such as tetrabromobisphenol-A (TBBPA). PBBs, PBDEs, HBCDDs, TBBPA and their derivatives are the most commonly used. These BFRs can leach out or evaporate from the products in which they are incorporated. They have been found to be ubiquitously present in remote areas in either abiotic and biota samples providing evidence that these substances are persistent in the environment, including long-range environmental transport, bioaccumulation in aquatic and terrestrial food and human biota. In 2009, HexaBBs, BDE congeners 47, 99, 153, 154, 175 and 183 were classified as new Persistent Organic Pollutants (POPs) under the Stockholm Convention; in 2013, HBCDDs were also added to the new POPs list. This has led to ban the production and use of certain formulations of these BFRs.

In order to assess the need for regulatory measures (or not), the European Commission asked the European Food Safety Authority (EFSA) to prepare a scientific opinion on the risks to human health related to the presence of BFRs in food. The Scientific panel on contaminants in food adopted several scientific opinions on the different classes of BFRs between 2010 and 2012 [2,3,4,5,6]. EFSA concluded that the most important BFRs (BDE congeners 28, 47, 100, 153, 154, 183, and 209; BB congener 153; HBCDD α,β,γ isomers; TBBP-A) have to be monitored based on the analytical feasibility to measure their occurrence in food and feed in accredited laboratories. The European Commission has adopted a recommendation (2014/118/EU) indicating that member states should perform the monitoring of BFRs during the year 2014 and 2015 for a wide variety of foodstuffs reflecting consumption habits [7]. Analytical methods have to reach a limit of quantification (LOQ) of 0.01 ng/g wet weight or lower for PBDEs and HBCDDs while 0.1 ng/g wet weight or lower is accepted as LOQ for TBBP-A and its derivatives.

Emerging and novel BFRs

Beside these 'established BFRs' a series of less well-known and studied BFRs were classified as 'emerging' and 'novel' BFRs [8]. According to the EFSA report on these new classes of BFRs and also based on the scientific publication of Bergman and co-workers [9], emerging BFRs are defined as chemicals which are applied as flame retardants that have been identified as anthropogenic chemicals in any environmental compartment, in wildlife, in food or in humans. Novel BFRs are defined as chemicals applied as flame retardants, and with confirmed presence in materials and/or goods in concentrations above 0.1% but not identified in environmental samples, wildlife, food or humans. These two groups of BFRs encompass 17 and 10 individual compounds, respectively. The complete list is available in the EFSA report [8]. It is rather difficult to estimate accurately the production of these new BFRs. The report from Harju and coworkers estimates the total volume of production around 180000 tons/year [10]. Regarding the analytical methodologies, the EFSA report pointed out the lack of specific analytical methods for many of them. However, amongst the list, Commission Recommendation 2014/118/EU asked to carry out analysis of tris(2,3-dibromopropyl) phosphate (TDBPP); N,N'-ethylenebis(tetrabromophthalimide) (EBTEBPI); hexabromocyclodecane (HBCYD); bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP); 2- ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) and dibromoneopentyl glycol (DBNPG) in fish and other seafood, meat and meat products, animal and vegetable fats and oils, milk and dairy products, eggs and egg products and food for infants and small children [7. A limit of quantification of 1 ng/g wet weight or lower is requested for those BFRs. One should note that the analytical challenges to develop accurate methods here is much more complicated compared to the methods developed a few years ago for established BFRs like PBDEs. A wide variety of analytical approaches for sample extraction, purification and instrumental analysis are needed [11]. In addition, a limited number of standards are available for emerging and novel BFRs, including some ^{13}C labeled standards for isotope dilution quantification by LC or GC-mass spectrometry (MS) based techniques, but not sufficiently. A large range of standards and reference materials need to be developed.

Scientific reports, opinions and publications revealed and identified a number of research gaps covering analytical aspects, environmental issues, levels in food, physico-chemical characteristics, toxicological hazards and human exposure to these emerging and novel BFRs. Studies and research projects need to be undertaken to gather additional experimental data. In that context, a recent publication reported possible concerns regarding the present of Dechloranes (Dechloranes Plus, Dechloranes 602, Dechloranes 603, Dechloranes 604, and Chlordane Plus) in human serum samples from Western Europe [12]. Despite the fact that these chlorinated and mix chloro-bromo FRs were never produced in Europe, they were measured at levels higher than the most common PBDEs. Dechloranes were further found in Belgian foodstuffs at the pg/g fat level, corresponding to an estimated daily intake of more than 100 pg [13]. As very little is known about their toxicity, these reports do not yet demonstrate the need for regular food-feed control, but at least highlight Dechloranes as amongst the possible next targets.

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G.Eppe@ulg.ac.be