FLAME RETARDANTS ON OUR DESKS

De Boer J*, Brandsma SH, Ballesteros-Gómez A, Leslie HA, Leonards PEG

VU University, Institute for Environmental Studies (IVM), De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

Introduction

Environmental studies on flame retardants (FRs) took off in the late 1990s. Triggered by publications on the occurrence and increasing concentrations of brominated FRs (BFRs) in human milk[1] and sperm whales[2], many research groups started studies on BFRs and found substantial environmental concentrations of mainly tetra- and pentabrominated diphenylethers (BDEs), both originating from to the use of PentaMix as FR in upholstery textile and electrical and electronic equipment. Not much later, toxic and bioaccumulative properties of BFRs started to be identified[4]. It soon became apparent that another BDE mixture, decaBDE, was applied in even higher volumes in textiles and housing of electronics. These high volumes were reflected in the high concentrations of decaBDE which were detected in the sediments. Bioaccumulative properties of decaBDE and its possible degradation to toxic lower brominated BDE congeners[3] sparked a debate as to the environmental safety of this technical mixture. In addition to the numerous BDEs, two other BFRs were detected in the environment: the strongly lipofilic and bioaccumulative hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A)[5,6] which is less lipophilic. Ricklund et al.[7] analysed sediments and found decabromodiphenylethane (DBDPE), an alternative to decaBDE, with similar properties. Other BFRs were found[8,9], although most of them appeared to be present in somewhat lower concentrations in the environment compared to the pentaBDEs, decaBDE and HBCD.

Although organophosphorus-based flame retardants (PFRs) had already been used before, the concern about the BFRs triggered some companies to return to PFRs or opt for other halogen-free (HF) FRs as alternatives to BFRs. The European research project ENFIRO (www.enfiro.eu) investigated 15 HFFRs resulting in a comprehensive dataset on the viability of production and application, environmental safety, risk assessment and life cycle assessment. The conclusion was that in many applications it was technically possible to safely replace BFRs with alternative FRs, such as FRs based on metals (e.g. zinc stannate or aluminum trihydrate) or PFRs. Although the information on toxic properties and environmental behavior of these compounds was limited, the ENFIRO project was able to recommend six possible alternatives for BFRs for which environmental damage was estimated to be marginal. These proved to be less toxic and accumulated less in the food chain. For example, 3,4:5,6-dibenzo-2H-1,2-oxaphosphorin-2-oxide (DOPO) was identified as a viable alternative for printed circuit boards. For epoxy resins, melamine polyphosphate (MPP) in combination with aluminum diethylphosphinate (Alpi) are good alternatives. The substitution of BFRs is not a simple one-to-one replacement: the combination of FR, matrix and application is important. The three-year ENFIRO project ended before it could find 'green chemistry' alternatives for all possible polymer blends and applications, but it did demonstrate how industry and science can collaborate to design products that are fire safe and environmentally safe.

The number of novel PFRs, including chlorinated PFRs detected over a short period of time was overwhelming[10,11]. PFRs appeared to be present in many different types of equipment. With the exception of the chlorinated ones, PFRs are less persistent than BFRs, although PFR hot spots in the environment are possible in places where ongoing PFR emissions occur[12].

Chlorinated (C) FRs in the environment are also still being reported. Chlorinated paraffins (CPs) are being produced in high volumes, more than 700,000 tons per year in China alone. Dechloranes have been found in the US and Canadian environments in substantial amounts[13], and their accumulation in dolphins in the Atlantic demonstrated their global distribution[14]. Although CPs and dechloranes are both chlorinated hydrocarbons and highly persistent, they have not been listed as official POPs under the Stockholm Convention yet. For CPs the delay is due to analytical difficulties, although interlaboratory studies show improvements in the comparability of data from laboratories analysing CPs[15].

After the initial surge in environmental FR contamination studies, the human health aspects of these substances soon demanded attention. Many authors have pointed to the importance of FR exposure in the indoor environment. FRs are present at high concentrations, in close proximity to where we live and work, at our desks, in our computers and phones, in the upholstery we sit on, as well as in the many products and materials in the buildings we spend time in. Worldwide, people are spending more time indoors, in well-insulated buildings, and are more heavily engaged with multiple electronic devices. FRs can be emitted from the equipment and furniture through evaporation (offgassing) or by wear and tear (small particles breaking off from foam, textile fibers, etc.). Consequently, the discussion of exposure of humans to FRs suddenly got a different character. Persistent and bioaccumulative compounds in the environment often lead to dietary exposure, e.g. through fish or milk consumption. But the high chemical concentrations in indoor dust and air result in the major human exposure routes being inhalation and (especially for young children) hand-mouth contact. The situation indoors is even more complex as some of the substances have multiple functions besides flame retardancy; some are also applied as plasticizers or as additives in waxes. This dual functionality increases the number of applications these chemicals are used in, and consequently increases the total indoor exposure for humans.

A growing family

Abassi et al.[16] estimated that considering only the first use (no reuse and/or storage) of PBDE-containing products, approximately 60% of the US/Canadian stock of PBDEs in 2014 (i.e. ca. 70,000 tonnes, 95% of which is BDE209), will still be in use in 2020. Given the persistence of BDE209 in sediments and the availability in products and future release into the environment, substantial decreases in BDE209 concentrations in sediments are not expected in the near future. This prompted the suggestion of the creation of large environmental reservoirs of BDE209[3]. Although it is known that BDE209 can degrade when exposed to light[6], the actual rate of degradation of BDE209 may be very low because of limited light penetration in water and sediment. Tokarz et al.[17] reported half-lives of between 6 and 50 years for reductive debromination of BDE209 in sediment. An eight-year monitoring program (Decamonitor) on trends in BDE209 in European predator birds' eggs, sewage sludge and sediments showed continuously high BDE209 levels in sediments in the UK and various other locations in Europe with hardly any decrease, apart from the Western Scheldt (Netherlands). That means that small amounts of lower brominated congeners may become available over a very long period. Similarly, HBCD applied in roof insulation polyurethane foam will only become available at the end of the material life, which is estimated at periods of ca.30-100 years. With that, both chemicals are clearly of concern to the next generation.

The family of FRs that has been found in the environment has grown substantially during the last two decades. The groups of HFFRs and PFRs are at least as large as the BFR group. In addition, there are many examples of combined applications of various FRs in the same product, often with one or more synergists[18,19]. The 'Future Market Insights' industry analysis report 2014-2020 confirms that FR markets will continue to grow, particularly in the Asia-Pacific region, driven by growth in the construction and automotive industries and by fire safety regulations. All FRs have their own physical-chemical characteristics and toxicity, which makes their analysis, evaluation and risk assessment complex. The list of FRs identified around the globe in indoor air and dust in homes, schools, offices, hotels, cars and airplanes is long and growing. The concentrations indoors - in close proximity to the products that contain them - appear relatively high compared to outside concentrations (Table 1), even when we are looking at BFRs, CFRs and PFRs in sediment and fish from some of the most contaminated areas of the world (Great Lakes, USA/Canada), Baltic Sea (Scandinavia), Western Scheldt (Netherlands) and some Spanish and Korean rivers. Clearly, the exceptionally high levels in dust stand out for all three FR groups. The low accumulation of the PFRs in fish compared to the BFRs and FRs is striking (Table 1). And the high levels of the CPs

and Dechlorane Plus are remarkable and emphasize the need for action. Ballesteros-Gómez identified tris(2,4,6-tribromophenoxy) 1,3,5-triazine (TTBP-TAZ) in plastic electronic products and house dust, showing that new BFRs are still entering the market[20]. Since the ban on the Penta and Octa BDE-mixes, the total BFR production has only grown. Leaching of two new FRs, used as alternatives for decaBDE, resorcinol bis(diphenylphosphate) (PBDPP) and bisphenol A bis(diphenylphosphate) (BPA-BDPP) from consumer products was shown by Kemmlein et al.[21] These substances were also reported by Brandsma et al. in dust in various EU countries, as well as in dust collected in cars[22]. A chlorinated PFR not previously recorded in the environment, namely 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate) and commercially known as 'V6', was identified in polyurethane foam from baby care products, in houses and in cars[23]. Depending on the polymers in which they are used, Alpi and zinc stannate can leach out. Obviously, in this way a large, unexpectedly complex cocktail of substances is created in

Table 1. FRs in sediment and fish from some of the most contaminated areas in the world compared to concentrations of the same FRs in indoor dust from Europe, USA and China.

FR	Sediment	Fish	Dust
BDE47	0.06[12]	1.6[12]	280[32]
BDE209	20[12]	0[12]	1,300[32]
HBCD	0.6[12]	0.5[12]	270[32]
DBDPE	0.2-11[7]	0[39]	<10-11,070[10]
Dechlorane Plus	8-586[37]	0.5[38]	124,000[31]
Total SCCP	210-1170[35]	19-286[34]	4,000-27,000[33]
Total MCCP	20-499[36]	25-260[34]	9,000-892,000[33]
TIBP	8.1[12]	2.1[12]	48[31]
TCEP	0.4[12]	0.9[12]	1,300[31]
TBOEP	7.0[12]	6.6[12]	22,000[31]
TPHP	0.5[12]	0[12]	820[31]
EHDP	0.2[12]	0[12]	350[31]

Sediment, house, office, hotel dust: ng/g dw, fish: ng/g ww; SCCP: short-chain chlorinated paraffins, MCCP: medium- chain chlorinated paraffins, TIBP: Tris(iso-butyl)phosphate, TCEP: Tris(2-chloroethyl)phosphate, TBOEP: Tris(2-butoxyethyl)phosphate, TPHP: Tris(phenyl)phosphate, EHDP: 2-Ethylhexyldiphenyl phosphate.

indoor environments. And where one might think that CFRs would have disappeared from the scene by now, the presence of CPs, although not exclusively used as FR, and that of dechloranes suggest this is not the case. Fridén et al. report that adult exposure to CPs was predominantly via inhalation, while dust ingestion was suggested to be more important for toddlers[24]. In China an increase of CP concentrations has been reported in the outdoor environment as well[25].

Indoor exposure

The risk of dietary exposure seems still to be the greatest for the legacy BFRs and possibly some CFRs. The less persistent PFRs and HFFRs have a lower ability to bioaccumulate. Some chlorinated PFRs were found in herring from the Western Scheldt, but that area is known to be a hot spot for these chemicals, so the continuous input of new PFRs may supersede metabolism and degradation[12]. Indoors, the situation is entirely different. Both legacy BFRs and many emerging HFFRs, CFRs and PFRs have been identified in indoor air and dust. Abdallah et al. concluded that compared to dietary and inhalation exposures, dust ingestion constitutes an important pathway of exposure to HBCD and TBBP-A for the UK population[26]. PFRs are rapidly metabolized in humans and many cannot be found as parent compounds in human tissues, milk

or blood, although a number has been found in human milk from Sweden[27]. Searching for metabolites in urine is an option, but not an easy one. Tris(o,o,o-cresyl)phosphate (TCP, or TMPP in the Bergman nomenclature system[28]) was suggested to be related to neurotoxic symptoms in airplane crew members (organophosphorus-induced delayed neuropathy)[29]. Its analysis in humans is technically difficult, so reliable values are currently lacking. On top of everything else, information on toxicity is scarce for almost all compounds discussed here. The perpetual problem of using chemicals without first testing them adequately prevails more than ever here. Although analytical instrumentation now enables very sensitive detection at the picogram level, the presence of so many FRs in indoor dust is clearly of concern with regard to possible human health effects. Such widespread contamination indoors calls for robust inhalation studies. Not only the toxicity of individual FRs needs to be addressed, alongside the mixture effects of FRs and multiple other chemicals present indoors such as plasticizers and components in waxes, and metabolites[19]. This is a huge task and will require collaboration by scientists, authorities and manufacturers. Meanwhile reduction efforts are welcome, such as in California where nowadays FR-free furniture is being marketed[30]. Most likely we can live safely with much lower amounts of FRs in many products. At the same time, we should not refrain from taking reasonable measures to prevent fire-death scenarios.

References

1. Norén K, Meyronité D 2000. Chemosphere 40:1111-1123.
2. De Boer J, de, Wester PG, Klamer JC, Lewis WE, Boon JP 1998. Nature 394:28-29.
3. Ross PS, Couillard CM, Ikonomou MG, Johannessen SC, Lebeuf M, MacDonald RW, Tomy GT 2009. Mar Pollut Bull 58:7-10.
4. De Boer J, De Boer K Boon JP 2000. In: Paasivirta J (Ed.): The Handbook of Environmental Chemistry, Vol. 3, part K: *New Types of Persistent Halogenated Compounds*. Springer Verlag, Heidelberg, Germany, pp 61-95.
5. Covaci, A., A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.V. Heeb, H. Leslie, C.R. Allchin, De Boer J 2006. Environ Sci Technol 40:3679-3688.
6. Stapleton HM, Dodder NG 2008. Environ, Toxicol. Chem. 27:306-312.
7. Ricklund N, Kierkegaard A, MacLachlan MS 2010. Environ Sci Technol 44:1987-1991.
8. Covaci A, Harrad S., Abdallah MAE, Ali N, Law RJ, Herzke D, De Wit CA 2011. Environ Int 37:532-556.
9. López P, Brandsma S, Leonards P, De Boer J 2011. Anal. Bioanal. Chem.400:871-883.
10. Stapleton HM, Allen JG, Kelly SM, Konstantinov A, Klosterhaus S, Watkins D, McClean MD, Webster TF 2008. Environ Sci Technol. 42:6910-6916.
11. Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF 2009. Environ Sci Technol 2009, 43:7490-7495.
12. Brandsma, SH, Leonards PEG, Leslie HA, De Boer J 2015. Sci Total Environ 505:22-31.
13. Shen L, Jobst KJ, Reiner EJ, Helm PA, McCrindle R, Taguchi VY,Marvin CH, Backus S,. MacPherson KA, Brindle ID 2014. Environ Sci Technol 48:11170−11177.
14. De la Torre A, Alonso MB, Martinez MA, Sanz P, Shen L, Reiner EJ, Lailson-Brito J, Torres JPM, Bertossi C, Marigo J, Barbosa L, Cremer M, Secchi E, Malm O, Eljarrat E, Barcelo D 2012. Environ Sci Technol 46:12364-12372.
15. Van Mourik L, Gaus C, Leonards PEG, De Boer J 2015. Chemosphere, in press.
16. Abbassi G, Buser AM, Soehl A, Murray MW, Diamond ML. 2015. Environ Sci Technol 49:1521-1528.
17. Tokarz J, Ahn M-Y, Leng J, Filley TR, Nies L. 2008. Environ Sci Technol 42:1157-1164.
18. Waaijers, SL. Ph D thesis, University of Amsterdam, The Netherlands, 2014, pp 31-50.
19. Hoffman K, Fang M, Horman B, Patisaul HB, Garantziotis S, Birnbaum LS, Stapleton HM 2014. Environ Health Perspect 122:963-969.
20. Ballesteros-Gómez A, De Boer J, Leonards PEG 2014. Environ Sci Technol, 48:4468-4474.
21. Kemmlein S, Hahn O, Jann O 2003. Atmos Environ 37:5485-5493.
22. Brandsma SH, De Boer J, Leonards PEG 2014. Chemosphere 116:3-9.
23. Fang M, Webster TF, Gooden D, Cooper EM, McClean MD, Carignan C, Makey C, Stapleton HM 2013. Environ. Sci. Technol. 47:4449-4454.
24. Fridén UE, McLachlan MS, Berger U, 2011. Environ Int 37:1169-1174.

25. Chen MY, Luo XJ, Zhang XL, He MJ, Chen SJ, Mai BX 2011. Environ Sci Technol 45:9936-9943.
26. Abdallah M, Harrad S, Covaci A 2008. Environ Sci Technol 42: 6855-6861.
27. Marklund S, Sundkvist A, Olofsson U, Haglund P 2010. J Environ Monit12:943-951.
28. Bergman Å, Rydén A, Law RJ, De Boer J, Covaci A, Alaee M, Birnbaum L, Petreas M, Rose M, Sakai S, Van den Eede N, Van der Veen I 2012. Environ Intern 49:57-82.
29. Winder C, Balouet J-C 2002. Environ Res A89:146-164.
30. Betts K 2015. Environ Health Perspect 123:A56-A63.
31. Cao Z, Xu F, Covaci A, Wu M, Wang H, Yu G, Wang B, Deng S, Huang J, Wang X 2014. Environ Sci Technol 48:8839-8846.
32. Shoeib M, Harner T, Webster GM, Sverko E, Cheng Y 2012. Environ Pollut 169:175-182.
33. Hilger B, Fromme H, Völkel W, Coelhan M 2013. Environ Pollut 175:16-21.
34. Reth M, Zencak Z, Oehme M 2005. Chemosphere 58:847-854.
35. Castells P, Parera J, Santos FJ, Galceran T 2007. Chemsophere 70:1552-1562.
36. Hüttig J, Oehme M 2005. Arch Environ Contam Toxicol 4:449-456.
37. Sverko E, Tomy GT, Marvin CH, Zaruk D, Reiner E, Helm PA, Hill B, McCarry BE 2008. Environ Sci Technol 42:361-366.
38. Kang JH, Kim JC, Jin G-Z, Park H, Baek S-Y, Chang Y-S 2010. Chemosphere 79:850-854.
39. Kierkegaard A, Björklund J, Friden 2004. Environ Sci Technol 38:3247–3253.