Persistent Organic Pollutants

Edited by

STUART HARRAD

School of Geography, Earth and Environmental Sciences,
University of Birmingham, UK

WILEY

Persistent Organic Pollutants

Persistent Organic Pollutants

Edited by

STUART HARRAD

School of Geography, Earth and Environmental Sciences,
University of Birmingham, UK

WILEY

A John Wiley and Sons, Ltd, Publication

Contents

Contributors

Henry Alegria, Department of Environmental and Occupational Health, College of Public Health, University of South Florida, Tampa, Florida, USA

Mirza U. Beg, Department of Environmental Science, Environment and Urban Development Division, Kuwait Institute for Scientific Research, Safat, Kuwait

Miriam Diamond, Department of Geography, University of Toronto, Toronto, Ontario, Canada

Bondi Gevao, Department of Environmental Science, Environment and Urban Development Division, Kuwait Institute for Scientific Research, Safat, Kuwait

Stuart Harrad, Division of Environmental Health and Risk Management, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, UK

Erin Hodge, Department of Geography, University of Toronto, Toronto, Ontario, Canada

Foday M. Jaward, Department of Environmental Science, Policy and Geography, University of South Florida, St Petersburg, Florida, USA

Robin J. Law, Centre for Environment, Fisheries, and Aquaculture Sciences (CEFAS), Lowestoft Laboratory, Lowestoft, Suffolk, UK

Scott Mabury, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Derek C. G. Muir, Water Science and Technology Directorate, Environment Canada, Burlington, Ontario, Canada

Naomi L. Stock, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Nicholas A. Warner, Department of Chemistry, University of Alberta, Edmonton, Canada

Charles S. Wong, Department of Chemistry, University of Alberta, Edmonton, Canada

1

Beyond the Stockholm Convention: An Introduction to Current Issues and Future Challenges in POPs Research

Stuart Harrad

Division of Environmental Health and Risk Management, School of Geography, Earth, and Environmental Sciences, University of Birmingham, UK

The international significance of research into the sources, behaviour, fate, and effects of persistent organic pollutants (POPs) is exemplified by the Stockholm Convention for which the host organisation is the United Nations Environment Programme (UNEP). Following extensive negotiation, it was adopted on 22 May 2001, entered into force 90 days after the 50th party had ratified it on 17 May 2004, and by late 2008 there were over 180 participants (http://chm.pops.int/). The objective of the Convention is 'to protect human health and the environment from persistent organic pollutants' Among other things, it recognises the need for global action in recognition of the facts that POPs are toxic, resistant to degradation, and bioaccumulative. Furthermore, they are capable of global transport via air, water, and migratory species, and are deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems.

As of 2008, there are 12 chemicals (or groups of chemicals) that are listed under the Convention. These 12 are listed in Table 1.1. The Convention also allows for the inclusion of additional chemicals under its scope. Parties to the Convention may propose such additions, and the case for their inclusion is considered by the POPs Review

Table 1.1 *Chemicals currently listed and under consideration for listing as POPs under the Stockholm Convention*

Currently listed	Under consideration
Aldrin	Chlordecone[a]
Chlordane	Endosulfan
DDT	Hexabromobiphenyl[a]
Dieldrin	Hexabromocyclododecane
Endrin	α-Hexachlorocyclohexane
Heptachlor	β-Hexachlorocyclohexane
Hexachlorobenzene	γ-Hexachlorocyclohexane (Lindane)[a]
Mirex	Octabromodiphenyl ether
Polychlorinated biphenyls	Pentabromodiphenyl ether[a]
Polychlorinated dibenzo-*p*-dioxins	Pentachlorobenzene
Polychlorinated dibenzofurans	Perfluorooctane sulfonate[a]
Toxaphene	Short chain chlorinated paraffins

[a]Already recommended by the POPs Review Committee (POPRC) for listing under the Convention.

Committee (POPRC). For a chemical to be included in the Convention, it must display the following:

Persistence,
Bioaccumulation,
Potential for long-range environmental transport, and
Adverse effects.

Full details of the evidence required for these criteria to be fulfilled are included under Annex A of the text of the Stockholm Convention. As of late 2008, a further 12 chemicals were under consideration by POPRC for inclusion under the Convention. These are also listed in Table 1.1.

Inspection of Table 1.1 reveals that while all those listed under the original test of the Convention are organochlorines, those under consideration for inclusion include one organofluorine and a number of organobromine chemicals. Hence while this book addresses, to at least some degree, most or all of the chemicals listed in Table 1.1, it focuses particularly on polychlorinated biphenyls (PCBs), hexabromocyclododecane (HBCD), perfluorinated chemicals (PFCs), and polybrominated diphenyl ethers (PBDEs). These are selected on the basis that they either:

(a) represent an example of a currently listed POP that, despite significant efforts, remains of concern (i.e. PCBs), or
(b) are under consideration by POPRC *and* have been the subject of an explosion in scientific interest in the last decade (HBCD, PFCs, and PBDEs).

Both HBCD and PBDEs are examples of brominated flame retardants (BFRs). The recent growth in the number of scientific papers addressing the environmental presence and impacts of such chemicals has been quite phenomenal. In a similar vein, there has been a dramatic rise in concerns related to the environmental presence and impacts of perfluorinated chemicals (PFCs). Chapters 2 and 3 thus address current knowledge and research

priorities related to these groups of contaminants – often referred to as 'new' or 'emerging' POPs.

Making progress with understanding the environmental processes and pathways by which POPs transfer from their sources into wildlife and humans requires the application of sophisticated measurement techniques. One such area that has seen particular recent growth is the exploitation of the chiral properties possessed by several POPs. Chapter 4 describes how recent research in this field has provided new insights into the environmental sources and cycling of POPs.

Given the global nature of the Convention, it recognises that the nature of the problems faced by developing countries, and their capacity to tackle these problems, are often distinct from those associated with the developed world. For example, while in regions such as North America and western Europe concerns are expressed about human exposure arising from indoor contamination with BFRs emitted from items like consumer electronics, developing world concerns about BFRs are more likely to be related to issues such as emissions arising from the uncontrolled dumping and burning of BFR-containing waste, often shipped from the developed world (Athanasiadou *et al.*, 2008). The vast majority of what is known about POPs concerns the developed world, despite evidence that substantial problems exist in developing countries. It is for this reason that Chapter 5 of this book addresses the situation regarding POP contamination in such regions.

The primarily agricultural applications of some organochlorine pesticides, combined with the bioaccumulative potential and persistence of POPs that confers their well-characterised capacity to accumulate in food chains, can lead to a perception that the problems associated with POPs are largely to be found in rural, food-producing regions. In reality the urban environment plays a pivotal role in driving the emissions of POPs. Coupled with the ever-increasing rate of urbanisation, the specific physical characteristics of our cities are also of interest as they interact with POPs in a very different fashion to rural regions. Chapter 6 therefore examines urban issues related to POPs.

Traditionally, because measurements of human exposure to POPs via the diet exceeded considerably that received via inhalation of outdoor air and ingestion of water, human exposure via pathways other than diet have in the past been largely ignored. Recently, however, researchers have realised that in instances where POPs have found appreciable indoor applications, the resultant elevated indoor contamination, coupled with the high proportion of time spent indoors (typically 90 % or more in many countries) renders pathways of exposure other than diet of importance. In particular, the past widespread deployment of PCBs in, for example, building sealants has led to concentrations in indoor air that considerably exceed those present outdoors, to the extent that inhalation of such air is an appreciable exposure pathway (Currado and Harrad, 1998). More recently, attention has been drawn to the potential of incidental ingestion of indoor dust as a vector for exposure to brominated flame retardants and perfluorinated stain-proofing chemicals that enter dust as a result of their widespread deployment in electronic goods and fabrics, etc. (Abdallah, Harrad, and Covaci, 2008; Jones-Otazo *et al.*, 2005; Shoeib *et al.*, 2005). This is of special concern for infants and toddlers owing to their lower body weights and likely high dust ingestion rates compared to adults. Chapter 7 therefore examines the state of knowledge regarding the sources, levels, and human exposure implications of indoor contamination with POPs.

Finally, there is a perception that banning manufacture and new use of a POP will suffice as a control measure. While such action will have a short-term beneficial impact, further reductions in contamination are likely to be limited for as long as goods and materials produced before the ban remain in use or are otherwise not destroyed. Where the 'turnover' or replacement time of such items is long, they will represent an ongoing emission source for some time after implementation of the ban on manufacture. One example is the existence of substantial stockpiles of unused organochlorine pesticides in developing countries. Another scenario more pertinent to the developed world is the burden of POPs associated with goods and materials contained within the built environment. In both such instances, the remaining burden of these chemicals requires urgent action if their release into the environment is to be prevented. The final chapter of this book describes how indoor contamination can migrate outdoors, enter the food chain and thus 'buffer' dietary exposure. Potentially more serious, however, is the potential for environmental contamination and concomitant human exposure that exists if emissions arising from the end-of-life disposal of POPs-treated goods and materials are incorrectly managed. Chapter 8 thus calls for a radical reevaluation of the way in which we manage the life cycle of goods and materials treated with POPs, so that environmental contamination at the end of their life is minimized.

In the four years since the Stockholm Convention came into force, there has been substantial progress in our understanding of the environmental sources, behaviour, and impacts of POPs. At the same time, new issues and challenges have emerged – not least the identification of 'new' POPs like BFRs and PFCs – alongside the development of new thinking and strategies to tackle the problems. This book is intended to go some way towards identifying and describing these. In the author's view, POPs are likely to continue to provide extremely fertile research ground for the foreseeable future. Given the number of new chemicals under consideration for listing under the Stockholm Convention – a trend that is unlikely to abate anytime soon – it is imperative that scientists and policy-makers learn as much as possible from current knowledge related to the sources, fate, behaviour, and effects of those POPs listed currently and which have already been the subject of study for several decades. Such action is essential to prevent us repeating the mistakes of the past.

References

Abdallah, M. A., Harrad, S., Covaci, A. (2008) Hexabromocyclododecanes and tetrabromobisphenol-A in indoor air and dust in Birmingham, UK: implications for human exposure. *Environ. Sci. Technol.*, **42**: 6855–6861.

Athanasiadou, M., Cuadra, S. N., Marsh, G., Bergman, Å., Jakobsson, K. (2008) Polybrominated diphenyl ethers (PBDEs) and bioaccumulative hydroxylated PBDE metabolites in young humans from Managua, Nicaragua. *Environ. Health Perspect.*, **116**: 400–408.

Currado, G. M., Harrad, S. (1998) A comparison of polychlorinated biphenyl concentrations in indoor and outdoor air and the potential significance of inhalation as a human exposure pathway. *Environ. Sci. Technol.*, **32**: 3043–3047.

Jones-Otazo, H. A., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J., Wilford, B. (2005) Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.*, **39**: 5121–5130.

Shoeib, M., Harner, T., Wilford, B. H., Jones, K. C., Zhu, J. (2005) Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: occurrence, partitioning, and human exposure. *Environ. Sci. Technol.*, **39**: 6599–6606.

2

Brominated Flame Retardants

Robin J. Law

Centre for Environment, Fisheries, and Aquaculture Sciences (CEFAS), Lowestoft Laboratory, Lowestoft, Suffolk, UK

2.1   Introduction

Brominated flame retardants (BFRs) are a diverse group of chemicals that are used to protect the public from accidental fires by reducing the flammability of combustible materials such as plastics and synthetic polymers (Watanabe and Sakai, 2003). The most widely used to date are the polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A) (see Figure 2.1), although many other compounds have been developed (Birnbaum and Staskal, 2004). Depending on the product being produced and the flame retardant compound used, the flame retardant may be incorporated either additively or reactively. In the former case the flame retardant is simply mixed with the product at the production stage, in the latter the flame retardant is chemically bound. If chemically incorporated, the flame retardant is less likely to leach from the product during its lifetime. Up-to-date information on the levels of production of brominated flame retardants are not available. The Bromine Science and Environmental Forum estimated the total market demand for the major commercial BFRs by region in 2001 (Table 2.1). Evidence of the environmental persistence of a number of BFRs has led to risk assessments and risk reduction measures in a number of legislative areas, as well as voluntary emissions control measures by industry. Subsequently, production and use of the penta-mix and octa-mix PBDE formulations has ceased in the European Union following regulation in 2004, and the deca-mix product was banned in 2008 following a ruling by the European Court of Justice. Risk assessments for HBCD and TBBP-A have been completed within the EU (European Commission, 2006, 2008; Eisenreich, Munn and Pakalin, 2007; Spiegelstein, 2007). The reports of these risk assessments can be accessed on the website
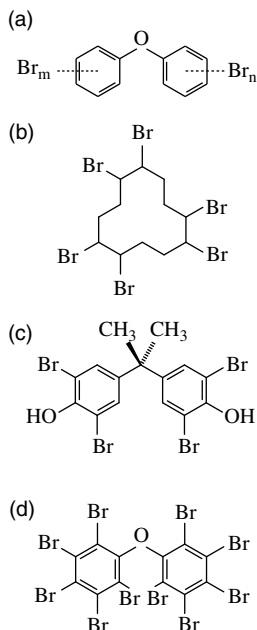
Figure 2.1   *Chemical structures of major flame retardant compounds: (a) polybrominated diphenyl ethers, (b) hexabromocyclododecane, (c) tetrabromobisphenol-A, (d) decabromo-diphenyl ether (BDE209)*

of the European Chemicals Bureau at http://ecb.jrc.ec.europa.eu/home.php?CONTENU=/ DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/.

In the USA, penta- and octa-PBDE formulations were also voluntarily phased out in 2004. In Japan, the consumption of PBDEs is declining due to effective regulation and voluntary restriction, while that of HBCD is increasing (Isobe *et al.*, 2007). TBBP-A, the most widely used BFR, is used primarily as a reactive flame retardant in printed circuit

Table 2.1   *The usage (tonnes) of selected brominated flame retardants in different areas of the world in 2001*

Product	Americas	Europe	Asia	Rest of the world	Total	% of total world usage
TBBP-A	18 000	11 600	89 400	600	119 700	59
HBCD	2800	9500	3900	500	16 700	8
Deca-mix PBDE formulation	24 500	7600	23 000	1050	56 100	27
Octa-mix PBDE formulation	1500	610	1500	180	3790	2
Penta-mix PBDE formulation	7100	150	150	100	7500	4
Total	53 900	29 460	117 950	2430	203 790	

boards (Birnbaum and Staskal, 2004), and so is be most likely to be observed close to locations at which TBBP-A is produced and used. These should mostly be in Asia, which currently has no controls in place on BFRs (BSEF, 2007; Law *et al.*, 2008b).

2.2 Sources

In general, POPs are used in industrial or agricultural applications, and exposure depends largely on proximity to these or to point-source discharges. For BFRs, the situation is different, other than close to sites of production and use, e.g. textile manufacture. Analysis of sewage sludges in a number of countries has demonstrated that there is little correlation between BFR levels and the degree of industrial discharge to wastewater treatment plants. The major source of background levels in sludge is from diffuse leaching of these compounds into wastewater streams from users, households and industries generally (Law *et al.*, 2006a). Study of BFR concentrations in atmospheric samples has shown that urban/suburban areas exhibit higher concentrations than semi-rural/rural areas (Harrad and Hunter, 2004). BFRs are incorporated into many household products and house building materials, and indoor air from buildings is acting as a source to the outdoor environment. Similarly, household dust can be contaminated to high concentrations with BFRs, and this forms a very significant exposure route, particularly for toddlers and small children (Ibarra *et al.*, 2007; Wilford *et al.*, 2005). Another area that is receiving considerable attention at present is the shredding and recycling of electronic waste (e-waste). In studies using Italian ryegrass as a passive sampler, Wanner *et al.* (2007) showed summed BDE concentrations up to 450 µg/kg dry weight around shredder plants in Bavaria. The highest concentrations were observed in the vicinity of the oldest plant, and congener patterns were linked to the material being processed, either containing the deca-PBDE or the penta- and octa-PBDE products.

Occupational exposure of workers at plants using BFRs has been assessed for both PBDEs and HBCD (e.g. see Sjödin *et al*., 2001). In the most recent study, Thomsen *et al.* (2007b) studied HBCD in workers at a factory manufacturing expanded polystyrene to which HBCD is added during production. As could be expected, workers exhibit serum levels of HBCD higher than those observed in the general population, as for PBDEs. The congener pattern for HBCD in the airborne dusts to which the workers were exposed closely resembled that of the technical HBCD mixture used at the factory (ca. 80% γ-HBCD), in contrast to the usual distribution in humans and wildlife in which α-HBCD dominates. Of particular concern in this respect is the situation in the Far East. In addition to areas such as the Pearl River Delta in China having large numbers of electronics manufacturing and assembling plants, e-waste is being imported into China at a current rate of 35 000 tonnes per annum. Guiyu in China has become an intensive e-waste recycling site, and incomplete combustion of e-waste and the dumping of processed materials are sources of various toxic chemicals, including PBDEs. This is leading to increasing pollution of rivers and coastal waters, and contamination of local fish and sediments (Guan *et al*., 2007; Luo, Cai and Wong, 2007; Wong *et al*., 2007). BDE209 is the dominant PBDE congener in both the serum of e-waste dismantling workers (Qu *et al*., 2007) and sediments in the area. The PBDE market in Asia in 2001 accounted for 37% of world demand: 23 000 tonnes of deca-PBDE, 1500 tonnes of octa-PBDE and 150 tonnes of penta-PBDE (Guan *et al*., 2007).

2.3   Overview of Measurement Techniques

This area has most recently been reviewed by Covaci *et al.* (2007a). Matrices commonly analysed include air, dust, soils, sediments, sewage sludges and a wide variety of biota samples, both terrestrial and aquatic (Law *et al.*, 2008b). BFRs have not been widely determined in water as these compounds are hydrophobic with high log K_{ow} values, and will tend to bind to soils and sediments in preference to remaining in the water column. Covaci *et al.* (2007a) have exhaustively covered extraction and clean-up techniques and it is not proposed to repeat this material here – readers are referred to their review. It is, however, worthwhile including some discussion on techniques for the determination of BFRs, certified reference materials, quality control and the current performance within intercomparison exercises.

Mass spectrometry (MS) is almost universally applied within BFR analysis, although the type of instrumentation applied and the mode of ionisation employed vary (Figure 2.2). For the BDEs, GC-MS is routinely applied, with both high- and low-resolution MS instruments in use. The ionisation mode used is either EIMS (electron impact MS mode) or ECNIMS (electron capture negative ion MS mode), in the latter case generally monitoring the bromine ions at 79 and 81 daltons. Essentially, GC-ECNIMS is functioning as a selective detector for organobromine compounds in general. For congeners in the tri- to hepta-BDE range (those deriving from the penta-mix PBDE formulation), the analysis and determination are relatively straightforward, and intercomparison exercises have shown a level of intercomparability increasing with time and experience. In the octa- to deca-bromo BDE congener range, which includes BDE183 (often considered a marker for the octa-mix formulation), BDE209 (the main congener found in the deca-mix product) and the intermediate octa- and nona-bromo congeners that could be generated by debromination of BDE209 (an issue at the heart of the debate over the environmental risk posed by the deca-mix), analysis is less simple. Taking BDE209 as the most extreme example, with a log $K_{ow} \sim 9$, due to its thermal instability, photosensitivity and its ability to bind strongly to surfaces, including laboratory glassware, determination of this congener is problematic. Achieving clean blanks and avoiding cross-contamination due to incompletely cleaned glassware are key, as is optimising the GC conditions. Lack of thermal stability can be circumvented by the use of short GC columns. Photosensitivity can be countered by using amber glassware or wrapping clear glassware in aluminium foil and using UV light filters on windows and fume cupboard fronts. ^{13}C-labelled BDE congeners are available for use as internal standards, and this is particularly important for BDE209. Protocols suitable for the determination of BDE209 have been developed (de Boer *et al.*, 2001) and need to be applied stringently if good interlaboratory agreement is to be achieved. This should not cause analysis of BDE209 to be neglected, as it is a high-production volume compound and widely distributed in the environment, but the best available methods should be used in all studies, with an appropriate level of quality control. Recently, a range of fluorinated BDE congeners have been produced as alternatives to ^{13}C-labelled congeners. Another technique that has been applied to the analysis of BDEs is comprehensive two-dimensional gas chromatography (GC × GC) (Korytár *et al.*, 2005, 2006) in order to try to solve problems of co-elution of some BDE congeners with other brominated compounds, which occurs on a single GC column. Even with the most effective combination of GC columns, the number of co-elutions was reduced but not eliminated entirely.
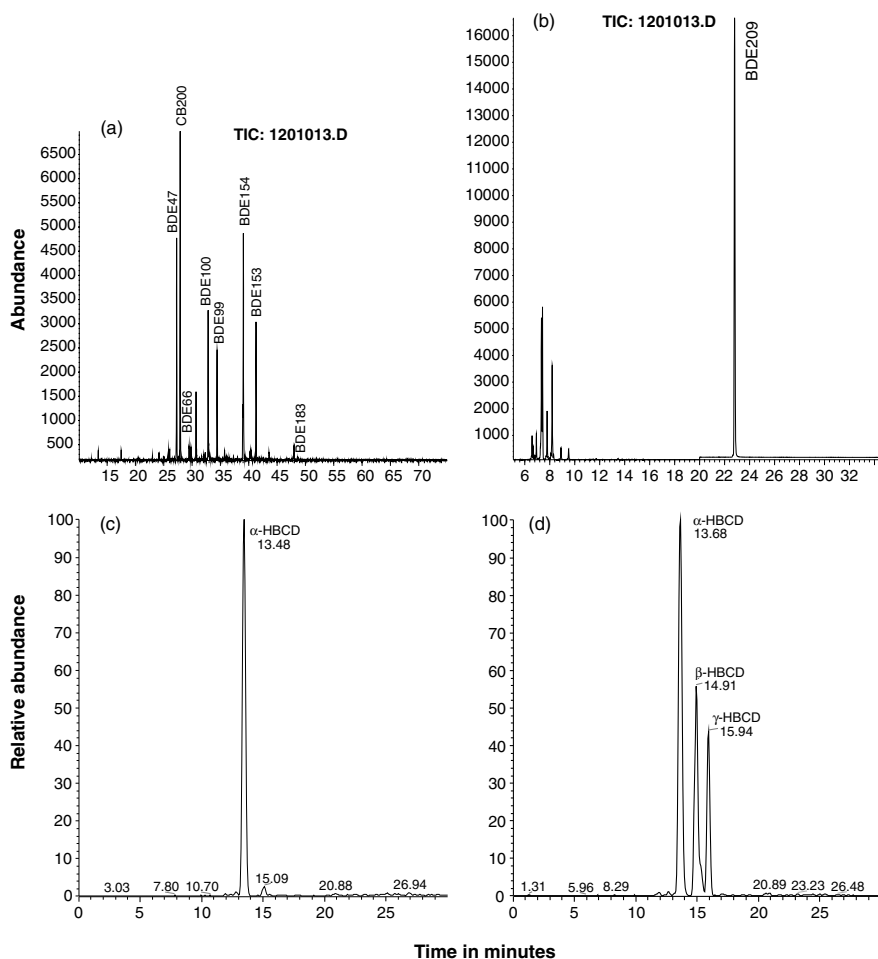
Figure 2.2 *Chromatograms of major BFRs: (a) tri- to octa-BDE congeners, (b) BDE209 (decabromodiphenyl ether), both analysed by gas chromatography–electron capture negative ion mass spectrometry using a column of 50 m length in (a) and of 15 m length in (b), where in (a) CB200 is the internal standard; (c and d) HBCD analysed on a diastereoisomer-specific basis by LC-MS. TBBP-A can be analysed in the same analytical run, but is seldom detected in UK samples. Samples analysed were: (a) blubber from a harbour porpoise SW2003/186 stranded at Hell's Mouth, Gwynedd, 26 March 2003, (b) dredged sediment from Billingham Reach, River Tees, 29 November 2005, (c) blubber from a harbour porpoise SW2005/34B stranded at Dunoon, Strathclyde, 19 February 2005, (d) blubber from a harbour porpoise SW2006/41 stranded at Putney Bridge, London, 21 January 2006*

HBCD has also been determined using GC-MS, but this approach cannot be recommended. This is because HBCD degrades on passage through the GC column due to its thermal instability, meaning that it is not possible to determine the three diastereoisomers (α-, β- and γ-HBCD) using this technique, and that even for the determination of total HBCD a broad peak is observed. The determination of HBCD on an individual

diastereoisomer basis by LC-MS is fully established (Budakowski and Tomy, 2003; Morris *et al.*, 2003, 2006; Tomy *et al.*, 2003). Care must be taken in establishing the method so as to avoid problems with ion suppression, and internal standards (^{13}C-labelled or deuterated HBCD isomers) (Morris *et al.*, 2006) should be used routinely for quantification. HPLC on chiral columns has also been used to identify the following separate HBCD enantiomer pairs, (+/–)α-, (+/–)β- and (+/–)γ-HBCD (Heeb *et al.*, 2005; Janák *et al.*, 2005).

TBBP-A is determined only rarely, probably because where it has been determined concentrations are significantly lower than those of the BDEs or HBCD (see, for example, Law *et al.*, 2006b). Even these may be overestimates due to analytical difficulties (Law *et al.*, 2008a). It can be determined using LC-MS, in the method described by Morris *et al.* (2006) concurrently with HBCD in a single analytical run. TBBP-A is used as a reactive flame retardant, primarily in printed circuit boards for electronic equipment such as computers, and so is less likely to leach from the products during use than additive flame retardants. Studies around areas of production and use, when the compound is in its unreacted state, are therefore recommended as a worst-case situation. This suggests that TBBP-A may be more important as an environmental contaminant in Asia than in Europe and North America.

The availability of certified or standard reference materials (CRMs/SRMs) is an important aspect of analytical quality control and method development, and only two are currently available for BFRs. These are SRM1589a (freeze-dried human serum) and SRM 2585 (household dust), both available from the National Institute of Standards and Technology in the USA. SRM1589a is certified for four BDE congeners, with indicative values for three more, while SRM2585 is certified for 15 congeners, including BDE209. In addition, indicative values have been developed for a range of other reference materials (Zhu and Hites, 2003; Kucklick *et al.*, 2004; Stapleton *et al.*, 2006, 2007).

Since 1999, a number of international intercomparison exercises have been organised with the aim of assessing and improving the quality of BFR analysis, the most important are summarised in Covaci *et al.* (2007a). A broad range of matrices have been used, including soils, sediments, fish and bird tissues, reindeer meat and whale blubber. Most have involved the determination of BDEs, but HBCD and TBBP-A were included in a few exercises. A series of exercises conducted within the laboratory proficiency scheme QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) has shown improved comparability over time for a number of BDE congeners (BDE47, BDE99, BDE100, BDE153 and BDE154) (de Boer and Wells, 2006). However, BDE183 and BDE209 still cause serious difficulties for most participating laboratories. Also, only a minority of laboratories can carry out reliable analyses for HBCD and TBBP-A. When examining data reported in the literature, for BDE209 and HBCD in particular, readers should carefully scrutinise the quality assurance information given before accepting data at face value.

2.4   Physicochemical Properties and Their Influence on Environmental Fate and Behaviour

The potential for organic compounds to bioaccumulate is a function of their lipophilicity, usually expressed as the logarithm of the octanol–water partition coefficient, or log K_{ow}. In the UK, the Chemicals Stakeholder Forum assesses compounds using criteria whereby

Table 2.2   Indicative log K_{ow} values for selected BFRs

Compound	Log K_{ow}	Reference
BDE3	4.8	Palm, Brorström-Lundén and Breivik, (2004)
BDE15	5.0	Wania and Dugani, (2003)
BDE28	5.5	Wania and Dugani, (2003)
BDE47	6.1	Wania and Dugani, (2003)
BDE99	6.6	Wania and Dugani, (2003)
BDE100	6.5	Wania and Dugani, (2003)
BDE153	7.1	Wania and Dugani, (2003)
BDE183	7.1	Wania and Dugani, (2003)
BDE209	10	Wania and Dugani, (2003)
HBCD	5.6	Commission on Life Sciences, (2000)
α-HBCD	4.9–5.3	Hayward, Lei and Wania, (2006)
β-HBCD	5.0–5.4	Hayward, Lei and Wania, (2006)
γ-HBCD	5.3–5.9	Hayward, Lei and Wania, (2006)
TBBP-A	5.9	European Commission, (2006)

potentially bioaccumulative compounds are defined as those for which log $K_{ow} > 4$, with those for which log $K_{ow} > 5$ being defined as potentially very bioaccumulative compounds. From the indicative values of log K_{ow} given in Table 2.2, all of these flame retardant compounds have bioaccumulation potential. (Values are described as indicative as they are derived from a variety of experimental and estimation studies and can carry large uncertainties; see Hayward, Lei and Wania, 2006). For large molecules, this tendency for accumulation is inhibited due to their large size, and BDE183 (722 daltons) and BDE209 (959 daltons) are less bioaccumulative than the di- to hepta-brominated congeners.

Modelling approaches to assess the long-range transport potential of both the BDEs and HBCD have been undertaken (Wania and Dugani, 2003; Drohmann, 2006). For HBCD and highly brominated BDE congeners such as BDE209, it was concluded that they have a very low potential to reach remote areas. The tetra- and penta-brominated congeners were shown to have a similar potential for long-range transport and accumulation in the Arctic as that of hexa- and hepta-chlorinated CBs. This suggests that some BDEs and other BFRs with similar physical properties will undergo long-range transport, deposition and revolatilisation (a process known as the 'grasshopper effect'; see de Wit, Alaee and Muir, 2006). Subsequently, Ter Schure *et al.* (2004) reported a dominance of particle-associated BDE209 in air over the Baltic Sea, and the detection of BDE209 and HBCD in both abiotic and biotic samples from Arctic and other remote locations (de Wit, Alaee and Muir, 2006; Law *et al.*, 2005, 2006a) forced a reconsideration of these conclusions. Gouin *et al.* (2006) and Breivik *et al.* (2006) have suggested that, as BDE209 is largely associated with atmospheric particles, it has an enhanced ability for long-range transport adsorbed to aerosol particles. For HBCD, modelling of degradation pathways indicated that HBCD is not expected to persist in the aquatic environment (Admon *et al.*, 2007). This work indicated that the first stages of degradation occurred under anaerobic conditions, during which HBCD can be sequentially debrominated to *t, t, t*-cyclodecatriene. Then, under aerobic conditions, this compound is mineralised to CO_2. The authors concluded that the major environmental sink for HBCD would be sediments, while environmental studies indicate very high concentrations in some aquatic biota, such as harbour porpoises (Law *et al.*, 2006b, 2006c).

2.5   Overview of Toxicology

Due to the persistence, bioaccumulation and potential for chronic toxicity in both wildlife and humans, BFRs are of concern (Birnbaum and Staskal, 2004), although the degree of toxicological knowledge to date is inadequate for a full assessment of risks to be made. Initially, it was assumed that the toxicology of BDEs would parallel that of CBs due to the structural similarities (Hooper and McDonald, 2000), possibly including dioxin-like activity for some congeners. Based upon structure–activity relationships with polychlorinated biphenyls, polychlorinated diphenyl ethers and other compounds, some of the persistent and bioaccumulative BDE congeners were thought likely to cause cancer and thyroid and/or neurodevelopmental toxicity in both humans and wildlife. Schechter *et al.* (2003) noted BDE209 as a possible human carcinogen following a 2 year chronic rodent bioassay, although this effect was observed in laboratory animals only at very high levels of exposure. The authors also noted that the penta- and octa-mix PBDE formulations are more bioactive, with possible endocrine, hepatic, reproductive and neurodevelopmental toxicities. Currently, work is also underway to elucidate the toxicity of common congeners of the BDEs (see, for example, Kuiper *et al.*, 2004; Cantón *et al.*, 2006; Muirhead *et al.*, 2006; Hu *et al.*, 2007; Lema *et al.*, 2007). In the most recent study of BDE toxicology, van den Berg (2007) concluded that BDEs can no longer be considered as dioxin-like compounds and that it is now accepted that they may have toxicological similarities with *ortho*-substituted CBs such as CB153. Endocrine-related effects have also been reported for several BDE congeners and their hydroxyl metabolites. *In vitro* effects of OH-BDEs have been observed with the oestrogen receptor, thyroid hormone transporting protein (transthyretin, TTR) and the stereoidogenic enzymes CYP17 and CYP19. Recent semi-chronic studies within the EU FIRE programme with several BFRs, including penta-BDE and deca-BDE, have shown that similar effects can also be seen *in vivo*.

Similar isomer-specific studies are also needed for HBCD. Acute toxicity tests sponsored by industry have shown low toxicity for the commercial formulation (dominated by γ-HBCD) (Drohmann, 2006). However, in wildlife, the α-HBCD isomer is predominant (Law *et al.*, 2006c). Also, Darnerud (2003) had concluded earlier that there was a lack of relevant studies of high quality that could form a basis for risk assessment of HBCD. Law *et al.* (2006c) noted that the database on nonlethal effects is still incomplete and highlighted the need for more information on neurotoxicology, developmental toxicity and the potential for endocrine disruption. Covaci *et al.* (2006) noted a range of effects from HBCDs including developmental toxicity and effects on the thyroid hormone system and indicated that further research on the levels at which these effects occur is required.

2.6   Environmental Levels – Present, Past and Future Temporal Trends

Initial concern regarding BFRs was raised by studies in Sweden in 1980, which demonstrated the presence of polybrominated compounds (PBDEs) in environmental samples (Andersson and Blomkvist, 1981). Subsequently, this concern was heightened by further studies, which showed an exponential increase in levels of BDEs in human milk samples during the 1990s (Meironyté, Norén and Bergman, 1999). This sparked an interest within the European Union and began a programme of risk assessments of the continued

production and use of BFRs, which is ongoing and has so far led to the removal of all three PBDE products from the EU market. Subsequently, BDE congener concentrations relevant to the penta- and octa-products in human milk in Sweden have begun to decline (Meironyté and Norén, 2001). In the USA and Canada, where use of the penta-BDE product has continued beyond the date of the EU ban, concentrations in human milk are much higher than those in Europe and the Far East (Figure 2.3) and are probably still increasing. Temporal trends for BFRs have been examined in a variety of matrices and locations, and I propose to concentrate on these rather than on a catalogue of environmental concentrations. Readers are referred to the original publications for these for the most part, or to recent comprehensive reviews (Covaci *et al.*, 2006; de Wit, Alaee and Muir, 2006; Law *et al.*, 2006a, 2008b) and the references therein.

BFRs bioaccumulate in both aquatic and terrestrial food chains and are commonly detected in samples of air, household dust, sediments and soils, sewage sludges, birds and their eggs, fish and marine mammals (Law *et al.*, 2006a). BDE209 is generally not detected in aquatic biota, but can accumulate in terrestrial food chains with a biomagnification factor < 1. Earthworms may be a significant vector for this (Law *et al.*, 2006a). BDE209 has been reported in fish, etc., at concentrations close to the limit of detection, but these data need to be treated with caution due to analytical difficulties in the determination of this congener listed above.

A number of recent trend studies are summarised below. Settled sediments from lakes and undisturbed (preferably anoxic) sediments represent a historical record of contaminant
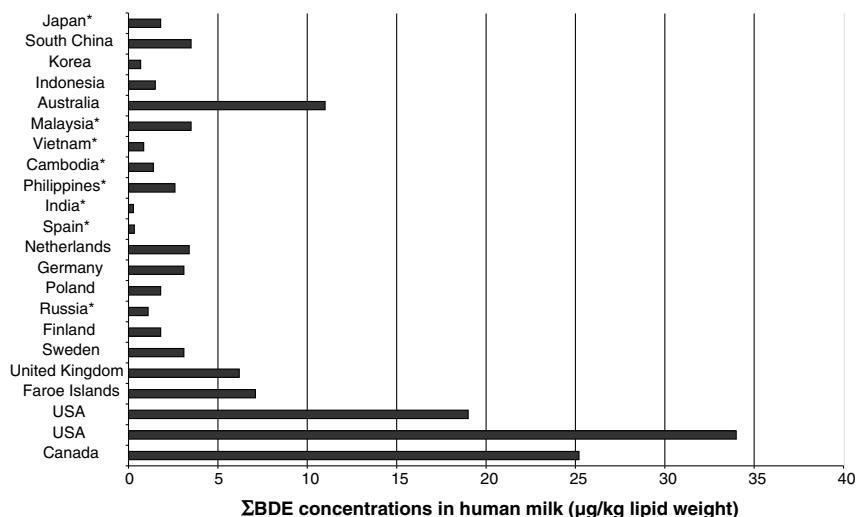
Figure 2.3 *International comparison of median (*mean) concentrations of summed BDE congeners (μg/kg lipid weight) in human milk. After Toms et al., 2007, with supplementary data. Data are taken from Baumann et al., 2003; Bi et al., 2006; Bordajandi, Abad and González, 2008; Darnerud et al., 2002; Eslami et al., 2006; Fangstrom et al., 2004; Fürst, 2006; Jaraczewska et al., 2006; Kalantzi et al., 2004; Ryan et al., 2002; Schechter et al., 2003, 2006; Strandman, Koistinen and Vartiainen, 2000; Sudaryanto et al., 2005; Toms et al., 2007; Tsydenova et al., 2007*

concentrations scavenged from the overlying waters by sediment particles, which are later deposited in the bed sediments. Three dated sediment cores from locations in western Europe (the Drammenfjord in Norway, the western Wadden Sea in the Netherlands and Lake Woserin in Germany) analysed for 14 BDE congeners showed a time-dependent pattern in BDE distribution (Zegers *et al.*, 2003). Two of the three commercial formulations could be distinguished. The penta-PBDE product was clearly present from the beginning of the 1970s, but the deca-PBDE product only appears in the late 1970s. This is in agreement with data for the industrial production of these two formulations and, in the environment overall, concentration trends generally parallel the production data as far as these can be accessed and assessed. The octa-PBDE product was not observed. In the cores from the Netherlands and Germany, concentrations of BDE congeners associated with the penta-PBDE product were levelling off in the most recent layers (1995 and 1997) whereas those in Norway were still increasing in 1999. The levels of BDE209 decreased in the most recent layers of all three cores. The absence of all BDE congeners in the older (deeper) layers of all three cores, as well as in several 100–150 million year old layers of clay from Kimmeridge, UK, indicated that these BDE congeners are not produced naturally, although some methoxy-BDEs are produced by marine animals (Teuten, Xu and Reddy, 2005). In a similar study of three sediment cores taken in Japan, the highest concentrations of summed BDEs, BDE209 and HBCD were observed in the surface layers of each core. PBDEs appeared in the layer dated to the mid 1940s, while HBCD was not detected until the early 1970s. Declining inputs of congeners from the penta- and octa-PBDE products following their discontinued use in the 1990s has stemmed increases in concentrations for these compounds (Tanabe *et al.*, 2007). Chen *et al.* (2007) studied three sediment cores from the Pearl River Estuary in south China. Summed BDE concentrations (without BDE209) increased gradually from the mid 1970s to the early 1990s, followed by differing trends in the three locations. BDE209 concentrations remained constant until 1990 and thereafter increased exponentially, with doubling times of 2.6 to 6.4 years, reflecting the increasing market demands for the deca-PBDE product in China in the 1990s due to growth in the electronics manufacturing industry. In a core from Lake Ontario, Canada, concentrations of BDEs (tri- to hepta-bromo BDEs, BDE209) and BTBPE (1,2-bis-(2,4,6-tribromophenoxy)ethane) began rising steeply during the early 1980s (Qiu, Marvin and Hites, 2007). Sudaryanto *et al.* (2007) determined BDEs in 119 sediment samples from several countries in Asia and three sediment cores from Tokyo Bay. Higher concentrations of BFRs were found in coastal waters of Korea, which is one of the major consumers in Asia. BDE209 was the dominant congener (80–100%) in all countries, whereas levels of BDE congeners deriving from the penta- and octa-PBDE products were much lower. Analyses of the sediment cores showed that concentrations of BDE209 and HBCD increased in the upper layers, coincident with the growing use of these commercial products.

Temporal trends of BFRs in lake trout from Ontario over the period 1979–2004 were studied by Tomy *et al.* (2007). Summed BDE concentrations showed a linear increase from 1979 to 1998, followed by an apparent decrease in 2004. Concentrations of HBCD were between 2.0 and 4.1 µg/kg lipid weight, and showed a declining trend during sampling years. BTBPE (now replacing the penta-PBDE product) showed a strong linear increase from 1979 to 1998, followed by a small decline in 2004. BDE209 showed a linear increase in concentrations over the whole period, consistent with usage patterns.

Takahashi *et al.* (2007) reviewed recent studies on BFRs in the Asia–Pacific region. BDE concentrations in mussels from Hong Kong and Korea were higher than in those from other

locations (Cambodia, China, India, Malaysia, the Philippines and Vietnam). The analysis of archived marine mammal samples from Asian waters taken from a specimen bank have demonstrated that, in general, environmental levels of BDEs and HBCD have risen significantly over the past 30 years (Tanabe *et al.*, 2007). In striped dolphin, for example, mean concentrations of summed BDEs increased from 13 μg/kg lipid weight in 1978 to 640 μg/kg lipid weight in 2003. An increasing trend was also observed for HBCD, from 12 μg/kg lipid weight in 1978 to 710 μg/kg lipid weight in 2003. In the UK, concentrations of BDEs, HBCD and TBBP-A have been determined in the blubber of harbour porpoises deriving from the national Cetacean Strandings Project. Maximum concentrations observed were:

Summed di- to octa-BDE congeners	15 700 μg/kg lipid weight
BDE209	Not detected in any samples
HBCD	21 300 μg/kg lipid weight
TBBP-A	38 μg/kg lipid weight

Investigation of possible time trends in HBCD concentrations in harbour porpoises from the UK indicated a sharp increase from about 2001 onward, which was not confounded by age, sex, nutritional status or location (Law *et al.*, 2006b). This may have been a result of changing patterns in the use of HBCD following controls on two PBDE formulations in the EU. A later study, however, showed a significant decrease in HBCD concentrations to have occurred between 2003 and 2004, possibly as a result of the closure of a manufacturing plant in NE England and the introduction of improved emission controls during use (Law *et al.*, 2008a).

Hassanin *et al.* (2005) determined BDEs in archived pasture samples collected in the UK between 1930 and 2004. BDEs could not be routinely detected in samples before 1970. The general trend thereafter was: (1) a rise through the 1970s, (2) a mini-peak in the mid 1980s and (3) a more recent decline consistent with controls on the use of the penta- and octa-mix commercial products in the EU (Law *et al.*, 2006a).

The presence of BDE209 at low but readily detectable concentrations in a variety of organisms and lake sediments from the Arctic shows that even very nonvolatile chemicals can reach this polar region (Muir, Alaee and de Wit, 2007), presumably due to transport on atmospheric particles. Overall, concentrations of BFRs measured to date in the Arctic are very low compared to those of 'legacy' POPs. There are a number of semi-volatile BFRs which, due to their relatively long predicted atmospheric half-lives, could undergo airborne transport and which therefore represent good candidates for future surveys of spatial and temporal trends, both in the Arctic and elsewhere (Muir and Howard, 2006). For discussion purposes, Muir and Howard list 30 chemicals with high predicted bioconcentration and a low rate of biodegradation and 28 with long-range atmospheric transport potential. There is now a vast quantity of data concerning BDEs, and some of this effort could in the future be diverted to the study of 'novel' compounds.

2.7 Human Exposure – Magnitude and Relative Significance of Pathways

In a number of studies, intake of BFRs from consumption of fish and shellfish have been shown to form a significant (or the dominant) part of the total dietary intake. In a US study,