THE ENVIRONMENTAL OCCURRENCE OF BROMINATED FLAME RETARDANTS

Jacob de Boer

Netherlands Institute for Fisheries Research, P.O. Box 68, 1970 AB IJmuiden, The Netherlands

Introduction

As long as humans inhabit the world, they have sought for means to protect themselves against fire. Still, fire is a major source of damage, leading to many deaths and injuries in each country in the world each year. For example, 465 deaths and 3,700 injuries are the result of 67,000 fires per year in Canada[1]. The idea of using flame retardants (FRs) goes back to 450 BC, when the Egyptians used alum to reduce the flammability of wood[2]. The need for FRs has grown enormously since the introduction of polymers in our modern society. Various types of FRs are nowadays available: chemicals based on halogenated organic compounds, phosphorous containing substances, aluminium based compounds and others. There are reactive FRs which have a covalent bond with the polymer, and additive flame are being dissolved in the polymer. The mechanism for flame retarding can be based on physical principles: i) cooling or ii) dilution, or chemical principles: iii) radical formation (flame termination), iv) removal by decomposition of polymer, and v) protection (coating) by carbonising[3]. Most brominated FRs (BFRs) work according to

Table 1. BFR product groups and applications[3].

BFR product group	Examples	Application
Bisphenol-A	TBBP-A	Epoxy, ABS
	Bisphenol-A bis-dibromopropyl-ether	Polypropylene, polyethylene, glow wire
	Carbonate oligomers of TBBP-A	GF PBT, PC sheet
Diphenylether	PBDEs: penta mix	Flexible and rigid PUR
	PBDEs: octa mix	ABS
	PBDEs: deca mix	HIPS for TVs (USA, Asia), upholstered furniture
Phthalic acid anhydrid	Tetrabromophthalic anhydride	Polyester
	Tetrabromophthalic ester	Flexible PVC
	Tetrabromophthalate diol	Rigid PVC
Phenol	2,4,6 Tribromophenol	Endcap for FR oligomers
	Bis (tribromophenoxy) ethane	UV stable ABS
Styrene	Polydibromo styrene	High heat glass reinforced PA
	Grafted polybromo styrene on polypropylene	Non-blooming polypropylene
Cyclododecane	HBCD	Polystyrene, HIPS, glow wire, upholstered furniture

ABS: acrylonitrile butadiene styrene; GF PBT: glass fiber reinforced polybutylene terephthalate; PUR: polyurethane; PC: polycarbonate; HIPS: high impact polystyrene; PVC: polyvinylchloride; PA: polyamide;

the principle of flame termination. Bromine is more effective than chlorine. Antimony oxide is often used as a catalyst, for a stepwise liberation of bromine at relatively low temperatures and to optimise the dose of the BFR. Hexabromocyclododecane (HBCD) in polystyrene is an example of a BFR based on the principle of removal: bromine radicals cause a rapid decomposition of the polymer, and because of the chain splitting, the material is removed from the heat. BFRs are used preferentially because i) a large group (ca. 75) of these compounds with various properties is available, ii) their efficiency in flame retarding, iii) their universal applicability, iv) for some polymers they are the only available FRs to meet the highest safety limits, v) there is a lot of information on these compounds and vi) they can easily be recycled. The 75 available BFRs can be distinguished in six groups (Table 1). Their main applications are being shown as well. This presentation will give an overview of the current knowledge on the environmental occurrence of BFRs. Because of the substantial differences in character of the various BFRs, until now laboratories have only developed analytical methods for the determination of a limited number of BFRs: polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBP-A), and HBCD, which are most likely the BFRs with the highest production figures. Consequently, the environmental occurrence of these substances will be discussed. Because of the limited space, this overview does not claim to be complete. The occurrence of BFRs in indoor air and in humans will not be discussed.

Analysis

The analysis of the various BFRs is complicated as all of them have their own specific characteristics which hinders the application of multi-residue schemes. Even within one group such as the PBDEs, properties differ considerably: decaBDE requires a different clean-up and gas chromatographic (GC) analysis than the penta and octa mix related congeners. An overview of analytical methods for the determination of BFRs is given by Covaci and de Boer[4]. GC combined with mass spectrometric (MS) detection is the most frequently used method for the determination of a number of BFRs. However, because of the instability at higher temperatures, HBCD is preferably analysed with liquid chromatography (LC)-MS. Also, TBBP-A can be analysed by LC/MS. The two international interlaboratory studies organised until now have revealed that the penta-mix related congeners can be analysed by most laboratories without major difficulties. However, the analysis of decaBDE is not under control by the majority of the laboratories. World-wide only a very small number of laboratories has methods available for the analysis of HBCD and TBBP-A[5,6]. A number of typical analytical difficulties can lead to erratic data. Most PBDEs need GC columns with sufficient resolution (sufficient length and/or narrow internal diameter, e.g. 50mx0.25mm, or 8mx0.1mm), to prevent coelution problems. DecaBDE requires a limited residence time in the injector and GC oven. Therefore, GC columns with a maximum length of 10-15m and a thin film (0.1 μm) are required. Interestingly, although it has been encouraged to carry out two separate analyses for the determination of decaBDE – on a short column – and of the other BDEs - on a long column -, the use of 0.1mm columns with a length of 8-10m and film thickness of 0.1 μm would allow a proper determination of all BDEs in one GC run[7]. The analysis of decaBDE is also very sensitive for blank problems, as decaBDE occurs in high concentrations in dust[8,9]. Blanks do not always show the true problems, as decaBDE requires a considerable amount of time to redissolve. Prolonged contact of extracts with contaminated glassware can therefore easily lead to false positive decaBDE results. HBCD consists of three diastereomers. Separation of these three diastereomers is not possible by GC. In addition, the three diatsereomers are transferred into each other at temperatures above 160 C. This effect causes broad peaks and and larger standard deviations. LC/MS with electrospray will separate the three diastereomers. The same method can be applied for the determination of TBBP-A. In that way the more complicated GC analysis after derivatisation is avoided. Certified reference materials for BFRs are not yet available, but during the second international interlaboratory study a lake trout was tentatively certified for a number of BDEs[6].

Environmental Occurrence

A number of reviews on the environmental occurrence of BFRs will appear in 2003[10-14]. Most of the available information is related to penta mix related BDEs. A smaller part of the reports includes decaBDE, while only a few reports include information on HBCD and TBBP-A. A comprehensive overview on earlier data was presented by de Wit[15].

Air. PBDE concentrations in Great Lakes air have been reported by Strandberg et al.[16]. PBDEs were found in all samples in concentrations comparable to those of total DDT and ranged from 5 (Lake Superior) to 52 pg/m^3 (Chicago) for total BDE (sum of BDEs 47, 99, 100, 153, 154, 190 and 209, 209 always < det. limit). The spatial trend was well correlated to that of PCBs, indicating a correlation with densely populated and industrialised areas. PBDEs can apparently be transported to remote areas, and particle-to-gas partitioning is an important process for these compounds. Total BDE concentrations (15 BDEs, no decaBDE) of ca. 3 and ca. 20 pg/m^3 were reported for sites in Ireland and the UK, respectively. At one site, near Oxford (UK) the presence of pentabromoethylbenzene was reported. Total BDE (excl. decaBDE) concentrations in the Canadian Arctic at Alert varied between 10 and 700 pg/ m^3 [1]. Nine BDE congeners including decaBDE in rain and particulate deposition were reported in southern Sweden (total deposition 2 ng/m^2/day)[18].

Water. Few reports are available on BFR concentrations in water. The solubility in water of most BFRs is very low. Actually, the extremely low solubility of decaBDE in water (< 0.1 μg/L) may explain the very limited uptake of decaBDE in fish, as decaBDE would not be able to be transferred from the suspended particulate matter (SPM) and sediment via the water to the fish. Concentrations of 4-13 pg/L were reported for dissolved PBDEs in Lake Ontario[19]. Semi-permeable membrane devices (SPMDs) may be the most suitable instruments for the determination of BFRs in water. Booij et al. reported concentrations of 4 pg/L for BDE 99 and 4 pg/L for decaBDE in Dutch coastal water[20].

Suspended particulate matter. Limited data are available for BFR concentrations in SPM. This is due to the fact that SPM sampling is labour-intensive and costly. De Boer et al. reported very high decaBDE concentrations (up to 4.6 mg/kg dry weight (dw)) in SPM from the Western Scheldt, downstream many small textile industry sites. Penta mix related BDE concentrations varied between 0.1 and 23 μg/kg dw[21]. It was concluded that SPM is an important carrier for PBDEs and for decaBDE in particular.

Sewage sludge. Hale et al. reported a high burden of penta-mix related BDEs in US sewage sludge, up to 3 mg/kg dw[22]. These levels are 10-100-fold higher than in European sludges[21,23,24]. DecaBDE was found in varying concentrations between 0.08 and 5 mg/kg dw, also substantially higher than in some Dutch sewage sludge samples (0.009-0.2 mg/kg dw)[21]. The higher BDE concentrations found in the US samples are of environmental concern, moreover because disposal of sewage sludge by application to agricultural and other land is widely practised in the US, whereas in - at least some - European countries sewage sludge is burned in waste incinerators. The presence of TBBP-A (up to 220 μg/kg wet weight) and 2,4,6-tribromophenol (0.9 μg/kg wet weight) in Swedish sewage sludge was recently reported by Öberg et al.[24]. Sellström et al. reported the presence of TBBP-A and HBCD in sewage sludge from Sweden, in concentrations of 2.9-76 and 11-120 µg/kg dw, respectively[23]. HBCD was also found in sewage sludge from the UK, Ireland and The Netherlands (<0.4-2,600 µg/kg dw, highest levels in Ireland), and in landfills from The Netherlands (<29-660 µg/kg dw, with two extreme values of 22 and 68 mg/kg dw).

Sediment. Numerous reports are available on the presence of PBDEs in sediments[15]. Interesting is the substantial increase of penta-mix related congener and decaBDE concentrations in a number of European estuaries from 1996 to 2000, resulting in concentrations in 2000 of BDE 47 of 410, 140, 6.5 and 22 , and of decaBDE of 1,300, 105,000, 7,700, and 4,500 µg/kg org. C in the rivers Clyde, Mersey, Scheldt and Liffey (Ireland), respectively, which points to recent inputs of penta-mix related BDEs in the UK and of decaBDE in the UK, Ireland and The Netherlands[25]. The analysis of sediment cores is an elegant way to look back into history. Several reports have confirmed the relationship between the production of PBDEs and their concentrations in sediments[25,26]. Sellström et al. reported the presence of HBCD in sediment from the Swedish Viskan river, and pointed to a relationship between the textile industry and the concentrations of HBCD (max. 7.6 mg/kg organic C) and decaBDE (max. 16 mg/kg organic C) found[27]. This relationship was confirmed in an extensive diastereomer-specific study on HBCD in the Scheldt basin in Belgium. Both γ-HBCD and α-HBCD were found in the Scheldt downstream textile industry sites. Technical HBCD normally consist of ca. 80% γ-HBCD[28]. When heated to temperatures above 160 °C, γ-HBCD is transferred into α-HBCD. Such elevated temperatures are being used during impregnation of HBCD into plastics and furniture. The presence of α-HBCD therefore indicated losses during these impregnation processes. TBBP-A concentrations in the same sediment samples from the Scheldt were much lower than the HBCD concentrations. Voordeckers et al. reported the anaerobic biotransformation of TBBP-A down to bisphenol-A under conditions promoting methanogenesis or sulfate reduction[29].

Biota. Interestingly, in the study on HBCD in the Scheldt basin, mainly α-HBCD was found in eel (total HBCD concentrations up to 33 mg/kg lipid weight, α/γ ratios 2.5-3.5). Biotransformation within the eel is unlikely, as a bromine atom would need to change position. Consequently, selective uptake and/or excretion of one of the diastereomers would possibly take place. HBCD (also mainly α) was also found in starfish, whelks, cod liver, harbour porpoise blubber and liver and harbour seal blubber from the North Sea, and in eel, common tern eggs and gudgeon from the Netherlands. These results are strong indications for a highly bioaccumulative behaviour of HBCD. They show that, HBCD is of potential environmental concern. TBBP-A and dimethyl TBBP-A concentrations in biota were considerably lower than the HBCD concentrations in the same study. This can be explained by the more polar character of TBBP-A which makes that a large fraction of TBBP-A will be dissolved in the water phase. There are numerous reports on the occurrence of PBDEs in fish and other biota from all over the world, throughout many different food chains[1,10,15,30-35], all showing the bioaccumulative properties of penta-mix related BDE congeners, with generally higher levels in North America, compared to Europe and Asia. Norstrom et al. predicted that due to the ongoing use of pentaBDE formulation in polyurethane foam in the US, total PBDE levels will surpass total PCB levels in Great Lakes herring gulls within 10-15 from now[36]. As far as decaBDE has been analysed in fish, it has not been reported in measurable concentrations, apart from one report of Lepom on decaBDE in bream from the river Elbe in Germany[37]. DecaBDE was found in 11 out of 22 samples, but was not found in eel from the same locations, which may indicate that blank problems have played a role. Sellström et al. reported the presence of substantial amounts of decaBDE in Swedish peregrine falcon eggs[38]. This was the first report that showed that decaBDE would be able to bioaccumulate in birds. Meanwhile, a follow-up study on decaBDE in birds is ongoing as a contribution to the European risk assessment of decaBDE.

Conclusions

An increasing number of reports on the presence of BFRs in the environment is nowadays being produced. Most of them contain valuable information, but more information is needed in specific areas: i) more (preferably diastereomer-specific) data on the occurrence of HBCD, ii) more and better quality data on decaBDE in biota, iii) more information on the behaviour and possible degradation of decaBDE in sediments[39], iv) more data on the environmental occurrence of TBBP-A, v) more information on the possible presence of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs), and vi) more information on the toxicity of the BFRs in general.

Given the indications for increasing environmental concentrations of penta mix related BDEs, and based on the response of the bromine industry to the European ban of the penta mix, it is hoped that the industry will voluntarily reduce the penta mix production in North America. Few data are available on the octa mix, which, although analytical methods have initially not included the measurement of octa mix related BDE congeners, presumably reflects the lower production figures of this mixture. The European risk assessment process will soon conclude on the possible risks of decaBDE, and in a later stage on HBCD and TBBP-A. The recent information on environmental HBCD levels suggests that this compound is of potential environmental concern. The discussion will presumably eventually focus on the need for risk management. Possible options could be a termination of its production or measurements through product stewardship programmes.

Until now only one report on the occurrence of PBDDs and PBDFs in humans has shown the absence of a correlation between penta mix related BDE and PBDD and PBDF concentrations. However, the analysis of these compounds is complicated and the toxicity of these compounds is high at very low concentrations. Therefore, more information on PBDDs and PBDFs is needed.

Clearly, more information on the toxicology and behaviour of BFRs is needed to enable a better estimation of the risks associated with the environmental occurrence of BFRs. Meerts et al. have reported estrogen receptor-mediated luciferase induction by some BDEs, some hydroxylated BDEs and brominated bisphenol-A analogs[40]. Sandholm has shown that decaBDE has a short half-life (57 h) compared to PCBs (> 90 d), and that decaBDE is mainly distributed to the liver and plasma, rather than to the adipose tissue[41]. The European research project FIRE (Flame retardants – integrated risk assessment for endocrine disruption) will provide further information on the toxicology, as well as on the human and environmental exposure to BFRs. It is hoped that the current discussions and collaboration between authorities, research institutes and universities, and the bromine industry will lead to the right balance between the benefits of BFRs for society and their environmental and human risks.

References

1. Alaee, M., Bunce, N., Ikonomou, M., Lebeuf, M., Metcalf, C., Muir, D., Ryan, J., Sergeant, D., Solomon, K., Wakeford, B., and Whittle, M. (2002) Impact of polybrominated diphenylethers to Canadian environment and health of Canadians. TSRI report 237, National Water Research Institute, Burlington, Ontario, Canada.
2. Hindersinn, R.R. (1990) Historical aspects of polymer fire retardance. In: Nelson, G.L. (ed.): Fire and polymers hazard identification and prevention. Am. Chem. Soc. Symp. Series No. 415, New York, USA.

3. Drohman, D. Modern Flammschutzmittel für Kunststoffe. Presentation in Haus der Technik, Essen, Germany, 19-20 June 2001.
4. Covaci, A., Voorspoels, S., de Boer, J. (2003) Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples – a review. Environ. Intern., in press.
5. de Boer, J, Cofino, W.P. (2002) Chemosphere 46, 625.
6. de Boer, J., Wells, D.E., Norén, K. (2002) Organohalogen Compounds 58, 197.
7. Björklund, J. (2003) Gas chromatography and mass spectrometry of polybrominated diphenyl ethers. Ph.D. thesis, Stockholm University, Sweden.
8. Knoth, W., Mann, W., Nebhuth, J. (2002) Organohalogen Compounds 58, 213.
9. Leonards, P.E.G, Santillo, D., Brigden, K., van der Veen, I., Van Hesselingen, J., de Boer, J., Johnston, P. (2001) Proceed. BFR2001, 299, Stockholm, Sweden.
10. Law, R.J. et al. (2003) Levels and trends of PBDEs and other BFRs in wildlife. Environ. Intern., in press.
11. Watanabe, Sakai, S. (2003) Environmental release and behaviour of BFRs. Environ. Intern. in press.
12. Alcock (2003) Understanding levels and trends of BDE-47 in the UK and PBDE flame retardants in the North American Environment - an assessment of principal reservoirs and source inputs. Environ. Intern. in press.
13. Hale, R. et al. (2003) PBDE flame retardants in the North American environment. Environ. Intern. in press.
14. Hardy, M. et al. (2003) Industry sponsored reserch on the potential health and environmental effects of selected brominated flame retardants. Environ. Intern. in press.
15. de Wit, C. (2002) Chemosphere 46, 583.
16. Strandberg, B., Dodder, N.G., Basu, I., Hites, R. (2001) Environ. Sci. Technol. 35, 1078.
17. Lee, R.G.M., Thomas, G.O., Jones, K.C. (2002) Organohalogen Compounds 58, 193.
18. ter Schure, A.F.H., Larsson, P. (2002) Atmosph. Environ. 36, 4015.
19. Lucky, F., Fowler, B., Litten, S. (2001) Establishing baseline levels of polybrominated diphenylethers in Lake Ontario surface waters. Proceed. BFR2001, 337, Stockholm, Sweden.
20. Booij, K., Zegers, B.N., Boon, J.P. (2000).Organohalogen Compounds *47*, 89.
21. De Boer, J., Wester, P.G., van der Horst, A., Leonards, P.E.G. (2003) Environ. Pollut. 122, 63.
22. Hale, R.C., La Guardia, M.J., Harvey, E.P., Gaylor, M.O., Mainor, T.M., Duff, W.H. (2001) Nature 412, 140.
23. Sellström, U. (1999) Organohalogen Compounds 40, 383.
24. Öberg, K., Warman, K., ÖT. (2002) Chemosphere 48, 805.
25. de Boer, J., Allchin, C., (2001) Organohalogen Compounds 52, 13.
26. Sakai, S., Hayakawa, K., Okamoto, K., Takatsuki, H. (2002) Organohalogen Compounds 58, 189.
27. Sellström, U., Kierkegaard, A., de Wit, C., Jansson, B. (1998) Environ. Toxicol. Chem. 17, 1065.
28. Peled, M., Scharia, R., Sondack, D. (1995) Thermal rearrangement of hexabromocyclododecane (HCBD). In: Advances in Organic Chemistry II, Elsevier Publ., New York, p.92.
29. Voordeckers, J.W., Fennelli, D.E., Jones, K., Häggblom, M.M. (2002) Environ. Sci. Technol. 36, 696.

30. Zennegg, M., Kohler, M., Gerecke, A.C., Schmid, P. (2003) Chemosphere 51, 545.
31. Akutsu, K., Obana, H., Okihashi, M., Kitagawa, M., Nakazawa, H., Matsuki, Y., Makino, T., Oda, H., Hori, S. (2001) Chemosphere 44, 1325.
32. Boon, J.P., Lewis, W.E., Tjoen-a-Choy, M.R., Allchin, C.R., Law, R.J., de Boer, J., Ten Hallers-Tjabbes, C., Zegers, B. (2002) Environ. Sci. Technol. 36, 4025.
33. Petreas, M., She, J., Brown, F.R., Wnkler, J., Visita, P., Li, C., Chand, D., Dhaliwal, J., Rogers, E., Zhao, G., Charles, M.J. (2002) Organohalogen Compounds 58, 177.
34. Oliaei, F., King, P., Phillips, L. (2002) Organohalogen Compounds 58, 185.
35. Moon, H.-B., Choi, H.-G., Kim, S.-S., Lee, P.-Y., Ok, G. (2002) Organohalogen Compounds 58, 221.
36. Norstrom, R.J., Simon, M., Moisey, J., Wakeford, B., Weseloh, D.V.C. (2002*). Environ. Sci. Technol.* 36, 4783.
37. Lepom, P. Karasyova, T., Sawal, G. (2002) Organohalogen Compounds 58, 209.
38. Sellström, U., Lindbergh, P., Hagglund, L., de Wit, C. (2001) Proceed. BFR2001, 159, Stockholm, Sweden.
39. Palm, A., Cousins, I.T., Mackay, D., Tysklind, M., Metcalfe, C., Alaee, M. (2002) Environ. Pollut. 117, 195.
40. Meerts, I., Letcher, R.J., Hoving, S., Marsh, G., Bergman, Å., Lemmen, J.G., van den Burg, B., Brouwer, A. (2001) Environ. Health Perspect. 109, 399.
41. Sandholm, A. (2003) Metabolism of some polychlorinated biphenyl and polybrominated diphenylether congeners in the rat. Ph. D. thesis, Stockholm University, Stockholm, Sweden.