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Item 4 (a) of the provisional agenda*

Technical work: work programmes on new persistent organic pollutants as adopted by the Conference of the Parties

Supporting document for the draft technical paper developed in accordance with the work programmes on new persistent organic pollutants as adopted by the Conference of the Parties

Note by the Secretariat

The annex to the present note contains a supporting document for the draft technical paper developed in accordance with the work programmes on new persistent organic pollutants as adopted by the Conference of the Parties. The draft technical paper has been made available as document UNEP/POPS/POPRC.6/2/Rev.1. The annex has been reproduced as received, without formal editing.

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* UNEP/POPS/POPRC.6/1/Rev.1.

Annex

Supporting Document for

Technical Review of the Implications of Recycling Commercial Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether

September 2010

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This Appendix:

(a) Summarises the decisions by the Conference of the Parties and the Persistent Organic Pollutants Review Committee and details the rationale for the report;

(b) Describes the issues that are being considered in the report and the overall objective; Proposals, illustrated by examples, are included for definitions of the terms “article”, “recovery”, “recycling”, “reclamation”, “direct reuse” and “other disposal operations”.

(c) Indicates the structure of the report and content of the various chapters; and

(d) Provides detail of the methodology used to obtain data and describe how this is presented in the report.

(e) Introduces the production and usage of PentaBDE and OctaBDE.

(f) Provides background data on the levels of PBDE in the environment and human body burdens.

(g) Introduces unintentionally formed Brominated Dioxins and Furans (PBDD/DF)

Appendix 2 (a): The decisions by the Conference of the Parties and the Persistent Organic Pollutants Review Committee and the rationale for the report

This report has been prepared as a consequence of the decision of the Conference of the Parties at its fourth meeting to list in Annex A of the Stockholm Convention[1] certain congeners contained in commercial pentabromodiphenyl ether[2] and octabromodiphenyl ethers[3]. For the purposes of this report the PBDE which are listed in Annex A have been labelled ‘POP-BDE’. Article 6 of the Convention requires that wastes containing POPs be managed in a manner protective of human health and the environment. The decisions to list these POP-BDE include specific exemptions allowing for recycling and the subsequent use in articles of recycled materials containing these substances.

The objectives of the technical review are:

i. To assess the possible health and environmental impacts of recycling articles containing brominated diphenyl ethers;

ii. To review the long-term environmental desirability of the recycling of articles containing brominated diphenyl ethers;

iii. To identify the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers.

The study has considered the implications for developed and developing countries and countries with economies in transition.

Appendix 2 (b): Descriptions of terms used

Article 6(1)(d)(iii) of the Stockholm Convention does not permit wastes, including product and articles upon becoming waste, to be subjected to “*disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants*”.

The Stockholm Convention does not define these terms and proposals for definitions of “*article*”, “*recovery*”, “*recycling*”, “*reclamation*”, “*direct reuse*” and “*other disposal operations*” have been requested as part of this review.

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[1] Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether and SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.

[2] The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

[3] The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether. .

The Stockholm Convention, however, does not include the words "*other disposal operations*". The qualification "other" infers that the definition is in a certain context – for example "*Disposal at sea was banned in 1998 and other disposal operations are now the only lawful options*".

To be useful therefore it is more relevant to define the full extent of "disposal operations" – a term included in Article 6(1)(d)(iii) of the Convention.

The key definitions proposed are therefore:

***"Disposal operations"*:**

Disposal is defined by Article 2 (4) of the Basel Convention as:

"any operation specified in Annex IV to this Convention".

Annex IV in turn contains a list of Disposal Operations divided into two categories:

A) Operations which do not lead to the possibility of resource recovery, recycling, reclamation, direct re-use or alternative uses; and

B) Operations which may lead to resource recovery, recycling reclamation, direct re-use or alternative uses.

There are only minor differences between the lists of operations in these categories and the Annexes I and II respectively of both the current composited version (2006/12/EC) and the revised version (2008/98/EC) of the European Waste Framework Directive. The Basel Convention differs in referring to both categories A and B as "*disposal*" whilst the European Directive defines only operations in Annex I as "*disposal*" those in Annex "II" being "*recovery operations*".

This issue was discussed in a teleconference on 7th July 2010 and it was agreed that it is important for the international conventions to use consistent definitions. It is therefore recommended that the Basel Convention definition should be used for the purpose of this study except where it conflicts with Stockholm Convention requirements under Article 6. It follows that the definition of waste in this study would utilise Article 2 of the Basel Convention which defines "*Wastes*" as:

"substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law".

***"Article"*:**

It is proposed that the definition of "*Article*" should be the taken from the European REACH[4] Regulations (Article 3 (3)) (European Parliament and Council 2006b):

"an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition".

***"Recycling"*:**

Recycling is not defined in the Basel Convention but the European Standard defines recycling as:

"*activity in a production process to process waste for the original purpose or for other purposes, excluding energy recovery*" European Standard EN 13965-2:2004 (British Standards Institute 2004)

This can be compared with the definition in Annex A.2 of the Packaging Directive - Council Directive 94/62/EC (European Parliament and Council 1994):

"'recycling' shall mean the reprocessing in a production process of the waste materials for the original purpose or for other purposes including organic recycling but excluding energy recovery"

The packaging directive definition is recommended as being slightly more comprehensive. This would be consistent with the way in which recycling is used in the Basel Convention to include those operations which are listed in Annex IV B

"Recovery"

It would follows that this review should use a definition of "Recovery" which includes those operations in Annex IVB of the Basel Convention. Recovery is thus wider than recycling in including all recycling operations as well as energy recovery.

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[4] "Registration, Evaluation, Authorisation and Restriction of Chemicals"

It is noted that the revised version (2008/98/EC) of the European Waste Framework Directive to the EU[5] will define incineration facilities with an efficiency above a certain threshold to as recovery operations (*R1 – use principally as a fuel or other means of to generate energy*) rather than the current definition of disposal operations (*D10 – Incineration on Land*). The Basel Convention lists incineration as D10 – Incineration on Land – i.e. a waste disposal operation.

"*Reclamation*":

Reclamation does not appear to have been formally defined in commonly used legislative codes. It is more commonly defined in the context of contaminated sites[6] than for waste management. The ISWA review of 1,000 Terms in Solid Waste Management (International Solid Waste Association (ISWA) 1992) helpfully defines reclamation for waste management as:

The process of collecting and segregating wastes for reuse.

This helps to distinguish reclamation as a process distinct from recycling, for example: "*the computer housings were reclaimed in X and shipped to Y for recycling*". This distinction is helpful and is recommended.

"*Direct reuse*"

Direct reuse also does not appear to have been formally defined in commonly used legislative codes

Re-use can mean any operation by which end-of-life products and equipment or its components are used for the same purpose for which they were originally conceived. An example would be a mattress which has been used in a superior hotel. The policy of the owners may be to change the mattress after a relatively short period – say three to five years – which is much less than the design life of approximately ten years. The mattress might then be sold, either directly or through an agent, for re-use with no re-manufacturing or intervention apart from possibly cleaning.

It can be distinguished from "indirect re-use" where some re-manufacturing is involved before the article is used again – an example would be a domestic mattress which has been used for a much longer period and which is completely stripped down to the frame and springs, for repair and re-furbishment, the components washed, refitted and possibly a recovered with new material before sale.

Appendix 2 (c): The structure of the report

The contents and numbering of the Report and Appendices are included in the main report. The intention is that the Report can be used independently and the appendices provide more detailed information, discussion and comprehensive referencing to sources. The numbering in the Appendices reflects the report to facilitate cross-referencing.

Appendix 2 (d): The methodology used to obtain data

There is now an enormousa very large literature on PBDE and it is estimated that the library is increasing by the publication of an additional five to ten papers on PBDEs are currently published each week (Brooke et al. 2009).

A simple Google search for the term PBDE returns about 715,000 hits – adding 'recycling' reduces this to 39,200. Even searching for Penta BDE finds 254,000. Octa BDE has a slightly smaller web profile with 191,000 results.

Scirus[7], is more directed as would be expected from a search engine for scientific information, but still shows 15,277 hits for PBDE (2,154 of which are journal sources); 2,165 for Penta BDE (553 journal sources) and 1,801 for Octa BDE (388 journal sources). Again adding "recycling" reduces the total hits to 2,213. In many cases, however, these papers would not be the most relevant for parts of this review and the addition of 'recycling' omits many of the references to arisings and uses, other treatments such as pyrolysis and cement kilns, PBDD/DF formation, debromination and so on.

Narrowing the scope of the literature has, therefore, been an important part of this work. The consultants established a comprehensive library of the peer-reviewed and grey literature in the early stages of the project from the standard academic references sources and on-line libraries. The indexes in PubMed and citation trackers in Scopus were used at this stage together will with full collections of the papers to the Internationalinternational symposia on Brominated Flame Retardants for 2000, 2004, 2007 and 2010 and of the international Dioxin Conferences (published as

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[5] Certain parts of which are now in effect but which must be transposed by Member States in full by12th December 2010.

[6] "Restoring land to the natural state after destruction associated with some economic activity" Wyman, B. C. and L. H. Stevenson (2007). The Facts on File Dictionary of Environmental Science Facts on File.

[7] http://www.scirus.com/

'Organohalogen CompoundsCompounds') for each year from 1990 to date. Search terms included combinations of the CAS numbers, names and synonyms of Penta PentaBDE and OctaBDE together with the technologies of interest.

The focus on the collection of grey literature has been to work backwards through the Risk Profiles and Risk Management Evaluations produced previously by the POPRC together with publications from other major for a with responsibility for chemical regulation – notably USEPA and the European Commission.

The main producers of grey literature in relation to PentaPentaBDE and OctaBDE have been the US and European agencies, NGOs and special interest groups.

A combination of citation databases (Sente[8], Papers[9] and EndNote[10]) were used for indexing and together with "*DevonThink Pro Office*"[11] Data-mining software, for searching, classifying and linking documents, peer reviewed papers, web sites and grey literature.

Many contacts were also made with professional, experts and scientists working in this field.

One comment in relation to the advanced draft was a suggestion only the publically accessible literature should be used. Unfortunately much of the peer reviewed literature remains accessible only in hard copies of journals or from publishers websites with limited access. In practically all cases papers are available to users without specific access on payment. The use of such papers is inevitable given the scientific nature of much of the information incorporated in the review – the better informed and more useful grey literature, which is normally more readily available, almost invariably draws upon the library of peer reviewed literature in any case. Relying on the grey literature and secondary referencing increases the likelihood that data has been mis-transposed from the originals or is otherwise incomplete. The review therefore relies heavily on the original sources and the authors aplogise if this makes access to the references less convenient for some readers. This approach was endorsed by the members of the POPRC participating in the 7th July 2010 teleconference.

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[8] http://www.thirdstreetsoftware.com

[9] http://mekentosj.com/papers/

[10] http://www.endnote.com/

[11] http://www.devon-technologies.com

Appendix 2 (e): Production, Use and Stocks of PentaBDE and OctaBDE

Galieleo, claims Ferris, was the original source of the quotation "*Count what is countable, measure what is measurable. What is not measurable, make measurable*" (Ferris 2004). A more modern adaptation of Galileo's dictum is "*If you can't measure it, you can't manage it*". Unfortunately in the case of PBDE the published data on production and use is limited and is often inconsistent.

This appendix therefore summarises and assesses the varied information collected from the scientific and grey literature in relation to the production and use of the relevant polybrominated diphenyl ethers congeners. Most parties appear to have little additional information on this as only one of the replies received by the Secretariat in response to the request for further information contained even limited detailed information on inventory of the POP-BDE.

The first stage of the assessment reviews the make-up of the commercial mixtures, the production of these commercial mixtures, and the production in different parts of the world. Whilst the quality of the data in relation to the production and usage is mixed there have been several assessments undertaken and these are used to make an assessment of the total production volumes around the world.

The next section then considers the various uses of the main commercial mixtures and where these relevant congers might enter the recycling waste flows. An assessment of reservoir sources is included at this stage.

Penta and Octa BDE Commercial Mixtures:

PBDE were produced by the bromination of diphenyl oxide, the degree to which it was brominated resulted in products containing mixtures of brominated diphenyl ethers with the three principle commercial mixtures being PentaBDE, OctaBDE and DecaBDE.

A TetraBDE mixture was produced for a short time in Japan as an alternative to DecaBDE but production ceased by 1990 (Watanabe & Sakai 2003). Many of the commercial mixtures included Polybrominated dibenzo- p-dioxins and, more importantly, dibenzofurans (PBDD/DF) as a by-product of the production process (WHO & IPCS 1994)(Hanari et al. 2006b). These concentrations and relevance of these contaminants are considered in more detail in Appendix 2 (g).

The PBDE structure consists of a diphenyl ether unit, with one to ten of the hydrogen atoms substituted by bromine atoms:

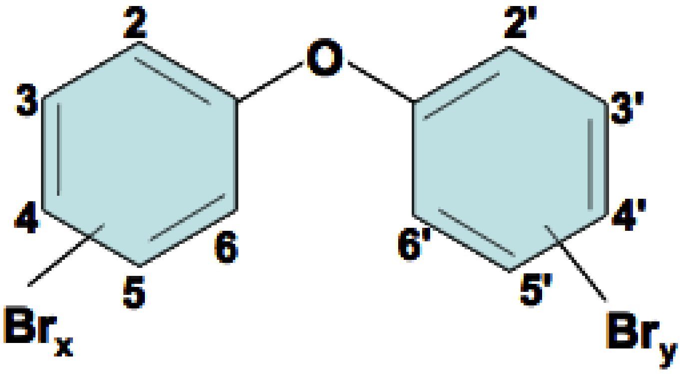


Figure 1: The structure of polybrominated diphenyl ethers (PBDE)

The formula is thus $C_{10}H_{10}Br_{x+y}O$, where x + y ranges from 1 to 10. When the different possibilities of geometric isomers are taken into account there are 209 possible individual congeners, as with polychlorinated biphenyls (PCBs) and they are numbered according to the position of the bromine atoms on the ring using the same IUPAC system as that used for numbering PCBs and similarly the nomenclature proposed by Ballschmiter for PCBs is also used for PBDE (Ballschmiter & Zell 1980). The total number of possible isomers for mono-, di-, tri- up to decabromodiphenyl ethers are: 3, 12, 24, 42, 46, 42, 24, 12, 3, and 1, respectively (WHO & IPCS 1994).

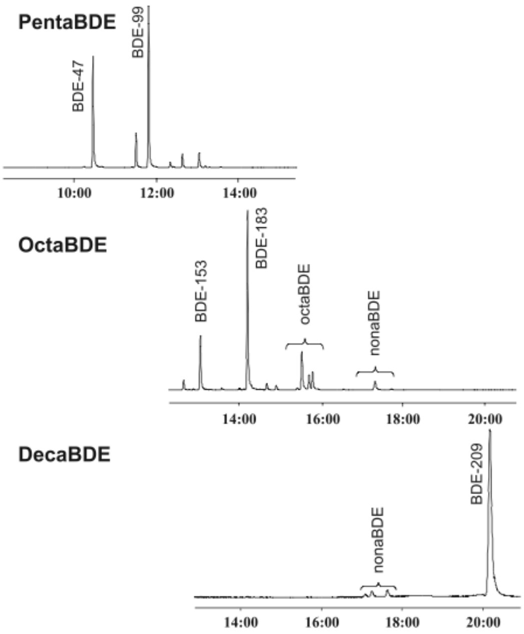
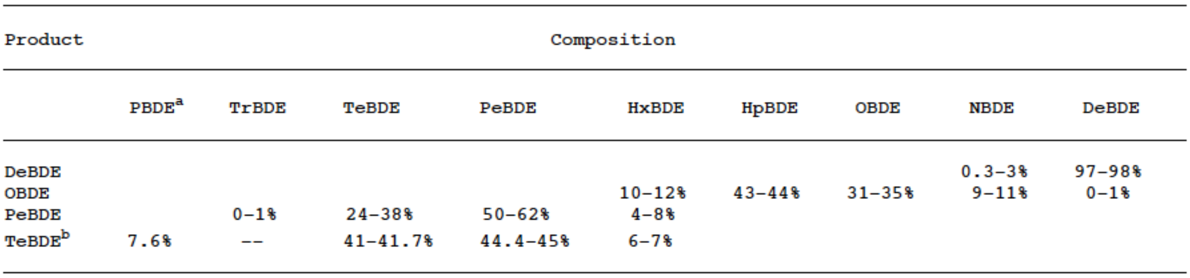


Figure 2: Chromatograms of three PBDE commercial products (from (Alaee et al. 2003))

The overlap between the Stockholm Listing as POPs and the commercial mixtures is not entirely straightforward and is a function of the composition of the mixtures – which varied over time and with different manufacturers as illustrated in the tables below:

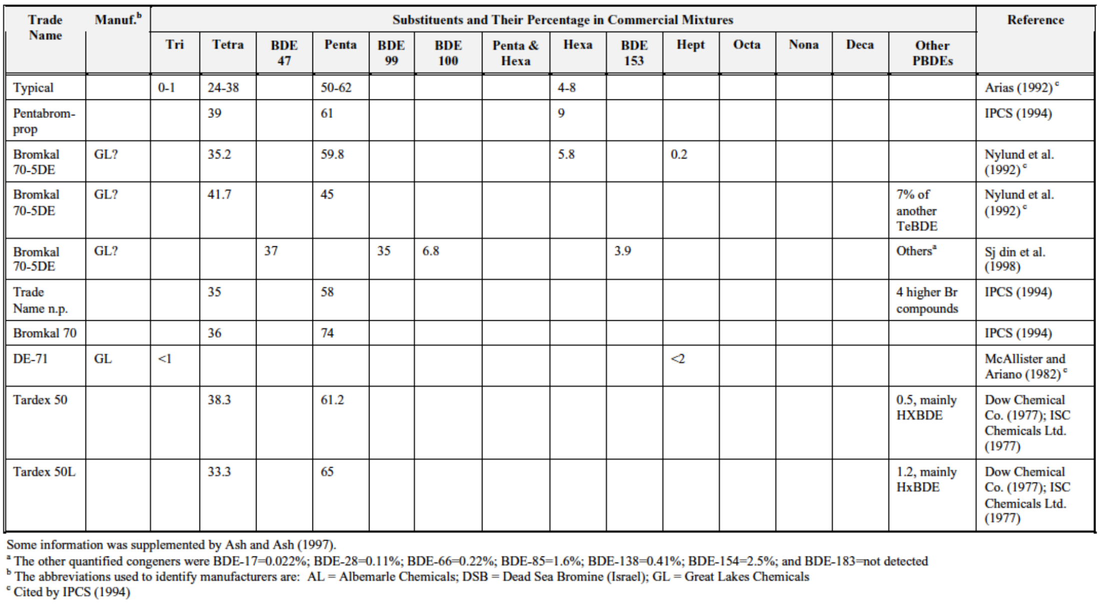
Table 1: Composition of commercial brominated diphenyl ethers (WHO & IPCS 1994).



Product	Composition								
	PBDE[a]	TrBDE	TeBDE	PeBDE	HxBDE	HpBDE	OBDE	NBDE	DeBDE
DeBDE								0.3–3%	97–98%
OBDE					10–12%	43–44%	31–35%	9–11%	0–1%
PeBDE		0–1%	24–38%	50–62%	4–8%				
TeBDE[b]	7.6%	--	41–41.7%	44.4–45%	6–7%				

More detailed summaries of the various PentaBDE and OctaBDE commercial mixtures were provided in a review for the US National Institute of Environmental Health Sciences by Integrated Laboratory Systems (Integrated Laboratory Systems 2001):

Table 2: Constituents of Technical Pentabromodiphenyl Ether - PentaBDE



Trade Name	Manuf.[b]	Substituents and Their Percentage in Commercial Mixtures														Reference
		Tri	Tetra	BDE 47	Penta	BDE 99	BDE 100	Penta & Hexa	Hexa	BDE 153	Hept	Octa	Nona	Deca	Other PBDEs	
Typical		0-1	24-38		50-62				4-8							Arias (1992)[c]
Pentabrom-prop			39		61				9							IPCS (1994)
Bromkal 70-5DE	GL?		35.2		59.8				5.8		0.2					Nylund et al. (1992)[c]
Bromkal 70-5DE	GL?		41.7		45										7% of another TeBDE	Nylund et al. (1992)[c]
Bromkal 70-5DE	GL?			37		35	6.8			3.9					Others[a]	Sj din et al. (1998)
Trade Name n.p.			35		58										4 higher Br compounds	IPCS (1994)
Bromkal 70			36		74											IPCS (1994)
DE-71	GL	<1									<2					McAllister and Ariano (1982)[c]
Tardex 50			38.3		61.2										0.5, mainly HXBDE	Dow Chemical Co. (1977); ISC Chemicals Ltd. (1977)
Tardex 50L			33.3		65										1.2, mainly HxBDE	Dow Chemical Co. (1977); ISC Chemicals Ltd. (1977)

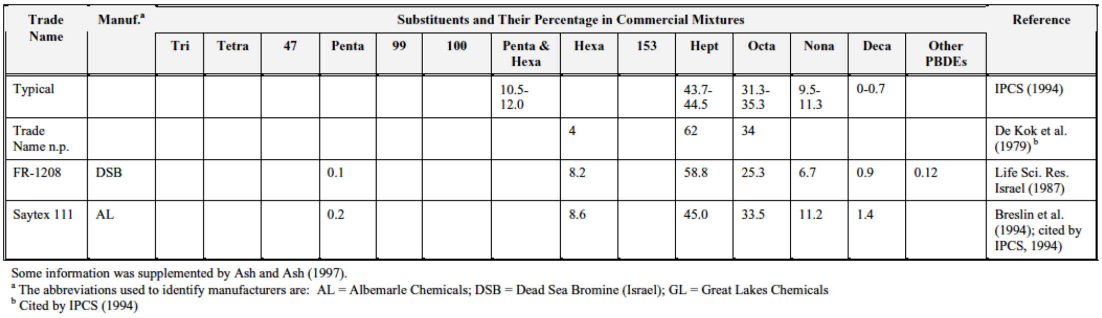
Some information was supplemented by Ash and Ash (1997).

[a] The other quantified congeners were BDE-17=0.022%; BDE-28=0.11%; BDE-66=0.22%; BDE-85=1.6%; BDE-138=0.41%; BDE-154=2.5%; and BDE-183=not detected

[b] The abbreviations used to identify manufacturers are: AL = Albemarle Chemicals; DSB = Dead Sea Bromine (Israel); GL = Great Lakes Chemicals

[c] Cited by IPCS (1994)

Table 3: Constituents of Technical Octabromodiphenyl Ether - OctaBDE



Trade Name	Manuf.[a]	Substituents and Their Percentage in Commercial Mixtures														Reference
		Tri	Tetra	47	Penta	99	100	Penta & Hexa	Hexa	153	Hept	Octa	Nona	Deca	Other PBDEs	
Typical								10.5-12.0			43.7-44.5	31.3-35.3	9.5-11.3	0-0.7		IPCS (1994)
Trade Name n.p.									4		62	34				De Kok et al. (1979)[b]
FR-1208	DSB				0.1				8.2		58.8	25.3	6.7	0.9	0.12	Life Sci. Res. Israel (1987)
Saytex 111	AL				0.2				8.6		45.0	33.5	11.2	1.4		Breslin et al. (1994); cited by IPCS, 1994)

Some information was supplemented by Ash and Ash (1997).

[a] The abbreviations used to identify manufacturers are: AL = Albemarle Chemicals; DSB = Dead Sea Bromine (Israel); GL = Great Lakes Chemicals

[b] Cited by IPCS (1994)

Focussing exclusively on the listed congeners presents significant challenges because of relation to the way that much of the data is presented in the literature – and even by those responding to the information request from the Secretariat - and this issue is addressed further in the relevant sections of this review.

The POP-BDE and the most commonly reported congeners (USEPA 2010) are:

Table 4: POP-BDE Congeners.

PBDE	*Congeners*
TetraBDE	47, 49, 66, 71, 75, 77
PentaBDE	85, 99, 100, 105, 116, 118, 119, 126, 138, 140
HexaBDE	153, 154, 155, 166
HeptaBDE	181, 183, 190

It is likely that each of the congeners listed in this table has been a component of one of the Penta or OctaBDE commercial mixtures at some stage, albeit possibly at very low levels, and that all are thus Stockholm POPs.

Commercial Pentabromodiphenyl Ether

Commercial pentabromodiphenyl ether (cPentaBDE) refers to mixtures of bromodiphenyl ether congeners in which the main components are 2,2', 4,4'- tetrabromodiphenyl ether which is BDE-47[12] and 2,2',4,4',5-pentabromodiphenyl ether which is BDE-99[13] which have the highest concentration by weight with respect to the other components of the mixture. The formulation of C-PentaBDE most widely used in North America and Europe contains 4-12% HexaBDE (Stockholm Convention 2007a).

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[12] CAS No. 40088-47-9

[13] CAS No. 32534-81-9, $C_{12}H_5Br_5O$

Synonyms of pentabromodiphenyl ether include:

- Benzene, 1,1’-oxybis-, pentabromo deriv. (9CI)
- Pentabromophenoxybenzene
- PentaBDE

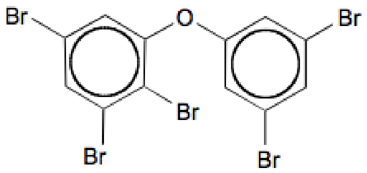

Figure 3: Pentabromodiphenyl ether isomer

Technical pentabromodiphenyl ether and the various commercial mixtures are also called:

- Benzene, 1,1«-oxybis-, pentabromo deriv. (9CI)
- PentaBDE
- Bromkal 70
- Pentabromodiphenyl ether
- Bromkal 70-5 DE
- Pentabromodiphenyl oxide
- Bromkal G1
- Pentabromprop
- DE 60FTM
- Planetron PB501
- DE 71
- Saytex 125
- FR 1205/1215
- Tardex 50

A further letter is sometimes added to the beginning of the abbreviation to indicate the degree of bromination (European Chemicals Bureau 2001):

Pentabromodiphenyl ether ≡ PeBBE ≡ PeBBO ≡ PeBDPE ≡ PeBDPO ≡ PentaBDPE

PentaBDE is used in this report to refer to the commercially available product. Individual components have been identified more specifically where appropriate.

The chromatogram of technical PentaBDE (Kemmlein et al. 2003c) shows that there are at least minor components of a majority of the congeners listed in

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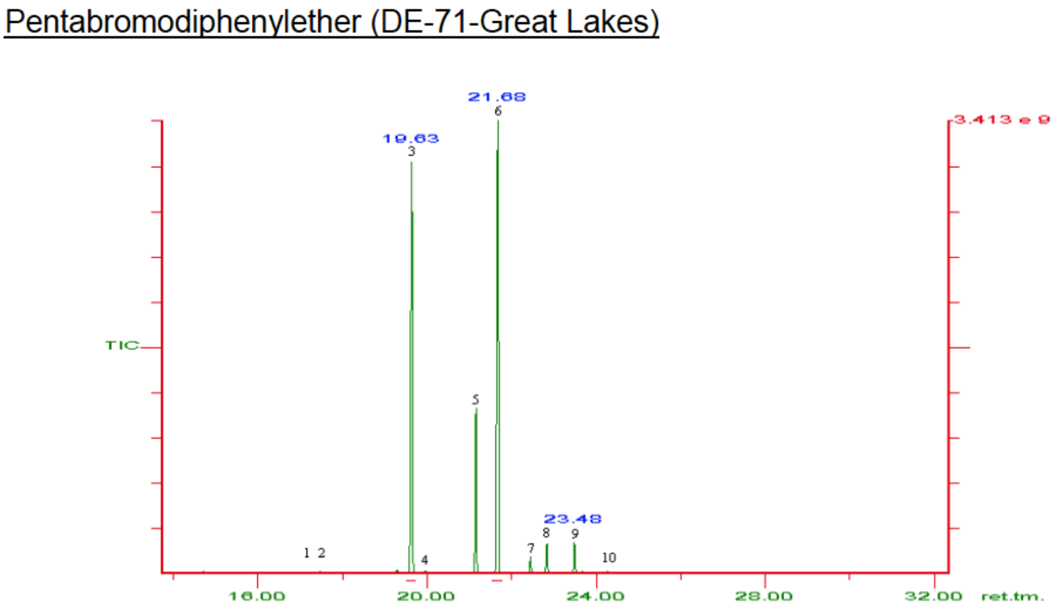
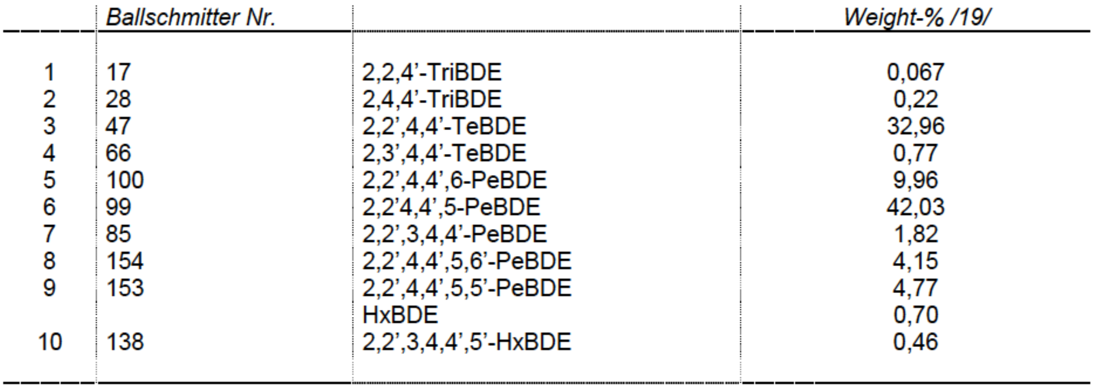


Pentabromodiphenylether (DE-71-Great Lakes)

Figure 4: Chromatogram and composition of technical PentaBDE (DE-71) (Kemmlein et al. 2003a)

Table 5: Congeners identified from the chromatogram of technical PentaBDE (DE-71) (Kemmlein et al. 2003a).



	Ballschmitter Nr.		Weight-% /19/
1	17	2,2,4'-TriBDE	0,067
2	28	2,4,4'-TriBDE	0,22
3	47	2,2',4,4'-TeBDE	32,96
4	66	2,3',4,4'-TeBDE	0,77
5	100	2,2',4,4',6-PeBDE	9,96
6	99	2,2'4,4',5-PeBDE	42,03
7	85	2,2',3,4,4'-PeBDE	1,82
8	154	2,2',4,4',5,6'-PeBDE	4,15
9	153	2,2',4,4',5,5'-PeBDE	4,77
		HxBDE	0,70
10	138	2,2',3,4,4',5'-HxBDE	0,46

Commercial Octabromodiphenyl ether

The c-OctaBDE mixture typically consisted of Penta- to Deca- isomers and contained approximately 79% (by weight) organically bound bromine. This bromine content corresponds to a true OctaBDE molecule and so the commercial products were often called "*OctaBDE*"[14] even though the product contained a range of PBDE (Stockholm Convention 2008d).

The commercially supplied OctaBDE was a complex mixture (LaGuardia et al. found 15 distinct PBDE congeners in DE-79) and was subject to significant variations in composition over time – note, for example, the 2006 analysis of the widely-used Bromkal 79-8DE which shows that nearly 50% of the Bromkal by the mass was DecaBDE (La Guardia et al. 2006). Typical compositions of OctaBDE are:

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[14] CAS: 32536-52-0; $C_{12}H_2Br_8O$; mol. wt. =801.47

Table 6: Typical composition of c-OctaBDE flame retardants (% by weight) adapted from (Stockholm Convention 2008d).

Main components	Up to 1994[a]	1997[c]	2000[d]	2001[e]	2006[f]	2006[g]
PentaBDE	10.5-12.0[b]		1.4-12.0[b]	≤0.5		
HexaBDE		5.5		≤12	10.5	0.3
HeptaBDE	43.7-44.5	42.3	43.0-58.0	≤45	45.5	12.8
OctaBDE	31.3-35.3	36.1	26.0-35.0	≤33	37.9	21.8
NonaBDE	9.5-11.3	13.9	8.0-14.0	≤10	13.1	18.9
DecaBDE	0-0.7	2.1	0-3.0	≤0.7	1.3	49.6

Note: a) 1994 data are taken from WHO (WHO & IPCS 1994).
b) This value is for the total amount of PentaBDE + HexaBDE.
c) 1997 data are from a composite sample from three suppliers to the EU (Stenzel and Nixon, 1997 cited by (European Chemicals Bureau 2003a)).
d) 2000 data are taken from an RPA report for the UK Environment Department (Risk & Policy Analysts Limited (RPA) for DEFRA 2002) and represent the composition reported to the OECD under a Voluntary Industry Commitment to "further reduce the possibility of negative environmental impact"[15].
e) 2001 data from the Great Lakes Chemical Corporation represent the upper bound composition based on random sampling of selected production lots from August 2000 to August 2001.
f) Data for DE-79 manufactured by Great Lakes Chemical Corporation, USA (La Guardia et al. 2006).
g) Data for Bromkal 79-8DE manufactured by Chemische Fabrik Kalk, Germany (La Guardia et al. 2006).

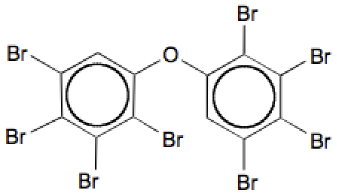

Figure 5: octabromodiphenyl ether isomer

Octabromodiphenyl ether was also called:

- Benzene, 1,1«-oxybis-, octabromo deriv. (9CI)
- Adine 404
- Bromkal 79-8DE
- CD 79
- DE 71
- DE 79
- EB 8

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[15] The voluntary commitment included:

- an undertaking not to manufacture or import/export the non-commercial PBDE, except when present as part of the three commercial products;
- to use the best available techniques, without incurring excessive costs, to improve the purity of deca- and octabromodiphenyl ether (specifically minimising levels of hexa- and lower-brominated congeners in commercial octabromodiphenyl ether); and
- to evaluate the ways in which the levels of hexa- and lower-brominated congeners in commercial octabromodiphenyl ether can be reduced.

- FR 1208
- FR 143
- Octabromodiphenyl ether
- Octabromodiphenyl oxide
- Phenyl ether, octabromo deriv.
- Saytex 111
- Tardex 80

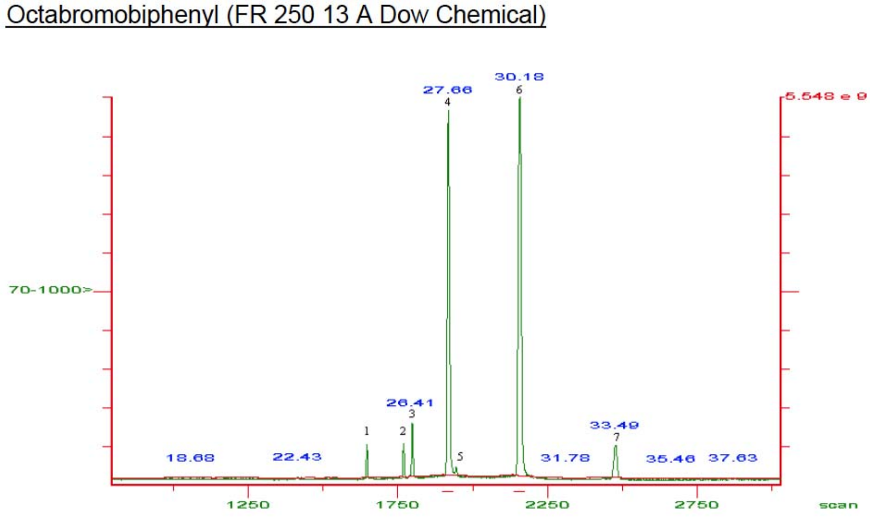
A further letter is sometimes added to the beginning of the abbreviation to indicate the degree of bromination (European Chemicals Bureau 2001).

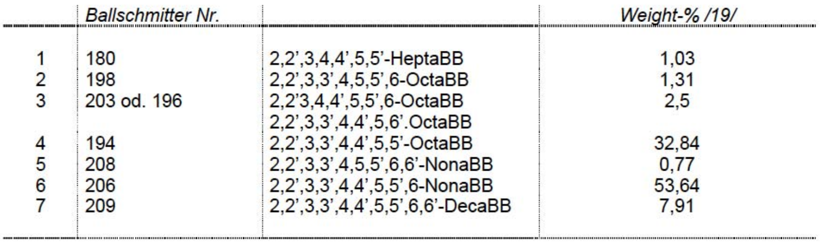
Octabromodiphenyl ether ≡OBBE ≡OBBO ≡OBDPE ≡OBDPO ≡OctaBDPE

OctaBDE has been used in this report to refer to the commercially available product. Individual components have been identified more specifically where appropriate.

Examples of chromatograms and the associated composition of the two technical OctaBDE from Kemmlein et al. are illustrated in the figures below (Kemmlein et al. 2003c):

Figure 6: Chromatogram of technical OctaBDE FR 250 13 A and table of congeners identified (Kemmlein et al. 2003a)

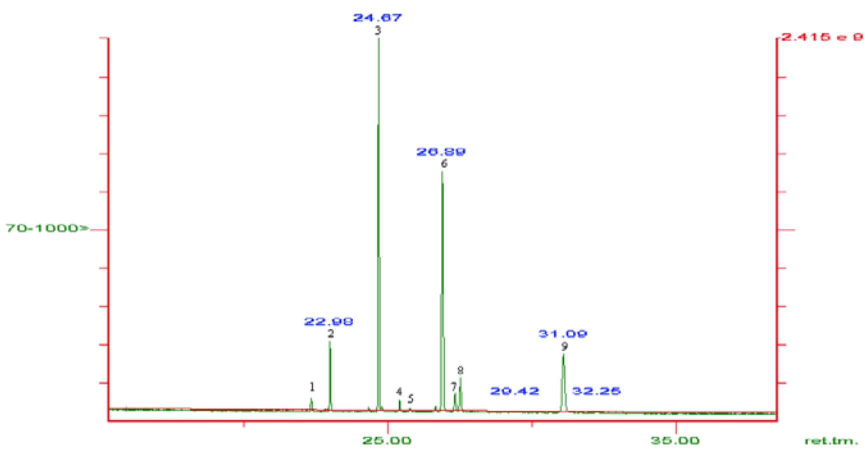




	Ballschmitter Nr.		Weight-% /19/
1	180	2,2’,3,4,4’,5,5’-HeptaBB	1,03
2	198	2,2’,3,3’,4,5,5’,6-OctaBB	1,31
3	203 od. 196	2,2’3,4,4’,5,5’,6-OctaBB 2,2’,3,3’,4,4’,5,6’.OctaBB	2,5
4	194	2,2’,3,3’,4,4’,5,5’-OctaBB	32,84
5	208	2,2’,3,3’,4,5,5’,6,6’-NonaBB	0,77
6	206	2,2’,3,3’,4,4’,5,5’,6-NonaBB	53,64
7	209	2,2’,3,3’,4,4’,5,5’,6,6’-DecaBB	7,91

Figure 7: Chromatogram of technical OctaBDE DE-79 and table of congeners identified (Kemmlein et al. 2003a)

Octabromodiphenylether (DE-79-Great Lakes)



	Ballschmitter Nr.		Weight-% /19/
1	154	2,2',4,4',5,6'-HexaBDE	1,19
2	153	2,2',4,4',5,5'-HexaBDE	8,10
3		HeptaBDE	40,17
4		HeptaBDE	2,01
5	190	2,3,3',4,4',5,6-HeptaBDE	0,84
6		OctaBDE	21,42
7		OctaBDE	5,51
8		OctaBDE	8,27
9		NonaBDE	12,49

Penta and Octa BDE Production/Market Volume:

Muir (Muir & de Wit) summarized the paucity of production data in a recent review paper confirming that there is "*very little current information on global BFR production volumes or geographical use patterns" yet this information "is needed in order to understand temporal and spatial trends".*

Muir noted, for example, *"China is now producing BFRs but production volumes are unknown*" (Muir & de Wit). During a meeting in Beijing at the end of June Chinese officials have been helpful in relation to the discussions about the production of PentaBDE in China and might provide data that can be incorporated in the final report.

Unfortunately the data from the Bromine Industry in general has tended to be rather vague. Production of PentaBDE in the US, for example was described in a 2003 for (then) Great Lakes Chemicals[16] simply as "*several million pounds per year*" based on a "*personal communication*" with the company (ENVIRON 2003b).

These uncertainties are reflected in the earlier reports for the POPRC which are somewhat vague in relation to total or regional production and use and, for example, give wide ranges in relation to US production of Penta and OctaBDE:

- US production of PentaBDE in the Risk management evaluation for commercial pentabromodiphenyl ether - *"The US EPA (2007) estimates that US production and import were between 4,500 and 23,000 tons in 2002, but specific figures are confidential to the industry". (Stockholm Convention 2007c)*
- US production of OctaBDE in the Risk management evaluation for commercial octabromodiphenyl ether - *"U.S. production of c-OctaBDE was estimated in the range of 450 to 4,500 tonnes"* (Stockholm Convention 2008d).

This problem is confounded because data is often aggregated in relation to other additives or fame retardants yet PBDE represent only a small part of total world market for performance additives (flame retardants, stabilizers, anti-oxidants, modifiers, and lubricants) for polymers. Murphy estimated that the total market amounted to about 2.72 million tonnes

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[16] now Chemtura

with a value, in 2001, of nearly US$16 billion (Murphy 2001).

Flame retardants, of which WHO/IPCS (WHO & IPCS 1997) listed more 175 in 1979, make up 31% of the volume of total polymer additives. This still represents nearly 850,000 tonnes with a value of c.US$2 billion. The Western European sector in 1995 was 316,000 tonnes. Other stabilizers, modifiers, and lubricants each account for around 16-17% (about 430,000 to 460,000 tonnes). Many articles contain a wide range of additives as well the polymer and any flame retardant.

A further difficulty is that the industry has only released market volume or demand data rather than actual production figures and that these have been aggregated over large geographical regions.

The market volume by type of brominated flame retardants (BFRs) in Japan and Western Europe is indicated in the table below which shows that PBDE were a relatively small component of the overall European market for brominated flame retardants even during the period of peak use:

Table 7: Market volume for brominated flame-retardants in Japan and Western Europe data from (Lassen et al. 1999)

Flame	Japan 1994		Benelux, France, UK, and Germany 1996		W. Europe 1998	
Retardant	Volume tonnes	%	Volume tonnes	%	Volume tonnes	%
TBBPA	24,000	47	9,700	31	13,150	21
TBBPA deriv.	9,500	18	-	-	3,650	6
PBDE	6,000	12	8,300	26	7,050	11
HBCD	1,600	3	2,200	7	8,950	14
EBTBP	2,500	5			5,250	8
TBPA			1,900	6		
Other	7,850	15	9,200	29	24,450	39
Total	51,450	100	31,300	100	62,500	100

The relatively small contribution from PBDE – and especially the POP-BDE - is even more obvious when plotted on a global trend basis as from Morf (Morf et al. 2003):

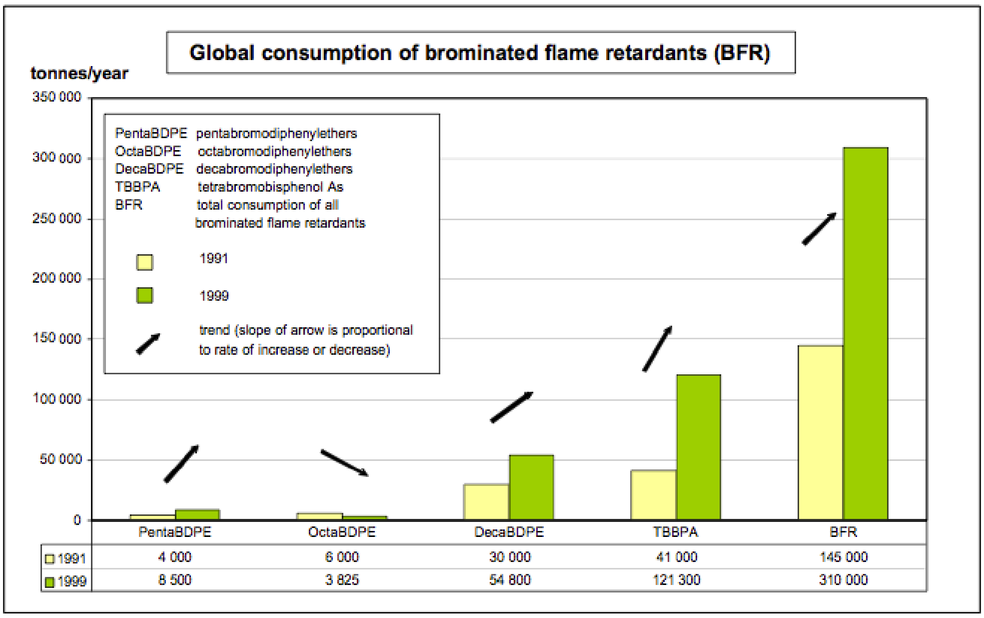

Figure 8: Comparison of world consumption for selected BFR, PBDE sources 1991 (WHO & IPCS 1994)(Morf et al. 2003).

Although Morf indicates that PentaBDE demand was rising from 1991 to 1999 the latest information on total market demand of cPentaBDE from Bromine Science and Environmental Forum shows that the total market demand decreased from 8,500 tons in 1999 to 7,500 tons in 2001 as in the table below.

The last years for which figures have been made publicly available by the bromine industry are 2001 with a limited update to 2003[17]. In 2001 almost 70,000 metric tons of polybrominated diphenyl ethers (PBDE) were produced globally, nearly half of which was used in products sold in America. The region covered in these data by "America" includes North, Central and South America combined and there are no further breakdowns by country (USEPA 2010). USEPA estimate that the United States accounts for 80% of the total use of Penta, Octa and DecaBDE used in the America region in 2001(USEPA 2010).

Table 8: PBDE volume estimates: Total market demand by region in 2001 in tonnes (and by percent) (BSEF, 2001).

Mixtures	America	Europe	Asia	Rest of the world	Total	% of total world usage
TBBP-A	18,000	11,600	89,400	600	119,700	59
HBCD	2,800	9,500	3,900	500	16,700	8
DecaBDE	24,500	7,600	23,000	1,050	56,100	27
OctaBDE	1,500	610	1,500	180	3,790	2
PentaBDE	7,100	150	150	100	7,500	4
Total	**53,900**	**117,950**	**117,950**	**2,430**	**203,790**	**100**

These figures differ from those presented by the American Chemical Society in an editorial (Renner 2005) which claims that the in 2001, c.34,000 tonnes[18] of PBDE were distributed worldwide. Of this DecaBDE constituted c.24,300 tonnes[19] (72%); Octa-BDE 1,400 tonnes[20] (4%); and PentaBDE made up 8,300 tonnes[21] (24%) – said to be c.98% of the global demand for PentaBDE[22].

The world market demand of PBDE as reported by BSEF in 2006 for 2003, by far the most significant demand by that time being for DecaBDE in America and Asia (where a high proportion is likely to have been exported in finished goods):

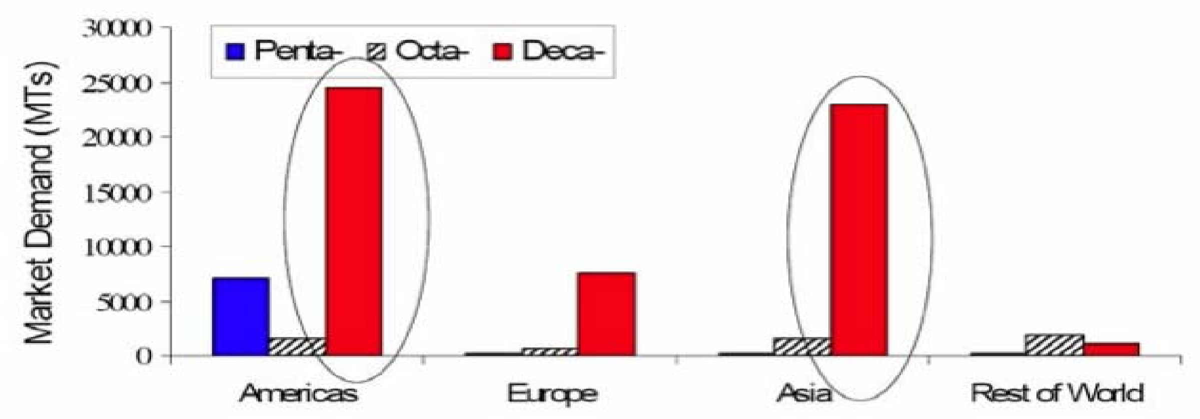

Figure 9: PBDE commercial mixture world market demand as reported in 2003 (original source: www.bsef.com)

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[17] Limited 2003 market volume figures were shown on the BSEF web site until 2006 but have since been removed.

[18] 74.9 million lb in the original

[19] 53.6 million lb in the original

[20] 3.0 million lb in the original

[21] 18.3 million lb in the original

[22] based on 1999 data

Morf (Morf et al. 2007) reviewed materials flow in Switzerland but found that data on production of Penta and Octa BDE was not readily available – even from the industry – and they had to rely on the published data available for only 1999 and 2001:

Table 9: Industrial Consumption of PBDE worldwide (kt/yr) and in Europe from BSEF (Morf et al. 2007)

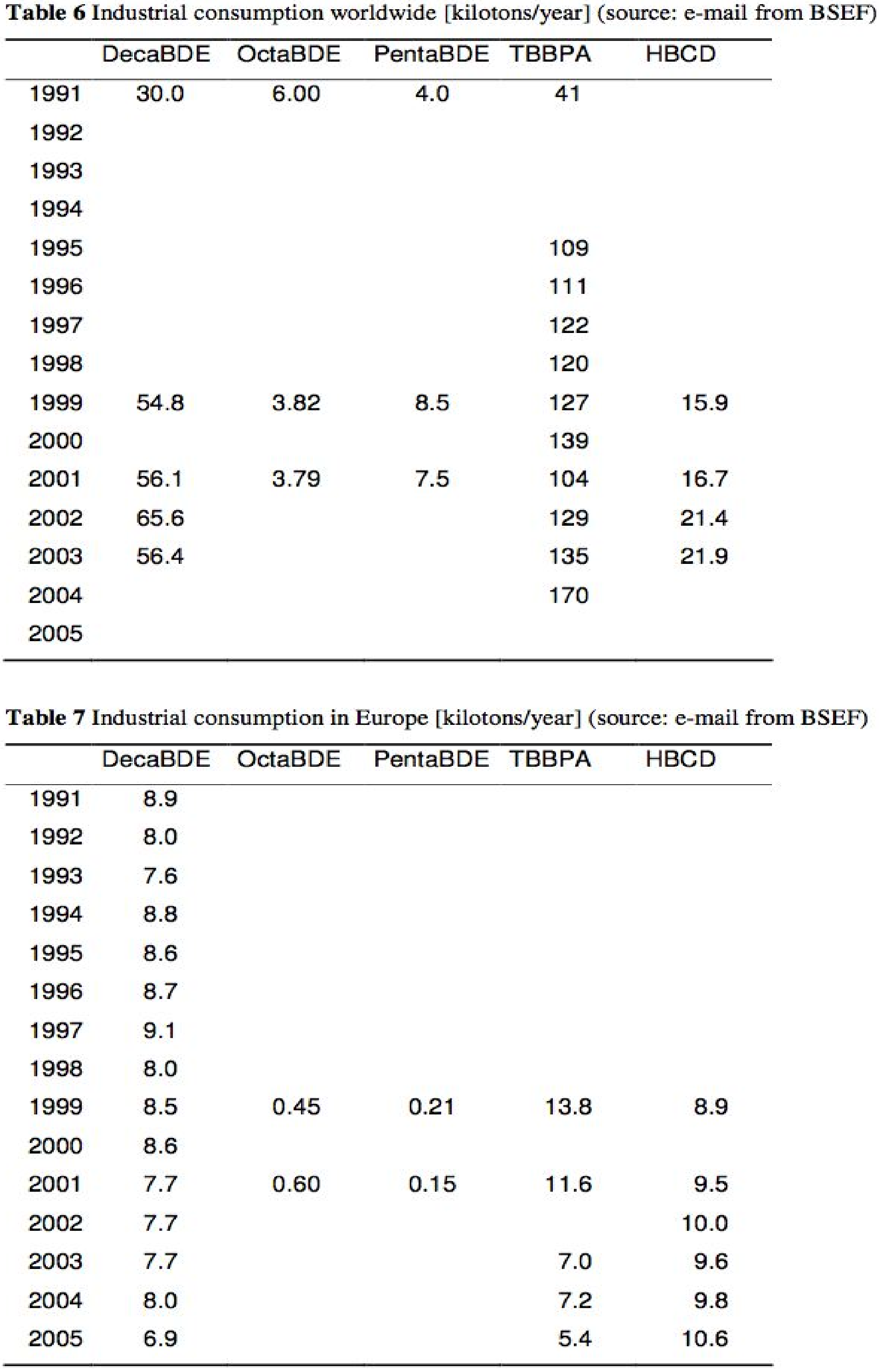

Table 6 Industrial consumption worldwide [kilotons/year] (source: e-mail from BSEF)

	DecaBDE	OctaBDE	PentaBDE	TBBPA	HBCD
1991	30.0	6.00	4.0	41	
1992					
1993					
1994					
1995				109	
1996				111	
1997				122	
1998				120	
1999	54.8	3.82	8.5	127	15.9
2000				139	
2001	56.1	3.79	7.5	104	16.7
2002	65.6			129	21.4
2003	56.4			135	21.9
2004				170	
2005					

Table 7 Industrial consumption in Europe [kilotons/year] (source: e-mail from BSEF)

	DecaBDE	OctaBDE	PentaBDE	TBBPA	HBCD
1991	8.9				
1992	8.0				
1993	7.6				
1994	8.8				
1995	8.6				
1996	8.7				
1997	9.1				
1998	8.0				
1999	8.5	0.45	0.21	13.8	8.9
2000	8.6				
2001	7.7	0.60	0.15	11.6	9.5
2002	7.7				10.0
2003	7.7			7.0	9.6
2004	8.0			7.2	9.8
2005	6.9			5.4	10.6

Schenker estimated PBDE consumption worldwide using a combination of values derived from literature combined with linear interpolations of literature values (Schenker et al. 2008):

Table 10: Estimated PBDE consumption worldwide (in tonnes).

PBDE-production				share of different PBDE - mixtures		
year	world bromine production (t/y)[1]	BFR production / bromine production (%)[1]	PBDE production / BFR production (%)	deca-BDE mixture (%)	octa-BDE mixture (%)	penta-BDE mixture (%)
1970	**2.10×10^5**	**1.0**	1.0	75.0	15.0	10.0
1971	**2.19×10^5**	**1.0**	1.0	75.0	15.0	10.0
1972	**2.37×10^5**	**1.0**	2.0	75.0	15.0	10.0
1973	**2.78×10^5**	**1.0**	3.0	75.0	15.0	10.0
1974	**2.92×10^5**	**1.0**	4.0	75.0	15.0	10.0
1975	**2.78×10^5**	**1.0**	5.0	75.0	15.0	10.0
1976	**2.97×10^5**	**1.0**	6.0	75.0	15.0	10.0
1977	**3.07×10^5**	**1.0**	7.0	75.0	15.0	10.0
1978	**3.09×10^5**	**1.0**	8.0	75.0	15.0	10.0
1979	**3.46×10^5**	**1.0**	9.0	75.0	15.0	10.0
1980	**2.95×10^5**	2.9	10.0	75.0	15.0	10.0
1981	**3.53×10^5**	4.8	11.0	75.0	15.0	10.0
1982	**3.81×10^5**	6.7	12.0	75.0	15.0	10.0
1983	**3.63×10^5**	8.6	13.0	75.0	15.0	10.0
1984	**3.88×10^5**	10.5	14.0	75.0	15.0	10.0
1985	**3.79×10^5**	12.4	15.0	75.0	15.0	10.0
1986	**3.71×10^5**	14.3	16.0	75.0	15.0	10.0
1987	**3.84×10^5**	16.2	17.0	75.0	15.0	10.0
1988	**4.05×10^5**	18.1	18.0	75.0	15.0	10.0
1989	**4.20×10^5**	20.0	19.0	75.0	15.0	10.0
1990	**4.40×10^5**	21.9	20.0	75.0	15.0	10.0
1991	**4.00×10^5**	23.8	21.0	75.0	15.0	10.0
1992	**3.70×10^5**	25.7	22.0	75.0	15.0	10.0
1993	**3.90×10^5**	27.6	23.0	75.0	15.0	10.0
1994	**4.10×10^5**	29.5	24.0	75.0	**15.0**[2]	**10.0**[2]
1995	**4.30×10^5**	31.4	25.0	76.2	13.7	10.1
1996	**4.50×10^5**	33.3	**26.0**[3]	77.3	12.4	10.3
1997	**4.70×10^5**	35.2	21.0	78.5	11.1	10.4
1998	**5.10×10^5**	37.1	16.0	79.6	9.8	10.6
1999	**5.30×10^5**	**39.0**	**11.0**[4]	80.8	8.5	10.7
2000	**5.42×10^5**	40.0	11.0	81.9	7.2	10.9
2001	**5.40×10^5**	**41.0**	11.0	83.0	**6.0**[5]	**11.0**[5]
2002	5.40×10^5	43.3	11.0	83.0	6.0	11.0
2003	5.50×10^5	45.5	11.0	83.0	6.0	11.0
2004	5.60×10^5	47.8	11.0	83.0	6.0	11.0
2005	5.80×10^5	50.0	11.0	83.0	6.0	11.0

Bold values are derived from literature; other values are linear interpolations of literature values (Schenker et al. 2008). World Bromine Production from Buckingham and Lyday (Buckingham et al. 2009)
1 - data from Prevedouros et al. (Prevedouros et al. 2004a, Prevedouros et al. 2004b) updated by Morf et al. (Morf et al. 2007)
2 - data from Law et al. (Law et al. 2006)
3 - data cited in (Lassen et al. 1999)
4 - data cited in (Lassen et al. 1999)
5 - data from chapter 4 of Paasivirta and Asplund (Paasivirta 2000)

This table reports results through to 2005 and this is the most relevant period for this review. It is interesting to note, however, that Buckingham has since updated the world Bromine production results which show that world bromine production has since decreased back to the levels of 1994 with 403,000 tonnes produced in 2007 and 413,000 tonnes in 2008 (Buckingham et al. 2009).

When this data is calculated and plotted then it can be seen how global use of BFRs has been the key driver for bromine production. PBDE has, however, been a minor element of this growth.

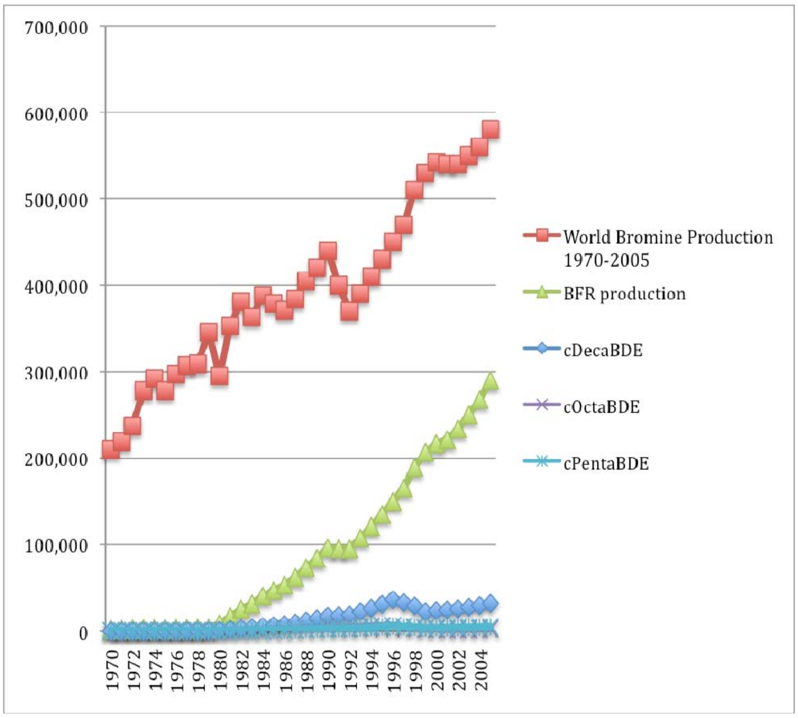

Figure 10: Global bromine and BFR production with Deca, Octa and PentaBDE (tonnes)

Looking more closely at the PBDE data the peak consumption of Octa and Penta can be seen in the mid-1990s with increasing growth again from 2000:

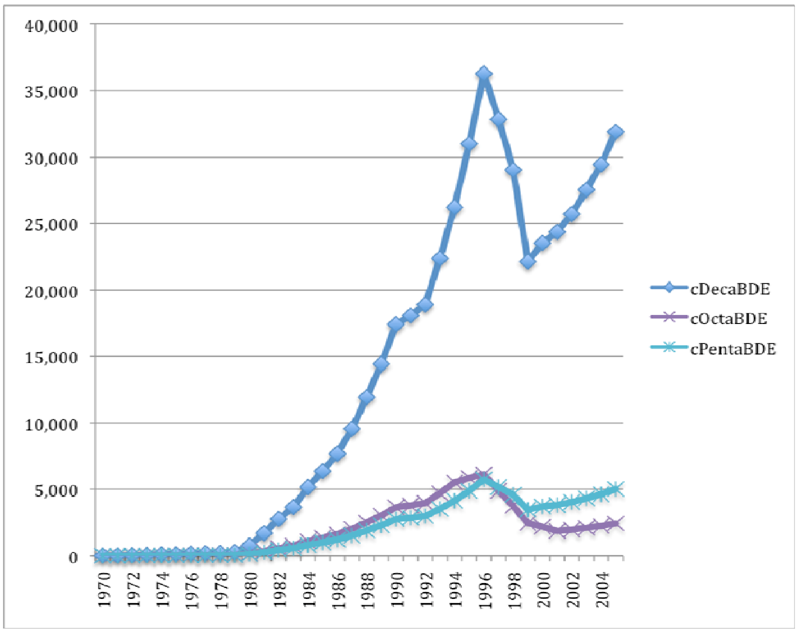

Figure 11: Global production of Deca, Octa and PentaBDE (tonnes) based on Schenker estimates

From the spreadsheet, however, it can be seen that the totals are significantly below the industry market demand figures and it is clear the Schenker has underestimated the total production. The cumulative PentaBDE production to 2001, for example, is just 57,960 tonnes according to these data yet it is widely accepted to be at least 100,000. Furthermore total PBDE production in 2001 is estimated to be just 30,031 tonnes whilst the BSEF data shows a global market demand of 67,390 tonnes. It is noted that although Schenker takes very conservative estimates of total production this has relatively little bearing on the paper which is essentially about the balance between the commercial mixtures and debromination as discussed later.

A conference presentation by Li et al. from Environment Canada reviewed the assumptions and re-plotted the graph validated against other sources (Li et al. 2010b):

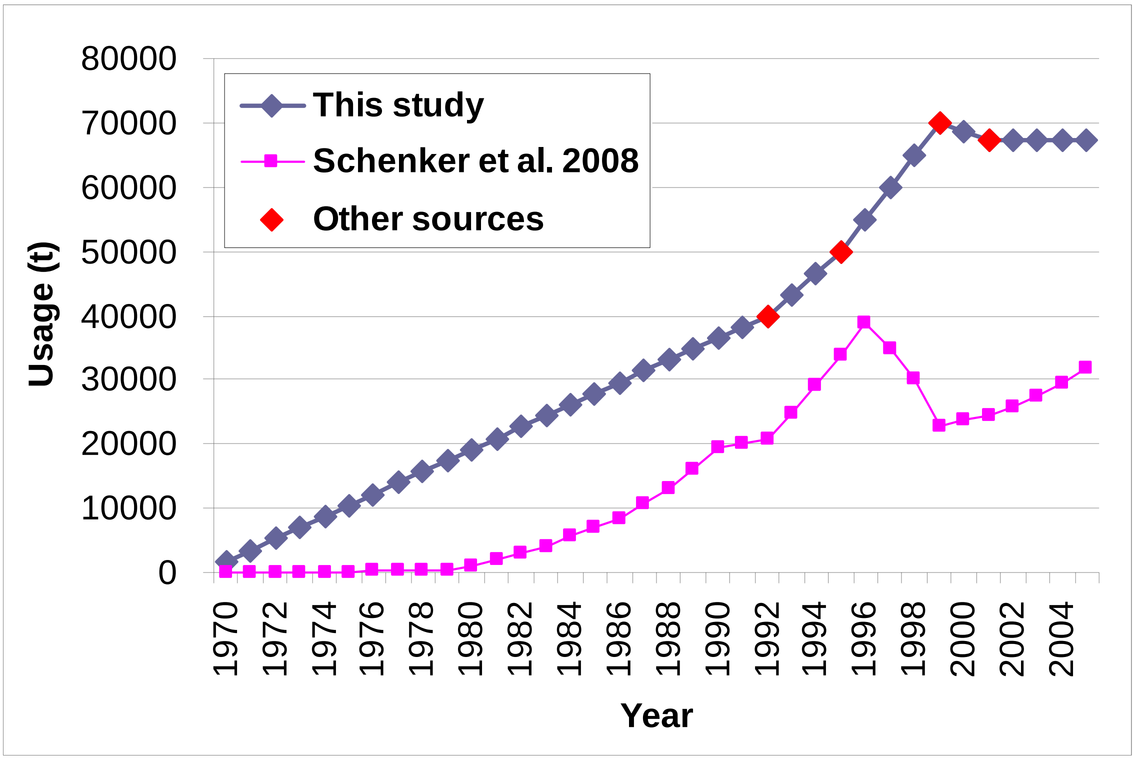

Figure 12: 'Top down' global emissions inventory of PBDE using published industry data (Li et al. 2010b).

This shows total global production of PBDE as approximately 1,300,000 tonnes rather than the 510,000 from the Schenker data. A 'bottom up' approach gives a slightly greater total of 1,500,000 tonnes:

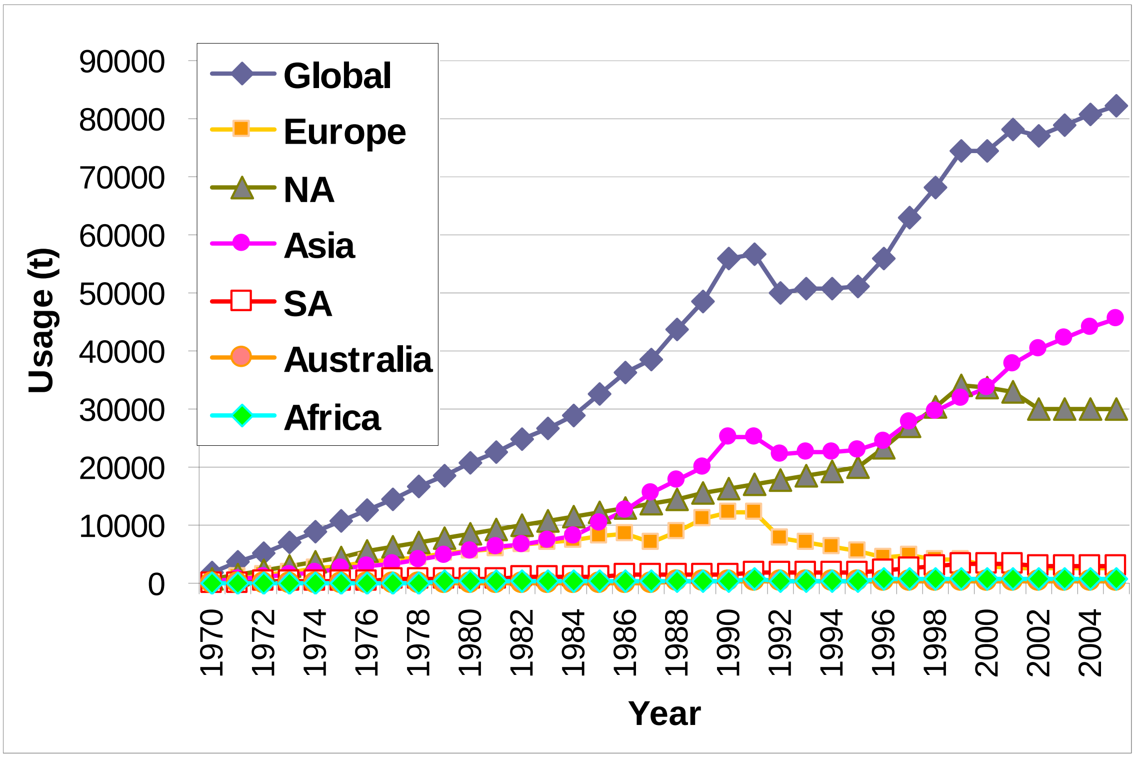

Figure 13: 'Bottom Up' global emissions inventory of PBDE (Li et al. 2010b).

It can be seen how Asia exceeded the usage in North America from c.2000 – although it must be noted that DecaBDE is over 80% of the total in the more recent data and about 77% of the global total over the entire period.

Assuming that the data from Schenker has a reasonable balance of the production between the mixtures, even if it underestimates the global production totals, these revised inventories would confirm that the total production of PentaBDE over the period from 1970 to 2005 is in the range from 91,000 to 105,000 tonnes and that the total production of OctaBDE over the same period was approximately 102,700 to 118,500 tonnes. A total of between about 1.1 and 1.25 million tonnes of DecaBDE was produced over the period. The results are summarised in Table 11:

Table 11: Estimated total production of PBDE commercial mixtures 1970 to 2005 (derived by the authors from (Schenker 2008, Li 2010)).

Commercial Mixture	*Tonnes*
DecaBDE	1,100,000 to 1,250,000
OctaBDE	102,700 to 118,500
PentaBDE	91,000 to 105,000

The scale of production of PBDE overall is therefore very similar to that of PCBs (Breivik 2002a, 2002b, 2007).

Li went a stage further and, using a GIS system, plotted global emissions and the corresponding atmospheric concentrations which were then validated against Global Atmospheric Passive Sampling (GAPS) Network data:

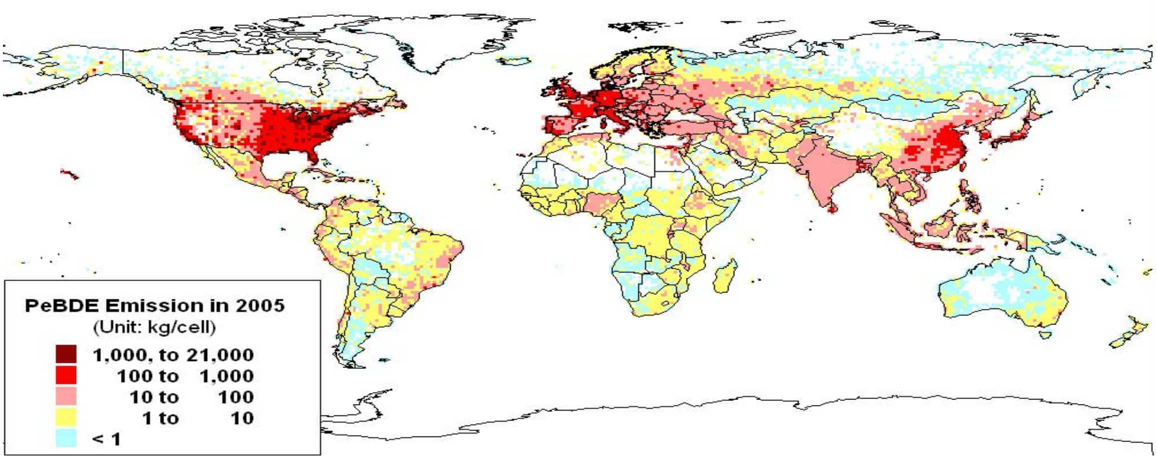

Figure 14: Global gridded PentaBDE emission in 2005 on a 1º latitude by 1º longitude resolution (trial output) (Li et al. 2010b).

This confirms the key concerns with PBDE are in the United States and Europe with some elevated concentrations in China. These conclusions are even clearer when the atmospheric concentrations are plotted:

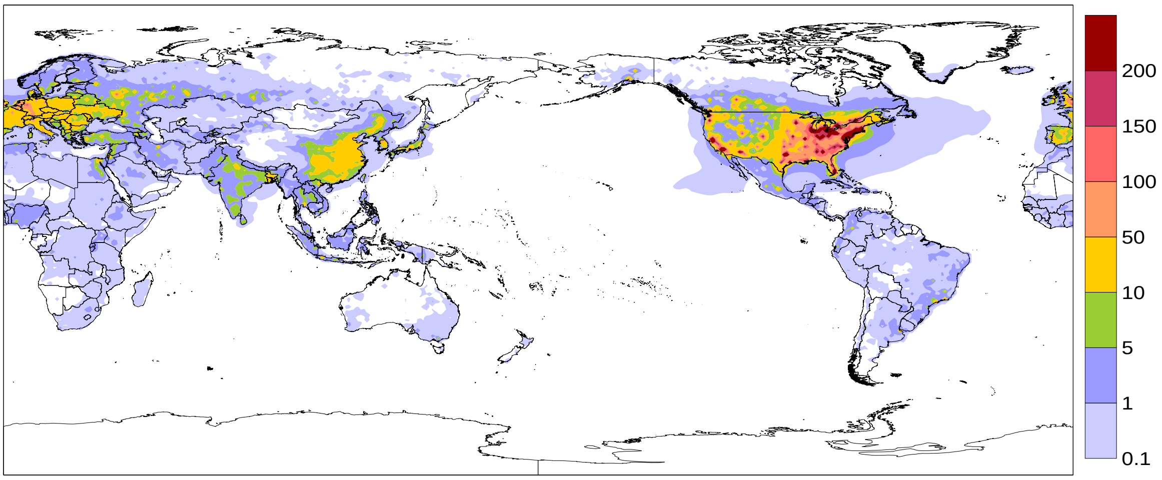

Figure 15: Global gridded annual mean air concentration of BDE-99 at 1.5 m height in 2005 on a 1º latitude by 1º longitude resolution (A trial version)(Li et al. 2010b).

Global Production/Market Demand of PentaBDE

It is noted that 'production' and 'use' are often used interchangeably, especially in the grey literature, in relation to regional data – and these terms are sometimes transposed from the original sources. Production does not necessarily reflect regional usage because commercial BDE mixtures were traded internationally. Nor does use necessarily reflect regional consumption because products containing BDE were often exported – this is likely to be particularly important in relation to Asia, for example, PBDE was used in products for export particularly to North America, Europe and Australia/New Zealand. In the case of DecaBDE this is probably still continuing in the case of North America at least).

It is known that PentaBDE has been produced in Israel, Japan, U.S, UK (Peltola & Yla-Mononen 2001) and probably China - where a patent was issued in 1999 on a new commercial mixture with a different congener balance but containing PentaBDE (Stockholm Convention 2006). Domestic production of BFRs in China is reported to have increased rapidly at that time– rising from 10,000 metric tons in 2000 to about 25,000 metric tons in 2004 (Xiang et al., 2007 quoted by Miyake (Miyake et al. 2008a)). It appears that most, and perhaps all, of this may have been DecaBDE production as Chen (Chen et al. 2007) notes that the estimated domestic production of the "*predominant commercial deca-BDE mixture in China increased by 200% between 2000 and 2005, from 10,000 to about 30,000 metric tons*". It still remains unclear, however, whether China ever produced any PentaBDE and, if so, how much and for how long.

Total market demand figures, which are assumed to match production figures at a global total level, were included in the risk profile (Stockholm Convention 2006) and were derived from the pre-2006 BSEF website:

PentaBDE Year	***America (%)***	***Europe (%)***	***Asia (%)***	***Rest of the world (%)***	***Total***
1999	8,290 (97.5%)	210 (2.5%)	-	-	**8,500**
2001	7,100 (94.7%)	150 (2%)	150 (2%)	100 (1.3%)	**7,500**

Table 12: Total market demand for PentaBDE from BSEF

The estimated cumulative use of PentaBDE between 1970 and 2001 was 100,000 t (BSEF, 2001)

This estimate is consistent with that of Alcock who broke it down further into 85,000 tonnes in the US and 15,000 tonnes in Europe (Alcock et al. 2003).

Prevedouros et al. (Prevedouros et al. 2004a) estimated, also consistently with these estimates, that a total of 3,000-5,000 t of PentaBDE were produced in Europe during the period from 1970-2000 with a further 9,000-10,000 t imported in finished articles.

The sole producer of cPentaBDE in US, the Great Lakes Chemical Corporation (now Chemtura) voluntarily ended their production of cPentaBDE in 2004.

Production in the EU_{15} stopped in 1997.

No information has been found for Eastern Europe countries outside EU.

In Japan, the technical TetraBDE, used as an alternative to cPentaBDE, was voluntarily withdrawn from the market in 1990 (Kajiwara et al. 2004). OctaBDE products were used as flame-retardants until 1999 (Watanabe & Sakai 2003). Japan is unique in having good consumption data for each flame retardant over the critical period through the 1990s (Watanabe & Sakai 2003):

Table 13: Annual consumption of flame retardants in Japan (Watanabe & Sakai 2003)

Amount (tons)

Type	Compound	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Brominated	TBBPA	12,000	14,000	18,000	20,000	23,000	24,500	23,000	22,000	24,000	30,000	29,000	31,000	29,500	31,000	32,300	27,300
	Deca-BDE	3000	4000	5000	6000	10,000	9800	6300	5800	5500	4900	4200	4450	4000	3800	2800	2500
	Octa-BDE	500	1000	1100	1100	1100	1500	1100	900	500	300	280	250	75	75	–	–
	Tetra-BDE	1000	1000	1000	1000	1000	–	–	–	–	–	–	–	–	–	–	–
	HBCD	600	600	700	700	700	1000	1400	1600	1600	1800	2000	2000	1850	1950	2000	2200
	Bis(tetrabromophthalimido)ethane	–	400	600	600	1000	1200	1300	1300	2500	2500	2500	2500	2000	2000	2000	1750
	Tribromophenol	100	250	450	450	450	1500	2000	2700	3500	4000	4100	4300	4300	4300	4300	3600
	Bis(tribromophenoxy)ethane	400	400	400	400	400	1000	1000	900	900	750	500	400	100	250	–	–
	TBBPA polycarbonate oligomer	–	–	–	–	–	2500	2500	2500	2500	2750	3000	3000	3000	2800	2900	1800
	Brominated polystyrene	–	–	–	–	–	1300	1300	1300	1300	1500	1600	2000	2000	3500	3300	2500
	TBBPA epoxy oligomer	–	–	–	1000	3000	4400	6,000	6500	7000	7450	9000	8500	8500	8500	8500	8500
	Bis(pentabromophenyl)ethane	–	–	–	–	–	–	–	1000	1600	2600	3000	4600	4600	5000	5000	4500
	TBBPA–bis(dibromopropyl ether)	–	–	–	–	–	–	–	–	–	–	–	700	1750	1750	2000	1000
	Poly(dibromophenylene oxide)	100	170	200	–	–	–	–	–	200	200	400	400	800	–	–	–
	Hexabromobenzene	–	–	–	–	–	–	–	–	350	350	350	350	350	350	350	350
	Others	2300	160	160	–	–	–	–	–	–	–	–	–	–	800	1800	1550
	Total	20,000	21,980	27,610	31,250	40,650	48,700	45,900	46,500	51,450	59,100	59,930	64,450	62,825	66,075	67,250	57,550
Chlorinated	Chlorinated paraffins	4000	4000	4500	4500	4500	4500	4500	4300	4300	4300	4300	4300	4300	4300	4300	4300
	Others	850	850	850	700	700	900	900	900	900	900	960	960	900	900	900	900
	Total	4850	4850	5350	5200	5200	5400	5400	5200	5200	5200	5260	5260	5200	5200	5200	5200
Phosphoric	Halogenated ester	3000	3000	3000	3000	3000	3100	3100	3100	3100	3100	3300	3100	4000	4000	4000	4000
	Nonhalogenated ester	4000	4000	4200	4400	4400	4400	4400	4400	4400	4000	4400	4600	22,000	22,000	22,000	20,000
	Others	1750	1750	1750	1750	1750	1810	1810	1810	3310	3310	1400	1000	2000	2500	2500	2500
	Total	8750	8750	8950	9150	9150	9310	9310	9310	10,810	10,410	9100	8700	28,000	28,500	28,500	26,500
Inorganic	Antimony oxide	8300	13,000	15,000	15,000	16,000	18,500	18,500	17,000	17,000	17,000	18,000	19,100	17,000	16,000	16,000	14,000
	Hydrated aluminum	48,000	30,000	33,000	35,000	37,000	42,000	42,000	42,000	42,000	42,000	42,000	42,000	42,000	42,000	42,000	42,000
	Others	7200	7200	8340	7700	8400	9000	9000	9000	9000	9000	10,000	10,000	10,000	10,000	10,500	11,000
	Total	63,500	50,200	56,340	57,700	61,400	69,500	69,500	68,000	68,000	68,000	70,000	71,100	69,000	68,000	68,500	67,000
Total		97,100	85,780	98,250	103,300	116,400	132,910	130,110	129,010	135,460	142,710	144,290	149,510	165,025	167,775	169,450	156,250

[a] Based on the investigation made by Kagaku Kogyo Nippo-Sha (Japan) (1987–2001).

Ota has taken the trend data forward to 2008 and plotted the results – showing that thre has been little (or no) Penta and OctaBDE consumption since 1995 (Ota et al. 2009):

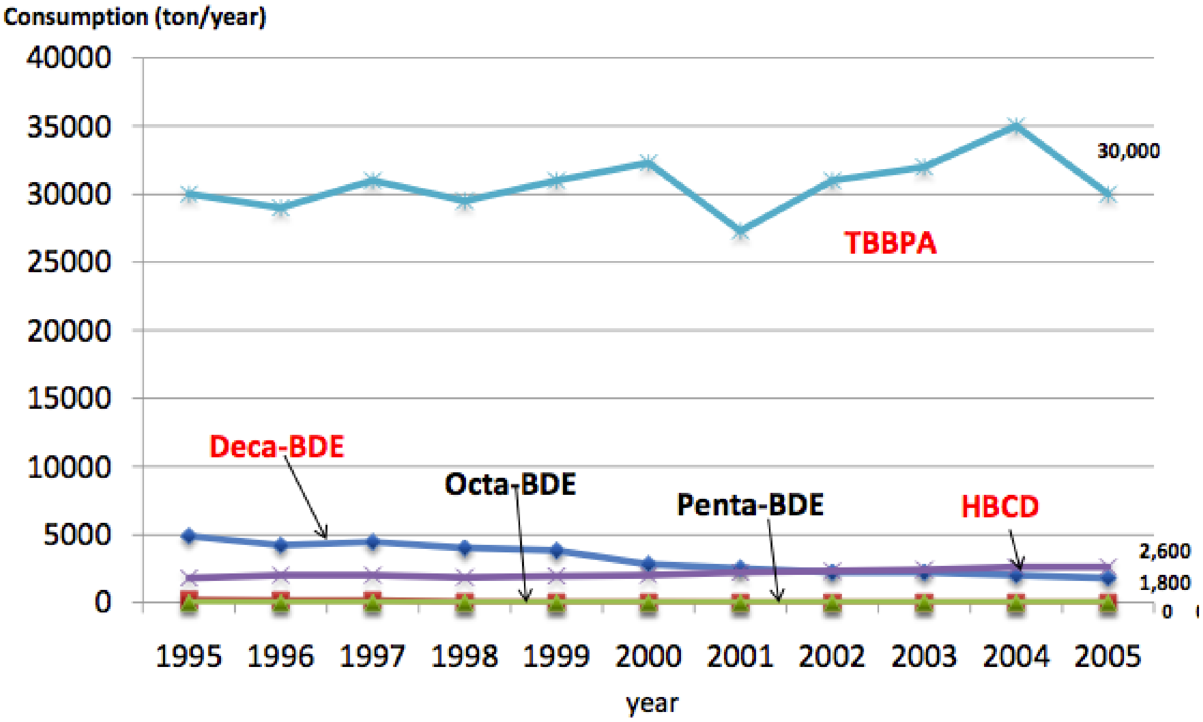

Figure 16: Trends of Annual Consumption of BFRs in Japan (Ota et al. 2009)

Production Trend data for PentaBDE Europe

Prevedouros used a number of plausible scenarios for production and use to develop estimates of historical consumption in Europe (Prevedouros et al. 2004a). The results, plotted in Figure 17 below show that most scenarios closely follow the increasing Bromine production and indicate that the peak of PentaBDE consumption in Europe occurred in the mid-1990s at c.1,050-1,250 t/year (Prevedouros et al. 2004a). Consumption was estimated to decline after the mid-1990s to c.175-200 t in 2000 in-line with the industry estimates of 210 and 150 t proposed in Table 12 above.

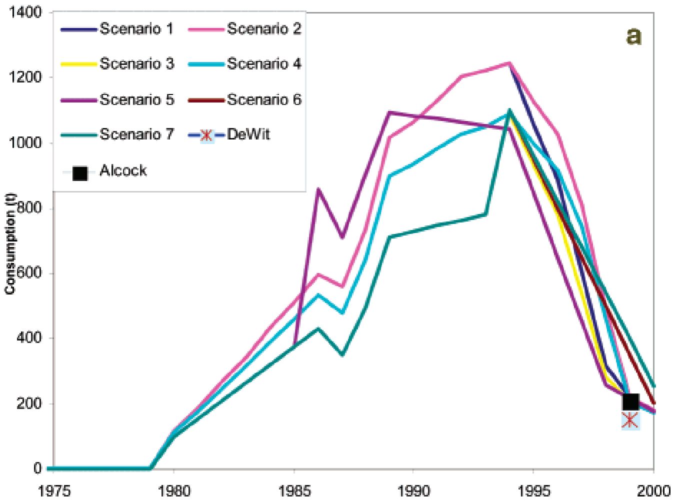

Figure 17: Estimated historical consumption of PentaBDE in Europe (t) (Prevedouros et al. 2004a). Based on seven separate scenarios and previously published consumption estimates (de Wit 2002) (Alcock et al. 2003)

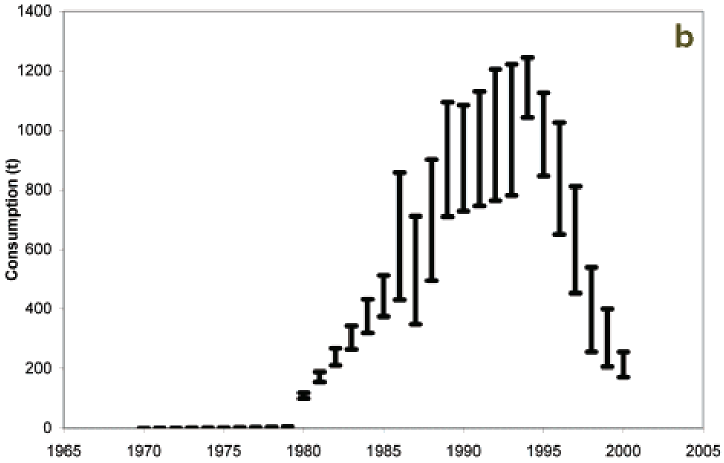

Figure 18: Estimated historical consumption of PentaBDE in Europe (t) (Prevedouros et al. 2004a). Computed range of the seven consumption scenarios

Congener-Specific Estimations:

The consumption data for individual BDE can be estimated by using the data on the commercial mixtures above. Prevedouros assessed the usage in Europe of congeners 47, 99, and 153 which constitute major components of the PentaBDE mix. This assumed that the majority of the composition was as the Bromkal mix which was produced in Europe together with some DE-71[23] entering through importation.

For BDE-47 the estimated production/use is 37,000 tonnes globally and 5,500 tonnes in the EU. The UK market for BDE-47 was assumed to be 20% of the EU total (Alcock et al. 2003):

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[23] Produced by (the then) Great Lakes Chemicals and with generally similar congener patterns to Bromkal but with the possible exception of around 15% higher levels of BDE-99 than BDE-47.

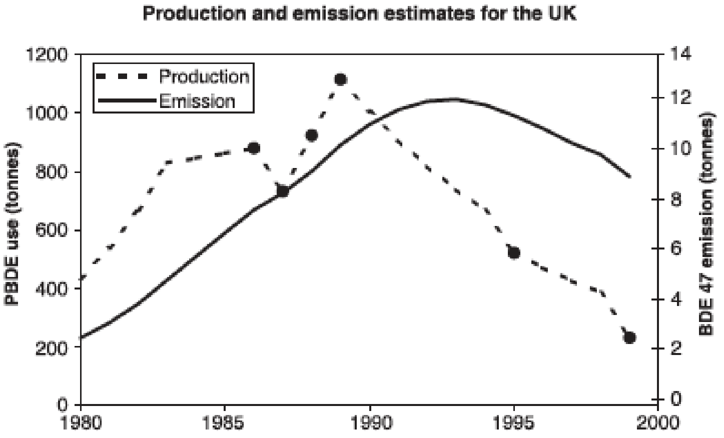

Figure 19: Estimated historical production and use of PentaBDE and emission estimates for BDE-47 in the UK (Alcock et al. 2003).

EU data from the review can therefore be extracted from the figure by simply multiplying the use or emissions by five.

These data, the authors warned, "*represent first estimates and as such are tentative and must be treated with extreme caution*". They hoped that improvements to our understanding of historical usage would occur "*as new data is published by both the manufacturers and also via knowledge of environmental time trends*" (Alcock et al. 2003). Unfortunately whilst there is now have some better information on the time trends, as detailed in the next chapter, little new information has been published by the manufacturers.

United States

It is particularly unfortunate given the extent of the usage of both Penta and OctaBDE in the United States that there is far less published data on production and consumption than in Japan and even than for Europe. It is consequently more difficult to establish trend data which makes it more difficult to establish the size of the remaining stocks of these POPs. Alcock relied on just three industry market demand points to plot US 'production' trends:

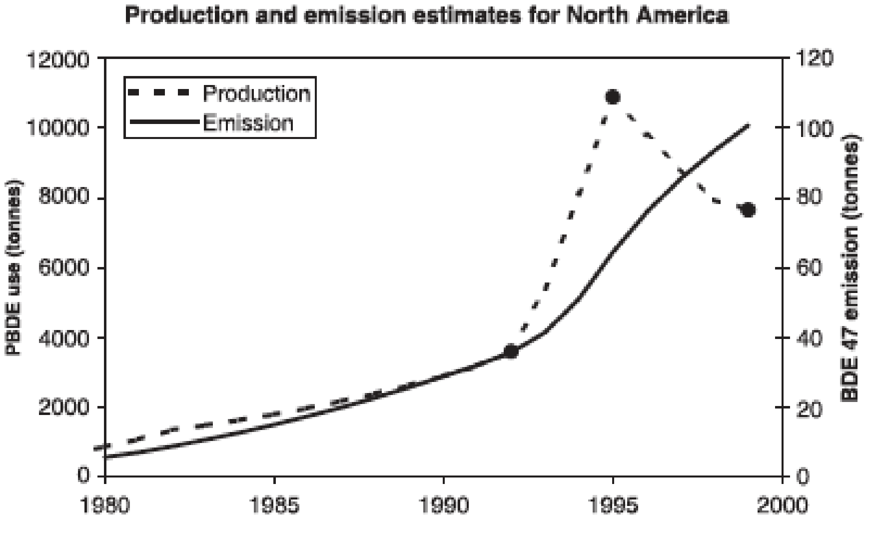

Figure 20: Production and emission estimates for North America (Alcock et al. 2003).

Penta and Octa BDE Uses:

The Response from the Dutch Government includes the quote "*Scott Masten (2001) mentions: "Determining which products contain PBDE and how much is difficult because many manufacturers do not report this and some may not* *even know if their products contain PBDE or some other flame retardant*" (the original reference for which is (Integrated Laboratory Systems 2001)[24]).

Followed by the recommendation:

"Dutch CA recommends to consult industry on amounts produced and applications of commercial octa- and pentaBDE in the past".

The first quotation has some resonance with the problems of establishing what products have been treated and, with even more uncertainty, how much has been treated.

Attempts have been made, as recommended, and in this case facilitated by the Dutch authorities, to meet with the Bromine Industry to establish the amounts and uses. Unfortunately the industry response was that:

C-OctaBDE and c-PentaBDE are legacy products. Because of the time which has passed since the last sales and production of these substances, people, systems and entire companies have changed. As a result, finding the historical data is a significant challenge.

Consequently no more information could be provided on these issues than the very limited production and use data which is already in the public domain in the POPRC Risk Profile, Risk Assessments and the EU Risk Assessment.

The European data, though limited in scope is still the best available, as confirmed in the ILS report cited by the Netherlands which says that for that (US) review:

"Much of the information about use of PBDE in products has been gathered by the European Community and is expected to be similar to products used in the United States since most European polymer products and U.S. products that would contain flame retardants come from the United States or Southeast Asia."

By far the majority of flame-retardants were used in the construction industry or in other non-consumer products. Of the 300,000 tpa of flame-retardants used in Europe in 1995 RPA (Risk & Policy Analysts Limited 2000) report that only around 17,000 tpa were used in consumer products (i.e. products which consumers can purchase). The POP-BDE were disproportionately represented in those BFRs used for consumer goods.

In the consumer products, over half (58%) of all European FR usage has been associated with upholstered furniture. This figure is much higher for the UK (90%) due to flammability regulations (Risk & Policy Analysts Limited 2000). Due to the high levels of FR use in furniture for the UK market, the UK accounts for almost 65% of all EU flame retardant usage.

Stevens and Mann (Stevens & Mann 1999) summarised the market for flame-retardants for use in consumer products for the UK Department of Trade and Industry:

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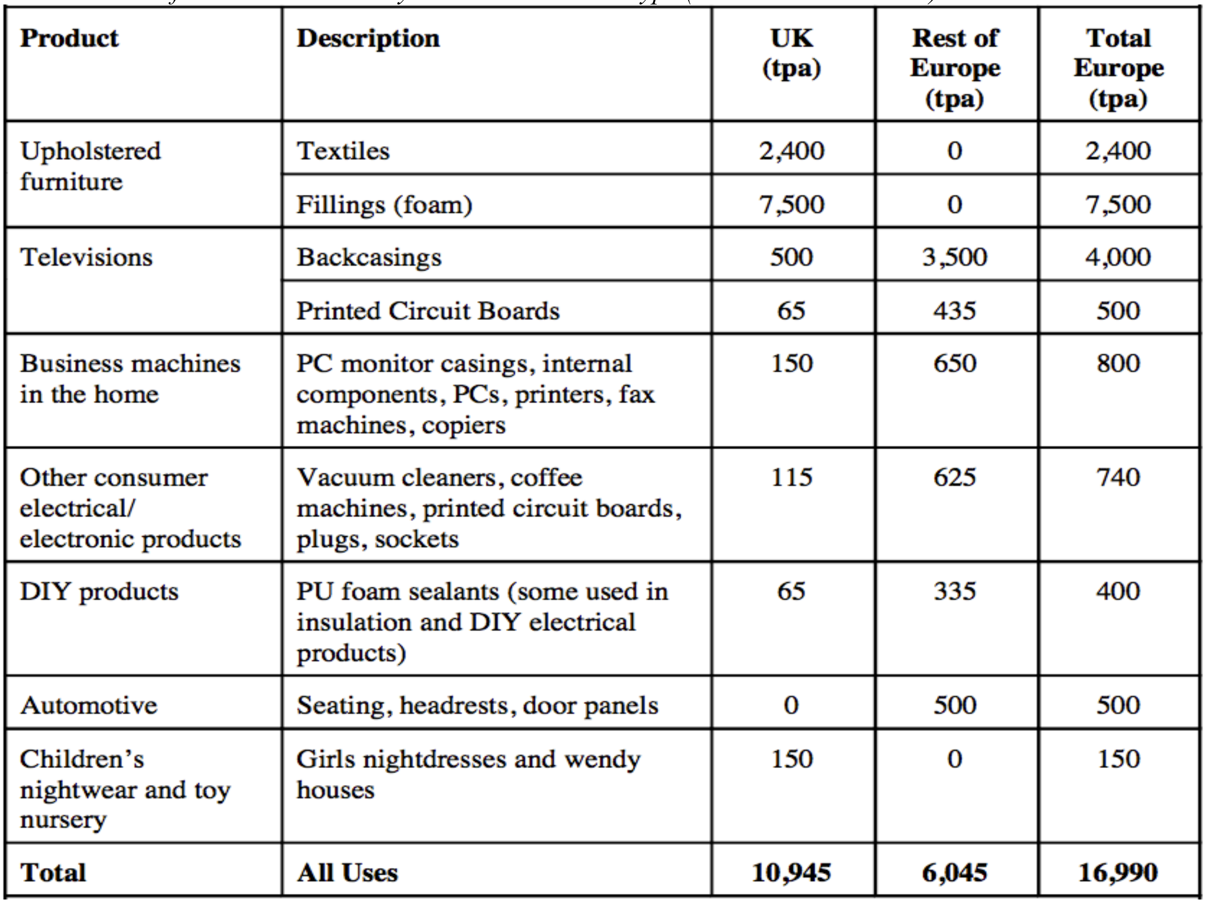
[24] Strictly speaking it is not a quote from Scot Masten as the report was prepared for him by Bonnie Carson of Integrated Laboratory Services.

Table 14: Use of Flame Retardants by Consumer Product Type (Stevens & Mann 1999)



Product	**Description**	**UK (tpa)**	**Rest of Europe (tpa)**	**Total Europe (tpa)**
Upholstered furniture	Textiles	2,400	0	2,400
	Fillings (foam)	7,500	0	7,500
Televisions	Backcasings	500	3,500	4,000
	Printed Circuit Boards	65	435	500
Business machines in the home	PC monitor casings, internal components, PCs, printers, fax machines, copiers	150	650	800
Other consumer electrical/ electronic products	Vacuum cleaners, coffee machines, printed circuit boards, plugs, sockets	115	625	740
DIY products	PU foam sealants (some used in insulation and DIY electrical products)	65	335	400
Automotive	Seating, headrests, door panels	0	500	500
Children's nightwear and toy nursery	Girls nightdresses and wendy houses	150	0	150
Total	**All Uses**	**10,945**	**6,045**	**16,990**

The later UK DEFRA report (Risk & Policy Analysts Limited 2000) says these data should at best be seen as indicative: use of flame retardants in upholstered furniture in European countries other than the UK is certainly not zero, for example. In addition the consultation indicated that flame-retardants (and in particular PentaBDPE) were indeed used in automotive products in the UK.

It has been reported that between 2 and 5% of WEEE plastics contain brominated flame-retardants although some reports have claimed that up to 12% of WEEE plastics contain some type of brominated flame retardant (Hall & Williams 2008).

Restrictions and Regulations on Penta and Octa BDE

The use of PentaBDE around the world varies significantly and has largely a function of the demand for products using the flame-retardants combined with the levels of regulatory control.

Most developed countries have taken some actions to limit the production and use of PentaBDE (Stockholm Convention 2007c):

- Australia: PentaBDE is effectively banned for use in new articles. Imports of articles containing BFRs are not regulated .
- EU: placing on the market and use in concentrations higher than 0.1 % by mass is banned from 2004 (EU-Directive 2003/11/EC). Use in electrical and electronic appliances was phased out from July 1st, 2006 under the EU's Restriction of Hazardous Substances in electrical and electronic equipment. Products containing more than 0.25 % PentaBDE or OctaBDE are classified as hazardous waste when they are discarded.
- US: the industry voluntarily ceased production of C-PentaBDE from 2005, and the use is forbidden in some states. USEPA requires notification and Agency review prior to restart of manufacture for any use (see rule at 40 CFR Part 721.10000).
- Japan: use of (the Japanese equivalent of) C-PentaBDE stopped voluntarily in 1990.

- Norway and Switzerland: both countries have banned production, import, export and marketing and use of PentaBDE and mixtures containing 0.1 percent per weight or more of PentaBDE. Products containing more than 0.25 % PentaBDE are classified as hazardous waste when they are discarded. In Norway recycling and reuse of PentaBDE and materials with PentaBDE are not allowed.
- Canada: no production of PentaBDE. Regulations on manufacture, use, sale and import were proposed in 2006. Canada will be implementing virtual elimination for the tetra-, penta- and hexa-BDE homologues contained in C-PentaBDE .
- China: use of PentaBDE in electric and electronic products was banned from 1st March 2007.

Fire Regulations

Consumption of flame-retardants is largely linked to regulatory requirements for fire regulation and thus the subsequent exposures have tended to be higher where there are more stringent regulations.

The usage of flame-retardants in the United Kingdom is higher than the European average - especially for textiles and furniture, for example, while it was lower in Scandinavian countries.

This follows the introduction to the UK, in 1988, of the upholstered furniture fire regulations requiring cigarette and match ignition resistance (HMSO 1988, HMSO 1989). This resulted in the ending of the use of non-combustion modified polyurethane foams in new furniture. Furniture sold since 1988 typically contains brominated/antimony trioxide or chlorinated phosphate treatments for textiles and chlorinated phosphate/melamine treatments for foam fillings (Horrocks & Price 2001). The main impact of this has probably been seen with DecaBDE rather than the POP-BDE levels.

Uses of PentaBDE:

The EU Risk Assessment comments "*Information on the exact uses of pentaBDPE is difficult to find*" (European Chemicals Bureau 2001). Such information has often been claimed to be commercially sensitive and therefore not disclosed. The passing of time has hardly reduced this barrier – but has added the barrier that production and usage records even from the 1990s are claimed to have been lost or that they are too obscure or difficult to retrieve.

Main Use:

Whilst there are differences in the usage of PentaBDE both temporally and in different regions the weight of evidence indicates that overall the major usage of PentaBDE has always been in polyurethane foams – mainly in flexible applications but to a minor extent also in rigid foams. The flexible foams were used mainly for furniture and upholstery in automotive and aviation industry and domestic furnishing and by the late 1990s practically all (>95-98%) PentaBDE was being used in this way (Risk & Policy Analysts Limited 2000)(USEPA 2010). Indeed some sources suggest that by c.2000 this was the only use and even add that this was confirmed by the industry (Peltola & Yla-Mononen 2001). A 2003 report for (then) Great Lakes Chemicals[25], the only manufacturer in the US, consultants ENVIRON wrote: "*The commercial pentaBDE product is used only for flame retardant purposes as an additive in consumer products manufactured by the furniture industry*" (ENVIRON 2003b). The report then went on to say, however, that "*a small percentage*" is used in *"commercial adhesive products*" (ENVIRON 2003b).

On the other hand the Danish EPA indicated in 1999 that the use of PentaBDPE in flexible PUR foams seems to have been discontinued (Lassen et al. 1999). This is not consistent with other evidence.

USEPA says the "*remaining 5% use of pentaBDE*" (after 95% usage in PUR foam) in 2004 prior to the end of US production was in the treatment of foam-based packaging materials and carpet padding (USEPA 2010).

Historical Uses:

Other historical uses of PentaBDE have included:

- epoxy resins (EPs) and phenolic resins used as protective coatings on circuit boards; unsaturated polyesters;
- textile fabrics used in upholstery for furniture and automobile seat covers;
- paper laminates;
- flexible polyvinyl chloride used as electrical wire coatings;

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[25] since merged with Crompton Chemical to form Chemtura (USEPA 2010).

- rubber; paints and lacquers;
- elastomer instrument casings[26]; and
- adhesives

For most of these applications there is little data on the quantities used, the regions in which they were used or the specific applications which required this treatment (WHO & IPCS 1994)(Rahman et al. 2001)(European Chemicals Bureau 2001, ATSDR 2004).

Resins for Printed Circuit Boards:

The exception is the use as protective coatings on printed circuit boards (also known as printed wire boards and the abbreviation PWB is used in this review). In 1978 Prescott ((Prescott 1978) cited by (European Chemicals Bureau 2001)) had indicated uses for PentaBDE in copper clad phenolic laminate circuit boards and so this usage, though often missed in the literature, may have been a longstanding one. RPA suggest that this relates only to printed circuit boards produced in Asia (Risk & Policy Analysts Limited 2000).

Lassen, for the Danish EPA, suggested that in the early 1990's European type FR2 (paper reinforced phenolic laminate) PWBs were flame retarded with TBBPA whereas Asian type FR2 laminates were flame retarded with PentaBDE (Lassen et al. 1999). For both types the content of a typical FR2 laminate has been estimated at 0.036 kg/m^2. Lassen indicated that there was a shift away from PeBDE through the 1990s and by 1999 "*most Asian FR2 laminates seem to be flame retarded with TBBPA*". As a rough estimate he assumed that PentaBDE still covered 30% of the FR2 laminates in consumer electronics other that TV-sets (Lassen et al. 1999).

The POPRC Risk Profile (Stockholm Convention 2006) for PentaBDE confirmed that analyses of dismantled FR2 circuit boards in electrical scrap show that about 35% of the PBDE used was PentaBDE and that the literature may have under-estimated the PBDE content of these boards as "*companies seldom provide all the information necessary to make accurate estimates*".

Prevedouros et al. (Prevedouros et al. 2004a) estimated production, consumption, and atmospheric emissions of PentaBDE in Europe between 1970 and 2000 based on literature data. According to that study, the flow of PentaBDE in discarded electrical and electronic appliances in Europe is in the range 17-60 metric tons per year for the period 2000-2005. These results seem rather low compared with the results reported from some e-waste including the PentaBDE congeners reported by Morf (Morf et al. 2005):

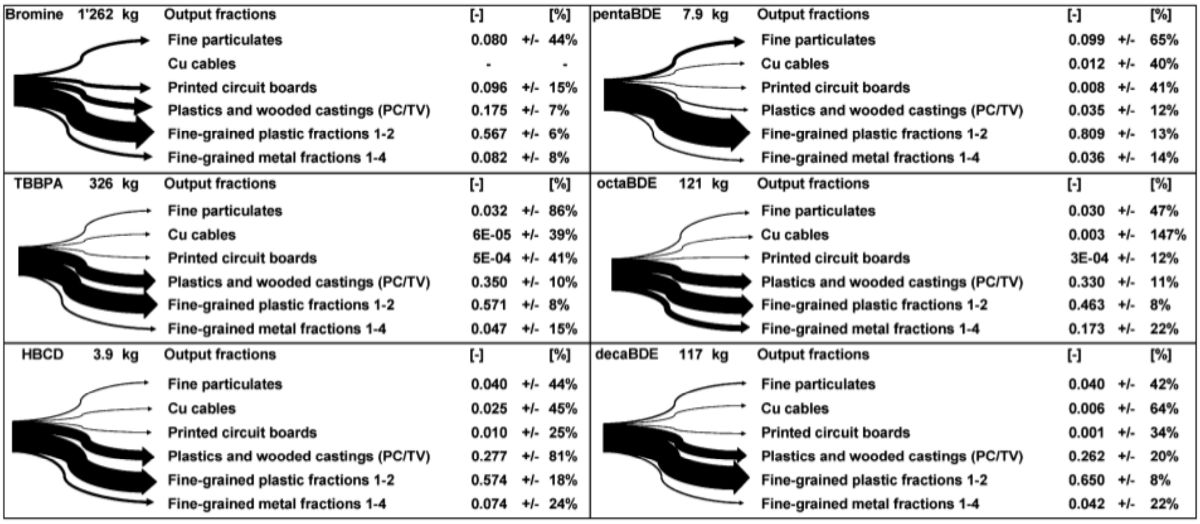

Figure 21: Input mass flow (kg) and mass transfer coefficients of selected BFRs and bromine from the WEEE input into output streams of the investigated WEEE treatment plant (Morf et al. 2005)

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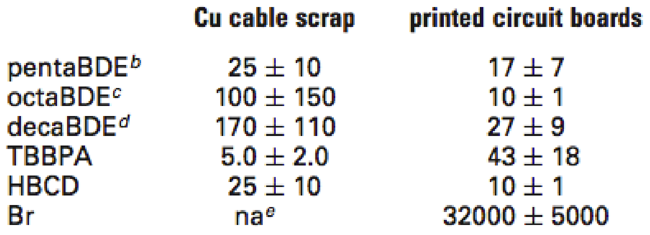
[26] The evidence for use in instrument casings in the EU, as mentioned in the POPRC PentaBDE Risk Profile (Stockholm Convention 2006), is not particularly strong. The original source for this appears to be simply a 'personal communication' with the UK DETR during the preparation of the EU Risk Assessment (European Chemicals Bureau 2001).



	Cu cable scrap	printed circuit boards
pentaBDE[b]	25 ± 10	17 ± 7
octaBDE[c]	100 ± 150	10 ± 1
decaBDE[d]	170 ± 110	27 ± 9
TBBPA	5.0 ± 2.0	43 ± 18
HBCD	25 ± 10	10 ± 1
Br	na[e]	32000 ± 5000

Table 15: Mean Concentration of Selected BFRs, Bromine, and Antimony in Separately Analysed Components of Representative WEEE from the Swiss Market (mg/kg) (Morf et al. 2005)

More recently it has been established that much of the recent production of PentaBDE in China has been used for circuit boards and that this has then been incorporated into products exported to (particularly) Europe and the US. Consequently the use of PentaBDE in circuit boards is likely to have continued until relatively recently. Hester commented in 2009 that "*pentabromodiphenyl ether is reportedly still used in a small percentage of Far East produced FR2 printed circuit board laminates*" (Hester & Harrison 2009). It was hoped that more details would have been provided about the volumes of PentaBDE involved following discussions in the New POPs Workshop held in Beijing at the end of June but no further details have been supplied at the time of this version of the review.

It is clear from the much higher bromine levels, however, that all the PBDE and 'conventional' flame retardants are only a small proportion of the total BFRs. Levels reported for PentaBDE in the other components were much lower than Octa and DecaBDE. Furthermore most of the evidence associated with these applications indicates that PentaBDE concentrations in circuit boards are likely to be much lower than the 0.1% RoHS threshold and in most cases below the current provisional "*low POPs*" threshold of 50 ppm for the original POPs (apart from PCDD/DF). This is discussed further in the risk assessment section of the appendices but the likely consequences are that circuit board uses would normally only require "*environmentally sound management*" and not destruction or irreversible transformation to comply with the requirements of Article 6 in any case.

Unconfirmed Uses:

Other uses for which there is robust confirmation include:

Speciality textiles: PentaBDE may also have been used in minor amounts in speciality textiles - although the EU BREF[27] says that Penta-BDE is not reported as being used in the textiles sector (European Commission 2003b). The BREF notes, however, that there are "*suspicions that deca- BDE, the major PBDE for textile applications, and octa-BDE could break down to penta-BDE and tetra-BDE after release into the environment*" (European Commission 2003b). This possibility is discussed further later in this appendix. One company at least, appears to have used PBDE in the production of rubber belts for the mining industry (Risk & Policy Analysts Limited 2000, Peltola & Yla-Mononen 2001). It is also possible that the use in conveyor belts was more widespread than mining. It is noted that the submission from Norway received at the beginning of July included reference to 7 years use of 75kg/year if PentaBDE for textiles. No more details are provided and it is hoped that further clarification can be provided about the nature of this usage.

Drilling Fluids for oil exploration and mining: Another possible historic use was as a hydraulic fluid for oil drilling (Peltola & Yla-Mononen 2001). This is a use that is regularly postulated but for which it has not been possible to find any supporting references. It has been suggested that this usage could "*explain the ubiquity of penta-BDPE in some biota in and near the North Sea (rather than emissions from polyurethane foam products)*" (Risk & Policy Analysts Limited 2000). Risk and Policy Analysts investigated this claim and were unable to verify that PentaBDE was actually used in these applications (Risk & Policy Analysts Limited 2000). The EU Risk Assessment comments that a survey by KEMI in 1999 indicated that one company looked into the possible use in this area "*15-20 years ago, but no product was marketed in Sweden*" (European Chemicals Bureau 2001). The survey did provide some circumstantial evidence that PentaBDPE may have been used in an early HFD flame resistant hydraulic fluid designed to be used as a heat exchange medium rather than hydraulic oil – in which cases any releases should have been relatively small. The OECD indicated in 1995 that c.10% of bromine production was used for drilling applications and listed the main compounds as calcium bromide, sodium bromide, zinc bromide but not PBDE (OECD 1995).

On balance it seems unlikely that hydraulic fluids and drilling have been significant sources of widespread

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[27] Best Available Techniques Reference Document

environmental contamination although the possibility of some local contamination cannot be dismissed[28]. The EU Risk Assessment, however, concluded in relation to the industry suggestions that these drilling uses could have been the explanation for marine contamination by PentaBDE that "*such speculation can not be considered further without substantiation*".

Similarly some early use was claimed in mining as a replacement and this was held responsible for contamination in rural areas away from obvious pollutions sources. The EU Risk Assessment again reports that "*after intensive investigation*" Kemi has not confirmed this use(European Chemicals Bureau 2001).

Usage in Polyurethane Foams:

The most common type of halogenated flame retardants used in polyurethane foams appear to be halogenated phosphorus based chemicals (European Chemicals Bureau 2001) – particularly chlorinated phosphate esters such as tris dichloro isopropyl phosphate (TDCP) and tris monochloro isopropyl phosphate (TCPP) (Eaves 2004). These retardants can, however, contribute to foam discolouration called 'scorch'. This does not affect the flame-retardancy and is an aesthetic effect unless severe (USEPA 2005).

PentaBDE gives much less scorch and was thus widely used in North America. PentaBDPE was generally used in flexible polyurethane foams as an admixture with aromatic phosphate esters (Larsen & Ecker 1988, European Chemicals Bureau 2001).

The level at which PentaBDE was added to PUR is clearly important. Many papers cite the 1994 WHO publication which says that flame-retardants were added at concentrations between 5 and 30% by weight (i.e. 1 kg of polymer would contain 50-300 g of flame retardant) (WHO & IPCS 1994). The RAPRA Handbook of Polymer Foams (Eaves 2004) suggests a maximum of 20% indicating that the 30% reported by WHO may be too high.

The Risk profile on commercial pentabromodiphenyl ether (Stockholm Convention 2006) suggests that treated foam contains "*between 10 and 18% of the commercial PentaBDE formulation (typically made up of 75% PentaBDE)*" this appears to be based on the original Norwegian submissions.

These assumptions appear to be much too high – at least for many of the common applications. In their 2003 report for Great Lakes Chemicals ENVIRON say that "*according to the limited data provided by companies that purchase the commercial pentaBDE product from GLCC*" for use as a flame retardant additive in FPUF levels were (ENVIRON 2003b):

- Mattress foam - approximately 2-3% flame retardant
- Cushion foam - 3-5% flame retardant

Scrap material from both industries have been used as padding beneath carpets, and, as a result, ENVIRON say, "*carpet padding likely contains 3-5% flame retardant similar to that for cushion FPUF*" (ENVIRON 2003b). Morf suggests a range of 4-13% (Morf et al. 2002).

Chemtura (Cambell 2010) confirmed that the levels of PentaBDE used in polyurethane foam for upholstered furniture that was intended to meet the California TB 117 flammability standard are influenced by the density of the foam:

Table 16: Usage of PentaBDE in PUR Foam (Cambell & Chemtura 2010)

PUR Foam Density	*% PentaBDE in Polymer (by wt)*
1.2 pcf or 19 kg/m3	5.45%
1.5 pcf or 24 kg/m3	4.30%
1.8 pcf or 29 kg/m3	2.77%

(pcf = pounds per cubic foot)

In both FPUF products and in carpet padding, only 75% of the flame retardant additive is the BDE portion of the commercial PentaBDE product. The remaining 25% is the aromatic phosphates. It is not clear whether the market demand figure reported by the industry are based on the content of the commercial mixtures alone or including additives like these aromatic phosphates. This needs clarification as it can influence the total inventory of PentaBDE significantly.

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[28] This may be the related to the methoxy and hydroxyBDE compounds found in some shellfish and this is discussed later in the appendices.

Penta-BDE has been used mostly in furniture for sale in California in order to comply with Technical Bulletin 117 (TB117), the state's 1975 performance- based furniture flammability standard (Zota et al. 2008). Regional differences in the US may be less obvious than might be expected, however, because some TB-117-compliant products have been distributed nationwide with about 25% of furniture sold in the U.S. outside California and in Canada meets TB117– and some even exported (Blum 2009). The chairs at the BFR2010 conference in Kyoto, Japan, for example, were TB-117 compliant:

Photograph 1: Chair with TB117 label at Kyoto BFR conference

The commercial PentaBDE was additively incorporated into foam polymers during an exothermic reaction (Alcock et al. 2003) the BFR is therefore easily liberated into dust (Zota et al. 2008).

The main uses of polyurethane containing PentaBDE in the EU have been identified as (European Chemicals Bureau 2001)(Risk & Policy Analysts Limited 2000):

a) foam-based laminated automotive applications such as headrests;

b) domestic furniture, including cot mattresses (where PentaBDE is used for commercial reasons by one company because it does not contain phosphorus); and

c) various small run and prototype components, such as non-foamed PUR instrument casings /packaging.

The manufacture of these products in the EU was estimated as being associated with <1% of PUR foam production (Risk & Policy Analysts Limited 2000).

Polyurethanes Foam Production

The impact of polyurethanes ('PUR') has been global but is mostly concentrated in the developed world (Thomson 2005). Global consumption of all PUR products had reached c.7.5 million tonnes by 1998 having grown at 6.1% over the period 1993–1998. Eaves says that approximately 70% of global consumption is accounted for by four sectors: automotive (15%), construction (17%), technical insulation (10%), and furniture and mattresses (28%)(Eaves 2001).

Alcock quoted the total US market for foam as 2.64 million tonnes (2001) – slightly higher than the total European PUR production of around 2.3 million tonnes in 1998 (Prevedouros et al. 2004a) – this highlighted, said Alcock, "*the huge global demand for this material*" (Alcock et al. 2003). Approximately half of this polyurethane usage is for flexible foams (Thomson 2005):

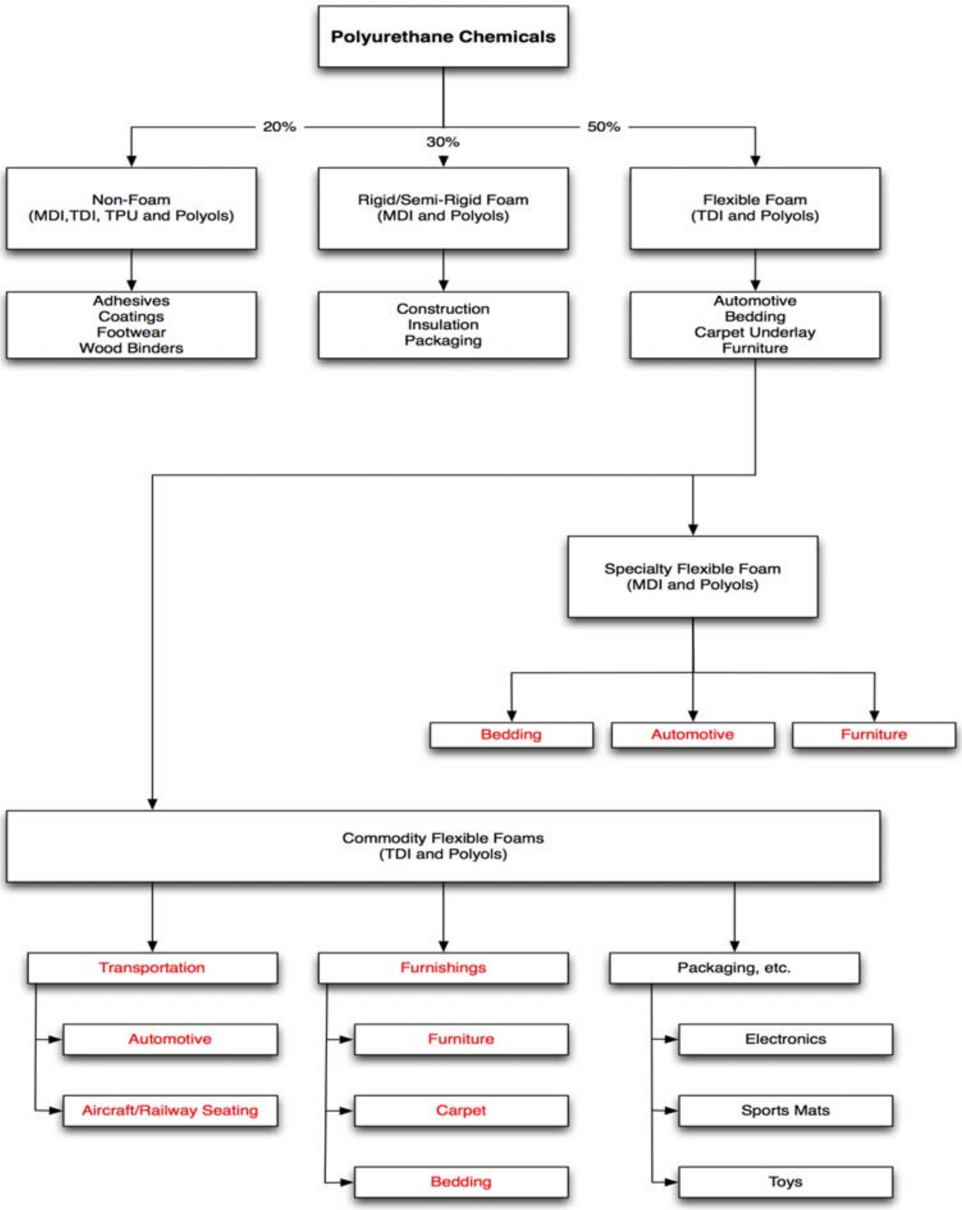

Figure 22:Uses of Polyurethanes with the applications most likely to be flame retarded with PentaBDE marked in red.
TDI -toluene diisocyanate is the conventional isocyanate used for slabstock foam,
MDI- diphenylmethane diisocyanate is a recent lower emissions isocyanate with greater recycling potential

Global foam production for 2001 was:

Tonnes foam	Asia-Pacific	Europe-Africa	Americas	Global
Polyether	530,000	620,000	880,000	2,030,000
HR	90,000	180,000	140,000	410,000
Polyester	60,000	120,000	60,000	240,000
Total Slab	**680,000**	**920,000**	**1,080,000**	**2,680,000**
Moulded	270,000	380,000	330,000	980,000
Total FPF	**950,000**	**1,300,000**	**1,410,000**	**3,660,000**

Table 17: Estimated foam production in 2001((Eaves 2004) based on data from IAL).

Alcock said 42% of PUR foam, equivalent to 1.08 million tonnes, is used for ‘flexible’ foam. The IAL data for US demand would therefore appear to be consistent with Alcock’s estimate – assuming that this was based on slabstock production and excluded moulded foam usage.

This slabstock usage was then split by Alcock into the main applications of which transportation uses, carpet underlay (unique to North America in practical terms), furniture and bedding form the most significant end use:

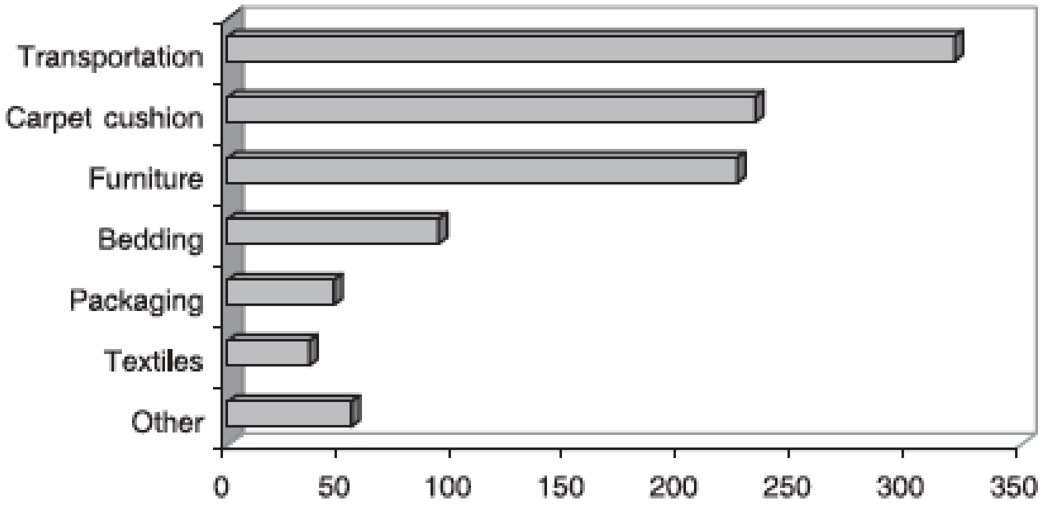

Figure 23: US market for flexible foams (1998) in tonnes (000s) (data from API (Alcock et al. 2003)).

Whilst transportation, particularly for automobiles, is the largest single use it represents just over 30% of the total flexible foam usage. Furniture, bedding and carpet cushion together with textiles associated with these uses represents nearly 60% of the total.

ATSDR included slightly lower figures and indicated that the US market was approximate 953,000 tonnes of flexible PUR foam (ATSDR 2004).

The POPRC Risk Profile for PentaBDE listed global production of PUR foam as only 150,000 tonnes/year (Stockholm Convention 2006). The same figure was used by BiPRO (BiPRO 2010) in the preliminary results of their work for the EU:

Polyurethane foam production	**Quantity of PentaBDE**	**Release of PentaBDE into waste water**	**Emissions of PentaBDE to air during production**
150,000 tonnes/year	15,000-27,000 tonnes/year	9,000-16,200 kg/year	7,500-13,500 kg/year

Table 18: Global production and use of C-PentaBDE in polyurethane foam production, and estimation of associated releases in 2000 (foam containing 10-18% PentaBDE). (Stockholm Convention 2006)

The total foam production of 150,000 tonnes is clearly much lower than the global PUR foam production of 3.66 million tonnes (2.68 million tonnes of slabstock) shown in Table 17 above. It is therefore assumed, although the text does not say so, that this is intended to represent the total quantity of PUR foam that has been treated with PentaBDE. This would therefore represent 4% of the total or 5.6% of the slabstock. This still seems rather low, as discussed below.

There is evidently an error in the POPRC table, however, as PentaBDE production has never risen as high as 15,000 tonnes/year (and certainly not 27,000 tonnes/year). It has been shown above that maximum annual production has always been less than 10,000 tonnes.

The dosing rate assumption in Table 18 is 10-18% which appears rather high when compared with those in the literature. Environ, for example, indicate that the average should be much lower – at around 3-5% - for mattresses, cushions and carpet padding (ENVIRON 2003b). The automotive industry has also indicated that 4% would be the most realistic figure for PUR foam in cars (Risk & Policy Analysts Limited 2000). Furthermore no analytical data has been found which supports the higher range suggested in the earlier reports. Stapleton analysed furniture foam for flame retardants replacing PentaBDE[29] and found that the Concentrations of tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and tris(1-chloro-2-propyl) phosphate (TCPP) and 'Firemaster 550' varied from 1 to 5%, 0.5 to 2.2%, and 4.2% by weight of the foam, respectively (Stapleton et al. 2009). These levels, she confirmed, were similar to reported concentrations of PentaBDE measured previously in polyurethane foam levels of less than 5%. This was reported by Allen in analysis of US PUR foams:

At an average loading of 4% then it would be anticipated that at the peak use of PentaBDE for treating PUR foam (about 8,000 tonnes/year) the total tonnage of treated foam would be approximately 200,000 tonnes year representing 5.5% of the global total or 7.5% of the slabstock. Nearly all of which would have been used in the US (Hale et al. 2002b).

This revised estimate, of 200,000 tpa of maximum global production of 200,000 tonnes/year of PentaBDE-treated foam at 4% loading is 33% higher than that previously assessed by POPRC. It is considered to be more robust, however, because it is can be reconciled with the PentaBDE production data available whilst the POPRC figures cannot. It is also consistent with the US ATSDR estimate that c.7.5% of PUR was treated with PentaBDE (ATSDR 2004).

The same approach can therefore be applied to European usage with the assumption that a maximum of c.1,000-1,050 tonnes/year of PentaBDE was used to treat PUR foam. then maximum consumption levels in Europe, including imports, would have been c.25,000 - 26,250 tonnes of PUR treated foam in the mid-1990s falling to less than 4,000 tonnes by 2000:

Table 19: Revised assessment of the total tonnage of PentaBDE-treated PUR foam.

Region	*PentaBDE-treated PUR foam production tpa*	*Quantity of PentaBDE tpa*
US	175,000	7000
Europe	25,000	1,000
Total	**200,000**	**8,000**

The EU Risk Assessment 2001 estimates that approximately 120,000 tonnes of polyurethanes were used in the United Kingdom each year (European Chemicals Bureau 2001). The European Risk Assessment appears to have assumed that all of this was flexible foam, however, whilst it is more likely that only about 50% would be as detailed above. RPA appears to confirm this as that report indicated that the UK production was 60,000 tpa of flexible PUR foams each year at that time (Risk & Policy Analysts Limited 2000)

The EU Assessment indicates that c.30% (36,000 tonnes) of the total was used in furniture and 18% (21,600 tonnes) is used in automotive applications. These are likely to be the major uses of polyurethane as flexible foam in the United Kingdom and the EU in general and those most likely to have required flame retardants and it seems reasonable to assume that this 57,600 tonnes represents the majority of the 60,000 tonnes flexible foam usage.

Some of the flexible foam will have contained BFRs but several different types of flame retardant could have been used and it is not known what fraction of this foam will contain PentaBDE (European Chemicals Bureau 2001).

Passenger cars make up the largest fraction of BFR consumption in the transport sector (Morf et al. 2007) and Andrady says that an average car contains approximately 10 kg of PUR (Andrady 2003). Thus the UK usage for the manufacture of the average of c1.7 million cars produced each year in the late 1990s would be expected to be about 17,000 tonnes plus any production wastage and would thus be consistent with these assumptions about the proportions of flexible foam. It is most unlikely that this was all treated with PentaBDE – not least because the peak European consumption was probably less than 26,000 tpa and UK manufactured cars are very unlikely to have represented more than 80% of this total.

RPA suggested that PentaBDE is associated with the production of just 350 tpa of foams for automotive applications in the UK and that this was only 0.6% of the 60,000 tpa of flexible PUR foams produced (Risk & Policy Analysts Limited 2000). These estimates seem low and the actual usage is probably somewhere in between.

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[29] It is notable that the detection frequencies for TDCPP and TPP in the dust samples were >96% and concentrations were similar to, and in some cases greater than, PBDE. This indicates that their use as replacements for PBDE may have been started several years before the sampling.

In the absence of any more robust data an appropriate starting point for further assessment of PentaBDE usage could be derived from the EU Risk assessment split of foam use between furniture and automotive uses:

- Furniture 36,000/60,000 = 60%
- Automotive Applications 21,600/60,000 = 36%
- Others 2,400/60,000 = 4%

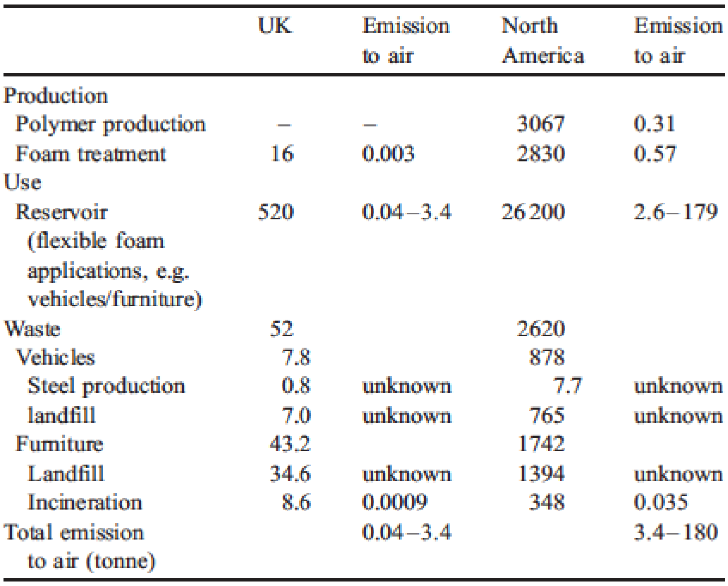
This would be broadly consistent with the US balance in Figure 23 above.

It is also broadly similar to the model developed by Alcock – although that estimates that even higher proportions of the PentaBDE are in furniture foams rather than cars for Europe in 1999 with differences between vehicles and furniture foam in the UK and North America as follows:

- UK—15% vehicles and 85% furniture foam.
- North America—35% vehicles and 65% furniture foam.

Alcock presented an assessment of a reservoir and with annual waste distribution (Alcock et al. 2003) for BDE-47[30]:

Table 20: BDE-47 in reservoirs, waste streams and estimated emissions to air for 1999 in the UK and North America (all units are in tonnes) (Alcock et al. 2003)



	UK	Emission to air	North America	Emission to air
Production				
Polymer production	–	–	3067	0.31
Foam treatment	16	0.003	2830	0.57
Use				
Reservoir (flexible foam applications, e.g. vehicles/furniture)	520	0.04–3.4	26 200	2.6–179
Waste	52		2620	
Vehicles	7.8		878	
Steel production	0.8	unknown	7.7	unknown
landfill	7.0	unknown	765	unknown
Furniture	43.2		1742	
Landfill	34.6	unknown	1394	unknown
Incineration	8.6	0.0009	348	0.035
Total emission to air (tonne)		0.04–3.4		3.4–180

The estimates made in this report assume that there is likely to be a similar balance in the imports to the EU which were estimated to contain the majority (800 tonnes vs. 300 tonnes (Risk & Policy Analysts Limited 2000)) of the PentaBDE that was in products in the 1990s and this assumption should be validated. This issue is explored below after a comment on the changes in usage of PentaBDE over time.

The much smaller use of PentaBDE suggested by RPA in their 2000 report (Risk & Policy Analysts Limited 2000) with just 350 tpa of foams for automotive applications may have been more appropriate by the end of the 1990s as the use of PentaBDE was declining rapidly and possibly at different rates in the automotive and furniture sectors. This automotive use, RPA said, was thus associated with between 14 tpa and 35 tpa of Penta-BDE usage – the lower usage being calculated in reliance on information supplied by the producers of automotive foams suggesting that such foams may contain only 4% Penta-BDE and thus seems more likely. Prevedouros (Prevedouros et al. 2004a) suggests, citing this report, that the European use of PentaBDE in cars has occurred mainly in the U.K and that 75-85% of all flexible foam applications in the U.K. were automotive with the rest in treated furniture foams. Whilst RPA had said "*levels of use in other Member States are not known, although trends in use suggest that it is likely to be small*" the data in the original report by RPA is completely inconsistent with a claim that automotive uses formed the majority of the applications. This is obvious from the fact that even RPA's (unreaslistically) high estimate of 35 tonnes of PentaBDE usage in cars was less than 20% of the EU consumption[31] by 2000.

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[30] BDE-47 represents approximately 37% of c.PentaBDE

[31] Based on combined market demand and imports of about 225 tonnes.

By 2000 it is likely that the use of PentaBDE in UK cars was mainly in the production of foams for ceilings and headrests. Whilst the submissions from New Zealand indicate that PentaBDE had been used in the seat cushions of older Japanese cars which had been tested (Geo & Hydro – K8 Ltd 2010) it appears that seating foam was a use which was phased out through the 1990s. By 2000 other flame retardants such as DecaBDE were generally used (Risk & Policy Analysts Limited 2000). This is consistent with the high levels of DecaBDE from UK manufactured cars in the samples tested by Lagalante (although it should be noted that the sample size is small):

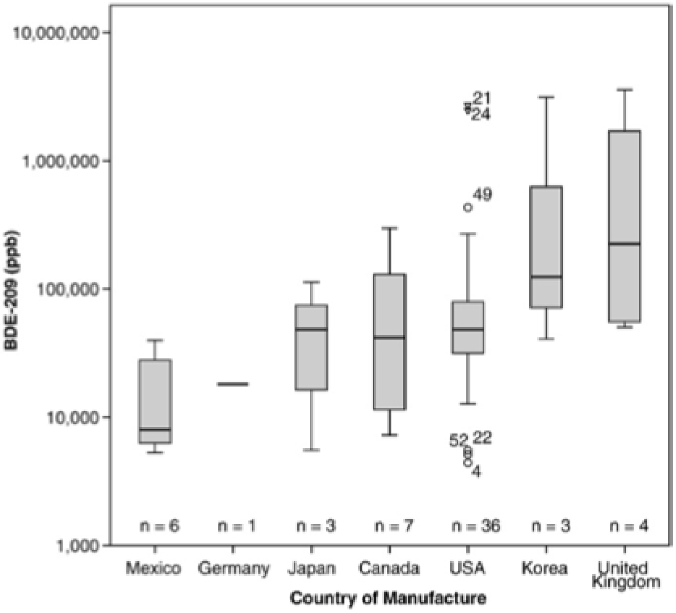

Figure 24: Boxplot of the BDE-209 concentrations (ng/g) measured in the automobile dust grouped by country of manufacture (Lagalante et al. 2009b).

In most of the rest of the EU the use of PentaBDE had stopped before 2000 and by that date it was not used in Spain, Germany, France, Italy or the Netherlands. RPA reported that globally, one car manufacturer has reported that PentaBDE was still being used in the automotive industry to quite a large extent in applications such as head-liners, carpeting and dashboards in 2000 (Risk & Policy Analysts Limited 2000).

PentaBDE imported in cars:

There were 1.167 million car imports into the EU in 1998 (Alcock et al. 2003). Alcock also estimated that each car produced in 1998 could contain c.250 g of PentaBDE (Alcock et al. 2003). Alcock therefore suggested that if 50% of these cars contained commercial PentaBDE at 250 g per car then approximately 50 tonnes of BDE-47 could be imported into Europe each year by this route – this would be equivalent to about 290 tonnes of cPentaBDE which would be, coincidentally, 36% of the assessed 800 tonnes of PentaBDE imported into Europe.

A potential confounder is that many of these cars would have been imported from Japan and use of PentaBDE in these vehicles would seem inconsistent with the Japanese data from Table 13 above showing that use of Tetra/Penta Mixes stopped in 1990.

However a submission received from New Zealand in the final stages of this draft (Geo & Hydro – K8 Ltd 2010) reveals that the highest levels of PentaBDE found in any of the consumer articles sampled was in the seat foam of a 1992 Mazda Astina car[32]. The only other sample containing any PentaBDE at levels above the LOD for the samples analysed by GCMS was in the seat foam of a 1996 Toyota Camry – though at much lower levels than the earlier car:

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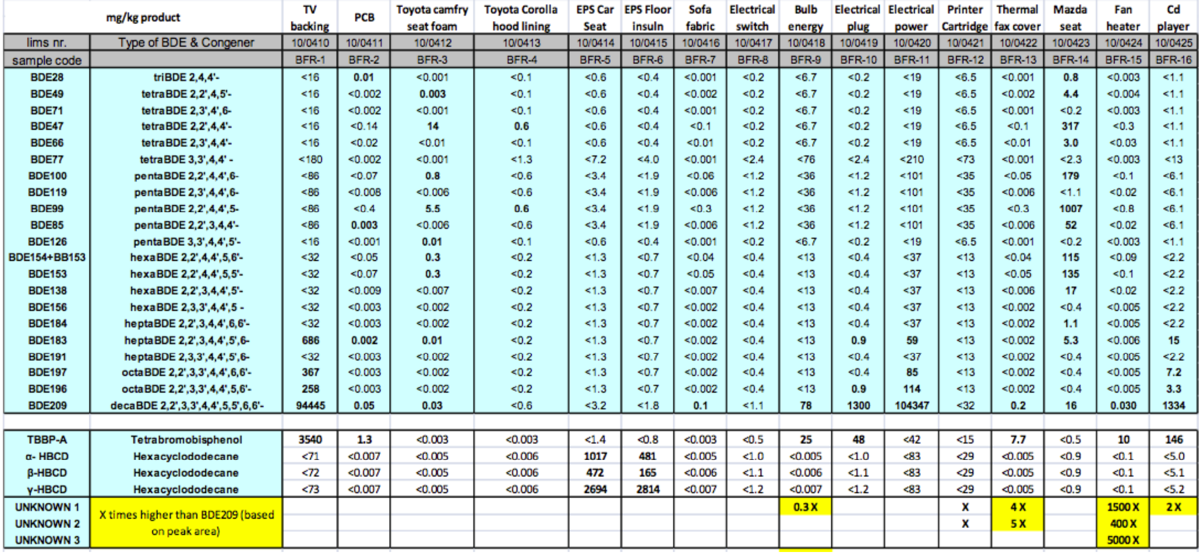
[32] It is interesting that this was mainly BDE-99 (1007 mg/kg); with lower levels of BDE-47 (317 mg/kg), BDE-100 (179 mg/kg) and BDE (153 mg kg).

Table 21:Results of analysis of consumer products in New Zealand (Geo & Hydro – K8 Ltd 2010)

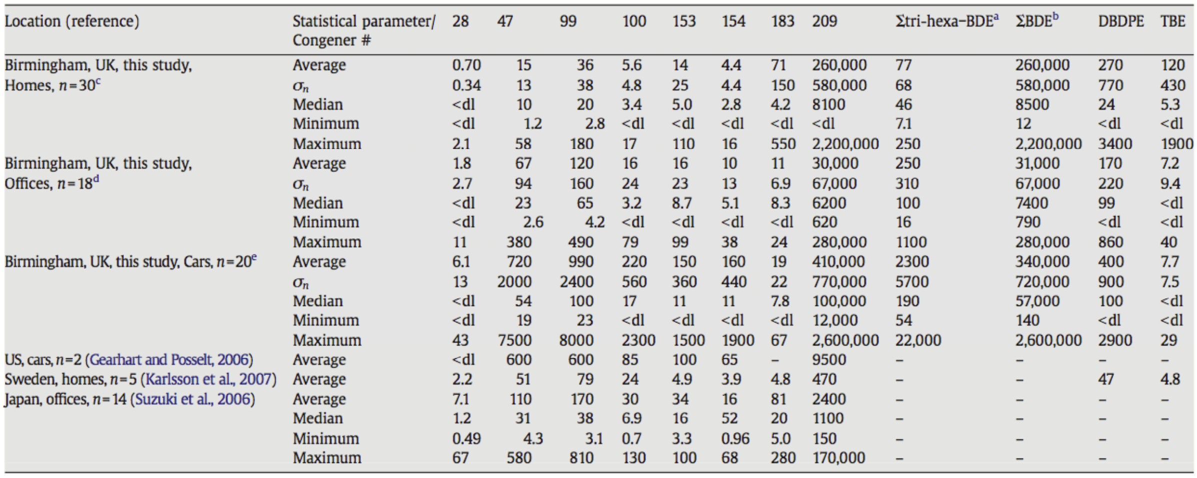


mg/kg product		TV backing	PCB	Toyota camfry seat foam	Toyota Corolla hood lining	EPS Car Seat	EPS Floor insuln	Sofa fabric	Electrical switch	Bulb energy	Electrical plug	Electrical power	Printer Cartridge	Thermal fax cover	Mazda seat	Fan heater	Cd player
lims nr.	Type of BDE & Congener	10/0410	10/0411	10/0412	10/0413	10/0414	10/0415	10/0416	10/0417	10/0418	10/0419	10/0420	10/0421	10/0422	10/0423	10/0424	10/0425
sample code		BFR-1	BFR-2	BFR-3	BFR-4	BFR-5	BFR-6	BFR-7	BFR-8	BFR-9	BFR-10	BFR-11	BFR-12	BFR-13	BFR-14	BFR-15	BFR-16
BDE28	triBDE 2,4,4'-	<16	**0.01**	<0.001	<0.1	<0.6	<0.4	<0.001	<0.2	<6.7	<0.2	<19	<6.5	<0.001	**0.8**	<0.003	<1.1
BDE49	tetraBDE 2,2',4,5'-	<16	<0.002	**0.003**	<0.1	<0.6	<0.4	<0.002	<0.2	<6.7	<0.2	<19	<6.5	<0.002	**4.4**	<0.004	<1.1
BDE71	tetraBDE 2,3',4',6-	<16	<0.002	<0.001	<0.1	<0.6	<0.4	<0.001	<0.2	<6.7	<0.2	<19	<6.5	<0.001	<0.2	<0.003	<1.1
BDE47	tetraBDE 2,2',4,4'-	<16	<0.14	**14**	**0.6**	<0.6	<0.4	<0.1	<0.2	<6.7	<0.2	<19	<6.5	<0.1	**317**	<0.3	<1.1
BDE66	tetraBDE 2,3',4,4'-	<16	<0.02	<0.01	<0.1	<0.6	<0.4	<0.01	<0.2	<6.7	<0.2	<19	<6.5	<0.01	**3.0**	<0.03	<1.1
BDE77	tetraBDE 3,3',4,4' -	<180	<0.002	<0.001	<1.3	<7.2	<4.0	<0.001	<2.4	<76	<2.4	<210	<73	<0.001	<2.3	<0.003	<13
BDE100	pentaBDE 2,2',4,4',6-	<86	<0.07	**0.8**	<0.6	<3.4	<1.9	<0.06	<1.2	<36	<1.2	<101	<35	<0.05	**179**	<0.1	<6.1
BDE119	pentaBDE 2,3',4,4',6-	<86	<0.008	<0.006	<0.6	<3.4	<1.9	<0.006	<1.2	<36	<1.2	<101	<35	<0.006	<1.1	<0.02	<6.1
BDE99	pentaBDE 2,2',4,4',5-	<86	<0.4	**5.5**	**0.6**	<3.4	<1.9	<0.3	<1.2	<36	<1.2	<101	<35	<0.3	**1007**	<0.8	<6.1
BDE85	pentaBDE 2,2',3,4,4'-	<86	**0.003**	<0.006	<0.6	<3.4	<1.9	<0.006	<1.2	<36	<1.2	<101	<35	<0.006	**52**	<0.02	<6.1
BDE126	pentaBDE 3,3',4,4',5'-	<16	<0.001	**0.01**	<0.1	<0.6	<0.4	<0.001	<0.2	<6.7	<0.2	<19	<6.5	<0.001	<0.2	<0.003	<1.1
BDE154+BB153	hexaBDE 2,2',4,4',5,6'-	<32	<0.05	**0.3**	<0.2	<1.3	<0.7	<0.04	<0.4	<13	<0.4	<37	<13	<0.04	**115**	<0.09	<2.2
BDE153	hexaBDE 2,2',4,4',5,5'-	<32	<0.07	**0.3**	<0.2	<1.3	<0.7	<0.05	<0.4	<13	<0.4	<37	<13	<0.05	**135**	<0.1	<2.2
BDE138	hexaBDE 2,2',3,4,4',5'-	<32	<0.009	<0.007	<0.2	<1.3	<0.7	<0.007	<0.4	<13	<0.4	<37	<13	<0.006	**17**	<0.02	<2.2
BDE156	hexaBDE 2,3,3',4,4',5 -	<32	<0.003	<0.002	<0.2	<1.3	<0.7	<0.002	<0.4	<13	<0.4	<37	<13	<0.002	<0.4	<0.005	<2.2
BDE184	heptaBDE 2,2',3,4,4',6,6'-	<32	<0.003	<0.002	<0.2	<1.3	<0.7	<0.002	<0.4	<13	<0.4	<37	<13	<0.002	**1.1**	<0.005	<2.2
BDE183	heptaBDE 2,2',3,4,4',5',6-	**686**	**0.002**	**0.01**	<0.2	<1.3	<0.7	<0.002	<0.4	<13	**0.9**	**59**	<13	<0.002	**5.3**	<0.006	**15**
BDE191	heptaBDE 2,3,3',4,4',5',6-	<32	<0.003	<0.002	<0.2	<1.3	<0.7	<0.002	<0.4	<13	<0.4	<37	<13	<0.002	<0.4	<0.005	<2.2
BDE197	octaBDE 2,2',3,3',4,4',6,6'-	**367**	<0.003	<0.002	<0.2	<1.3	<0.7	<0.002	<0.4	<13	<0.4	**85**	<13	<0.002	<0.4	<0.005	**7.2**
BDE196	octaBDE 2,2',3,3',4,4',5,6'-	**258**	<0.003	<0.002	<0.2	<1.3	<0.7	<0.002	<0.4	<13	**0.9**	**114**	<13	<0.002	<0.4	<0.005	**3.3**
BDE209	decaBDE 2,2',3,3',4,4',5,5',6,6'-	**94445**	**0.05**	**0.03**	<0.6	<3.2	<1.8	**0.1**	<1.1	**78**	**1300**	**104347**	<32	**0.2**	**16**	**0.030**	**1334**
TBBP-A	Tetrabromobisphenol	**3540**	**1.3**	<0.003	<0.003	<1.4	<0.8	<0.003	<0.5	**25**	**48**	<42	<15	**7.7**	<0.5	**10**	**146**
α- HBCD	Hexacyclododecane	<71	<0.007	<0.005	<0.006	**1017**	**481**	<0.005	<1.0	<0.005	<1.0	<83	<29	<0.005	<0.9	<0.1	<5.0
β-HBCD	Hexacyclododecane	<72	<0.007	<0.005	<0.006	**472**	**165**	<0.006	<1.1	<0.006	<1.1	<83	<29	<0.005	<0.9	<0.1	<5.1
γ-HBCD	Hexacyclododecane	<73	<0.007	<0.005	<0.006	**2694**	**2814**	<0.007	<1.2	<0.007	<1.2	<83	<29	<0.005	<0.9	<0.1	<5.2
UNKNOWN 1	X times higher than BDE209 (based on peak area)									**0.3 X**			**X**	**4 X**		**1500 X**	**2 X**
UNKNOWN 2													**X**	**5 X**		**400 X**	
UNKNOWN 3																**5000 X**	

This data indicates that Japanese cars may have included components manufactured elsewhere which still included PentaBDE even though not recorded as consumption in Japan.

Statistical analysis published by Harrad et al. (Harrad et al. 2008) of recent UK sampling showed that concentrations of PBDE 47, 49, 66, 99, 100, 154, and Σtri-hexa-BDE are significantly higher ($p<0.05$) in cars than in homes and offices which contained relatively low levels of POP-BDE contamination:

Table 22: Summary of concentrations (ng/g) of BFRs in dust samples from different indoor microenvironment categories in this and selected other studies (Harrad et al. 2008).



Location (reference)	Statistical parameter/ Congener #	28	47	99	100	153	154	183	209	Σtri-hexa-BDE[a]	ΣBDE[b]	DBDPE	TBE
Birmingham, UK, this study, Homes, $n=30$[c]	Average	0.70	15	36	5.6	14	4.4	71	260,000	77	260,000	270	120
	σ_n	0.34	13	38	4.8	25	4.4	150	580,000	68	580,000	770	430
	Median	<dl	10	20	3.4	5.0	2.8	4.2	8100	46	8500	24	5.3
	Minimum	<dl	1.2	2.8	<dl	<dl	<dl	<dl	<dl	7.1	12	<dl	<dl
	Maximum	2.1	58	180	17	110	16	550	2,200,000	250	2,200,000	3400	1900
Birmingham, UK, this study, Offices, $n=18$[d]	Average	1.8	67	120	16	16	10	11	30,000	250	31,000	170	7.2
	σ_n	2.7	94	160	24	23	13	6.9	67,000	310	67,000	220	9.4
	Median	<dl	23	65	3.2	8.7	5.1	8.3	6200	100	7400	99	<dl
	Minimum	<dl	2.6	4.2	<dl	<dl	<dl	<dl	620	16	790	<dl	<dl
	Maximum	11	380	490	79	99	38	24	280,000	1100	280,000	860	40
Birmingham, UK, this study, Cars, $n=20$[e]	Average	6.1	720	990	220	150	160	19	410,000	2300	340,000	400	7.7
	σ_n	13	2000	2400	560	360	440	22	770,000	5700	720,000	900	7.5
	Median	<dl	54	100	17	11	11	7.8	100,000	190	57,000	100	<dl
	Minimum	<dl	19	23	<dl	<dl	<dl	<dl	12,000	54	140	<dl	<dl
	Maximum	43	7500	8000	2300	1500	1900	67	2,600,000	22,000	2,600,000	2900	29
US, cars, $n=2$ (Gearhart and Posselt, 2006)	Average	<dl	600	600	85	100	65	–	9500	–	–	–	–
Sweden, homes, $n=5$ (Karlsson et al., 2007)	Average	2.2	51	79	24	4.9	3.9	4.8	470	–	–	47	4.8
Japan, offices, $n=14$ (Suzuki et al., 2006)	Average	7.1	110	170	30	34	16	81	2400	–	–	–	–
	Median	1.2	31	38	6.9	16	52	20	1100	–	–	–	–
	Minimum	0.49	4.3	3.1	0.7	3.3	0.96	5.0	150	–	–	–	–
	Maximum	67	580	810	130	100	68	280	170,000	–	–	–	–

This provides only aggregated data for the cars[33]. Most were UK models but it is not possible from the results to link levels in dust with a particular vehicle.

The US samples in the study by Gearhart had lower average contamination levels but the sample size was small (Grearhart & Posselt 2006). A more recent investigation examined 60 second-hand US cars and found significantly higher levels that those reported by Gearhart (Lagalante et al. 2009b):

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[33] The sampling was from 10 Fords, 4 Vauxhalls, 3 Fiats, 1 Hyundai, 1 Jaguar, and 1 Volvo. The average age of the vehicles studied was 5.5 ± 3.1 years ranging from 1 week to 12 years.

Table 23: Automobile specific variables and PBDE levels (ng/g) for the vehicles sampled (Lagalante et al. 2009b).

No.	Make	Model	Model year	Manufacture date	Odometer (km)	Country of manufacture	Vehicle top	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
1	Buick	Century	1998	Dec-97	215007	Canada	None	9.6	1900	1590	329	16600	702	5650	296000
2	Buick	Rendezvous	2002	Aug-01	113951	Mexico	None	116	729	1080	181	135	87.9	nd (<3.8)	12700
3	Chevrolet	Blazer	2002	Jun-02	99678	USA	None	321	815	1070	206	166	98.4	59.7	157000
4	Chevrolet	Colorado	2005	Nov-04	37197	USA	None	30.2	303	380	67.8	42.8	27.5	5.7	4380
5	Chevrolet	Equinox	2007	Nov-06	17665	Canada	None	129	672	926	156	483	65.2	1450	41900
6	Chevrolet	HHR	2006	Feb-06	26553	Mexico	Sunroof	383	1080	1910	348	267	195	nd (<3.8)	40000
7	Chevrolet	Malibu	2007	Jun-07	488	USA	None	119	5500	19500	3030	2970	2010	1270	109000
8	Chevrolet	Silverado	2005	Jun-05	58622	USA	None	4.4	457	569	96.6	107	21.4	63.6	203000
9	Chevrolet	Trailblazer	2004	Jun-04	71774	USA	Sunroof	372	1800	3570	585	527	365	94.1	36400
10	Chevrolet	Trailblazer	2004	Jul-03	89518	USA	None	91.4	504	1080	186	160	109	108	48300
11	Chevrolet	Trailblazer	2004	Mar-04	123171	USA	None	41.2	277	535	85.0	109	59.8	70.6	37700
12	Chevrolet	Trailblazer	2004	Nov-03	94096	USA	Sunroof	48.8	1090	1970	331	314	186	74.3	70100
13	Chevrolet	Trailblazer	2004	Nov-03	99784	USA	None	168	548	668	128	138	69.1	93.6	59400
14	Chevrolet	Trailblazer	2004	Jun-04	42532	USA	None	143	287	528	85.4	131	65.4	48.4	56700
15	Chevrolet	Trailblazer	2004	Feb-04	76843	USA	None	132	586	596	112	108	65.3	66.4	37100
16	Chevrolet	Trailblazer	2004	Aug-03	56083	USA	None	73.4	1700	2760	537	371	261	47.0	33800
17	Chevrolet	Trailblazer	2004	Oct-03	98135	USA	None	86.1	480	828	140	168	92.7	50.8	62600
18	Chevrolet	Trailblazer	2005	Aug-04	39131	USA	Sunroof	69.7	139	201	31.8	78.3	22.5	77.9	36900
19	Chevrolet	Trailblazer	2005	Dec-04	43717	USA	None	617	371	480	79.4	131	46.0	99.0	48700
20	Chevrolet	Trailblazer	2006	Mar-06	29464	USA	None	27.1	183	273	45.3	143	46.9	221	54300
21	Chevrolet	Uplander	2007	Aug-06	40626	USA	None	96.3	1120	1050	186	159	88.7	153	2480000
22	Chrysler	PT Cruiser	2005	Nov-04	152009	USA	None	91.8	1930	1710	343	165	118	35.7	5490
23	Dodge	Dakota	2004	Apr-04	46128	USA	None	180	13600	22900	3870	2130	2050	185	146000
24	Ford	Escape	2003	Mar-03	116887	USA	None	208	1180	1180	225	270	110	306	2710000
25	GMC	Envoy	2005	Apr-05	44787	USA	None	151	374	589	92.9	133	80.4	74.8	56100
26	Honda	Accord	2004	May-04	71475	USA	Sunroof	162	1310	2150	419	342	265	117	75300
27	Honda	Accord	2007	Jan-07	18674	USA	Sunroof	101	1190	1400	246	186	106	43.1	14500
28	Honda	Civic	2001	Feb-01	102437	Canada	None	200	1980	2650	470	295	221	18.0	11000
29	Honda	Civic	2006	Jan-06	51568	Canada	None	763	2660	2940	548	283	202	91.8	12000
30	Honda	Civic	2007	Oct-06	12502	Japan	None	nd (<3.2)	1680	2610	446	310	166	nd (<3.8)	48800
31	Honda	CR-V	2004	Nov-03	92044	UK	None	107	389	959	150	145	90.6	199	813000
32	Honda	CR-V	2004	Nov-03	54587	UK	Sunroof	46.6	518	623	110	95.9	47.4	520	3570000
33	Honda	CR-V	2005	Jan-05	66577	UK	Sunroof	86.6	1100	1610	301	158	140	41.2	61200
34	Honda	CR-V	2005	Feb-05	77076	UK	Sunroof	81.7	908	1090	206	120	91.6	18.1	50600
35	Honda	Element	2006	Feb-06	32048	USA	Sunroof	77.0	489	843	145	93.9	80.0	19.2	13000
36	Honda	Odyssey	2004	Aug-04	66017	USA	None	77.4	880	2250	352	455	277	125	62000
37	Honda	Odyssey	2004	Mar-04	41670	USA	None	125	239	335	57.5	85.4	35.5	140	47900
38	Honda	Odyssey	2004	Mar-04	46613	USA	None	113	379	642	113	120	66.9	24.4	83000
39	Honda	Odyssey	2006	Apr-06	39179	USA	None	67.8	336	567	114	85.9	69.8	25.7	13700
40	Honda	Pilot	2004	Nov-04	49205	Canada	None	325	802	747	135	144	69.7	31.6	83000
41	Honda	Pilot	2006	Sep-05	39766	Canada	None	237	915	1380	228	188	127	33.4	7250
42	Hyundai	Santa Fe	2006	Sep-05	30433	Korea	Sunroof	128	621	1030	179	158	100	247	41000
43	Hyundai	Sonata	2003	Aug-02	79349	Korea	None	44.3	365	598	109	86.2	64.5	71.1	124000
44	Jeep	Commander	2007	Oct-06	27358	USA	None	150	1020	1580	280	207	103	79.6	267000
45	Jeep	Liberty	2004	Oct-03	35097	USA	None	190	1440	1530	282	164	106	63.1	46900
46	Kia	Sorrento	2006	Jun-05	13993	Korea	None	101	726	1050	174	160	91.2	191	3130000
47	Mercedes-Benz	C-Class	2003	Sep-02	72366	Germany	Sunroof	126	1340	1470	289	146	118	72.6	18200
48	Mitsubishi	Eclipse	2002	Oct-01	66593	USA	Soft top	82.7	879	1280	233	199	139	15.2	14500
49	Mitsubishi	Eclipse	2003	Mar-03	74823	USA	Soft top	51.1	767	1460	257	261	146	635	429000
50	Nissan	Altima	2006	Aug-05	48881	USA	None	77.9	546	756	155	272	84.3	159	29900
51	Nissan	Altima	2006	Mar-06	11714	USA	None	95.9	1080	1370	257	152	100	29.2	35400
52	Nissan	Altima	2006	Aug-05	30656	USA	None	215	1360	1480	268	181	119	37.1	5120
53	Nissan	Pathfinder	2004	Jun-04	30211	Japan	Sunroof	216	2000	3270	551	620	377	240	5540
54	Nissan	Sentra	1999	Aug-99	146948	Mexico	None	359	1380	1700	326	162	143	202	6280
55	Nissan	Sentra	2000	Oct-03	198084	Mexico	Sunroof	216	828	1110	203	164	95.1	37.3	28100
56	Nissan	Sentra	2004	Sep-04	94701	Mexico	None	150	1030	1860	317	229	159	126	7050
57	Nissan	Sentra	2005	Jan-00	81448	Mexico	None	146	892	1150	216	149	120	18.4	5290
58	Toyota	4-Runner	2007	Feb-07	18090	Japan	None	135	374	859	144	135	108	99.3	113000
59	Toyota	Corolla	1990	Jan-90	255038	Canada	None	18.9	1380	1610	299	207	148	113	202000
60	Volkswagen	Jetta	2005	Jul-04	35515	Mexico	Sunroof	453	2530	3420	618	339	246	68.7	9050
							Low	nd (<3.2)	139	201	32	43	21	nd (<3.8)	4380
							5th percentile	18	275	378	67	86	35	5	5480
							Median	118	880	1130	211	163	105	73	48100
							Mean	154	1233	1989	345	552	194	238	272119
							95th percentile	387	2537	3428	587	695	393	667	2491500
							High	763	13600	22900	3870	16600	2050	5650	3570000

The data collected by Lagalante shows that even cars manufactured in the last few years in the US can have higher levels of POP-BDE than those sampled by Harrad in the UK. There are only three cars manufactured in Japan in the sample. However the results show that even recent Japanese cars can still contain quite high levels of PentaBDE in spite of the Japanese consumption pattern as a 2004 Nissan (no.53) and 2006 Honda (no.30) are in the top ten for PentaBDE levels. This is perhaps not surprising as car components are sourced globally and may not have been made in the country of manufacture of the car. Higher levels of PentaBDE could have been expected in older cars but as these results relate to dust they must be seen as indicative in any case.

It is concluded, therefore, that the import of 290 tonnes of PentaBDE to Europe in cars as suggested by Alcock (Alcock et al. 2003) is reasonable. This would leave the remaining 510 tonnes of PentaBDE assessed by the UK Environment Agency to be imported into Europe in other foam products.

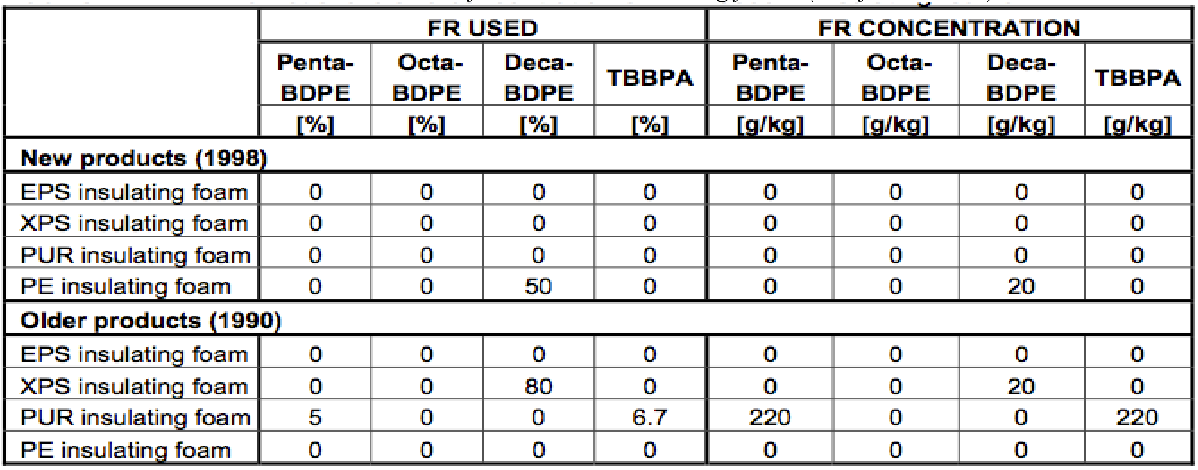
The balance of the evidence available, however, points to furniture being a larger user of PentaBDE in both Europe and the US rather than transport. An approximate distribution of 36% in cars, 60% in Furniture with a 4% residual for other articles is proposed as plausible on the basis of this assessment.

Rigid PU Foams:

There is even less clarity about the uses of PentaBDE in rigid foam insulation.

In 1999 the Danish EPA (Lassen et al. 1999) advised that brominated polyols were used as the almost exclusive flame retardant for rigid PUR foam for insulation and that no PBDE were used for this purpose[34]. Morf took a different perspective in relation to the substance flow analyses for Switzerland (Morf et al. 2003, Morf et al. 2007) and estimates some use of PentaBDE in rigid foam insulation in Switzerland in 1990 – by 1998 there was assumed to be no use in rigid foam:

Table 24: Market share and concentration of BFR used in insulating foams (Morf et al. 2002).



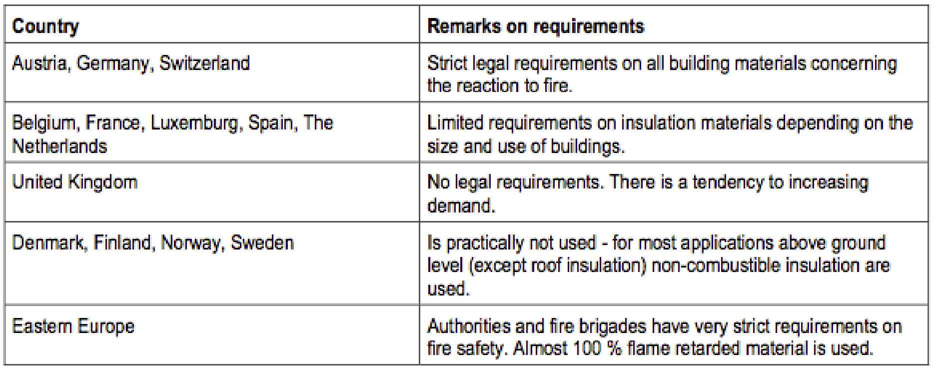
	FR USED				FR CONCENTRATION			
	Penta-BDPE [%]	Octa-BDPE [%]	Deca-BDPE [%]	TBBPA [%]	Penta-BDPE [g/kg]	Octa-BDPE [g/kg]	Deca-BDPE [g/kg]	TBBPA [g/kg]
New products (1998)								
EPS insulating foam	0	0	0	0	0	0	0	0
XPS insulating foam	0	0	0	0	0	0	0	0
PUR insulating foam	0	0	0	0	0	0	0	0
PE insulating foam	0	0	50	0	0	0	20	0
Older products (1990)								
EPS insulating foam	0	0	0	0	0	0	0	0
XPS insulating foam	0	0	80	0	0	0	20	0
PUR insulating foam	5	0	0	6.7	220	0	0	220
PE insulating foam	0	0	0	0	0	0	0	0

The FR concentration given refers only to commercial FR products, not to the substances under study. A distinction was made between previous (older products) and present-day (new products) applications. The % values under 'FR USED' mean that x % of the products consumed annually in Switzerland were treated with the given FR. The g/kg values indicate the concentration of FR in the plastic.

The data underpinning these estimates is not strong and it appears that the use may have been limited to Switzerland and possibly Germany (Morf et al. 2002).

Fire Regulations for insulation materials differ substantially across Europe and this could account for some differences in usage and inventory levels in different countries (European Commission 2008b):

Table 25: Requirements for using flame retarded insulation materials (D. Lausberg, BASF cited by (European Commission 2008b)).



Country	**Remarks on requirements**
Austria, Germany, Switzerland	Strict legal requirements on all building materials concerning the reaction to fire.
Belgium, France, Luxemburg, Spain, The Netherlands	Limited requirements on insulation materials depending on the size and use of buildings.
United Kingdom	No legal requirements. There is a tendency to increasing demand.
Denmark, Finland, Norway, Sweden	Is practically not used - for most applications above ground level (except roof insulation) non-combustible insulation are used.
Eastern Europe	Authorities and fire brigades have very strict requirements on fire safety. Almost 100 % flame retarded material is used.

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[34] Lassen indicated, however, that if flame retardancy requirements were particularly strict, other additives and reactives could be combined with the brominated polyol (Lassen et al. 1999).

The main application for rigid PU foam is in the construction industry for insulating boards and panels. It is also used as an in situ material for sprayed-in-place insulation and as a one component bonding foam. Boards are used in pitched and flat roofs, in suspended ceilings, in floor slabs with or without under floor heating, in walls for external, internal or cavity insulation (with rendering if required) and in a wide range of buildings from multi-storey car parks to farms (Eaves 2004).

The insulation market is dominated by what Eaves describes as "*less technically attractive*" alternatives - mineral or glass fibre wool with a 63% share in Europe followed by PS foam with 17.5%. Mineral wool has the compensating advantages of being cheaper and more easily meeting fire resistance requirements (Eaves 2004). Rigid PUR foam has a 14% market share (Eaves 2001) with the total worldwide use of PUR in construction applications being 1,050,000 tonnes in 1996 of which approximately 685,000 tonnes was used in Europe (Eaves 2001).

Whilst the building insulation foam requirements are more likely to have affected usage of HBCD than PentaBDE they may, at least in part, explain the higher levels in the Swiss building inventory.

Alcock says that evidence from the US foam industry highlights that the vast majority (87%) of contemporary applications of flexible foam are associated with interior rather than exterior uses (Alcock et al. 2003) but there is no indication of any usage or treatment of rigid foams.

This level of actual usage of PentaBDE in building insulation is important, as will be seen below, given the much longer lifetime of rigid foam insulation used in buildings compared most applications of flexible foams which have a much shorter lifespan. The difference is significant in terms of the ultimate stock of BDE-POPs that need treatment and also, clearly, in relation to the treatment options as there can be differences for rigid and flexible PUR. It appears most likely, however, that the use of PentaBDE for rigid foam was a short-term usage in the early 1990s which was phased out before the peak usage period in Europe. Consequently use will be significantly less than 5% overall and could easily be as little as 1% or less of the total European usage of PentaBDE.

Uses of OctaBDE:

Research commissioned for and published by Great Lakes Chemical Corporation (now Chemtura) suggests that in US practically all commercial OctaBDE was used by the plastics industry to additively flame retard acrylonitrile-butadiene-styrene (ABS) terpolymers (ENVIRON 2003a).

In the European Union, approximately 95% of the total commercial OctaBDE product sold to the electronics and plastics industries was used in ABS applications. ABS was typically used for the casings of computers, monitors and business machine cabinets (Lassen et al. 1999)(European Chemicals Bureau 2003a)(Integrated Laboratory Systems 2001).

OctaBDE product was used in ABS with loadings of 12–18% flame retardant by weight and always in conjunction with antimony trioxide (Integrated Laboratory Systems 2001)(ENVIRON 2003a). Other sources indicate that the loading was greater than this and both OECD and Dufton quote 20% OctaBDE with 6% antimony trioxide (Dufton 2003)(OECD 1995). These loadings are consistent with levels reported from actual samples:

The use of OctaBDE in ABS reduced throughout the 1990s as it was replaced by other brominated flame retardants (primarily tetrabromobisphenol A (TBBP-A)). This was mainly due to the relatively poor ultraviolet light instability of OctaBDE (Integrated Laboratory Systems 2001).

By 2003 OctaBDE was a relatively small component of electrical equipment even in waste streams in Europe (Morf et al. 2005):

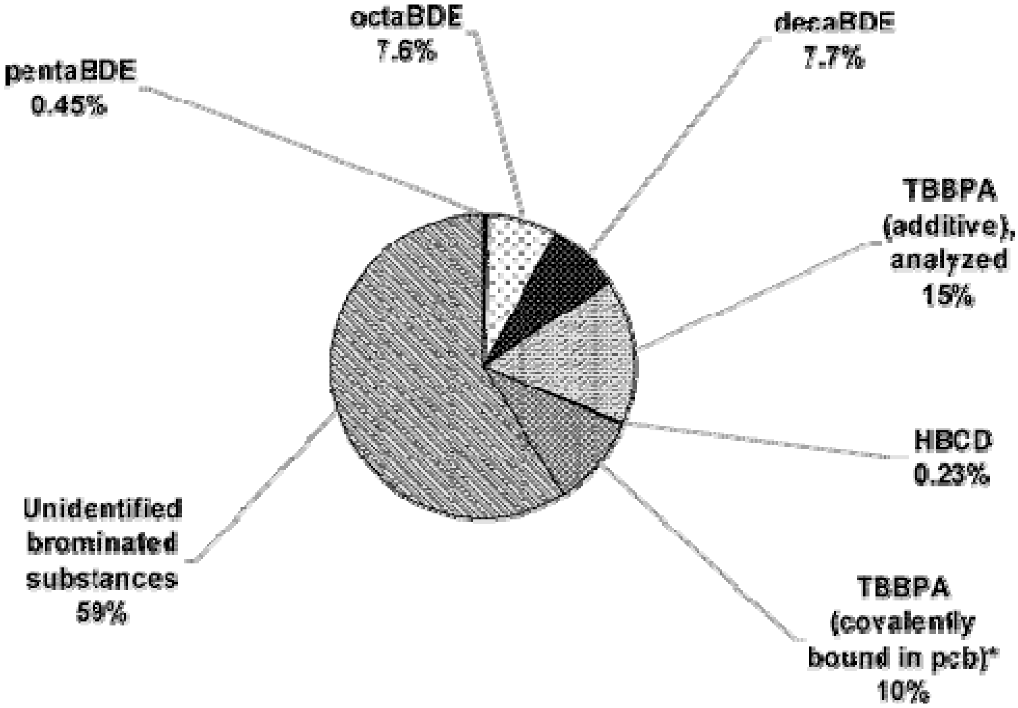

Figure 25: Bromine share of the investigated BFRs related to the total bromine input flow from a WEEE recycling plant in 2003(Morf et al. 2005).
Figures for penta- and octaBDE refer to the bromine content of the technical mixtures (Bromkal 70-5 DE and Great Lakes Chemicals DE-79, respectively) for decaBDE, TBBPA, and HBCD to the bromine content of the individual substances. For TBBPA, the estimated amount of bromine covalently bound in printed circuit boards (pcb's) estimated according to literature data is given (Morf et al. 2005).

Minor Uses of OctaBDE:

Minor uses for OctaBDE, accounting for the remaining 5% or less of usage, included high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers (with a 12-15% loading by weight) (European Chemicals Bureau 2003a).

Other possible applications of OctaBDE include use as additive flame retardant in polycarbonate, phenol-formaldehyde resins, unsaturated polyesters, nylon, thermoplastic elastomers, polyolefins, adhesives, and coatings (ATSDR 2004)(OECD 1995)(WHO & IPCS 1994).

These uses, if developed at all, are all minor and dispersed with little or no solid information about their scale or applications. It has therefore not been possible to pursue them further.

Appendix 2 (f): Human and Environmental Exposure to PBDE

This section gives some background on the environmental distribtion of PBDE, the levels that have been measured in humans and the temporal trends. Although not specifically listed in the terms of reference it is considered essential to assist the understanding of where higher background exposures are likely, to establish how effective previous regulation has been, as a basis for the assessment of risks associated with recycling oprations and to provide a datum when considering the discussions in Appenices 3 and 4 of the environmental and human exposures associated with particular disposal and recycling operations.

Appendix 2 (f)(i): Environmental Levels of PBDE

Up to 209 BDE congeners are theoretically possible, although only about 40 are routinely detected in the environment (Ross et al. 2009). The first report of PBDE being detected in the environment appears to be a paper by Vincent DeCarlo published in 1979 (DeCarlo 1979). The samples were collected near plants manufacturing and/or using polybrominated compounds in the USA.

Two years later the first environmental sample from the wider environment remote from a chemical plant was reported by Andersson who found Tri- to hexaBDE in fish from the Swedish river Viskan in 1981 (Andersson & Blomkvist 1981). These compounds had not been present in fish samples collected in the same area in 1977.

Over the past 30 years they have become global contaminants as can be seen from the spatial distribution of PBDE in the Global Atmospheric Passive Sampling (‘GAPS’) campaign[35] (Pozo et al. 2006):

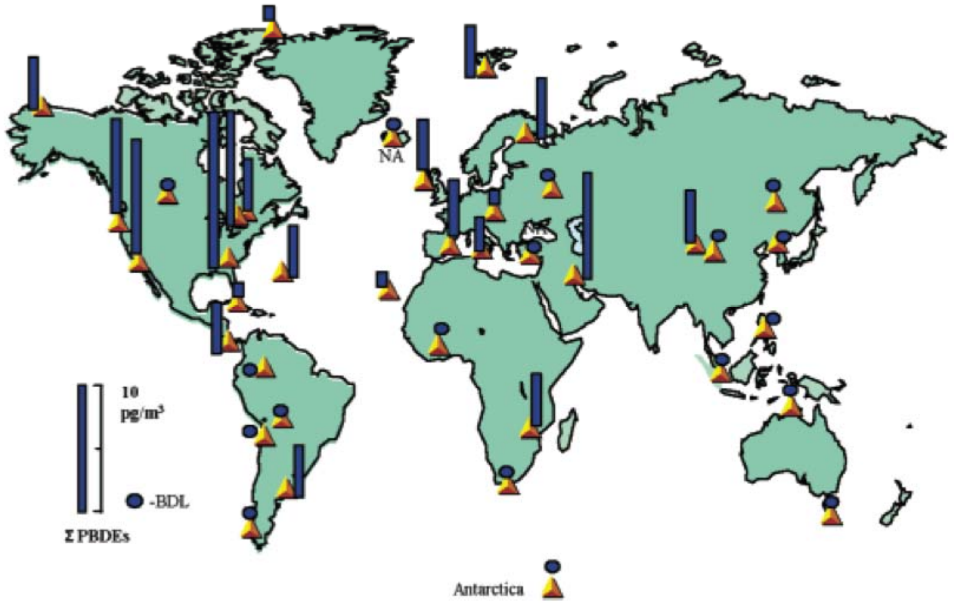

Figure 26: Air concentrations (pg/m^3) of PBDE between December 2004 and March 2005 at GAPS sites (Pozo et al. 2006).

The levels found in the GAPS campaign largely appear to reflect patterns of usage with North American samples generally being more heavily contaminated (Georgia was highest at 24 pg/m^3, followed by California at 19 pg/m^3) and Europe. It is notable, however, that the third highest concentration (17 pg/m^3) was measured at a site in Kuwait. Gevao (Gevao et al. 2010) notes that there are no known sources of PBDE in Kuwait apart from their presence in consumer products. He suggests, however, that PBDE were manufactured in Israel by the Dead Sea Bromine Company and “*releases that occur during the production of these chemicals may influence levels in the region*” (Gevao et al. 2010).

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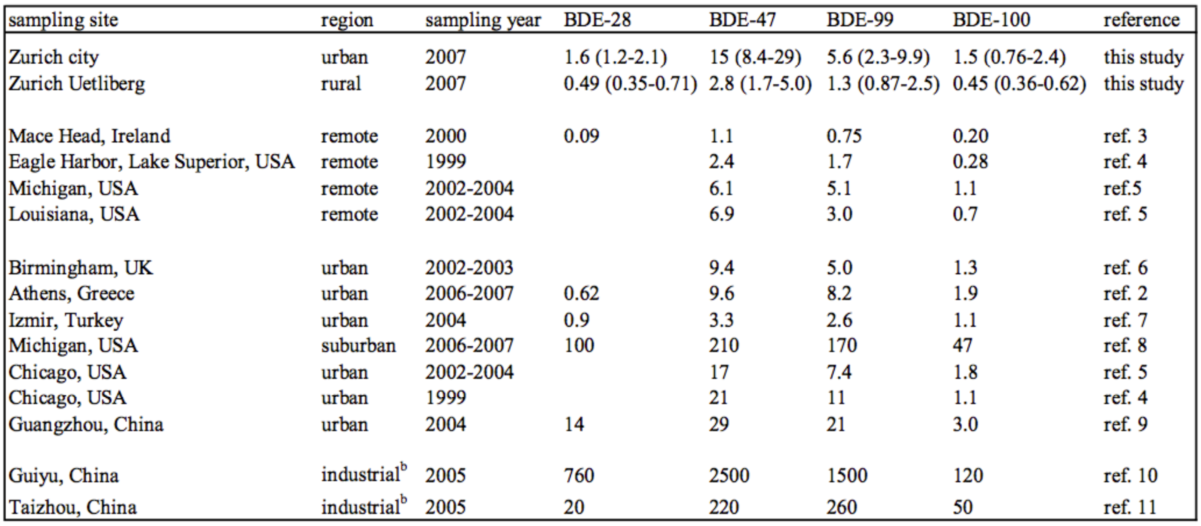
[35] GAPS measured

Relatively high concentrations were also measured in the southern part of Africa, South America and China. Gevao proposes that these levels " *may reflect releases from e-waste recycling activities that are carried out in developing countries*" (Gevao et al. 2010).

The GAPS levels are generally consistent with other airborne concentrations reported in the literature – although it should be noted that meteorological conditions and sampling times can make a significant difference (Moeckel et al. 2010). The results summarised by Moeckel show that some sites, particularly those which have been directly impacted by e-waste recycling such as Guiyu – where levels of 2,500 pg/m^3 far exceed the global medians (Moeckel et al. 2010) – even when the components are broken down into individual POP-BDE rather than taken as the aggregated totals presented in GAPS:

Table 26 Airborne concentrations [pg m^{-3}] of selected PBDE (Moeckel et al. 2010).



sampling site	region	sampling year	BDE-28	BDE-47	BDE-99	BDE-100	reference
Zurich city	urban	2007	1.6 (1.2-2.1)	15 (8.4-29)	5.6 (2.3-9.9)	1.5 (0.76-2.4)	this study
Zurich Uetliberg	rural	2007	0.49 (0.35-0.71)	2.8 (1.7-5.0)	1.3 (0.87-2.5)	0.45 (0.36-0.62)	this study
Mace Head, Ireland	remote	2000	0.09	1.1	0.75	0.20	ref. 3
Eagle Harbor, Lake Superior, USA	remote	1999		2.4	1.7	0.28	ref. 4
Michigan, USA	remote	2002-2004		6.1	5.1	1.1	ref.5
Louisiana, USA	remote	2002-2004		6.9	3.0	0.7	ref. 5
Birmingham, UK	urban	2002-2003		9.4	5.0	1.3	ref. 6
Athens, Greece	urban	2006-2007	0.62	9.6	8.2	1.9	ref. 2
Izmir, Turkey	urban	2004	0.9	3.3	2.6	1.1	ref. 7
Michigan, USA	suburban	2006-2007	100	210	170	47	ref. 8
Chicago, USA	urban	2002-2004		17	7.4	1.8	ref. 5
Chicago, USA	urban	1999		21	11	1.1	ref. 4
Guangzhou, China	urban	2004	14	29	21	3.0	ref. 9
Guiyu, China	industrial^b	2005	760	2500	1500	120	ref. 10
Taizhou, China	industrial^b	2005	20	220	260	50	ref. 11

a averages over the whole sampling period, ranges are given in brackets
b electronic waste dismantling site
References: (3) (Lee et al. 2003); (4) (Strandberg et al. 2001); (5) (Hoh & Hites 2005)(Hoh and Hites 2005); (6) (Harrad et al. 2004); (7) (Cetin & Odabasi 2008) (8) (Batterman et al. 2009); (9) (Chen et al. 2006); (10) (Chen et al. 2009a); (11) (Li et al. 2008b).

In general these data show higher levels in the USA, as expected from the usage of POP-BDE but highlight the extremely high levels to which some workers and their families are likely to be exposed in primitive e-waste rcycling conditions.

Human and environmental levels are now fairly well characterised with levels in North America being ten to one hundred times higher than in the EU and other countries. Only heavily exposed e-waste workers and associated populations in developing/transition countries have body burdens as high as those in North America.

Trend data indicates that levels in the environment and in human milk have been falling in the EU since about 2000. There is less trend data in the US but the indications are that levels are stable or possibly still rising in the US.

There is still considerable uncertainty about exposure routes. The literature indicates an enormous range of different balances of intakes between food and dust/indoor exposure – ranging from estimates that food is accounting for up to 97% of the intake (Fromme et al. 2009) to dust being responsible for up to 90% of total exposure (Lorber 2008). The apparently conflicting reports are not irreconcilable, however. Whilst food contamination levels appear to be broadly similar, certainly between the EU and the USA the dust concentrations vary by an order of magnitude – or more when outliers are considered, as discussed below. The weight of evidence in the literature points to dust/indoor exposure as being an increasingly important contribution to total BDE intakes as the concentration of PBDE in the dust increases.

There are still outstanding uncertainties, however as even dust exposure seems unable to explain the very high exposure of the outliers with extremely high PBDE exposure (USEPA 2010).

Appendix 2 (f)(ii): Temporal Trends of PBDE

The studies of temporal trends in the European Environment are reassuring and support the earlier conclusions that the POP-BDE issue has largely been addressed in Europe (with the possible exception of legacy stocks in landfill sites and possible longer life applications in buildings).

A trend study on guillemot eggs from the Baltic Sea, from Sellstrom, for example, shows a rapid initial increase from c1970 to about 1990 followed by a rapid fall to 2000. Levels in pike trend are somewhat different as they peak in the the mid-1980s and the PBDE concentrations decrease much more slowly (Sellstrom et al. 2003):

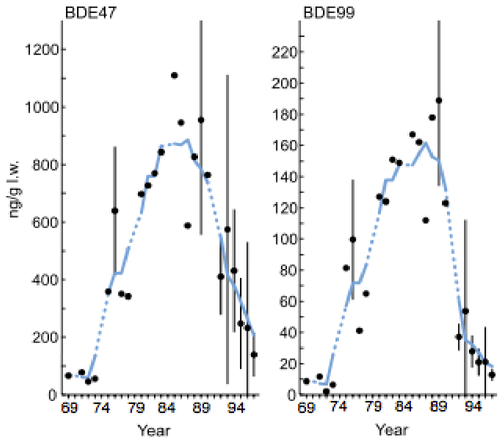


Figure 27: Temporal trends of BDE-47 and BDE-99 in guillemot egg from Stora Karlso1(Sellstrom et al. 2003). The line represents a five-point running mean smoother (p < 0.001), and the dots represent the arithmetic means with 95% confidence intervals indicated

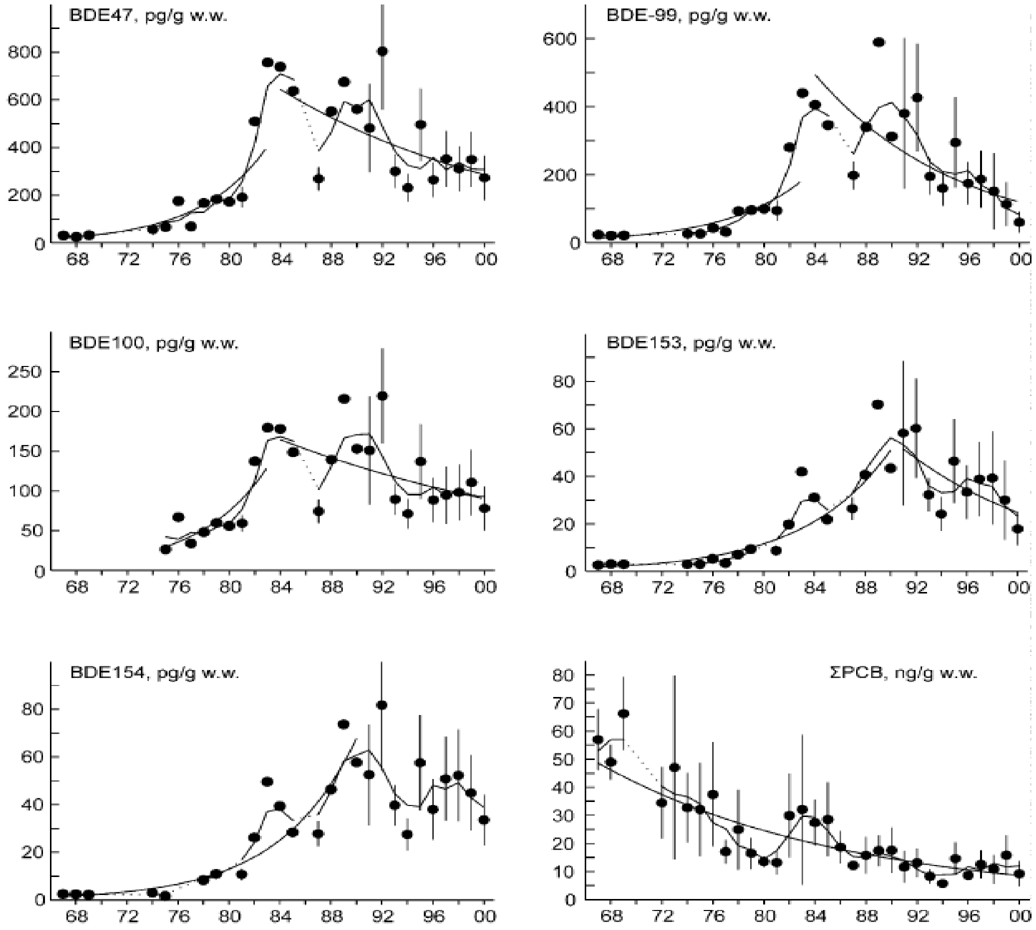


Figure 28: Temporal trends of tetra- to hexaBDE and SPCB (on wet weight basis) in pike from Lake Bolmen (Sellstrom et al. 2003).
The line represents a three-point running mean smoother (P<0.001), the dots the arithmetic means with the 95% confidence interval indicated. The curves represent the log-linear regression for selected time periods (P<0.05).

In Swedish mother's milk the PBDE concentrations increased alamingly in the 1990s. The report submitted by New Zealand (Geo & Hydro – K8 Ltd 2010) includes a figure from a 1999 page by Meironyté (Meironyté et al. 1999) captioned "*Often called "the graph that launched a thousand papers'*"":

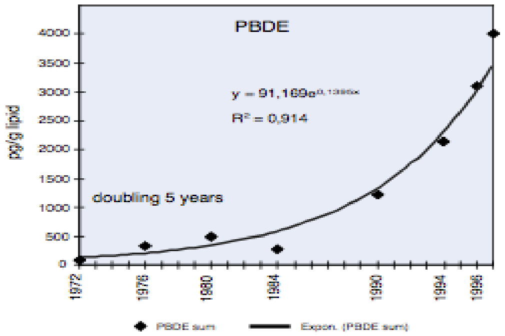


Figure 29:Graph from (Meironyté et al. 1999) cited by (Geo & Hydro – K8 Ltd 2010)

Fortunately, however, the growth did not continue - as Lind et al. demonstrated in 2003 (Lind et al. 2003):

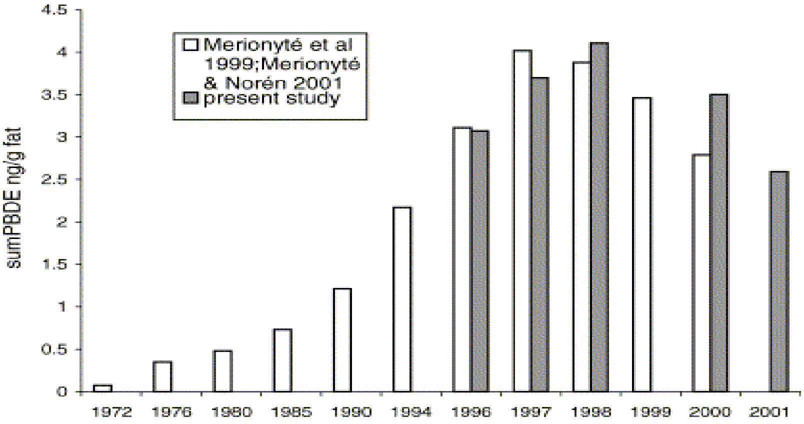


Figure 30: A comparison between data on PBDE levels in pooled breast milk from Meironyté, Norén, and co-workers (Meironyté et al. 1999) and mean values of individuals from the Lind study (1996–2001)(Lind et al. 2003) The mean value from 1999 was omitted from the graph because of the small number of observations (n=4; mean 3.05 ng ΣPBDE/g fat). During the comparable period (1996–2001) the two data sets are concordant.

Whilst the European trend data for breast milk might still look alarming in isolation it is important to put it into perspective with US exposures – the steep Swedish graph is the almost flat line on the combined plot:

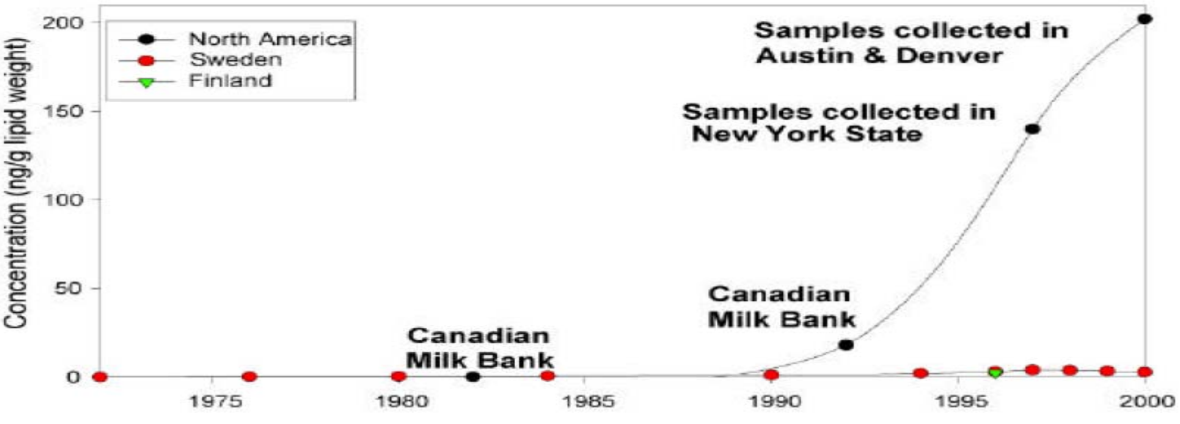


Figure 31: Comparison between the concentrations of BDE reported in human milk from North America and Europe (ENVIRON 2003a).

Recently several reports have indicated increasing concentration of BDE-153, at concentrations similar or even higher than BDE-47 (Thomsen et al. 2005)(Fängström et al. 2005c)(Fängström et al. 2005a)(Schecter et al. 2003).

The concentrations of the lower-brominated PBDE congeners, i.e. BDE-47, BDE-99 and BDE-100, have been decreasing since the middle of 1990's. The concentrations of BDE-153, however, have been increasing. This is in consistent with indications from previous studies performed in human milk from Sweden were the influence of BDE-153 have increase and BDE-47 have decreased. The ratio of BDE-153/BDE-47 (ng/g lipids) in 1980 to 2004 has changed from 30 % to 99 %:

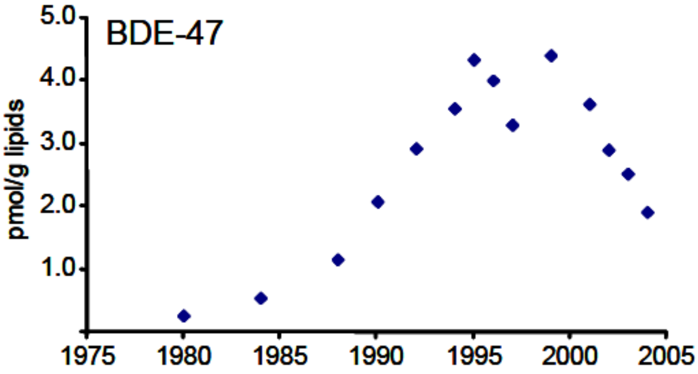


Figure 32: BDE-47 concentrations in pmol/g lipids in pooled milk samples from Sweden 1980 to 2004 (Fängström et al. 2005b).

Contrasting with BDE 153 and HBCDD (albeit at lower concentrations):

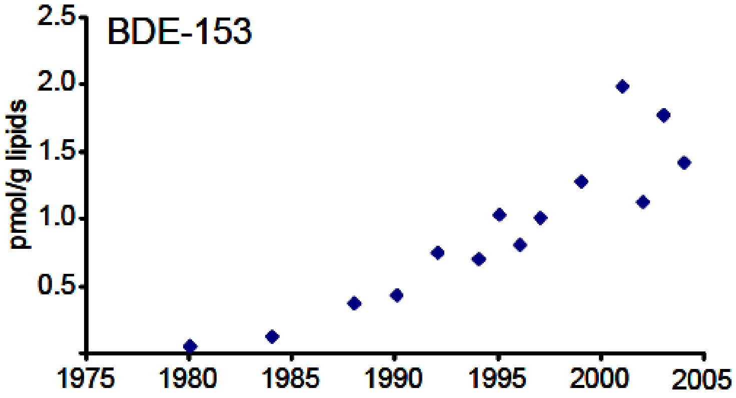


Figure 33: BDE-153 concentrations in pmol/g lipids in pooled milk samples from Sweden 1980 to 2004 (Fängström et al. 2005b)

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The increase in BDE-153 levels is disturbing as it is not a major component of any commercial mixture and yet is sometimes now found as the largest contaminant in humans. The linkage with PBDD/DF as a pre-dioxin is discussed later. It is too early to dismiss the hypothesis of BDE-153 being formed abiotically or via metabolism from BDE-209 (Fängström et al. 2005b).

In Norway, PBDE concentrations in human milk increased from 1986 to 2001 (*11*), within a similar concentration range as reported in Sweden and in Japan (*8-10,12*). These temporal trend studies all indicate decreasing PBDE concentrations, all driven by decreasing BDE-47 concentrations.

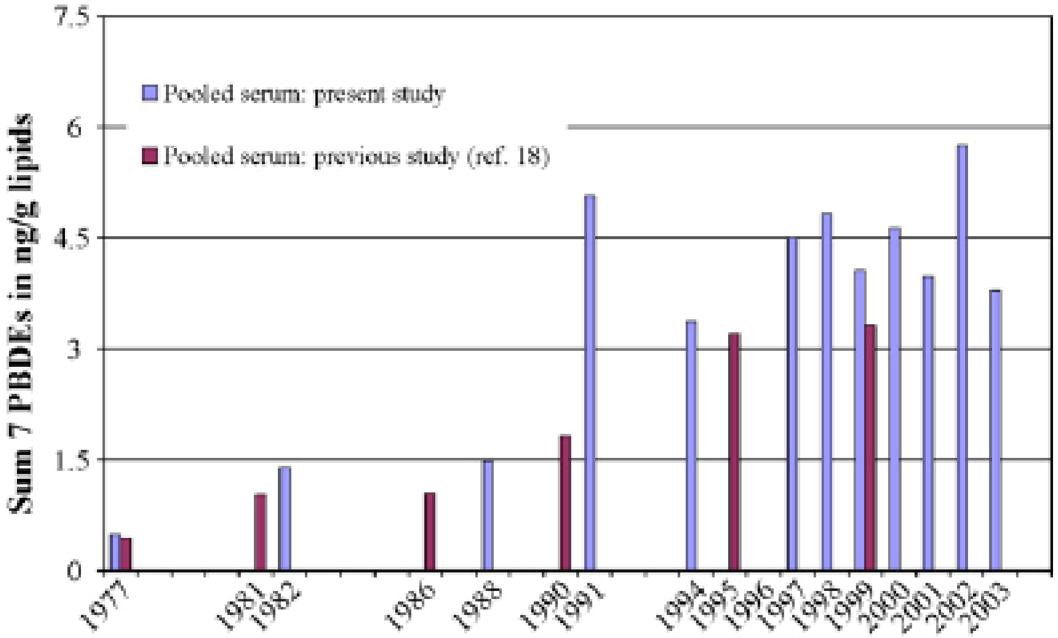

Figure 34: The concentration of the sum of seven PBDE (BDE 28, 47, 99, 100, 153, 154 and 183) in ng/g lipids in pooled serum samples from 40 to 50 year old Norwegian men sampled from 1977 to 2003 (Thomsen et al. 2007)

Appendix 2 (f)(iii): Human Exposure and Levels of PBDE

Hale notes that "*in many locales PBDE burdens ..... now surpass those of PCBs*"(Hale et al. 2006). This was clearly demonstrated by Johnson-Restrepo in research comparing levels of PBDE and PCB in human adipose tissue samples collected in New York City (Johnson-Restrepo et al. 2005):

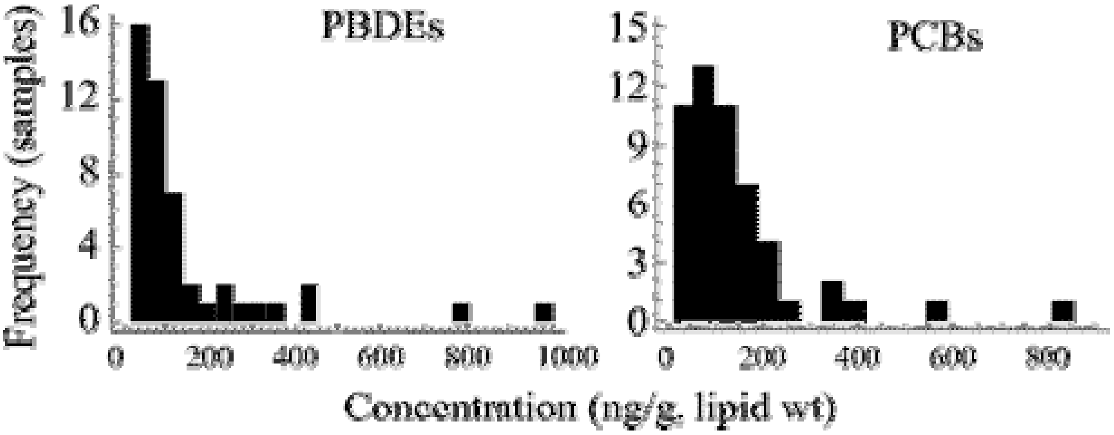

Figure 35: Frequency distributions of concentrations of PBDE and PCBs in human adipose tissue samples from New York City (two outliers were excluded for PBDE) (Johnson-Restrepo et al. 2005)

Johnson-Restrepo wrote (Johnson-Restrepo et al. 2005):

The results of this study suggest that the concentrations of PBDE in human adipose tissues from New York City are 10- to 100-fold greater than levels reported for European populations. A total PBDE concentration of 9630 ng/g, lipid wt, found in a sample of adipose tissue was the highest ever reported. PBDE congener profiles in human tissues varied, suggesting that individual exposures are associated with occupational and environmental settings. Average concentrations of PBDE were similar to those of PCBs in human adipose tissues, and substantially higher with the inclusion of PBDE outliers in the analysis. This was despite the fact that several congeners associated with octa- or deca-BDE mixtures were not quantified in this study"(Johnson-Restrepo et al. 2005).

Only two studies appear to have undertaken a comprehensive exposure evaluation including all the major pathways and different age groups – these are Johnson-Restrepo (Johnson-Restrepo & Kannan 2009) and the more recent USEPA Exposure Assessment (USEPA 2010).

Harrad and Diamond (Harrad & Diamond 2006) postulate that there may be two peaks to exposure – the initial direct exposure from products in households and work places, followed by a secondary peak as the brominated compounds eventually build up in the food chain:

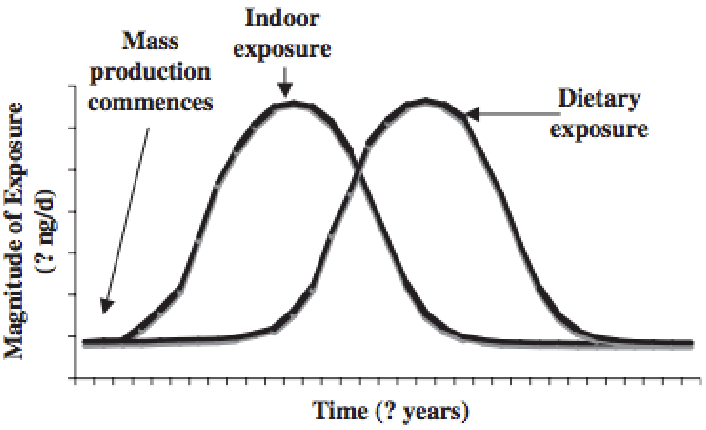

Figure 36: Illustrative Hypothetical time course in the relative magnitude of human exposure to PCBs and PBDE due to (a) indoor exposure, and (b) dietary exposure (Harrad & Diamond 2006).

Note that the exact and relative magnitude of exposures and time frame of trends are illustrative.

Harrad warned "*Our fear is that the current elevated indoor burden of PBDE represents a ''time bomb''. Specifically, this indoor reservoir is slowly ''bleeding'' these chemicals into the outdoor environment, whence, due to regional and long range atmospheric transport and their persistence, they will be incorporated into and magnified by terrestrial and aquatic food chains"*.

"*Currently, we can reduce our exposure to PBDE by minimizing their accumulation in the indoor environment; however, it will be much more difficult to reduce exposure once they are in the food supply. We urge concerted action to not only ban current manufacture and use of PBDE, but to find ways of reducing the existing indoor reservoir of these compounds and managing the end-of-life of PBDE-containing products*" (Harrad & Diamond 2006).

Developing Countries

In what is believed to be the first study reporting on PBDE in human serum from Africa Linderholm et al (Linderholm et al.) detected PBDE in all the samples they analysed in Guinea-Bissa. The PBDE were found only at low levels with the exception of BDE-209 which they found at surprisingly high concentration (up to 23 ng/g fat).

The BDE-153 levels over the period 2005– 2007 are similar to the levels observed in Sweden in the mid 1990's (Meironyté et al., 1999).

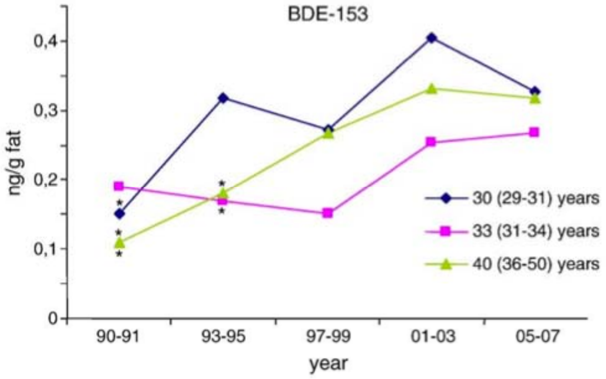

Figure 37: Concentration (ng/g fat) of BDE-153 in five pooled serum samples from Guinea- Bissau sampled at five occasions between 1990 and 2007(Linderholm et al.).

The source of exposure generating the elevated BDE-209 levels was unknown but given the very short half-life of BDE-209 in humans clearly represent ongoing exposure. Tens of thousands of tonnes of electrical and electronic waste are exported to Africa (Brigden et al. 2008, Greenpeace 2008)(Widmer et al. 2005, Cobbing 2006, European Environment Agency 2009) but there is no evidence of export of e-waste to Guinea-Bissau. Levels in Guinea-Bissau are increasing and the population doubling time for BDE-153 was calculated as c.10 years. This can be compared to observations in Sweden, with a doubling of BDE-153 about every 5 years between 1972 and 1997 (Meironyté et al. 1999).

Much higher levels of PBDE in a developing country have also been observed in Central America (Athanasiadou et al. 2008). The occupational exposure to PBDE in children working at a waste disposal site, and a substantial background level of exposure to PBDE in the urban population, are clearly shown. The PBDE concentrations in the serum of children working and living at the waste disposal site are among the highest ever reported. Athanasiadou also found that hydroxylated PBDE metabolites are retained in human serum, in the same way as OH-PCBs. They compared the OH-PBDE profiles with the profile obtained in an experimental study of rats given equimolar doses of the major PBDE (Malmberg et al. 2005). At least six of the OH-PBDE in the previous rat study were also formed and retained in the serum of the child workers.

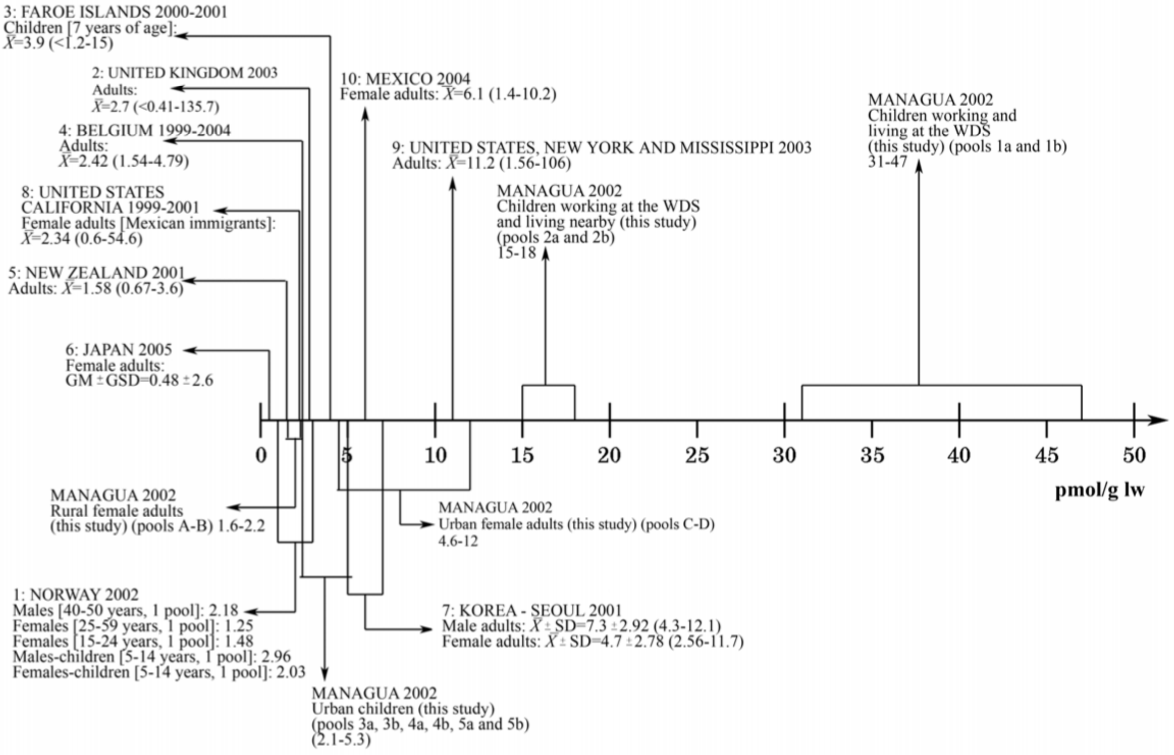

Figure 38: Serum levels of BDE-153 (pmol/g l.w.) in different regions (Athanasiadou et al. 2008) .
Data are from: 1: Thomsen et al. 2007; 2: Thomas et al. 2006; 3: Fängström et al. 2005; 4: Covaci and Voorspoels 2005; 5: Harrad and Porter 2007; 6: Inoue et al. 2006; 7: Kim et al. 2005; 8: Bradman et al. 2007; 9: Schecter et al. 2005; 10: Lopez et al. 2004. For comparison, reported concentrations were transformed into serum concentrations in pmol/g l.w. when needed; $\tilde{X}$ = median; GM, geometric mean; GSD, standard deviation of GM; WDS, waste disposal site.

Appendix 2 (g): Unintentionally formed Brominated Dioxins/Furans (PBDD/DF) and Brominated-Chlorinated Dioxins/Furans (PXDD/DF)

This Appendix provides an introduction to the brominated (PBDD/DF) and mixed chloro-bromo (PXDD/DF) dioxins. Brominated flame retardants, especially PBDE but also, to a lesser extent, PBBs, are a major source of toxic tri[36] - to octa-brominated dioxin and furan contamination (World Health Organisation 1998)(Zennegg et al. 2009)(Suzuki et al. 2010)(Weber & Kuch 2003)(WHO IPCS 1994)(Ota et al. 2010).

The section includes part of the details required by paragraph 3 (b) of the Terms of Reference. It is sensible, however, to provide an introductory assessment of PBDD.DF and PXDD/DF before considering the operational issues in Appendix 3. Further to this introduction specific details of PBDD/DF and PXDD/DF production relating to those particular technologies are included in Appendix 3.

PBDD/DF and PXDD/DF are important both as contaminants of the commercial mixtures and because of their production in use and, more importantly, in the waste management, including recycling, of PBDE. More detailed assessments of the research relating to emissions from particular processes and treatments are included in the Appendices which follow.

Relevance of PBDD/PBDF to the Recycling of POP-BDE via Environmental, Food, House dust and Human background exposure

The potential for formation of brominated and mixed halogenated dioxins and furans at various stages during the production, use, recycling and disposal of articles containing PBDE has been raised as a potential concern. To address this it has first been necessary to screen the relevance of PBDD/DF to this review by considering whether these compounds are relevant to the POP-BDE and particularly in relation to potential recycling operations.

Compelling evidence has accumulated over the past twenty years or so that brominated flame-retardants, especially PBDE (and to a lesser extent PBBs) are a major source of toxic tri[37] - to octa-brominated dioxin and furan contamination. There is an extensive literature on this and examples are included in the footnote[38]. The peer-reviewed and grey literature clearly shows that consideration of the generation, emissions and impacts of

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[36] For PCDD/DF the most relevant toxic compounds for TEFs are the tetra to octa chlorinated but bio-TEFs have been determined for some tribrominated PBDD/DF (Behnisch et al. 2003). Due to the relatively high levels detected in food (Rose & Fernandes 2010) the tribrominated DF might be of toxicological/epidemiological relevance.

[37] See previous footnote.

[38] (Thoma et al. 1987b, Dumler et al. 1989a, Dumler et al. 1989b, Hutzinger et al. 1989, Donnelly et al. 1990, Dumler et al. 1990, McAllister et al. 1990, Thies et al. 1990, Luijk & Govers 1992, Lorenz & Bahadir 1993, Zelinski et al. 1993, Lenoir et al. 1994, WHO & IPCS 1994, World Health Organisation International Programme on Chemical Safety (WHO IPCS) 1994, Ott & Zober 1996, World Health Organisation 1998, Rieß et al. 2000, Hamm et al. 2001, Sakai et al. 2001, BIPRO 2002, Nakao et al. 2002, Scientific Committee on Toxicity 2002, Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) 2002, Soderstrom & Marklund 2002, Behnisch et al. 2003, Birnbaum et al. 2003, Choi et al. 2003, Ebert & Bahadir 2003, Weber & Kuch 2003, Ashizuka 2004, D'Silva et al. 2004, Drohmann et al. 2004, Hayakawa et al. 2004, Schlummer et al. 2004, Ashizuka et al. 2005, Committee on Toxicity 2005, Kotz et al. 2005, Malmvärn et al. 2005, Rupp & Metzger 2005, Barontini & Cozzani 2006, Brigden & Santillo 2006, Fernandes et al. 2006, Food Standards Agency 2006b, Food Standards Agency 2006a, Hanari et al. 2006a, Löthgren et al. 2006, Olsman et al. 2006, Sakai et al. 2006, Schlummer et al. 2006, Suzuki et al. 2006, Takahashi et al. 2006, UK Committee On Toxicity of Chemicals in Food & Consumer Products and the Environment 2006, Guan et al. 2007, Gullett et al. 2007, Lai et al. 2007, Leung et al. 2007, Nose et al. 2007, Schlummer et al. 2007, Suzuki et al. 2007, Colles et al. 2008, Concannon 2008, Hirai et al. 2008, Malmvärn et al. 2008, Mandalakis et al. 2008, Miyake et al. 2008b, Nnorom & Osibanjo 2008, Takigami et al. 2008, Wyrzykowska et al. 2008, Yosuke et al. 2008, Yu et al. 2008, ChemSec & Action. 2009, Hagberg 2009, Lundstedt 2009, Steen et al. 2009, Takigami et al. 2009, Terauchi et al. 2009, Wang et al. 2009b, Wyrzykowska et al. 2009, Zennegg et al. 2009, Ericson Jogsten et al. 2010, Kajiwara & Takigami 2010, Sepulveda et al. 2010, Suzuki et al. 2010, Wang et al. 2010b, Wang et al. 2010c)

PBDD/DF are relevant considerations in relation to the manufacture/processing[39], recycling[40] and disposal[41] of products containing, or contaminated with, PBDE and related compounds.

In 2003 Alcock identified six points at which PBDD/DF could be released via PBDE use into the environment after the original production (Alcock et al. 2003):

(1) blending of PBDE within polymers;

(2) formation during textile finishing with PBDE;

(3) emissions from products in use containing PBDE;

(4) recycling of plastic products containing PBDE;

(5) formation during accidental fires of products containing PBDE; and

(6) formation during the combustion of waste containing PBDE;

Since 2003 it has also become clear that formation during lifetime should be added to this list (Kajiwara et al. 2008)(Kajiwara & Takigami 2010).

In a 2009 summary of the Japanese assessment of the generation and releases of PBDD/DF from the use of BFRs Ota et al. (Ota et al. 2009) concluded that:

- PBDD/DF occur in relatively high concentrations in emission gas from BFR related facilities (e.g., flame-retarded plastics moulding facilities) in the supply chain of BFR-containing products as well as in effluents from those facilities.
- high emission of BFRs (PBDE in particular) was also found at the facilities emitting high concentrations of PBDD/DF. The presence of PBDD/DF (mainly PBDF) is closely associated with BFRs (mainly PBDE).

It is apparent from the above that brominated dioxins and, in particular, brominated furans are relevant contaminants which are inexorably linked with aspects of the production, use, recycling and disposal of PBDE. It can be seen that there are obvious risks of exposure of humans and the environment and that PBDD/DF

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[39] (Brandt-Rauf et al. 1988, Thies et al. 1990, Brenner 1993a, World Health Organisation 1993, WHO & IPCS 1994, World Health Organisation International Programme on Chemical Safety (WHO IPCS) 1994, Sidhu et al. 1995, Ott & Zober 1996, Sedlak et al. 1998, World Health Organisation 1998, Borojovich & Aizenshtat 2002b, Borojovich & Aizenshtat 2002a, Ebert & Bahadir 2003, Imai et al. 2003, Weber & Kuch 2003, D'Silva et al. 2004, Hayakawa et al. 2004, Nammari et al. 2004, Ashizuka et al. 2005, Greenpeace 2005, Malmvärn et al. 2005, Brigden & Santillo 2006, Hanari et al. 2006a, Sakai et al. 2006, Schlummer et al. 2006, Guan et al. 2007, Gullett et al. 2007, Leung et al. 2007, Nose et al. 2007, Schlummer et al. 2007, Concannon 2008, Nnorom & Osibanjo 2008, Yosuke et al. 2008, Brigden & Labunska 2009, ChemSec 2009, ChemSec & Action. 2009, ChemSec et al. 2009, Kawamoto 2009, Terauchi et al. 2009)

[40] (Lorenz & Bahadir 1993, Ritterbusch et al. 1994, World Health Organisation 1998, Rieß et al. 2000, Behnisch et al. 2001, Hamm et al. 2001, Ebert & Bahadir 2003, Imai et al. 2003, Weber & Kuch 2003, Balabanovich et al. 2004, Schlummer et al. 2004, Rupp & Metzger 2005, Brigden & Santillo 2006, Sakai et al. 2006, Schlummer et al. 2006, Gullett et al. 2007, Leung et al. 2007, Li et al. 2007b, Schlummer et al. 2007, Hirai et al. 2008, Nnorom & Osibanjo 2008, Wyrzykowska et al. 2008, Yosuke et al. 2008, Yu et al. 2008, Terauchi et al. 2009, Zennegg et al. 2009, Sepulveda et al. 2010)

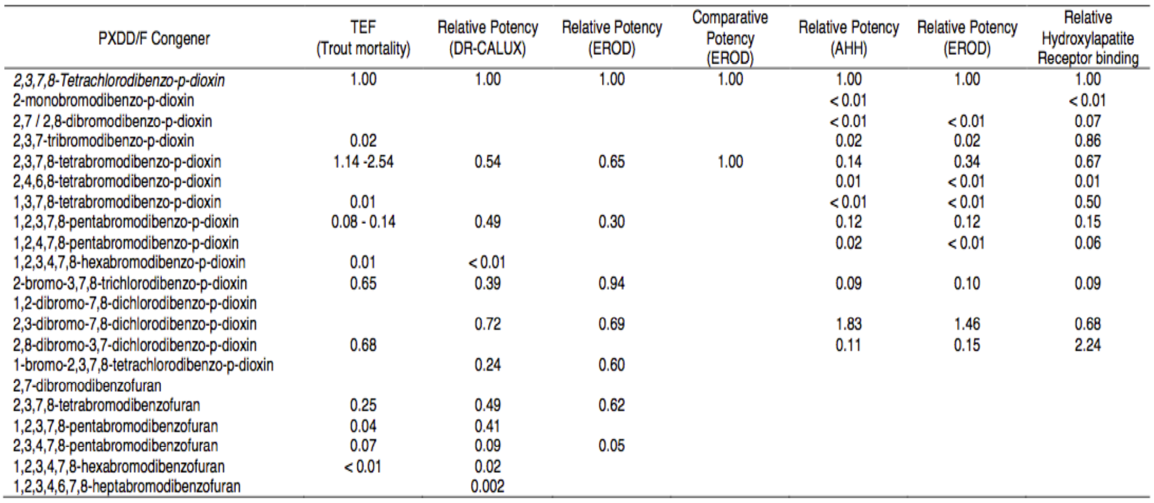
[41] (Brandt-Rauf et al. 1988, Dumler et al. 1989b, Donnelly et al. 1990, Lutes et al. 1992, Riggs et al. 1992, Brenner 1993a, World Health Organisation 1993, Lenoir et al. 1994, Ritterbusch et al. 1994, World Health Organisation International Programme on Chemical Safety (WHO IPCS) 1994, Heeb et al. 1995, Funcke & Hemminghaus 1997, World Health Organisation 1998, Behnisch et al. 2001, Sakai et al. 2001, Behnisch et al. 2002, BIPRO 2002, Borojovich & Aizenshtat 2002a, Lemieux et al. 2002, Nakao et al. 2002, Scientific Committee on Toxicity 2002, Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) 2002, Soderstrom & Marklund 2002, Ebert & Bahadir 2003, Liljelind et al. 2003, Vehlow et al. 2003, Weber & Kuch 2003, Balabanovich et al. 2004, Hayakawa et al. 2004, Nammari et al. 2004, Schlummer et al. 2004, Schuler & Jager 2004, Rupp & Metzger 2005, Brigden & Santillo 2006, Löthgren et al. 2006, Sakai et al. 2006, Gullett et al. 2007, Lai et al. 2007, Leung et al. 2007, Li et al. 2007b, Schlummer et al. 2007, Concannon 2008, Horii et al. 2008, Nnorom & Osibanjo 2008, Wyrzykowska et al. 2008, Yosuke et al. 2008, Yu et al. 2008, Brigden & Labunska 2009, ChemSec et al. 2009, Kawamoto 2009, Molto et al. 2009, Terauchi et al. 2009, Zennegg et al. 2009, Sepulveda et al. 2010)

contamination and emissions are therefore an important issue which should be addressed in relation to the recycling of PBDE.

Toxicity of Brominated Dioxins and Furans

Brominated dioxins and furans have been shown to have toxicities similar to, and in some cases greater than, their chlorinated counterparts in human cell lines and mammalian species (World Health Organisation 1998)(Birnbaum et al. 2003)(Weber & Greim 1997)(Behnisch et al. 2003)(Samara et al. 2010)(Olsman et al. 2007)(Matsuda et al. 2010)(D'Silva et al. 2004). It is particularly notable that 2,3-Dibromo-7,8-dichlorodibenzo-p-dioxin and 2,3,7,8-T_4BDD are shown to elicit upto 2.5 times the toxic response of 2,3,7,8-T_4CDD – often though to be the most toxic anthropogenic chemical:

Table 27: Toxicity of PBDD/Fs and PBrClDD/DF relative to 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)(D'Silva et al. 2004)



PXDD/F Congener	TEF (Trout mortality)	Relative Potency (DR-CALUX)	Relative Potency (EROD)	Comparative Potency (EROD)	Relative Potency (AHH)	Relative Potency (EROD)	Relative Hydroxylapatite Receptor binding
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2-monobromodibenzo-p-dioxin					< 0.01		< 0.01
2,7 / 2,8-dibromodibenzo-p-dioxin					< 0.01	< 0.01	0.07
2,3,7-tribromodibenzo-p-dioxin	0.02				0.02	0.02	0.86
2,3,7,8-tetrabromodibenzo-p-dioxin	1.14 -2.54	0.54	0.65	1.00	0.14	0.34	0.67
2,4,6,8-tetrabromodibenzo-p-dioxin					0.01	< 0.01	0.01
1,3,7,8-tetrabromodibenzo-p-dioxin	0.01				< 0.01	< 0.01	0.50
1,2,3,7,8-pentabromodibenzo-p-dioxin	0.08 - 0.14	0.49	0.30		0.12	0.12	0.15
1,2,4,7,8-pentabromodibenzo-p-dioxin					0.02	< 0.01	0.06
1,2,3,4,7,8-hexabromodibenzo-p-dioxin	0.01	< 0.01					
2-bromo-3,7,8-trichlorodibenzo-p-dioxin	0.65	0.39	0.94		0.09	0.10	0.09
1,2-dibromo-7,8-dichlorodibenzo-p-dioxin							
2,3-dibromo-7,8-dichlorodibenzo-p-dioxin		0.72	0.69		1.83	1.46	0.68
2,8-dibromo-3,7-dichlorodibenzo-p-dioxin	0.68				0.11	0.15	2.24
1-bromo-2,3,7,8-tetrachlorodibenzo-p-dioxin		0.24	0.60				
2,7-dibromodibenzofuran							
2,3,7,8-tetrabromodibenzofuran	0.25	0.49	0.62				
1,2,3,7,8-pentabromodibenzofuran	0.04	0.41					
2,3,4,7,8-pentabromodibenzofuran	0.07	0.09	0.05				
1,2,3,4,7,8-hexabromodibenzofuran	< 0.01	0.02					
1,2,3,4,6,7,8-heptabromodibenzofuran		0.002					

More relevant to formation from PBDE is that 2,3,7,8-Tetrabromodibenzofuran has a dioxin-like toxicity close to 2,3,7,8-TCDD (Matsuda et al. 2010)(Behnisch et al. 2003)(Samara et al. 2009)(Samara et al. 2010) and is therefore far more toxic than the 2,3,7,8-TCDF. This is of particular concern because 2,3,7,8-TBDF is one of the most prevalent PBDD/PBDF congeners in human tissue (Ericson Jogsten et al. 2010) and human milk samples (Kotz et al. 2005) but can also be rather high in flame retarded plastics from WEEE (Riess et al. 2000)[42].

Thymic atrophy, wasting of body mass, lethality, teraterogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T_4 and vitamin A, and increased hepatic porphyrins have been observed in animal studies of both brominated and chlorinated dioxins and furans (World Health Organisation 1998)(Birnbaum et al. 2003)(Weber & Greim 1997). *In vitro* responses of brominated PBDD/DF are similar to chlorinated PCDD/PCDF, including enzyme induction, anti-oestrogen activity in human breast cancer cells, and transformation of mouse macrophages into tumour cells and standard bio assays for dioxin-like toxicity testing (World Health Organisation 1998)(Behnisch et al. 2003) (Samara et al. 2010)(Samara et al. 2009)(Olsman et al. 2007)(Matsuda et al. 2010).

Recent studies indicate that some brominated-chlorinated (PXDD/DF) dioxins/furans also have similar – and for some mixed congeners possibly greater - toxicity compared to their chlorinated homologues (Behnisch et al. 2003)(Mennear and Lee 1994; (Birnbaum et al. 2003)(Olsman et al. 2007)(Matsuda et al. 2010).

Regulation of PBDD/DF

The available evidence indicates that there are currently only two jurisdictions which regulate PBDD/DF contents or releases. In addition there is also a live discussion in the current USEPA consultation process relating to the relevance of PBDD/DF and PXDD/DF standards for dedicated potentially polluted areas in the establishment of new limits for Remediation Goals for Dioxin in Soil at CERCLA and RCRA Sites.

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[42] The source of 2,3,7,8-TBDF in WEEE plastic stem most probably from PBDE#153 (2,2',4,4',5,5'-HxBDE) which is a direct precursor of 2,3,7,8-TBDF via Br_2 Elimination being a preferred formation pathway to PBDF from PBDE (Weber & Kuch 2003).

Germany: Ordinance on Chemicals (Chemikalienverbotsverordnung)

Only the German ordinance on prohibition of certain chemical (German Federal Ministry of Justice 2003) has defined a limit for PBDD/DF in products:

Table 28: Limit value for PBDD/DF in materials according the German ordinance for chemicals (German Federal Ministry of Justice 2003).

Class	*Compounds*	*Limits*
Class I	2,3,7,8-TBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PBDD, 1,2,3,7,8-PBDF	Sum class I < 1 µg/kg
Class II	1,2,3,7,8-PBDF, 1,2,3,6,7,8-HBDD, 1,2,3,7,8,9-HBDD, 1,2,3,4,7,8-HBDD	Sum (I + II) < 5 µg/kg

Components weighing less than 50 grams were excluded from these requirements until July 1999. All components are now required to comply.

Turkey: Degree on air emission from industrial sources

The Turkish by-law on ‘Air Pollution Prevention and Control in the Industrial Sectors’ includes an air emission limit for the following dioxin-like compounds (Turkish Ministry of Environment, 2009):

- Chlorinated PCDD and PCDF
- Dioxin-like PCBs
- Brominated PBDD and PBDF
- Brominated-chlorinated PXDD and PXDF

Turkey has a large metal industry from which the emissions have been of increasing scientific concern and this might have been part of the reason that emission limits for PBDD/DF and PXDD/DF were established for these industrial emissions. The limits set are demanding, both in terms of compliance and the country’s analytical capacity to effectively regulate emissions and to confirm compliance.

USA: Comment of the American Soil Science Society to EPA Remediation Goals for Dioxin in Soil

Currently US EPA is establishing new remediation guidelines and has published a “*Draft Recommended Interim Preliminary Remediation Goals for Dioxin in Soil at CERCLA and RCRA Sites (DPRGDS)*” (United States Environmental Protection Agency (USEPA) 2009, United States Federal Register 2009).

In it’s response to the consultation the Dioxin Work Group of the Soil Science Society of America (Glasener 2010) has highlighted that for certain sites potentially contaminated by dioxin PBDD/DF and PXDD/DF should be considered. The Recommendation mentions, inter alia, the following areas where PBDD/DF and mixed halogenated PXDD/DF can be relevant:

- Production of PBDE and BFRs
- Application areas of BFRs (production of BFR plastic; PUF foam, BFR textiles etc)
- Recycling areas of flame retarded plastic (WEEE), flame-retardant PUF foam (furniture, mattresses, car shredders, other shredders, etc.) and other BFR materials
- Thermal recycling where BFRs are included (e.g. smelters)
- Areas where open burning of waste occurred; landfill areas

SSSA highlight that in all of these areas that any assessment which does not include an evaluation of soil contamination by PBDD/DF (and in some cases also PXDD/DF) is limited in respect of the risks associated with dioxin-like compounds.

Recommendation of the WHO TEF group

A key reason why PBDD/DF have been addressed by national legislation in only a few cases, and hardly at all at an international level, is that no official TEFs have yet been established by the WHO.

The WHO-IPCS expert review of Brominated Dioxins had already suggested in 1998 that development of TEFs for selected PBDD and PBDF is justified given their existing similarities in structure, mechanism, and potency to PCDD and PCDF. The report said that “*Owing to the accumulating and toxic potential of some PBDDs/PBDFs, every effort should be made to prevent exposure of humans to, and pollution of the environment by, these compounds*” (World Health Organisation 1998).

The WHO-IPCS expert group (Van den Berg et al. 2006) reviewed the TEF scheme in 2006 and concluded that, based on mechanistic considerations “*PBDDs, PBDFs, PXCDDs, PXCDFs, PCNs, PBNs and PBBs undoubtedly belong in the TEF concept*”. The report says “*if the presence of PBDDs and PBDFs in human food* *as well as in people is more extensively demonstrated there will be a clear need for assigning TEFs to these compounds".* Because of the lack of human exposure data, WHO proposed that preliminary exposure assessments should be done in the near future to indicate if these compounds are relevant for humans with respect to TEQ dietary intake. The conclusion was that "*among all compounds proposed….for development of WHO TEFs*" the PBDD and PBDF "*should be given high priority*".

The relevance of PBDD/DF exposure

The evidence base for the relevance of human exposure to PBDD/DF has increased significantly since 2006. There is now a steady flow of new scientific work being published on these compounds confirming both the extent of contamination and the human and environmental hazards of these dioxins. It is therefore anticipated that there will be much greater international regulatory interest in these compounds in the near future.

The importance and relevance of PBDD/DF has been demonstrated by the significant contribution they are now making to dietary intake. It is therefore considered sensible that the formation and presence of PBDD/DF in the production, treatment and recycling of PBDE and, where available, the related exposure should be addressed so far as it possible to do so in this review.

Exposure to PBDD/DF

Having established the relevance to processes involving recycling of PBDE and the toxicity of PBDD/DF consideration has been given to whether there are:

- Significant background contamination levels
- Vulnerable population groups
- Occupational exposure risks
- Contaminated sites with exposure risks

The evidence in relation to each of these cases, as shown below, is that there are concerns which must be addressed.

The third step, therefore, is that further and more detailed consideration needs to be given to the extent and impacts of any generation or contamination of PBDD/DF through any potential processing, recycling and/or disposal of POP-BDE. The evidence available to us and detailed in this section indicates that this is likely to be the case and that brominated dioxins and, in particular, brominated furans are relevant contaminants inexorably linked with aspects of the production, use and disposal of PBDE. This has significant impacts in relation to exposure of humans and the environment.

Human background exposure

Brominated dioxins and furans have been found in humans (Choi et al. 2003)(Kotz et al. 2005)(Ericson Jogsten et al. 2010) and in biota (Ashizuka et al. 2008)(Fernandes et al. 2008). A recent food survey in the UK indicates that PBDD/DF contributed approximately 30% of the dioxin-like toxicity in food (Rose & Fernandes 2010).

A Swedish study of adipose tissue samples from individuals in the general population suggest that PBDD/DF contributed up to 14% of the total dioxin toxic equivalence (TEQ) (Ericson Jogsten et al. 2010).

There are still relatively few data for levels in human milk. In 1992 Wiberg reported that PBDD/DF and PXDD/DF were either non-existent or extremely low (< 20 ng/kg) (Wiberg et al. 1992). Subsequent research, however has established that PBDD/DF are now a contaminant of human milk. PBDD/DF were analysed in a follow up study using in the pooled human milk samples from the 3rd WHO human milk survey for PBDE, PBDD/DF and PXDD/DF to assess dioxin-like toxicity in human milk (Kotz et al. 2005). Kotz confirmed the very high levels of PBDE in US milk samples as 40 to > 100 times higher than in Europe. He detected 2,3,7,8-TBDF was detected in almost every sample which is of particular concern due to the relatively high toxicity of this compound compred with 2,3,7,8 –TCDF as discussed further below. The brominated dioxins contributed were present at levels upto 25% of the chlorinated dioxins measured as toxic equivalence. These compounds adds to the exposure of infants worldwide to that from chlorinated dioxins and furans and dioxin-like PCBs – exposure which already exceeds the WHO recommended tolerable daily intake by one to two orders of magnitude (van Leeuwen et al. 2000).

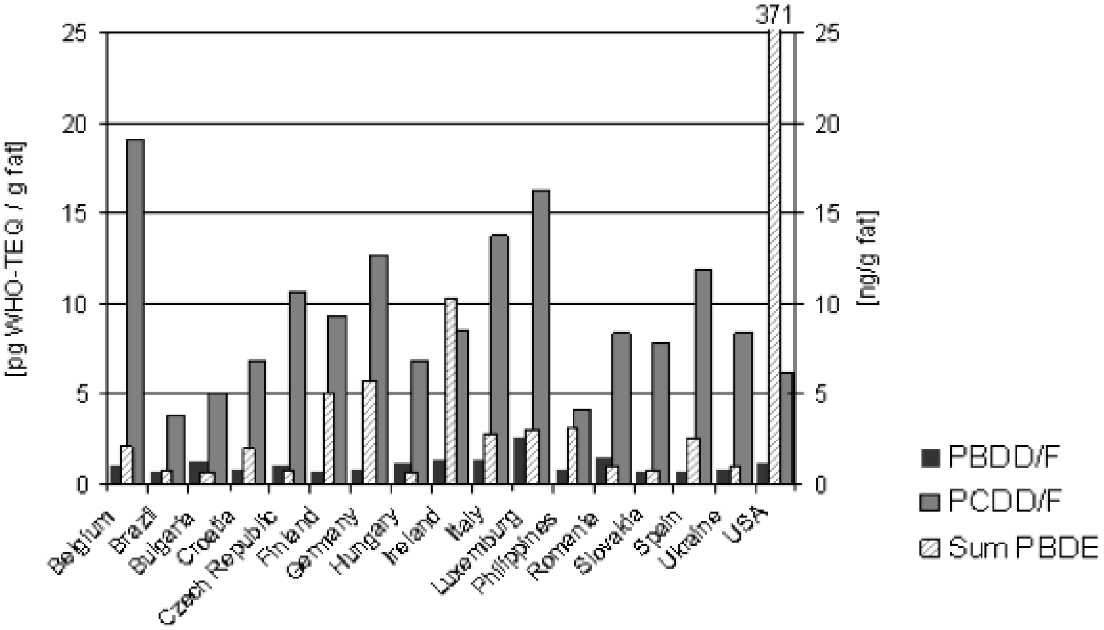


Figure 39: Comparison of "WHO"-PBDD/F- and WHO-PCDD/F-TEQs (pg/g fat WHO-TEQ, upper-bound limit) and PBDE (ng/g fat) in the pooled human milk samples.

It is notable that the TEQ PBDD/DF levels in breast milk reported in the US are not, unlike the PBDE levels, the highest in the countries sampled. This is probably due to the higher proportions of cPentaBDE (with the predominance of Tetra and PentaBDE congeners) in the USA. These compounds are not precursors for 2,3,7,8 substituted-PentaBDF and probably only precursors to a very limited extent for for 2,3,7,8-TetraBDF. A key congener for the formation of the more toxic for 2,3,7,8-PBDD/DF congeners is 2,2',4,4',5,5'-HexaBDE (BDE-153) together, to a lesser extent, with other Hexa and HeptaBDE. The results from Kotz support this hypothesis as there are much higher proportions of BDE-153 in the human milk samples in Europe (such as those from Belgium shown in Figure 39) than in those from the US which are dominated by BDE-47, -99 and 100 with a relatively low proportion of BDE-153:

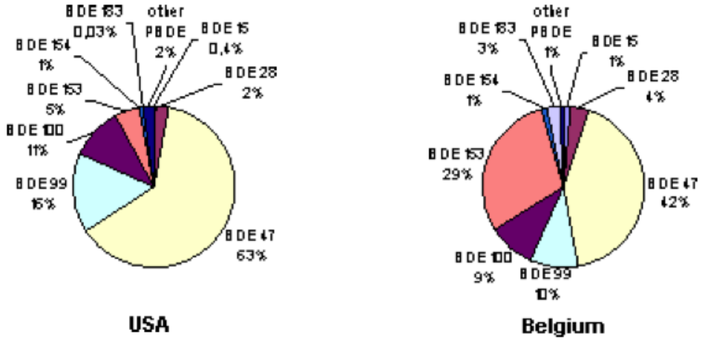


Figure 40: Relative BDE contribution to total PBDE in the human milk from USA and Belgium (Kotz et al. 2005).

Some studies have documented what appears to be a shift in the PBDE congener patterns in human tissues from the dominance of BDE-47 as the largest contributor to the PBDE body burden to a PBDE body burden dominated by BDE 153 (Johnson-Restrepo et al. 2005)(Fernandez et al. 2007)(Fängström et al. 2005a)(Meneses et al. 1999)(Covaci et al. 2002)

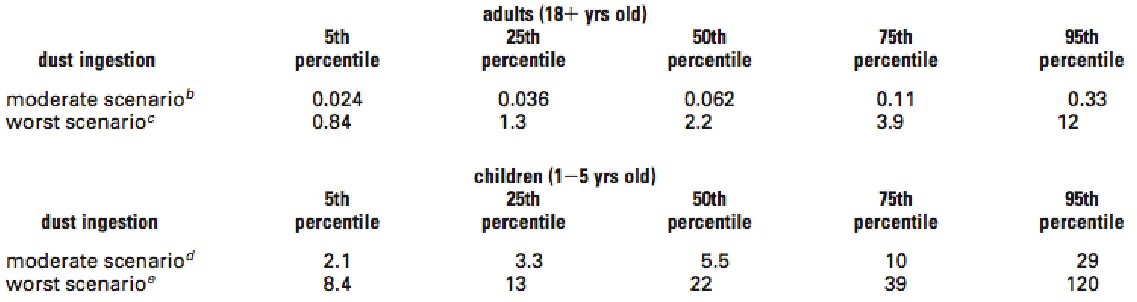
Fangstrom (Fängström et al. 2005a) and Stapleton (Stapleton 2006a) have both proposed that a possible explanation for this could be the metabolism of BDE-209, leading to the formation of BDE- 153. An alternative explanation may be related to BDE-153 having a higher persistence than BDE-47. The linkage between BDE

153 and PBDF is a concern and it is recommended that particular attention should be paid to this congener in any recycling operations.

PBDD/PBDF have been found around the world in house dust (Franzblau et al. 2009)(Takigami et al. 2008)(Suzuki et al. 2006)(Ma et al. 2009)(Suzuki et al. 2010). Japan is the only country to have performed a systematic screening of total dioxin-like compounds in house and office dust (Suzuki et al. 2010). It was found that PBDF are the major contributors to dioxin-like toxicity in this particularly relevant exposure matrix. Suzuki showed that dioxin-like PBDF toxicity considerably exceeded the combined amount from chlorinated PCDD, PCDF and dioxin-like PCBs in the samples from 19 households and 14 offices/laboratories (Suzuki et al. 2010). The bio-TEQ levels in these dusts were up to 1,400 ng (median 160 ng) CALUX-TEQ/kg. These levels are three to five orders of magnitude higher than those in food samples. As there was a difference of approximately three orders of magnitude for dioxin-like PCBs and PBDD/DF concentrations in these indoor dusts Suzuki concluded that this indicated the specific source of PBDD/DF as the indoor environment (Suzuki et al. 2010).

An assessment of daily intake of dioxin-like compounds for children (1-5 years) revealed a significant contribution to daily intake from dust even for a moderate intake scenario of 50 mg dust/day. A simple calculation for the highest concentration shows that a child could be ingesting 280 pg TEQ/day. Child specific exposure factors from USEPA (United States Environmental Protection Agency 2002) show that the mean bodyweight over this age range is between approximately 11 kg at 1 year to 19.5 kg at 5 years. Consequently the daily intake can range from about 14 to over 25 pg/kg bw/day from dust alone. These exposures far exceed of the WHO and European Tolerable Daily Intakes for chlorinated dioxins. For a high dust exposure scenario of 200 mg dust/day and median dust concentrations levels the daily intake of dioxin-like compounds of children via dust exceeded the daily intake of TEQ from PCDD/PCDF via food (Suzuki et al. 2007):

Table 29: Average Daily Doses (ADDs; in pg CALUX-TEQ/day) of Dioxin-Like Compounds via House Dust for Adults (at Least 18 Years) and Children (1-5 Years) (Suzuki et al. 2007)



		adults (18+ yrs old)			
dust ingestion	**5th percentile**	**25th percentile**	**50th percentile**	**75th percentile**	**95th percentile**
moderate scenario[b]	0.024	0.036	0.062	0.11	0.33
worst scenario[c]	0.84	1.3	2.2	3.9	12

		children (1—5 yrs old)			
dust ingestion	**5th percentile**	**25th percentile**	**50th percentile**	**75th percentile**	**95th percentile**
moderate scenario[d]	2.1	3.3	5.5	10	29
worst scenario[e]	8.4	13	22	39	120

In their follow-up study it was revealed that 50% of this TEQ came from PBDF as the main contributor to dioxin-like TEQ (Suzuki et al. 2010).

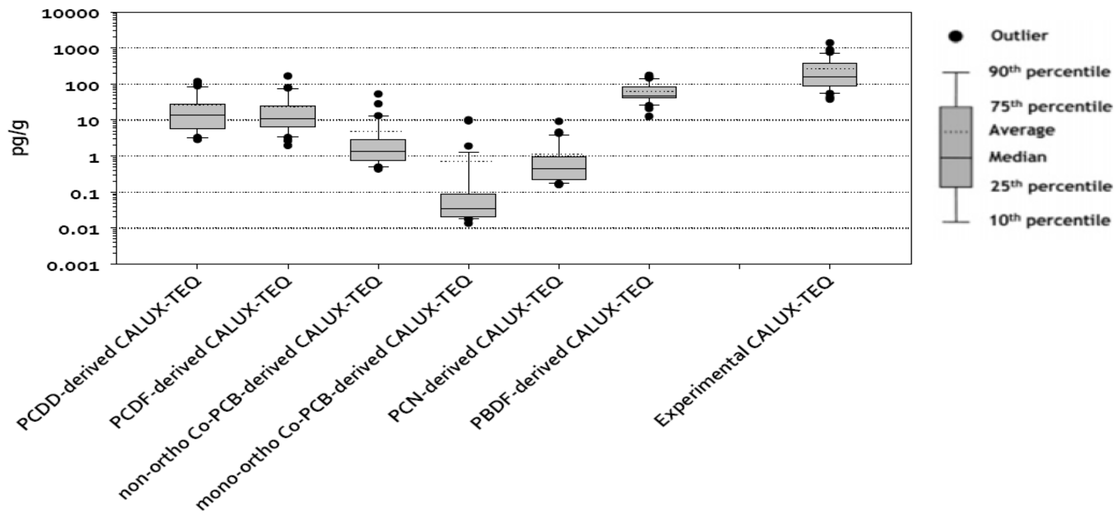


Figure 41: Dioxin-like contribution of PCDD/DF, Co-PCBs, PCNs, and PBDF concentrations in Japanese indoor dusts (from instrumental analysis recalculated to CALUX-TEQs) compared to total measured CALUX-TEQ (Suzuki et al. 2007, Suzuki et al. 2010).

The most comprehensive study to date of dietary exposure to PBDD/DF in food has been performed by the UK Food Standards Agency and revealed that PBDD/DF can contribute more than 30% of the dioxin-like toxicity in food. The UK dietary intakes for adults of PBDD/DF were 0.4 pg/kg bw/day through to 0.8 ng/kg bw/day, with the largest contribution coming from dairy milk (Food Standards Agency 2006b). In children aged 1.5 to 2.5 years the dietary intake rises to up to 3.0 pg/kg bw/day for high-level consumers (Food Standards Agency 2006b)(Fernandes et al. 2006). These exposures, which are well above the EU recommendations for chlorinated dioxins, arise from brominated dioxins alone. The exposure from chlorinated dioxins and dioxin-like PCBs is, of course, supplementary to this exposure. The exposure of infants from contamination of breast milk were not addressed in this study but, based on the experience with chlorinated dioxins, is likely to be very significantly higher than exposure from the diet. Diet is the main exposure pathway for PCDD/DF and a 30% TEQ additional burden from PBDD/DF is a significant contribution to the daily intake in the UK (Food Standards Agency 2006b)(Fernandes et al. 2006). Martin Rose of UK Food Standards Agency also presented the first data on brominated-chlorinated PXDD/DF in food samples at the BFR2010 meeting indicating that these levels were in the same concentration range or even higher compared to PBDD/DF (Rose & Fernandes 2010).

The levels detected in UK food indicates that PBDD/DF make a significant contribution to the dioxin toxicity of dietary intake in the UK population. The relative contribution from PBDD/DF to current exposures need to be investigated further in other countries.

Potentially highly exposed occupational groups

Of particular concern are the occupational exposures of certain workers including:

- historically, those chemical workers in PBDE production
- staff processing PBDE plastic in shredding, moulding and similar processes in recycling operations.
- Fire-fighters and rescue workers exposed to uncontrolled combustion of current stocks (and stores for recycling).
- workers collecting, handling, treating, shredding, recycling and disposing of BFR-containing waste.
- Carpet fitters and furniture upholsterers who may come into regular contact with recycled PBDE-treated materials.

Studies on PBDD/F levels with relevance to human exposure have been conducted in industries using PBDE (Ota et al. 2010). However, there appears to be no information available for workers in factories producing PBDE and levels in workers have not been measured (or reported). This is, however, mainly of historical significance and has not been pursued.

People working but also living in e-waste recycling and open burning areas are high-risk human populations for PBDD/DF, PBDE and other toxic releases (Jin et al. 2009)(Bi et al. 2007)(Deng et al. 2007, Luo et al. 2007a, Luo et al. 2007b, Wong et al. 2007a, Wong et al. 2007b, Wong et al. 2008b)(Wu et al. 2010).

Fire fighters are another occupation with elevated exposure to PBDD/DF and PCDD/DF (Birnbaum et al. 2003) where high PBDD/DF levels are formed in accidental fires from BFRs under uncontrolled combustion conditions (Weber & Kuch 2003)(Ebert & Bahadir 2003)- see below.

Fire-fighters are exposed to complex mixtures of contaminants in smoke from the fire and during clean up after fires (LeMasters et al. 2006)(Brandt-Rauf et al. 1988). Studies show an association between fire fighting and significantly elevated rates of specific types of cancer, including multiple myeloma, non-Hodgkin's lymphoma, prostate, and testicular cancer (reviewed in (LeMasters et al. 2006)(Kang et al. 2008). These four types of cancer are potentially related to exposure to dioxins and/or furans (PCDD/DF, PBDD/DF, PXDD/DF) formed via combustion processes during and after fires (LeMasters et al. 2006).

Analysis of PBDD/DF and brominated-chlorinated PXDD/DF

The congener specific GC/MS analysis of PBDD/DF including quantification of 2,3,7,8-PBDD/DF is well established. In industrial countries there are several commercial laboratories that have been offering PBDD/DF analysis since for many years. Recent publication from China and Taiwan in demonstrate that research institutions in these countries have also established PBDD/DF analysis.

Congener specific analysis of brominated-chlorinated PXDD/DF is more problematic, not least because these classes of compounds include 1,550 PXDD congeners and 3,050 PXDF congeners (D'Silva et al. 2004):

Table 30: Numbers of PBDD/F, PCDD/F, and PXDD/PXDF Congeners from (Buser 1987) and (D'Silva et al. 2004)

	Substitution								
Compound	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Total
PBDD	2	10	14	22	14	10	2	1	75
PBDF	4	16	28	38	28	16	4	1	135
PCDD	2	10	14	22	14	10	2	1	75
PCDF	4	16	28	38	28	16	4	1	135
PBrClDD	0	14	84	254	420	452	252	74	1550
PBrClDF	0	28	168	496	840	880	504	134	3050
Grand total PXDD/F congeners									5020

More than 400 congeners are 2,3,78-PXDD/DF substituted and therefore of particular interest. It is currently not possible to separate these from non-2,3,78-PXDD/DF congeners and assign TEFs to individual 2,3,78-PXDD/DF congeners – nor is this likely to be possible in the near future at least. Therefore bio-TEF factors must generally be used – but these have been assigned to only relatively small numbers of these compounds to date.

The complexity of the large numbers of congener and homologues is the main reason that comprehensive analysis of the full range of these compounds is still unusual and that only a few studies such as those of Zennegg (Zennegg et al. 2009) have measured the full range of PXDD/DF. In other studies often only Monobromo-polychloroDD/DF are measured for PXDD/DF.

The complexity of the PXDD/DF analysis, and the consequential gaps in the emissions data, should to be taken into account when thermal or chemical processes with significant levels of brominated and chlorinated organics need to be assessed for their total dioxin-like risk. The limited number of determinands currently analysed means that the hazards associated with many of the emissions are probably under-estimated.

Currently the only method to determine dioxin-like contamination and hazard is the assessment with established bio-assays measuring total dioxin-like potential like EROD, CALUX or DR CALUX.

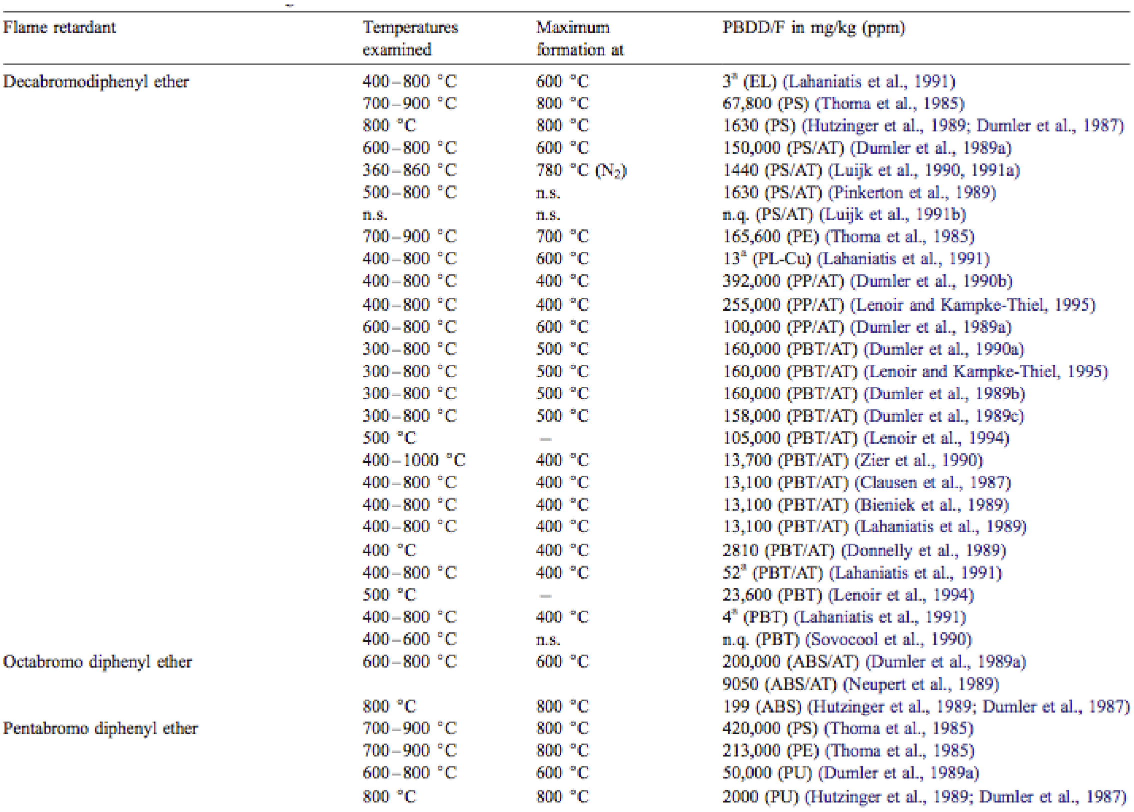
PBDE as precursors for PBDD/PBDF

The project brief requires examination of the release and emission data on PBDE and other unintentionally produced organic pollutants (e.g., brominated dioxins and furans) from various disposal operations, such as incineration, landfilling and open burning. This is examination should cover both high and low-technology operations;

PBDE are excellent precursor for PBDD/DF and high yields of PBDD/DF have been reported from thermolysis of PBDE or PBDE-containing materials (Weber & Kuch 2003)(Ebert & Bahadir 2003)(Buser 1986)(Thoma et al. 1987a, Thoma et al. 1987b) (Dumler et al. 1989a, Dumler et al. 1989b, Hutzinger et al. 1989)(Dumler et al. 1990)(Zacharewski et al. 1988)(Luijk & Govers 1992). The maximum reported values are 10% for c-PentaBDE and 5% for c-OctaBDE (Buser 1986) with the highest yield for DecaBDE conversion somewhat lower at 1 to 2% conversion (see below) (Buser 1986).

Ebert and Bahadir (Ebert & Bahadir 2003) helpfully summarised some of the published data on the formation of PBDD/DF after thermal degradation of various BFRs at temperatures above 300°C:

Table 31: Formation of PBDD/Fs after thermal degradation of BFRs above 300^{o}C from Ebert and Bahadir 2003 (Ebert & Bahadir 2003).



Flame retardant	Temperatures examined	Maximum formation at	PBDD/F in mg/kg (ppm)
Decabromodiphenyl ether	400–800 °C	600 °C	3[a] (EL) (Lahaniatis et al., 1991)
	700–900 °C	800 °C	67,800 (PS) (Thoma et al., 1985)
	800 °C	800 °C	1630 (PS) (Hutzinger et al., 1989; Dumler et al., 1987)
	600–800 °C	600 °C	150,000 (PS/AT) (Dumler et al., 1989a)
	360–860 °C	780 °C (N_2)	1440 (PS/AT) (Luijk et al., 1990, 1991a)
	500–800 °C	n.s.	1630 (PS/AT) (Pinkerton et al., 1989)
	n.s.	n.s.	n.q. (PS/AT) (Luijk et al., 1991b)
	700–900 °C	700 °C	165,600 (PE) (Thoma et al., 1985)
	400–800 °C	600 °C	13[a] (PL-Cu) (Lahaniatis et al., 1991)
	400–800 °C	400 °C	392,000 (PP/AT) (Dumler et al., 1990b)
	400–800 °C	400 °C	255,000 (PP/AT) (Lenoir and Kampke-Thiel, 1995)
	600–800 °C	600 °C	100,000 (PP/AT) (Dumler et al., 1989a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1990a)
	300–800 °C	500 °C	160,000 (PBT/AT) (Lenoir and Kampke-Thiel, 1995)
	300–800 °C	500 °C	160,000 (PBT/AT) (Dumler et al., 1989b)
	300–800 °C	500 °C	158,000 (PBT/AT) (Dumler et al., 1989c)
	500 °C	–	105,000 (PBT/AT) (Lenoir et al., 1994)
	400–1000 °C	400 °C	13,700 (PBT/AT) (Zier et al., 1990)
	400–800 °C	400 °C	13,100 (PBT/AT) (Clausen et al., 1987)
	400–800 °C	400 °C	13,100 (PBT/AT) (Bieniek et al., 1989)
	400–800 °C	400 °C	13,100 (PBT/AT) (Lahaniatis et al., 1989)
	400 °C	400 °C	2810 (PBT/AT) (Donnelly et al., 1989)
	400–800 °C	400 °C	52[a] (PBT/AT) (Lahaniatis et al., 1991)
	500 °C	–	23,600 (PBT) (Lenoir et al., 1994)
	400–800 °C	400 °C	4[a] (PBT) (Lahaniatis et al., 1991)
	400–600 °C	n.s.	n.q. (PBT) (Sovocool et al., 1990)
Octabromo diphenyl ether	600–800 °C	600 °C	200,000 (ABS/AT) (Dumler et al., 1989a) 9050 (ABS/AT) (Neupert et al., 1989)
	800 °C	800 °C	199 (ABS) (Hutzinger et al., 1989; Dumler et al., 1987)
Pentabromo diphenyl ether	700–900 °C	800 °C	420,000 (PS) (Thoma et al., 1985)
	700–900 °C	800 °C	213,000 (PE) (Thoma et al., 1985)
	600–800 °C	600 °C	50,000 (PU) (Dumler et al., 1989a)
	800 °C	800 °C	2000 (PU) (Hutzinger et al., 1989; Dumler et al., 1987)

It is clear, therefore that the efficiency of PBDE as PBDD/PBDF[43] precursors is comparable to that of PCBs as precursors for PCDD/DF where similar conversion rates in the lower percentage range have been demonstrated under pyrolysis conditions or low temperature oxidation (Buser 1986)(Weber 2007).

It is widely accepted that PBDE have the potential to form brominated dioxins/furans during processing and disposal and the European Chemical Industry Council says(European Chemical Industry Council (CEFIC) & European Flame Retardants Association 2005):

"*Because it [DecaBDE] is a bromine-containing compound whose structure is such that there may be potential for forming brominated dibenzodioxins or furans (PBDD/F) in uncontrolled thermal processes. Therefore, all handling operations of DBDE-containing plastics, such as compounding, converting, cleaning, recovery and recycling, have to be carried out under strictly controlled temperature conditions*".

And:

"*DecaBDE is a brominated compound so conditions conducive to the formation of dioxins/furans in thermal processes should be avoided in processing and disposal".*

The Role of debromination in the formation of PBDE and PBDD/PBDF

The formation of PBDD/DF through Debromination is an important contributor to the hazards associated with PBDE. Appendix 6 (b) reviews the science of debromination in more detail.

It should additionally be noted that PXDD/DF may also be pre-cursors for PCDD/DF. In laboratory experiments it has been shown, for example, that the bromine substituents of PXDD/DF are more easily removed by UV-light than the chlorine substituents, both in solution and in crystalline form (Buser 1988)(Wiberg et al. 1992). In this way monobromo-polychlorodibenzo-p-dioxins/dibenzofurans may degrade and form PCDD/DF.

Other BFRs

In determining the relationship between the POP-BDE and PBDD/DF consideration needs to be given also to the fact that the key brominated flame retardants on the market are aromatic compounds (with the exemption of HBCD) and can therefore act to more or less extent as PBDD/DF precursors (Weber & Kuch 2003, Weber

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[43] A direct elimination of HBr

2007). However even for a non-aromatic flame retardants like HBCD considerable PBDD/DF formation has been reported at temperatures, normally around 300°C, in the GC/MS injector block (Brenner & Knies 1994). Brenner (Brenner 1993b)(Brenner & Knies 1994) noted that HBCD "*can produce high amounts of PBDFs/Ds in the GC-injection block, leading to entirely wrong positive results*". In the same study the author reported thermolysis of HBCD containing polymers at 700°C and reported on concentrations of PBDD/PBDF from 30 to 100 ppb (for tri to hexa).

Söderström and Marklund (Soderstrom & Marklund 2002) tested the combustion of municipal waste with addition of PBDE, TBBPA and HBCD in a laboratory scale incinerator. Combustion of all three types of flame-retardants resulted in the formation of PBDD/DF and brominated-chlorinated PXDD/DF (Soderstrom & Marklund 2002).

This suggests that all BFRs and BFR retarded material including the non aromatic compunds have a certain risk of forming PBDD/DF in thermal processes and need appropriate management and destruction.

The allocation of PBDD/DF and PXDD/DF between POP-BDE and other BFRs is therefore a complex issue which needs more research – the POP-BDE appear, however, to be the most potent sources – although DecaBDE is almost the largest overall source, combining enormous stocks with high potential for PBDD/DF generation.

Source of PBDD/PBDF already in PBDE retarded products entering recycling at the end-of-life

While the majority of the relevant PBDD/DF are formed at the end-of-life stage (see below), PBDE flame retarded goods and products already contain PBDD/DF arising from:

- Production of PBDE and subsequent contamination of the commercial mixtures.
- Formation during production processes of the PBDE-containing product such as moulding and extrusion of polymers.
- Formation during life- time and use of PBDE-containing materials.

PBDD/DF in commercial PBDE

The USEPA warned about the potential for generation of brominated dioxins and furans during the manufacture of PBDE in the their 1987 report about the Manufacture of Halogenated Organic Chemicals (USEPA et al. 1987). They noted, however, that "*relatively little recent data are available due to the confidential nature of business information in the organic chemicals industry*".

During production of halogenated aromatic compounds halogenated dioxins are formed as unintentionally produced POPs and the World Health Organisation commented in 1998 that "*PBDDs/PBDFs have been found as contaminants in brominated organic chemicals (e.g. bromophenols) and, in particular, in flame retardants, such as polybrominated diphenyl ethers (PBDEs), decabromobiphenyl (decaBB or DBB), 1,2-bis(tribromophenoxy)ethane, tetrabromobisphenol A (TBBPA), and others*"[44] (World Health Organisation 1998).

Hanari et al. (Hanari et al. 2006b) have since analysed a number of Commercial PBDE mixtures and found that as well as PBDD/DF all additionally contained unintentionally produced PBB with the highest levels in the PentaBDE[45]:

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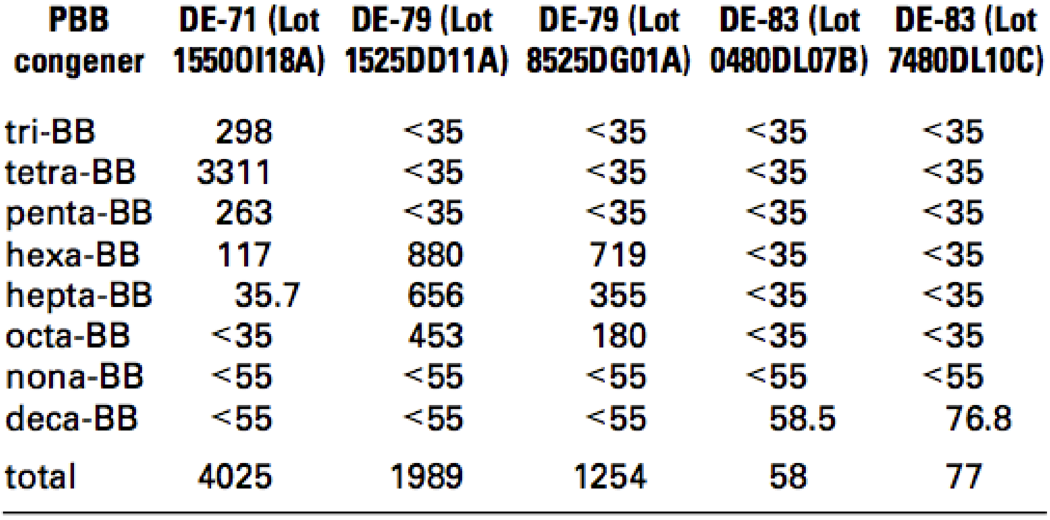
[44] Also HBCD were found to contain PBDF (20 ppb TetraBDF and 30 ppb PentaBDF) (Brenner & Knies 1994)

[45] this could, at least in part, help to explain the surprise that is sometimes expressed in the literature when PBBs are found in recent wastes along with PBDE.

Table 32: Concentrations of Polybrominated Biphenyls (ng/g) in Commercial PBDE Mixtures DE-71 (Penta), DE-79 Octa and DE-83 Deca (Hanari et al. 2006b)



PBB congener	DE-71 (Lot 1550OI18A)	DE-79 (Lot 1525DD11A)	DE-79 (Lot 8525DG01A)	DE-83 (Lot 0480DL07B)	DE-83 (Lot 7480DL10C)
tri-BB	298	<35	<35	<35	<35
tetra-BB	3311	<35	<35	<35	<35
penta-BB	263	<35	<35	<35	<35
hexa-BB	117	880	719	<35	<35
hepta-BB	35.7	656	355	<35	<35
octa-BB	<35	453	180	<35	<35
nona-BB	<55	<55	<55	<55	<55
deca-BB	<55	<55	<55	58.5	76.8
total	4025	1989	1254	58	77

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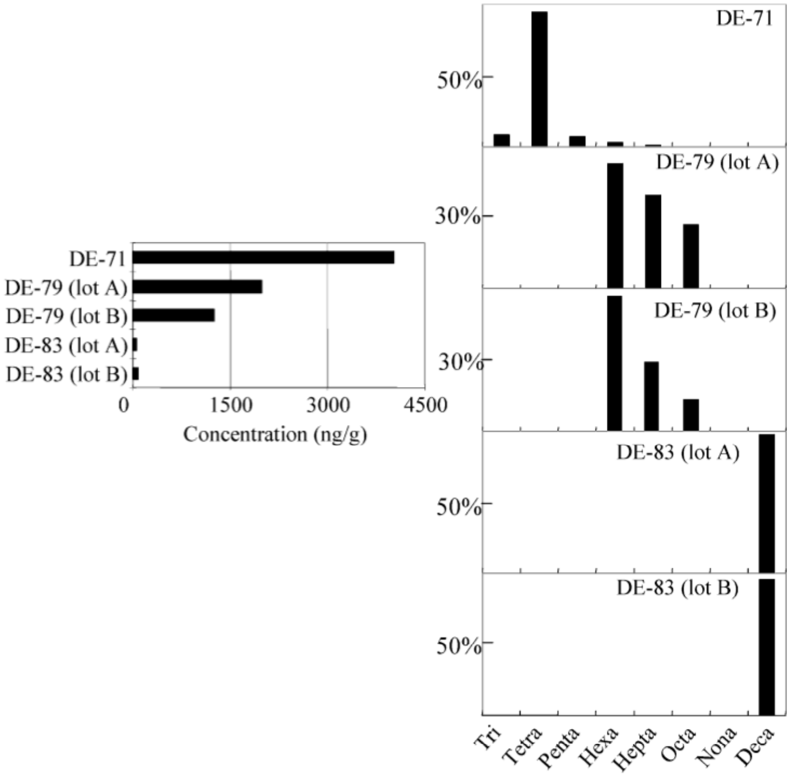

Figure 42: Concentrations of total PBBs (left) and relative proportions of individual PBB homologue groups (right) in three commercial PBDE preparations: DE-71 (Penta), DE-79 Octa and DE-83 Deca (Hanari et al. 2006b).

As with the unintentionally produced PBBs the PBDD/DF concentrations in PBDE vary significantly with the source and specification of the commercial mixtures. Unlike with PBBs, however, where the highest levels are in the PentaBDE and Octa mixtures the highest total[46] PBDD/DF levels (30.8 and 49.6 ppm) were found in the DecaBDE mixture :

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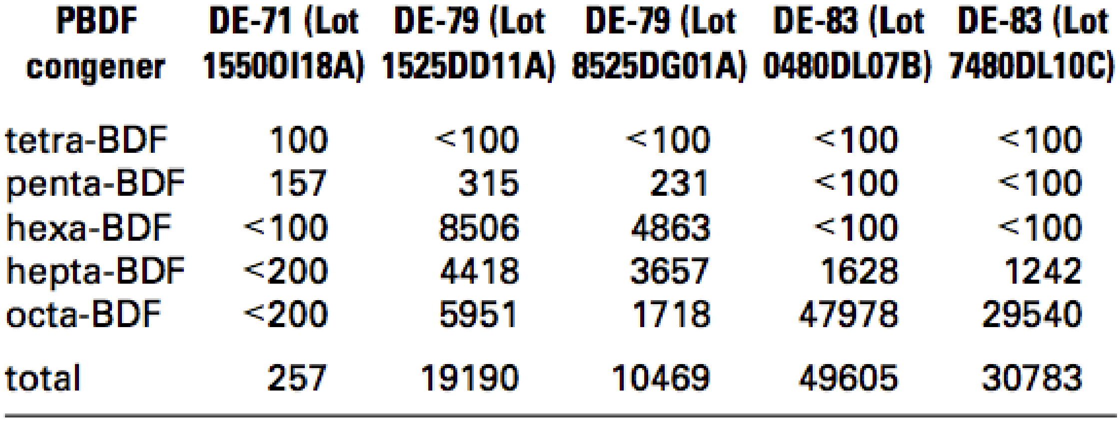
[46] TEQ/TEF results were not reported.

Table 33: Concentrations of Polybrominated Dibenzofurans (ng/g) in Commercial PBDE Mixtures: DE-71 (Penta), DE-79 Octa and DE-83 Deca (Hanari et al. 2006b)



PBDF congener	DE-71 (Lot 1550OI18A)	DE-79 (Lot 1525DD11A)	DE-79 (Lot 8525DG01A)	DE-83 (Lot 0480DL07B)	DE-83 (Lot 7480DL10C)
tetra-BDF	100	<100	<100	<100	<100
penta-BDF	157	315	231	<100	<100
hexa-BDF	<100	8506	4863	<100	<100
hepta-BDF	<200	4418	3657	1628	1242
octa-BDF	<200	5951	1718	47978	29540
total	257	19190	10469	49605	30783

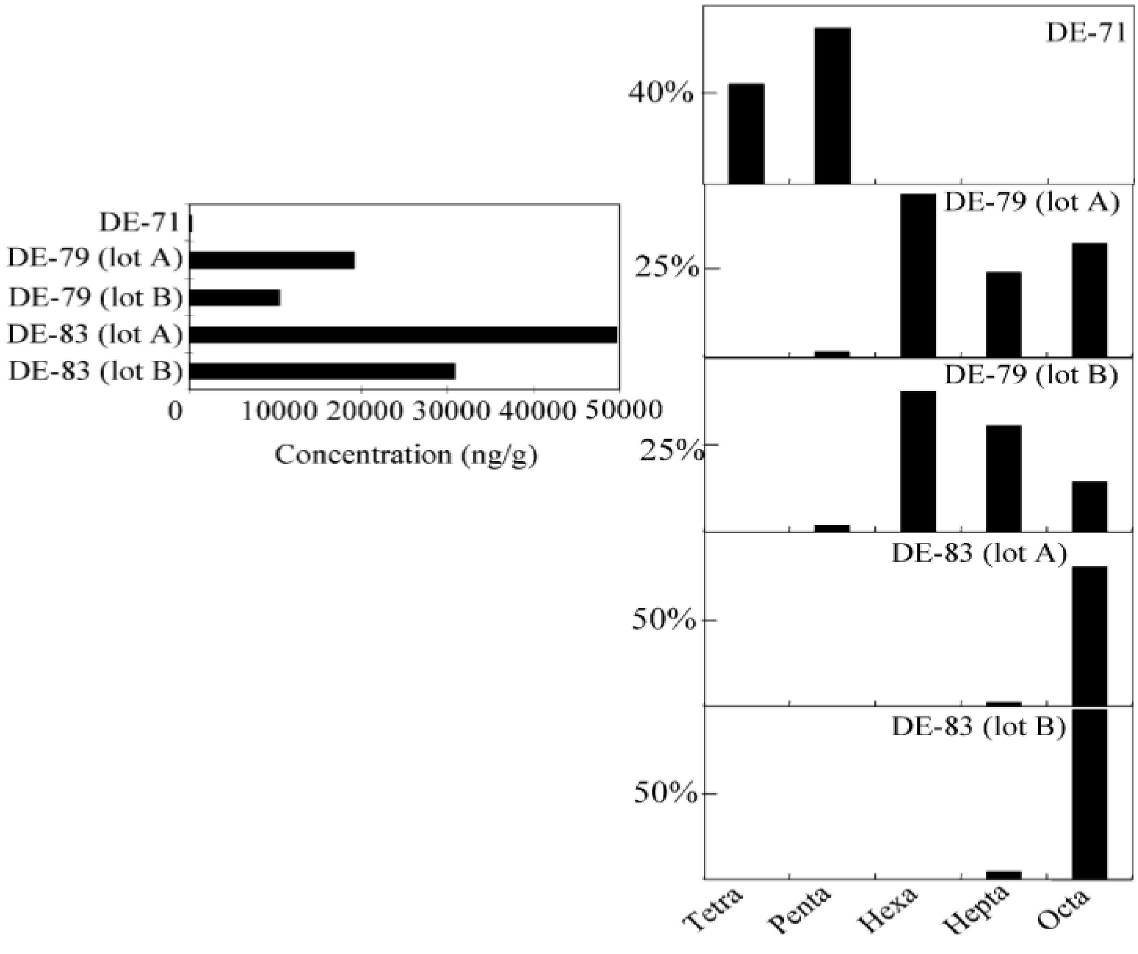
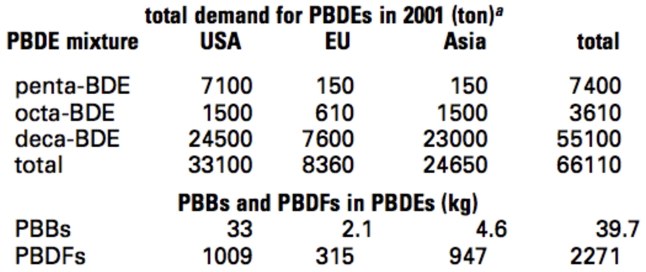


Figure 43: Concentrations of total PBDF (left) and relative proportions of individual PBDF homologue groups (right) groups (right) in three commercial PBDE preparations: DE-71 (Penta), DE-79 Octa and DE-83 Deca (Hanari et al. 2006b).

On the basis of the production/usage of commercial PBDE mixtures in 2001, Hanari calculated that the potential global annual emissions of unintentionally produced PBDFs were 2,271 kg (Hanari et al. 2006b):

Table 34: Global Demand for Commercial PBDE Mixtures (Tons) in 2001 and Estimated Content (kg) of PBBs and PBDF in Commercial PBDE Mixtures (Hanari et al. 2006b).



	total demand for PBDEs in 2001 (ton)[a]			
PBDE mixture	**USA**	**EU**	**Asia**	**total**
penta-BDE	7100	150	150	7400
octa-BDE	1500	610	1500	3610
deca-BDE	24500	7600	23000	55100
total	33100	8360	24650	66110
	PBBs and PBDFs in PBDEs (kg)			
PBBs	33	2.1	4.6	39.7
PBDFs	1009	315	947	2271

It should be noted that the POP-BDE are not the only source of PBDD/DF contamination in products. A recent publication of the Japanese Environmental Ministry reported PBDD/DF in DecaBDE and HBCD applied in Japanese manufacturing (Ota et al. 2010). The conclusions were that the presence of PBDD/DF was "*closely associated*" with PBDE but also that increases found in processes using HBCD "*suggest PBDD/DF in the effluent may be mainly due to impurities in HBCD*".

With the limited data available it is not possible to quantify more specifically the relative importance of each BFR as a source of PBDD/DF arising from contaminants in production.

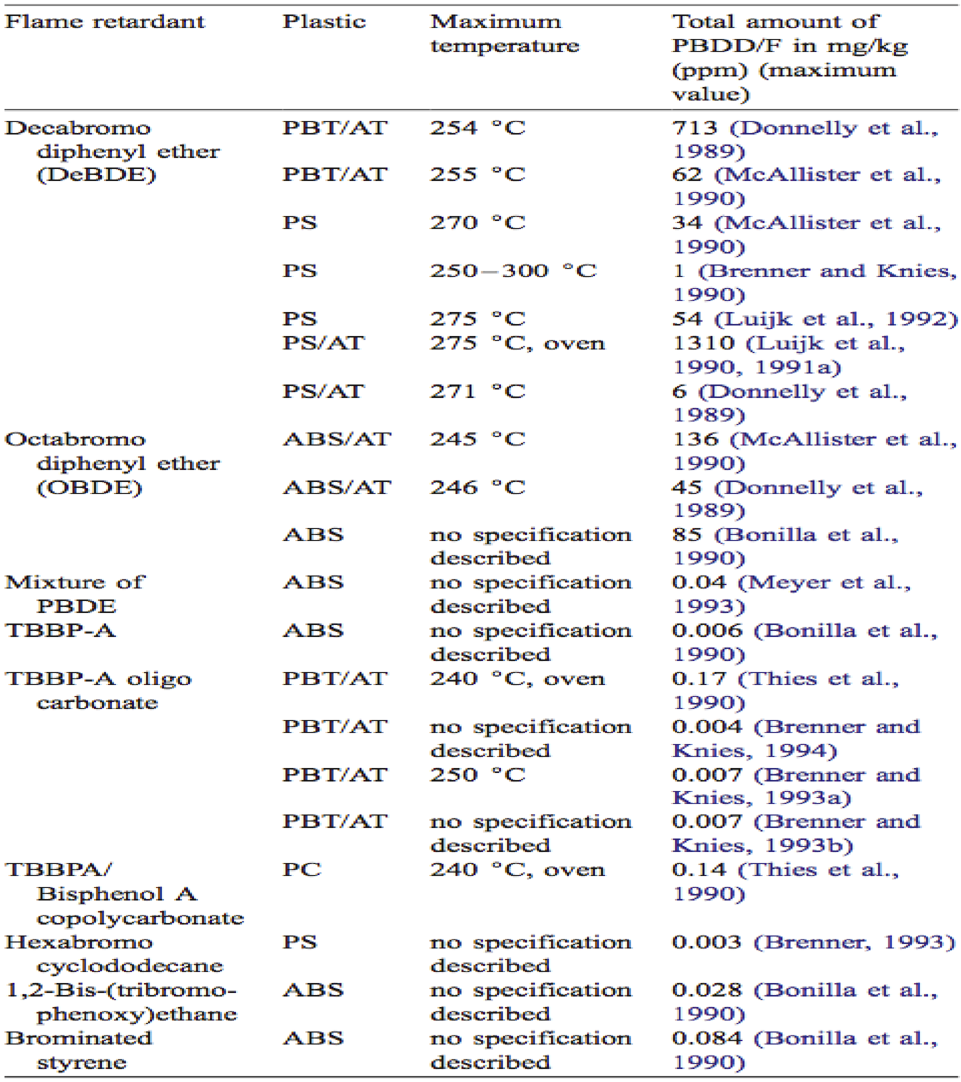
It is likely, however, that in the case of the POP-BDE these unintentionally produced PBDD/DF impurities remain associated with related exposure to workers (including repair staff), collectors, recyclers, disposal operatives and consumer during the entire life cycle of treated articles.

PBDD/DF formation during (re)manufacturing of materials containing PBDE/BFR retarded materials

PBDD/PBDF are also formed in the production of PBDE retarded plastics involving thermal processes like moulding and extrusion operated at temperature between 240°C to 300°C. (Weber & Kuch 2003)(Ebert & Bahadir 2003)(McAllister et al. 1990)(Zober et al. 1992). The highest PBDD/PBDF levels were found in production where PBDE (OctaBDE and DecaBDE were used as shown in **Error! Reference source not found.**Table 35). While other major BFR (TBBA, HBCD, Brominated Styrene) generated PBDD/DF levels several orders of magnitude lower.

In 1992 Zober reported test results for five production employees extrusion blending polybutylene terephthalate who were all positive for PBDF and PBDD. While no health impacts were established the body burdens of the operators were significantly elevated with 2,3,7,8-TBDD detected at concentrations of 100 to 500 ng/kg and 2,3,7,8-TBDF at concentrations of 100 to 200 ng/kg respectively. Among the control group, PBDF and PBDD were either not detected or were marginally present (Zober et al. 1992).

Table 35: Formation of PBDD/F during production/recycling processes of plastics (Ebert & Bahadir 2003).



Flame retardant	Plastic	Maximum temperature	Total amount of PBDD/F in mg/kg (ppm) (maximum value)
Decabromo diphenyl ether (DeBDE)	PBT/AT	254 °C	713 (Donnelly et al., 1989)
	PBT/AT	255 °C	62 (McAllister et al., 1990)
	PS	270 °C	34 (McAllister et al., 1990)
	PS	250–300 °C	1 (Brenner and Knies, 1990)
	PS	275 °C	54 (Luijk et al., 1992)
	PS/AT	275 °C, oven	1310 (Luijk et al., 1990, 1991a)
	PS/AT	271 °C	6 (Donnelly et al., 1989)
Octabromo diphenyl ether (OBDE)	ABS/AT	245 °C	136 (McAllister et al., 1990)
	ABS/AT	246 °C	45 (Donnelly et al., 1989)
	ABS	no specification described	85 (Bonilla et al., 1990)
Mixture of PBDE	ABS	no specification described	0.04 (Meyer et al., 1993)
TBBP-A	ABS	no specification described	0.006 (Bonilla et al., 1990)
TBBP-A oligo carbonate	PBT/AT	240 °C, oven	0.17 (Thies et al., 1990)
	PBT/AT	no specification described	0.004 (Brenner and Knies, 1994)
	PBT/AT	250 °C	0.007 (Brenner and Knies, 1993a)
	PBT/AT	no specification described	0.007 (Brenner and Knies, 1993b)
TBBPA/ Bisphenol A copolycarbonate	PC	240 °C, oven	0.14 (Thies et al., 1990)
Hexabromo cyclododecane	PS	no specification described	0.003 (Brenner, 1993)
1,2-Bis-(tribromo-phenoxy)ethane	ABS	no specification described	0.028 (Bonilla et al., 1990)
Brominated styrene	ABS	no specification described	0.084 (Bonilla et al., 1990)

A contemporary survey on the current status of PBDD/DF emissions in Japan confirmed that facilities handling high concentrations of BFRs (e.g., flame-retarded plastics moulding facilities, textile manufacturing) also exhibit high concentration of PBDD/DF emissions (Ota et al. 2009)(Ota et al. 2010). The correlation coefficients between the concentration of PBDD/F and PBDE in plastic moulding facility and textile manufacturing facilities were very high (0.86 and 0.92 respectively) (Ota et al. 2010).

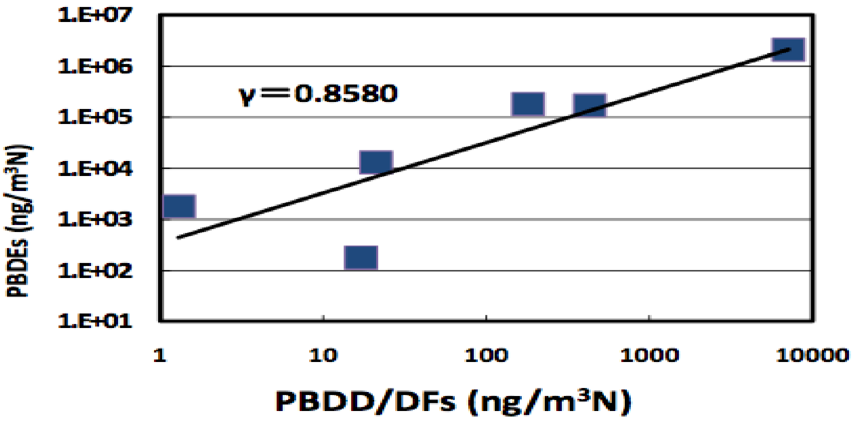


Figure 44: PBDE vs PBDD/DF in the gas emissions from facilities moulding flame retarted plastics (Ota et al. 2009)

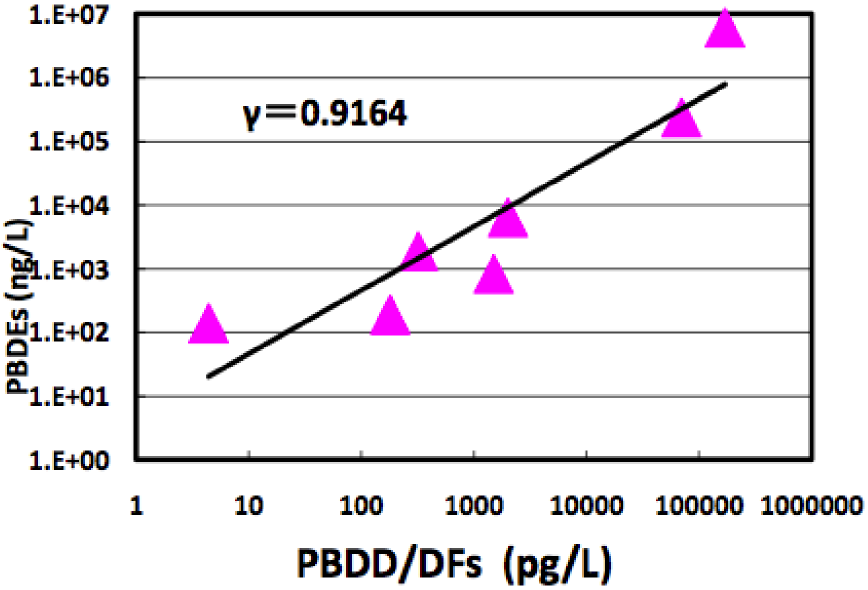


Figure 45: Correlation between PBDD/DF and PBDE concentration in the effluents from textile manufacturing facilities in Japan (Ota et al. 2009)

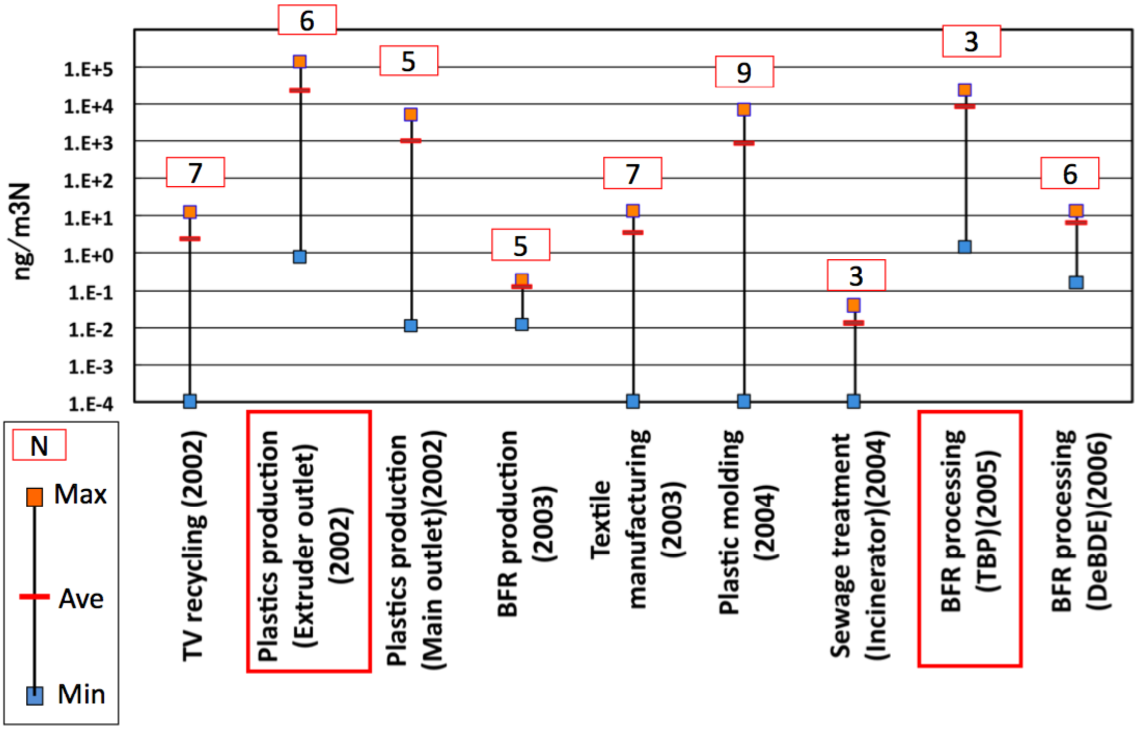
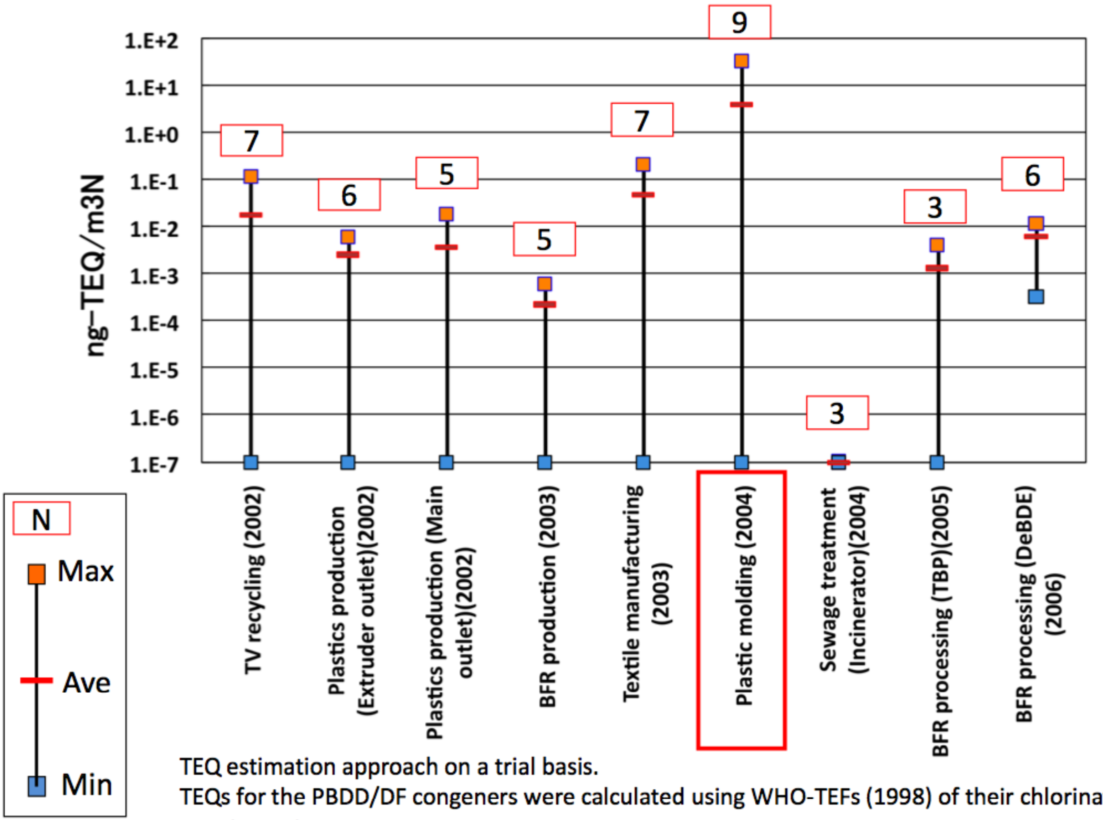


Figure 46: Levels of PBDD/DF in emission gas from various sources (Actual concentration) (Ota et al. 2009).

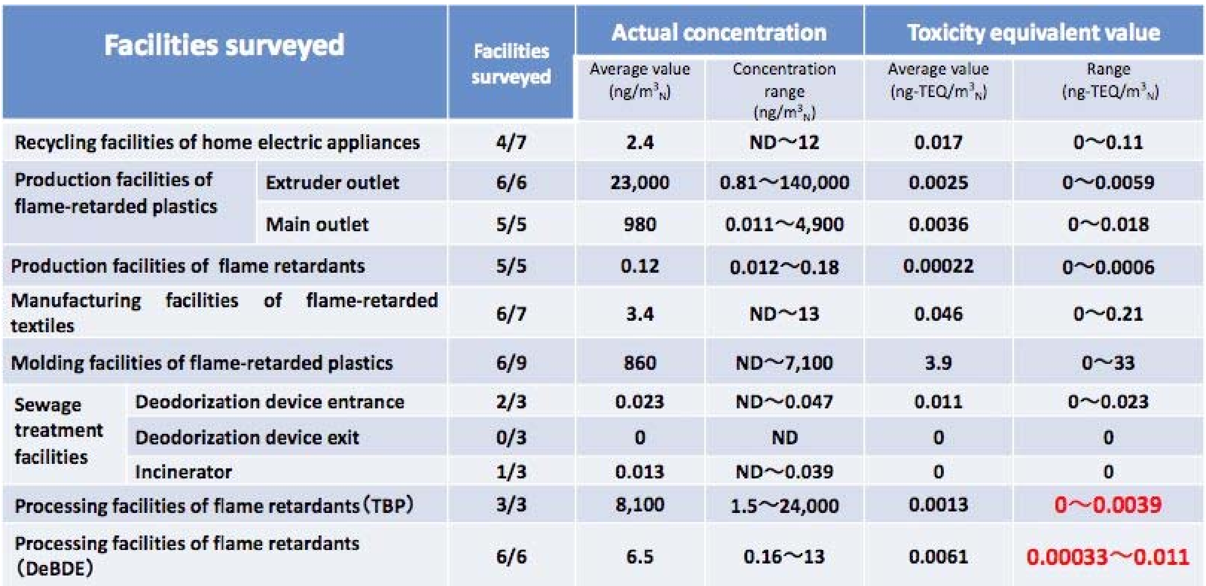
The plastic moulding levels are particularly relevant to recycling and are the highest emissions by a clear margin when presented as TEQ:



TEQ estimation approach on a trial basis.
TEQs for the PBDD/DF congeners were calculated using WHO-TEFs (1998) of their chlorinated counterparts.

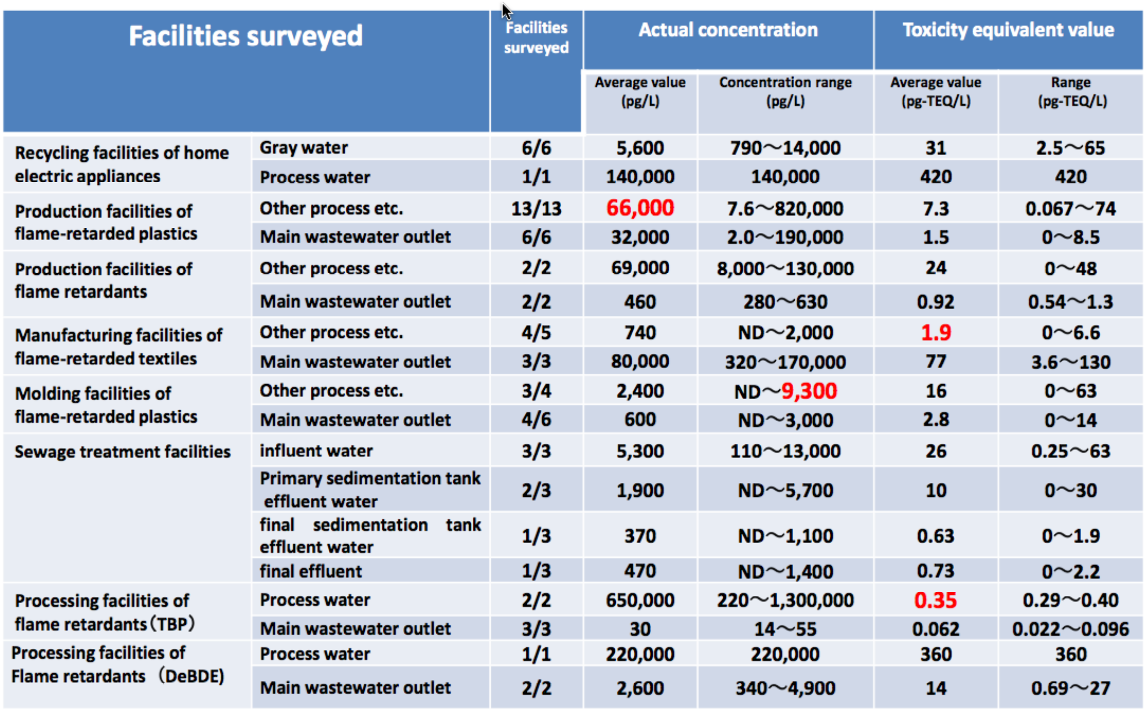
Figure 47: Levels of PBDD/DF in emission gas from various sources (TEQ) (Ota et al. 2009)

Table 36: Levels of PBDD/DF in emission gas from various sources (Ota et al. 2009).



Facilities surveyed		Facilities surveyed	Actual concentration		Toxicity equivalent value	
			Average value (ng/m^3_N)	Concentration range (ng/m^3_N)	Average value (ng-TEQ/m^3_N)	Range (ng-TEQ/m^3_N)
Recycling facilities of home electric appliances		4/7	2.4	ND～12	0.017	0～0.11
Production facilities of flame-retarded plastics	Extruder outlet	6/6	23,000	0.81～140,000	0.0025	0～0.0059
	Main outlet	5/5	980	0.011～4,900	0.0036	0～0.018
Production facilities of flame retardants		5/5	0.12	0.012～0.18	0.00022	0～0.0006
Manufacturing facilities of flame-retarded textiles		6/7	3.4	ND～13	0.046	0～0.21
Molding facilities of flame-retarded plastics		6/9	860	ND～7,100	3.9	0～33
Sewage treatment facilities	Deodorization device entrance	2/3	0.023	ND～0.047	0.011	0～0.023
	Deodorization device exit	0/3	0	ND	0	0
	Incinerator	1/3	0.013	ND～0.039	0	0
Processing facilities of flame retardants（TBP）		3/3	8,100	1.5～24,000	0.0013	0～0.0039
Processing facilities of flame retardants（DeBDE）		6/6	6.5	0.16～13	0.0061	0.00033～0.011

Table 37: Levels of PBDD/DF in process water from various sources (Ota et al. 2009)



Facilities surveyed		Facilities surveyed	Actual concentration		Toxicity equivalent value	
			Average value (pg/L)	Concentration range (pg/L)	Average value (pg-TEQ/L)	Range (pg-TEQ/L)
Recycling facilities of home electric appliances	Gray water	6/6	5,600	790～14,000	31	2.5～65
	Process water	1/1	140,000	140,000	420	420
Production facilities of flame-retarded plastics	Other process etc.	13/13	66,000	7.6～820,000	7.3	0.067～74
	Main wastewater outlet	6/6	32,000	2.0～190,000	1.5	0～8.5
Production facilities of flame retardants	Other process etc.	2/2	69,000	8,000～130,000	24	0～48
	Main wastewater outlet	2/2	460	280～630	0.92	0.54～1.3
Manufacturing facilities of flame-retarded textiles	Other process etc.	4/5	740	ND～2,000	1.9	0～6.6
	Main wastewater outlet	3/3	80,000	320～170,000	77	3.6～130
Molding facilities of flame-retarded plastics	Other process etc.	3/4	2,400	ND～9,300	16	0～63
	Main wastewater outlet	4/6	600	ND～3,000	2.8	0～14
Sewage treatment facilities	influent water	3/3	5,300	110～13,000	26	0.25～63
	Primary sedimentation tank effluent water	2/3	1,900	ND～5,700	10	0～30
	final sedimentation tank effluent water	1/3	370	ND～1,100	0.63	0～1.9
	final effluent	1/3	470	ND～1,400	0.73	0～2.2
Processing facilities of flame retardants（TBP）	Process water	2/2	650,000	220～1,300,000	0.35	0.29～0.40
	Main wastewater outlet	3/3	30	14～55	0.062	0.022～0.096
Processing facilities of Flame retardants （DeBDE）	Process water	1/1	220,000	220,000	360	360
	Main wastewater outlet	2/2	2,600	340～4,900	14	0.69～27

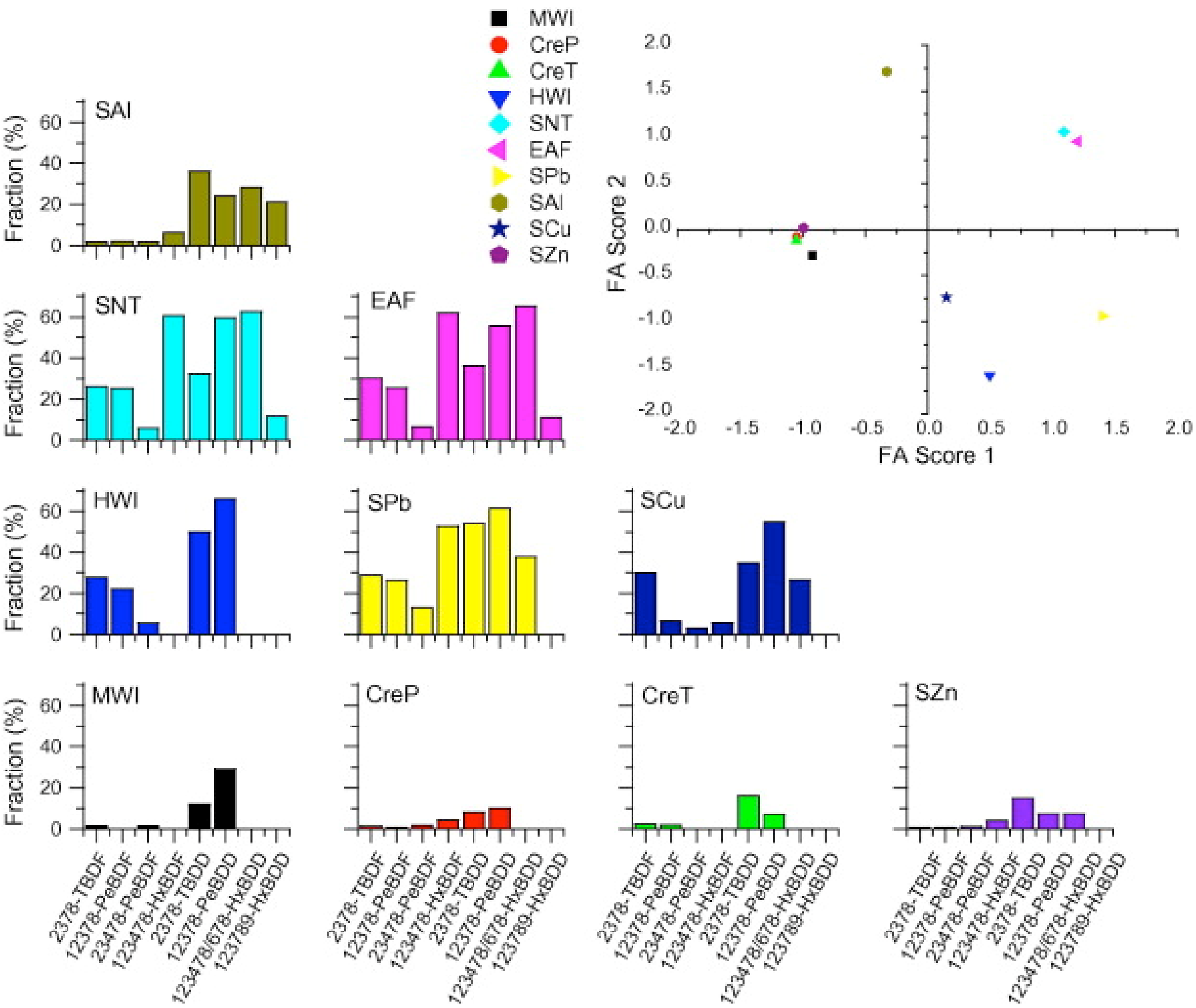


Figure 48: Congener profiles of PBDD/F by the ratio of 2,3,7,8-substituted congeners to corresponding homologues classified by factor analysis (Du et al.)

Conversion during life span of product (e.g UV or thermal stress)

For PBDE the levels of PBDD/PBDF contamination increases during the life span by photolytic conversion which can take place, for example, in plastic matrices (Kajiwara et al. 2008) or treated textile (Kajiwara & Takigami 2010).

In the textile experiment, involving exposure of an indoor sample to sunlight behind a window for 371 days, thus simulating the exposure of curtains and similar textiles, the total PBDF concentrations in the samples reached 17,000 ng/g – equivalent to approximately 142 ppm on the basis of DecaBDE levels of 120 mg/g in the textile. The levels after a year were approximately 7 times the initial levels at 2,400 ng/g – equivalent to approximately 20 ppm on the basis of DecaBDE levels of 120 mg/g.

Among the congeners analysed, OctaBDF was the predominant congener throughout the exposure, constituting 50% to 80% of the total PBDF. The concentrations of mono- to PentaBDF congeners showed a continuous increase during the experimental period. The authors suggest that flame-retarded products under daily usage have the potential to be major sources of PBDF contamination in indoor air and dust (Kajiwara & Takigami 2010). These results suggest that BDE 209 added to the curtain material photodegraded and contributed to the synthesis of the full range of PBDF (MonoBDF to OcaBDF). A similar trend was found in a television casing reported previously (Kajiwara et al. 2008). It should be noted that as well as the PBDD/DF the experiments also §resulted in a small, but increasing, level of the POP-BDE in the sunlight exposed samples over time.

Electronic waste containing PBDE but also other BFRs can contain high levels of PBDD/DF at the end-of-life. Sakai et al detected high levels of PBDD/DF (3,000 to 130,000 ng/g) in flame retarded plastic, waste television cabinets and printed circuit boards at their end-of-life (Sakai et al. 2001). The DecaBDE formed significant quantities of POP-BDE in the residues along with the PBDD/DF. In these circumstances it is extremely difficult (and from an environmental/health perspective, probably not sensible) to attempt to distinguish between PBDD/DF associated entirely with the POP-BDE and with DecaBDE:

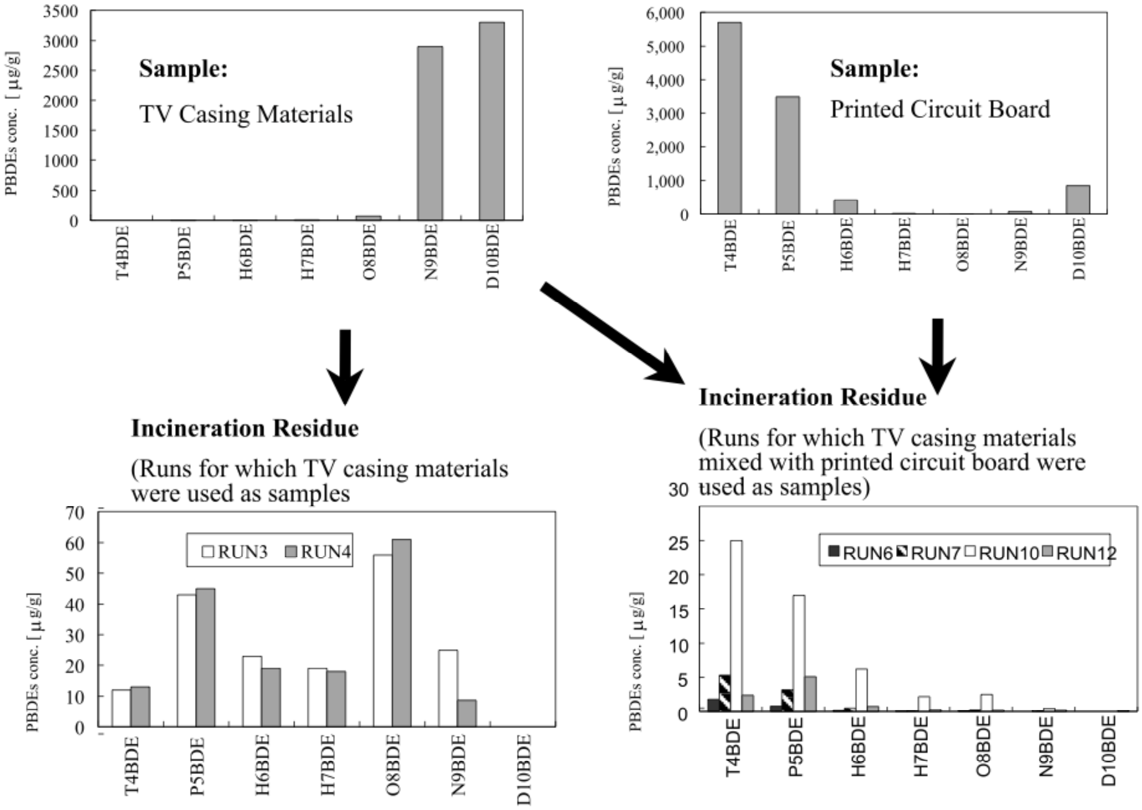


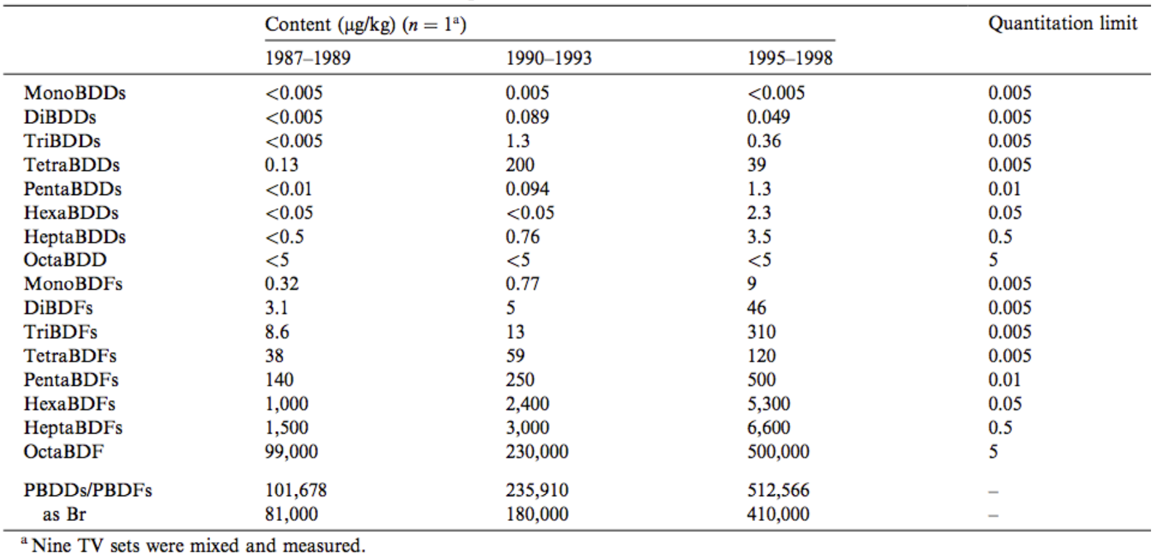
Figure 49: Samples and PBDE homologues profiles in incineration residues (Sakai et al. 2001)

Table 38: concentrations of flame retardant compounds and dioxins (PBDD/DF, PCDD/DF and BFRs) in end-of-life WEEE materials (Sakai et al. 2001).

Analytical item	Samples			
	PBDEs/PE	TBBP-A/ABS	TV casing materials	Printed circuit boards
Chlorine (Cl) (%)	ND < 0.025	2.0	0.021	1.1
Bromine (Br) (%)	8.8	8.8	3.7	2.2
Flame retardant PBDEs (µg/g)	20,000	–	6300	11,000
Flame retardant TBBP-A (µg/g)	–	420	2.4	500
PBDDs/DFs (ng/g)	3100	0.62	3000	130,000
PCDDs/DFs (ng/g)	–	0.04	0.69	0.31
PCDDs/DFs (ng-TEQ/g)	–	0.002	0.0008	0
Br$_1$ Cl$_y$DDs/DFs (ng/g)	–	–	ND	ND
Br$_2$ Cl$_y$DDs/DFs (ng/g)	–	–	ND	ND
Br$_x$Cl$_1$DDs/DFs (ng/g)	–	–	ND	9.5
Bromobenzene(PBBz) (ng/g)	–	–	5800	95,000
Bromophenol (PBP) (ng/g)	–	–	79,000	20,000

Significant levels of PBDD/DF have also been detected in waste television cabinets and other flame-retarded plastics (Watanabe & Sakai 2003). Tasaki et al. also reported high levels of brominated dioxins in the rear covers of end-of-life TV sets with an increasing time trend from 1987 to 1998 (Tasaki et al. 2004b). PBDD/DF levels rose from 100 ppm (1987 to 1989) to 500 ppm (1995 to 1998). The levels were therefore about an order of magnitude higher compared to the high levels of PBDD/DF reported as contamination of DecaBDE product thus indicating significant PBDD/DF formation during lifespan of the TV sets:

Table 39: Contents of PBDD/DF in rear covers of TV sets in Japan (Tasaki et al. 2004b)



	Content (μg/kg) ($n = 1^a$)			Quantitation limit
	1987–1989	1990–1993	1995–1998	
MonoBDDs	<0.005	0.005	<0.005	0.005
DiBDDs	<0.005	0.089	0.049	0.005
TriBDDs	<0.005	1.3	0.36	0.005
TetraBDDs	0.13	200	39	0.005
PentaBDDs	<0.01	0.094	1.3	0.01
HexaBDDs	<0.05	<0.05	2.3	0.05
HeptaBDDs	<0.5	0.76	3.5	0.5
OctaBDD	<5	<5	<5	5
MonoBDFs	0.32	0.77	9	0.005
DiBDFs	3.1	5	46	0.005
TriBDFs	8.6	13	310	0.005
TetraBDFs	38	59	120	0.005
PentaBDFs	140	250	500	0.01
HexaBDFs	1,000	2,400	5,300	0.05
HeptaBDFs	1,500	3,000	6,600	0.5
OctaBDF	99,000	230,000	500,000	5
PBDDs/PBDFs	101,678	235,910	512,566	–
as Br	81,000	180,000	410,000	–

[a] Nine TV sets were mixed and measured.

These increases are similar to the seven fold increase in PBDF from DecaBDE in textiles within the first year sunlight exposure found by Kajiwara and described above (Kajiwara & Takigami 2010). The levels of PBDD/DF levels in the end-of-life products are an order of magnitude higher than the levels of contamination in commercial PBDE (Hanari et al. 2006b). Consequently the inventory of 2,271 kg PBDD/DF from contamination of commercial PBDE products might increase during production and lifetime by an order of magnitude which would imply c.20,000 kg PBDD/DF per year. This might be at least part of the explanation for the high PBDF levels found in Japanese house dust

The extent to which the PBDD/DF in plastics and on textiles result in an actual indoor exposure of consumers is currently unclear. The high potential of such an exposure has been demonstrated and there is evidently a significant threat of PBDD/DF release and exposure from both usage (where dust is an obvious potential pathway (Suzuki et al. 2010)) and in recycling and end-of-life treatment scenarios. These are discussed further in the following Appendix.

Conclusions

During the entire life cycle of PBDE-containing materials PBDD/DF are formed in tonnes scale. The contemporary levels of PBDD/DF in indoor dust, food, human tissue and human milk demonstrate that part of these PBDD/DF are released and have already accumulated in the food chain. This highlight the importance to address these compound class and to minimise and avoid further releases. While PBDE (including DecaBDE) are found to have a key relevance for formation and release of PBDD/DF (and if chlorine is present in thermal processes also PXDD/DF) it is clear that also other BFR (in particular brominated aromatic compounds) are precursor for PBDD/DF depending on the thermal formation conditions.

The increase in levels of PBDD/DF during the life cycle of PBDE-containing materials highlight the crucial importance of responsible end-of-life treatments and management of residues in rder to minimise the releases of these hazardous substances.

Appendix 3: Operations to recycle and recover articles containing POP-BDE and an assessment of their possible health and environmental impacts

This Appendix summarises and assesses the information collected from Parties and observers, scientific and gray literature with the goal of describing the health and environmental impacts of recycling activities, including transport and storage, and of using recycled articles containing PBDE.

The appendix, together with Appendix 5(c) includes an assessment of possible impacts on the environment and health impacts on workers, local populations, vulnerable populations and consumers.

The previous section introduced brominated dioxins and furans and similar unintentionally produced organic pollutants[47].

This section describes release and emission data on PBDE and other unintentionally produced organic pollutants (including process specific information in relation to brominated dioxins and furans) for

(a) The more common and important operations to recycle various materials and products. Operations described include shredding and re-moulding of plastics and the fabrication of rebonded carpet underlay from scrap polyurethane foam[48].

For each of these operations the information in the literature has been reviewed and summarised in relation to:

(i) Possible emissions that may occur through existing processing and recycling operations

(ii) Information on relevant monitoring and exposure data such as occupational exposure and levels of pollutants in local environments and biota;

(b) Tertiary recycling operations

(c) From disposal operations including incineration, landfilling and open burning;

(d) Reviews and summarises information on the presence of PBDE in articles produced from recycled materials and health risk from use of such articles;

Knowledge gaps identified in this section are included in the Appendix 6.

The ranking of exposure scenarios from recycling and disposal operations according to estimated risks to health and the environment is included with the selection of BAT in Appendix 4 (c).

The principle operations considered in relation to the common recycling operations are the re-use and recycling of:

a) Flexible polyurethane foams (for PentaBDE), and

b) ABS plastics and other polymers (for OctaBDE)

c) Printed circuit boards (PWBs)

These are the two main categories of materials that have been identified in Appendix 2 (e) as being most relevant to recycling of POP-BDE materials and together they are estimated to cover at least 90% of the total usage. A third category, Printed Circuit Boards, has also been included to address the likely recent use of PentaBDE formulations from China which are likely to have been used in these applications. In the case of the PWBs the main interest is in recycling the precious metals rather than polymers and so the approach can be different from that adopted for the polymers in any case.

Many of the minor uses of the POP-BDE will be addressed by the sections dealing with shredder wastes as many of those wastes are likely to ultimately partition to this fraction.

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[47] Para 3 (b) (ii) of the original Terms of Reference

[48] This was the only recycling operation confirmed by any party in their responses to the Secretariat. Canada confirmed that there were two manufacturers who "*believe their rebonded foam carpet cushion may contain Penta and OctaBDE*". The Canadian submission added that "*more information is not forthcoming until analysis of this product can be performed*". Although there was no response from the USA it is known also that there are Rebond manufacturers using foam containing PentaBDE.

Recycling processes can be classified in a variety of ways. In 1991, the United States Environmental Protection Agency (USEPA) introduced a nomenclature that describes the three distinct approaches to categorisation for recycling polymers:

a) Primary - applications producing the same or similar products (e.g returning of pre-consumer production scrap to the process)

b) Secondary - producing products with less demanding specifications by physical reprocessing (e.g. shredding, grinding and melting) and reformation of post-consumer recyclate.

c) Tertiary - using the recyclate as a chemical raw material where the components are isolated and reprocessed for use in manufacture.

A fourth catergory is sometimes added to this list (Selke 2006):

d) Quaternary - using the recyclate as a source of energy

Selke notes, however, that the quaternary category "*is often not considered to be true recycling*". In most regulatory regimes use for energy is classed not as recycling but as "*recovery*" or even just as "*disposal*"[49].

In Euorpe it is more common to use the terms mechanical recycling and feedstock recycling. Mechanical recycling cover primary and secondary recycling and, as the name indicates, uses mechanical processes to convert the polymer to a usable form. Feedstock recycling is equivalent to tertiary recycling and the use of the polymer to produce a chemical raw material. This is generally used for the production of new plastics but could be used for fuel, or other industrial processes. The term "recovery" is often used to encompass both mechanical and feedstock recycling plus, sometimes, incineration with energy recovery or combustion as an alternative fuel, such as in a cement kiln.

To avoid confusion, therefore, it is proposed to use the terms Primary, Secondary and Tertiary recycling in this report but then to use "energy recovery" instead of "quaternary recycling". The consideration of options for energy recovery are included in Appendix 3 (c) on 'end-of-life options'.

The USEPA approach considers "recycling" to be the processing of waste to make new articles. Because, for example, bottles intended for re-use are not made to be discarded and become waste, re-use is not considered recycling by EPA. Re-use would also generally be included in the European Environment Agency[50] definition of "*Waste minimisation*":

"Measures and/or techniques that reduce the amount of wastes generated during any domestic, commercial and industrial process".

Thus reuse is generally regarded as one form of source reduction i.e. minimising the amount of material entering the environment. However the OECD working definition of waste minimisation covers not only re-use but also recycling:

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[49] See, for example, the decision of the European Court of Justice in relation to the EU interpretation (European Court of Justice 2002). This will changing somewhat when the revisions to the Waste Framework Directive are implemented in December 2010 (European Union 2008).

[50] http://scp.eionet.europa.eu/definitions/minimisation

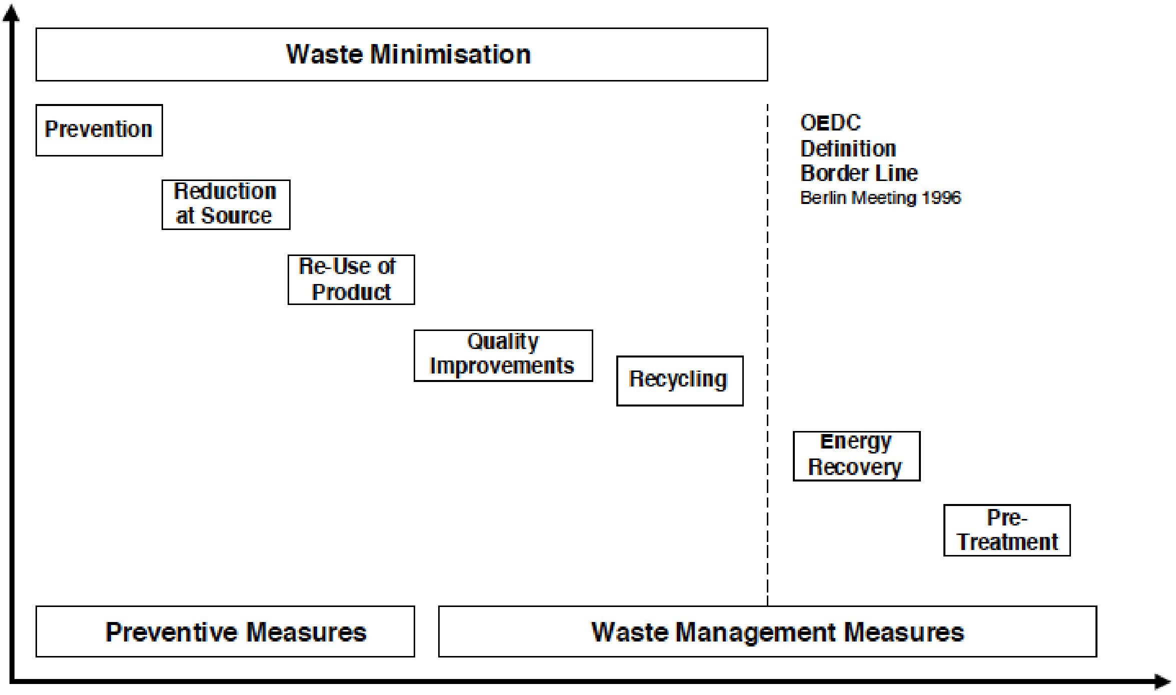

Figure 50: OECD working definition of waste management from 1996 as reported by the European Environment Agency (Riemer & Kristoffersen 1999)

In simple reuse, an article remains intact and is re-used in its original form. In secondary and tertiary recycling, the original article is destroyed and a new, possibly very different, article is made from the remains. Simply focusing on recycling does not address the issue of exposure to POP-BDE and so reuse options will be briefly discussed in this section.

The operations which will be considered in each case are:

Primary Recycling - Pre-Consumer Scrap

Primary recycling is the recycling of industrial scrap produced during the manufacture of articles. This was defined as "*home scrap*" by the USEPA[51]. Historically this would have included, in the case of PentaBDE, the use of processing scrap for “rebond” (carpet padding). As the POP-BDE are no longer produced then there should no longer be any primary recycling issues as no manufacturing process should be using POP-BDE in the manufature of virgin material (that has not yet been processed, used and collected) articles.

Secondary Recycling - Physical Reprocessing

Secondary recycling involes the physical shredding, grinding, melting, and/or reforming of post-consumer recyclate (polymer material a material that has already been processed, used and collected). The basic polymer is not altered during the process of secondary recylcing. In the case of this study the principle operations which need to be addressed:

1) Using PentaBDE-treated PUR foam in rebond; and
2) Using OctaBDE-treated ABS for plastics.

There are normally two different polymer fractions available on the market. Well-defined polymer fractions are separated from, for example, mattresses or from WEEE in dismantling plants, especially in the later case, in the course of cathode-ray tube glass recovery. The main part of WEEE plastics and a proportion of PUR foam, however, is found as a mixed shredder residue produced as a by-product in metal recovery processes – either from autoshredders or e-waste shredders. It can be isolated from bulk WEEE by means of shredders, magnetic separators and cyclones (Cui & Forssberg 2003)(Schlummer et al. 2007). The details of the separation technologies available are discussed in the next Appendix.

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[51] The term "*home scrap*" means those scrap materials virgin content of a material or by-products generated from and commonly reused within an original manufacturing process.

Tertiary Recycling - Chemical Reprocessing

Two types of feedstock recycling can be distinguished: chemical processes and thermal processes (Lundquist et al. 2001). A basic schematic adapted form Lundquist helps to illustrate the distinction:

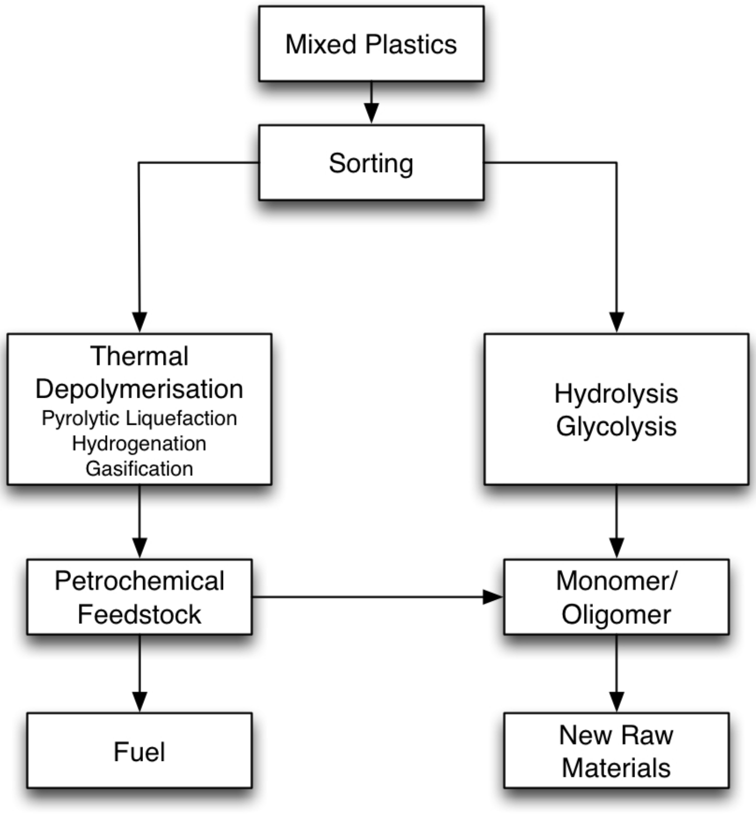

Figure 51: thermal and chemical feedstock recycling (adapted from (Lundquist et al. 2001)).

The primary goal of tertiary recycling is the regeneration of purified starting materials. Chemical reprocessing may involve depolymerisation of the article with subsequent regeneration and purification of resulting monomers (or oligomers).

The monomers may then repolymerised and the regenerated or reconstituted polymer is formed into new articles. Regenerated monomer, polymer (or both) may be blended with virgin materials. The regeneration process may involve a variety of monomer/polymer purification steps in addition to washings, such as distillation, crystallization, and additional chemical reaction (USFDA 2006). In some cases the depolymerised material is used to recover energy rather than materials. In these circumstances the use of thermal depolymerisation moves to the energy recovery section rather than being a form of recycling.

Feedstock recycling can be used for contaminated and heterogeneous plastics waste. Plastics have to meet certain minimum quality standards and must be preceded by extraction of contaminants, i.e. dehalogenation and degrading extrusion to separate halogens and heavy metals contained in additives (Dreher et al. 2004).

Energy Recovery:

Common treatment options in which energy is recovered include the use of incineration, cement kilns. Metallurgical processes also fall into this category in relation to the POP-BDE as whilst metals are recovered for recycling the polymer to which the POP-BDE had been added is used for the recovery of energy. The presence, and recovery, of the metal in these cases is due to the mixing processes, usually shredding, used in disassembly rather than to any specific use of POP-BDE in metal components. Metallurgical processes are therefore included with the other energy recovery options and considered in more detail in the end-of-life section below.

The main recycling options can therefore be summarised as:

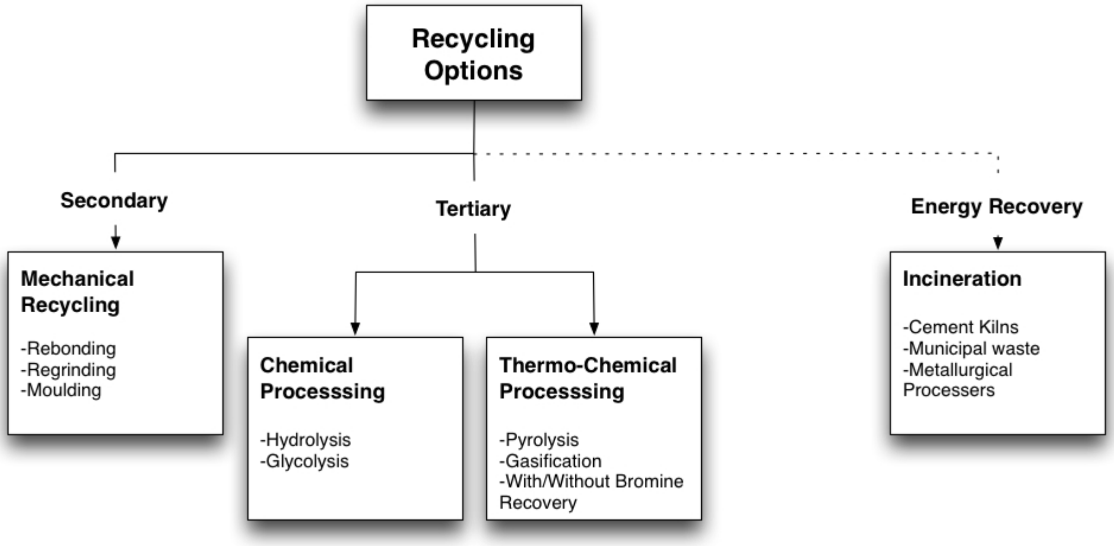

Figure 52: Recycling options for polymers containing BFRs and particularly PUR foams.

Appendix 3 (a): Re-Use and Secondary Recycling Operations

Appendix 3 (a) (i): Re-Use of Articles

Direct re-use relating to POP-BDE is most relevant to furniture and mattresses with a more limited relevance to car-parts. ABS casings and printed wire boards are almost invariably recycled involving industrial processing and remanufactured rather than re-used – although there are minor exceptions, some of which can involve risks associated with human and animal exposures:

Photograph 2: Minor examples of computer component direct re-use
http://www.unplggd.com/ol-images/hometech/uploads/2007-10-10-hillbillymouse.jpg,
http://lynnepope.net/images/recycling.jpg,
http://1.bp.blogspot.com/_aOVUVB-gmBA/StHIxobHjSI/AAAAAAAAN2M/-UeHJIL8Ye0/s1600-h/ComputerPartsReuse+%282%29.jpg

There are an increasing number of companies who specialise in recycling mattresses for in-direct re-use. No accurate statistics exist on how many units of used mattresses are renovated and resold. In 1995 the International Sleep Product Association estimated that this market could be up to 35% of the new units sold annually (equivalent to 13.9 million units in the US in 2003) (International Sleep Products Association 2004).

The approach used for marketing mattresses for re-use varies from simple cleaning of the mattresses before returning them to the market through to complete dismantling and reconstruction. Many used mattresses from parts of the US are also exported to Mexico for reuse(Rowe 2010).

The operational exposure risks associated with the recycling of mattresses are clear from an article in the San Francisco Chronicle (DeBare 2008) describing a mattress recycling operation in San Leandro, California:

"*Sergio Solarez smoothly ran his utility knife around the side of a queen-size mattress, like slicing a cake into two layers. He pulled off the flowered fabric and two layers of foam, flipped the mattress over with an explosion of dust, and sliced and stripped the other side until he was left with a bare set of springs.*

……

The bigger hazard is dust, which seems to billow endlessly out of the mattresses.

"Even the nice ones have dust,""

Unfortunately there seem to be no data of the levels of POP-BDE in the high levels of mattress dust to which these workers are clearly regularly exposed.

Appendix 3 (a) (ii): Physical Reprocessing

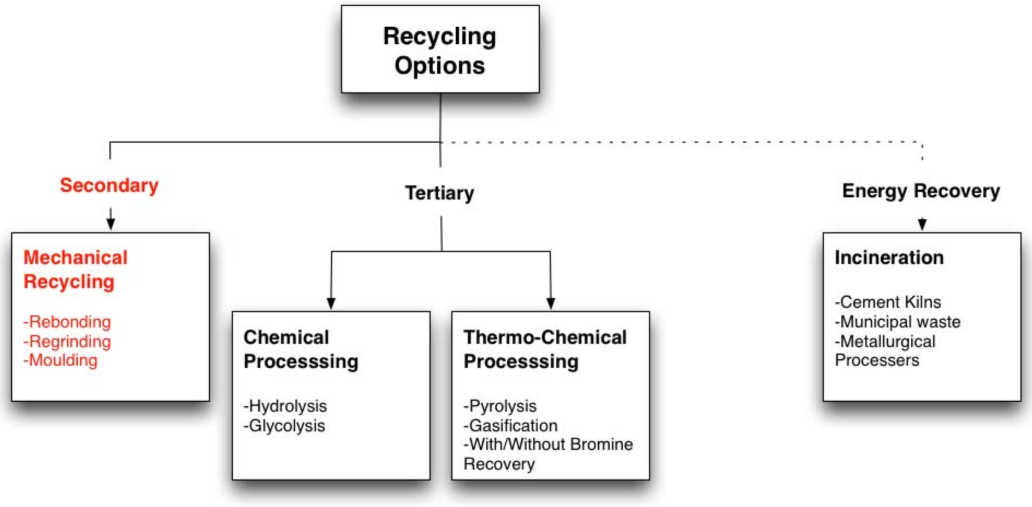

Figure 53: Secondary recycling options.

Before recycling the materials must be collected from waste. The foams to be recycled can arise from a number of sources. The principal ones being:

- Mattresses
- Furniture/ carpet padding
- Cars and transport

For the consistent bulk supplies needed for recycling emphasis is placed on mattresses - together with scrapped cars. Recycling of vehicles is normally a process involving the depolluting of the vehicle in which batteries and all fluids are removed, increasingly combined with the manual stripping of components which can be re-used or recycled. This is then followed by fragmentation in a shredder, where the metals are separated from other materials. Plastics, rubber, paper, wood, dirt, etc. end up in several fractions of shredder residues. The plastic parts mainly end up in a shredder residue fraction called "automotive fluff". Whilst both sources have been used to recover foam the source segregated route gives a much cleaner and more useful output – and a better chance of effectively sorting any residues contaminated with POP-BDE along with other hazardous components. A more detailed discussion of shredding is included below.

A review of mattress recycling by the International Sleep Products Association summarises some of the key issues with materials recovery for mattresses (International Sleep Products Association 2004):

- The economics of recycling are finely balanced and the value of the recovered mattress materials alone cannot sustain a mattress disposal operation
- Finding a sustainable income source to supplement the scrap revenue is therefore key to a successful operation (fees from consumers, retailers, manufacturers or municipalities equal to the “*tipping fee*” that a landfill would otherwise have charged had the mattress instead been dumped at the landfill).
- Facility location and security are critical as it is important to minimise the cost of moving product to the facility and when selling the recovered materials to potential customers.
- Preparing recovered scrap in saleable form can be challenging – particularly for the steel scrap which is by far the most valuable and easily recovered mattress material.
- Consistent product volume is necessary to maintain an efficient dismantling operation.
- Low-tech manual dismantling appears to be more efficient than more automated alternatives, although new technologies are under development a manual approach using relatively low-skilled manual labourers equipped with box-cutters is the preferred approach at present. Capital expenditures are still needed, however, to shred product that cannot be quickly dismantled by hand. These include magnetic separators, bailers, forklifts to handle the product and the scrap, etc.

- A sustainable supplemental income source is necessary on top of the value of the recovered steel scrap. Furthermore, many facilities cannot process mattresses efficiently without cutting the units into smaller pieces[52].

Rebond – Recycling PentaBDE-treated PUR Foam:

Rebonding is the process whereby scrap PUR foam is shredded into small pieces and then reconstituted with a polyurethane adhesive or isocyanate binder to produce an aggregated polyurethane foam product (USEPA 1996a). The main use is in the production of carpet cushions (Eaves 2004) as shown in Figure 54 below. The major slabstock PUR foam producers tend to produce little waste from cutting or moulding processes because most scrap is used in these rebond operations for the production of carpet backing:

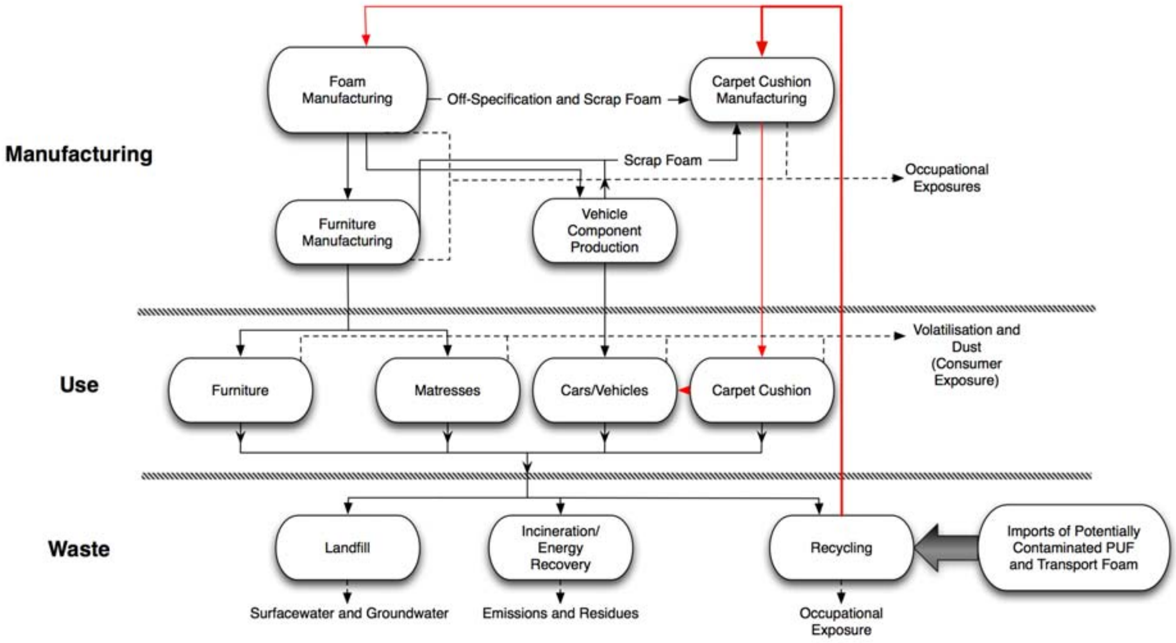

Figure 54: Simplified materials flow of foam and recycling routes (marked in red) to carpet cushions (adapted from (USEPA 2005)).

Other uses of rebond include school bus seats (USEPA 1996b) and floor mats for gymnasia (Zia et al. 2007).

Eaves (Eaves 2004) describes carpet-cushioning foams as "*a North American phenomenon*" [53] noting that this application "*is almost non-existent in the rest of the world*". Carpet cushion can be either high-density prime or rebond foam. Polyurethane recycling, other than rebond has been "*quite limited*" in the United States (Selke 2006). Media reports indicate that other recycling uses for foams which are not re-used in the refurbishment of mattresses or for rebond include pet bedding and insulation (Rowe 2010). It is assumed that these are relatively low volume outlets for foams.

Whilst the use of carpet cushion may be almost unique to North America it is noted that the European Isocyanates Producers' Association says that "*up to 50,000 tonnes of rebonded foam are processed each year in Western Europe and new applications are constantly being developed*" (ISOPA 2001). It is assumed that this rebounded foam is more likely to be used for transport than carpet padding and that it is much less likely than foam in the US to contain PentaBDE given the much smaller levels of intitial use in Europe.

There are few publicly available data on the volumes of material involved – and USEPA was unable to assist with more specific details. However literature sources indicates that in 2002, 850 million pounds (385,000 tonnes) of polyurethane was used to make carpet cushion (Zia et al. 2007). Of this 830 million pounds (376,000

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[52] The consultants are aware that many grate incinerator operators refuse to handle mattresses because of the problems the steel springs can cause with the operation of the rocker grates.

[53] Rebond is used in Canada

tonnes) was made from scrap polyurethane foam. Approximately 50 million pounds (23,000 tonnes) came from post-consumer waste (Zia et al. 2007).

Many slabstock foam facilities in the US include rebond operations but some rebond operations are free-standing. There is also increasing evidence of production in Asia exporting to the US to meet that market demand.

The '*free-standing'* facilities also acquire bales of scrap from plants that do not have rebond operations (USEPA 1996a). Rebond creates a large market for scrap foam as a raw material and the demand is so great for this material that scrap urethane foam is imported from Europe into the United States (Andrady 2003). The POPRC Risk Management Evaluation for PentaBDE says that the "*EU has been an exporter of scrap foam (around 40,000 tonnes/year) to the United States for this use (RPA 2000)*". The original source for this, however, is an article in ENDS in 1998 (ENDS 1998) which relates to off-cuts and scraps from the slabstock industry. This says that large quantities of production waste are generated - an average 20% of input, and up to 40% when cutting more intricate shapes. It is not clear, however, how much post-consumer waste, if any, might also have been exported – nor what quantity of PentaBDE might have been included in the export.

There are concerns that higher legislative targets for vehicle recycling could mean that the amount of scrap will "*significantly outpace demand for rebond*" (Eaves 2004).

Mattresses contain large amounts of foam (roughly 10% by weight) (International Sleep Products Association 2004). In the 2004 International Sleep Products Association review of mattress recycling the demand for scrap foam for the production of carpet underlay through a rebonding process was reported as being strong, with the United States being "*a net importer of roughly 150 million lbs. of used flexible foam at prices ranging from 25 to 35 cents/lb*" (International Sleep Products Association 2004).

There have been increasing concerns amongst recyclers of the consequences of the regulatory interest in PBDE. International Sleep Products Association (ISPA) created the Mattress Disposal Task Force (MDTF) in 2003, for example, to review Used Mattress Disposal and Component Recycling (International Sleep Products Association 2004). One of their recommendations was that:

"The mattress industry should work with the polyurethane foam industry to remove and prevent further legal restrictions on the recycling of foam: Specifically several states have or are considering bans on the use of certain PBDE fire retardants in foam. These laws may have the effect of limiting the use of post-consumer foam in foam carpet underlay, the primary market for used mattress foam".

It is not clear at this stage whether the increased regulations have had any affect on diversion and recycling routes. Much of the industry literature is silent on the issues about PBDE and other flame-retardants and the impression given is that recyclers only occasionally consider the issue of contamination by retardants.

Obviously, this could have important implications for human exposure to POP-BDE and any future risk assessment scenarios. This also has implications for releases to the atmosphere, as indoor air environments are likely to become preferentially contaminated. Releases to outdoor air will then occur as result of evaporative losses from building/ vehicle interiors and ventilation.

Regrinding

Eaves notes that the declining use of scrap foam in North American carpet cushion has spurred the uptake of innovative processes allowing manufacturers to non-cryogenically grind foam scrap from the manufacturing process. The ultrafine powder is then used to displace more than 20% of the virgin chemicals in the manufacture of new foam.

With minor formulation adjustment, the resulting foam is said to have properties equal to the original foam. The economics are driven largely by the difference between the value of scrap and the price of chemical raw materials and this has led to its rapid adoption (Eaves 2004).

This technology also has potential to allow the recycling of significant amounts of post- consumer foams – although that is probably dependent on obtaining large consistent streams with similar additives such as those from hospitals and hotels.

Shredder plants

The simpler academic life-cycle approaches tend to define separation efficiency only for the different individual materials. This ignores the fact that recycling streams are a complex combination of materials and often does not reflect common industrial practice. Because many mixed materials cannot be easily physical separated they are often mixed and treated together. This can seriously affect the quality of the waste streams for recycling and the assessment of the benefits associated with recycling. With the current approach to product design and production together with only limited legislation requiring producer responsibility for post consumer products it is not possible recover all materials as segregated waste streams even in more developed countries.

van Schaik (van Schaik & Reuter 2010) warns:

This argument holds even more for the minor toxic elements, which are often present in low concentrations and cannot be ignored for their toxic and harmful nature and obliged control and monitoring as imposed in Annex II of the WEEE directive. "…These toxic elements, present in different physical materials (e.g. flame retardants plastics) could be 'dragged' along with the (un-liberated) physical particles to various recyclate streams (e.g. plastic with flame retardant connected to steel ending up in the steel stream and being processed in the steel convertor) where their destination and behaviour needs to be predicted in order to control the dispersion and recovery of toxic elements" (van Schaik & Reuter 2010).

Shredder plants are one example of where this problem occurs in practice. Indeed Shredder plants for treatment of end-of-life vehicles already listed in Annex C of the Stockholm Convention as a source that has the potential to form and release chemicals listed in Annex C. The BAT/BEP guidelines also include a chapter on these facilities. E-waste can be shredded in large multi-purpose shredders with cars and other household goods or in smaller units dedicated to e-waste – normally the printed circuit boards and plastic materials discarded after the recovery of metals (Sakai et al. 2000). While automobile shredder residues consist of a high percentage of fine materials, mainly glass and others, about 90% of electronic goods shredder residues can be plastics (Sakai et al. 2000).

End-of-life-vehicles (ELVs) are processed through shredders. The normal practice in most countries is to shred them along with other end-of-life metal products (such as bicycles, office furniture, vending machines and household appliances). Shredders are large-scale machines equipped with one or more anvils or breaker bars and lined with alloy steel wear plates. The scrap processors normally use 3,000 to 8,000-hp hammer mills in which electric motor drive rotors with free-swinging alloy steel hammers. Beneath the shredder is a vibratory pan, which receives the shredded material discharged through the grates. Processing-unit operations vary but the basic process involves air classification of the "lights" fraction followed by one or more stages of magnetic separation to recover the ferrous metals. Trommels and screens are then used to remove particles smaller than about 15 mm followed by one or more stages of eddy-current separations to recover the nonferrous metals. Typically a ferrous metal stream is produced, which is relatively clean and consists of small (50 mm) pieces of steel and a shredder residue or '*fluff*' stream.

Photograph 3: Typical shredder residue (CalEPA 2006).

The fluff contains the fragments of non-ferrous metals and other materials that entered the shredder typically a mix of polymers (plastics, rubber, and polyurethane foam), a "fines" fraction that includes metal oxides, glass, and dirt, together with residual amounts of ferrous and nonferrous metals.

The shredder is also known as a fragmentiser and thus the shredder residue is sometimes colloquially called "frag". Occasionally and not particularly accurate in the light of the mixed feedstock of which cars may be 50% or less it is also called autoshredder residue ('ASR').

The normal processing of cars for shredding includes (Ecobalance 2002):

- Materials and parts e.g. tyres, batteries are removed provided it is financially worthwhile to do so. Parts may be cleaned for resale and materials are separately collected.
- Materials collected by the dismantler are periodically collected and transported to an appropriate facility for further processing and treatment, e.g. smelter, where secondary material is produced for sale.
- The dismantled ELV may be crushed using a number of methods, these being shearing, baling or flattening. Such activities may occur at the dismantler or at a dedicated site (a scrapyard or feeder site).
- Ultimately, the ELV ends up at a shredder which breaks the vehicle into small pieces that are subsequently divided and sorted into ferrous metal, a heavy fraction (non ferrous metal (NFM) fraction) and light fraction (fluff).
- The ferrous fraction is relatively pure, having been removed from other material using magnetic separation after shredding. It is transported for further processing in an electric arc furnace where it is made into a secondary material for resale.
- The NFM fraction consists of aluminium, lead, copper, zinc, etc as well as glass, rubber and some plastics. It is transported to a heavy media separation plant for further processing. This plant separates out non-ferrous metals from other material (plastics, etc) on the basis of differences in density. All separated metals are then transported for further processing.

A schematic of the shredding process is:

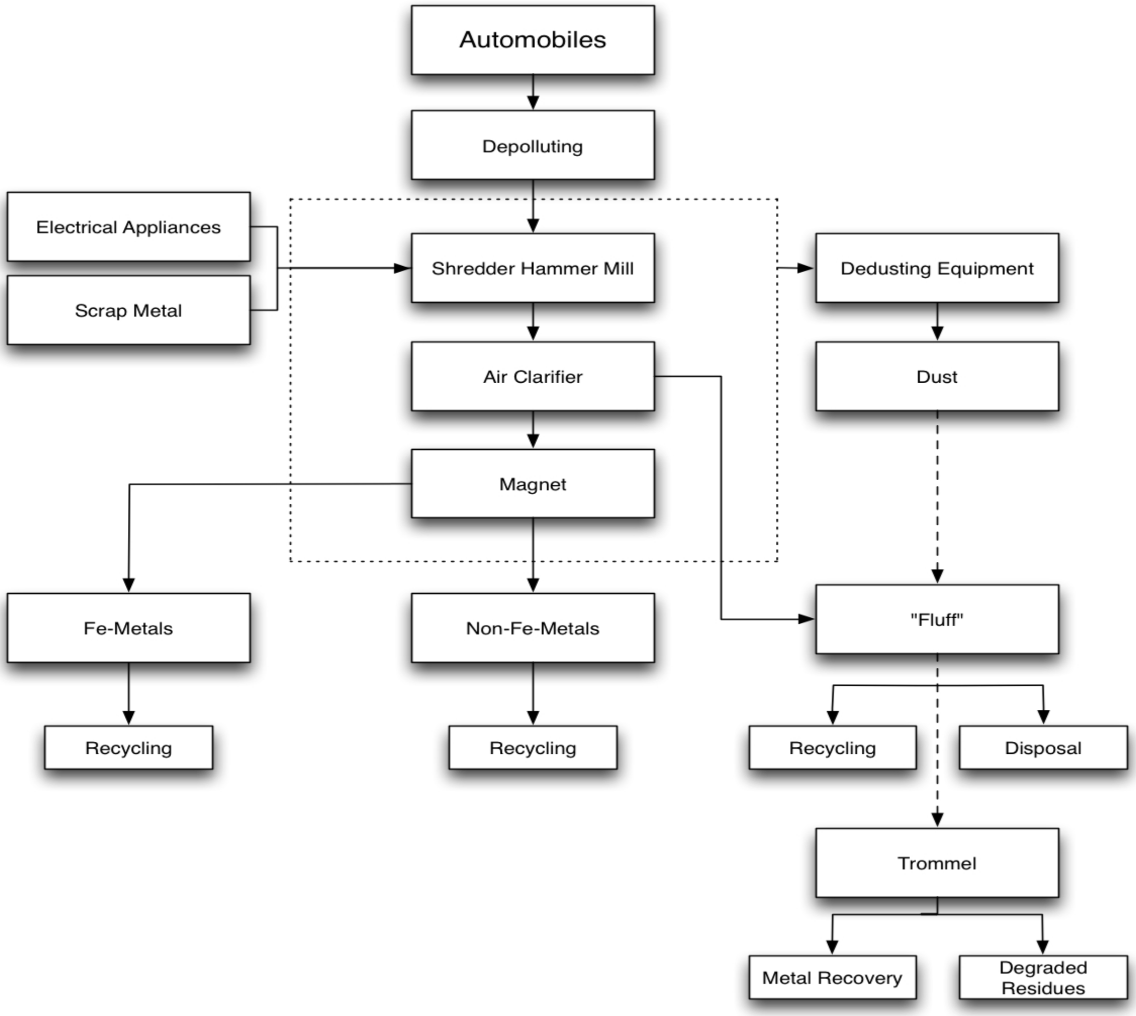


Figure 55: Overview on the shredder process

About 12 million tonnes per year of steel and non-ferrous metals are recycled at over 200 dedicated shredding operations in the United States (Boughton 2007). The shredder waste is estimated to be between 20% and 35% of the vehicle weight depending on the level of component removal before shredding (Stockholm Convention 2007b). Thus over 3 million tonnes of shredder residues are generated in the US each year. Nearly all of these residues are landfilled, often being used as ‘daily cover’(Boughton 2007). Most of the residues in Europe are similarly disposed to landfill “*because of its complexity*” (Nourreddine 2007). In Japan shredder residues total more than one million tons per year in Japan and Sakai reports that “*most of them have been landfilled in non-controlled landfill sites*” furthermore he notes that “*about 500 000 tons of shredder residues have also landfilled illegally on Teshima Island in Kagawa Prefecture, some of which have been burned in the open*”(Sakai et al. 1998)[54].

The Stockholm Convention BAT-BEP guidance (Stockholm Convention 2007b) recommendation is that:

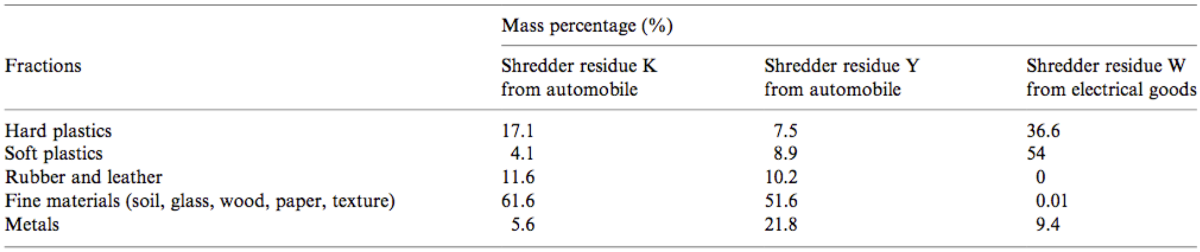
“*shredder residues are always contaminated and must only be disposed of in an incineration dedicated plant*” (sic).

Whilst the appropriate treatment is deemed to be incineration in a facility meeting the requirements of BAT/BEP the guidance says, as a secondary measure “*if such a facility is not available, disposal in a sanitary landfill may be preferred to other forms of disposal*”. The guidance emphasises that “*shredder residues should never be burned in an open fire or in inappropriate facilities*”.

Notwithstanding the advice in the guidance that disposal is the preferred option in this case there have been a number of proposals to recover more material from the shredder residues.

The composition of shredder fluff will vary considerably from batch to batch and shredder to shredder – the outputs obviously depends upon the inputs which change due to the different mixes of raw materials being processed; and the differing levels of pre-processing and inspection by shredder operators. It should also be noted that shredder fluff is likely to vary significantly between shredders due to varying requirements under State and Territory licensing conditions, and the changes in those conditions over time. One important factor is the age of the cars that are being dismantled - automotive polymer applications have increased more than 600% by volume per vehicle since 1970, and current vehicles contain “*an astounding 50% by volume of polymer*” (Bhattacharya et al. 2009). An average range for shredder residues has been reported as: plastics (19–31%), rubber (20%), textiles and fibre materials (10–42%) and wood (2–5%), which are contaminated with metals (8%), oils (5%), and other substances, some of which may be hazardous (about 10%), e.g. PCB, cadmium and lead (Morselli et al.)(Nourreddine 2007). Another typical composition of shredder waste is included in the table below:

Table 40: Physical fractions of shredder residues (Sakai et al. 2000).



Fractions	Mass percentage (%)		
	Shredder residue K from automobile	Shredder residue Y from automobile	Shredder residue W from electrical goods
Hard plastics	17.1	7.5	36.6
Soft plastics	4.1	8.9	54
Rubber and leather	11.6	10.2	0
Fine materials (soil, glass, wood, paper, texture)	61.6	51.6	0.01
Metals	5.6	21.8	9.4

Copper and chlorine are present in significant quantities and are likely to promote the formation of PCDD/DF and other unintentional releases of POPs in the case of burning (Stockholm Convention 2007b).

Petreas examined the BFR content of shredder residues in California in a systematic survey, during which samples were collected from all seven operational facilities in 2004–2005. Five to ten sample points from each autoshredder pile. These samples were air dried, sieved through a 2 mm sieve, and analysed for regulated metals, PCBs and PBDE. Considering the sampling was undertaken in California the results show surprisingly low levels of total BDE. The average for POP-BDE was less than 10 mg/kg (Petreas & Oros 2009):

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[54] Action has since been taken to clean up the illegally dumped wastes in this national park (Weber et al. 2008a).

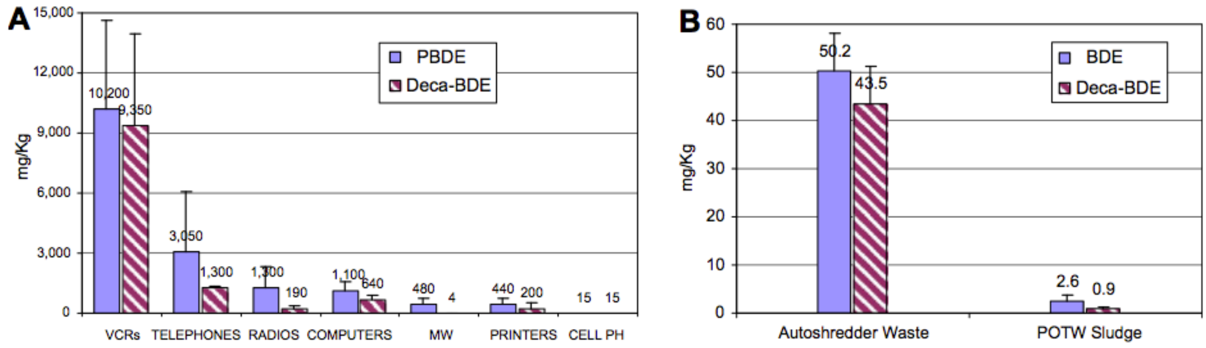
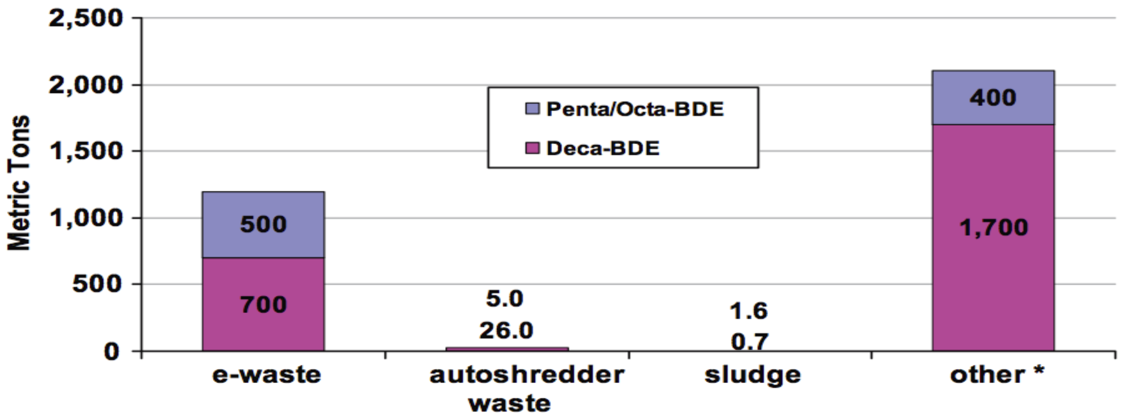


Figure 56: Concentrations of PBDE and BDE-209 in e-waste (A) and autoshredder waste and POTW sludge (B) (Petreas & Oros 2009)

These levels are lower than the total PBDE reported from Japan (Sakai et al. 2006) but unfortunately Sakai provided no results for the lower-brominated BDE. Petreas comments (as discussed in the previous Appendix) that autoshredder waste generated at a point in time reflects concentrations of PBDE (and other contaminants) present in products sold and used several years earlier and that the average lag between manufacturing and shredding of automobiles and major electric appliances may be over a decade. Whilst in a European context that means that peak levels could be expected at the time that Petreas sampled the later peak of usage in the US means that the data presented from autoshredder facilities sampled in 2004–2005 may not represent the peak of PBDE use in cars and major appliances. She therefore concluded that these data "*can serve as a warning for higher PBDE concentrations expected in autoshredder waste in the future*".

Based on these data Petreas estimated the total content PBDE content of e-waste, autoshredder waste and sewage sludge in California:



Production, MT	ΣPBDE	BDE-209	Penta-/Octa-BDE	Notes
N America	33,100	24,500	8,600	BSEF 2003
California	3,310	2,450	860	Assuming CA=0.10*N. America

Figure 57: Estimated mass of PBDE in three Californian waste streams (Petreas & Oros 2009)

Unfortunately the balance between the POP-BDE was not presented. However this shows one hundred times more POP-BDE in e-waste than in shredder residues. Patreas then assumed that California consumption of PBDE was equivalent to the 10% of North American usage. The results shows that whilst these waste streams are estimated to be responsible for just over half of the POP-BDE they do not contain the majority of total PBDE.

This finding is consistent with the conclusions reached by Morf et al who, in the case of Switzerland, determined that WEEE accounts for the largest volume of BFRs (in particular, PBDE) compared to other wastes such as autoshredder waste with approximately 75% of all OctaBDE and 44% of DecaBDE imported to the EU disposed via WEEE in the late 1990s (Morf et al. 2005).

Sinkkonen found lower levels than Petreas when sampling shredder residues from Sweden. Total Concentrations of PBDE were c. 245 ng/g with c. 60% being PentaBDE and only around 10 ng/g DecaBDE (Sinkkonen et al. 2004).

Concerns have been raised about the potential formation of PBDD/DF during shredding operations where increased surface temperatures and pressures are common (Schlummer et al. 2007).

Ma found very different proportions of PBDE and PBDD/DF for shredder waste than in dust from the e-waste workshops in China (Ma et al. 2009):

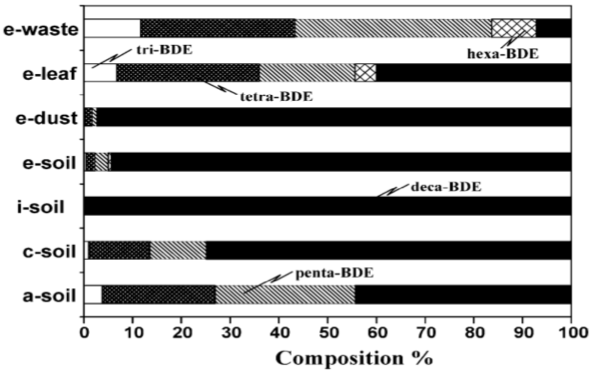


Figure 58: Composition (%) of PBDE homologues in electronic shredder residues (e-waste), leaves (e-leaf), floor dust (e-dust), and soil (e-soil) from an e-waste recycling facility and in soil from a chemical industrial complex (i-soil) and in soil from the vicinity of a copper mine (c-soil) and agricultural soil (a-soil) (Ma et al. 2009)

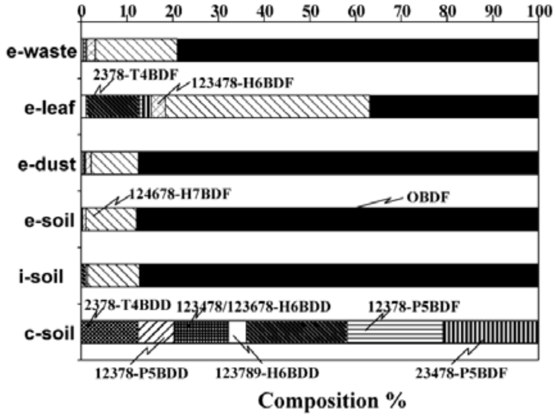


Figure 59: Composition (%) of 11 2,3,7,8-sbustituted PBDD/F congeners in electronic shredder residues (e-waste), leaves (e-leaf), floor dust (e-dust), and soil (e-soil) from an e-waste recycling facility and in soil from a chemical industrial complex (i-soil) and in soil from the vicinity of a copper mine (c-soil) (Ma et al. 2009).

The authors found a significant correlation was found between the concentrations of ΣPBDD/Fs and ΣPBDE (r^2=0.769, $p < 0.01$). Whilst some BDE 209 were released from the e-waste recycling operations and accumulate in soil and dust they also noted that "*BDE 209 is more readily debrominated to lower BDE congeners under the changes of pressure and temperature used during the low-tech recycling operations, so the composition of some BDE congeners were altered in e-wastes themselves*" during the processing. They found significant correlation among various PBDE congeners in matrices collected from the e-waste facility which supported a common source (Ma et al. 2009).

There are likely to be emissions and diffuse pollution from shredder plants, but they have not been reported and there are few data for off-site emissions of PBDE or PBDD/DF from these plants. The conditions for emissions can be assumed to be similar as for recycling plants of EE-appliances. For facilities not equipped with an efficient air pollution control device a significant flow of dust-borne PBDE may be transferred into the environment. In plants with off-gas filtering a large portion of PBDE will end in the collected fraction of gas.

The BAT/BEP guidance warns about the contents of shredder residues which are dioxin precursors which may result in the formation of PCDD/DF when burnt. These include PCB-containing condensers, PCB- or chlorobenzene contaminated waste oils or textiles, and polymers containing brominated flame retardants with the risk of formation of PBDD/DF (Stockholm Convention 2007b).

Soderstrom tested the burning of wastes containing high levels of brominated flame-retardants in a laboratory scale pilot fluidised bed incinerator and found that mixtures containing both chlorine and bromine lead to the formation of a complex mixture of PXDD/DF. It may also increase the total levels of chlorinated dioxins generated when these wastes are burned or incinerated (Soderstrom & Marklund 2002). Soderstrom reported that when bromine levels were increased chlorination levels increased and that more bromination than chlorination was seen. The most favoured reactions led to the formation of dibromodichlorodibenzo-p-dioxin and dibromodichlorodibenzofuran (Soderstrom & Marklund 2002). It is not clear how reproducible these results would be when extended to larger scale operations but it is important to test this at an operational scale to ascertain the impacts associated with burning shredder residues containing POP-BDE.

Recommended measures to reduce the formation of PCDD/DF, PBDD/DF and PXDD/DF have previously focused on the control of the treated scrap. This has involved the indentification of electric devices, transformers and condensers together with their separate treatment to avoid introduction of PCB into the plant. Whilst this was seen as a measure to reduce the contamination of shredder residues by PCB (Stockholm Convention 2007b) it will also be helpful for reducing contamination by PBDE.

Similarly the removal of foams and other polymers from vehicles before shredding can result in a significant improvement in the recovery rate and a reduction in the contamination of the resulting shredder waste.

The BAT-BEP guidance says that nevertheless the shredder residues is always contaminated and have to be disposed of only in a dedicated incineration plant (Stockholm Convention 2007b). Special care needs to be taken for the slags/ash due to their high heavy metal content.

However Directive 2000/53/EC of the European Parliament stipulates technical requirements for car design as well as minimum reuse and recovery rates for end-of-life vehicles. The Directive requires that by 1st January 2015 95% of the mass of end-of-life vehicles shall be recovered or recycled. Furthermore 85% of this must be by materials recycling rather than by incineration. This has increased pressures to recover more useful material from shredder residues by, for example, eddy current separation which allows a significant proportion of the non-ferrous metals, such as copper and aluminium to be recovered.

Given the very high levels of polymers in modern vehicles the 2015 targets will be especially challenging. It will be necessary to either reduce the quantity of shredder residues generated by stripping more polymers from vehicles before shredding or to recycle more of the shredder residues rather than to incinerate or dispose of them. This will need upgrades and improvements to the technologies used for processing the light and heavy fraction of the automotive shredder residue. It may also require the development of separation technologies and developing more recycling possibilities for the products gained from the separation. (Ferrao & Amaral 2006).

Further treatments for shredder residues have been proposed to give higher levels of recycling than have been achieved in the past and to reduce or eliminate the residual waste needing final disposal. Kurose et al, for example, has shown that shredder residue in Japan can be recycled after a separation process, followed by washing at acidic pH (Kurose et al. 2006) as illustrated below:

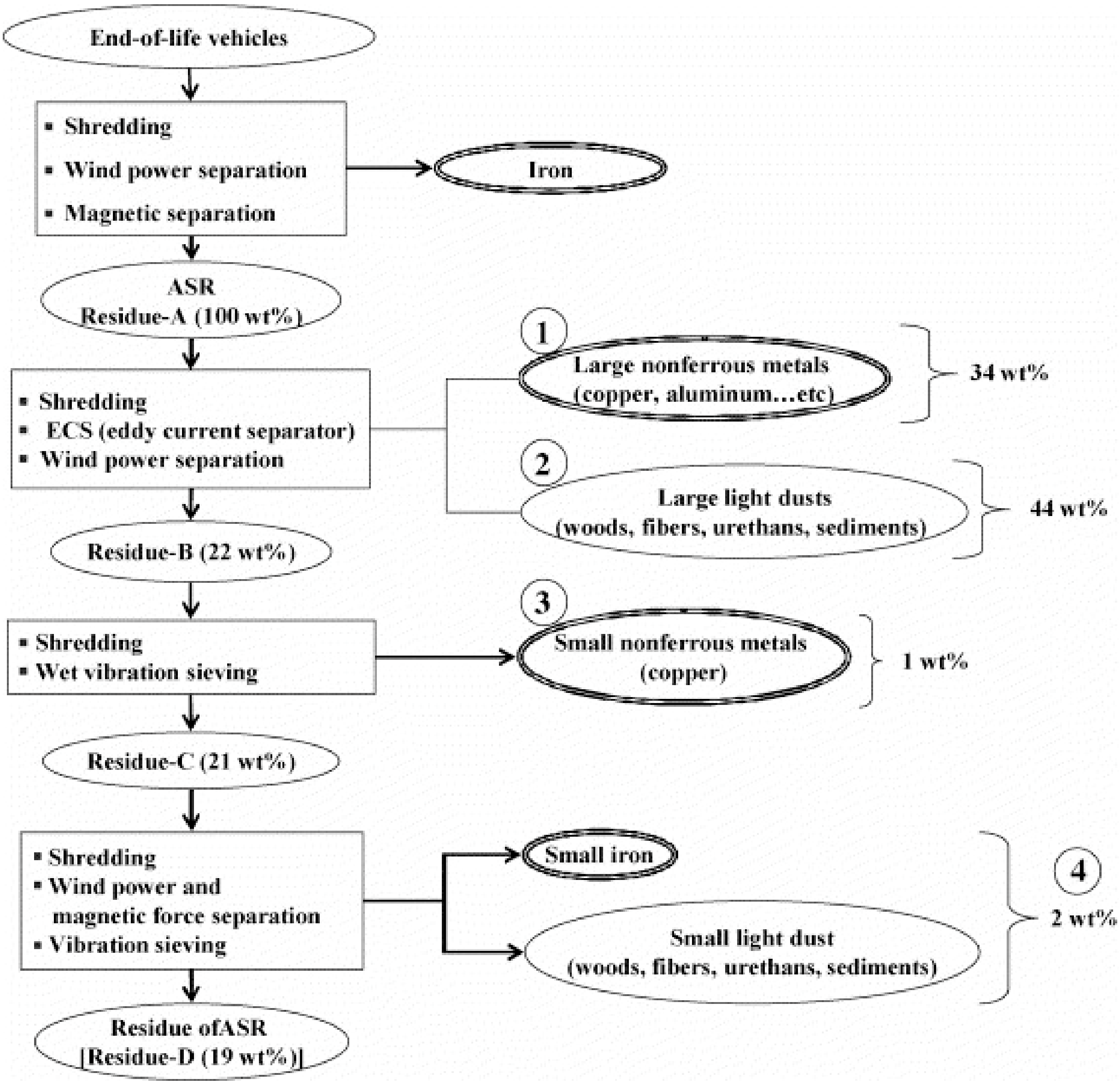


Figure 60: Flow diagram for the separation process (Kurose et al. 2006).

The final fraction (‘Residue D’) is mainly composed of small particles (approximately 2–4 mm) of heavy plastics. Due to As, Se, and Pb in the leachate from the residue additional washing is required to decrease the concentration of heavy metals to levels that satisfy the Japanese standards for elution.

PUR Foam recovery from Shredder Residues

Though the PUR foam is only (depending upon the input) approximately 5% of shredder residue, it amounts to over 30% of its volume (Hoffman 2008). The residues are increasingly difficult and expensive to dispose of and there is increasing interest in recovering more material from it.

The US industry says that the viability of foam recovered from shredder residue for the foam-rebond market depends on two key factors: Development of an economical process for recovering foam from shredder residue, and confirmation that the recovered foam meets quality requirements (Hoffman 2008).

Argonne National Laboratory has developed a plastics separation system based on froth flotation. A series of six tanks is used, each with a specific function, depending on the plastic being recovered. The chemical solutions in each tank are chosen for the particular application. It has been used for recovering selected plastics from automobile shredder residue, disassembled car parts, industrial scrap plastics, and consumer electronics (Selke 2006). Argonne finds the highest-quality foam comes from dismantling and then washing the foam from seats.

But they claim that manual separation of the foam is not economical (Hoffman 2008). It says this is the only technology that can successfully recycle >80% of ABS with a purity greater than 99 percent (Selke 2006).

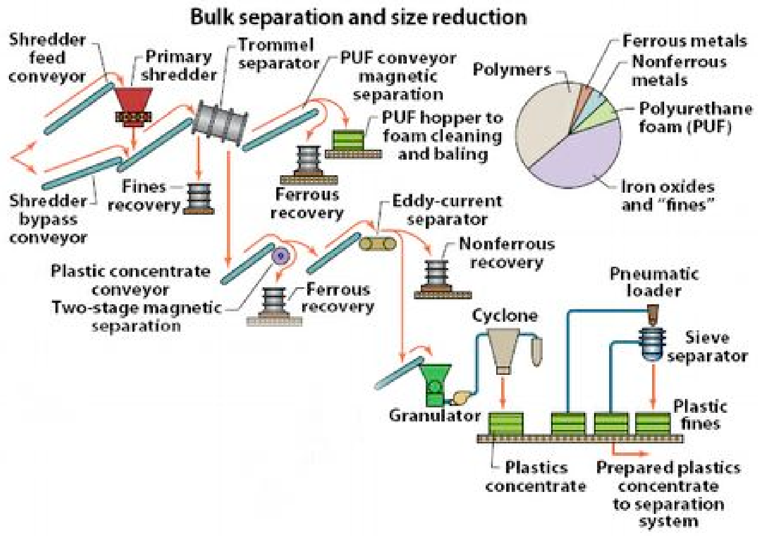


Figure 61: Argonne's mechanical-separation plant (Hoffman 2008)

Argonne's mechanical-separation plant's unit operations can operate in different sequences. It typically starts with the manual removal of large metallic, PUF objects and rubble. In full-scale shredders these larger pieces are screened by a trommel and/or a destoner and then separated to recover the metals and polyurethane foam (Hoffman 2008).

Argonne's process is designed to efficiently separate polymers of equivalent densities by a process called froth flotation. This was originally developed to separate ABS from high-impact polystyrene (HIPS). A large-scale (450 kg/hr) pilot plant was built and operated in Minneapolis to confirm process economics and to test the effectiveness of Argonne's froth-flotation process.

In 2004 NV Salyp of Ypres, Belgium, commissioned the Salyp ELV Centre which operates the Argonne technology under license to recover polyurethane foam and other plastics from shredder residue. It is reported to have an operational process capacity of 6 tonnes of ASR per hour. The plant also uses technology licensed from a German firm, KUTEC, for separating different types of thermoplastics from the Argonne technology reject stream. About 5 percent of automotive shredder residue, the material remaining after metals are recovered, is polyurethane. The Argonne technology separates the fluff into three streams: fines, foam, and a thermoplastic-rich stream. The foam stream is cleaned and sold for markets such as rebond foam in carpet underlay and for padding in automobiles. The thermoplastic stream is sorted further for recovery of a variety of pure resins. The fines stream may also be recovered for applications such as cement as a substitute for iron or mill scales (Selke 2006).

In a one-shift operation, Salyp has been recycling approximately 50 tonnes of ASR per day of which 20% is recovered in metal-rich streams, 20% in plastics streams and 50% for energy recovery.

Salyp reports that the process can also recover PUR foam from shredded mattresses (Selke 2006).

Energy Recovery

The higher specific energy of shredder residue was reported by Lanoir (Lanoir et al. 1997) to be 19,000 kJ kg^{-1} and the ash content 38%. However, residues normally contains between 1% and 4 % of chlorine (Tai et al. 2007) – Lanoir for example, found 3.5% (Lanoir et al. 1997). These levels are too high for municipal waste incinerators which should maintain halogen levels below 1%[55].

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[55] The EU Waste Incineration Directive, for example, requires that if hazardous wastes with a content of more than 1% of halogenated organic substances, expressed as chlorine, are co-incinerated, the temperature has to be raised from 850 °C to 1,100 °C (European Commission 2000)

Thus dechlorination of shredder waste may be necessary prior to incineration or other thermal treatment processes (Tai et al. 2007). One approach that has been proposed for dechlorination of shredder residues (which should also be suitable for wastes containing bromine) is extraction with a $Ca(OH)_2$ solution (pH 12.5) which may reduce the chlorine in the waste by 15%. Extraction with the $Ca(OH)_2$ solution at 373 K led to a further reduction of chlorine in the waste to 34%. Incineration of ASR with Ca(OH)2 at 1100K gave significant reductions (75–85%) in chlorine emissions (Tai et al. 2007)(Tai et al. 2006). It is not clear whether, or where, this approach has been used at a commercial scale.

The BREF warns that burning shredder residues may also increase CO emissions and, because of the higher calorific value, reduce the throughput of MSW (European Commission 2006).

Landfill and Leaching

Leaching concentrations of PCDD/DF and PCBs from shredder residues are strongly affected by surfactants. It is very likely that there will be similar impacts in relation to the leachability of PBDE residues. Sakai found leaching of PCBs from shredder residues when using 1000 mg/l of linear alkylbenzene sulfonate (as found in synthetic detergents and common in landfill sites) the leachate concentrations were about 70 times higher than that of distilled water. Similarly he reported that the concentration with humic acid 200 mg/l solution was about 4.6 times higher compared to the results from distilled water (Sakai et al. 2000).

Recycling of Articles Containing OctaBDE

Most OctaBDE will arise from the casings on office equipment such as computers and printers. Some articles containing OctaBDE will be processed through the shredder streams described above. Whilst the recycling options relevant to PentaBDE-containing materials are largely relevant to OctaBDE, the more common options are shown in the schematic below:

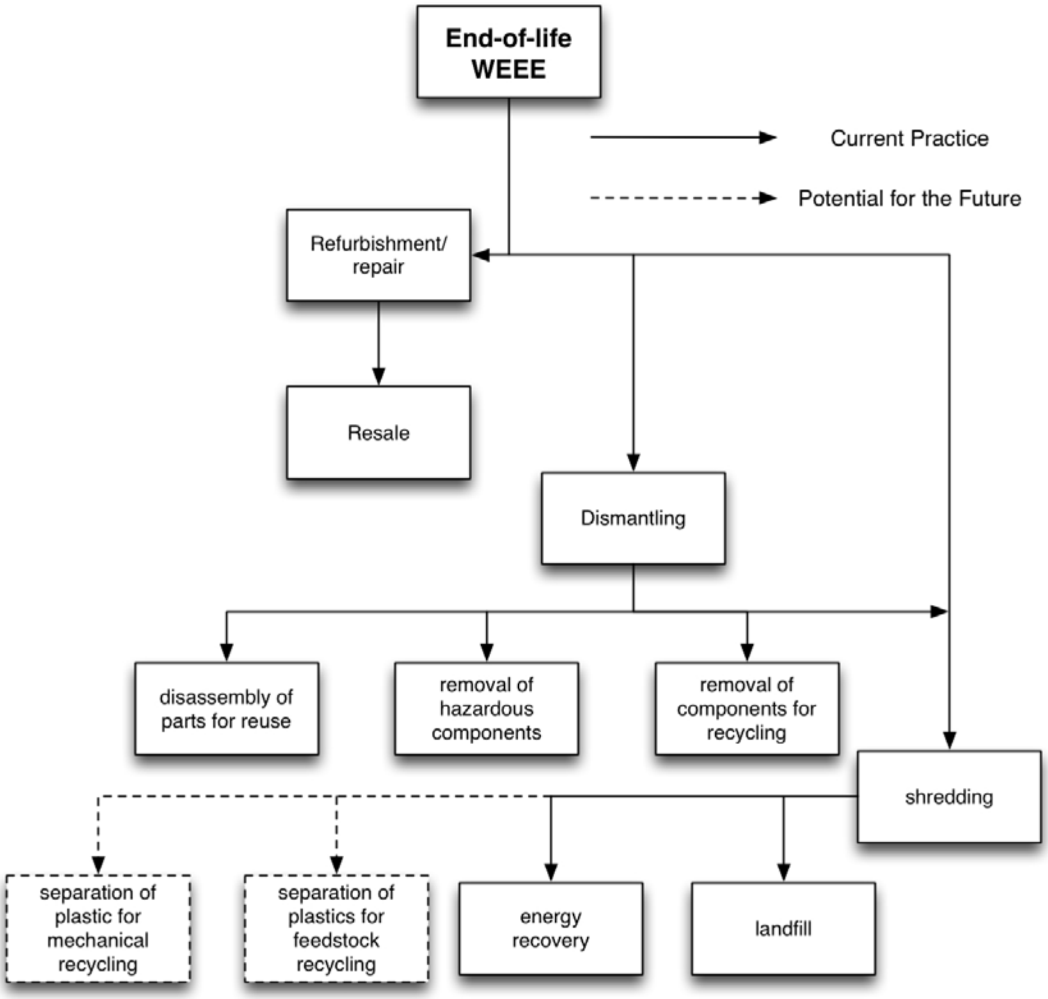
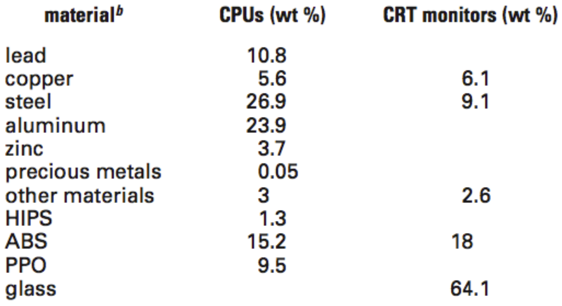


Figure 62: Waste management and recycling options for End-of-life WEEE

Computers, monitors, CRT monitors and television sets are recycled by removing the plastic outer casing before separation of the glass screen from the electronic components. On average around 20% of the weight of PCs and monitors is likely to be polymer – mainly ABS:

Table 41: Representative Materials Composition Assumed for the Central Processing Units and Cathode Ray Tube Monitors (Kang & Schoenung 2006a)



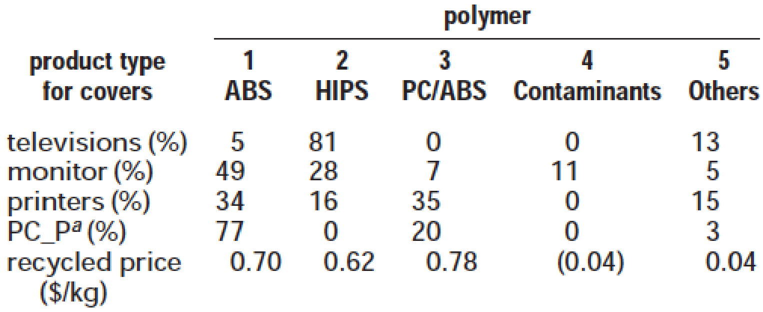
material[b]	CPUs (wt %)	CRT monitors (wt %)
lead	10.8	
copper	5.6	6.1
steel	26.9	9.1
aluminum	23.9	
zinc	3.7	
precious metals	0.05	
other materials	3	2.6
HIPS	1.3	
ABS	15.2	18
PPO	9.5	
glass		64.1

The glass and circuit boards are separated for recycling. The collection of casings in this way can, in principle, give large volumes or relatively homogeneous materials for reprocessing. These are normally shredded in a much smaller shredder than used for cars and are ground into small flakes of approximately 10–20 mm in size.

Because of the more carefully selected inputs the outputs are much cleaner than autoshredder residues but prior to melting and reforming, the ground, flaked, or pelletised polymer is generally washed to remove contaminants. The size of the polymer flakes or pellets can influence the effectiveness of the washing. Smaller particles provide a greater surface area for enhancing the effectiveness of the wash. Different polymers may also undergo different reforming conditions, such as different processing temperatures, the use of vacuum stripping, or other procedures, that could influence contaminant levels. In some cases, during the grinding or melting phases, the reprocessed material may be blended with virgin polymer (USFDA 2006).

The price of recovered polymers varies as does the contribution from different equipment but most PCs, about half of monitors and one third of printers are likely to have ABS cases:

Table 42: Average Product Cover Polymer Composition, and Revenue (Rios et al. 2003)



	polymer				
product type for covers	**1 ABS**	**2 HIPS**	**3 PC/ABS**	**4 Contaminants**	**5 Others**
televisions (%)	5	81	0	0	13
monitor (%)	49	28	7	11	5
printers (%)	34	16	35	0	15
PC_P[a] (%)	77	0	20	0	3
recycled price ($/kg)	0.70	0.62	0.78	(0.04)	0.04

The impact strength and appearance of recycled ABS is often significantly lower than virgin polymers, however:

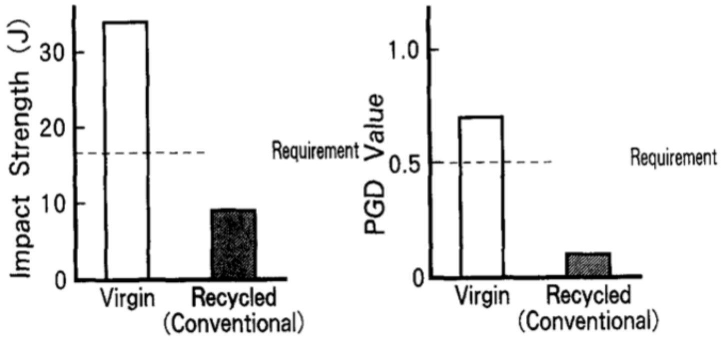


Figure 63: Comparison of virgin ABS and recycled ABS in impact strength and appearance (Tatemichi & Tomizawa 1997)

In most administrations it is only when there are specific regulated uses that the recycler must be able to demonstrate that contaminant levels in the reformed plastic have been reduced to sufficiently low levels to be suitable for its intended use. To produce a polymer with the desired qualities, however, additional antioxidants, processing aids, or other adjuvants may need to be added to the recycled polymer (USFDA 2006).

Depending on the quality of the input materials and the mixture the graded polymers can be used for relatively high quality applications with mixed plastics being sold for low level recycling applications, such as "*plastic fencing, pallets, garden furniture, and traffic cones*" (Hall & Williams 2007).

The more common and important recycling operations include:

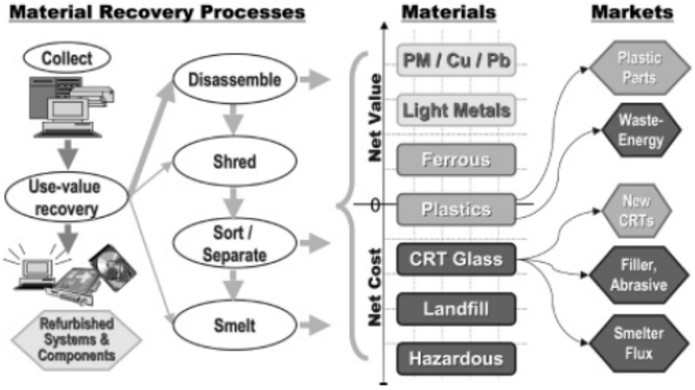


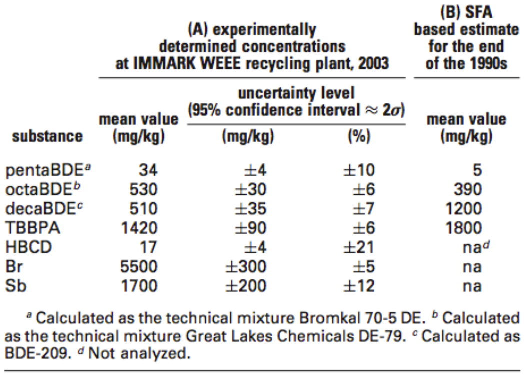
Figure 64: Schematic of EOL electronic material recovery pathways (Atlee, 2006)

Printed Circuit Boards

Whilst there is little doubt that some PentaBDE was used in the early 1990s for FR2 printed circuit boards (PWB) it is still a moot point whether more recently produced PWBs contain any PentaBDE. This issue was discussed in some detail in Appendix 2.

Morf reported levels of PentaBDE and OctaBDE from a WEEE recycling plant in 2003 (Morf et al. 2005) which showed low levels of PentaBDE:

Table 43: Average Concentrations of Selected BFRs, Bromine and Antimony in sWEEE in Switzerland (A) Experimentally Determined in the Present Study and (B) Estimated in a Literature-Based National Substance Flow Analysis for Switzerland (Morf et al. 2005)



	(A) experimentally determined concentrations at IMMARK WEEE recycling plant, 2003			(B) SFA based estimate for the end of the 1990s
		uncertainty level (95% confidence interval ≈ 2σ)		
substance	mean value (mg/kg)	(mg/kg)	(%)	mean value (mg/kg)
pentaBDE[a]	34	±4	±10	5
octaBDE[b]	530	±30	±6	390
decaBDE[c]	510	±35	±7	1200
TBBPA	1420	±90	±6	1800
HBCD	17	±4	±21	na[d]
Br	5500	±300	±5	na
Sb	1700	±200	±12	na

[a] Calculated as the technical mixture Bromkal 70-5 DE. [b] Calculated as the technical mixture Great Lakes Chemicals DE-79. [c] Calculated as BDE-209. [d] Not analyzed.

The relative range of uncertainty quoted corresponds approximately to the 95% confidence interval.

Although the levels reported by Morf are quite low they were still higher than anticipated based on the substance flow analysis. It is not clear whether this is due to new usage of PentaBDE, older stocks of e-waste being treated or simply assumptions in the SFA which underestimated the concentrations and quantities of usage. In these circumstances it is prudent to assume that some PWBs will contain PentaBDE as suggested in Appendix 2.

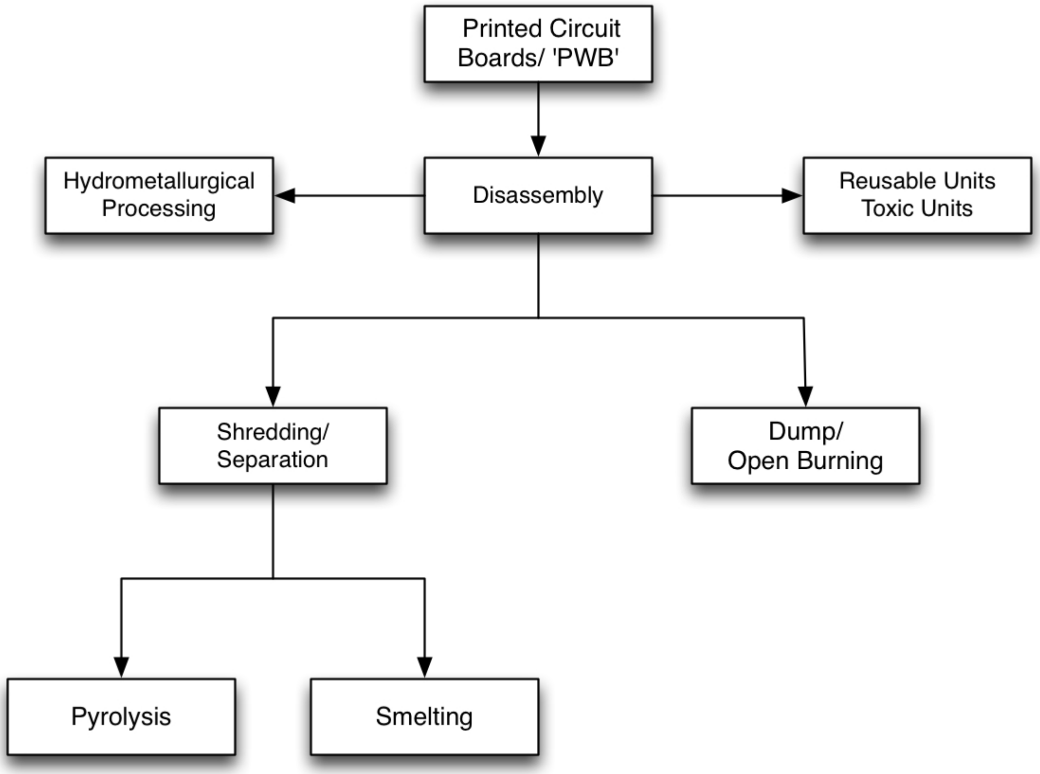


Figure 65: PWB recycling / waste management including non-BAT realities

The PWB recycling process can involve both thermal processing - smelting to recover precious metals, and nonthermal processing - disassembly, shredding, separation, and chemical treatment. The potential level of exposure to workers and the general population that results from these processes will obviously vary depending on the type of operation. The options that are likely to be used for circuit boards have been addressed in relation to the recycling/recovery of other articles containing PentaBDE or OctaBDE in this appendix. It is noted however, that the principal economic motivation in the case of PWBs is likely to be the recovery of copper and other precious metals including gold.

A report for the UK Department of Trade and Industry (Goosey et al. 2002), indicates that this may present unanticipated additional exposure and emissions routes as the report suggested that PWB waste "*may be subject to pyrolysis for both ultimate copper recovery or the generation of a copper ash for application in fertiliser production*". This is also included in a more recent Royal Society of Chemistry book on e-waste recycling.

In neither case is there any apparent consideration or comment on the implications of thermal processing of PBDE in the presence of copper (an effective catalyst (Weber et al. 2002a)(Stanmore 2004)(Halonen et al. 1997, Hatanaka et al. 2004)) and in a reducing environment – representing conditions with a very high risk of high levels of dioxin formation (Weber & Kuch 2003). The suggestion of use for fertiliser production is a surprising use of such residues with a high risk of contamination of the human food chain. If the application is real and continuing then particular care needs to be taken that no POPs and no dioxin precursors are present.

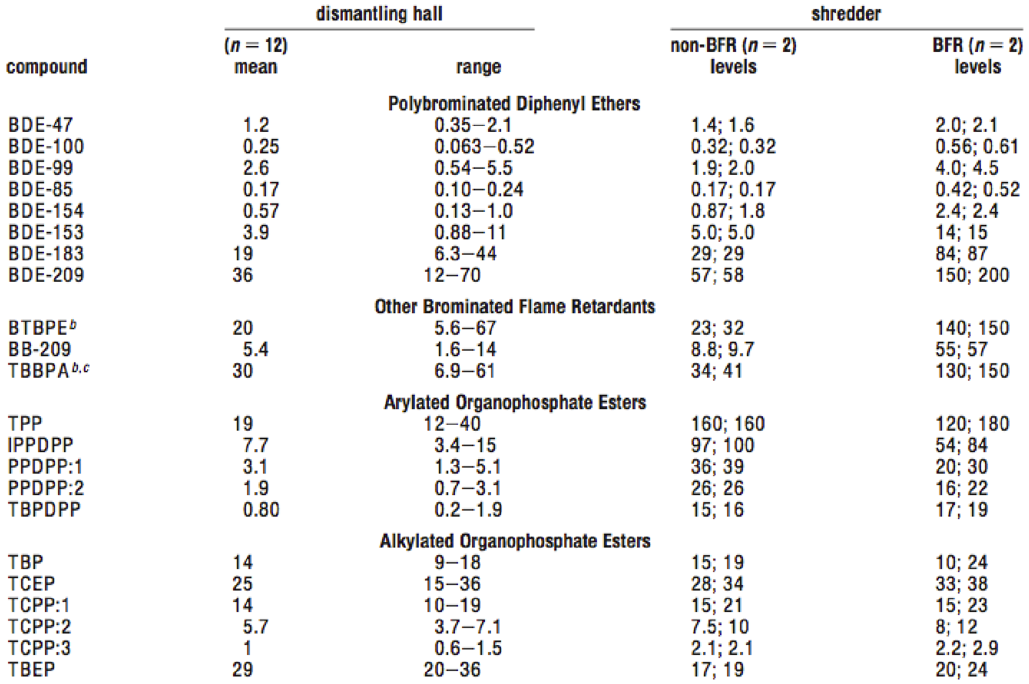
PBDE and PBDD/DF releases and exposure from Secondary recycling facilities

There are reports of elevated body burden levels to BFRs for e-waste recycling workers within the formal recycling sector in Europe. Studies have demonstrated higher levels of PBDE in the blood of workers employed in the formal e-waste recycling sector, at an e-waste recycling facility in Sweden (Sjődin et al. 1999)(Thuresson et al. 2006a, Thuresson et al. 2006b) and also one from Norway (Thomsen et al. 2001). These exposures are more strictly relevant to the stripping and shredding operations as preparation for secondary recycling.

Modern e-waste recycling

Sjődin et al. reported levels of PBDE and other brominated flame retardants in air samples collected at a Swedish plant involved in the recycling of e-waste (Sjődin et al. 2001). This plant dismantled discarded electronic equipment including computers, printers, TV sets, microwave ovens, and "*numerous other electronic goods*" in order to recover valuable metals (Sjődin et al. 2001).

Table 44: Total Concentrations (ng/m^3) of Particle-Associated and Semivolatile Brominated Flame Retardants and of Particle-Associated Organophosphate Esters in Air from the Plant for Recycling Electronic Products ((Sjődin et al. 2001).



	dismantling hall		shredder	
compound	(*n* = 12) mean	range	non-BFR (*n* = 2) levels	BFR (*n* = 2) levels
		Polybrominated Diphenyl Ethers		
BDE-47	1.2	0.35–2.1	1.4; 1.6	2.0; 2.1
BDE-100	0.25	0.063–0.52	0.32; 0.32	0.56; 0.61
BDE-99	2.6	0.54–5.5	1.9; 2.0	4.0; 4.5
BDE-85	0.17	0.10–0.24	0.17; 0.17	0.42; 0.52
BDE-154	0.57	0.13–1.0	0.87; 1.8	2.4; 2.4
BDE-153	3.9	0.88–11	5.0; 5.0	14; 15
BDE-183	19	6.3–44	29; 29	84; 87
BDE-209	36	12–70	57; 58	150; 200
		Other Brominated Flame Retardants		
BTBPE[b]	20	5.6–67	23; 32	140; 150
BB-209	5.4	1.6–14	8.8; 9.7	55; 57
TBBPA[b,c]	30	6.9–61	34; 41	130; 150
		Arylated Organophosphate Esters		
TPP	19	12–40	160; 160	120; 180
IPPDPP	7.7	3.4–15	97; 100	54; 84
PPDPP:1	3.1	1.3–5.1	36; 39	20; 30
PPDPP:2	1.9	0.7–3.1	26; 26	16; 22
TBPDPP	0.80	0.2–1.9	15; 16	17; 19
		Alkylated Organophosphate Esters		
TBP	14	9–18	15; 19	10; 24
TCEP	25	15–36	28; 34	33; 38
TCPP:1	14	10–19	15; 21	15; 23
TCPP:2	5.7	3.7–7.1	7.5; 10	8; 12
TCPP:3	1	0.6–1.5	2.1; 2.1	2.2; 2.9
TBEP	29	20–36	17; 19	20; 24

The study by Sjődin (Sjődin et al. 2001) found fairly high concentrations of some flame retardants in the indoor air particularly in the vicinity of shredding equipment. The most notable DecaBDE (BDE-209), tetrabromobisphenol A (TBBPA), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), tris(2-chloroethyl) phosphate (TCEP) and tris(2-butoxyethyl) phosphate (TBEP) . The concentrations of POP-BDE generally low with only BDE-183 and BDE-153 being particularly elevated. BDE-183 is a major component of OctaBDE and BDE-153 a minor one. In addition, the authors commented, a total of seven octa- and nona- BDE were detected in the same air, but "*the levels of these PBDE congeners could not be quantitated* [quantified]*, because authentic reference substances were not available*". They suggested that the patterns of octa- and nona-BDE present in the air resemble those encountered in the technical product Bromkal 79- 8DE. These congeners almost certainly arose from the use as flame retardants in ABS casings (Sjődin et al. 2001).

In a separate study Sjődin et al. compared the serum concentrations of PBDE in the workers from the plant studied here and who wore dust masks while shredding the plastics, with computer clerks and hospital cleaners (Sjődin et al. 1999):

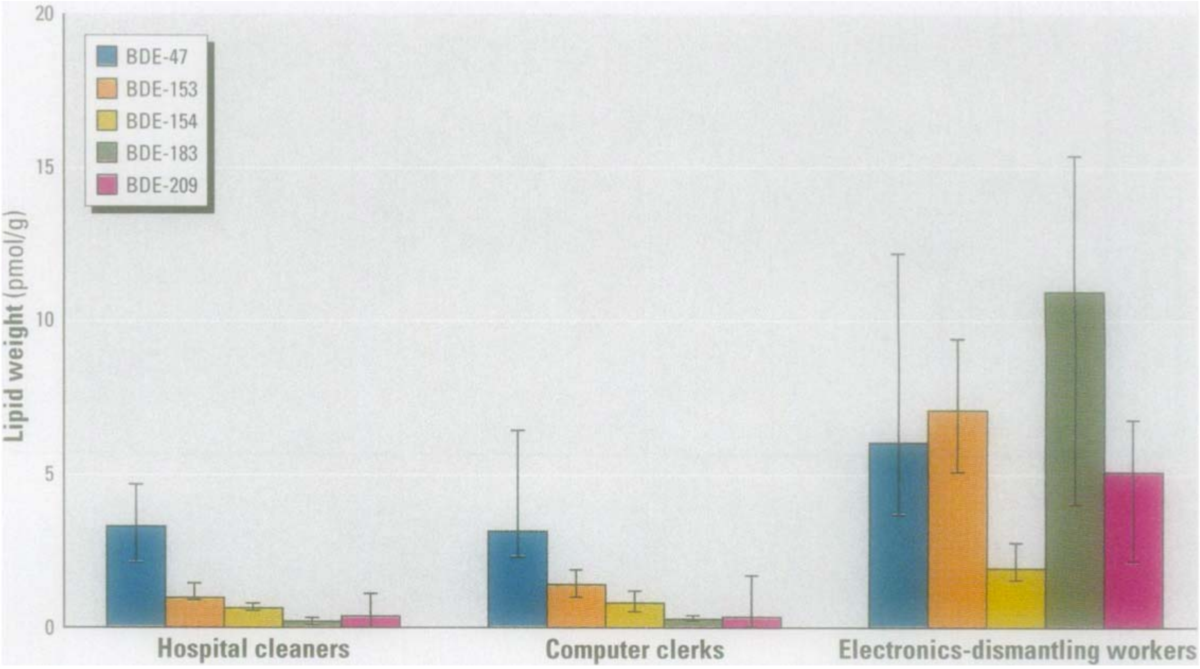


Figure 66: Median concentrations (pmol/g lipid weight) of five polybrominated diphenyl ether congeners in the study groups (Sjődin et al. 1999).
Quartile limits are indicated with error bars. Limit of detection is used for nonquantified polybrominated diphenyl ethers and non-detects was set to 0. Two PentaBDE, BDE-99 and BDE-100, were present in all samples but are not reported here as it was not possible to accurately quantify them.

Apart from BDE-209, which was detected in 45 out of 59 samples, the PBDE congeners shown in Table 44were detected in all the blood samples analysed. The levels and patterns were different between the groups with the electronic dismantling workers being significantly higher than for the hospital cleaners and computer clerks (Sjődin et al. 1999). It is notable that the BDE-47 levels were elevated in spite of the apparently low concentrations reported in the later study, reported above (Sjődin et al. 2001). This may be due to earlier exposures and/or the longer half-life of BDE-47.

The serum levels of BDE-47 in the serum of hospital cleaners and computer clerks were similar to levels from male blood donors in Sweden (Klasson-Wehler et al. 1997)[56].

Pettersson-Julander et al. (Pettersson-Julander et al. 2004) evaluated exposure to BFRs by staff in an e-waste recycling facility in Sweden by using personal air monitoring over a two year period.

Twenty-two PBDE and two other bromine-containing organic compounds were analysed and evaluated in 17 personal air samples. The most abundant congeners were BDE-209 (<0.7–61 ng/m^3), BDE-183 (<0.1–32 ng/m^3) followed by BDE-99 and BDE-47 (<1.3–25 and <0.9–16 ng/m^3, respectively) (these congeners indicates the presence of DecaBDE, OctaBDE and PentaBDE). The second most abundant peak in the chromatogram from all samples was identified as 1,2-bis(2,4,6-tribromophenyxy)ethane (BTBPE) in the concentration range (<0.6–39 ng/m^3)[57].

The workers were distinguished in three different categories: dismantlers, other workers and unexposed. There was a significant difference among the dismantlers and the unexposed categories for PBDE congeners BDE-47, BDE-100, BDE-99, BDE-154; BDE-153, BDE-183, BDE-209 and BTBPE:

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[56] This was the first paper to report the presence of PBDE in human blood. PBDE had previously been reported in adipose tissue (Haglund 1997) and in human breast milk in Germany.

[57] A second bromine-containing compound was also detected, structurally similar to decabromodiphenyl ethane (DeBDethane), however no definite identification could be made

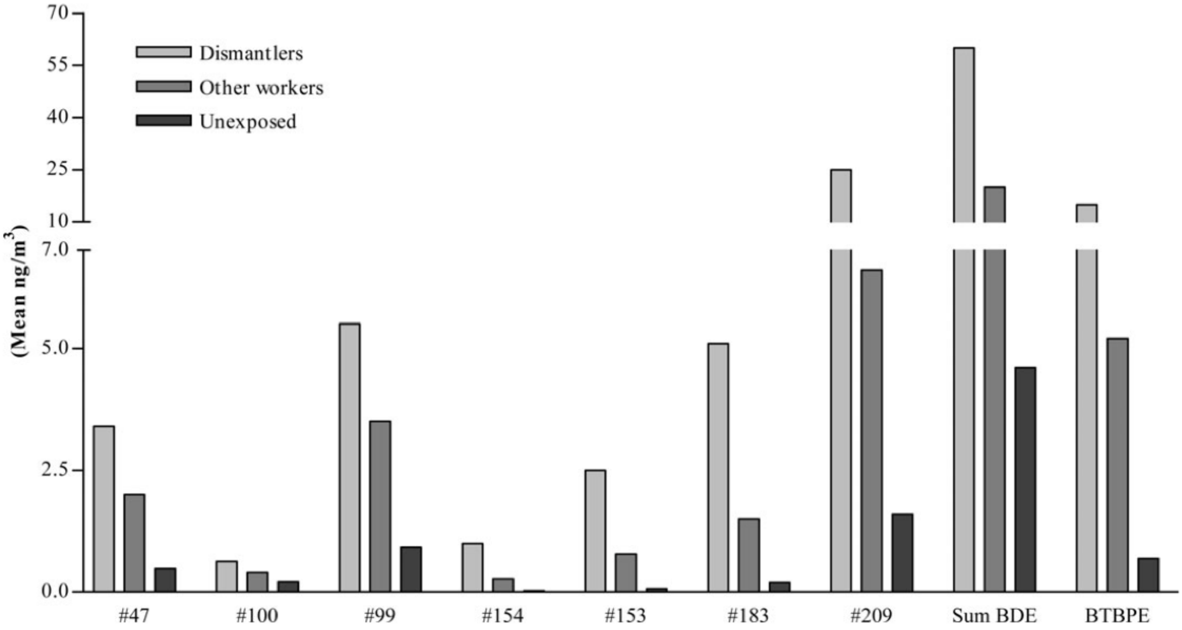
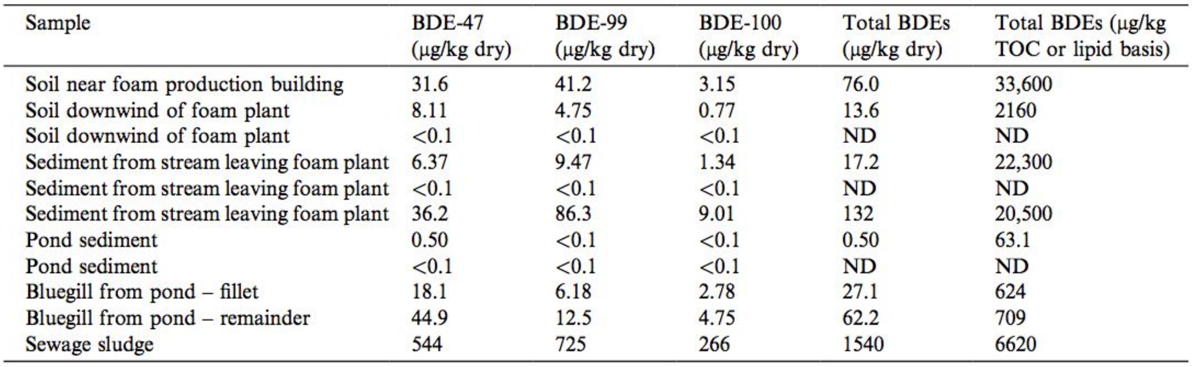


Figure 67: Air concentration of PBDE and BTBPE in the breathing zone for the three different exposure categories at the electronic dismantling facility
Dismantlers (n = 11), other work (n = 2), and control (n = 3)

Emissions from Foam Processing:

Reduction strategies for volatile emissions from foam-producing facilities in the US restricted emissions to air after about 1997. Before these were in place significant releases are likely to have occurred. Hale et al. (Hale et al. 2002b) examined concentrations of BDE in soil, sediment and fish collected near a polyurethane foam manufacturing facility:

Table 45: Concentrations of BDE in soil, sediment and fish collected near a polyurethane foam manufacturing facility (Hale et al. 2002b)



Sample	BDE-47 (μg/kg dry)	BDE-99 (μg/kg dry)	BDE-100 (μg/kg dry)	Total BDEs (μg/kg dry)	Total BDEs (μg/kg TOC or lipid basis)
Soil near foam production building	31.6	41.2	3.15	76.0	33,600
Soil downwind of foam plant	8.11	4.75	0.77	13.6	2160
Soil downwind of foam plant	<0.1	<0.1	<0.1	ND	ND
Sediment from stream leaving foam plant	6.37	9.47	1.34	17.2	22,300
Sediment from stream leaving foam plant	<0.1	<0.1	<0.1	ND	ND
Sediment from stream leaving foam plant	36.2	86.3	9.01	132	20,500
Pond sediment	0.50	<0.1	<0.1	0.50	63.1
Pond sediment	<0.1	<0.1	<0.1	ND	ND
Bluegill from pond – fillet	18.1	6.18	2.78	27.1	624
Bluegill from pond – remainder	44.9	12.5	4.75	62.2	709
Sewage sludge	544	725	266	1540	6620

Totals provided were for the sum of BDE-47, -99 and -100. BDE-209 was only detected in the sludge (but at rather high levels - 1,470 µg/kg). Fish from the river to which the treatment plant discharged had previously been found to contain high burdens of tetra- to hexabrominated diphenyl ethers (Hale et al. 2001). These emissions are more likely related to the intitial usage of POP-BDE in products rather than to recycling operations.

Handling and recycling PUR Foams:

Although there are no data from recycling operations the operational exposure risks associated with the recycling of mattresses are clear from an article in the San Francisco Chronicle (DeBare 2008) describing a mattress recycling operation in San Leandro, California:

"*Sergio Solarez smoothly ran his utility knife around the side of a queen-size mattress, like slicing a cake into two layers. He pulled off the flowered fabric and two layers of foam, flipped the mattress over with an explosion of dust, and sliced and stripped the other side until he was left with a bare set of springs.*

……

The bigger hazard is dust, which seems to billow endlessly out of the mattresses.

"Even the nice ones have dust,""

There are an increasing number of companies who specialise in recycling mattresses for in-direct re-use.

Lower grade remoulding Operations:

As a high proportion of POP-BDE-contaminated polymers are exported, either as components of e-waste or as collected and sorted polymers, it is likely that most of the remoulding to recycled products will take place in facilities with relatively low operational and health and safety standards. In Taiwan, for example, Tsai notes, due to the low-grade uses of recycled plastics, most of the facilities which adopt material recycling methods for treating plastic waste simply use basic filters in the local ventilation system to treat the melting fumes generated from electrically-heated extruders. Although some of these plants also use scrubbers to treat the exhaust, "*both fumes and odour eliminations are unsatisfactory*" (Tsai et al. 2009). Bromomethane was measured in the emission from a polypropylene production line at 8 ug/m^3 and it was suggested that this could be generated from the "*additive brominated flame retardants (BFRs) in PP plastic products, as BFRs, particularly polybrominated diphenyl ethers*" (Tsai et al. 2009).

PBDD/PBDF formation during state of art recycling operations of plastic – reused in new products

The Bromine industry has warned about the hazards associated with PBDD/DF production from recycling WEEE plastics for more than a decade (Mark & Lehner 2000). Although the work published by APME contained only very limited data it confirmed that analysis had been "*carried out for halogen-containing organic compounds: chlorinated PCDD/Fs, brominated PBDD/Fs and mixed brominated and chlorinated PBCDD/Fs*" and that the "*values found varied quite significantly*". It was claimed, unlike in reports from other investigators (such as Schlummer (Schlummer et al. 2004)), that "*the average*"[58] PXDD/DF content "*of all the samples of waste E+E plastics so far investigated by APME*" had met the German regulations. Nonetheless it still continued "*potentially high content of these organic compounds may well provide an extra reason for large-scale handling, automatic fragmentation, Syngas production and post-combustion, thus minimising the impact on the internal and external environment*". Adding the warning "*[F]urthermore, potentially significant amounts of these impurities suggest that mechanical recycling of old plastics from the WEEE should be looked at with great care*" (Mark & Lehner 2000).

There is a growing recognition that a wide range of brominated hydrocarbons, including PBDD/DF, are formed and emitted during the thermal treatment of brominated flame retardants in fabrics, plastics and electronic materials (Ebert & Bahadir 2003)(Cormier et al. 2006).

The Swiss authorities were warning before 2000 about the dangers of dioxin production from "*flame retardants containing bromine (e.g. in printed circuit boards, housings, cables)*" because they "*can form brominated dioxins and furans when they are incinerated*". The Swiss guidance said that "*thermal treatment of the printed circuit boards or their baseplates with or without energy recovery is only permitted in suitable plants*"(Monteil 2000).

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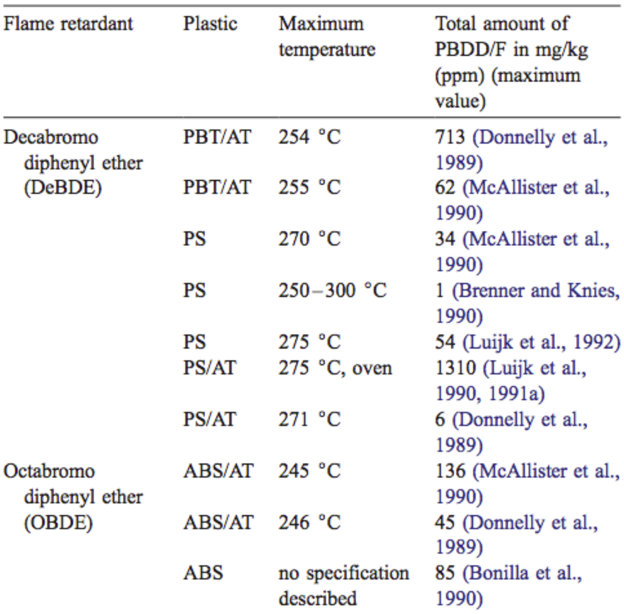
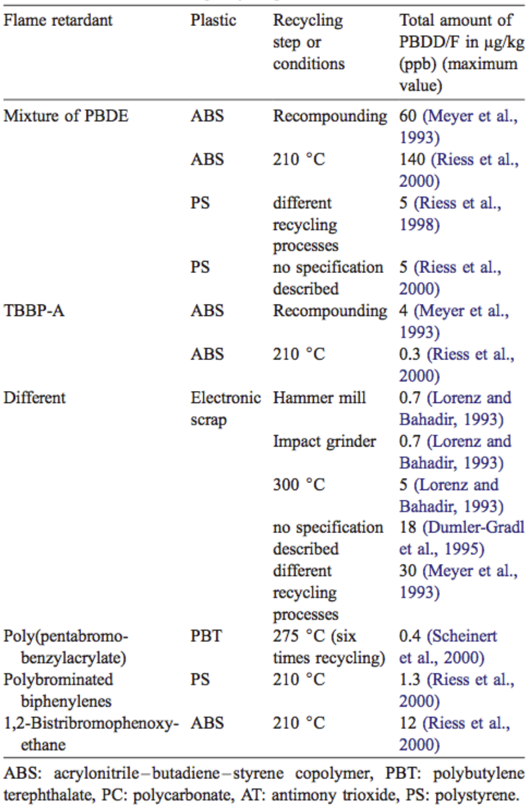
[58] As no data is presented it is difficult to assess what size and composition of sample the average here relates to – and also whether PXDD/F is being used to represent PBDD rather than the more conventional usage of mixed chloro/bromo dioxins and furans.

Table 46: Formation of PBDD/F during production/recycling operations (which do not involve burning or incineration) (Ebert & Bahadir 2003):



Flame retardant	Plastic	Maximum temperature	Total amount of PBDD/F in mg/kg (ppm) (maximum value)
Decabromo diphenyl ether (DeBDE)	PBT/AT	254 °C	713 (Donnelly et al., 1989)
	PBT/AT	255 °C	62 (McAllister et al., 1990)
	PS	270 °C	34 (McAllister et al., 1990)
	PS	250–300 °C	1 (Brenner and Knies, 1990)
	PS	275 °C	54 (Luijk et al., 1992)
	PS/AT	275 °C, oven	1310 (Luijk et al., 1990, 1991a)
	PS/AT	271 °C	6 (Donnelly et al., 1989)
Octabromo diphenyl ether (OBDE)	ABS/AT	245 °C	136 (McAllister et al., 1990)
	ABS/AT	246 °C	45 (Donnelly et al., 1989)
	ABS	no specification described	85 (Bonilla et al., 1990)

Table 47: Formation of PBDD/F during recycling (Ebert & Bahadir 2003).



Flame retardant	Plastic	Recycling step or conditions	Total amount of PBDD/F in µg/kg (ppb) (maximum value)
Mixture of PBDE	ABS	Recompounding	60 (Meyer et al., 1993)
	ABS	210 °C	140 (Riess et al., 2000)
	PS	different recycling processes	5 (Riess et al., 1998)
	PS	no specification described	5 (Riess et al., 2000)
TBBP-A	ABS	Recompounding	4 (Meyer et al., 1993)
	ABS	210 °C	0.3 (Riess et al., 2000)
Different	Electronic scrap	Hammer mill	0.7 (Lorenz and Bahadir, 1993)
		Impact grinder	0.7 (Lorenz and Bahadir, 1993)
		300 °C	5 (Lorenz and Bahadir, 1993)
		no specification described	18 (Dumler-Gradl et al., 1995)
		different recycling processes	30 (Meyer et al., 1993)
Poly(pentabromo-benzylacrylate)	PBT	275 °C (six times recycling)	0.4 (Scheinert et al., 2000)
Polybrominated biphenylenes	PS	210 °C	1.3 (Riess et al., 2000)
1,2-Bistribromophenoxy-ethane	ABS	210 °C	12 (Riess et al., 2000)

ABS: acrylonitrile–butadiene–styrene copolymer, PBT: polybutylene terephthalate, PC: polycarbonate, AT: antimony trioxide, PS: polystyrene.

There are differing reviews, however, about whether the levels of PBDD/DF increase during recycling operations. Riess (Riess et al. 1998)(Riess et al. 2000) assessed a total of 78 TV housings and 34 personal computer housings for polymer types and flame retardant composition. Representative samples of the most common were, including high impact polystyrene (HIPS) treated with PBDE flame retardants, were then sampled and analysed for PBDD/DF. Following this the material was ground to a 4 mm size and processed by a screw extruder which was used with a processing temperature of 190°C. It was then re-analysed. The conclusion was that that the PBDE flame-retardants tend to form lower-brominated products as well as PBDD/DF during recycling processes. Although there was a slight fall in the total concentrations measured for compliance with the German Ordnance there was nearly a 10% increase in 2,3,7,8-PBDF and given the high TEF of this compound the total toxicity almost certainly increased during recycling (Riess et al. 1998)(Riess et al. 2000):

Table 48: Levels of brominated dibenzofurans and dibenzo-p-dioxins in impact modified polystyrene containing brominated diphenyl ether both before and after recycling (Riess et al. 1998) quoted by (European Chemicals Bureau 2001).

No	Isomer	Level before recycling	Level after recycling
1	2,3,7,8-TBDD	<0.009 µg/kg	<0.016 µg/kg
2	1,2,3,7,8-PeBDD	<0.027 µg/kg	<0.032 µg/kg
3	2,3,7,8-TBDF	0.407 µg/kg	0.431 µg/kg
4	2,3,4,7,8-PeBDF	5.45 µg/kg	4.05 µg/kg
5	1,2,3,4,7,8-HxBDD + 1,2,3,6,7,8-HxBDD	<0.11 µg/kg	<0.023 µg/kg
6	1,2,3,7,8,9-HxBDD	<0.11 µg/kg	<0.023 µg/kg
7	1,2,3,7,8-PeBDF	<0.019 µg/kg	<0.021 µg/kg
Sum 1-4		5.90 µg/kg	4.53 µg/kg
Sum 1-7		6.14 µg/kg	4.59 µg/kg

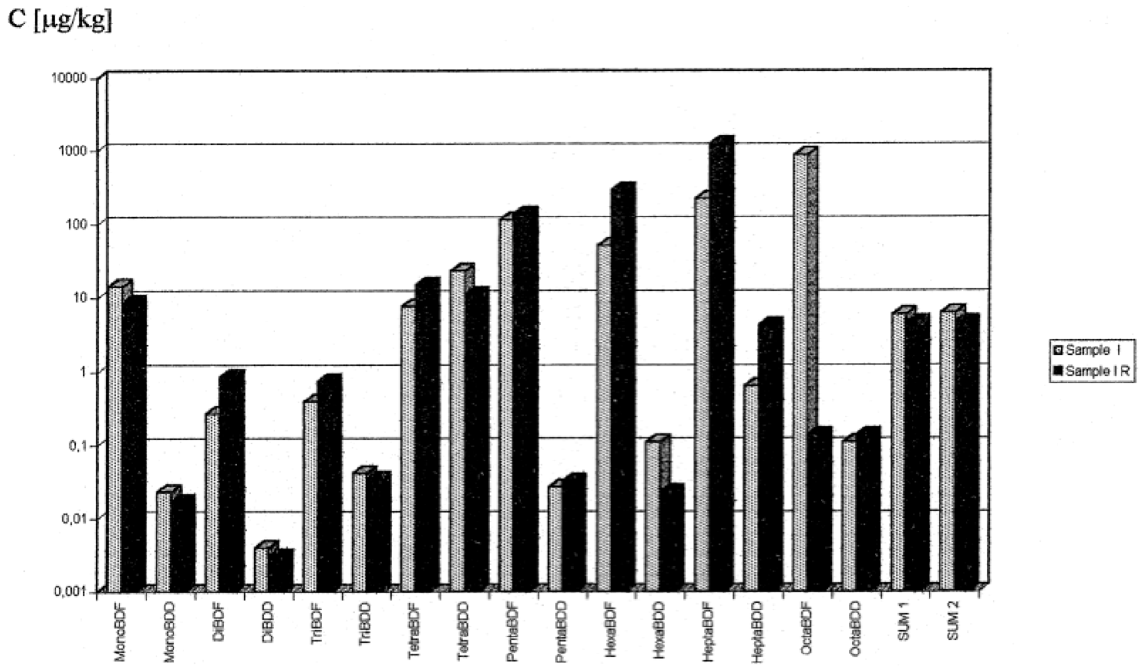
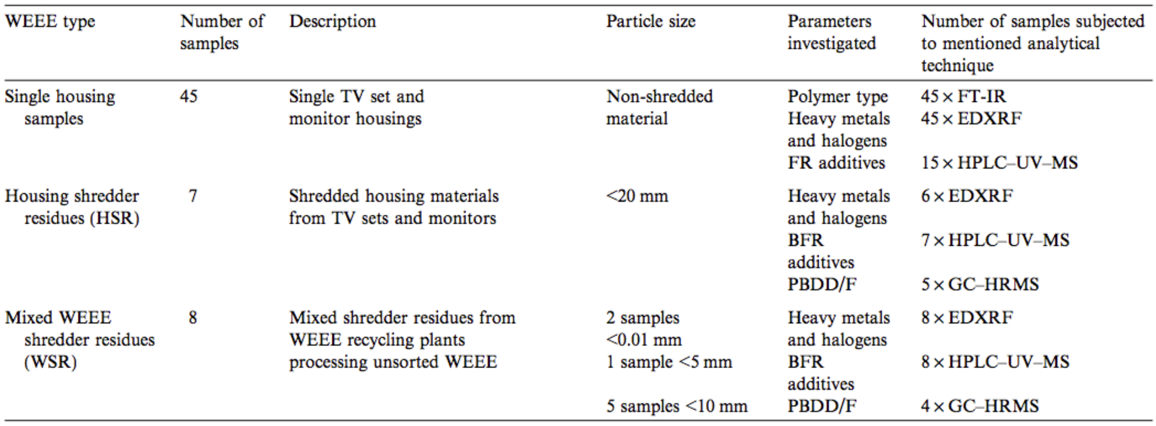


Figure 68: Influence of material recycling on PBDD/F concentrations (Riess et al. 2000).

Since this report was published the thresholds in the Chemikalienverbotsverordnung have been reduced to 1 ppb (µg/kg) as above (German Federal Ministry of Justice 2003) – consequently the results would no longer be in compliance with the order.

More recently, Schlummer (Schlummer et al. 2007) sampled a wide range of WEEE:

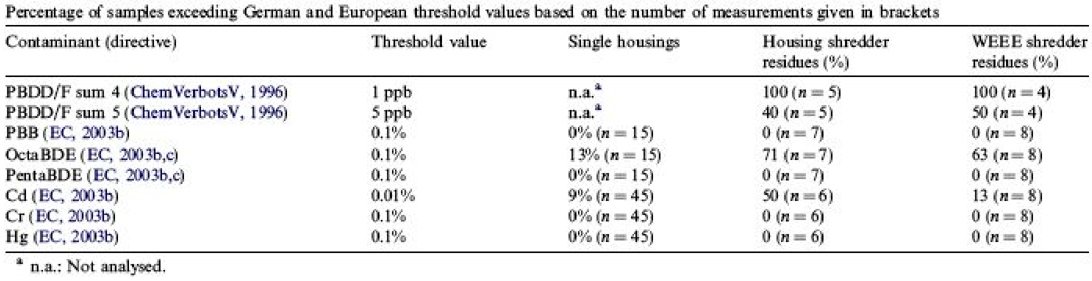
Table 49: Description of samples investigated in Schlummer's study and monitoring program (Schlummer et al. 2007)



WEEE type	Number of samples	Description	Particle size	Parameters investigated	Number of samples subjected to mentioned analytical technique
Single housing samples	45	Single TV set and monitor housings	Non-shredded material	Polymer type Heavy metals and halogens FR additives	45 × FT-IR 45 × EDXRF 15 × HPLC–UV–MS
Housing shredder residues (HSR)	7	Shredded housing materials from TV sets and monitors	<20 mm	Heavy metals and halogens BFR additives PBDD/F	6 × EDXRF 7 × HPLC–UV–MS 5 × GC–HRMS
Mixed WEEE shredder residues (WSR)	8	Mixed shredder residues from WEEE recycling plants processing unsorted WEEE	2 samples <0.01 mm 1 sample <5 mm 5 samples <10 mm	Heavy metals and halogens BFR additives PBDD/F	8 × EDXRF 8 × HPLC–UV–MS 4 × GC–HRMS

Schlummer reported that contamination of all four samples of mixed WEEE plastics tested exceeded the German limit value of 1 ppb for brominated dioxin/furan contamination (sum 4[59]), and two of the four samples exceeded the sum 5 limits, as reproduced below. Of these plastic samples, all four contained PBDE, three contained TBBPA and two contained BTBPE (Schlummer et al. 2007):

Table 50:Percentage of samples exceeding German threshold values in the Chemikalienverbotsverordnung Schlummer, 2007 #34170}.



Percentage of samples exceeding German and European threshold values based on the number of measurements given in brackets

Contaminant (directive)	Threshold value	Single housings	Housing shredder residues (%)	WEEE shredder residues (%)
PBDD/F sum 4 (ChemVerbotsV, 1996)	1 ppb	n.a.[a]	100 ($n = 5$)	100 ($n = 4$)
PBDD/F sum 5 (ChemVerbotsV, 1996)	5 ppb	n.a.[a]	40 ($n = 5$)	50 ($n = 4$)
PBB (EC, 2003b)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
OctaBDE (EC, 2003b,c)	0.1%	13% ($n = 15$)	71 ($n = 7$)	63 ($n = 8$)
PentaBDE (EC, 2003b,c)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
Cd (EC, 2003b)	0.01%	9% ($n = 45$)	50 ($n = 6$)	13 ($n = 8$)
Cr (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)
Hg (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)

[a] n.a.: Not analysed.

Schlummer notes that the levels found are the same range as reported by Fluthwedel and Pohle (Fluthwedel & Pohle 1996) for housing materials and notes that no substantial decrease in PBDD/DF levels can be observed despite the reducing trends in PBDE application.

The APME report warns about the risks of worker exposure in recycling facilities "*mechanical recycling of WEEE with increased detectable levels of PXDD/Fs will give rise to potential costs of handling and exposure to recyclates made from these WEEE plastics*" (Mark & Lehner 2000).

More details are needed of the actual levels of PBDD/DF production during recycling and the resulting levels of exposure.

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[59] the sum of 2,3,7,8-TeBDF, 2,3,7,8-TeBDD, 2,3,4,7,8-PeBDF and 1,2,3,7,8-PeBDD, as well as in terms of PBDD/F. Sum 5 is the sum of sum 4 plus 1,2,3,7,8-PeBDF, 1,2,3,6,7,8-HxBDD, 1,2,3,4,7,8-HxBDD and 1,2,3,7,8,9- HxBDD.

Appendix 3 (b): Tertiary Recycling Operations

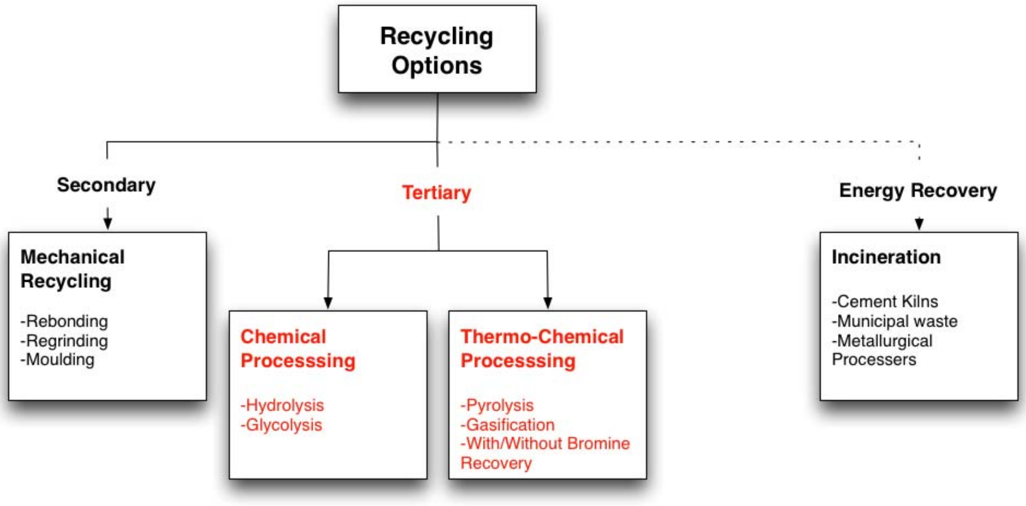

Figure 69: Tertiary recycling options – chemical and thermo-chemical processing

Appendix 3 (b) (i): Chemical Reprocessing

Glycolysis is a process in which polyurethane is chemically mixed and heated to 200°C producing polyol, which can be used to make more polyure- thane or it, can be used as a fuel. Hydrolysis is like glycolysis, however it produces polyol and amine intermediates which can be used for fuel and for producing more polyurethane (Zia et al. 2007).

Glycolysis

Glycolysis offers the opportunity to recycle scrap foam by chemically reconstituting it into new raw materials. Many companies use glycolysis to process their relatively pure PU scrap whilst other wastes are dealt with by a mechanical process. Glycolysis turns the PU waste back into polyols for new rigid PU slabstock production and is a process which has been used for many years (Eaves 2004).

InfiChem Polymers[60] in Michigan, USA claims to be the first North American company to convert scrap polyurethane foam into new polyols (PlastEurope.com 2010). The new process, developed with project aid from a number of sources, is being used for the first time in a new production facility, completed last year at the Michigan site.

ICP’s glycolysis technology chemically depolymerises polyurethanes into liquid initiators to produce the polyols, which it says are the first of their kind to be commercially available. Recyclate content is said to exceed 60%. The polyols can also be used in spray foam applications, flexible foams, elastomers, and other traditional polyurethane applications, the company says (PlastEurope.com 2010).

In a recycling method developed by Puren Schaumstoffe, PU waste is mixed with scrap PET from, for example, soft drink bottles. This has the advantage of reducing methylene diphenylamine levels arising from MDI based PU which can reach undesirable levels if only PU waste is used (Eaves 2004).

Contaminated waste, i.e., waste containing PU foam mixed with covering paper, mineral wool, glass wool, aluminium sheet, etc., is first separated and pressed into briquettes which are then granulated and transported to a mixing system. An MDI-based binder is added and the mixture pressed at 140-160 °C at a pressure of 1-3 MPa for about 30- 60 seconds to form boards which are subsequently cut to size. The product is said to have good mechanical properties, low heat conduction and is moisture resistant. Thicknesses range from 5 to 60 mm and densities from 250 to 850 kg/m^3. Various construction applications are envisaged, including floor insulation

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[60] http://www.infichempolymers.com/

and sandwich elements. The process was sufficiently successful for Puren to decide in 1997 to build a second plant to increase capacity.

BASF have developed a ‘second generation chemistry’ using glycolysis to recover polyols from a variety of PU systems including rigid PU foam. Residual amine is claimed to be less than 1%. The polyols are said to be reusable in polyisocyanurate foam, insulation non-critical foam, structural foam, friable energy-absorbing foam, low density void filling foam, elastomeric coatings, rigid non-cellular PU, and moulded semi-rigid foam.

Hydrolysis

Hydrolysis is the reaction of polyurethane with water, and can produce both polyols and amine intermediates from polyurethane process and post-consumer scrap. When recovered, the polyols can be used as effective fuels, and the intermediates can be re-used to produce other polyurethane components. This method uses a heated, oxygen-free environment to break down polyurethane and plastics into gases, oils and solids. Material recovery by hydrolysis has applied to PU foam waste from scrap cars since the 1970s in the USA (Zia et al. 2007).

Appendix 3 (b) (ii): Thermo-chemical Reprocessing

PBDE/BFR are mainly used in materials with high calorific value (plastics, polyurethane foam, polystyrene foam, textiles). One option for the recycling of such materials is the utilization of the energy present in the material and metals attached to the PBDE-treated polymer. The potential energy value of polymers is nearly 40 MJ/kg which corresponds to €80/mton (at €2/GJ) (Tange & Drohmann 2005). The Basel Convention "*Technical guidelines for the identification and environmentally sound management of plastic wastes and for their disposal*" recommends feedstock recycling and thermal energy recovery for PBDE-containing plastic (Basel Convention 2002):

"*Plastic wastes which contain polybrominated diphenyl ethers (PBDE) should be excluded from material recycling because of the possibility of emitting dioxins and furans. Instead such plastic wastes should be treated in feedstock recycling facilities or in controlled incinerators recovering energy*".

Since these materials are flame retarded their flamability is reduced and this can result in increased formation of products of incomplete combustion in facilities which are not the best available technology with appropriate combustion efficiency (Weber & Kuch 2003). For materials containing PBDE being excellent precursors for PBDF, the formation of the more toxic PBDF is a crucial parameter to be considered and evaluated in thermal treatments and destruction (Sakai et al. 2001)(Weber & Kuch 2003)(WHO 1998)(Vehlow et al. 2002).

Pyrolysis and gasification of PBDE/BFR-containing plastic

In its simplest definition pyrolysis is the degradation of polymers at moderate to high temperatures under nonoxidative conditions to yield marketable products (e.g. fuels, oils or activated carbon). Pyrolysis is capable of converting plastic waste into fuels, monomers, or other valuable materials by thermal and catalytic cracking processes (Tange & Drohmann 2005) (Scheirs & Kaminsky 2006). This method can be applied to transform both thermoplastics and thermosets in high-quality fuels and chemicals. Moreover it allows the treatment of mixed, unwashed plastic wastes (Scheirs & Kaminsky 2006). Considering the results from laboratory thermolysis (Thoma 1987a, Clausen et al. 1987, Dumler 1989a, 1990, Buser 1986a, Zacharewski et al. 1988, Luijk et al. 1991, Bieniek et al. 1989), however, elevated concentrations of PBDD/DF can be expected from pyrolysis processes when PBDE is present in the waste. Therefore for the feedstock recycling via pyrolysis/gasification of PBDE and BFR-containing waste the formation of PBDD/DF need to be considered and depending on the chlorine content also the formation of brominated-chlorinated PXDD/DF have to be considered (Weber & Kuch 2003). Furthermore since pyrolysis and gasification are thermal processes in reducing atmosphere, debromination and dechlorination processes are taking place, leading e.g. for pyrolysis of chlorine-rich automotive shredder waste to a PCDD/PCDF homologue pattern with maximum at DiCDD/F to TetraCDD/F (Weber and Sakurai 2001). The pyrolysis of DecaBDE-containing HIPS at 500ºC generated mainly mono to pentabrominated PBDE (Hall & Williams 2008). The main TriBDE to PentaBDE formed from DecaBDE were 3,3',4-TrBDE (PBDE #77), 3,3',4.4'-TetraBDE and 3,3',4.4'5-PentaBDE (Hall & Williams 2008). The study highlights that significant debromination of DecaBDE to lower-brominated PBDE takes place under pyrolysis conditions. Therefore for all pyrolysis and gasification processes (and also for incineration processes in particular under transient conditions; see below) the fate of debromination of DecaBDE to POPs PBDE needs to be considered and assessed for feedstock recycling of PBDE (c-Penta/c-OctaBDE and DecaBDE). Furthermore the conversion to PBDF during thermal degradation of c-PentaBDE, c-OctaBDE and DecaBDE-containing materials in feedstock recycling needs to be taken into consideration and evaluated.

In a laboratory study on pyrolysis of TV casings it was concluded that the elimination of hazardous toxic compounds, mainly those containing bromine, is necessary before the pyrolysis oils are able to safely be used as fuels or in refinery or petrochemical industry flows (Vasile et al. 2006)(Vasile et al. 2007).

Pyrolysis and gasification with recovery of bromine

The price for elemental bromine has increased in recent years and is currently around $2500/t (Hofland 2010). Therefore the recovery of bromine can be of economic interest.

Several treatment options have possibilities for bromine recovery as summarised by Tange et al. (Tange & Drohmann 2002):

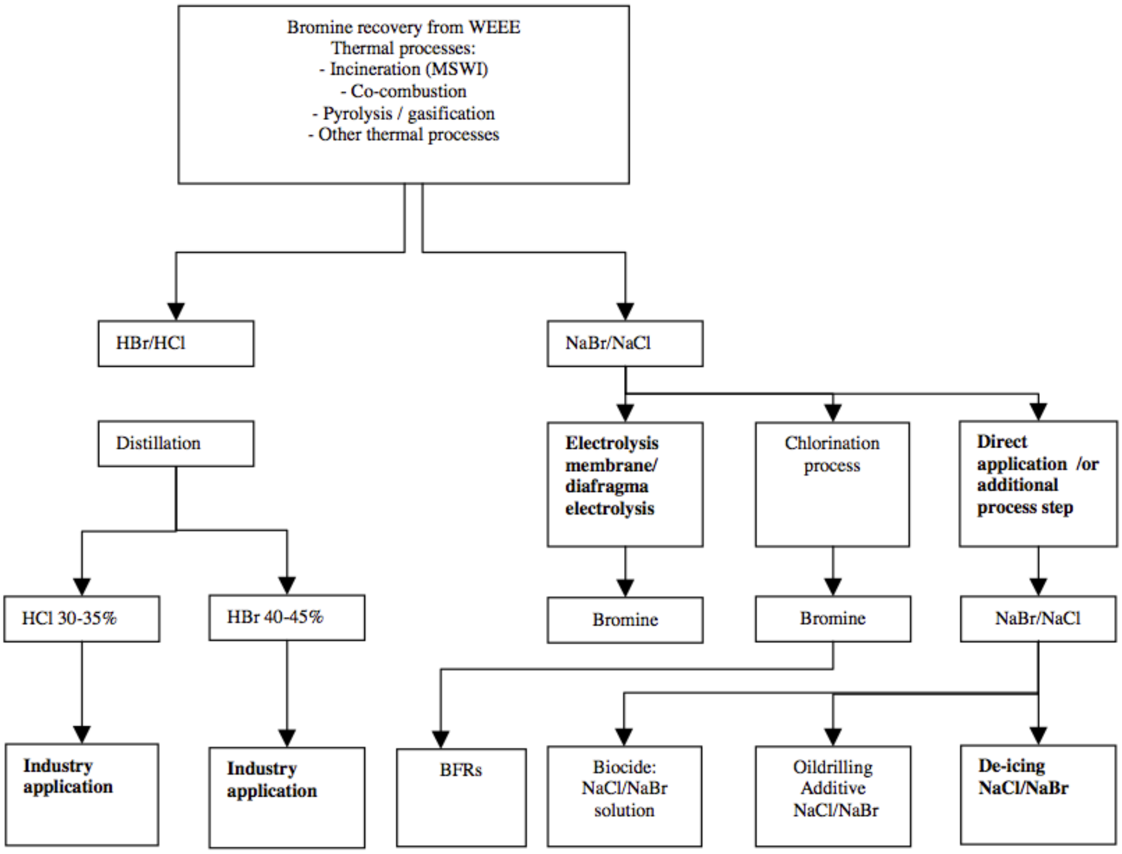

Figure 70: Potential options for the bromine recovery process and closing the bromine cycle (Tange & Drohmann 2002).

Whilst none of these post-combustion recovery processes are operating commercially two thermal processes utilising pyrolysis have been developed to pilot scale where the recovery of bromine from electronic waste and waste plastic was one project feature.

A) The Haloclean process

The Haloclean process is a low temperature pyrolysis developed as a thermal-chemical process for the treatment of waste electrical and electronic equipment (Hornung and Seiffert 2006, Koch 2007). The Haloclean® reactor was developed with a gas-tight rotary kiln. The process tries to divide shredded electronic scrap into a valuable material stream and an energy flow. In a two-stage pyrolysis the plastic components are converted into oil and gas. A further chemical process step (called “Polypropylene Reactor”) aims to strip and recover bromine and other halogens out of these products. From the remaining pyroylsis residue precious metals and other metals can be separated (Hornung and Seiffert 2006, Koch 2007). To date only a demonstration plant has been developed. The process is currently used for biomass pyrolysis.

B) Recovery of bromine by two stage pyrolysis-gasification

In a pilot trial carried out for the bromine industry (EBFRIP) at Energy Research Centre (ECN) (Boerrigter 2001)(Tange & Drohmann 2005) in Holland it was shown that it is possible to recover bromine via thermal processes. The process (“Pyromaat”) consisted of a staged gasification, comprising pyrolysis (550 ºC) and a high temperature gasification (>1230 ºC). In pilot test runs, the HBr was recovered by wet alkaline scrubbing of the syngas from treating plastic fraction of WEEE (Boerrigter 2001)(Tange & Drohmann 2005):

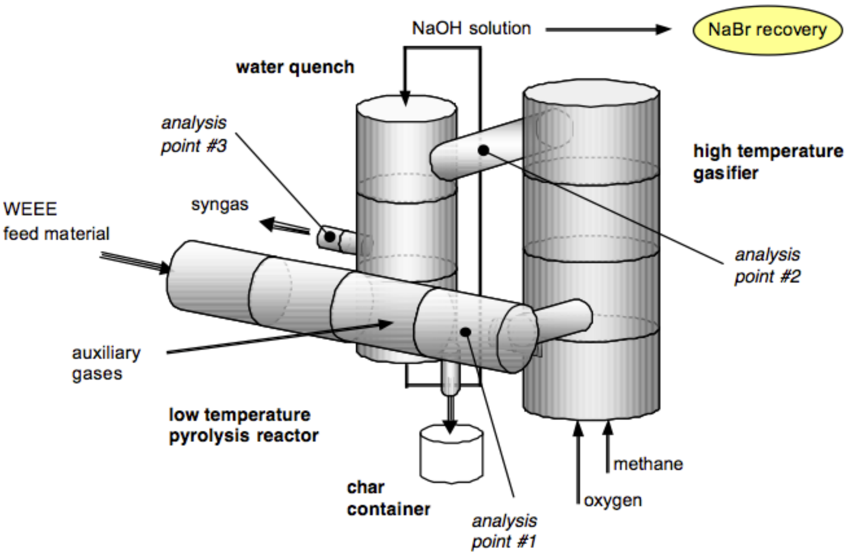

Figure 71: Impression of the 'Pyromaat' with the material flows (Boerrigter 2001)

This system was only operated at a pilot scale (Tange & Drohmann 2005).

C) Br recovery ammonia treatment

These novel techniques have been tested at a laboratory/pilot scale as that reported by Brebu (Brebu & Sakata 2006)(Brebu et al. 2006). Brebu describes a process for debromination of brominated flame-retardant treated high impact polystyrene (HIPS-Br) performed at 450 ^{o}C by ammonia treatment (Brebu & Sakata 2006). All inorganic and most organic Br compounds were successfully removed and converted to inorganic NH_4Br powder, which then allows easy bromine recovery. The liquid degradation products are rich in benzene derivatives and Brebu suggests that they can be used as feedstock or fuel (Brebu et al. 2006).

D) Full scale plant

There were no reports available showing whether thermal plants (pyrolysis or incinerator) to recover bromine has only been tested and operated as research trials (Boerrigter 2001) or whether there are any facilities operating at full-scale to recover bromine from PBDE/BFR-containing wastes. Since such facilities would have a high bromine/halogen input and halogen in the flue gas it can be assumed that high PBDD/PBDF, PBB and PBDE depending on the chlorine content also high PXDD/PXDF and PXB can be generated within the system. Therefore highly efficient flue gas treatment technologies would be necessary for such facilities. Within the process of Stockholm Convention implementation it should be assessed if such recovery plants are operated. Here the quality of the flue gas treatment systems and the releases of PBDD/PBDF, PXDD/PXDF and PBDE to air, water and solids should be assessed.

Alternatives to coal. A Japanese process involves the production of "a new artificial solid fuel, Eco-fuel, that uses both waste PU foam and coal" (Kim et al. 2006). The advantages are said to be related to the controlling of "the emissions of environmental pollutants from coal combustion". The "Eco-fuel" is composed of about 10 % by mass of PU foam and 90 % by mass of low-grade coal. The material is combined and briquetted under high pressure (3 ton/cm^2). No reference is made in the published literature to the likelihood of releases of PBDE nor of the production of brominated and mixed halogenated dioxins (Kim et al. 2006).

Pyrolysis and gasification of PBDE-containing materials for production of fuel without bromine recovery

Some plastic fractions even from E-waste are low in bromine (and PBDE) content. For example in the mixed plastic fraction from E-waste (after separation of TV casings and casings of monitors used for material recycling) being the major part of e-waste plastic (for Sweden approximately 80%) the bromine content is often below 1%[61] (Schlummer 2010, MBA polymers 2010) and first data for the Europe region indicate that PBDE content are below 1000 ppm (Austrian ministry of environment 2010; MBA polymers 2010). Also the concentration in Swiss automotive shredder is normally below 1% Bromine (Fahrni 2010). Since bromine recovery at this low content is probably not commercially useful, these major polymer fractions might be used for feedstock recycling via pyrolysis or gasification to produce alternative fuels or raw materials for chemical industry. A range of pyrolysis and gasification technologies have been developed for materials containing halogens and other heteroatoms and were reviewed (Hornung and Seifert 2006). Data and information on current commercial full scale application are however not available but should be gathered for the Stockholm Convention implementation. Hornung and Seifert emphasise in their review that any post-consumer plastic stream will contain some halogens in form of brominated flame retardants, polyvinylchloride and other sources and that gas streams from the depolymerization of plastic must be scrubbed to remove halogenated impurities to satisfy emission control, and halogens in the liquid product must be minimized to increase its value and marketability (Hornung and Seifert 2006). Furthermore in all pyrolysis and gasification processes the formation of unintentionally formed brominated and chlorinated POPs but also PAHs need to be considered. For chlorine-rich fractions (e.g. car shredder containing PVC) the oil after pyrolysis contain high levels of PCDD/DF (Weber and Sakuarai 2001, Rosemann et al 1998).

PBDE & PBDD/PBDF formation and releases from Pyrolysis and Gasification and UPOPs formation

Considering the results from laboratory thermolysis (Thoma 1987a, Clausen et al. 1987, Dumler 1989, 1990, Buser 1986, Zacharewski et al. 1988, Luijk et al. 1991, Bieniek et al. 1989), elevated concentrations of PBDDs/PBDFs can be expected from pyrolysis processes when PBDE is present in the waste (Weber and Kuch 2003). For chlorine-rich fractions (e.g. car shredder containing PVC) the oil after pyrolysis contained high levels of PCDD/PCDF up to 10 ng TEQ/g oil which corresponds to approximately 5000 µg TEQ/ton input (Weber and Sakurai 2001, Rosemann et al 1998). Therefore for pyrolysis/gasification of PBDE/BFR-containing materials/waste[62] (e.g. feedstock recycling of plastics or destruction of waste) formation of PBDD/PBDF needs to be considered and depending on the chlorine content also the formation of brominated-chlorinated PXDD/PXDF (Weber and Kuch 2003). Since pyrolysis and gasification are thermal processes under oxygen deficiency, dehalogenation (debromination and dechlorination) processes of the input materials are taking place (Hagenmaier 1987, Weber 2007). Here the pyrolysis of DecaBDE-containing HIPS at 500ºC resulted in the formation of mainly mono- to pentabrominated PBDE revealing significant debromination of DecaBDE under these conditions to mainly Mono to PentaBDE including the formation of POPs PBDE (Hall and Williams 2008). The main TriBDE to PentaBDE formed were 3,3’,4-TrBDE (PBDE #77), 3,3’,4.4’-TetraBDE and 3,3’,4.4’5-PentaBDE (Hall and Williams 2008). These congeners are for PCB the most toxic compounds but have not been evaluated in detail for PBDE. The study highlights that significant debromination of DecaBDE to lower-brominated PBDE takes place under pyrolysis conditions. Therefore for all pyrolysis and gasification[63] processes the fate of debromination of DecaBDE to POPs PBDE need to be considered and assessed for feedstock recycling of PBDE-containing waste (c-Penta/c-OctaBDE and DecaBDE).

However data and information on current commercial full scale operation of pyrolysis and gasification of PBDE-containing waste are not available. Levels of releases can however be estimated to be very high.

Therefore information which should be gathered on pyrolysis and gasification processes in the context of the implementation of the Stockholm Convention are:

a) The total amount of PBDE waste entering pyrolysis and gasification processes and the fate of the products

b) The dependence of debromination and conversion on the reaction conditions and to what extent this can be overcome by applying appropriate temperatures and residence time or appropriate post treatment technologies

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[61] However there are some other highly flame retarded ewaste fraction (e.g. office equipment) potentially containing PBDE.

[62] Hornung and Seifert emphasise in their review on “Rotary kiln pyrolysis of polymers containing heteroatoms” that any post-consumer plastic stream will contain some halogens in form of brominated flame retardants, polyvinylchloride and other sources and that gas streams from the depolymerization of plastic must be scrubbed to remove halogenated impurities to satisfy emission control and halogens in the liquid product must be minimized to increase its value and marketability (Hornung and Seifert 2006).

[63] In the fuel bed of gasification and even in the fuel bed of incineration processes pyrolysis conditions exist (Hunsinger et al 2002).

(e.g. pyrolysis/gasification in combination with a high temperature incineration (Boerrigter et al 2001) or melting step.

Appendix 3 (c): Energy Recovery and end-of-life Options

This section considers the more common and important energy recovery and end-of-life options for articles containing PBDE. In relation to energy recovery the technologies considered are:

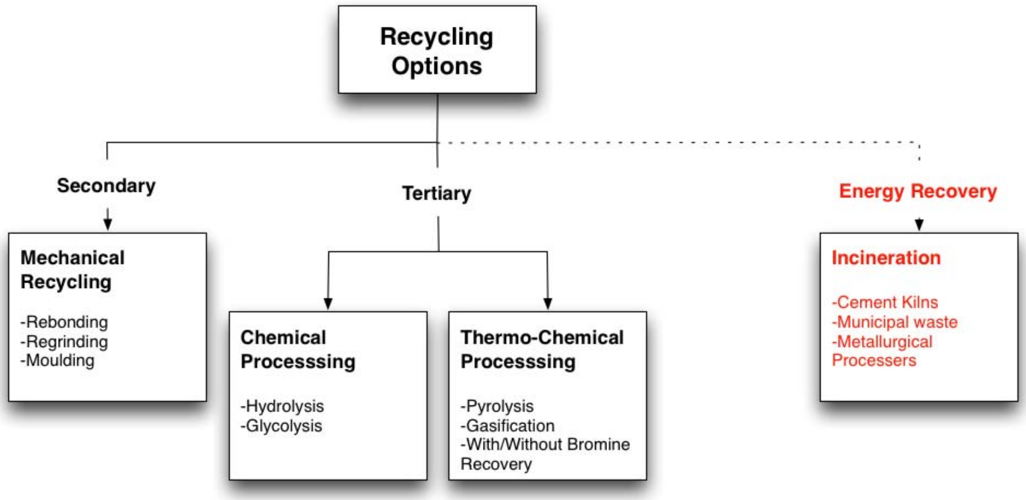

Figure 72: Energy recovery options

The EU risk assessment of PentaBDE said (European Chemicals Bureau 2001):

"Overall, for disposal by incineration and landfill, metal recycling and accidental fires, it can be concluded that the polybrominated diphenyl ethers, as a source of bromine, can contribute to the formation of halogenated dibenzo-p-dioxins and furans generated during such processes but it is not possible to quantify the amounts or assess the environmental significance of these products."

In the light of the likely hazards associated with these compounds there is still a remarkable imbalance between the literature on brominated compared with chlorinated dioxins. The seriousness of the problem associated with PBDD and PBDFs is, however, now becoming more clear than when the EU risk assessment was published in 2001 due to the growing library of relevant data. This adds to the uncertainties particularly associated with the energy recovery and end-of-life options.

Appendix 3 (c) (i): Energy recovery from PBDE/BFR-containing waste in cement kilns

Cement kilns are increasingly used in waste management schemes (Holcim & GTZ 2006, Reijnders 2007). The facilities have been/are used for destruction of PCB contaminated oil (Karstensen et al. 2010) and some pilot tests for destruction of pesticides (Schimpf 1998, Karstensen et al. 2006)and tyres (Carrasco et al. 1998, Giugliano et al. 1999) (Court 2005) have been performed and the results published.

The Stockholm Convention guidelines on Best Available Techniques (Stockholm Convention 2007b) includes "*Electronic Waste*" on the negative list of "*waste not recommended for co-processing in cement plants*". The guidelines expand upon this and say:

"Electronic waste is composed of computer and accessories, entertainment electronics, communication electronics, toys and also white goods such as kitchen devices or medical apparatus. The average composition shows that electronic waste contains, on the one hand, substances harmful to health and the environment such as Cl, Br, P, Cd, Ni, Hg, PCB and brominated flame retardants in high concentrations, often higher than threshold limit values. On the other hand, electronic waste contains such a high scarce precious metal content that all efforts have to be undertaken to recycle it. Co-processing of the plastic parts of electronic waste would be an interesting option, but requires disassembling and segregation first (after Holcim, 2006)".

This reflects the interest by the industry in cement kilns as possible energy recovery option for plastic waste containing PBDE from electrical and electronic equipment (Tange & Drohmann 2005).

However no study has yet been published with monitoring of releases of PBDE and PBDD/PBDF. It is therefore not possible to be confident about the effectiveness of cement kilns for wastes containing PBDE.

The destruction efficiency of PBDE in the waste will depend to a significant extent on the feeding point in the kiln. Stable molecules (and Dioxin precursor) like PCB or POPs pesticides need to be fed at the hot end of the kiln into the burner flame with temperature up to 2000ºC and residence time of more then 2 seconds above 1100 ºC to guarantee a high destruction efficiency. This should assure also destruction of PBDE in secondary fuels and suppression of PBDD/DF formation at this feeding point. However PBDE-containing waste (e.g. E&E plastic, automotive/transport shredder, polyurethane foam from furniture and construction, mattresses, insulation foams) are solid waste fractions. Such solid waste fractions are normally fed from the ‘cold’ end of the kiln where temperatures between 700 and 1000ºC exist and the residence time depends strongly on the plant configuration of the respective cement kiln.

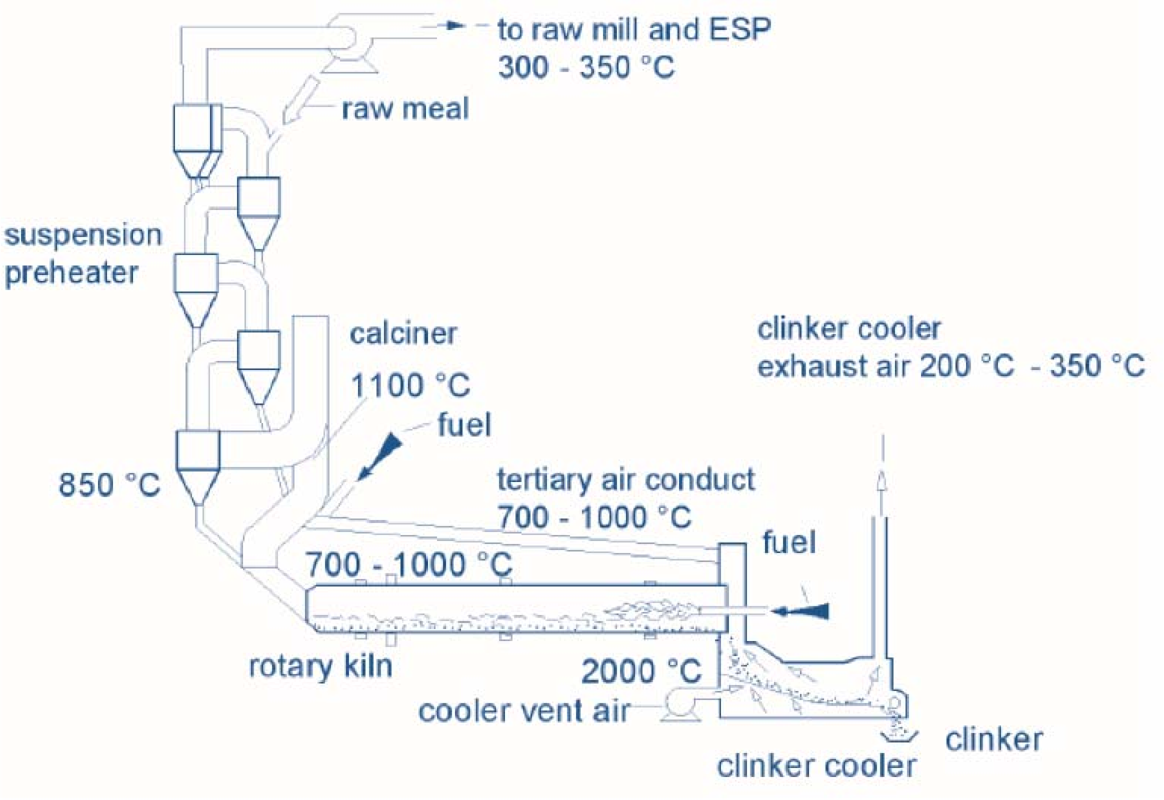

Figure 73: Temperatures in a modern cement kiln(Stockholm Convention 2007b)

Therefore the current situation of accepting and treating PBDE/BFR-containing waste in cement kiln requires a detailed and site-specific assessment including feeding points, temperature, residence time, PBDE destruction efficiencies (in particular if the waste types are not appropriate for feeding with fuel in the burner but would be fed from the cold end) and related emissions. A properly configured test-burn, together with the establishment of the destruction efficiency which incorporates analysis of all emissions from the process including from products and the bypass stack, should always be carried out before any POPs waste is considered for routine disposal.

A second important consideration for treating PBDE/BFR-containing waste in cement kilns is the sensitivity of some cement kilns types to halogen input. For a pre-heater kiln (with or without a pre-calciner) – the main kiln type considered from the Stockholm Convention BAT/BEP guidelines as an option for waste treatment (Stockholm Convention 2007b) - the average total chlorine input from the combination of raw material, fuel and other materials (including waste) should really stay below 0.03% (total input recalculated to clinker) to avoid clogging (Waltisberg 2010). Here, chloride entering the cement kilns builds up within the kiln (around kiln inlet zone) resulting in hot meal (meal at kiln inlet) levels of up to 2% chlorine within this area and circulates within the system with possible negative impact on the operation by clogging at the colder areas at kiln inlet/lower cyclone stages (Waltisberg 2010). If an alkali bypass system is installed between the feed end of the rotary kiln and the pre-heater tower then high chlorine-containing cement kiln dust (CKD) can be generated in the system. The chlorine content of this CKD presents particular problems for future disposal options. Furthermore while cement kilns preheater normally have PCDD/DF emission levels well below 0.1 ng TEQ/Nm^3 (Karstensen et al. 2006) but with high chlorine levels wet and dry kilns can reach emission levels well above 1 ng TEQ/Nm^3 and levels as high as 136 ng TEQ/Nm^3 have been reported (Stockholm Convention 2007b, Karstensen 2008). As bromine has similar physico-chemical properties to chlorine it will probably act in a similar way within a cement kiln. The behaviour of bromine in cement kilns and associated releases of unintentionally produced POPs/byproducts or elemental Bromine has to our knowledge, however, not been investigated and described. Therefore with increased input of bromine via PBDE and other BFRs containing waste fractions, the risk of increased clogging in preheater kilns and a possible formation of brominated & brominated-chlorinated PXDD/DF and other brominated organics for all kiln types (but in particular for wet and long dry kilns) needS to be considered and assessed.

Therefore the options and limitations for the destruction of wastes containing PBDE such as sorted plastics from electrical and electronic equipment, automotive/transport shredder, polyurethane foam from furniture and construction, mattresses, insulation foams) in cement kiln need an urgent evaluation to decide the options and limits of recovery energy from PBDE/BFR-containing materials in cement kilns. Such assessment should include a comprehensive monitoring of release of POPs PBDE and other unintentionally produced brominated and brominated-chlorinated toxic substances including PBDD/DF and PXDD/DF. Considering that the built-up of chloride within a cement kiln can take weeks, an assessment of the fate of PBDE/BFR-containing materials on associated POPs releases can best be performed with long term monitoring (Reinmann et al 2010) over extended time frame of weeks and months. In this respect also the releases from bypass operations should be assessed including the contamination levels of cement kiln dust (CKD) and the necessity of environmentally sound management of such solid residue.

Appendix 3 (c) (ii): Energy recovery from PBDE/BFR-containing waste in incinerators

Most of the PBDE/BFR retarded waste has been produced in North America and Europe where BAT waste incinerators operated according Best Environmental Practice (BEP) should normally be able to cope with the contaminated residues at moderate concentrations (Sakai et al. 2001)(Vehlow et al. 2002)(Weber & Kuch 2003).

In Sweden there is currently no materials recycling of WEEE plastics in the form of re-processing into raw material. WEEE plastics from TV and computer casings containing BFR are separated at the pre- treatment plants and sent for incineration at authorised plants (in Sweden). The BFR-free WEEE plastics are exported for materials recycling (Retegan et al. 2010).

For incinerators treating relatively high levels of PBDE/BFR-containing wastes Vehlow suggested that bromine recovery might be possible (Vehlow et al. 2002). It was suggested that a typical MSW combustion line treats 20 tonnes of MSW per hour and that normally, to achieve suitable economies of scale, several lines operate alongside each other. On the basis that 3% of WEEE plastics containing 2.5 wt% bromine was added to three lines, (1800 kg/h WEEE plastics), this would represent 45 kg/h of bromine in the feed. At a typical scrubber efficiency of >97% and a bromine recycling yield of >90%, such a unit could in theory recycle 310 tonnes of bromine per year. It is possible to distil HBr as a 48% solution, in which case the recycling level would be around 660 tonnes of 48% HBr per year. This, Kennedy and Donkin had calculated, could contribute 7% to the income of a municipal waste incinerator. Whilst the bromine industry proposals in Europe (as described in Appendix 5 (a)) were for high levels of chemical recycling with bromine recovery it is not clear that this has ever been applied in practice.

It must be highlighted that extremely high levels of PCDD/DF were formed intermediately during solid fuel burnout when incinerating fractions from waste electrical and electronic scrap (WEEE) with a mixture of municipal waste (Hunsinger et al. 2002). The formation of mixed brominated-chlorinated PXDD/DF in relation to PCDD/DF depends strongly on Cl/Br ratio of the waste mixture. When co-combusting WEEE at very high share (Cl/Br ≈3-4 of the fuel mixture) PXDD/DF were formed some orders of magnitude higher then PCDD/DF[64] (Hunsinger 2010 personal communication). These PCDD/DF and PXDD/DF were efficiently

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[64] In another experimental series in this incinerator an addition of 0.06% bromine to the fuel feed (containing approximately 0.6% chlorine) resulted in the formation of high levels of PXDD/DF (mainly mono bromo- and dibromo-polychloroDD/DFs) in the first combustion zone at levels higher then the PCDD/DF. This demonstrate that despite thehigh Cl/Br ratio of >10 in the fuel input considerable PXDD/DF can be formed) (Hunsinger et al. 2001)

destroyed during controlled flue gas burnout in the secondary combustion zone finally resulting in moderate PCDD/DF and PXDD/DF levels in the raw gas and low levels in the clean gas (Tange & Drohmann 2005)(Vehlow et al. 2002). These tests demonstrate that BAT incineration can cope with addition of PBDE/BFR-containing plastic and the resulting high levels of unintentionally formed chlorinated, brominated and brominated-chlorinated dioxins formed and released from the fuel bed could be destroyed in the secondary combustion zone operated according to BAT (sufficient residence time (2 seconds), temperature (>850ºC) and turbulence (Stockholm Convention 2007b)(European Commission 2006). But the test also highlights the associated risk of incinerating PBDE/BFR-containing WEEE in incinerators with lower combustion quality (see below).

Corrosion in incinerators in particular the boiler section is of concern also from economic perspective and as all halogens enhance corrosion, operators of incinerators are reluctant to burn large amounts of bromine-containing waste (Rademakers et al. 2002). When incinerating PBDE/BFR-containing waste the corrosion of boilers in waste incinerators and other incineration plants must therefore be taken into consideration. If bromine (from PBDE and other BFRs from e.g. WEEE in fuel) is considerably lower compared to the chlorine input (Cl is around 0.7% in household waste), the corrosion is mainly caused by chlorine (Rademakers et al. 2002). When however high levels of PBDE/BFR-containing wastes are processed e.g. for recovery of bromine then such corrosion needs to be considered and closely observed and economic benefits and drawbacks assessed.

PBDE & PBDD/PBDF formation and releases from waste incineration of PBDE-containing materials

A larger part of PBDE-containing materials end up in waste incinerators of different quality. In industrial countries most incinerators are BAT/BEP. However the PCDD/PCDF inventories of the Stockholm Convention indicate that many of the incinerators in transition and developing countries are not state of the art.

BAT/BEP incinerators and PBDD/PBDF and PXDD/PXDF formation and release

When incinerating waste with a high share of PBDE-containing materials like WEEE, extreme high levels of PBDD/DF, brominated-chlorinated PXDD/DF and PCDD/DF are formed in the first combustion zone even in BAT incinerators (Hunsinger et al 2002, Hunsinger 2010). The PCDD/DF levels alone were up to around 10,000 ng /Nm^3 (Hunsinger 2002). Considering that the ratio of TEQ to total PCDD/DF in incinerators is around 1/30 to 1/100, the related TEQ levels can be estimated to 100 ng TEQ/Nm^3 to several hundreds of ng/TEQ. PXDD/DF in these tests were approximately an order of magnitude higher compared to PCDD/DF (Hunsinger 2010) and considering a similar dioxin-like toxicity of PBDD/DF & PXDD/DF compared to PCDD/DF (see Annex PBDD/DF), the total dioxin-like toxicity of the gas phase in the first combustion zone can be estimated in the order of 1000 ng TEQ/Nm^3.

In BAT/BEP incinerators the PCDD/DF, PXDD/DF and PBDD/DF formed in the first combustion zone were efficiently destroyed during controlled flue gas burnout in the secondary combustion zone finally resulting in moderate PCDD/DF, PXDD/DF and PBDD/PBDF levels in the raw gas and low levels (below 0.1 ng TEQ/Nm^3) in the clean gas (Tange and Drohmann 2005, Vehlow et al 2008, Hunsinger 2010). The high combustion efficiency results additionally in the formation of low levels of products of incomplete combustion (soot, PAH etc.) resulting in low de novo synthesis rates in the post combustion zone. Therefore PBDD/DF, PBDE/BFR-containing waste can be destroyed in BAT waste incinerators operated according to Best Environmental Practice (BEP) with final low values in the stack gas (Sakai et al 2001, Vehlow et al 1997, Weber and Kuch 2003).

In recent measurements in municipal waste incinerator in the US and Taiwan without specific feed of PBDE-containing materials PBDE and PBDD/PBDF were detected.

The PBDD/DF air emission levels in the Taiwanese municipal waste incinerator (without specific PBDE input) had mean value of 2.28 and 18.2 pg N/m^3, respectively (sum of seven 2,3,7,8-Br-substituted tetra- to hexaBDD/DFs). Furthermore the Taiwanese study has shown that in a BAT grate municipal waste incinerator, elevated PBDD/DF and PBDE levels were found in the bottom ashes (BA) (Wang et al. 2010b).

The authors commented:

> *"BA exhibited much higher PBDE distributions than those of other ashes and stack flue gases in the MSWI systems. The reutilization of BA of MSWIs should contribute PBDE into the environment, and not be ignored from the developing PBDE inventory. Furthermore, the high PBDE content in BA may also contribute the PBDE exposures of the workers who handle and operate BA-related work"* (Wang et al. 2010b).

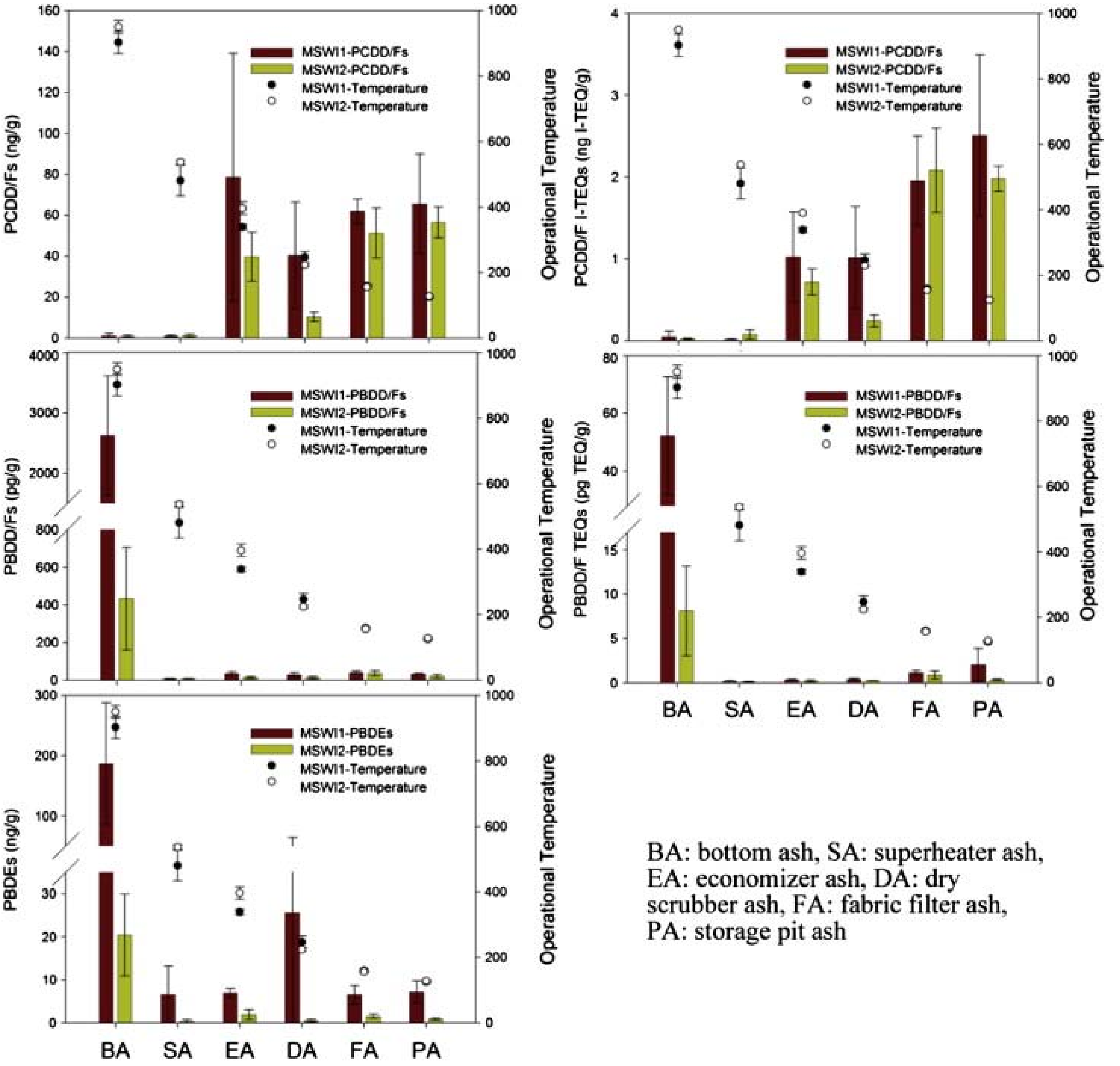

Figure 74: PCDD/DF, PBDD/DF and PBDE contents in the ashes from MSWIs (Wang et al. 2010b).

The source of the PBDD/DF most probably resulted from insufficient burn out of PBDE/BFR-containing waste in the fuel bed or by combining the bottom ash with particulate matter falling through the grate (grate siftings which are usually c.1 to 3% of waste input) and are not subject to complete combustion. Grate incinerators are the main incineration technology used for municipal waste worldwide and grate siftings are generated in all these facilities. In incinerators operated according BEP, grate siftings need to be returned into the incinerator and must not be combined with the bottom ash. The Stockholm Convention BAT/BEP guidance does not specifically recommend this approach and in Section V.A Part II for waste incinerators includes siftings in the mass of bottom ash – inferring that they are mixed together. Consideration might be given to a clarification of this issue in a future update of the BAT/BEP guidelines in the light of BEP practice in e.g. European incinerators and the results from Wang (Wang et al. 2010b). **Further studies would be valuable to estimate the relevance of PBDD/DF and PXDD/DF in bottom ash if PBDE/BFR-containing materials are incinerated.**

In a recent study of a full scale municipal waste incinerator in the US PBDE and PBDD/DF release in raw gas and stack gas have been reported (Wyrzykowska et al. 2008). PBDE und PBDD/Fs in stack gases were at levels of 1.41 to 16.5 pg/Nm^3 (sum of 17 tri- to octa-BDD/DF) (Wyrzykowska et al 2008).

Both the shut-down and the start-up of the MWI were found to considerably increase the yields of ΣPBDE in the flue gas (with at least 10- to 30-fold increases in concentrations during transients compared to steady state operation). The transient conditions also had an effect on the BDE congener and homologue patterns in the flue gas. Even though the isomers found in technical product BDE dominated in all stages of the combustion process, some of the measurement of the transient conditions exhibited specific enrichment of congeners which are minor or not present in the technical mixtures, (*e.g.,* DiBDE-15, TriBDE-17, TriBDE-28, TeBDE-49) (Wyrzykowska et al. 2008). The higher contribution of di- through tetraBDE congeners during the transients suggests that debromination likely occurs at some point of the disturbed combustion (Wyrzykowska et al. 2008). A likely explanation is that during start-up and shut down the oxygen supply is not optimised and therefore pyrolysis/gasification condition prevail which support significant debromination of PBDE (as highlighted above for pyrolysis and gasification technologies). The US study concluded that MWI emissions should be considered as a source of both lowly and highly brominated PBDE and PBDD/DF to the atmosphere (Wyrzykowska et al. 2008).

In the Taiwanese and the US study no particular addition of PBDE/BFR-containing waste were done for the study highlight that PBDE are present in waste of ordinary municipal waste in the US and Taiwan and depending on the levels of disturbed combustion can be released from BAT incinerators when not operated according to BEP[65].

In another measurement PBDD/F concentrations levels in an industrial waste incinerator with elevated bromine input in the feeding waste were relatively low (7 congeners, 4.17 pg TEQ/Nm^3) (Wang and Chang-Chien, 2007).

These data indicate that BAT/BEP incinerators have measurable releases of PBDD/DF indicating PBDE/BFR input in municipal waste but that they are under normal operation at relatively low level in stack gas (considerably below 0.1 ng TEQ/Nm^3).

On the other hand the high PBDD/DF, PXDD/DF and PCDD/DF levels in the first combustion zone at an incineration test with high levels of WEEE input demonstrate that at such WEEE destruction projects specific care has to be taken for optimized operation.

It should be noted that the May 2010 USEPA Exposure Assessment made "*no attempt*" to "*estimate stack air releases of PBDDs and PBDFs during the incineration of MSW*" (USEPA 2010).

Non-BAT/BEP incinerators

Most incinerators in developing and transition countries do not meet BAT standards and are often inadequately maintained and not operated according to Best Environmental Practice (BEP). There are no dedicated studies available on incineration of PBDE-containing waste and associated releases. However considering the excellent precursor quality of PBDE for PBDF formation (Buser 2006, Weber and Kuch 2003) high releases of PBDD/DF and depending on the levels of chlorine also PXDD/DF can be expected (Weber and Kuch 2003, Hunsinger 2010). A rough estimate on releases can be done with information from the above mention study in BAT pilot scale incinerator: The formation of extreme high levels of PXDD/DF in the first combustion zone before entering secondary combustion (Hunsinger 2010, Hunsinger et al 2001) for incineration of high level WEEE containing waste (Hunsinger 2010) indicate that for incinerators without an excellent secondary combustion zone the PBDD/DF and particularly the PXDD/DF release from co-incineration of WEEE would be extremely high. Levels can be expected at several 100 ng or even 1000 ng dioxin-like toxicity/Nm^3 (considering PCDD/DF, PXDD/DF and PBDD/DF).

The final release of PBDE from waste input will depend on the temperature and the residence time in the fuel bed and flue gas above 800ºC and additionally on the burn out of the fuel bed. As mentioned above even in BAT incinerators PBDE are found in bottom ashes, fly ashes and flue gas (Wang et al 2010, (Wyrzykowska et al. 2008). Levels in non-BAT incinerators can be expected to be considerably higher than levels reported in these BAT or near BAT studies.

Furthermore the study of Wyrzykowska (2008) further suggest significant debromination of PBDE under disturbed condition which are virtually permanent for non-BAT incinerators. Therefore it need to be highlighted that the incineration of DecaBDE-containing waste in non-BAT incinerators can be expected to lead to the formation and release of POPs PBDE (and PBDD/DF) via debromination and degradation of DecaBDE.

In conclusion, if PBDE-containing waste is incinerated in non-BAT incinerators there are likely to be high of PBDE, PBDD/DF and PXDD/DF in both emissions and residues leading to relevant exposure risk.

Appendix 3 (c) (iii): Recovery of PBDE-containing materials in smelters and other metal industries

Some PBDE/BFR-containing materials are treated or end up in copper smelters and other metal industries such as electric arc furnaces or secondary alumina smelters.

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[65] The US incinerator were operated non-continuous with daily start-up and shut-down

Copper smelters are used for recovering metals from Printed Circuit Boards, cables and other plastic materials which are firmly combined with the metals to be recovered.

Recent studies have reported on releases of PBDE and polybrominated dioxins and furans (PBDD/DF) from electric arc furnaces, sinter plants and aluminium smelters revealing that also PBDE and BFR-containing materials are processed in these facilities (Du et al.)(Odabasi et al. 2009)(Wang et al. 2010c). The latest review by Du also reports releases of PXDD/DF (Du et al. 2010). Whilst the type of feeding materials was not specifically measured[66] or documented in this literature these emissions indicate that PBDE-containing waste have been processed in these facilities.

Since thermal processes can lead to debromination of DecaBDE to lower-brominated PBDE the emission pattern of PBDE in these studies only allow limited conclusions on the actual input of c-PentaBDE and c-OctaBDE into these processes. Nor, without specific details of the concentration levels of brominated compounds in the inputs can the destruction efficiency or appropriateness of treatment for PBDE-containing waste be assessed.

Therefore only limited conclusions can be made of the effectiveness and environmental impacts of these processes for recovering energy and materials from articles containing c-PentaBDE and c-OctaBDE.

Material recovery and energy recovery in smelters

Smelters treat a wide range of mixed waste streams such as shredder residues (which can contain high concentrations of PBDE), PVC, and catalytic metals such as copper (Hwang et al. 2008). Other flame retarded materials, notably printed circuit/wiring boards (‘PWB’ is used as an acronym instead of PCB to avoid confusion with Polychlorinated biphenyls), are often processed in secondary copper smelters for recovery of the copper and other precious metals. The polymers containing the PBDE/BFRs are firmly combined with precious and other metals to be recovered. The plastics/resin content serves a dual function as a reducing agent and as a source of energy for the smelting process. There have been full-scale tests to additionally utilise PBDE/BFR-containing plastic from WEEE as substitute for coke or oil as reduction agent for the metals and as fuel for smelting (Mark & Lehner 2000)(Hagelüken 2006)(Brusselaers et al. 2006).

State-of-the-art integrated smelters require investments of well above US$ 1 billion. Currently, only 5-10 plants feature the technological performance necessary for the described operations. These include e.g. the plants run by UMICORE[67] (Belgium) the Norddeutsche Affinerie AG (Germany), Boliden[68] (Sweden/Finland), Johnson Noranda (Canada) and DOWA (Japan).

Since the scale of these feedstock recycling operations as practiced for printed circuit boards involves tens of thousands of tonnes/year (see table 12) and is currently recommended for PBDE/BFR-containing plastic from electronics by industry (Mark & Lehner 2000)(Hagelüken 2006)(Brusselaers et al. 2006) the releases of PBDE and PBDD/DF could be substantial depending on destruction efficiency of these facilities.

Two larger pilot studies on BFR WEEE plastic recycling in smelters have been documented in Europe. One in an integrated smelter in at Sweden (Boliden[69]) and the second at in an integrated smelter in Antwerp/Belgium (Umicore[70]).

Table 51: European Smelter Capacity from BSEF[71]

Plants	*Existing Recycling capacity (per year)*
Boliden, Sweden	35,000 tons of E&E scrap (25% plastic)
Umicore, Belgium	Can treat >10,000 tons per year (mainly circuit board)

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[66] Although the Du study does provide some limited information on feedstock in the supporting information (Du et al. 2010)

[67] http://www.umicore.com/en/

[68] http://www.boliden.com/

[69] http://www.boliden.com/

[70] http://www.umicore.com/en/

[71] BSEF http://www.bsef.com/science/brominated-flame-retardants-and-recycling/technical-recycling-and-waste-solutions/

Norddeutsche Affinerie AG, Germany	Treats 10,000 tons of circuit boards plus an other >15,000 tons of E&E plastics

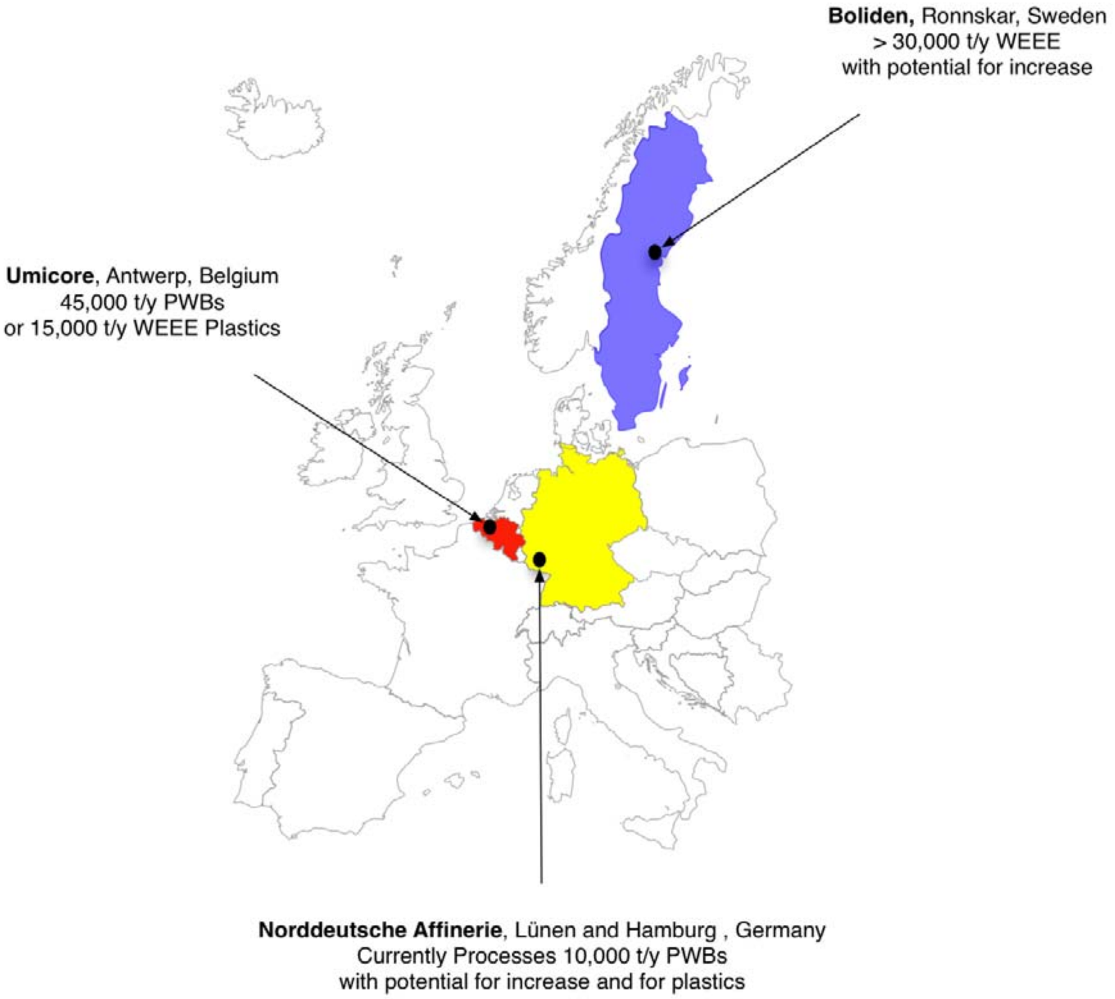

Figure 75: Capacity for use of WEEE plastics in precious metal smelters in Europe (adapted from (Tange et al. 2006))

While the temperature in the molten metal bath is high (above 1100°C), the temperature from the charging point to the surface of the bath ranges through a full temperature gradient from ambient conditions to the bath temperature. Smelters can be described as thermal processes with incomplete combustion occurring at the charging of the material. While coke is mainly oxidized in the melting bath, the more flammable resin of printed circuit boards together with the plastics from WEEE charged to the smelter is ignited and burns/pyrolyse to some extent on top of the melting operation.

As described above, experience with waste incinerators demonstrates the concentration of PCDD/DF and the brominated and brominated-chlorinated PXDD/DF in the off gas of the first combustion zone is high (up to one thousand ng TEQ/Nm^3) when adding a high proportion of WEEE (Hunsinger et al. 2002), Hunsinger 2010). These high levels of unintentionally produced POPs are largely destroyed in the secondary combustion zone of the incinerator (Hunsinger et al. 2002). From this evidence together with basic consideration of dioxin formation, it can be expected that high levels of brominated PBDD/DF - and depending on the chlorine content of the WEEE or the other fuel also high levels of brominated-chlorinated PXDD/DF and PCDD/DF - will be formed and released from smelter furnaces treating PBDE and other BFR-containing plastic.

The European "*Draft Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries*" mention that "*If major amounts of electronic scrap with brominated flame-retardants are used as feedstocks, this may result in the formation of brominated and mixed halogenated PXDD/F*" (European Commission 2008a). Unfortunately, however, even the latest draft of the BREF contains no actual monitoring data.

The use of an afterburner could possibly substitute for a secondary combustion chamber but PCDD/DF emissions up to 5 ng/m^3 are reported in the updated Draft BREF (European Commission 2008a) even with after-burners (which it is understood are not fitted to all smelters and are not reported in most of the literature (Mark & Lehner 2000)(Hagelüken 2006)(Brusselaers et al. 2006)). According to information from UMICORE staff, an afterburner is necessary for the treatment of off-gases after a non-ferrous smelting process where e.g. printed circuit boards are treated (Kegels 2010).

In the two larger pilot projects utilizing brominated flame retarded material in smelters (Mark and Lehner 2000, (Hagelüken 2006)(Brusselaers et al. 2006), PBDD/DF and brominated-chlorinated PXDD/DF have not been measured or were not reported. PCDD/DF were mentioned for both case studies. The value in the fuming plant during recycling of PC scrap in the Swedish study was found to be 0.08-0.12 ng TEQ/m^3, (around the limit of stack emissions for waste incinerators) (Mark & Lehner 2000) and therefore above the German workplace level of 0.05 ng TEQ/Nm^3 (TRGS 557 2000) even without considering the PBDD/DF or PXDD/DF. Also in the pilot test at the smelter in Belgium only PCDD/DF were measured and only at the stack after flue gas treatment (Hagelüken 2006)(Brusselaers et al. 2006).

Therefore no adequate study has yet been performed (or at least published) to assess the release of PBDE and the formation and releases of PBDD/DF and PXDD/DF from the feedstock recycling of PBDE/BFR-containing materials in smelters. This type of feedstock recycling is used for tens of thousands of tonnes of printed circuit boards every year and has been recommended for PBDE/BFR-containing plastic from electronics (Mark & Lehner 2000)(Hagelüken 2006)(Brusselaers et al. 2006). There is clearly an urgent need to fill the major data gaps and to assess the releases of PBDE, PBDD/DF and PXDD/DF from these practices.

Material recovery and energy recovery in electric arc furnaces

Electric arc furnaces (EAFs) have not been widely considered to be facilities for recovery of PBDE/BFR-containing waste. It has been established for a number of years that electric arc furnaces processing scrap metals can generate high levels of PCDD/DF in solid wastes and dust from flue gas cleaning (ENDS 1997). More recently, however, emissions of PBDE and PBDD/DF from EAFs have been reported for China, Taiwan and Turkey (Du et al. 2010)(Du et al.)(Odabasi et al. 2009)(Wang et al. 2010c). The levels from metallurgical processes were "*markedly higher than combustion processes*" (Du et al.). This demonstrates that feedstock wastes containing PBDE is entering EAFs and need to be addressed in the Stockholm Convention implementation. Since EAFs recover metal, such cases might fall into the category of recycling and recovery of materials containing PBDE. As materials recovered/recycled in EAF possibly containing PBDE following categories need to be considered:

- car scrap and components of other transport vehicles (busses, trains, aeroplanes) containing PBDE in polyurethane foam from seats and roof, plastic from interior or cables
- white goods containing PBDE in plastic part or PWBs.

Therefore EAFs need to be evaluated for the sources of PBDE input. Additionally it needs to be assessed to which extent EAFs using BAT with afterburners might be able to safely process PBDE/BFR-containing material input. Alternatively even for BAT EAFs input material containing PBDE may need an additional separation step before the thermal recovery of the metals in the furnace.

Feedstock recycling of PBDE-containing plastic in primary steel industry

Plastic is used in the primary steel industry either directly in the blast furnace to substitute coke or in the coking plant as a substitute for coal in the production of coke (Japan National Institute for Environmental Studies 2010)(European Commission 2009). In a life-cycle assessment for PBDE-containing TV casings, Hirai et al. (Hirai et al. 2007) assessed four scenarios: material recycling, feedstock recycling, incineration and landfilling. Whilst the assessment was based on DecaBDE in polystyrene the results are likely to be more broadly applicable to PBDE in thermoset polymers. They concluded that feedstock recycling in the primary steel industry would be preferable compared to material recycling or incineration for energy recovery. However in their assessment the bromine/halogen content was one factor limiting the extent of use in the primary steel industry. The Japanese steel industry accepts a halogen content of up to 0.5%[72] (bromine or chlorine). The bromine content of waste TV casings generated in Japan each year is 705 tons or nearly twice the 400 tonnes of total halogen which could be accepted/managed by plastic feedstock recycling in the Japanese primary steel industry. Consequently a maximum of about 50% of the TV plastics could be recovered via this route for Japan (Hirai et al. 2007). Considering the additional chlorine content normally present in waste plastic and shredder residues the total quantity of TV casings which could be utilised in the Japanese primary steel industry would be even less. The study concluded that the TV casings in Japan would need to use other treatment options as well (Hirai et al. 2007) and also other BFR-containing plastic fractions would need other treatments. However plastic waste containing bromine (or chlorine) could first be treated with a pyrolysis process or other HCl/HBr removing process and as such a coke or other low halogen fuel produced could then be utilised by the steel industry (Tange & Drohmann 2005).

According to European data (which will need to be confirmed for other regions) the plastic fraction of mixed electronics and automotive/transport shredder residues seems to have a lower bromine/halogen (and also PBDE) content compared to TV or computer casings. Therefore such material might be more suitable for use for feedstock recycling in the steel industry and are available in larger amounts. The European BAT reference document mentions shredder residue as a used feedstock in primary steel production. However for an assessment of the options and limitations of the feedstock use of such plastic rich fractions (mixed electronics and or car shredder) the heavy metal content, particularly mercury, is crucial for the evaluation of options and limitation for their use[73] (European Commission 2009).

Furthermore no PBDE/BFR and PBDD/DF measurements have been performed (or, if so they are not published) for feedstock recycling of PBDE/BFR-containing materials in the primary steel industry – including direct use in blast furnace or for use in coke plants. On the other hand, the recent study on PBDE. PBDD/DF and PXDD/DF emissions from sinter plants in Taiwan and China demonstrate their presence and release from this industry (Wang et al. 2010c)(Du et al. , Du et al. 2010).

Wang noted that "*surprisingly*" PBDE and PBDD/DF were found in the stack flue gases of sinter plants whose feedstock contained coke, lime and iron ore, but not any BFRs-containing wastes. This, they suggested, revealed that sinter plants could generate PBDE and PBDD/DF through similar formation conditions to those generating PCDD/DF (Wang et al. 2010c). They had not measured the bromine content in the feedstock of the sinter plants but suggested one of the bromine sources for PBDE and PBDD/DF formation "*is believed to originate from coal*". Unfortunately the reference given for this in the paper is incorrect[74] and makes no mention of coal and so it has not been possible to check this source. The input materials - coke and iron ore - are actually very unlikely to be the direct source for these purely brominated organic compounds[75], it is most probable that PBDE-containing plastic materials have either been used here in the blast furnace and PBDE and PBDD/DF have been transferred via recycling of the ash into the sinter plant, or that PBDE-containing plastic have been used for production of coal/coke used as energy source in the sinter process. Another possible PBDE source could be PBDE-containing conveyer belts used extensively in these facilities.

The use of PBDE/BFR-containing materials in the primary steel industry and the related emissions of PBDE and PBDD/PBDF need a detailed assessment in the frame of Stockholm Convention implementation.

PBDE-containing materials in secondary aluminium industries

PBDD/DF and PXDD/DF have been detected in stack gas from secondary Aluminium smelters (Du et al. , Du et al. 2010) .

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[72] In Europe the Chlorine content of up to 1.5% (Bremen/Germany) (Tukker 2002) and 2% (Linz/Austria) (European Commission 2009) is reported to be accepted from steel industry.

[73] The European Steel BREF mention limits for Cobalt, Chromium, Arsen, Lead, Nickel, Mercury, Cadmium and Zinc in plastic feedstock recycling in a blast furnace (European Commission 2009).

[74] Marklund, S.,Andersson, R.,Tysklind, M.,Rappe, C.,Egeback, K.-E.,Bjorkman, E. Grigoriadis, V., (1990). Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20(5): 553-561 (Marklund et al. 1990)

[75] Chlorine is present in one to two orders of magnitude higher concentration compared to bromine. Therefore it is from basic consideration of formation mechanism not possible to form highly brominated compounds like the detected DecaBDE (which was detected as the PBDE with the highest emission value from the sinter plants by Wang (Wang et al. 2010c). In formation experiments using synthetic fly ashes with an equal ratio of chlorine and bromine, the bromine was found at even lower concentration compared to chlorine (Weber et al. 2002b).

PBDE have also been found in the waste input of an aluminium recycling plant. Samples were taken from waste from handling of electric and electronic plastics, filter dust from electronic crusher, cyclone dust from electronic crusher and light residues from a car shredder. In the screening analyses, PBDE were identified in all samples in amounts of 245–67,450 ng/g. The highest levels were found in the plastics from electronics. Other brominated flame retardants were also observed in all samples. The major PBDE congeners found were PentaBDE (150 ng/g), HexBDE (20 ng/g) and DecaBDE (10 ng/g)(Sinkkonen et al. 2004).

Therefore, secondary aluminium plants should further be assessed for PBDE-containing material input and for the release of PBDE, PBDD/DF and PXDD/DF to air and solid residue.

Antimony smelters

Some flame retarded WEEE plastic is recovered in antimony smelters where Sb_2O_3 (used as flame retardant synergist with halogenated flame retardants) is recovered and the plastic serves a function as a reducing agent. No data on volumes treated, PBDE destruction efficiency, or PBDE and PBDD/DF release are available for these processes.

Appendix 3 (c) (iv): Landfill

Globally the majority of PBDE end up in landfills.

Even in industrialized countries a large proportion of flame retarded wastes are deposited in landfill sites. This has been confirmed by material flow analyses were recently documented for California (Petreas & Oros 2009) and Switzerland (Morf et al. 2003, Morf et al. 2007).

In countries such as Australia and New Zealand with no waste incineration capacity practically all the flame retarded waste will finally be sent to landfill. The subsequent degradation processes are largely unknown.

PBDE & PBDD/PBDF formation and releases from landfills

PBDE releases from landfills

Previous reviews have largely dismissed the possibility of releases from landfill sites. BiPRO, for example, in their assessment of management options for OctaBDE for the European Commission in relation to the UNECE comment (BiPRO 2007):

"*No experiments appear to have been carried out on the leachability of c-octaBDE from polymers in landfills, but, by comparison with the decabromodiphenyl ether (see the risk assessment report of decabromodiphenyl ether (European Commission, 2002)), it would not be expected to leach to a significant extent from polymers, unless the polymer itself undergoes some form of degradation*" (BiPRO 2007).

They therefore concluded:

"*releases after disposal are considered to be negligible. It is assumed that this conclusion applies to the whole UNECE region*"(BiPRO 2007).

A similar conclusion was reached in the report prepared for the New Zealand Department of the Environment for the POPRC process (Geo & Hydro – K8 Ltd 2010). The executive summary concludes:

"Disposal to landfill is in the New Zealand situation a well developed and controlled activity. Only very low levels of BDE were present in the leachate of three landfills tested. This study supports disposal of BDE-plastics to secure landfills as an environmentally sound means to dispose of BDE containing polymers / plastics. Compared to the quantities of these products stored, the quantity of BDE leaving the landfill in leachate is infinitesimal" (Geo & Hydro – K8 Ltd 2010).

This conclusion is caveated, however, by the additional comment:

"*These initial findings should be more widely validated*" (Geo & Hydro – K8 Ltd 2010).

There is, however, growing evidence that brominated flame retardants including also PBDE are leaching from landfills and contaminating the environment (Oliaei et al. 2002, Osako et al. 2004, Odusanya et al. 2009, Danon-Schaffer 2010, Danon-Schaffer & Mahecha-Botero 2010)(Oliaei et al. 2010).

In the Oliaei study (Oliaei et al. 2002) leachates of five landfills with different waste characteristics (three municipal, one industrial, and one demolition landfill) were analyses for PBDE. The total PBDE concentrations ranged from 29-248 ng/L. The demolition landfill had the highest total PBDE concentrations. The sewage sludge samples from two wastewater treatment plants that receive landfill leachates showed the total PBDE concentrations up to 5,300 ng/g (dry weight). These levels may not seem particularly high but as part of their study, sediment and fish samples from rivers receiving the related wastewater effluent discharges were also analysed for PBDE. The total PBDE concentration in fish samples were high and ranges from 113-3,400 ng/g lipid wt, and the sediment samples showed PBDE contamination up to 1,950 ng/g TOC.

Substantial concentrations of PBDE were also present in the soils adjacent to all landfills and dumpsites in various regions of Canada (Danon-Schaffer 2010), indicating atmospheric PBDE release and deposition from landfills.

Recently, PBDE-contaminated groundwater from South African landfills has been reported (Odusanya et al. 2009), indicating that new POPs PBDE are present in significant amounts in the end-of-life stage in developing/transition countries. For developing countries it has also been demonstrated that releases of PBDE from landfills reach human communities living near or on the landfills. Elevated levels of PBDE have been reported in breast milk from women living near a landfill site in India (Kunisue et al. 2006) and young people (11 to 14 years) living and rag picking on a landfill in Managua/Nicaragua (Athanasiadou et al. 2008).

These cases detail the releases of PBDE from landfills and related waste water treatment plant and highlight the necessity of careful management of treatment residues and effluents. It appears, therefore, that the relatively low/moderate levels in leachate cannot prevent environmentally relevant contamination and bio-accumulation. There are possible risks to via fish and contaminated agricultural soils to the human foodchain.

Furthermore neither the New Zealand review (Geo & Hydro – K8 Ltd 2010) nor BiPRO (BiPRO 2007) appear to have considered the long-term nature of landfill storage. Because of their persistence (and relative moderate mobility), PBDE (and other POPs) will persist in landfills for many decades and probably centuries or even longer.

Dannon Schaffer recently modelled the debromination of DecaBDE in landfills to lower PBDE in landfills (including the POP-BDE) (Danon-Schaffer & Mahecha-Botero 2010). Debrominaton rates were derived from other debromination studies. Depending on selected debromination rates one model suggests significant debromination within the next 30 years.

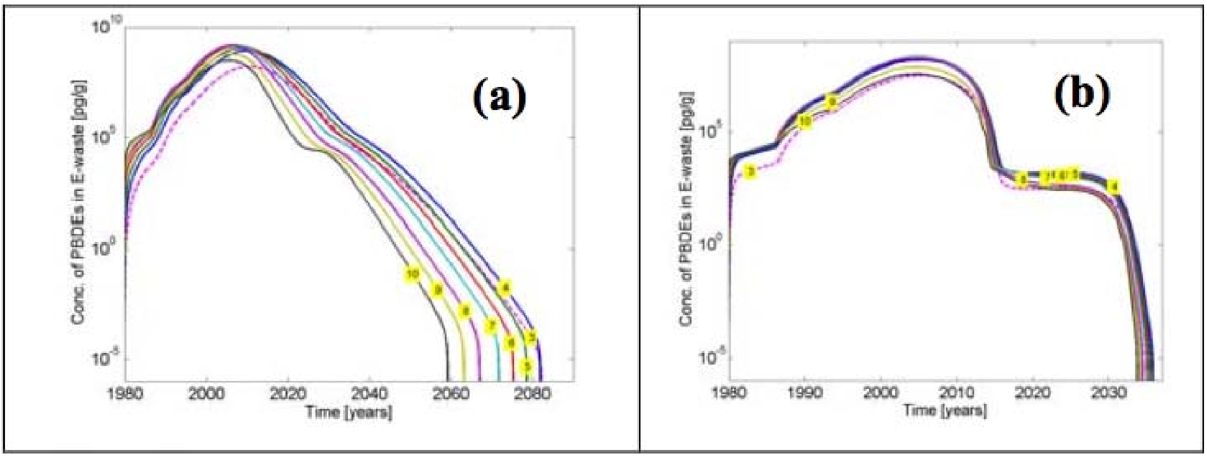

Figure 76: Predicted PBDE concentrations of the eight congener groups in the e-waste *subsystem* vs. *time. (a) Kinetic parameters from Table 2, column 6. (b) Kinetic parameters increase ten fold (Danon-Schaffer & Mahecha-Botero 2010)*
Numbers indicate the number of bromine atoms for each BDE group (i.e. 10 = deca-BDE, 9 = nona-BDE to lowBDE = mono- di-, tri-BDE).

Another model suggested debromination taking considerably longer then 2150 which is probably a more likely scenario in modern landfill sites.

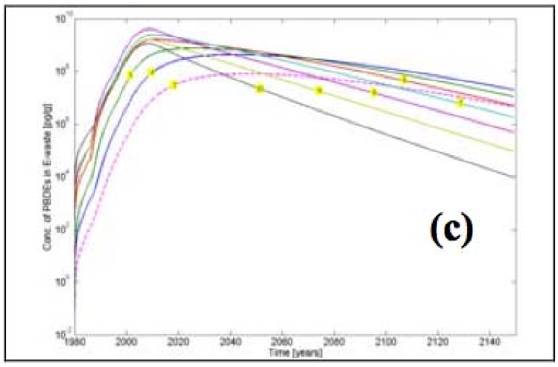

Figure 77: Predicted PBDE concentrations of the eight congener groups in the e-waste subsystem vs. time. (c) Kinetic parameters decrease ten fold (Danon-Schaffer & Mahecha-Botero 2010).

The problem in each case is that the hazards of the PBDE mixture steadily increases through debromination whilst over these extended time frames engineered landfill systems, including basal and capping liners, gas and leachate collection systems will inevitably degrade and lose their structural integrity and capability to contain contamination (Buss et al. 1995, Allen 2001)(Simon & Muller 2004). The guarantee for lining systems is often around 25 years and compacted clay liners are particularly vulnerable to failure (Simon & Muller 2004) and there is "*considerable concern*" about the common usage of compacted clay liners as a single liner in a capping system (Müller 2006). Failure of the capping system after pumping has ceased and before failure of the basal liner can lead to flooding of the landfill sites and contamination of surrounding areas. The loss of structural integrity and containment capability is dependent upon the materials used and construction practices. However, ultimately all engineered landfills will degrade and allow containment releases over time. When considering the disposal of PCBs to landfill USEPA expressed concerns that the "*large amounts of PCBs already contained in land disposal sites present a severe hazard for the future*" (USEPA 1979). The risks presented by PBDE appear to be similar and these concerns are likely to be equally applicable.

It is therefore inevitable that the landfilled PBDE (and other POPs) will eventually leach into the environment over extended periods of decades or even centuries via escaping leachate, contaminating ground or surface water as well as escaping to atmosphere by volatilisation.

Furthermore over the extended timescales of a century or longer, consideration needs to be given to the impacts of climate change and extreme weather events. This may include increased flooding, posing problems with the integrity of the containment systems and possibly increasing the rate of future leakage. Climate change is likely to result in higher temperatures, increasing the volatalisation of semi-volatile and volatile compounds. In some areas, longer drying periods may enhance drying or dessication of surface (or liner) caps, increasing the opportunity for gaseous escape and higher water infiltration from rainfall. In other areas, higher intensity rainfall events and increased flooding will impose risks on the integrity of the containment systems and depending upon the lining system, will probably result in increased leachate production and leakage. It is therefore likely that climate change and warming may induce greater levels of deposited POPs to leach into rivers, lakes and the larger environment via escaping leachate, ground or surface water as well as to the atmosphere by volatilisation. Furthermore the sea level is expected to rise nearly a metre by 2100, together with storm surges between 10 and 20 times more frequently, this will result in permanent flooding of coastal areas and even some low lying inland areas will be innundated (Bebb & Kersey 2003). Landfills and contaminated sites in these areas will then be compromised by the sea-water.

Release of PBDE and other contaminants is likely to lead to exposure and subsequent bioaccumulation of contaminants to fish in these areas.

Landfill fires

A long-standing concern with landfill fires is that the presence of chlorophenols and PCB compounds in municipal wastes can form PCDDs and PCDFs during the incomplete combustion and smouldering (Ettala et al. 1996). Due to the excellent PBDD/DF precursor properties of PBDE there are similar or even greater risks associated with the formation and release of PBDD and, particularly, PBDF from PBDE as precursors in landfill fires. The WHO-IPCS expert review noted this concern although no data were then available on the scale of this source (WHO & IPCS 1994).

Whilst comprehensive data is scarce it is clear that many landfill sites do catch fire. The Stockholm Convention PCDD/DF National Action Plans, inventories, and "Dioxin toolkit" (UNEP 2005) landfill fires are a relevant source of PCDD/DF in particular for developing and transition countries. However landfill fires are also common in industrial countries.

A survey in Finland, for example showed that, on average, 0.6 fires per landfill site occurred annually. One-quarter of fires were deep fires at a depth of more than 2 m where pyrolitic conditions conducive to the production of PBDD and PBDFs. There was an average of 633 sanitary landfills in operation in Finland in 1990–92 and thus it could be expected that 380 landfill fires probably occurred annually in Finland (Ettala et al. 1996). Ruokojarvi, concluded:

"During the fires, the concentrations of polychlorinated dibenzo-p-dioxin and -dibenzofurans in the air of the landfills were high; even the limit value for waste incineration plants in many European countries, 0.1 ng/m^3 was exceeded during the active fire".

PBDD/DF and PBDE have to date only be measured in fires on dumps in Mexico in a project (supported by UNEP Chemicals and USEPA) where the waste has been ignited on purpose for a scientific study on emission factors for open burning on dump sites (prevailing for developing/transition countries) (Gullett et al. 2009). In these studies emissions of 40 PBDE averaged 724 μg/kg carbon burned (Gullett et al. 2009) and had congener patterns similar to those of reported atmospheric sampling demonstrating that the PBDE likely originating from commercial brominated flame retardants and were not formed in the fire.

In this study high emissions of PBDD/DF averaging 470 ng TEQ/kg carbon burned were similar in magnitude to their chlorinated counterparts (PCDD/DF). The authors suggested that these PBDD/DF originate either from reaction products of PBDE combustion or as thermally desorbed impurities from the commercial PBDE flame retardant (Gullett et al. 2009).

The research group noted that emission factors appear to be related to combustion quality, as conditions conducive to smouldering combustion, rather than flaming combustion, resulted in higher emission factors (Gullett et al. 2009).

Since landfill fires are to a large portion smouldering fires partly taking place within the landfill body with lack of oxygen close to pyrolysis/gasification the fate of debromination in particular of DecaBDE to lower POP-BDE (Hall et al 2008) need to be assessed. Such DekaBDE conversion might contribute to a significant formation of POPs PBDE and PBDD/DF.

Appendix 3 (c) (v): primitive e-waste recycling and the open burning of waste

The majority of PBDD/DF and PXDD/DF are formed in end-of-life stage in particular during primitive recycling of electronic waste in transition and developing countries (Ma et al. 2009)(Zennegg et al. 2009).

A large share of electronic waste (e-waste) from industrialized countries ends up in China, India, Pakistan, Vietnam, the Philippines, other South East Asian countries (Basel Action Network & Silicon Valley Toxics Coalition (SVTC) 2002)(UNEP et al. 2005)(Cobbing 2006)(United Nations Environment Programme & United Nations University 2010) but also African countries like Nigeria or Ghana for cheap recycling due to the low labour costs and less stringent environmental regulations in these countries. Recycling of e-waste has been undertaken for 10-20 years in some of these countries[76].

The PCDD/DF inventories developed in the frame of Stockholm Convention implementation have revealed that large quantities of waste are burned in the open. Since PBDE and other BFR are included in household and other wastes along with PCDD/DF also PBDD/DF are formed and emitted.

PBDD/DF and PBDE, as noted in the section on landfill fires above, have so far only been measured in an open burning study (supported by UNEP Chemicals and US EPA) on a dump site in Mexico (Gullett et al. 2009) with high emission factors for 40 PBDE (averaged 724 μg/kg carbon burned) and high emission factors for PBDD/DF (averaging 470 ng TEQ/kg carbon burned). These PBDD/DF emissions are of the same magnitude as the chlorinated counterparts (Gullett et al. 2009). The authors suggested that these PBDD/DF originate either from reaction products of PBDE combustion or as thermally desorbed impurities from the commercial PBDE flame retardant (Gullett et al. 2009).

Landfill fires/open burning of (household) waste is contributing PCDD/DF emissions in the order of tens of kilogrammes TEQ to the global PCDD/DF inventory. The emission factor found in the open burning experiments in Mexico suggest that PBDD/DF from PBDE also are emitted in similar orders of magnitude and that the emission of PBDE from open burning are in the range of several tens of thousands of kilogrammes. Since these emission factors have been derived from only a few open burning experiment, these estimates should be seen only as a preliminary indication of the total order of magnitude. However this first estimate highlights that PBDE and PBDD/DF releases from landfill fires/open (household) waste burning are significant on a global scale and are therefore highly relevant.

It is noted in Appendix 6 (b) that Schenker suggests reducing open burnings of waste might be an efficient measure to reduce current levels of DecaBDE in the environment because a majority of DecaBDE originates from this process (Schenker et al. 2008). This would help to reduce the atmospheric availability of DecaBDE for debromination and thus the increase in generation of POP-BDE from this important source.

Primitive recycling practices of PBDE-containing materials

At informal e-waste recycling workshops/areas in Asia and Africa, a number of methods are used to recover metals from e-waste.

Open burning of electrical/electronic wastes to remove plastics and recover metals is a common treatment step in informal e-waste recycling.

Solder is recovered from printed circuit boards using open flames or hot plates. Subsequently the electronic components are removed, either for re-use, or to be ground down to recover metals. Also, in some locations, printed circuit boards are shredded and the metals separated by vibration.

Another non thermal primitive technique applied for recovery of precious metals is acid leaching

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[76] China and several other countries recently restricted the importation of e-waste and are attempting to regulate and control primitive e-waste recycling (Li and Zhao 2010).

The burning/heating processes result in emission to air of hazardous substances. These include halogenated substances contained within the e-waste, other organic substances generated during the combustion processes and a range of heavy metals.

Levels of PBDE and unintentionally produced POPs pollution from primitive recycling practices

The primitive recycling has produced contaminated mega-sites with a multitude of contaminants (Wong et al. 2007b)(Yu et al. 2006)(Yu et al. 2008)(Ramu et al. 2008). The best investigated area is probably Guiyu city located in the Chaoyang District in Southeast China, with a total area of 52 km^2 and a population of 150,000. It is a rice-growing region and its industry has been dominated by e-waste recycling since the early 1990s. The practices of primitive e-waste recycling over more than a decade with the associated emissions of high levels of POPs and heavy metals from many open burning sites and hundreds of small recycling shops has resulted in these contaminants accumulating in soils and sediments and biota. One consequence is that the drinking water of Guiyu city has been identified unfit for consumption and clean water is now routinely imported from Ninjing (Basel Action Network & Silicon Valley Toxics Coalition (SVTC) 2002)(Yu et al. 2006).

While Guiyu is the most prominent and best investigated e-waste recycling area, there are probably hundreds or even thousands of sites where primitive e-waste recycling contaminates large areas with pollutants including PBDE, PBDD/DF and PXDD/DF.

Air contamination

Air pollution around primitive e-waste dismantling and recycling areas in Guiyu/China was investigated by Li et al (Li et al. 2007b)(Wong et al. 2007b).

PBDE levels in ambient air were more than 100 times higher than other published ambient air data. PBDE POPs (BDE-47, 66, 100, 99, 154, 153, and 183) were the major contaminants detected [77] (Wong et al. 2007b).

Li et al detected high levels of PCDD/DF and PBDD/DF. Atmospheric concentrations of PCDD/PCDFs were .0.909 to 48.9 pg TEQ/m^3. Several of the individual measurements where higher then the highest ambient air levels reported in other ambient air studies globally (Li et al. 2007b). The PBDD and PBDF (eight 2,3,7,8-substituted congeners) levels in ambient air were also extremely high with average levels of 4.5 pg TEQ/Nm^3 in summer time and 27 pg TEQ/Nm^3[78] in winter time. The average TEQ levels of PBDD/DF in air were even higher than those of PCDD/PCDF. Brominated-chlorinated PXDD/DF have not yet been measured in air in e-waste recycling areas.

The total daily PCDD/PCDF intake of Guiyu residents were estimated to be between 1.88 to 6.08 pg of I-TEQ/kg/day (Li et al. 2007b). Therefore the population in Guiyu reached and often exceeded the recommended TDI of WHO (1-4 pg) by inhalation alone – an exposure route which normally accounts for less than 1% of daily intake. Considering the even higher TEQ levels from PBDD/DF the daily intakes were dramatically above WHO recommendation. Furthermore the daily intake of children per kg of bodyweight were approximately twice those of adults.

Li et al. (Li et al. 2007b) measured only ambient air in Guiyu but the levels in the working environment at some recycling shops will certainly be even higher. Li commented that the migrant workers employed by the e-waste recycling factories, numbering approximately 100,000 in all, who are breathing poisonous air in their workplace for more than 10 h per day without any protective measures might be particularly badly affected (Li et al. 2007b).

Li et al (Li et al. 2007b) did not measure PXDD/DF but it is likely that this class of compounds would have increased the exceedances of the tolerable daily intake much further as these were the compounds found in Guiyu by Yu (Yu et al. 2008) to have the highest concentrations of all the dioxins in soils from open e-waste burning. This is discussed further below.

China has recently introduced new regulations on e-waste import and management and have enacted a large program in an attempt to improve e-waste recycling in Guiyu. However e-waste flows have now diverted to

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[77] DecaBDE and NonaBDE were not measured.

[78] The authors used the TEF of PCDD/PCDF for PBDD/F. Since 2,3,7,8-TBDF were the most prominent PBDD/F the use of PCDD/F lead to a considerable considerably underestimation of the dioxin-like toxicity (TEF factor of 2378-TBDF was selected from 2378-TCDF (0.1) while the TEF factor from bio-assay indicate that the TEF factor of TBDF is around 0.8) ..

other South East Asian countries including Vietnam, The Philippines, India or African countries and the primitive practices described in this section continue in those countries (Yoshida & Terazono 2010).

Soil contamination

Leung *et al.* (Leung et al. 2006) conducted a detailed study at the Guiyu area to quantify the pollution levels generated from e-waste recycling, and identify sources. They found PBDE levels up to 1,169 ng/g (dry weight) in soils near the recycling areas which were 10–60 times higher than PBDE contamination reported at other locations in the world. In 2007 this study was extended (Leung et al. 2007) to surface soils and combusted residue in the Guiyu area and found total PBDE concentrations were highest in the combustion residue of plastic chips and cables collected from a residential area (33,000–97,400 ng/g, dry wt); in soils from an acid leaching site (2,720–4,250 ng/g, dry wt); and a printer roller dump site (593–2,890 ng/g, dry wt). The authors also found that DecaBDE was the dominant congener (35–82%) among the study sites.

Yu et al (Yu et al. 2008) and Zennegg et al (Zennegg et al. 2009) reported extremely high levels of PCDD/DF, PBDD/DF and PXDD/DF in soil in Guiyu. PCDD/DF levels at two open burning sites were 13,900 ng TEQ/kg and 13,300 ng TEQ/kg respectively and therefore exceeded levels and which remediation is often required even for industrial sites (Weber et al. 2008b).

PBDD/DF were also detected in all soil samples. For the circuit board smouldering site PBDD/DF values were 45 times higher compared to PCDD/PCDF and also for the open burning sites PBDD/PBDF exceeded PCDD/DF level (see Figure 78) (Yu et al. 2008). Regarding mixed brominated-chlorinated PXDD/DF and PCDD/DF at both e-waste burning sites (Site C and D in Figure 78). The concentration of PXDD/F were lower than PBDD/DF only for the area where printed circuit boards were smouldered (Site A Figure 78).

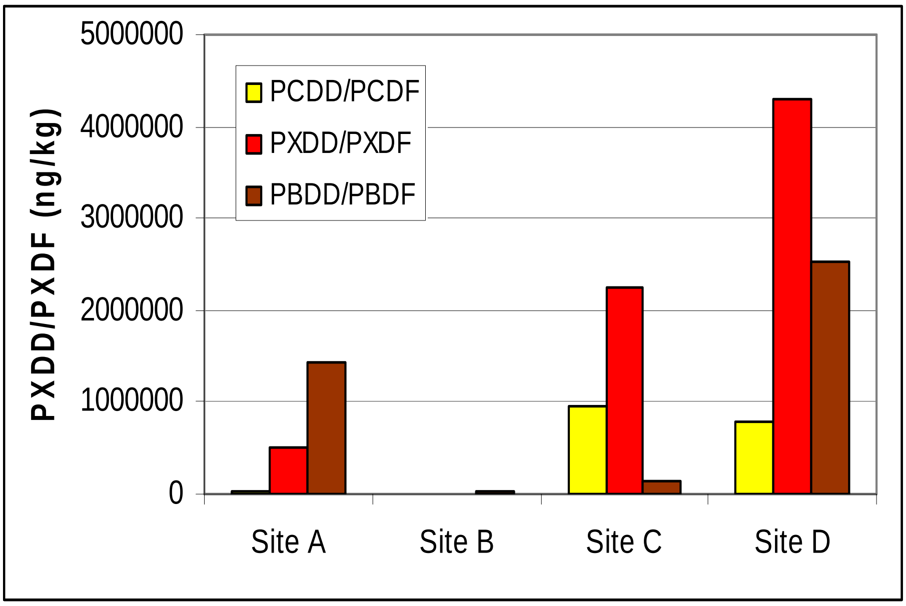

Figure 78: PCDD/DF, PBDD/DF and PXDD/DF in soil from Printed Circuit Board smouldering (A), open Ewaste burning (C and D) compared to an open burning area for household waste (B) in Guiyu (Yu et al. 2008).

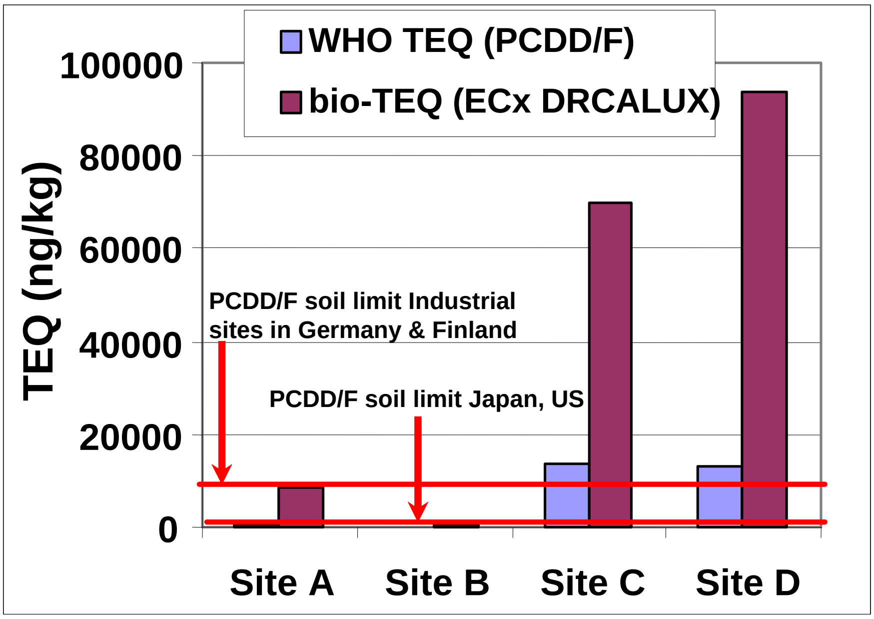

Figure 79: Soil contamination in Guiyu at Ewaste burning/smouldering sites A, C and D: Comparison of WHO TEQ (PCDDs, PCDFs, PCBs) and bio-TEQ (DRCALUX) with soil guidelines for remediation in some countries (Yu et al. 2008). At site B mainly household waste was burned.

Total Dioxin-like toxicity was estimated by a standard bio-assay assessing dioxin-like compounds (DR CALUX). The dioxin-like toxicity for site A, C and D were five to fourteen times higher compared to the PCDD/F derived TEQ (Figure 27). The bio-TEQ levels were approximately 10, 70 and 90 times above the 1,000 ng TEQ/kg limit used for a range of countries as remediation limit for industrial sites (e.g. US and Japan).

These extreme high soil contamination levels reveal that the Dioxin levels after decades of primitive ewaste recycling are extremely high at levels making them one of the highest dioxin polluted sites.

PBDE were also present in high concentrations in the soil. Total total PBDE levels were in the ppm level (up to 44,400 ng/g) with mainly DecaBDE (31,200 ng/g). TetraBDE to NonaBDE were an one order of magnitude lower concentrations at low ppm level.

These studies further demonstrated that PBDE were the key precursor for dioxin-like compounds in primitive E-waste recycling (Yu et al. 2008)(Zennegg et al. 2009). Furthermore Zennegg et al concluded that "*Considering that several 1000 tons of PBDE in the 20 to 50 million tons of Ewaste reaching the waste recycling sector every year mainly in developing countries around the world utilizing primitive thermal processes, the load of halogenated PXDD/PXDF can be expected to be in the tons scale and therefore possibly higher than all other current PCDD/PCDF sources combined*" (Zennegg et al 2009).

The authors note that "*People still work and live on/around these sites without any protective measures; children play without any awareness of the health threats and farmers still grow their rice and vegetables just nearby. This situation calls for an immediate significant improvement of e-waste recycling practices in developing/transition countries. Additionally, appropriate remediation measures need to be evaluated and started*" (Zennegg et al. 2009).

Sediments

All together 23 PBDE (from mono- to hepta-BDE and deca-BDE) were found in the sediment samples. In general, the total PBDE concentrations in sediments ranged from 4 to 407 µg/kgdw (average 125.2 mg/kg) which were much higher than those reported in other sediments around the world. (Wong et al 2007).

Human contamination of PBDE, PCDD/PCDF and PCBs at primitive Ewaste sites[79]

Human milk, placenta and hair were collected from donors at the e-waste recycling area in Guiyu and Taisho and compared to background area in China (Chan et al, 2007; 2008, Xing et al 2007). Mothers living at the e-waste site contained substantially higher values of ΣPCDD/DF (WHO-TEQ) (by over 2, 3, and 6 times for milk, placenta and hair, respectively) and ΣPBDE in their tissues (by over 57, 19 and 31 times for milk, placenta and hair respectively), when compared with their counterparts residing at the reference site. Also PCB levels (ΣPCBs (ng/g)) of all the human tissues collected from the e-waste site were substantially (over 3, 5, and 7.6 times, respectively, for ΣPCBs in milk, placenta and hair) higher than those collected from the reference site.

The high levels of PCDD/DF, PCBs and PBDE in human milk implied that infants at the e-waste processing sites were potentially threatened by greater health risks than adults *(Xing et al. 2007)(Chan et al. 2007)*(Wong et al. 2008a):

Table 52: PCDD/Ds in human specimens from Taizhou and Lin'an (Chan et al. 2007)(Wong et al. 2008a)

Site	***E-waste site: Taizhou (n=5)***			***Reference site: Lin'an (n=5)***		
Human specimens	Milk fat	Placenta fat	Hair dry wt	Milk Fat	Placenta fat	Hair dry wt
ΣPCDD/F (WHO-TEQ) pg/g	21.0±13.81	35.1±15.6*	33.8±17.7*	9.35±7.39	11.9±7.05	5.59±4.36
Range	11.5-44.6	18.1-43.2	14.57-62.43	2.04-21.35	4.89-13.3	2.41-13.3
ΣPBDE ng/g	116±191*	19.5±29.9*	110±210	2.06±0.94	1.02±0.36	3.57±2.03
Range	8.89-457	1.28-72.0	8.47-485	1.0-3.56	0.59-1.42	1.56-5.61

**Significant difference between e-waste site and reference site at $p<0.05$*

Table 53: PCBs in human specimens from Taizhou , compared with Lin'an (Xing et al. 2007)

Site	***E-waste site: Taizhou (n=25)***			***Reference site: Lin'an (n=25)***		
Human specimens	Milk fat	Placenta fat	Hair dry wt	Milk Fat	Placenta fat	Hair dry wt
ΣPCBs ng/g	363±470*	223±97.0 *	385±465*	116±108	44.5±76.9	50.9±37.2
Range	13.6-1957	99.4-435	23.2-1704	33.0-405	0.15-263	17.0-139
Range	27.1-457	8.32-285	3.43-146	5.41-239	N.D.-510	5.83-208

** Significant difference between e-waste site and reference site at $p<0.05$*

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[79] In addition to PBDE, PCDD/PCDF, PBDD/PBDF, a wide range of other toxic chemicals in electronic waste and unintentionally formed pollutants from thermal treatment of e-waste are released. E.g. today dozens of brominated flame retardants are in use and additionally chlorinated and non-chlorinated phosphor organic flame retardants are applied. Furthermore, chlorine (PVC) and fluorine-containing plastic are included in e-waste resulting in a complex mixture of chlorine, bromine and fluorine containing organic pollutants from the primitive/thermal recycling operations. In addition to a wide range of toxic heavy metals are released (lead, mercury, cadmium, chromium, antimony etc). This large variety of pollutants question risk assessments based on evaluation of single compounds. The Stockholm Convention POPs Reviewing Committee has recently started with activities on toxicological interactions between POPs. The multiple POPs contamination of humans by primitive e-waste recycling could be one important contemporary issue to be addressed in this respect considering the global relevance of this problem and the amount of Stockholm Convention POPs (PCDD, PCDF, PCB, HCB, PeCB, c-PentaBDE, c-OctaBDE,) and other POPs proposed for inclusion into the Convention (HBCD, SCCP). These are present as contaminants in e-waste recycling with other persistent toxic substances and warrant evaluation of their toxicological relevance including toxicological interactions.

The estimated daily intake of PBDE by breast-fed infants from the e-waste processing site within 6 months of age was 572±839 ng/kg body wt/day, which was 57 times higher than that of infants from the reference site (10.12±4.60 ng/kg body wt/day).

The maximum value measured (2240 ng/kg body wt/day) exceeded the chronic oral reference dose for PentaBDE (2,000 ng/kg/day) established by US EPA. Also the daily intake of PCDD/DF for infants were significantly above the WHO guideline of 1-4 pg/kg/day. These dioxin-like intakes, however, do not consider the possible intake of PBDD/DF, mixed halogenated PXDD/DF (and other possible dioxin-like compounds) which could have a significant contribution considering their relative high impact in soils and air at the open burning sites: State media estimated that almost 9 out of 10 people in Guiyu suffered from problems with skin, nervous, respiratory, or digestive systems, which may be linked to e-waste recycling practices (Chisholm and Bu 2007; United States Environmental Protection Agency (USEPA) 2008; United States Environmental Protection Agency (USEPA) 2008).

According to epidemiological data (for adults) provided by the Centre for Disease Control and Prevention in another e-waste recycling area (Taizhou), there has been an obvious increase in morbidity between 2004 to 2006 for a range of diseases (Figure 80). Therefore there seems to be an urgent need to find out if the high body burdens of POPs of residents of Taizhou is related to the increased incidence of diseases. Furthermore a more comprehensive epidemiological study of health impacts caused by e-waste recycling operations is essential. In these heath studies the effect of toxic interactions should be taken in consideration and evaluated.

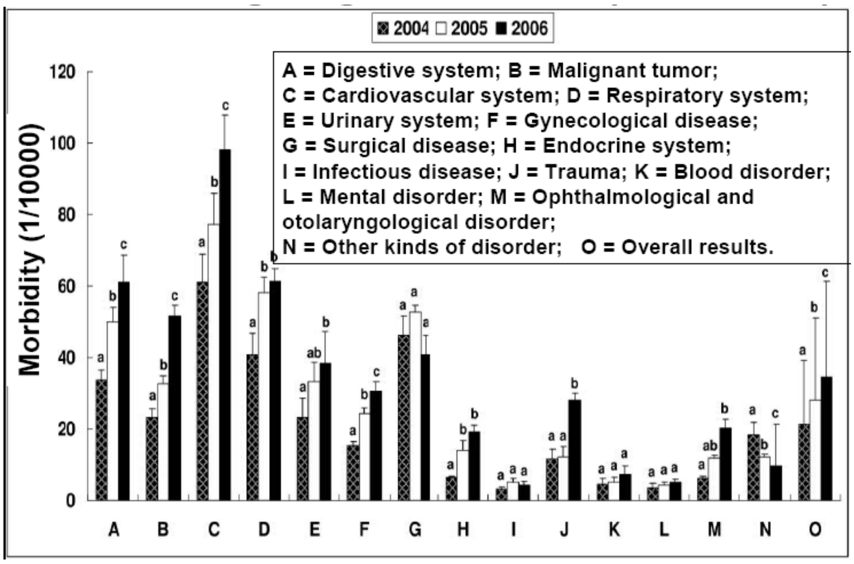

Figure 80: Epidemiological data from Taizhou; (a) 2004; b) 2005 and c) 2006) (Leung et al. 2010).

Appendix 3 (c) (vi): Accidental Fires

The possible generation of PBDD and PBDFs in accidental fires is important if PBDE which can act as the precursor for those brominated dioxins are to be re-used in products which are subsequently at risk of being burned.

Zelinski (Zelinski et al. 1993) examined fire residues from three different accidental fires in private residences for PBDD/DF and brominated flame retardants. In most samples brominated substances and particularly PBDE could be detected in a concentration range from 1 to 100 mg/kg. One sample, a plastic TV case, however, contained 5 % PBDE. The concentrations of PBDD/F were in the range from 1 to 173 µg/kg with the exception of another TV-case, which contained 14,910 µg/kg PBDD/DF.

The content of PBDF of this TV exceeds the limit of 0.1 mg/kg TEQ specified in the Ger- man hazardous chemical regulations (German Federal Ministry of Justice 2003). Accordingly issues arise in relation to health and safety, waste disposal and decontamination and these all need to be taken into account.

Blomqvist et al (Blomqvist et al. 2004a) compared emissions from an EU and US TV in a fire scenario. The US TV housing was treated with BDE. The results from these tests highlight the effects on the combustion products of the presence of a flame retardant additive. The yields of all the products of incomplete combustion measured, including: CO, VOC, PAH together with chlorinated and brominated dioxins were significantly higher for the TV-set with a fire retarded enclosure (US TV). Both brominated dioxin species and brominated furans were found from the US TV, although the brominated furans dominated. The authors warned that comparison is difficult, however, as the fire scenario differs considerably between the tests conducted on the EU and US TV, which required a large ignition source to remain in contact with the TV during the complete test in order to maintain combustion. The authors considered that the test conditions for the US TV could be a more relevant model for a fire in a landfill or other deposit, where TV-sets containing brominated flame retardants might be stored together with other more easily ignitable plastic materials. When TVs were included in a room fire, however, the product distribution was ventilation controlled and less sensitive to the specific organic makeup of the fuel load (Blomqvist et al. 2004b).

The German health office (Bundesgesundheitsamt, BGA, 1990) has published a recommendation for cleaning houses after fires with proposals for the disposal of waste. According to this guidance any residues of electrical or electronic equipment have to be separated and treated as hazardous waste. The remaining fire damaged material, ash and char can be handled as ordinary waste.

Zelinski indicated that implementation of these proposals may be difficult because:

1. The fire residues may not be separated in that way that would be necessary because often equipment is too badly burned to be readily identified.
2. The PBDD/DF results show that only some of the electrical commodities represent a danger. On the other hand articles apart from electrical equipment could contain these substances, depending on the producing company or country and the levels of recycling. It is difficult to correctly identify things equipped with PBDE and potentially contaminated with PBDD/DF.

These are valid concerns. Zelinski therefore suggested that for safety and environmental reasons, all fire residues should be disposed off as PBDD/DF containing hazardous waste and disposed of appropriately. This can be considered to represent a precautionary approach to BAT/BEP in relation to potentially PBDE-contaminated wastes found in fires.

In recent years large accidental fires triggered by drought due to climate change have occurred. In some of these fire events whole villages or city districts have been affected - most notably in Australia and California where hundreds of homes and cars have been damaged by fire. In these cases thousands of items of electrical equipment and other PBDE-treated articles have been burned. The associated releases of PBDE and PBDD/DF are likely to have been enormous but they have not been monitored (or at least reported). As climate change will inevitably lead to more drought and large scale fire events the increased release of POP-BDE and PBDD/DF from this source is potentially important and should be assessed. Recycling of POP-BDE into articles which are subsequently burned in open fires of this sort is potentially a major release route.

Appendix 3 (d): Review and summarise information on the presence of PBDE in articles produced from recycled materials and health risk from use of such articles

There key concerns in relation to recycled articles containing POP-BDE which relate to PentaBDE in carpet padding and OctaBDE in recycled plastics, particularly those used for sensitive uses including toys.

The first concerns principally PentaBDE and is the long-standing recycling in North America of post-consumer PUR foam into carpet cushion ('rebond'). This recycling route has traditionally been a major outlet for used foams and production off-cuts in the USA and Canada[80]:

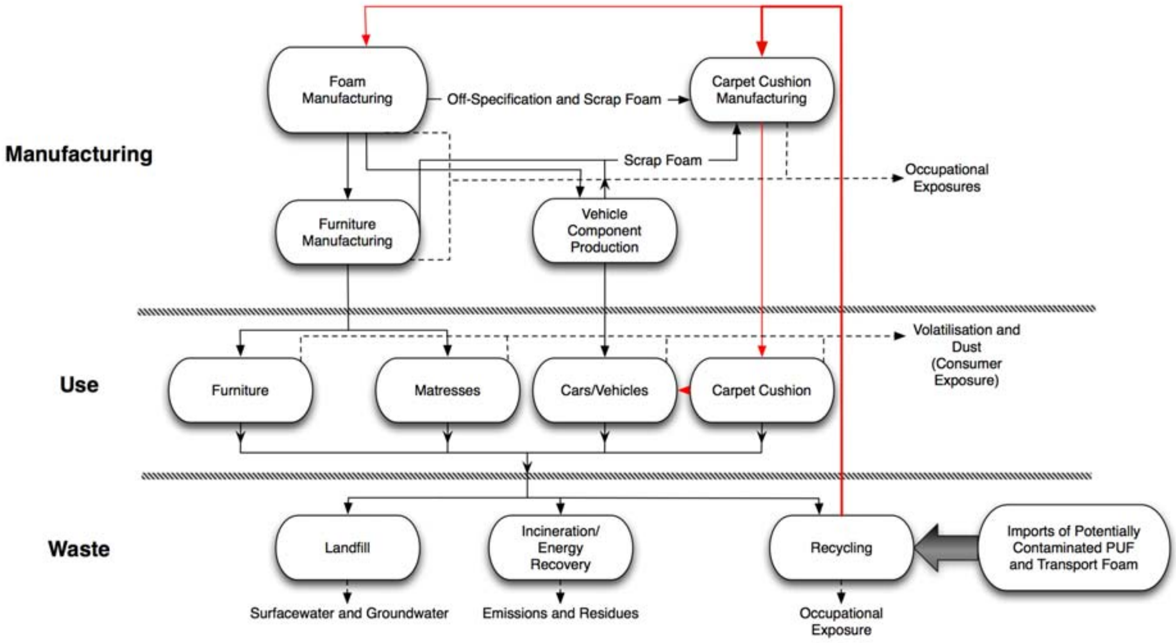

Figure 81: Simplified materials flow of foam and recycling routes (marked in red) to carpet cushions (adapted from (USEPA 2005)).

Given the long-established use of foam for rebond there is a surprising lack of information about the scale of the usage and the level of contamination. USEPA were unable to provide any details and the only data found for this indicated that in 2002 the rebond industry used 376,000 tonnes of scrap polyurethane foam and that of this approximately 23,000 tonnes came from post-consumer waste (Zia et al. 2007). There is no indication of how much of this post consumer waste contained PentaBDE but if it is conservatively assumed that this all contained PentaBDE at the maximum likely loading of c.5% this would represent 1,150 tonnes of PentaBDE being recycled into carpet padding.

The dust from carpets and padding is of particular concern in circumstances where carpet cushion can contain PentaBDE and considering the high exposures of carpet layers reported by Stapleton (Stapleton et al. 2008). The health risks associated with worker exposure are considered in more detail in Appendix 5 (c).

USEPA has published a detailed assessment titled "*Resuspension and Tracking of Particulate Matter From Carpet Due to Human Activity*" (RTI International 2007) which quantifies how effectively dust can be re-suspended.

Walking on medium carpet re-suspended almost 2% of the PM between 1 and 10 µm available on the carpet fibres, but up to 40% could be re-suspended under the proper conditions. Carpet age, applied force, and relative humidity determined the emission factors. Emission factors of less than 1% were obtained for new carpet at low humidity and low applied force (e.g., walking). Emission factors between 20 and 40% were obtained for older carpet at high force (e.g., stomping) and low humidity. On average, the re-suspended concentration at 36 inches above the floor was 1.8 times lower than the concentration measured at 18 inches.

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[80] The reply from Canada to the questionnaire was the only response confirming the likely recycling of POP-BDEBDE. This relates to two manufacturers who "*believe their rebonded foam carpet cushion may contain Penta and OctaBDE*". The Canadian submission added that "*more information is not forthcoming until analysis of this product can be performed*"

It is notable that older carpets had significantly higher emission factors, possibly because of the weaker adhesion forces between the dust and carpet fibres. The consequences of increased exposure of toddlers and children playing close to the floor together with the higher dust intake is consistent with the much higher levels of PBDE reported in children compared with adults (Fischer et al. 2006, Toms et al. 2009, Lunder et al. 2010). It is likely, for example, that the higher emission factors for older carpets might, at least in part, help explain the higher body burdens reported from low income families (Zota et al. 2010).

There is increasing awareness about the use of PBDE-contaminated wastes in rebond (and some manufacturers now advertise their rebond with labels including "*PBDE free*" or "*no 'post consumer' scrap*"). Knowledge is far more limited about the recycling of OctaBDE-treated plastics into alternative plastic products.

Indeed there is little evidence that BFRs are taken into account at all in many operations where recycling of plastics and PUR currently takes place. A UK Industry Department report on recycling of WEEE in Japan is typical in reporting that *there was no visual evidence of at-line analysis of polymer type or any attempt to stream the casings by brominated flame- retardant content" (DTI 2005).* Yet, the report continues *"[I]t was stated at two companies that up to 60% of the TV casings do contain brominated additives"*. As a consequence *"the shredded plastic from this particular stream is finding its way into lower-grade applications in non-E&E goods*"(DTI 2005).

There may be circumstances in which the recycling in this way reduces the need to add supplementary flame retardants and an example is given of the production of a cable-tray conduit used for the laying of power cables alongside railway lines. This, the authors say "*is a durable product application where the flame-retardant properties are of continued lifelong benefit"*(DTI 2005).

There is certainly evidence of contamination in current products – most obviously where there are mixtures of different types of flame retardant in products and where the bromine levels are lower than would be used for flame retardancy, especially those where there are no requirements for flame retardancy.

In the survey by Bantelman (Bantelmann et al. 2010), for example, many of the investigated electronic articles contained bromine at levels too low for flame retardancy. These parts were probably made from recycled plastic:

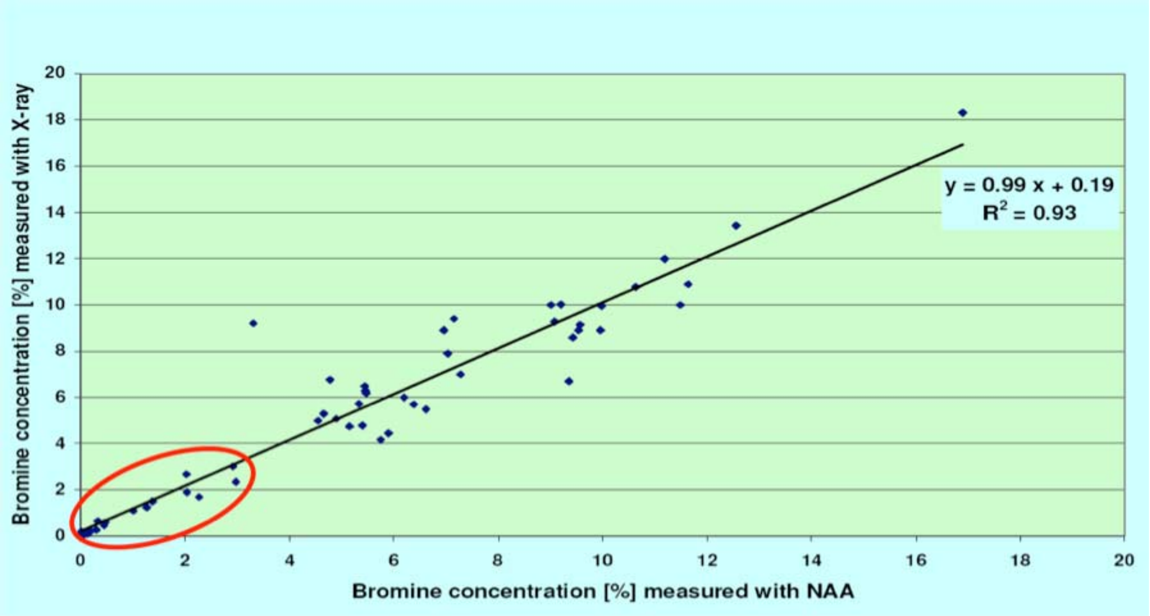

Figure 82:Survey of Swiss products showing brominated compounds at below flame retardancy levels (Bantelmann et al. 2010).

Another example is PBDE/BFR in video tape casings imported to Japan from China and Korea (Hirai & Sakai 2007). The concentrations of PBDE ranged from <0.05 mg/kg to 6700 mg/kg (average 2000 mg/kg = 0.2%). These concentrations were lower than those of the plastics to which BDE were intentionally added (10%). Interestingly the one sample from Japan (3c) appears to contain just DecaBDE whilst the others from Korea and China contain heptaBDE and hexaBDE – either from contamination with OctaBDE or possibly debromination of DecaBDE:

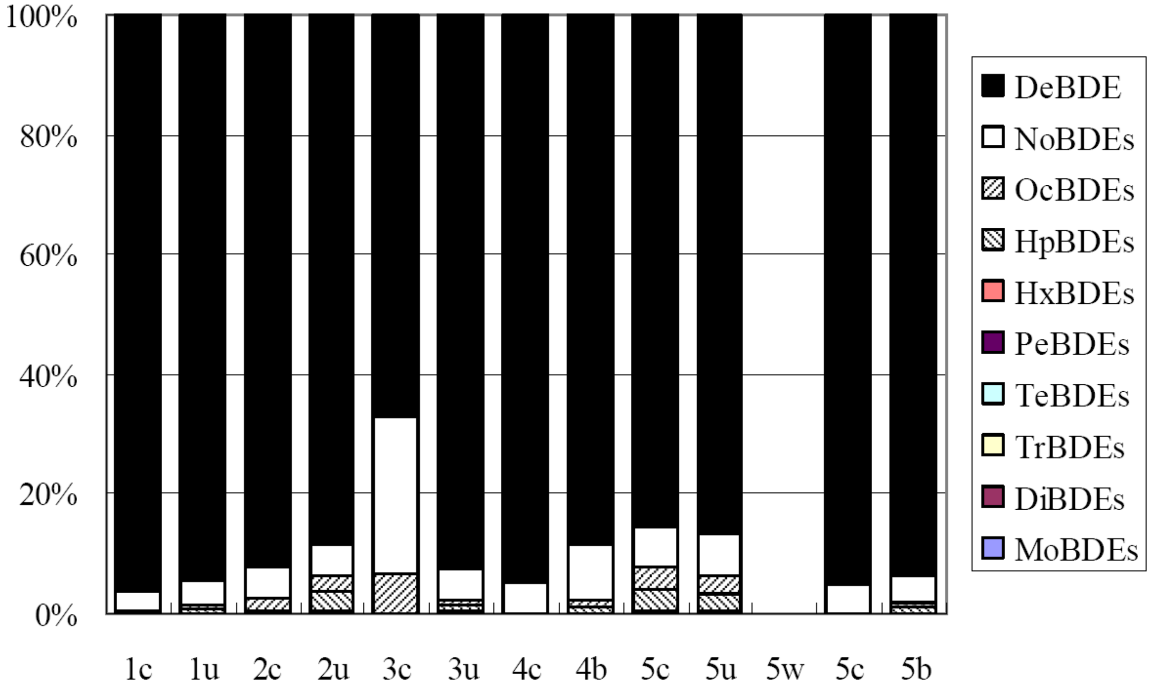

Figure 83: PBDE/BFR in video tape casings imported to Japan from China and Korea (Hirai & Sakai 2007)

The report commissioned by the New Zealand Ministry of the Environment as part of the POPRC review process also reported finding plastics containing BFRs which had been recycled (Geo & Hydro – K8 Ltd 2010):

"From the BDE analysis results we obtained in this study we can see some articles have not only high Deca-BDE levels but also contain some TBBP-A. The interpretation by researchers at the Institute for Environmental Studies in the Free University of Amsterdam, Holland, is that during the manufacture of these goods or of the polymers to make these goods some recycled polymers have been blended with virgin polymers" (Geo & Hydro – K8 Ltd 2010) .

The articles thought to include recycled polymers and BFRs included the backing for an LCD TV; Chinese electrical plugs; and the handle of a CD player.

The literature reviewed contains relatively little information on the presence of PBDE in recycled articles.

Imai (Imai et al. 2003) compared characteristics of ABS-plastic treated with Tetrabromobisphenol A (TBBPA) and brominated epoxy oligomers (BEO). They commented that that due to the "*superior recycling properties*":

"a major manufacturer of business machines [Richoh] has started to use an ABS/BEO plastic for producing the plastic parts for the cabinet of its copy machines. These contain up to 30% of recycled plastic material. Plastic parts are being collected and actually being recycled". (Imai et al. 2003)

Low results were also obtained in relation to the levels of PBDD/DF after several simulations of recycling operations. No reference is made by Imai to the recycling of polymers containing PBDE and so the relevance of this review is moot.

Chen et al. published data on children's exposure together with a risk assessment for BFRs in children's toys in South China (Chen et al. 2009b, Chen et al. 2010a). A critical response was made by the industry (Banasik et al. 2010) to which Chen responded (Chen et al. 2010b).

Chen notes that whilst many countries have passed toy safety regulations, few of them have limited the content of BFRs. The EU RoHS (Restriction of Hazardous Substances) regulations (see earlier) restrict the threshold values of PBDE and PBBs to 1,000 ppm only in only certain electrical and electronic toys. The majority of the world's toys and not subject to any controls on levels of PBDE. At least 70% of the world's toys are estimated to be produced in China. Furthermore approximately 50% of the global production comes from Guangdong Province in South China. Between 70% and 80% of US toys are imported from China (Chen et al. 2009b).

Chen et al. purchased sixty-nine toy samples from the two largest toy markets in Guangzhou City (the capital of Guangdong Province) and the largest toy trading centre in China. These were categorised as:

- hard plastic toys (such as racing cars, vehicles, weapons, action figures, and hand-held video game consoles (n=30);
- foam toys (such as mats, puzzles, and swords (n=18);
- rubber/ soft plastic toys (such as Barbie dolls and teethers (n=15); and
- textile and stuffed toys (such as animals, dolls, and Christmas toys (n= 6).

Toys have no "*ingredient labelling*" requirements and the only way to identify their constituents is by analysis. The results of the analysis for BFRs for each group in this case were:

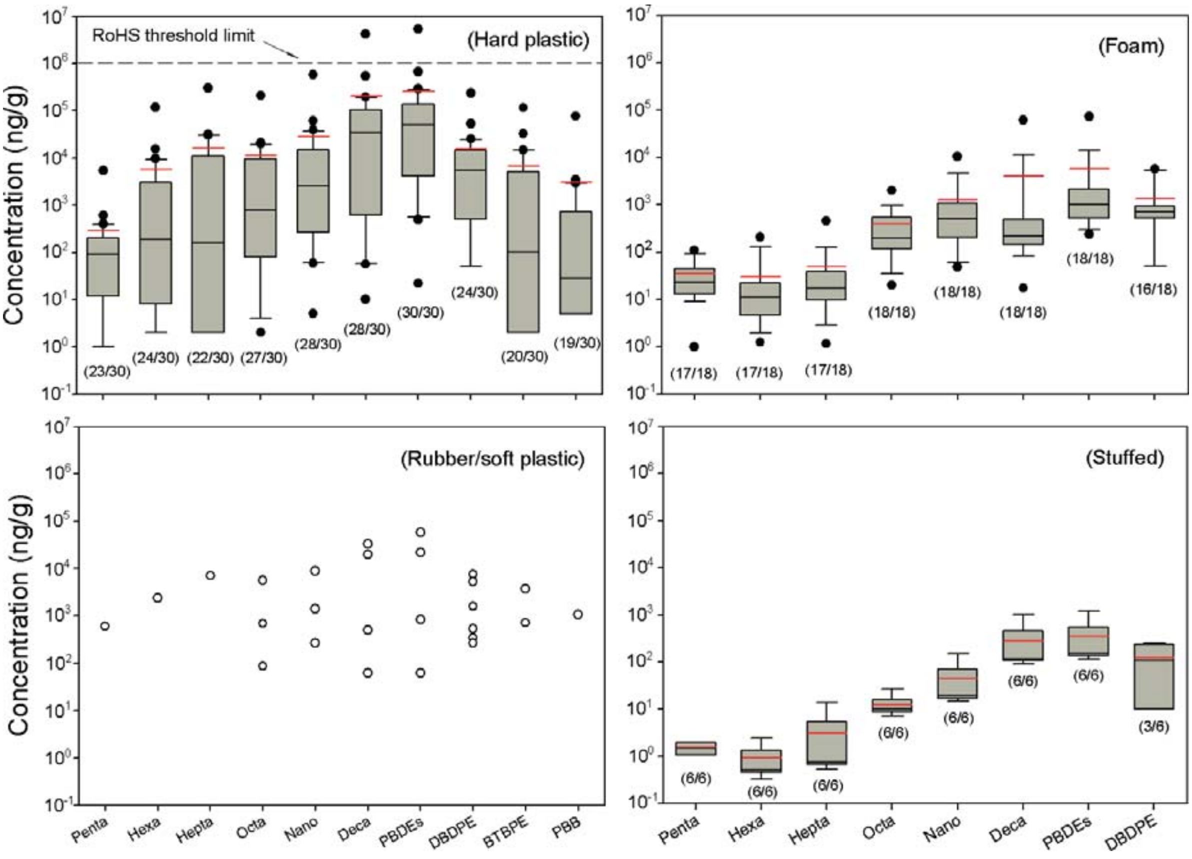

Figure 84: Concentrations (ng/g) of BFRs in each type of toy. The horizontal lines represent the 10th, 50th, and 90th percentiles; the box represent the 25-75th percentiles; the red lines represent the means; individual points are outliers; circles represent BFR concentrations in rubber/soft plastic toys; values in brackets are detection frequencies (Chen et al. 2009b).

The RoHS threshold limit marked on the first figure is equivalent to 0.1% (1000 ppm). This is twenty times higher than the concentration of the provisional "*low POPs*" level for the original AnnexA POPs pesticides and PCBs of 50 ppm[81].

Decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), polybrominated biphenyls (PBBs) and PBDE were found in the toys. PBDE were the predominant BFRs and accounted for, on average, 77.6%, 60.3%, 78.8%, and 45.1% of the BFRs in the hard plastic, foam, rubber/soft plastic, and stuffed toys, respectively. One hard plastic toy had a total PBDE concentration (5,344,000 ng/g) exceeding the RoHS threshold limit. PBBs – which may have been present as a co-contaminant of PBDE as detailed in the PBDD/DF section - was 1.0% of the BFRs. The lowest concentrations were generally found for Penta- and HexaBDE which is not surprising given the majority usage in PUR rather than plastics. Congeners from Octa- and PentaBDE products (tri through heptaBDE) constituted small percentage distributions (<27.4% and <11.5%, respectively) compared with Deca as the major component of PBDE in all of the toys except two. Chen comments that it is noticeable in the principal component analysis of the congeners that BDE-28, -99, and -100,

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[81] The provisional limit for PCDD/DF is 15 ppb.

which were commonly derived from PentaBDE product, are actually grouped with BDE183 which is a major congener of OctaBDE product (rather than BDE47 as a major congener of PentaBDE as would have been expected if PentaBDE was the source). These results, Chen says "*were probably indicative of both commercial and decomposition origins for these less brominated congeners*". It is also notable that the values of Nona- and OctaBDE exceeded those of the DecaBDE in 14 of the 18 foam toys. Chen commented that "*given that neither nona- nor octaBDE are predominant congeners in commercial deca or octaBDE products, the relatively high concentrations in foam toys were likely a result of photo- or thermal-decomposition of decaBDE*". They concluded "*that some less brominated BDE in the environment may be derived from the decomposition of higher brominated PBDE in PBDE-containing products during the process of the manufacturing, use and/or recycling in addition to degradation in the environment*" (Chen et al. 2009b).

Chen does not say where the BFRs in the toys are likely to have come from. Robonson, referring to this review suggests tentatively that "*it is conceivable that recycled materials from E-waste, which may contain PBDE or PCBs, are used in the manufacture of products for export*" (Robinson 2009). As no other explanation has been put forward to explain the presence of flame retardants in plastics which are significantly below the levels at which they would be useful as flame retardants (and there is, in any case, no requirement to flame retard most of these toys) then this seems the most plausible explanation. The risk of "*re-exportation of E-waste contaminants*" says Robinson "*warrants further investigation*" (Robinson 2009).

Table 54: Assessed children's Daily Exposure to PBDE via Toys (Chen et al. 2009b)

	exposure (pg/kg bw day)						
age group	penta[a]	hexa	hepta	octa	nona	deca	ΣPBDEs
			inhalation				
3–12 months	17.5	2.20	8.27	2.76	1.47	0.55	32.7
1–3 years	65.2	8.23	30.9	10.3	5.49	2.06	122
3–5 years	47.7	6.02	22.6	7.53	4.02	1.51	89.3
5–9 years	34.6	4.37	16.4	5.47	2.92	1.09	64.9
9–14 years	27.8	3.51	13.2	4.39	2.34	0.88	52.1
			mouthing				
3–18 months	5.88	109	400	1031	2370	5001	8916
19–36 months	0.52	9.58	35.1	90.4	208	439	782
			dermal contact				
3–12 months	23.1	2.92	11.0	3.65	1.95	0.73	43.3
1–3 years	20.9	2.64	9.89	3.30	1.76	0.66	39.1
3–5 years	22.9	2.83	10.6	3.53	1.89	0.71	42.0
5–9 years	17.2	2.17	8.15	2.72	1.45	0.54	32.2
9–14 years	16.3	2.06	7.71	2.57	1.37	0.51	30.5
			oral ingestion (hand-to-mouth)				
3–12 months	16.5	2.09	7.83	2.61	1.39	0.52	31.0
1–3 years	7.83	0.99	3.71	1.24	0.66	0.25	14.7
3–5 years	4.79	0.60	2.27	0.76	0.40	0.15	8.97
5–9 years	1.50	0.19	0.71	0.24	0.13	0.05	2.82
9–14 years	0.97	0.12	0.46	0.15	0.08	0.03	1.82

[a] Refers to the sum of tri- through pentaBDEs (BDE28, -47, -66, -100, and -99).

When the exposures from use of toys, and particularly mouthing in those cases where this was anticipated or was likely, then the contributions made by the POP-BDE generally contributed more than half of the intake from oral ingestion, dermal contact and inhalation (due to the higher volatility of the lower-brominated congeners) but significantly lower in the case of mouthing behaviour which was the largest exposure route for young children. The total PBDE exposures via mouthing hard plastic toys were 8,916 and 782 pg/kg bw/day for infants and toddlers, respectively, estimated by the median migration rates. However, it is significant that the exposures calculated for the 95th percentile migration rates were much higher at 65,180 pg/kg bw/day for infants and 5,717 pg/kg bw/day for toddlers.

The children's median exposure via toys was comparable to the exposure via human milk (7,100 pg/kg bw/day) for infants and was higher than that via fish consumption (110-395 pg/kg bw/day) and inhalation (230-343 pg/kg bw/day) for toddlers reported by Meng et al. (Meng et al. 2007) for China.

The results were comparable or lower than the median exposures via dust ingestion (4,750-6,990 pg/kg bw/day) and food (4,330- 6,370 pg/kg bw/day) for British children (6-24 months) reported by Harrad et al. (Harrad et al. 2006) – although exposure from toys could be additional to that from dust intake and so supplement the body burden.

The overall exposure (from diet, inhalation, dust ingestion, and dermal contact) of American children to PBDE ranged from 9.1 to 49.3 ng/ kg bw/day (Lorber 2008) and these levels are much higher than assessed by Chen – although as with the UK exposure the mouthing of toys would be additional to that from dust intake and so supplement the body burden.

The hazard quotients calculated by Chen ranged from 4×10^{-9} to 8×10^{-3} with the higher values for infants. They concluded "*the hazard quotients for the four congeners were all far below 1, even calculated on the basis of the observed worst-case exposure, suggesting a low deleterious risk associated with children's toys with regard to BFRs*". However, they added "*it is noteworthy that children can be exposed to a significant amount of non-PBDE BFRs, as well as highly brominated BDE, in addition to BDE209 via toys. Toxicological data of these chemicals are currently very limited. Additionally, young children may be much more sensitive to xenobiotic toxic chemicals than adults, and the EPA's confidence in this RfD is low*". They therefore concluded that despite the "*low deleterious risk associated with household products with regard to PBDE, they are of special concern because of the relatively higher exposures observed for young children and further work is required*".

The majority of the exposure in the examples sampled by Chen was from the higher brominated BDE but given the lack of quality control and analysis in the recycling programmes other samples are likely to contain higher proportions of POP-BDE.

Appendix 4: Identification of the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers

Based on the analysis in the previous section and information provided by parties and observers this section examines and identifies, subject to the uncertainties highlighted, the best available techniques (BAT) and best environmental practices (BEP) associated with recycling articles containing PBDE.

There are three main treatment scenarios to be considered in relation to BAT technologies for recycling with particular relevance to the POP-BDE are, as outlined in the previous Appendix:

(a) PUR foams – from furniture and transport.

(b) ABS and other polymer casings - from computers and business machines.

(c) Printed wire boards – from electrical and electronic equipment.

This Appendix describes:

(a) Current methods to identify articles/recycled articles containing PBDE

(b) How to separate articles containing PBDE from other components of the waste stream and how to remove PBDE from articles containing them;

(c) The assessment of BAT Technologies for recycling PBDE-containing articles considering exposures from recycling and disposal options.

(d) The capacity of developing/transition countries to implement BAT/BEP.

(e) Regulatory approaches and strategies used to support the implementation of BAT/BEP.

Knowledge gaps are listed in Appendix 6.

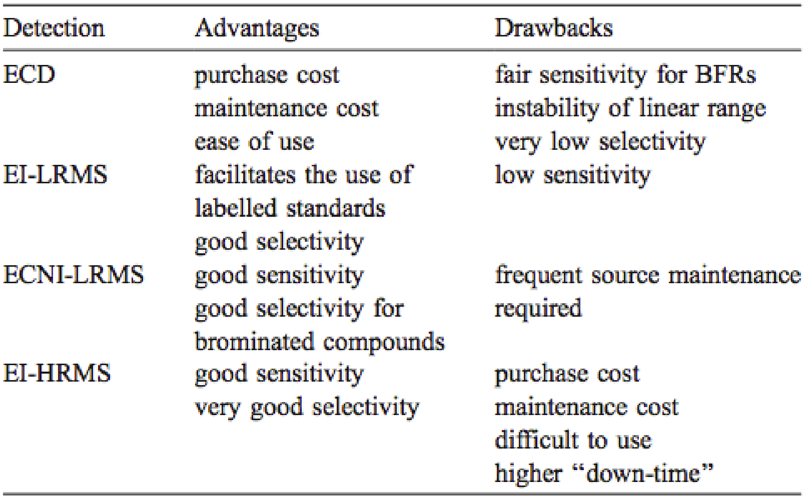
The work already completed by the Stockholm Convention BAT/BEP Expert group in the published BAT/BEP guidelines has been relied upon where relevant. The relevant guidance produced by the Basel Convention has also been taken into account.

Appendix 4 (a): State of the art identification of PBDE in articles

The state of art analytical technique for PBDE analysis of the PBDE congeners addressed by the Convention (TetraBDE to HeptaBDE) are chromatographic techniques coupled with a mass spectrometer (Rieß et al. 1998, Rieß et al. 2000)(Covaci et al. 2003) (Kemmlein et al. 2005)(International Electrotechnical Commission 2008).

As chromatographic technique gas chromatography is normally used (Kemmlein et al. 2005)(International Electrotechnical Commission 2008). Liquid chromatography (LC, HPLC) has been applied however the separation efficiency is lower (Covaci et al. 2007)(Schlummer et al. 2005).

Different detection mass spectrometric technologies can be used and the advantages and drawbacks of different detection techniques for BFRs are hightlighted in the table (Covaci et al. 2003) (Covaci et al. 2007):



Detection	Advantages	Drawbacks
ECD	purchase cost maintenance cost ease of use	fair sensitivity for BFRs instability of linear range very low selectivity
EI-LRMS	facilitates the use of labelled standards good selectivity	low sensitivity
ECNI-LRMS	good sensitivity good selectivity for brominated compounds	frequent source maintenance required
EI-HRMS	good sensitivity very good selectivity	purchase cost maintenance cost difficult to use higher "down-time"

Table 55: advantages and drawbacks of different detection techniques for BFRs are hightlighted in the table(Covaci et al. 2003) (Covaci et al. 2007)

In principle also other detectors can be used for the detection of PBDE including Electron Capture Detector (ECD), UV detector or Flame Ionisation Detector (FID) (Covaci et al. 2003) (Covaci et al. 2007). However since brominated flame retardants can overlap with retention times in the gas chromatograph (Vetter & Rosenfelder 2008) detectors like ECD, FID and UV have some uncertainty and need experience in the interpretation of chromatograms. This will be more critical in future since the number of brominated flame retardants are increasing (according to the bromine industry there are currently already approximately 75 BFRs on the market) and the retention time of these emerging flame retardants have not been assessed for the GC columns used.

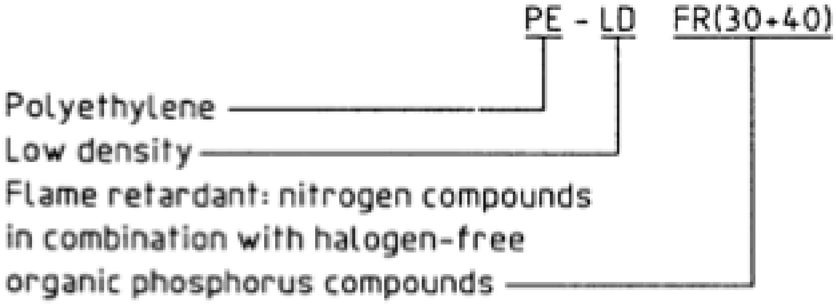
According to experts working for more than a decade in the area of screening BFRs in plastic from electronics and other matrices, the advantage of the ECD detector is the robustness (Schlummer et al. 2005). A recent interlaboratory comparison study reveals a good agreement of GC-ECD and various GC-MS techniques (Zeleny et al. 2010).

For the concentrations which need to be detected in the PBDE-containing materials (plastic, foams, textiles etc.) then low resolution MS would be adequate for considering, for example, a hypothetical low POPs content of say 50 ppm.

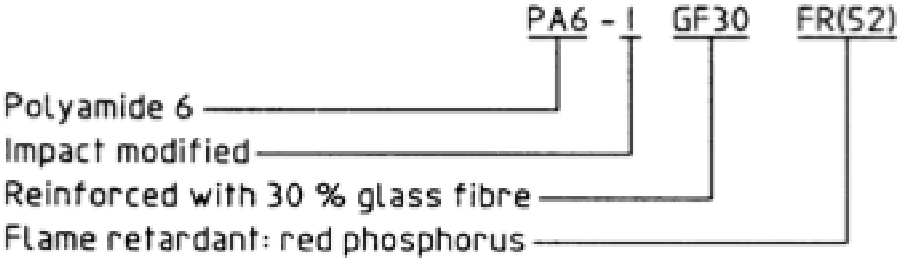
International Standards for Labelling

It should be noted that there are some labelling requirements for flame retarded plastics. The text of the International Standard from Technical Committee ISO/TC 61 "Plastics" of the International Organization for Standardization (ISO) has been taken over as an European Standard by Technical Committee CEN/TC 249 "Plastics". As a CEN European standard it is obliged to be given the status of a national standard, either by publication of an identical text or by endorsement. The latest date for implementation was November 1999 (BSI 1999). The current standard, ISO 1043, provides uniform symbols for flame retardants added to plastics materials. The symbols are written with the abbreviated term "FR" and one or more succeeding code numbers (International Organisation for Standards 1998):

EXAMPLE 1:



EXAMPLE 2:



Different PBDE are not distinguished by the standard and the relevant codes are:

18	*polybrominated diphenyl ether*
19	*polybrominated diphenyl ether in combination with antimony compounds*

Note that only flame retardants exceeding 1 % (*m*/*m*) have to be identified (International Organisation for Standards 1998).

International Standards for determination of PBDE:

International Standard for determination of regulated substances in electronics (IEC 62321)

An International Standard IEC 62321 ed.1 (International Electrotechnical Commission 2008) has been developed for “Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)”. The method describe details on sample preparation and analysis. The Determination of PBDE (MonoBDE to DecaBDE) and PBB (MonBB to DecaBB) in polymers by GC-MS is described in Annex A - including extraction, analysis and quality assurance. The method has especially been optimized for the concentration range of 100 mg/kg and 1000 mg/kg due to the requirements of EU RoHS Directive compliance.

It has, however, been discovered in a inter-laboratory comparison study, that even considering that the GC-MS analysis of PBDE in plastics has an established standard procedure that it had a low precision for DecaBDE determination (Linsinger et al. 2009). Since the DecaBDE is not included as POPs in the Convention the difficulty with determination of DecaBDE does not have a direct consequence for compliance measurements for the Convention. As noted earlier in this review, however, the reliable determination of OctaBDE to DecaBDE congeners is important for the further assessment of the relevance of debromination to the current POPs burden. Further debromination of DecaBDE (and other highly brominated BDE) during analysis can result in an overestimation of POPs BDE.

A working group (IEC TC111 WG 3) is currently drafting the 2nd edition of the international standard (IS 62321; 2nd editions) and this version is expected by December 2012.

German national standard for determination of PentaBDE and OctaBDE in plastic materials in respect to the RoHS directive

A standard method for determination of PentaBDE and OctaBDE in plastic materials in respect to the RoHS directive (Directive 2003/11/EC, Directive 76/769/EEC) has been developed on behalf of the German Environmental Agency (Kemmlein et al. 2005). The method includes extraction, clean-up and measurement procedures. The study has also validated the method for different polymers and assessed for reproducibility and repeatability. The compounds analysed in this method are however limited to certain PentaBDE (BDE85 (2,2',3,4,4'-pentaBDE), BDE99 (2,2',4,4',5-pentaBDE), BDE100 (2,2',4,4',6-pentaBDE)) and OctaBDE BDE203 (2,2',3,4,4',5,5',6-octaBDE), BDE196 (2,2',3,3',4,4',5,6'-octaBDE), BDE197 (2,2',3,3',4,4',6,6'-OctaBDE) since the current RoHS limit is defined for Σ PentaBDE and ΣOctaBDE with a limit of 0.1% each.

Development of a measurement standard for PBDE relevant to the Stockholm Convention

A measurement method for PBDE for Stockholm Convention purposes would need to focus on the ΣTetraBDE to HeptaPBDE with less emphasis on the relevance of OctaBDE to DecaBDE. For Stockholm Convention purposes also another calibration range might have to be used if a different 'low POPs' limit was established from the 0.1% limit used for RoHS. This seems likely as the 0.1% RoHS limit is not based on risk considerations and is 20 times higher than the current provisional 'low POPs' limit for POP pesticides and PCBs.

Further, the currently developed international/national standards focus on PBDE in plastics from electronics/WEEE. Application to the Stockholm Convention requirements requires a broader range of matrices for which additional sampling, sample preparation and extraction protocols are needed.

Commercial availability of PBDE analysis

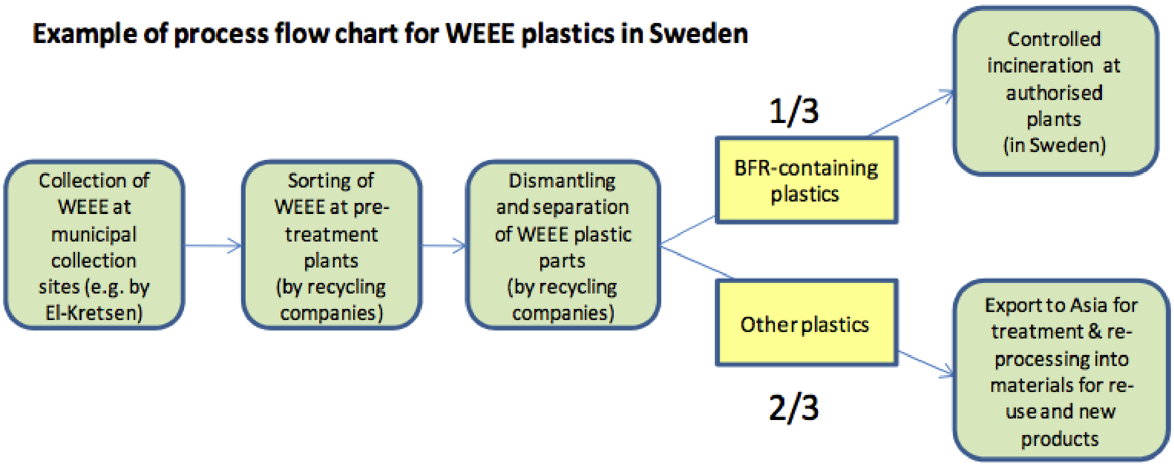
Standard commercial GC/MS analysis of PBDE in plastic and other materials is widely available in industrial countries. This is largely because of the demand that has arisen over the past few years due to the requirement of RoHS compliance. The Commercial GC/MS analysis of brominated flame retardants are, however, still relatively expensive. The Price in Europe for PBDE starts from approximately $180 per sample. This can be compared to PCB analysis in transformer oil which is currently available with GC/MS from approximately $60/ sample. Much of this (significant) cost difference can be explained by the more complex and time consuming extraction and clean-up of the polymer matrix required for PBDE analysis.

Limitation and options of practical applicability of using standard PBDE analysis as a screening approach

The current "state-of-the-art" analytical GC/MS techniques for PBDE requires appropriate extraction and clean-up. This takes a lot of time - normally days from delivering a sample to receiving the results from the laboratory. If a large investment in equipment was to made then such an analysis could be established in-house with automated preparation. In such cases the "*turn-around*" time frame might be reduced to several hours. Even this would present practical difficulties for routine use in the screening of the PBDE levels of recyclate at pre-treatment plant. Most recycling operators would have to rely on commercial laboratory services for GC/MS analysis, however, and the timescale of those services makes this type of screening entirely impractical.

Furthermore the relatively high price of GC/MS analysis will not allow a comprehensive screening of PBDE-containing equipment even for the larger equipment like TV sets, computers, car seats or mattresses. It can easily be calculated that to screen mattresses alone would be extremely costly. In the US, for example, if is assumed that disposals are equivalent to 2003 sales - estimated to be about 39.7 million units (International Sleep Products Association 2004) - then the costs for GC/MS analysis of just half of these disposals would be of the order of $4 billion/year. A similar or slightly lower amount would be necessary for TV sets/computers and for cars respectively.

Sweden submitted a report on "*WEEE Plastics Containing Brominated Flame Retardants*" (Retegan et al. 2010) to the Stockholm Convention Secretariat as part of their response to the request for relevant data. This report concluded that "*It is not feasible for the pre-treatment plants to determine what type of BFR is present in all the different types of WEEE plastics*". Therefore, it continues "*the pre-treatment plants work to separate all BFR-containing plastics, and not only those containing PBB/PBDE. This is also stipulated in the Swedish legislation for pre-treatment of WEEE (Swedish National Ordinance 2005)"*. The consequence in Sweden, therefore, is that the waste distribution is as illustrated below:



Rapid determination techniques for PBDE analysis

Status, options and possible limitations of rapid analysis techniques for PBDE

To achieve a practical screening method it is necessary to use faster (but less effective) extraction techniques and to omit the clean-up steps. Pöhlein et al. (Pöhlein et al. 2008) developed a rapid screening method for BFR including PBB and PBDE in polymer samples using ultra sonic extraction and GC-MS analysis. The time of analysis is 9 min (GC/MS) or 15 min (GC/ECD) and this method was validated for suitability to determine PBB, PBDE and other brominated flame retardants in styrenic industrial polymers from WEEE.

An alternative method to screen brominated flame retardants including PBDE in a selective mode without extraction and clean-up has been established. Danzer et al. (Danzer et al. 1997) used online pyrolysis of pulverised plastic and analysed with gas chromatography coupled to mass spectroscopic detection (py-GC/MS). This thermo-desorption method for polymers was optimised for more than a decade and was used by Rieß in the rapid screening of approximately 100 TVs and 80 computers (Rieß et al. 2000).

The pyrolysis GC/MS method has since been developed to a commercially available application by Shimadzu with a 48 sample auto-sampler (Shimadzu 2010).

A number of other rapid analysis systems for PBDE measurement have been presented at a meeting for establishing the second edition of IEC 62321 standard for determining PBDE and PBB in electronic equipment (Tange 2010).

An independent evaluation of the quality of results of such rapid screenings has not been performed. This will be necessary since the approach of rapid extraction might lead to an underestimation of PBDE concentrations. The pyrolysis of matrices might also lead to degradation of PBDE including the debromination reactions which have been reported for GC/MS analysis.

Rapid analytical techniques with reduced (or no) clean-up steps will reduces the number of injections between GC/MS (or other instrument) maintenance and shortens the lifetime of the relatively expensive GC columns (even if pre-columns are used). Both possible drawbacks need to be assessed if such rapid analysis might be used as options for PBDE screening.

Such quick chromatographic methods optimized for time would still require at least 30 to 60 minutes per sample when the sampling, grinding, pyrolysis, minimum GC separation on short column, data aquisition and data interpretation are included.

Even time requirements of 30-minutes for a sample would be still much too long and, given the use of still sophisticated and high capital cost equipment, expensive for most practical application in a WEE or other recycling plant.

Approximate Costs for rapid screening using GC/MS with minimum preparation time

Assumptions:

- As there is no clean-up the GC column will only last for a limited number of injections. A optimistic estimate might be 100 samples.
- Without clean-up the detector will need frequent cleaning probably on a daily basis. Time for cleaning which includes shut down of the system, cleaning of MS and start-up of the system can be estimated to be at least 4 hours for simple systems. Considering a three shift operation of the equipment 3 people would be employed and, depending on expertise and sampling arrangements, they could probably process between 20 and 80 samples per day.
- Equipment life under these conditions

From these assumptions an approximate costs would be:

- cost for 3 people (depending on laboratory and country) EURO 15-30,000 Euro per year and person
- capital cost for equipment (low resolution) EURO 200,000
- cost for column EURO 250
- cost for workplace depending on lab and country

The cost per analysis would therefore still be significant- and prohibitive for small to medium sized operations. Furthermore even 80 samples per day would be too few for proper operation of a recycling facility and it is concluded that a pyrolysis GC/MS approach would be unlikely to be practical for most recycling facilities having throughputs averaging several hundred TV sets or computers per day unless the facility was treating more homogeneous materials and could be confident, possibly supported by staff expertise and other rapid screening methods, that batches of wastes had very similar characteristics and contamination levels. An example could be recyclers treating equipment in a manufacturers take back scheme or operating on a contract basis for governments or large organisations where large quantities of very similar materials would be processed together.

Status and Options for development of online PBDE screening technique

Currently no system is applied for online screening of PBDE. The most rapid method which can practically be applied for screening PBDE in plastic is currently the pyrolysis GC/MS method mentioned above. This requires at least 15 minutes for data generation.

However there have been 20 years research and development for online monitoring of PCDD/DF, PCB or other chlorinated aromatic compounds in waste incineration (Tsuruga et al. 2007)(Blumenstock et al. 2001)(Oser et al. 2001). The developed systems are however not applied in practice in incinerators or other PCDD/F emitting industries for different reasons (Weber 2005) and only in a Japanese PCB destruction plant such an instrument for monitoring off gas from PCB destruction (a technology developed by Mitsubishi (Tsuruga et al. 2007)) is used (Umea, 2007). Therefore in principle from an instrumental perspective an on-line screening of PBDE with similar technologies might be possible. Since the relevant concentration levels of PBDE in contaminated materials are in the range of 50 ppm (depending how the “low POPs” content is eventually defined) to 20% the detection should be considerably more straight-forward than analysis of PCDD/DF present at < 1 ng/Nm^3 in incinerators.

From the experience of equipment for online detection of PCDD/DF such equipment is relatively expensive - in the order of hundreds of thousands of dollars.

Practical considerations require that such screenings would need to be undertaken before equipment was crushed or shredded. This means that whole television or computer casings would be screened. Polyurethane in mattresses, couches etc. could also be screened in a similar way.

By such a method e.g. PentaBDE or OctaBDE might be scanned within few minutes or even seconds. Assuming an operation time between 1 and 5 minutes, 300 to 1,440 samples per day could be screened.

Considering time and price for current GC/MS analysis, such a system might be cheaper in the long run and perhaps be the only method which would have a screening throughput for PBDE sufficient for a smooth operation of a recycling facility.

Developing and Transition country consideration

GC/MS techniques are not readily available in most developing and transition countries. The use of GC/ECD might be an option in these countries. However the use of an ECD detector which just confirms the presence of a compound by retention time needs experience in understanding chromatographic fingerprints as highlighted above. It is evident, therefore, that the establishment of specific PBDE analysis capacity in developing countries will need significant efforts and resources directed towards capacity building.

Previous experiences from the Stockholm Convention capacity building programes on POPs analysis have revealed that even basic POPs pesticides which have been analysed in developing and transition countries for decades often still lack effective QA/QC. The precision of analytical measurements and QA/QC needs to be considerably improved even for these relatively "*standard*" compounds. PBDE are a new class of compounds for most developing countries. They present a range of new challenges and expertise in analysis has been established in only a handful of research groups to date (e.g. Odabasi in South Africa). Expanding this capacity will be challenging.

Experience in analysis of the original POPs (even the POPs pesticides) has also revealed that laboratories in developing countries often lack even the basic necessities such as analytical standards. For the development of the analysis of new classes of compounds like PBDE such standards are essential both for establishing the techniques and subsequently for the calibration/quantification and for QA/QC in routine analysis.

One drawback of the rapid screening technologies discussed above is the increased maintenance time required for the instruments. This is a particular challenge for developing countries. Appropriately qualified technical support for maintenance of instruments is rarely available locally and technical personnel might have to come from abroad. This is obviously associated with high costs.

Furthermore the shorter lifetime of the relatively expensive GC columns would be a particular a challenge for developing and transition country laboratories. Not only is the cost an issue but as lead times for delivery are likely to be longer there may be difficulties in maintaining high levels of availability of analytical capacity.

The evidence available indicates that developing countries might have relatively low stocks of POP-BDE-containing materials. Therefore occasional representative sampling and analysis of key waste/recycling streams with might justify the conclusion that the respective waste/recycling steam is not contaminated by relevant amounts of POP-BDE and special treatment is not required. Obviously such sampling should focus on the streams most likely to be impacted including e-wastes and shredder residues.

In situ (and non-destructive) measurement of bromine in articles

An alternative monitoring method could aim for the elimination of BFR-containing materials by screening of Bromine using XRF/Sliding spark type equipment. From a practical perspective a separation of BFR materials from non-BFR-containing material is preferable to an attempt to sort POP-BDE containing materials alone given the limited capacity of the general waste management streams to deal with any brominated wastes in most developing/transition countries.

For the screening of bromine several rapid screening methods which can be performed within seconds are commercially available and are applied in full scale WEEE recycling.

X-Ray Fluorescence (XRF)

For rapid screening of the presence of BFRs (including PBDE), X-Ray Fluorescence (XRF) seems to be the method of choice (Bantelmann et al. 2010)(Riess et al. 2000)(Allen et al. 2008b)[82]. Several types of hand-held equipment are available on the market. This method is relatively cheap, does not require any special or long-term training and analysis can be done on site. Also the method is non-destructive without physical alteration of the material[83]. However the method can not differentiate between the different brominated flame retardants and therefore result in the separation of brominated flame retarded material and material which does not contain brominated flame retardants. The measurements need to be calibrated before and after a measurement series and including this procedure single data are generated within minutes (Lienemann, 2007).

In a recent Swiss survey of brominated flame retardants in electronic goods more then 1000 samples were screened with XRF as pre-selection method. The reliability of the x-ray method for bromine content was confirmed by comparing its results with the neutron activation analysis (NAA). Based on measurements of 60 polymer containing components from different articles:

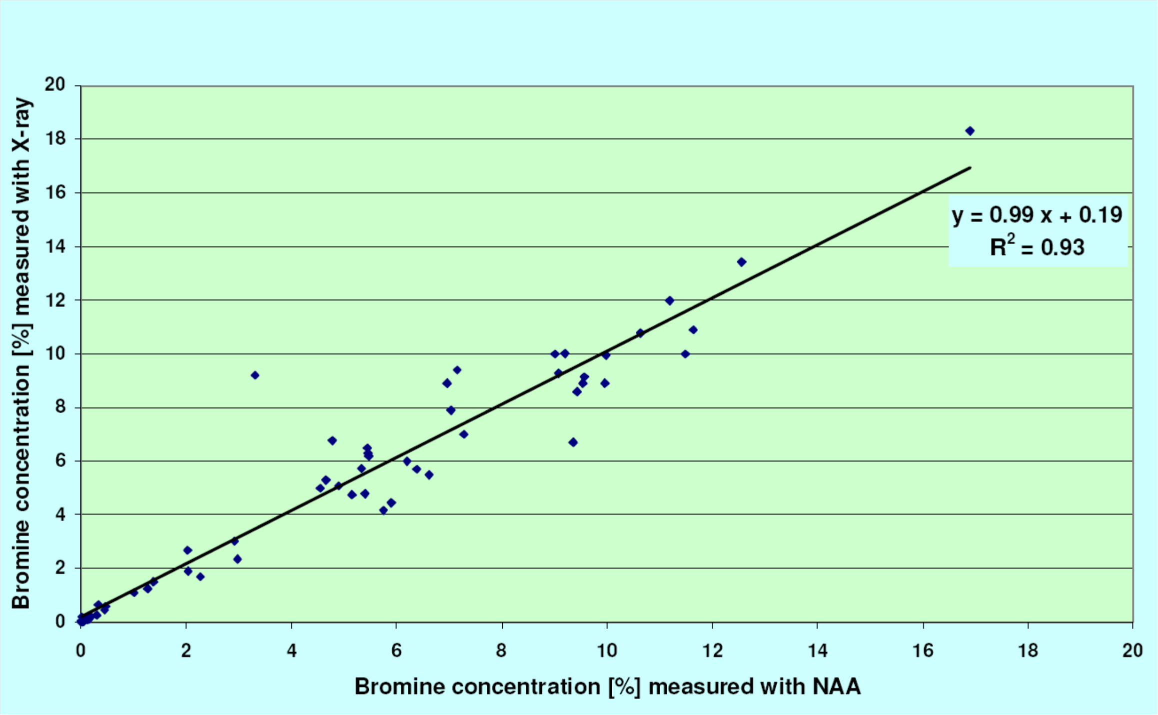


Figure 85: Comparison of bromine measurement methods: neutron activation analysis (NAA) and X-ray fluorescence (n = 60) (Bantelmann et al. 2010)

The comparison of these two independent methods showed an excellent correlation for bromine. Therefore the method seems not only reliable in a qualitative sense (no false positive or false negative) but also a quantification of bromine is possible. The method would however need to be validated for the respective low POPs content.

According to Swedish experience XRF is not used continuously (on-line) in their sorting facilities but only for random sample control of the accuracy of applied sorting methods (manual separation by work experience and manuals, density separation of shredded plastic). According to this report the technique is perceived to be costly and inefficient as an on-line analysis tool for sorting out BFR-containing plastics – although this appears to be based on use for plastic separation after shredding. Before shredding it is not particularly difficult to screen TV or computer casings – and these are the principal relevant plastics recycled in Sweden. The report confirms that

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P[83] The detection limit of the method for bromine is in the range of 10 to 100 ppm and so would be useful for screening if a low POPs content of PBDE was to be established at similar levels to the current provisional levels for PCBs and POPs pesticides of 50 ppm.

compared to the methods currently in use for detecting brominated flame retardants in different materials and discussed above XRF seems to be superior in respect of accuracy (Retegan et al. 2010).

Systems are commercially available e.g. from innovx or niton:

- http://www.innovx.com/themes/IX/graphics/demo/demo/compliance/InnovX_compliance.html
- http://www.niton.com/RoHS-Compliance-Hi-Rel.aspx?sflang=de

The price for an XRF sampler is in the order of € 35,000.

Sliding Spark Technology

Another approach for rapid bromine analysis is the sliding spark spectroscopy (IoSys 2010). This method allows an identification and semi-quantitative analysis of bromine in homogenous materials like plastic, polymer foams or textiles (since it analyses the surface only).

The technology is applied in full scale globally to separate halogen containing plastic for WEEE separation but also to phase out PVC in plastic used as fuel e.g. in cement kilns. In at least two Bavarian WEEE dismantling facilities the system is used in order to separate high bromine-containing TV-sets and monitors from bromine free equipment.

The screening time is a few seconds and therefore allows a rapid screening. The quantification limit of the method can be set in the detector. The lowest limit is 1000 ppm. For practical reasons the system is normally set at 1% BFR by the recycler. This allows the operator to screen out BFR-containing polymers which normally contain between 3 and 20% BFRs. The equipment is commercially available at a price of approximately $6,000 (Seidel 2010).

The method requires a direct contact of the monitoring nozzle onto the sample. Therefore the technology is applied manually and is not automated.

The method can also screen for chlorine and phosphorous.

Since the method also can describe different plastic types in the instrumental version combining NIR in the same equipment (the cost for such tandem equipment is approx $25,000), the method has a potential for practical separation not only of PBDE/BFR and non PBDE/BFR plastic but also for separation of plastic types at e-waste dismantling for WEEE plastic recycling.

X-ray transmission (XRT)

X-ray transmission can detect BFR and /PBDE-containing polymers and BFR-containing other materials. XRT is used in full scale to screen and sort out BFR and PVC-containing plastic in WEEE recycling.

XRT is available e.g. from TiTEch (http://www.titech.com/). The automated method is relatively expensive with a price in the range of $400,000.

The method can also detect and eliminate other contaminants like chlorine-containing plastic.

Neutron activation analysis

The neutron activation analysis is a radiochemical multi-element analysis described as a “*supreme technique*” for elemental analysis by Bart (Bart 2005). The method can be utilised for the determination of bromine content in plastic and was used for the Swiss market survey of BFR in products in 2004 and as validation method in the 2009 survey(Bantelmann et al. 2010)(Kuhn et al. 2004). Key advantages and disadvantages are detailed by Bart (Bart 2005) but the technique it is of limited relevance to this review as nuclear expertise is required and the sample is rendered radioactive. This method is not suitable for rapid screening.

Near Infrared (NIR) screening technology

Near Infrared NIR technology is applied in full scale WEEE plastic separation and can be applied in automated systems. The technology can detect some types of brominated flame retardants (e.g. TBBP A and Derivates) however it can not differentiate PBDE-containing and PBDE-free polymers.

Mid Infrared (MIR) screening technology

Also in the mid infrared region, plastic and BFR can be screened. Commercially available technology includes, for example, the Sony Plastics ID system mid-infra red reflectance spectroscopy. While it has a very high accuracy it needs 35 seconds for the screening which according to the WRAP report is too long and impractical for recycling lines (WRAP 2006a).

FT-IR

Also FT-IR instruments are on the market for screening of plastics including detection of BFRs. The PolyAna Avatar (Wolfson Electrostatics), for example, uses FT-IR reflectance spectroscopy operating in the spectral range 3-20µm. The blue section contains the special optics to bring the IR beam to the sample held at the nozzle. Cost is € 35,000 (WRAP 2006a). While the system is quick and simple in operation, it has not been proven that the full range of BFR can be measured (WRAP 2006a). Since NIR has difficulties with PBDE it is unlikely that this IR system will be able to detect PBDE in polymer matrices – it might, however, be able to detect TBBA.

Comparison of approved systems with practical applicability in WEEE separation facilities

From the above mentioned systems four have been tested in long time trials (WRAP 2006) and/or are used in full scale facilities:

- XRF
- Sliding spark
- XRT
- FT-IR

XRT is only used in automated systems and due to the relative high cost (€ 400,000) can only be applied in large WEEE separation plants. The FT-IR system can also be discounted as it cannot detect PBDE and therefore is not applicable.

Table 56: Comparison of the hand held methods for separation of BFR and non-BFR-containing plastic (WRAP 2006 with modifications).
The FT-IR system can detect some BFR but not PBDE and so has not been included in the table

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
Prime Function	Detect and quantify additives	Detect + quantify bromine and chlorine
Method of operation	Low power X-ray penetrates ~10mm into sample, detector measures distinct energy peaks from florescence of a range of elements to give ID and % concentration of additives	High voltage spark on surface creates plasma of vaporised material. Light spectra analysed for know peaks at Br and Cl wavelength to estimate % concentration.
Weight approx	1.7 kilos	0.75 kilo (gun)
Portability	Excellent – battery powered, no cables.	Reasonable – light to carry, but needs mains power.
Ruggedness	Excellent – built for on-site use in scrap-yards	Good – but care needed for fibre optic cable
Start-up speed	OK – 2-3 mins	Fast - < 1min
Operator manual	Good	Very good
1.Ergonomics	Easy – but careful to point away from user	Easy – but low flex cable to gun
2 .Sample presentation & speed	Easy – hold gun on sample for 15 – 30 seconds	Very easy – 1 second to ‘fire’ spark
3.Read-out	OK – but need to interpret ppm numbers on screen	Simple & clear
4.Adjustment	Not a problem	Easy to adjust base level reading to remove noise. Simple sensor cleaning method.
Sample preparation	Thicker samples better (> 5mm). Will detect surface contamination & coatings. Good for	Clean surface required and flat area for good spark contact. Will detect dirt and

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
	granular plastics.	coatings on surface.
1.Accuracy	Very good – ppm levels of elements.	Sufficient – to nearest 1% on Br / Cl concentration.
2.Repeatability	Excellent	Good – some noise around 0-1% level
3. Reliability	Very good	Very good
4. Speed	Slow 15-30 seconds	Fast – 1 second
5. User confidence	Good on primary elements, lower on chlorine.	High – except at 1% concentration level.
Price	Approx. $40-50,000	Approx. $6,000
Operator Skill level required	Technical operator to interpret results	Factory operator with basic training

It has also been shown that it is possible to manually separate BFR-containing plastic components from other plastic components using relatively low-cost detectors.

Richard Hull reflected the conclusions of many delegates at the BFR2010 conference with his conclusions that *"…it is essential that waste treatment processes are able to identify, separate and treat materials containing halogenated flame retardants properly, and ensure that they do not end up in halogen free waste streams"* (Hull 2010). Unfortunately in most circumstances, the manual identification and sorting of plastics parts from automobiles or computer and business equipment housings using fast infrared and hand held scanner techniques has significant throughput limitations. Andrady reports that the overall identification and sorting rates of about 250 lb (c.100 kg) per hour for car interior trim plastics and c. 900 lb (c.400 kg) per hour for computer and business equipment housings can be expected (Andrady 2003).

This is, Andrady notes "*not very impressive when compared to the fully automated flake-sorting rates near 10,000 lb(4,500 kg) per hour achieved using state-of-the-art density separation methods*" (Andrady 2003).

These automated separation systems are considered further in Appendix 4 (b).

Developing and transition country consideration on use of Bromine screening

Screening methods to determine polymers containing PBDE/BFR for developing countries need to be straightforward to use, reliable and economical. The XRF and Sliding Spark Technology are established, relatively simple and robust methods (as detailed in Table 56) and therefore appear appropriate for use in developing countries in WEEE recycling and similar facilities. Both methods are labour intensive and this is a disadvantage in industrial countries where they are relatively expensive to use because of the associated operational costs. The lower wages in developing/transition countries and the need to provide employment means that these handheld screening technologies might be seen as an advantage for these countries.

The cost of the XRF equipment is in the range of $40,000 to 50,000 and therefore might be too costly for (small and medium size) WEEE recycling companies in developing countries.

The sliding spark technology for the detection of halogens (IoSys 2010) is cheaper and costs around $6,000. A German producer of sliding spark technology has confirmed that equipment has been supplied to China (Seidel 2010) thus indicating that the technology is already used in a transition country.

Such handheld sliding spark equipment is available with additional detectors (NIR) for determination of the plastic type and can be used for producing clean polymer fractions with associated higher market values. The manual determination of polymer type to produce clean polymer fractions might be an attractive option for recovery of high quality plastic from developing and transition countries and this could be combined with the separation of PBDE/BFR-containing plastic.

The use of these technologies needs to be further assessed. International projects on WEEE recycling in developing/transition countries could determine whether such equipment is already used for selection of the polymer types and if there is already any experience on determining bromine content in practical operations.

The automated XRT method, by contrast, is a relatively expensive technology which can be used for automated screening. The method has recently been applied to full scale operations in industrial countries (Switzerland and Germany) and it’s usefulness for developing countries should probably be evaluated after more experience has been gained in industrial countries and the longer term reliability, robustness and effectiveness has been demonstrated.

Appendix 4 (b): Separation of articles containing PBDE from other components

The online detection and separation of PBDE from PBDE/BFR-containing materials (plastic, foam, textiles etc.) is currently not feasible. Given the challenging demands for making quick and reliable analyses of PBDE, as described in the earlier section, the only feasible approach, currently at least, is the separation of materials containing any brominated flame retardants from non-BFR-treated material.

This approach is already applied in some full-scale operational facilities although it is mainly applied for computers and TV casings. A few full scale plants have been established to separate mixed plastics from WEEE (Table 59 below). These separation techniques have currently mainly been established for plastics, and particularly plastics from electronic waste, and would need to be developed further to be useful for other key applications of PBDE/BFRs containing materials. This presents economic challenges as the separation of other materials for recycling is less economically attractive compared with the high specification plastics used in TV and PC casings.

Reasons for sorting plastics

The main driving forces encouraging the separation of plastics are a) recycling targets set in legislation, such as the WEEE Directive in Europe and b) the market value of plastic which can be recycled and used as a substitute for increasingly expensive virgin materials.

Japan has already established a Japanese Industrial Standard (JIS) for plastics for use in electric home appliances, "*marking for identification of plastic parts for electrical and electronic equipment (C9912).*" This standard requires the marking of plastic parts such as flame retardants (FR), recycled plastics and dismantling assistance. In particular, the marking system includes plastics already recycled by 'closed-loop recycling' (recycling from plastics of electric home appliances to plastics of electric home appliances). Target recycling rates for different electronic categories have also been set (Aizawa et al. 2010).

Whilst there are several WEEE recycling plants in Europe using 'state-of-the-art' technologies for the separation of plastics there are still only a handful of facilities for comprehensive treatment integrating plastic separation and recycling and only a very few plants separate BFR-containing plastic. Most WEEE recycling companies dismantle and sort equipment into various streams and then pass the plastic rich fraction to other specialised operators. Some aim for the recovery of residual metals in these polymer-rich fractions, others recycle parts of the plastic fraction, a third group recovers energy and a large proportion of WEEE plastics are sold as mixed plastic for export - mainly to China. This is discussed in more detail in Appendix 5 (b). In many parts of the world the plastic fraction, particularly in shredder residues, is sent to landfill or incinerated, often in non-BAT/BEP facilities.

The four main reasons for the limited number of approaches for recycling plastics from WEEE are:

a) Industry using secondary plastic materials has tight specifications in relation to polymer quality, both chemically (RoHS compliance) and with respect to material properties. This is also used as an argument to depress the prices of recyclate thus increasing the economic challenges.
b) WEEE plastics contain at least 15 different plastic types (Dimitrakakis et al. 2009). Whilst three polymers (ABS, PS, PP) account for between 70% and 85% of total the efficient sorting of the mixtures presents difficult technical challenges and a degree of cross-contamination is inevitable in practice.
c) WEEE plastics contain RoHS listed BFRs (PentaBDE, OctaBDE, DecaBDE; but normally no PBB which is also listed) along with BFRs which may be more heavily regulated in the future. Potential customers are therefore risk adverse to contaminated recyclate.
d) Production of larger volumes with identical properties and performance, as required by many major manufacturers, requires consistent quality and composition of inputs.

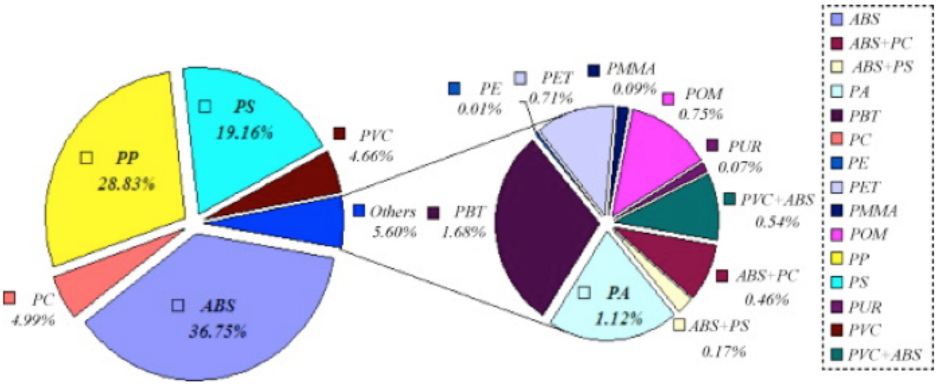

Figure 86: Polymer types identified in small WEEE plastic samples (%, w/w) (Dimitrakakis et al. 2009)

TV casing and PC monitors

Of the many EEE classified products, TV and computer monitors provide two of the richest sources of plastics: the plastic content in these two product groups varies between 10 and 40 weight percent. The major plastic part of a monitor is the rear part of the housing and this is separated for recycling and to gain access to the cathode ray tube. These plastic parts are normally removed by hand in the facilities and result therefore in a clean plastic fraction consisting mainly of ABS and HIPS which can then be recycled.

Mixed plastic from WEEE

Since the recycling industry collects different categories (TV/monitors, PCs, white goods, small electronics, lamps, etc. eventually, others) and uses different plant designs to recover metals and other recyclable materials, the final polymer rich fraction differs significantly with respects to polymer types; distribution; BFR content; PBDE/PBB content; and levels of heavy metals.

Currently most WEEE recycling facilities do not separate these mixed plastic fractions. For the EU these fractions are mostly exported, mainly to China. Only a few companies seem to separate these mixed plastic fractions (see below).

Technologies to separate PBDE/BFR-containing plastic

The separation of PBDE/BFR-containing plastic needs to be effectively integrated with the technologies used for separation of plastics for polymer material recycling as these are really the main driving force of a recycling plant.

The following techniques are used in full-scale plants for recycling plastics and may be used in a plant recycling plastics from WEEE.

a) Manual pre-sorting
b) XRF and Sliding spark spectra analysis (SSS[84]).
c) Sink and float technologies (S/F):
d) NIR (near infrared) sorting
e) Electrostatic separation[85]

None of the single techniques, however, has the ability to separate mixed plastic from WEEE; to ensure that the plastic is separated into marketable polymer fractions; and that at the same time PBDE/BFR-containing polymers are separated.

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[84] Strictly “sliding spark spectroscopy” but both terms are used.

[85] Electrostatic separation has been applied to polymers from computer keyboards from one company, where three well-defined polymers have to be separated. If more than tree polymer types are in the input or the input quality changes, electrostatic separation does not work very well. Thus, this technique is not applicable to mixed WEEE as a stand-alone technique. However, it may be used to separate fractions from S/F separation.

Table 57: Key separation techniques applied for the separation of WEEE plastic.

	Automation	***Polymer Separation***	***Separation interfering substances***	***Elimination/ Reduction BFR***
Sink and Float	4	%	4	% (+)
NIR	4	%	4	8
Electrostatic	4	%	4	8
X-ray transmission	4	%	4	4
Sliding spark spectroscopy	8	4 / %	4	4

4: Yes, **%**: To some extent, 8: No

Separation of PBDE/BFR-containing plastic in the pre-sorting stage (XRF & SSS)

It is theoretically possible to screen and separate materials using the technologies for detecting PBDE and for detecting bromine as described in the analytical section above. For practical reasons only technologies which are quick, cheap and reliable are useful or relevant to these processes in normal operational practice. Consequently the more complex methods for analysis of PBDE are (at least currently) not practical for use in pre-sorting PBDE-containing waste. Instead the screening of wastes is based on bromine content and subsequent separation is between those elements of the waste which contain bromine and those which do not.

The three technologies applied in practice (industrial/full-scale) to separate BFR and non-BFR-containing plastics are XRF, XRT and the Sliding spark spectroscopy.

XRF technology

The XRF technology can be used for detection and separation of PBDE/BFR-containing plastic with a detection limit of 10 to 100 ppm. XRF analysis is limited to the detection of bromine in the material, without any capacity to identify the type of compound. It is not possible by XRF alone, for example, to distinguish between Octa- and Deca-BDE.

The cost of an instrument is approximately $40,000 to $50,000. Therefore the use in small, and even medium size enterprises, may be limited. The time requirement for a measurement is less then a minute.

According to information supplied to the Secretariat by Sweden (Retegan et al. 2010), XRF is currently not used continuously in Swedish sorting facilities but instead is used for random checks on the accuracy of manual sorting (based on the experience of operators to distinguish, particularly, older equipment). The technique is perceived as costly and inefficient as an on-line analysis tool for the sorting of BFR-containing plastics.

Sliding spark spectroscopy

Sliding spark spectroscopy using hand-held instruments is used in various dismantling plants and other fields for screening halogens in plastic all over the world. It allows operators to distinguish between BFR-containing and almost BFR free components. The scanning time is very quick and takes only a few seconds. However, the SSS instrument needs a direct contact to the material surface and it is therefore not applicable for use in automated sorting systems but is used in the dismantling stage. Each instrument costs approximately $6,000 (Seidel, 2010). The quantification limit of the method can be set in the detector. The lowest detection limit for bromine is 0.1%. For practical reasons the system is normally set at 1% BFR by the recyclers in order to screen out PBDE/BFR-containing polymers which normally contain between 3 and 20% PBDE/BFR.

With dual-function equipment including NIR this method can also distinguish different plastic types. Instruments with this integrated function therefore have the potential for practical separation not only of PBDE/BFR and non-PBDE/BFR plastic but also for separation of plastic types at e-waste dismantling and recycling facilities at the dismantling stage.

Separation of PBDE/BFR-containing plastic by manual pre-sorting

The principal method currently used in the Swedish recycling industry for the assessment and separation of plastics from TVs and computer monitors containing BFRs from those without is manual pre-separation (Retegan et al. 2010) . This approach is used only for TVs and Monitors and not for other WEEE.

Operators use written instructions and guidelines listing various WEEE plastic components which are most likely to contain BFR. The listed items are removed manually from the waste stream (Retegan et al. 2010). More experienced staff and those with formal training and experience of manually sorting WEEE plastics and parts containing BFR can effectively sort plastics and remove those components which their experience has shown to contain BFRs (Retegan et al. 2010).

Even experienced manual sorting operatives cannot ascertain which type of BFR is incorporated in the plastics. Furthermore the use of manual sorting relies on the expertise of experienced and motivated personal. According to the Swedish report the accuracy of such sorting can be supervised by spot-checks using XRF measurements (Retegan et al. 2010).

The Swedish report did not include information about the effectiveness of this approach. It claimed, however, that for waste TV and PC monitors the accuracy of these sorting methods are satisfactory for complying with the European directives/legislation (Retegan et al. 2010). This is not surprising as the numbers of residual articles still containing Penta and OctaBDE has now dropped to low levels in Europe as explained in Appendix 3 above (i.e. the lifespan of the articles in which POP-BDE were used is short and there has very little use of POP-BDE for the past decade). In Europe and probably in most other countries apart from the US, therefore, it is only the 'tail end' of the disposal of POP-BDE-contaminated items that is now being processed. Whilst there are obvious attractions in the simplicity of this approach a more detailed analysis of the correlation between the visual assessments and the XRF spot-checks would really be necessary before such an approach could be recommended.

Applicability for other regions

The effectiveness of manual separation would also need to be evaluated in other countries or regions where the composition of BFR in the different WEEE categories is likely to be different.

The separation of a larger share of potentially PentaBDE and OctaBDE-containing equipment might be possible in particular for regions where PentaBDE and OctaBDE were phased out in the 1990s (e.g. Japan or Europe). Here mainly older TVs, monitors, and other electronics produced in the 1990s and earlier, would need separation and could be separated. For regions where PentaBDE and OctaBDE were used until 2004, and particularly in the US where volumes were very high, even relatively new equipment can contain PentaBDE and OctaBDE and manual separation of PBDE-containing equipment is likely to be less effective.

Separation of PBDE/BFR-containing plastic by "Sink and float" technologies (S/F)

Polymer types exhibit different specific weights and therefore liquid media with appropriate densities allow for separation of different thermoplastics into density groups. The salinity, and hence the density, of the liquid media can be changed by adding different salts. If water is being used, for example, the density can be raised to 1.15 by the addition of magnesium sulphate. Bromine-free polystyrene will float while bromine-containing polystyrene will sink, thus separating the plastics containing bromine from other polymers. For selected input fractions the sink and float technology produces very clean and qualitatively good products in respect to separation of BFR-containing materials. TV-cases contain mainly HIPS and exhibit higher densities, in Europe about 30%[86] of the casings contain BFR and S/F is a good way to separate them. With respect to BFRs, and especially PBDE, S/F has been reported to effectively separate BFR-containing from non-BFR types of ABS and/or HIPS. For Sweden, S/F has been reported separation of BFR rich fractions of TV/PC from low BFR fraction intended for recycling purposes.

With respect to plastics from small electronic equipments and mixed WEEE plastic from recycling of mixed WEEE (which in the case of e.g. Sweden are about 80% of total WEEE plastic), S/F can produce almost bromine-free plastic fractions, which consist of largely of ABS, PS (incl. HIPS) and polyolefins. However, due to a large share of black polymers in these low-bromine fractions it is challenging to produce high quality polymers with a good market price as useful output. Currently, therefore, the yield of these techniques does not normally allow economic recovery of polymers. Unless the bromine free fraction can be converted into

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[86] The content of BFR will depend on the region and the legislation for flammability standards - in the US/Canada most of the casings contain flame retardants.

valuable recyclate then S/F is unlikely to be widely used as operators are (understandably) unwilling to use a separation technique to produce what might be, in effect, two new waste streams without adding value to the output.

Near infrared technology

Near infrared technology ('NIR') is performed with manual sensors (e.g. IOSYS) in dismantling plants or in automatic sorting systems (e.g. TiTech, RTT). NIR light is directed to the waste plastic and the reflected NIR spectrum is captured and analysed. Programmable operational databases allow the identification of the different plastic types the machine has been 'taught'. However, WEEE plastics normally contain a high proportion dark-coloured or black plastics and the reflected spectra from these are weak so that they are often inadequate for accurate polymer identification. Furthermore whilst TBBPA and derivates can be detected with NIR the technique is not capable of detecting and separating plastics containing PBB or PBDE. These problems severely limit the operational utility of NIR for WEEE waste streams.

X-ray transmission technology (XRT)

X-ray transmission (e.g. X-Tract, TiTEch) has been developed to separate materials with different optical densities. According to TiTech their system is able to clean and separate alumina fractions, CRT glass fraction (Pb vs non-Pb), RDF fractions from metals, glass and PVC and to remove halogen-containing materials. X-ray transmission technology uses an electric X-ray source which creates a broad-band radiation in the energy range of 80 KeV to 160 KeV. This radiation penetrates the segregation material and, when attenuated, hits an X-ray camera sensor using two independent sensor lines with different spectral sensitivity. The data supplied by this camera is classified using high speed X-ray processing. The atomic density of the materials can therefore be identified and this is largely accomplished regardless of the material thickness.

The technology has successfully been applied to separate BFR/PBDE-containing plastics from BFR-free types (Krämer et al. 2010). It may, therefore play an important role in WEEE plastic recycling plants particularly if combined with NIR.

Sorting machines based on X-ray transmission are available at an industrial scale. They cost several hundred thousand Euros (the system from TiTEch, for example costs approximately € 400,000) and consequently may be too expensive for small to medium recycling and WEEE dismantling operations.

Polymer identification methods	Device	Advantages	Limitations
Experience/Inspection of producer information on the equipment	Manual	low capital costs	– No marking on all pieces – Automation difficult – Reliability of the markings
Near infrared spectroscopy (NIR)	PolySort (RTT-Systemtechnik GmbH)	– Fast, non intrusive – Automation possible	–No identification of dark/black plastics –Particle size and shape must fulfill the requirements
Infrared spectroscopy (IR)	Nicolet 380 FT-IR Spectrometer (Thermo Scientific)	–Reliable technology	– Surface impurities can influence the result
Sliding-spark-spectroscopy	SlideSpec-S2 (IoSys)	– Fast, non intrusive – Identification of additives - no problems with black samples	– Automation not feasible – Some uncertainty as to whether some plastic types can be identified
X-ray transmission	X-Tract, TiTEch	– can separate BFR plastics	– Expensive

Table 58: Summary of sorting techniques (adapted from (Chancerel & Rotter 2009).

Technologies for separating PBDE/BFRs from Plastic

Technologies of separating BFRs (including PBDE) from materials has only been established for:

a) PBDE/BFR-containing plastic; and

b) Printed circuit boards.

These two PBDE/BFR-containing material categories have commercial market value and this has been the main driving force for the development of improved recycling technologies. Neither of the separation technologies is currently operating at an industrial scale. For PBDE/BFR separation from plastic the technology now seems ready for industrial application. For printed circuit board, the PBDE/BFR separation technology is still only operating at a laboratory scale (see below).

For other materials only bromine recovery by separation via high temperature thermal processes like incineration and pyrolysis is discussed later in this chapter and has been suggested for separating and recovering bromine.

Separating of BFRs/Bromine from BFR-containing plastics with polymer recovery

The common sorting approaches are based on "*cherry picking*" the most valuable components of the electronics/polymers from the input. Yields are generally fairly low and are normally in the range of 20% to 60% depending on input, the plant design and technologies used. The PBDE/BFR and bromine load however is enriched in the residual waste fraction. This residual is then typically landfilled, sent for incineration/thermal recovery or exported to transition countries for recycling to products with low polymer quality requirements.

The CreaSolv® process extracts PBDE/BFRs from target polymers from plastic-rich fraction and is able to remove undissolved (e.g. non-target polymers and other interfering materials) and dissolved contamination (e.g. PBDE, PBB or other brominated flame retardants) from the target polymers (Schlummer et al. 2006). BFR from flame retarded plastics is extracted using a proprietary CreaSolv® solvent formulation and produces a by-product with high levels of BFR. The market price of Bromine is approximately 2500$/t (Hofland 2010a) so this by-product might be used for bromine recovery by the bromine industry. Alternatively it could be chemically treated or incinerated. It has been developed and optimised to WEEE plastic fractions and is able to produce RoHS compliant polymers even from BFR-rich fractions (Schlummer et al. 2006). The extracted recycled polymers are of high quality and intended for applications such as EEE production.

An assessment of practical and commercial applicability of the technology has been performed in the UK (WRAP 2006a). The study shows that the Creasolv® process for extraction of brominated flame retardants from WEEE polymers has potential to be commercially viable in the UK context at a throughput of 10,000 tonnes/year.

According to Fraunhofer-Institute IVV, where the process was developed, the process could be developed commercially with plant capacities of 2000 t/year and greater (Schlummer 2010).

The process should be able to compete with incineration ($100+ per tonne gate fee) or landfill[87] disposal (cost of landfill gate fee depends strongly on region and country policy) or as treatment methods for segregated polymer streams (WRAP 2006a). Creasolv will compete for BFR removal processes using spectroscopic sorting techniques, since it reaches higher yields due to the fact, that also most of PBDE/BFR-containing plastics are converted to RoHS compatible and marketable polymer products (WRAP 2006a).

The assessment concluded that the process could compete with export of mixed WEEE polymer outside the EU (current sales value around $100/tonne) if the finished high grade compounded recyclate can be sold at about 80% of the virgin compound price (WRAP 2006a).

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[87] According to the convention POPs waste need to be destroyed or irreversibly transformed. Landfilling Should be avoided if possible as it is not, in most circumstances, an approach which can guarantees long-term security. POPs Studies from different regions are documenting that PBDE are released from landfills and contaminate ground and surface water, the surrounding soil and for developing and transition countries contamination of humans working on or living around the landfill sites has been documented as discussed in the section on final disposal.

Recovery of metals, energy and bromine from printed circuit board (PWB)

The mechanical recycling of printed circuit boards which also separates the BFRs from other materials in the recovery process has been developed at a laboratory scale (Kolbe 2010a). Full scale operation of the process is planned for 2011 (Kolbe 2010b).

Within the complete material recovery strategy also the bromine is planed to be recovered (Kolbe 2010a). The main parts of metals are mechanically removed from PWB in a first step. In a second step the PWB resin is dissolved and the remaining metals and the glass-fibre is recovered. The metals are further recovered in metal smelters. The dissolved resin is debrominated and the bromine recovered (as NaBr). The resulting debrominated oil is used in a power plant (Kolbe 2010a). The glass-fibre is pressed, washed and dried and can be reused as filler material.

The company also plans to recycle the residues and dust from the production of printed circuit boards (Kolbe 2010b).

Separation of PBDE/BFR-containing materials other then WEEE plastic

While the separation of PBDE/BFR plastic by separation of BFR-containing fractions has been developed for different types of WEEE and types of plastic, there has been no information on such separation for other PBDE/BFR materials. Separation options need to be considered for materials like polyurethane foams which are to some extent recycled.

For larger polyurethane foam items like mattresses (or furniture) the same screening methods used for plastic items can be applied with handheld XRF or sliding spark spectroscopy.

Similar approaches to screening and separation can be used for other articles which may contain POP-BDE, this may include, for example, larger textile items such as curtains from public buildings. Furthermore in some countries with strict fire safety requirements it is possible that other articles not considered above may contain POP-BDE, either as original flame retardants or as subsequent contaminants. This might include any goods containing PUR foam from the US and other countries with particularly stringent flame retardant regulations.

Consideration should also be given to possibilities for labelling of suitability for export of articles after screening and sorting and whether it is appropriate to issue certification that sorted articles are PBDE free.

Appendix 4 (c): BAT Technologies for recycling PBDE-containing Articles considering exposures from recycling and disposal options

There are three main treatment scenarios to be considered in relation to BAT technologies for recycling with particular relevance to the POP-BDE are, as outlined in the previous Appendix:

(1) PUR foams – from furniture and transport.

(2) ABS and other polymers - largely from computers and business machines.

(3) Printed wire boards – from electrical and electronic equipment.

Technical systems developed for WEEE plastic recycling

There are a limited number of full scale operating plant, and a few pilot operations, which in response to the obligations arising WEEE Directive have to some extent considered PBDE/BFR separation from WEEE plastic. These have been discussed earlier.

Some companies perform full scale recycling of plastics from WEEE (including: Axion Recycling, UK; MBA, Austria/China; RUAG Switzerland, WERSAG, Germany). Unfortunately, however, most do not disclose the details of the separation techniques used. All the technologies report further material recycling of WEEE polymers. Currently there is little or no public evaluation of the resulting plastic fractions.

Table 59: Operational Industrial Scale WEEE separation technologies and their potential to separate PBDE-containing plastic (compiled by the authors from various sources)

WEEE input	Separation techniques	Success of separationPlastics Separated	Quality of separated polymers	PBDE Elimination (RoHS compliant products)	Development Stage*	Reference
Mixed plastic from WEEE (Austria, China)	Not disclosed	A) Low-BFR types of ABS, HIPS and ABS-HIPS-Mix B) Mixed plastic fraction	A) Good (Customers specify) B) Not for Electronics	Yes No (Deca failed)	Industrial scale	MBA Polymer Patent
Small electronic equipment, White goods (Switzerland)	Includes XRT (X-ray Transmission)	BFR and PVC free polymers	Good	Yes	Industrial scale	{Gerig, 2010 #51685}(Gerig 2010)
Small electronic equipment (Germany)	Smasher→ NIR (Near Infra Red) → NIR → XRT	Low-BFR types of ABS and HIPS	Not reported yet.	low Br levels	Industrial and pilot scale	{Krämer, 2010 #50539}(Krämer 2010)
WEEE plastics (UK)	Undisclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	{Morton, 2007 #18613}(Morton 2007)
WEEE plastics (Germany)	Undisclosed (incl. S/F [sink and float] and Electrostatic)	Low-BFR types of PP, ABS and HIPS	Undisclosed	Undisclosed	Industrial scale	{Schlummer, 2010 #50546}(Schlummer 2010)
TV and computer casings (Sweden)	Manual, not disclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	{Retegan, 2010 #46789}(Retegan 2010)

Table 60: Operational Pilot Scale WEEE separation technologies and their potential to separate PBDE -containing plastic plastic (compiled by the authors from various sources)

TV and monitor housings (Germany)	Dismantling → S/F	Low-BFR types of ABS, HIPS and ABS-HIPS-Mix	Good	Yes	Pilot scale	{Schlummer, 2006 #13132}(Schlummer 2006b)
Small electronic equipment (Austria)	Smasher→ S/F → CreaSolv®	Low-BFR types of ABS, HIPS and ABS-HIPS-Mix	Good	Yes	Pilot scale	{Schlummer, 2006 #41493}(Schlummer 2006a)

TV housings (UK)	Dismantling → BFR rich fraction → CreaSolv®	Low-BFR types of HIPS-ABS-Mix	Good	Yes	Pilot scale	{WRAP, 2006 #35179}(WRAP 2006)
TV housings (Germany)	Dismantling → S/F (heavy BFR rich fraction) → CreaSolv®	Low-BFR types of HIPS-ABS-Mix	Good	Yes	Pilot scale	{Schlummer, 2010 #50546}(Schlummer 2010)
Monitor housings (Germany)	Dismantling → NIR → S/F	Low-BFR types of ABS, HIPS and PC/ABS	Good	Yes	Pilot scale	{Schlummer, 2009 #50544}(Schlummer 2009)
Monitor and TV-set housings (Germany)	Dismantling → SSL → S/F	Low-BFR types of ABS and HIPS	Not yet tested	Yes	Pilot scale	{Schlummer, 2009 #50544}(Schlummer 2009)

Life Cycle Assessment and the Waste Hierarchy

The Stockholm Convention guidelines on Best Available Techniques (BAT) and Best Environmental Practices (BEP) provide a useful starting point for the assessment of waste management options. These guidelines confirm that society can manage wastes in a number of ways, depending on their physical and chemical nature, and on the economic, social, and environmental context in which they are produced. Specific decisions will always be influenced by local circumstances such as the availability of waste treatment facilities, alternative markets for materials, and the infrastructure available to safely collect, manage and transport waste materials.

Section III C (ii) of the BAT-BEP Guidelines, shows a hierarchy of decision-making for waste management:

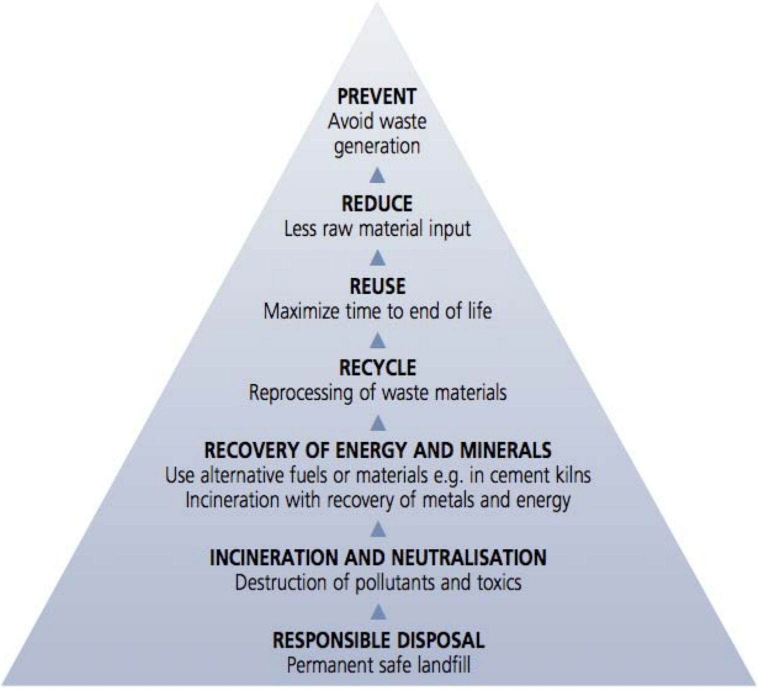

Figure 87: Waste management hierarchy (Stockholm Convention 2007b)

Waste hierarchies similar to this example have gained practically universal support as a starting point for managing waste. They are typically used together with life cycle assessments and similar techniques to ensure that the principles are applied soundly to any particular case. In the case of the BAT-BEP Guidelines the hierarchy is recommended to be used along with a number of principles one of which is that (in general) priority should be given to approaches that prevent the formation and release of chemicals listed in Annex C of the Convention.

The benefits of materials recycling are obvious in some of the applications for POP-BDE. Scrap PWBs, for example, have an average composition which includes 22% copper and 0.035% gold (350 ppm) (Lee et al. 2004). This can be compared with gold ores which can be economically mined with concentrations as low as 0.5 ppm[88]. Typical ore grades in open mines are 1–5 ppm and in hard rock mines are usually at least 3 ppm. Most copper is mined as copper sulphide from deposits that contain 0.4 to 1.0% copper. The recycling of precious metals including gold from circuit boards is thus self-evidently attractive.

For plastics the justification for materials recycling is not quite so clear. Most life cycle assessments of plastics have focussed on the range of polymers which are arise in normal municipal waste, generally those from packaging. Few, if any, have focussed on ABS plastics containing PBDE. Even those detailed specialist reviews, including a major study by USEPA in 2001 on the life cycle assessment of computer monitors didn't address the BFR impacts as part of the assessment (USEPA 2001).

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[88] http://en.wikipedia.org/wiki/Gold

Today, plastics are almost completely derived from petrochemicals produced from fossil oil and gas. Hopewell (Hopewell et al. 2009) suggested that around 4 per cent of annual petroleum production is converted directly into plastics from petrochemical feedstock. Furthermore as the manufacture of plastics also requires energy, its production is responsible for the consumption of a similar additional quantity of fossil fuels (Hopewell et al. 2009). In spite of the fossil fuel intensity of plastics, and the low thermal efficiency of most energy recovery processes (17- 30% without combined heat and power for a modern incinerator (European Commission 2006)) some countries burn most of their plastic waste:

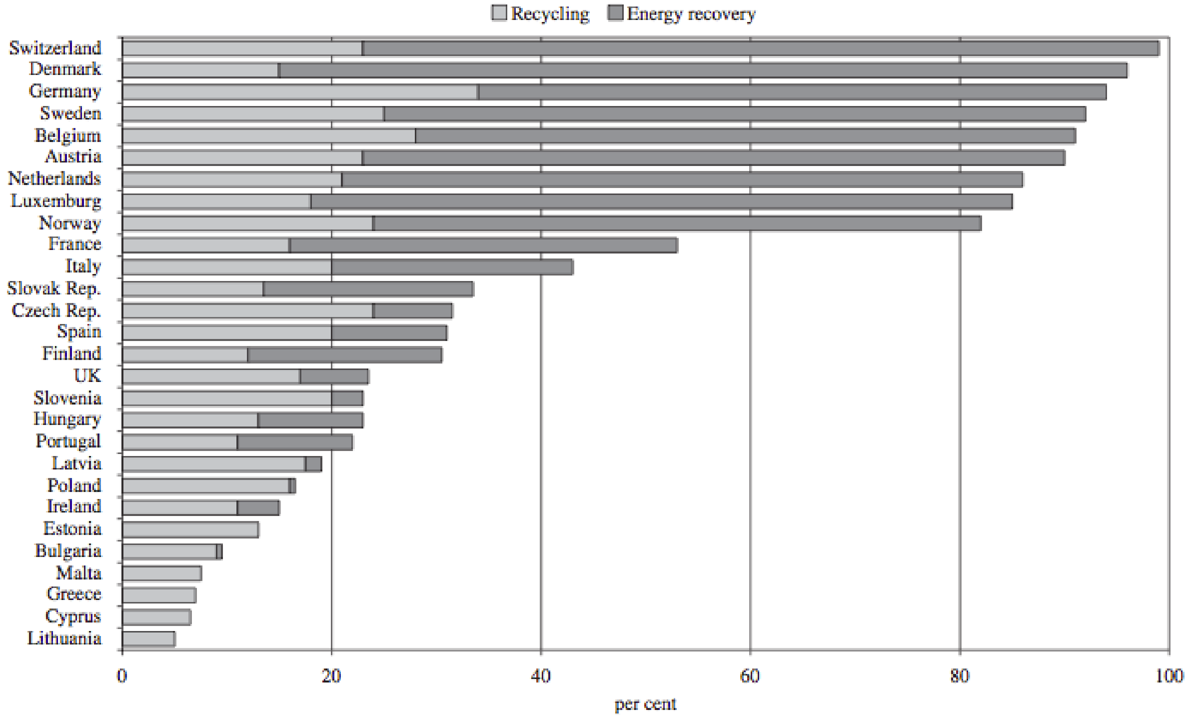

Figure 88: Rates of mechanical recycling and energy recovery as waste-management strategies for plastics waste in European nations (Hopewell et al. 2009).

Hischier et al. (Hischier et al. 2005) examined the question of whether WEEE recycling makes sense from an environmental perspective by a detailed life cycle assessment approach focusing on the environmental impacts of the Swiss take-back and recycling systems. The results of the LCA study demonstrated that for waste electrical and electronic equipment a take-back and recycling system as established in Switzerland has "*clear environmental advantages*" compared with the baseline scenario assuming a complete incineration of all WEEE. This was even true if only the primary production of the raw materials was considered in the baseline scenario and the disposal of the WEEE (i.e. its incineration) was ignored. The impact from recycling was assessed to be much smaller than that from the respective primary production.

The conclusion was that as recycling shows such clear environmental advantages over incineration a recycling goal "*as high as possible*" should be aimed for (Hischier et al. 2005). There appears to be general consensus on this issue – a press release issued by BSEF in relation to trials of metal recovery at the Umicore smelter emphasised (BSEF 2007b):

"*The intention of the test was not to promote the treatment of mixed, entire WEEE devices in integrated smelters, which clearly focus on non-ferrous metals recovery. Wherever plastics can be removed beforehand in an eco-efficient way, this is further regarded as the preferred option*".

In the United Kingdom the Waste Resources Action Programme, a Government sponsored organisation promoting efficient waste management commissioned an extensive review of international studies examining the environmental benefits of recycling (WRAP 2006b). The conclusions of this review included:

- In the vast majority of cases, the recycling of materials has greater environmental benefits than incineration or landfill.

- In the UK the current recycling of these materials saves 18 million tonnes of CO_2 equivalent greenhouse gases per year, compared to applying the current mix of landfill and incineration with energy recovery to the same materials.

Evidence from WRAP to a UK Parliamentary Audit committee (House of Commons Environmental Audit Committee 2008) said:

14. The message of this 2006 study is unequivocal. Recycling is good for the environment, saves energy, reduces raw material extraction and combats climate change. It has a vital role to play as waste and resource strategies are reviewed to meet the challenges posed by European Directives, as well as in moving the UK towards more sustainable patterns of consumption and production, and in combating climate change by reducing greenhouse gas emissions.

WRAP tabulated the results of their review showing the numbers of studies in each category:

Table 61: Summary of WRAP review of life cycle papers for waste management options (WRAP 2006b)

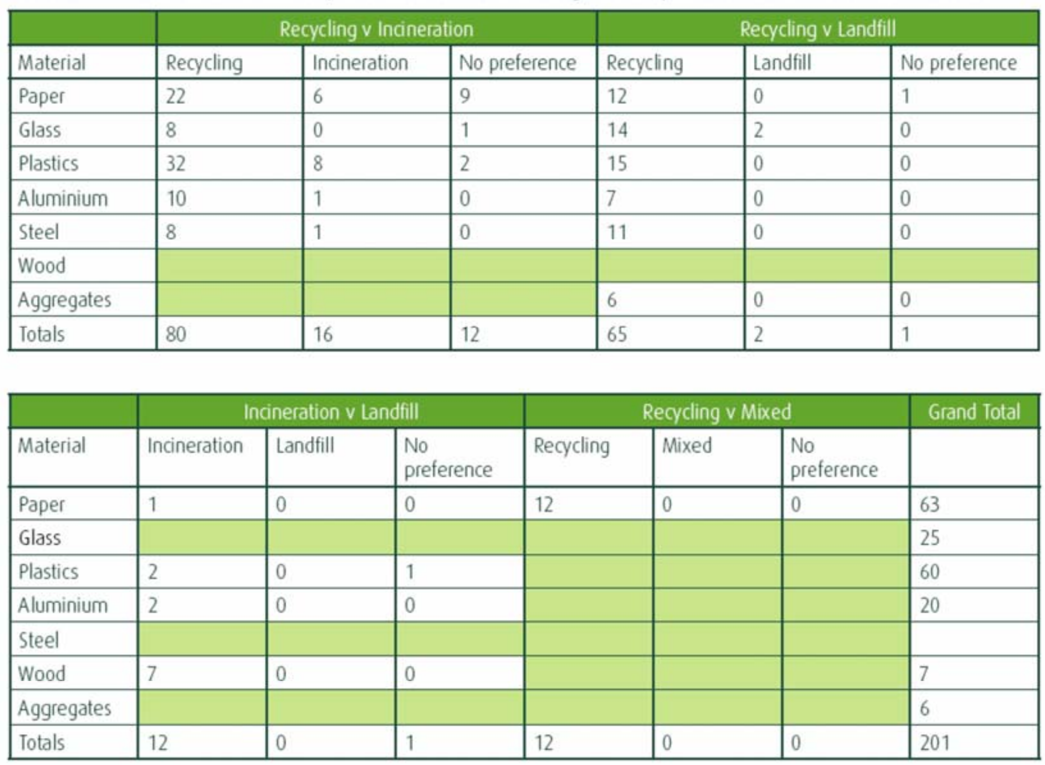

Table ES 4: Overall environmental preference of waste management options across all reviewed scenarios

	Recycling v Incineration			Recycling v Landfill		
Material	Recycling	Incineration	No preference	Recycling	Landfill	No preference
Paper	22	6	9	12	0	1
Glass	8	0	1	14	2	0
Plastics	32	8	2	15	0	0
Aluminium	10	1	0	7	0	0
Steel	8	1	0	11	0	0
Wood						
Aggregates				6	0	0
Totals	80	16	12	65	2	1

	Incineration v Landfill			Recycling v Mixed			Grand Total
Material	Incineration	Landfill	No preference	Recycling	Mixed	No preference	
Paper	1	0	0	12	0	0	63
Glass							25
Plastics	2	0	1				60
Aluminium	2	0	0				20
Steel							
Wood	7	0	0				7
Aggregates							6
Totals	12	0	1	12	0	0	201

It is clear that for all material streams recycling the balance of evidence indicates that materials recovery is preferable to incineration/energy recovery.

Practical reason to separate all BFR-containing plastic

Whilst separation of material containing any BFRs, including those which are not currently regulated as POPs, from waste streams goes beyond the requirements arising from the decision of the Stockholm COP there are good reasons to promote this approach.

These include:

- Compliance with legislation on Restriction of Hazardous (RoHS) limit on PBDE in Europe (where DecaBDE is included following the 2008 judgement of the European Court of Justice (ENDS 2008, European Court of Justice 2008)). China has similar, and in some cases more stringent requirements in the Chinese RoHS. If properly enforced this is likely to require better separation of BFR plastic to avoid potentially problematic contamination of plastic streams used in the production of new EEE.
- There is a current debate if in an updated RoHS regulation restriction should cover all BFRs – largely driven by consumer demand. Only the development of a strict recycling scheme with near complete separation of BFR and non-BFR-containing plastic will be able to produce plastic fractions suitable for such a market demand.

- When recycling polymers BFR-retarded materials should only be reused in plastics which require flame retardant properties and PBDE/BFR-retarded plastic should not enter non-flame retarded plastic streams. All BFRs investigated have certain toxic properties and their unnecessary incorporation into recycling streams is, in practical terms, the use of dilution to treat hazardous wastes contrary to accepted good practice in waste management. Furthermore if risk assessments had been undertaken for a BFR, the risk scenarios would only cover the original design usage. If the BFR is subsequently used for another product then the risk assessment and exposure pathways can be very different from the original use. This has been shown recently with assessments by Chen et al. of the risks associated with recycled plastics containing BFRs being used for the production of children toys which are vulnerable to exposure routes, such as mouthing, which were not anticipated in the original use (Chen et al. 2009b, Chen et al. 2010a)[89]. Chen demonstrated that such uses of contaminated recycled plastics carry unacceptable risk and uncertainties for human health.
- The control of the substance flow of BFRs can only realistically be achieved if the global recycling industry separates the FR and non FR plastic streams.
- A separation of BFR and non-BFR plastic will improve the recyclability of the plastic streams.
- Some global producers of electronics have phased out brominated flame retardants and aim to recycle only BFR-free plastic fractions. They are faced with challenges to avoid cross contamination which are made more much more difficult if BFRs are diluted through the stock of plastics.
- Many BFRs are aromatic compounds and therefore have varying degrees of potential to form PBDD/DF during their useful life, from end-of-life treatment and to contain PBDD/DF from production. These chemicals therefore need to be carefully controlled when there is any possibility that they could enter thermal processes which favour PBDD/DF formation such as feedstock recycling to fuels; incomplete combustion processes, pyrolysis, gasification or thermal stress in metal recycling (Weber & Kuch 2003). Separation can assure compliance with the German Chemikalienverbotsverordnung (for brominated dibenzo-p-dioxins and dibenzofurans) (German Federal Ministry of Justice 2003, Schlummer et al. 2006).
- DecaBDE, which is a major global BFR with a historic production of well over 1,000,000 tonnes (see Appendix 2), is a precursor of POP-BDE in some environmentally relevant circumstances and technical processes, as described in Appendix 4 (e) below and a PBDF precursor during lifespan of some applications and in some end-of-life treatment scenarios (see Appendices 2 (g) and 3 (c)). It therefore needs careful control to avoid its entering non-BAT processes including feedstock recycling processes (e.g. fuel production) and other processes where pyrolysis conditions are prevalent, to avoid the formation of POP-BDE during these processes (Hall & Williams 2008).
- It is estimated that a large share of POP-BDE in atmospheric stem from debromination of DecaBDE as described in above (Schenker et al. 2008). DecaBDE will ultimately all be degraded with lower-brominated PBDE and PBDFs as significant degradation products. The question is essentially not "*whether*" DecaBDE will be degraded but "*how long will it take*" to degrade and what the degradation products will be.

Considerations of BAT-BEP for Waste Management:

a) Plastic containing PBDE

Recent studies have shown that plastics containing PBDE have been used to produce articles for which no flame retardancy is required including children's toys, household goods and video tapes (Hirai & Sakai 2007, Chen et al. 2009b, Chen et al. 2010a, Chen et al. 2010c). This shows that the flow of plastics containing PBDE/BFR for recycling are not well controlled and that plastic containing POP-BDE is being mixed with the non-flame retarded plastic streams.

From a waste hierarchy and life cycle assessment perspective the mechanical recycling of plastic for further use is strongly favoured. When plastics are contaminated with hazardous POPs, however, particular care has to be given to how the waste hierarchy is followed. It can be seen from Appendix 5 (c) of the report that current exposures to POP-BDE are at levels where serious health effects are being measured in epidemiological studies. In these circumstances it is clearly not sensible to recycle materials containing POP-BDE into uses where

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[89] A critical response was made by the industry (Banasik et al. 2010) to which Chen responded (Chen et al. 2010b).

exposures cannot be controlled and may be significantly more harmful than in the original use (from a printer housing into a toy that may be chewed by a young child, for example). Furthermore such recycling is not necessary because technologies to separate PBDE-containing fractions have been developed and are operating in full scale. Currently these technologies seems mainly available in Europe. However at least one international company operates a plant in China. Furthermore affordable handheld systems allow sorting and separation of the (normally much smaller) waste streams containing BFRs to be applied even in transition/developing as described below.

Several options exist for the treatment of separated PBDE/BFR-enriched fraction. Further material recycling could be performed after a separation step to remove the PBDE/BFR by the Creasolv process for example. From the remaining highly PBDE/BFR-enriched fraction bromine could be recycled. This is an increasingly attractive option given the very high prices for bromine.

This option, assessed to be competitive with alternatives when operating at a moderate scale meets the aims of the waste hierarchy in relation to achieving high levels of materials recovery whilst reducing exposure to POP-BDE. Whilst it appears to be the preferable option in principle it cannot currently be unequivocally recommended as full-scale operational performance has not yet been evaluated. However a comprehensive assessment of pilot tests including cost estimates have been made and published (WRAP 2006a).

Depending on the bromine content, the PBDE/BFR rich fraction could be thermally recovered in cement plants or the primary metal industry. However considering the knowledge gaps on emissions from these two facility types (see comparison tables and Appendix 3), both types of facility need further assessment before any final recommendation can be given. Currently, therefore, the only tested and commercially operating technology for treating the high PBDE/BFR fraction is BAT incineration (Stockholm Convention 2007b). Depending upon the plant configuration this gives the additional possibility of recovering bromine. BAT Incineration is available mainly in industrial countries.

Feedstock recycling to produce by pyrolysis technologies fuel has been suggested as another option (Hornung et al. 2003, Zia et al. 2007). Again, however, information is only available for pilot plants. In these cases the resulting oils need additional treatment to remove (or debrominate) the resulting contaminants. Particular care has to be taken to reduce the formation of POP-BDE and PBDF by debromination of DecaBDE.

An alternative approach, further down the waste hierarchy, is energy recovery of the entire WEEE plastic fraction in primary steel industry. This approach is available in all regions of the world but not necessarily in each country. Hirai (Hirai et al. 2007) assessed this to be the most favourable choice from an LCA perspective subject to consideration about limitations on the bromine/halogen content as a limiting factor in the primary steel industry. The Japanese steel industry accepts a halogen content of up to 0.5%[90] (bromine or chlorine). However it is also not clear to which extent the present antimony and bromine could have negative impacts on the performance or emissions at the blast furnace or by transfer via ash residues in the sinter plant. PBDD/DF emissions have not been assessed/reported in this route.

b) PUF containing PBDE

For polyurethane foam large recycling activities used for carpet padding are ongoing in the US. High levels of exposure of workers and carpet installers have been revealed in a first study. The extent of this recycling activity for other regions is unknown. PBDE-containing foams could be separated by screening with hand held bromine scanning (XRF or SSS). The

For PBDE-containing PUF no technology has been developed yet for separation of PBDE/BFR to reuse the polymer.

Since PUF has a high calorific value similar considerations apply to the energy recovery options as for plastics. The main difference is however the large volume (low density) which can lead to large logistic challenges for transport and therefore can only be treated relatively locally[91]. The low density also (probably) does not allow the use in blast furnaces.

c) Textiles containing PBDE

The extent of recycling of PBDE-containing textiles is unclear but can be assumed to be small for composite materials such as those used in transport. There may be some limited recycling also for other PBDE-containing

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[90] In Europe the Chlorine content of up to 1.5% (Bremen/Germany) (Tukker 2002) and 2% (Linz/Austria) (European Commission 2009) is reported to be accepted from steel industry.

[91] Although it is noted that this has not prevented export of foam from the UK to the US for recycling into rebond.

textiles. Textiles containing PBDE could be separated and thermally treated with the same considerations mentioned in (b) above.

d) Printed circuit/wire board (PWB) containing PBDE

Material recycling of PWB by mechanical means is still operating only at a laboratory scale and therefore materials recycling of printed circuit board can not be considered further here.
The current main recycling path is copper smelters which recover the copper and precious metals and utilise the plastics and resins as reducing agent. Smelters processing PWB need an after burner for the destruction of UPOPs and other emissions from the furnace. There is currently no data on PBDE, PBDD/DF and PXDD/DF emission levels available from the five to ten BAT integrated smelters worldwide.

Comparative emissions and impacts of the various recycling and recovery technologies are included in the table below:

Table 62: Assessment of different treatment scenarios

Scenario (Material)	***Applied in practice***	***Waste Hierarchy LCA***	***Economics *****	***BFR Removal/ Destruction***	***PBDD/DF***	***Worker Exposure***	***Consumer Exposure***
Rebonding (PUF)	🟩	🟩	🟧	🟥	🟨	🟥	🟥
Regrinding (Polymer)	🟩	🟩	🟧	🟥	🟨	🟥	🟥
Moulding (Polymer)	🟩	🟩	🟧	🟥	🟧	🟥	🟥
Creasolv (Polymer)	🟨	🟩	🟨	🟩	🟩	🟨	🟩
Hydrolysis	🟧	🟨	🟧	🟧	🟩	🟨	🟩
Glycolysis	🟧	🟨	🟧	🟧	🟨	🟨	🟩
Pyrolysis for fuel/feed	🟨	🟨	🟧	🟧	🟥	🟧	🟨
Pyrolysis/ Gasification	🟩	🟧	🟨	🟨	🟧	🟨	🟩
Blast Furnace (Polymer)	🟩	🟧	🟩	🟩	🟨	🟨	🟩
Copper Smelters (PWB)	🟩	🟧	🟩	🟩	🟥	🟧	🟩
Antimony Smelter	🟩	🟧	🟨	🟩	🟥	🟧	🟩
Electric Arc* Furnace (EAF)*	🟧	🟧	🟨	🟩	🟥	🟧	🟩
Secondary Aluminium*	🟧	🟧	🟨	🟩	🟥	🟧	🟩
Cement Kilns (All)	🟩	🟧	🟨	🟩	🟨	🟨	🟩
HW/MW Incineration (All)	🟩	🟧	🟥	🟩	🟧	🟨	🟩
Landfill (All)	🟩	🟥	🟨	🟥	🟧	🟧	🟧
Open Burning (All)**	🟩	🟥	🟥	🟥	🟥	🟥	🟥

* The PBDE material is just introduced with the metal fraction and therefore EAF and secondary aluminium industries are not actual treatment technologies

** Economics includes external cost considerations

🟩	Yes/ **Scoring:**
🟩	Positive – e.g. low emissions/ environmental/ health impacts
🟨	Uncertain - probably OK
🟧	Uncertain - possibly negative
🟥	No/Negative – high emissions/ environmental/ health impacts

Scenario (Material)	*Applied in practice*	*Waste Hierarchy LCA*	*Economics ***	*BFR Removal/ Destruction*	*PBDD/DF*	*Worker Exposure*	*Consumer Exposure*
Rebonding (PUF)	🟩	🟩	🟧	🟥	🟨	🟥	🟥
Regrinding (Polymer)	🟩	🟩	🟧	🟥	🟨	🟥	🟥
Moulding (Polymer)	🟩	🟩	🟧	🟥	🟧	🟥	🟥
Creasolv (Polymer)	🟨	🟩	🟨	🟩	🟩	🟨	🟩
Hydrolysis	🟧	🟨	🟧	🟧	🟩	🟨	🟩
Glycolysis	🟧	🟨	🟧	🟧	🟨	🟨	🟩
Pyrolysis for fuel/feed	🟨	🟨	🟧	🟧	🟥	🟧	🟨
Pyrolysis/ Gasification	🟩	🟧	🟨	🟨	🟧	🟨	🟩
Blast Furnace (Polymer)	🟩	🟧	🟩	🟩	🟨	🟨	🟩
Copper Smelters (PWB)	🟩	🟧	🟩	🟩	🟥	🟧	🟩
Antimony Smelter	🟩	🟧	🟨	🟩	🟥	🟧	🟩
Electric Arc* Furnace (EAF)*	🟧	🟧	🟨	🟩	🟥	🟧	🟩
Secondary Aluminium*	🟧	🟧	🟨	🟩	🟥	🟧	🟩
Cement Kilns (All)	🟩	🟧	🟨	🟩	🟨	🟨	🟩
HW/MW Incineration (All)	🟩	🟧	🟥	🟩	🟧	🟨	🟩
Landfill (All)	🟩	🟥	🟨	🟥	🟧	🟧	🟧
Open Burning (All)**	🟩	🟥	🟥	🟥	🟥	🟥	🟥

* The PBDE material is just introduced with the metal fraction and therefore EAF and secondary aluminium industries are not actual treatment technologies

** Economics includes external cost considerations

🟩	Yes/ **Scoring:**
🟩	Positive – e.g. low emissions/ environmental/ health impacts
🟨	Uncertain - probably OK
🟧	Uncertain - possibly negative
🟥	No/Negative – high emissions/ environmental/ health impacts

Appendix 4 (d): Identify Capacity of developing/transition countries to implement BAT/BEP

4 (d) I) Material recycling of PBDE-containing articles

Currently plastic in developing and transition countries are recycled without the determination of the PBDE or bromine content. Furthermore PBDE/BFR plastic from material recycling is entering sensitive plastic stream (see above and Annex 4a). As mentioned above and described in Annex 4 several technologies are used in developed countries (Annex 4f).

a) Recycling of plastic including detection of PBDE/BFR

Manual separation of PBDE/BFR-containing plastic

Manual separation of PBDE-containing materials without instrumental help might be an option to some extent. However considering the complexity of the thousands of different electronics (different types, different producers and different series from same type and same producer) and the uncertainty of producers having used a BFR type, manual separation seems a huge challenge. To some extent there are stamps showing that plastic contain BFR materials. However it is not clear how many of the non-marked plastic do contain PBDE/BFRs.

Separation by means of instrumental PBDE/BFR screening

Also for developing/transition countries only the screening and separation in respect to bromine content might be practical in particular since wages are lower for manual separation. Here XRF and SSS might be applied. From price and simplicity in operation the sliding spark technology seems favourable for developing/transition countries. Such handheld sliding spark equipment is available with additional NIR spectrometer for the identification of plastic type (cost is then approx. $25,000) and could be used for producing clean polymer fractions with associated market value. The options should be further assessed.

b) Recycling of plastic into non-sensitive uses without determining of PBDE/BFR content

There might be other uses where lower concentrations of PBDE/BFR might not consist a threat to humans and the environment. One important consideration for such less sensitive uses for recycled products possibly containing PBDE/BFR are further end-of-life considerations and the need of ESM. This is a challenge for developing/transition countries when considering their limited waste management, regulatory and analytical capacities.

c) Material recovery of PBDE-containing PUF

Developing/transition countries with particularly strong links to the US market, and/or those countries receiving goods as aid from the US might receive articles such as cars, commercial vehicles, mattresses, furniture, textiles etc. containing significant levels of POP-BDE. The screening options mentioned for plastics can be applied to the separation of articles containing or contaminated with POP-BDE and articles recycled. Experiences in the US have revealed high occupational PBDE exposure for PUF recycling (Stapleton et al. 2008). Therefore options and limitations of PUF recycling need to be further assessed for the different regions.

4 (d) II) Material recovery and energy recovery of PBDE-containing materials in metal industries

As mentioned above, recent studies in China, Taiwan and Turkey have reported releases of PBDE and PBDD/DF from metal industries (copper smelters, electric arc furnaces, sinter plants, secondary aluminium industry) revealing that also PBDE/BFR-containing materials are entering these facilities (Du et al. , Du et al. 2010)(Odabasi et al. 2009)(Wang et al. 2010c). Many developing/transition countries have some of these facilities and therefore possible releases.

It is currently not clear whether metal industries in developed countries are appropriate to treat waste containing PBDE due to the lower average technology levels than in industrial countries. There are large knowledge gaps in this respect (see also Appendix 3).

Since there are still considerable knowledge gaps for the differaent metal industries in developed countries (copper smelters, electric arc furnaces, secondary aluminium, antimony smelters) currently no recommendation can be given for such practices for developing/transition countries.

4(d) III) Feedstock recycling and thermal recovery of energy in thermal processes

a) Energy recovery (and bromine recovery) from PBDE/BFR-containing materials in incinerators

Only BAT incinerators should be used to treat PBDE-containing materials. However the construction of BAT incinerators in developing/transition countries is questionable considering the high cost of waste treatment (normally above $100) and the generally high levels of wet organic wastes(Brunner & Fellner 2007)(World Bank 2005). Therefore waste incineration is unlikely to be a feasible option for treatment of PBDE-containing waste in developing countries.

b) Energy recovery from PBDE/BFR-containing waste in cement kilns

Cement kilns are increasingly used in waste management schemes also in developing/transition countries for energy and material recovery (Holcim & GTZ 2006). The facilities have been/are used for destruction of PCB-contaminated oil and some pilot tests for destruction of pesticides have been performed in developing countries (Karstensen et al. 2006). Since no study has been published yet on the destruction of PBDE/BFR-containing waste with monitoring of releases of PBDE and PBDD/PBDF even in developed countries (see Appendix 3c), no final recommendation can currently be given even for dry BAT kilns. However from experience with long dry kilns without pre-heaters and pre-calciners and wet kilns the PCDD/DF formation and release potential is known in particular when chlorine-rich (alternative) fuel/feed is brought into such kilns these two types of kilns can not be used for recovery of PBDE-containing materials. Only BAT/BEP cement kilns with multi-stage pre-heater /pre-calciners which are already operating in compliance with the conditions of their permits should be considered for waste management (Holcim & GTZ 2006). A properly configured test-burn, including the assessment of the destruction efficiency of the kiln which incorporates analysis of all emissions (including sampling for PBDD/DF) from the process and the bypass stack together with the concentrations in clinker and cement kiln dust, should always be carried out before any POP-BDE waste is considered for routine disposal.

c) Pyrolysis and gasification of PBDE/BFR-containing polymers/articles

No recommendation can currently be given for using pyrolysis or gasification of PBDE-containing materials for developing/transition countries due to the lack of full scale experiences also in industrial countries (see Appendix 3b).

Appendix 4 (e): Regulatory approaches and strategies used to support the implementation of BAT/BEP

This section includes considerations of the capacity of countries to safely handle POP-BDE and discusses the regulatory approaches necessary.

The expression "*if you can't measure it, you can't manage it*" from Appendix 2 is particularly relevant to the regulation of the POP-BDE. The limited information provided in the country questionnaire responses together with knowledge gaps sections of this review highlight some crucial deficiencies in the information on arisings, uses, stocks, emissions, impacts and the (uncertain) permanence of final sinks. All of these gaps really need to be addressed in order to ensure effective regulation of these POPs.

Even without full information it is clear that some areas deserve urgent regulatory attention.

In the inventory of PBDE in California waste streams Petreas highlights the "*striking relative magnitude of e-waste as the largest repository for PBDEs*" and argues that this "*cannot be ignored*" (Petreas & Oros 2009).

This is certainly true when it is estimated that upto about 80% of all the e-waste collected for recycling in industrialised countries ends up being exported to China, India, Pakistan, Vietnam, the Philippines (Wong et al. 2007b)(Robinson 2009) but also to countries in Africa, and that up to 99% of PBDE-contaminated ABS wastes are exported to developing/transition countries (Schut 2007). These countries often lack appropriate regulatory structures to be able to safely handle these hazardous materials.

The scale of the informal sector in these countries indicates the scale of the challenge. In China alone, it is estimated that 700,000 people earn their income in the collection and recycling of e-waste (Manhart et al. 2008). Approximately 98% of these work in informal conditions (Manhart 2007)(Manhart et al. 2008). If there are no alternative employment opportunities, sector-reforms are likely to get undermined by these stakeholders (Manhart et al. 2008).

The recent UNEP report "*Recycling from E-Waste to Resources*" confirms this dilemna and notes that China "*has already shown how the financing of state-of-the-art e-waste recycling plants fails when not supported by a proper collection network and suffers the completion of informal sector, notwithstanding the economic effort of the government: western high tech equipment could not come as universal cure to financial and social problems hidden behind the e-waste issue*" (United Nations Environment Programme & United Nations University 2010).

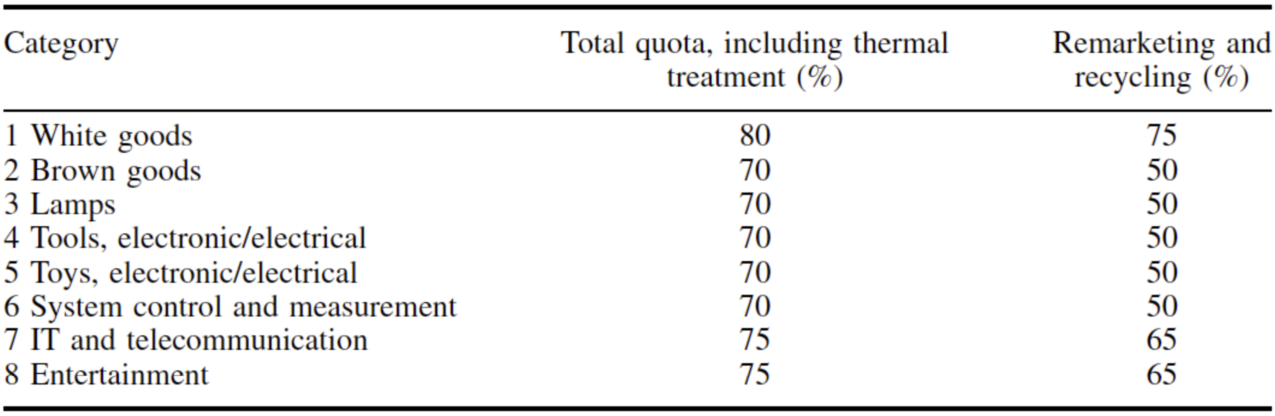
Petreas argues that as "*e-wastes contain the majority of PBDEs in California waste streams and, therefore, waste management practices should focus on them*". The response that is most pressing is to ensure that export is only allowed for genuine recovery of materials and that the often illegal shipments that are currently handling much of the e-waste must be stopped.

Perhaps even more striking, however, was the magnitude of the unaccounted PBDE, included in the Californian survey in the "*other*" category of wastes. Characterisation of these types of wastes, as Petreas urges, "*is critically needed to avoid ecological catastrophes. Accounting for chemical use from cradle to grave is just another step toward responsible and sound waste management*".

Legislation and policy related on separation of BFR-containing plastic

Directive 2002/96/EC of the European Parliament and the Council of 27 January 2003 on waste electrical and electronic equipment (the 'WEEE' Directive) (European Commission 2003a) entered into force on 13th February 2003 and establishes a legislative framework for the requirement in the EU to treat and recycle electrical and electronic equipment. The WEEE Directive gives priority to the reuse of WEEE and its components, sub-assemblies and consumables and Member States have to ensure that, on average, more than four kilograms of WEEE per inhabitant per year are separately collected. It required that, by December 2006, Member States must ensure that EEE producers achieve targets for recovery of e-waste (70-80% by weight, for different types of equipment) and for component, material and substance reuse and recycling (50-75%):

Table 63: European Union recycling quotas from article 7 of Directive 2002/96/EC (Scheirs & Kaminsky 2006).



Category	Total quota, including thermal treatment (%)	Remarketing and recycling (%)
1 White goods	80	75
2 Brown goods	70	50
3 Lamps	70	50
4 Tools, electronic/electrical	70	50
5 Toys, electronic/electrical	70	50
6 System control and measurement	70	50
7 IT and telecommunication	75	65
8 Entertainment	75	65

Producers have to establish systems to treat collected WEEE by using best available techniques and where it is demonstrated that reuse is not the preferable option then all WEEE collected separately should be sent for recovery.

Annex II of the WEEE Directive prescribes the selective treatment for materials and components of waste electrical and electronic equipment in accordance with Article 6(1). The Annex requires "*as a minimum"* that the listed *"substances, preparations and components*" including, inter alia, "*plastic containing brominated flame retardants*" have to be removed from any separately collected WEEE. These "*substances, preparations and components*" are then required be "*disposed of or recovered*" in compliance with the obligations of Article 4 of the Waste Framework Directive[92] – which means, in essence, "*without endangering human health and without using processes or methods which could harm the environment*". Many countries interpret this obligation as a requirement to remove the plastics containing brominated flame retardants as an identifiable waste stream. There is debate about how effectively this requirement of the WEEE Directive is being applied and enforced across EU Member States (Bio Intelligence Service for European Commission DG Environment 2006).

National legislation in some countries fully implements the requirements of the Directive. In Sweden, for example, the Swedish national ordinance on the pre-treatment of WEEE, requires plastics containing BFRs to be separated (NFS 2005, (Retegan et al. 2010). However only 20% of WEEE plastic is separated.

In Switzerland there has historically been a policy to incinerate plastic from WEEE. The consequence of this has been to effectively eliminate the stock of Penta and Octa BDE in plastics and electronics (Morf et al. 2007). Switzerland is now switching to promoting more material recycling with separation of BFR/non-BFR plastic only incinerating the BFR-containing fraction.

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[92] (then 75/442/EEC, since codified as 2006/12/EC (European Parliament and Council 2006a) and currently being superseded by 2008/98/EC (European Union 2008)). This obligation is interpreted by many countries as meaning the removal as an identifiable waste stream. – also the formulation in the WEEE recast from Dec 3, 2008).

Appendix 5: Review of the long-term environmental desirability of the recycling of articles containing PBDE

This Appendix discusses the environmental desirability of recycling articles containing PBDE in the context of sustainable development and the environmental and health impacts identified in the previous sections. It takes into account the life cycle and the durability of new articles made from recycled material containing PBDE.

For this Appendix the literature has been reviewed and information sought in order to provide:

(a) A prediction of the volumes and types of articles containing PBDE and an anticipation of levels of PBDE in articles in the waste stream and in new articles produced from recycled materials, with a view to considering the fate of PBDE in waste materials and new products;

(b) Information on the potential trade volume of recycled articles containing PBDE, including from developed to developing countries;

(c) An assessment of the costs and benefits of removing or maintaining the exemption on recycling articles containing PBDE;

(d) Consideration of the particular needs of developing countries and countries with economies in transition in the event that, first, the exemption on recycling articles containing PBDE is removed; and, second, the exemption is maintained;

(e) Recommendations on the long-term environmental desirability of the recycling of articles containing PBDE;

(f) Recommendations for the elimination of PBDE from the waste stream.

In some cases no relevant or reliable information has been found.

Appendix 5 (a): Penta and Octa BDE Stocks and implications for levels in recycling and recyclate

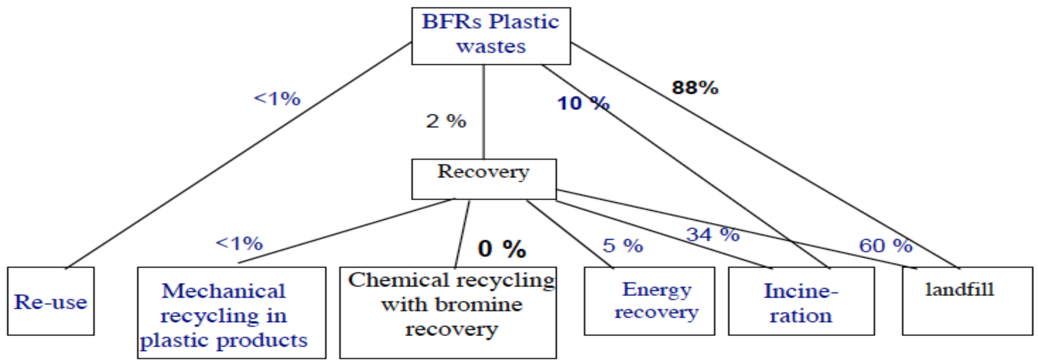
In order to assess the likely presence of POP-BDE in articles it is first necessary to try to establish how large, and in what form, the existing stocks of Penta and OctaBDE may be. This section should be read together with

Appendix 2 (e): Production, Use and Stocks of PentaBDE and OctaBDE. Here the analysis is taken a step further and provides a prediction of the volumes and types of articles containing PBDE and an anticipation of levels of PBDE in articles in the waste stream and in new articles produced from recycled materials, with a view to considering the fate of PBDE in waste materials and new products.

It had been hoped that industry data, supported by information from the Parties, would allow stocks and uses to be established. Unfortunately neither the industry nor the Parties provided any detailed information on these issues.

Early reports were therefore reviewed in an attempt to establish more robust details. The BSEF[93] report "*Introduction to Brominated Flame Retardants*" (Bromine Science and Environment Forum 2000), for example, considered the waste flows in 2000 together with projections for "*after 2004*":

Current situation in Europe



Situation in Europe after 2004

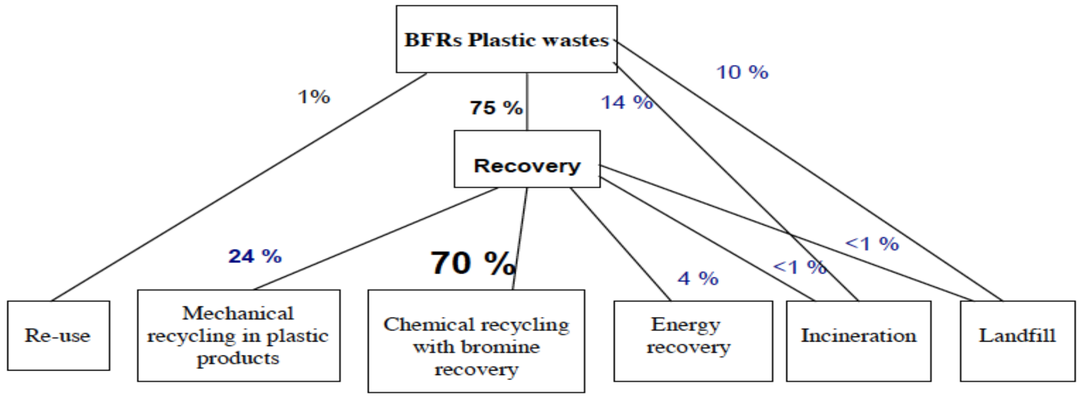


Figure 89: Waste flows in Europe as suggested by BSEF (Bromine Science and Environment Forum 2000)

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[93] Another BSEF report by Kennedy & Donkin Ltd. suggested (first noted as an "unpublished report" cited by Prevedouros (Prevedouros et al. 2004a)) that there is a measurable pool of brominated flame-retardants currently residing in electrical goods and electronic equipment. Their study calculated that approximately 11,000 tonnes of bromine was available for recovery from all plastic waste streams in Western Europe. The full report is not yet published but the Bromine Industry has provided a copy of the executive summary - unfortunately this provides no information about the stock of bromine in plastics and nothing about the POP-BDEBDE (PB Kennedy & Donkin Ltd 1999).

It appears that these predictions were not well founded – there is still very little, if any, commercial scale chemical recycling with bromine recovery in practice - and that the pre-2004 situation remains a more realistic assessment of the current situation. There has, however, probably been an increase in the mechanical recycling in plastic products after the export of articles containing POP-BDE. As there has been no response to the questionnaire from the Secretariat from those countries principally involved in these recycling operations (and especially China and the US) it has been particularly difficult to establish how much is being processed in practice.

Estimated Stocks of PentaBDE:

Given the major use of PentaBDE is in flexible foams typically in automotive and upholstery applications it is important to consider what stocks are likely to remain in products in use and where those that have been disposed of have gone.

In summary it is considered that the largest use of PentaBDE (90-95%) was the treatment of polyurethane foam and that aboutapproximately 90% of the market in the mid-1990s was in the USA with most of the rest being located in Europe. The US share increased to aboutapproximately 95% by 2000..

Balancing the evidence available in the literature indicates furniture being as the largest single user of PentaBDE in both Europe and the US with transport significantly smaller. An approximate distribution of known production is 36% in cars, 60% in furniture with a 4% residual in other articles. These percentages are considered to be reasonable and isare generally consistent with analytical data for different waste streams. A schematic diagram of the life cycle of PentaBDE and the potential for emissions is:

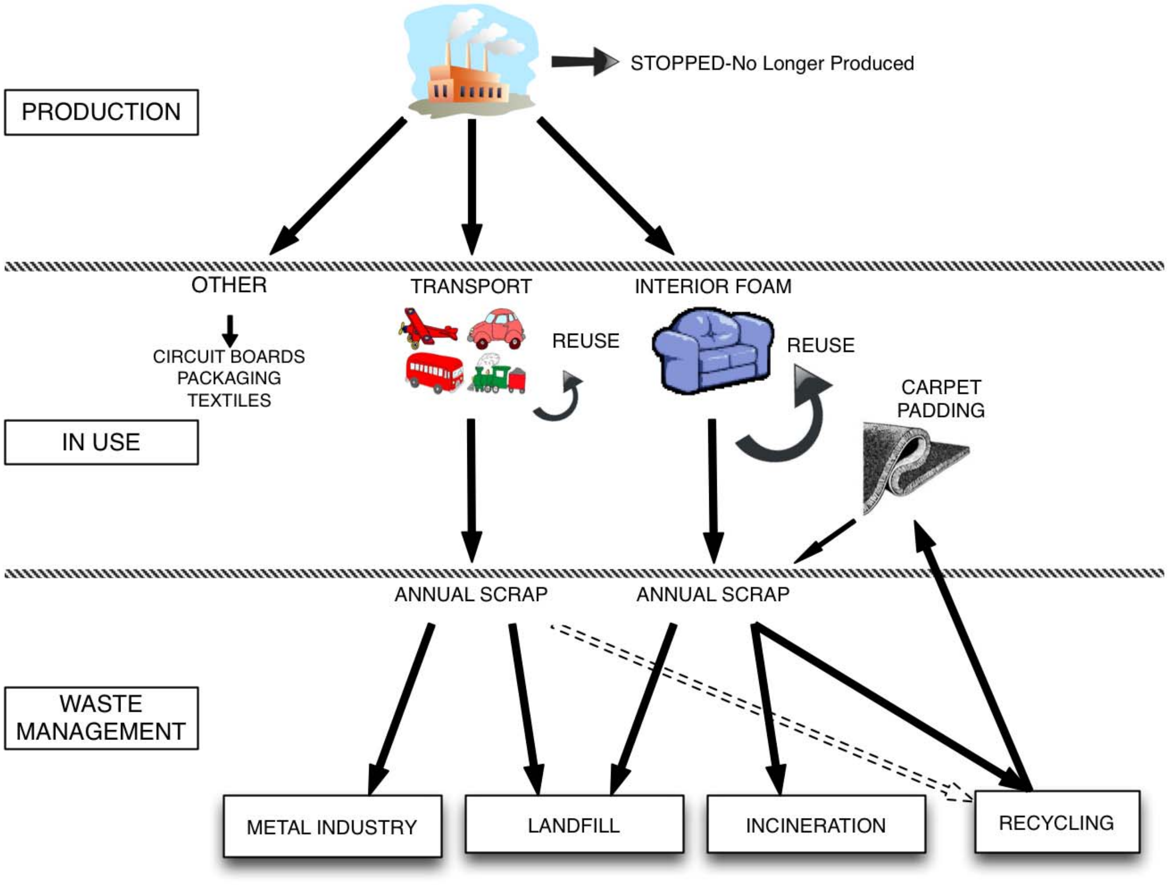

Figure 90: Schematic diagram of the life cycle of PentaBDE and the potential for emissions (emissions in the use period are discussed in the text but have been omitted from this schematic to improve clarity) (adapted from Alcock (Alcock et al. 2003)).

The only minor use 'other' uses are estimated to account for PentaBDE to be targeted is in 5% or less of the total usage. There is, however, significant uncertainty in relation to the use of PentaBDE in Printed Circuit (Printed Wire) Boards ('PWB') and this is therefore addressed in some detail by this review. PentaBDE was used as resin in some early boards but more recently China appears to have produced PentaBDE largely for use in PWBs. It is notable, for example, that triBDE to pentaBDE were the predominant homologs in Chinese electronic shredder waste from printed circuit boards and plastics remaining after the recovery of metals) as reported by Ma (Ma 2009). Although other levels reported (only in Europe) are much lower (Morf 2005, Schlummer 2007) some PentaBDE treated circuit boards have probably been exported to other countries including the US and Europe. Further information has been sought from the Chinese Environment Ministry about this but no reply had been received at the time of finalising this version of the report.

The schematic diagram shows that there are no longer emissions from production processes for PentaBDE as those have now stopped. There is some direct re-use and whilst data is difficult to obtain this is much more common with interior foam in furniture and mattresses than in transport application. Direct re-use can include sales of vehicles after the first user and the sometimes significant levels of export before end-of operational life. After end-of-life re-use is largely limited to replacement components from car scrap yards and is thus generally restricted to the particular model of car. The re-use of interior foams can be either through sales/donations of old furniture or from repair and refurbishment operations which are often run as charitable organisation.

Of the total production of c.100,000 tonnes of PentaBDE it appears that approximately 15,000 tonnes was used in Europe and the remainder in North America. The recycling of foam into rebond, as discussed earlier, has been the major recycling pathway. There appears to be little good data about the total quantity of waste foam containing PentaBDE which has been recycled into rebond – a crucial part of the jigsaw in relation to stocks in the US.

There has been some usage of PentaBDE in FR2 circuit boards as discussed in Appendix 2. Again there has been limited recycling in most countries. Goosey and Kellner noted in 2002 "*50,000 tonnes of PCB scrap is produced each year in the UK and of this only around 15% is currently subjected to any form of recycling. The remaining 85% is consigned to landfill. Currently, the only board waste being recycled is the proportion having an inherent value because of its precious metal content and this is limited to recovery of the metal content via smelting*." Some of the more esoteric recycled articles do, however, present a particular risk to users which was not envisaged in the first applications:

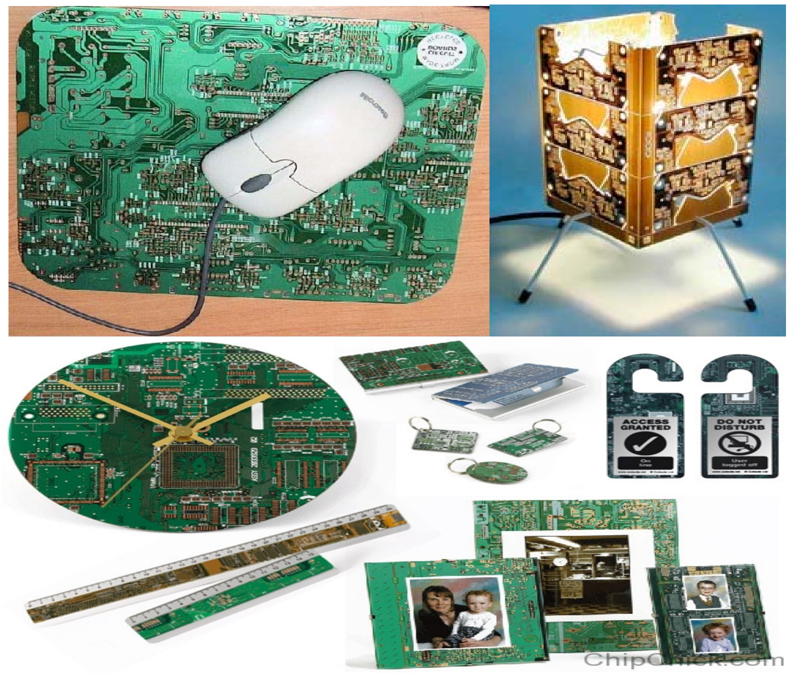

Figure 91: Recycled Circuit Board Mouse Mat (http://www.greenerstyle.co.uk/recycled-circuit-board-mouse-mat-p-324.html?zenid=64ab03ed89b2d6d492a59f88c0122533) Recycled Circuit Board lighting stand (http://www.electrickery.uk.com/html/lighting.html) Assorted recycled circuit board items (http://www.chipchick.com/2008/08/recycled_circuit_boards_become_picture_frames_and_mouse_pads.html)

The other key issue in the determination of the residual stocks is obviously the lifetime of the products in which PentaBDE was used. These have been examined in some detail by Morf et al. as part of the substance flow analyses for Switzerland (Morf et al. 2003, Morf et al. 2007):

Electrical and Electronic Equipment: Morf says that the total lifetime of office and consumer electronics consists of a service life of 5–6 years followed by an additional period averaging 3–4 years where the appliances are stored until they are disposed of. The implications of this additional storage are discussed below.

Consequently the lifetime in the use phase is currently approximately 9 years. In the mid 1990s, the mean lifetime was longer at 11 years and as this trend towards faster turnover is increasing Morf anticipates a decrease to 7 years in future.

Freezers, washing machines and larger household appliances have a longer lifetime of c.15 years or more but these are likely to be less relevant to the POP-BDE. Small household appliances like vacuum cleaners or coffee percolators have similar, or possibly even shorter, lifetimes than office and consumer electronics.

Transport: Eurostat (quoted by (Prevedouros et al. 2004a)) estimated the average age of passenger cars in the EU as 7.6 yr in 1999. Two sources cited by Morf showed that the service life of passenger cars to be 10 years[94] and to have remained constant over the past twenty-years. Marsh supports this lifetime (Marsh 2005). Spielmann, in another study indicated that the current average life was about 12 years (Spielmann & Althaus 2006). Morf also quotes Reinhardt and Richers in 2004 claiming the mean service life until disposal to be approximately 14 years, and it seems reasonable to assume a mean lifetime of c.12 years(Morf et al. 2007).

Vehicle lifetimes in the US appears to be slightly longer with a median lifetime of c.13 years (Davis SC et al. 2009) while Lagalante says 16.9 years (Lagalante et al. 2009a).

There have been and are certainly some exports of old cars from Europe as well as exports of commercial vehicles – particularly to East Europe, Caucasus, Africa and Middle East and from the US to Mexico, Middle- and South America. These are likely to be older cars with higher levels of PentaBDE and so those countries which have imported these older vehicles should be aware of the potential risks arising from the likely POP-BDE content.

Other vehicle types such as lorries, buses and planes are likely to have longer average service lives and are also more likely to be exported from the country of first use to less developed countries. Estimates by Morf, however, indicate that comparative volumes are such that the majority of PentaBDE-treated foam is likely to be moved in cars rather than commercial vehicles (Morf et al. 2003, Morf et al. 2007).

Furniture Foam: No estimates are made by Morf but the EU Risk assessments suggested a 10-yr average lifetime for furniture applications using foam (European Chemicals Bureau 2001).

Effects of Assumptions on Product Lifetime:

The effect of using product lifetimes of 5, 10, and 20 yr was analysed by Prevedouros (Prevedouros et al. 2004a) and is illustrated in the figure below. With longer lifetime values the projected year of maximum emission is delayed. Thus, doubling the lifetime to 20 yr produced a maximum emission in 1999, which is around 25% higher than with the default ten-year lifetime, whereas a 5-yr lifetime generated an emission peak at 1995 and a decrease in peak emission of c.40%. It can be seen that using the default assumption the model indicates that emission levels should now be approaching zero:

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[94] The references given were Leidner, 1981 and Hirai and Sakai, 2004. Unfortunately the citation for the Hirai paper was not included in the citation list and so it has not been possible to track this down to confirm the basis for this assumption.

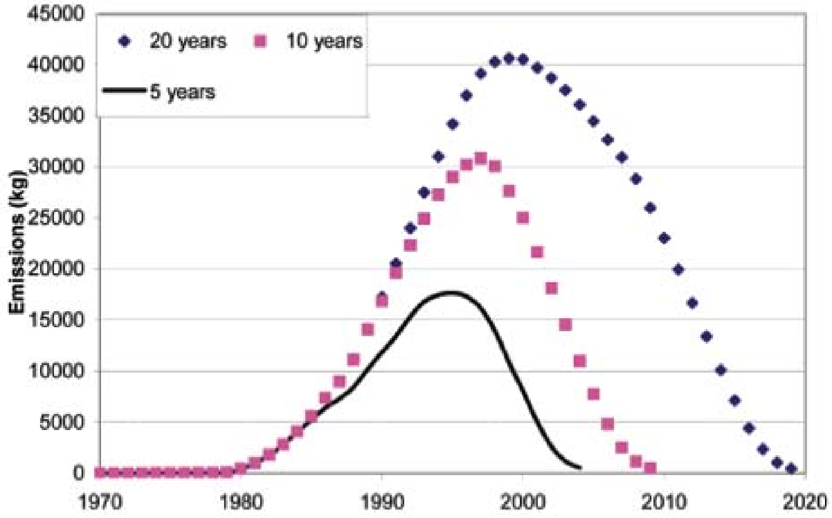


Figure 92: Illustration of the product lifetime effect on BDE-47 emissions (kg) with 5-, 10-, and 20-yr assumptions (Prevedouros et al. 2004a).
Note that the peak years for emissions are 1995, 1997, and 1999 for the 5-, 10-, and 20-yr lifetime assumptions. The recycling of PUF to rebond is not taken into account in these scenarios – such recycling will effectively extend the product lifetime and move the distribution to the right.

The conclusions reached by Morf (Morf et al. 2007) were similar with a strong decline in all stocks as products were disposed, incinerated and landfilled. The only remaining stocks are those in longer life construction applications (as discussed above). This is discussed above and may be a situation unique to Switzerland. With the exception of Germany there is no evidence that there may similar stocks in construction applications in other countries:

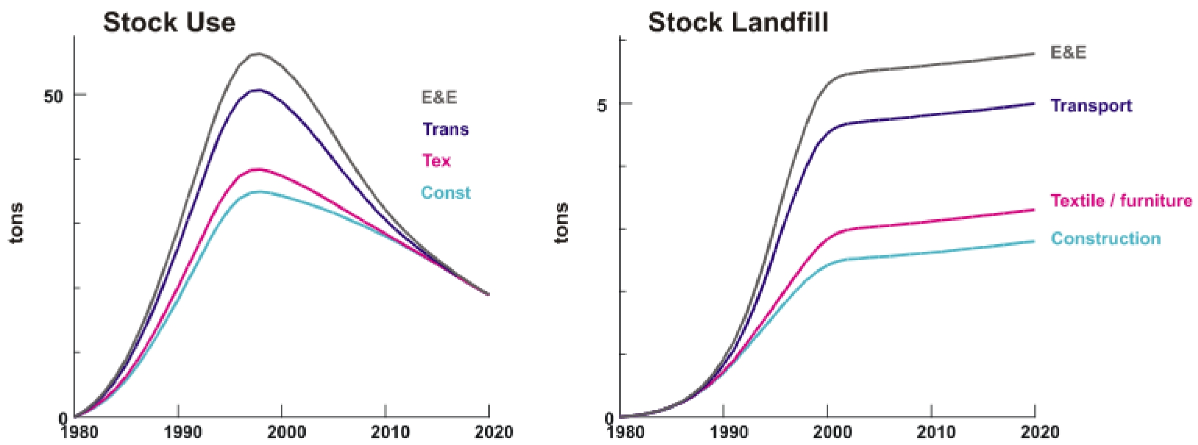


Figure 93: Trends of stocks of BDE-47 in the processes use and landfill (cumulative graphics) (Morf et al. 2007)

In conclusion, therefore the peak of the POP-BDE being delivered to waste in the EU would have been in the period 2005-7 and the balance depends upon the balance of usage between foam in cars and in furniture (about which there is conflicting evidence). The amount of Penta and Octa being included in waste since 2005 should have fallen with a profile similar to the reduction of their use a decade earlier.

Only minor residual POP-BDE should now be included in wastes being delivered for disposal. There will of course, be examples of older cars and furniture which are kept in use for much longer than the average life expectancy of these articles. Those articles may be exposing their users to particularly high levels of POP-BDE if, for example, the original protective covers are worn and exposing the foam – particularly in circumstance where young children are exposed. Children often play with foam cushions for example and are exposed to clouds of fine dusts which are likely to be rich in flame-retardants. It is, however, difficult to limit these exposures unless, for example, the original manufacturers, who are those parties best informed about the usage of particular flame retardants and which of their products contained POP-BDE, take steps to inform those users of their remaining products about the hazards associated with them.

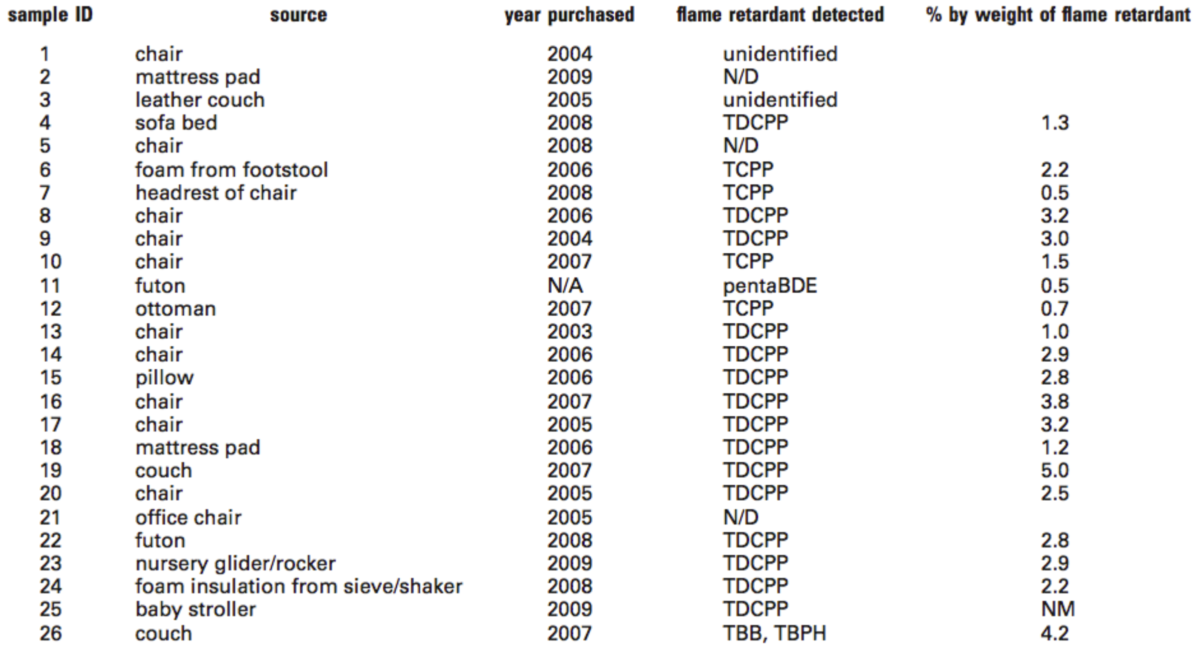
It appears likely, therefore, that in the case of Europe 80%-95% of the Penta BDE stocks have now been landfilled or incinerated leaving 750-3,000 tonnes that have been exported (mainly to the US for rebond) together with minor quantities that are left in long life uses such as rigid foam insulation, some mass transit systems and a decreasing number of elderly cars.

The US and North American situation is much more ambiguous.

There has been with much higher usage, a later effective phase out date, together with much greater levels of recycling of PentaBDE into homes and cars via carpet padding applications which tend to have longer service lives than the original uses. There will certainly have been some reduction through waste management, largely to landfill and export, but not as much as in Europe. In the Table 23 (above) showing the results of dust samples from cars the six highest levels of BDE-47 and BDE 99 were all in vehicles which were made in or after 2004. Furthermore the three highest levels were from cars manufactured in the USA (quite likely as a consequence of the use of rebond in cars).

There are reasons to be optimistic about the reduction of use of PentaBDE in furniture, however, following sampling by Heather Stapleton of a range of foam furniture to establish the flame retardants used as replacements for PentaBDE(Stapleton et al. 2009). She found TDCPP and TPP in >96% of dust samples – furthermore concentrations were similar to, and in some cases greater than, PBDE. This indicates that their use as replacements for PBDE may have been started several years before the sampling. Only one sample of foam from the 26 different pieces of furniture purchased between 2003 and 2009 contained PentaBDE (just 0.5%). This sample was collected from a futon (probably) purchased prior to 2004. This may have been re-used foam with contamination from a previous use as the loading was below the normal concentrations of 3-5% as discussed in Appendix 2. It can be seen that the loading of BFRs in all samples are less than 5%:

Table 64: Flame retardants used in polyurethane foam from furniture sampled by Stapleton in the United States (Stapleton et al. 2009).



sample ID	source	year purchased	flame retardant detected	% by weight of flame retardant
1	chair	2004	unidentified	
2	mattress pad	2009	N/D	
3	leather couch	2005	unidentified	
4	sofa bed	2008	TDCPP	1.3
5	chair	2008	N/D	
6	foam from footstool	2006	TCPP	2.2
7	headrest of chair	2008	TCPP	0.5
8	chair	2006	TDCPP	3.2
9	chair	2004	TDCPP	3.0
10	chair	2007	TCPP	1.5
11	futon	N/A	pentaBDE	0.5
12	ottoman	2007	TCPP	0.7
13	chair	2003	TDCPP	1.0
14	chair	2006	TDCPP	2.9
15	pillow	2006	TDCPP	2.8
16	chair	2007	TDCPP	3.8
17	chair	2005	TDCPP	3.2
18	mattress pad	2006	TDCPP	1.2
19	couch	2007	TDCPP	5.0
20	chair	2005	TDCPP	2.5
21	office chair	2005	N/D	
22	futon	2008	TDCPP	2.8
23	nursery glider/rocker	2009	TDCPP	2.9
24	foam insulation from sieve/shaker	2008	TDCPP	2.2
25	baby stroller	2009	TDCPP	NM
26	couch	2007	TBB, TBPH	4.2

N/A - Not available. N/D - Not detected. NM - not measured due to low mass of foam available. TDCPP - Tris-(1,3-dichloro-2-propyl)phosphate. TCPP - Tris(1-chloro-2-propyl)phosphate. PentaBDE - Pentabromodiphenyl ether commercial mixture. TBB - ethylhexyl 2,3,4,5-tetrabromobenzoate. TBPH - bis(2-ethylhexyl) tetrabromophthalate.

The residual stocks and their life depend very largely on the proportion of treated foam which has already been recycled as rebond. Demand has been consistently high (although it has reduced recently with the economic downturn) and publically available data on levels of recycling to date is very limited. USEPA were consulted about this but appeared to have no more information available at this stage to help narrow this major uncertainty.

The only data found on volumes of post-consumer foam used in rebond are from Zia (Zia et al. 2007). This indicates that in 2002 the rebond industry used 376,000 tonnes of scrap polyurethane foam and that of this approximately 23,000 tonnes came from post-consumer waste. There is no indication of how much of this post consumer waste contained PentaBDE but if it is assumed that this all contained PentaBDE at the maximum likely loading of c.5% this would represent a maximum 1,150 tonnes of PentaBDE being recycled.

The earlier discussion in Appendix 2 about the likely concentration of PentaBDE in PUR foam is an important one for both the recovery options and the consequences of recycling. Environ indicated that "*carpet padding likely contains 3-5% flame retardant similar to that for cushion FPUF*" (ENVIRON 2003b).

Estimated Stocks of OctaBDE:

Given the uncertainty associated with the minor uses of OctaBDE it can be assumed, for practical purposes, that the majority use of OctaBDE was used for casings for business machines, computers and monitors. The OctaBDE Risk Management Evaluation (Stockholm Convention 2008c) suggests that globally 70% of c-OctaBDE has been used in acrylonitrile butadiene styrene (ABS). Other minor uses include high impact polystyrene (HIPS), polybutylene terephthalate (PBT) and polyamide polymers :

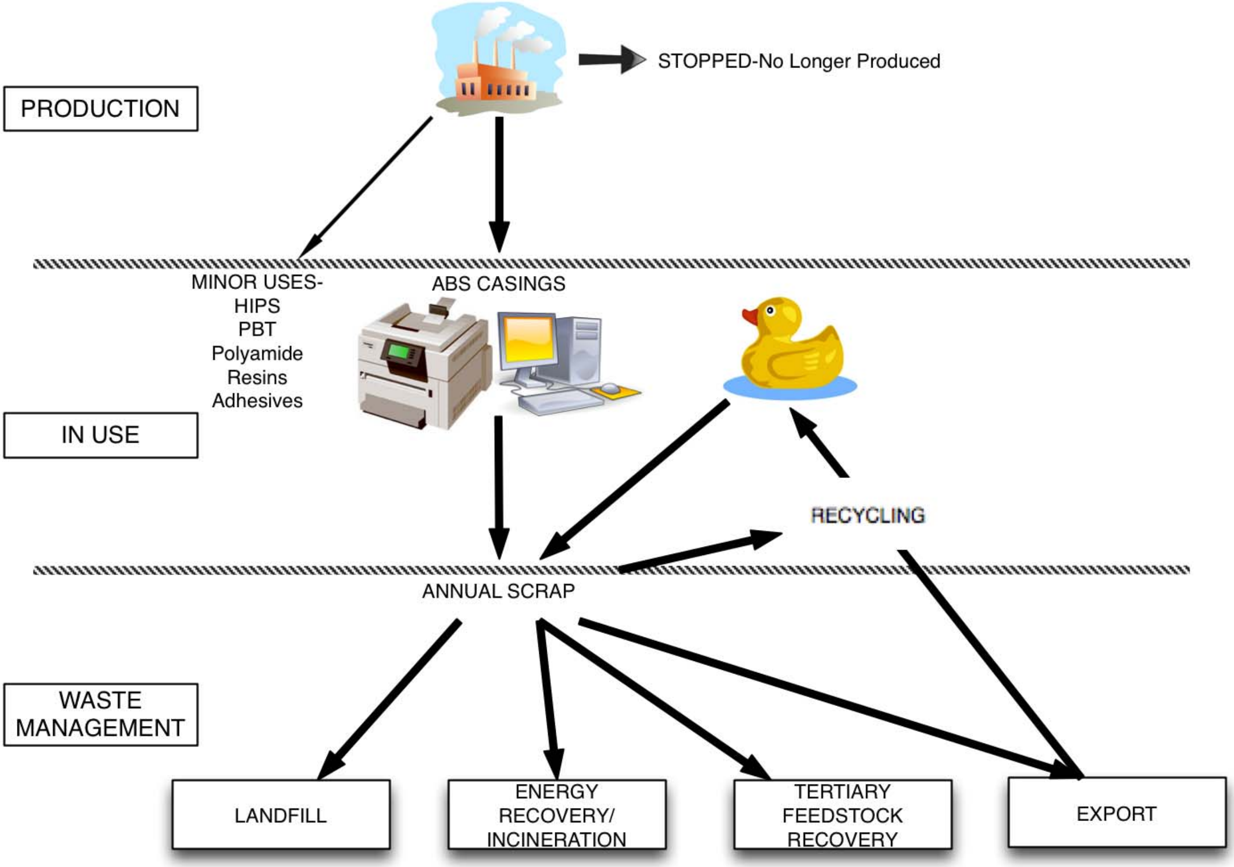


Figure 94: A schematic diagram of the life cycle of OctaBDE and the potential for emissions (emissions in the use period are discussed in the text but have been omitted from this schematic to improve clarity).

ABS is a relatively expensive polymer and is used for higher value items and for those where performance is more critical. The distribution of the usage, and stocks, should therefore be related to the penetration rates for computers for which data has recently been presented by Yu et al. (Yu et al. 2010b):

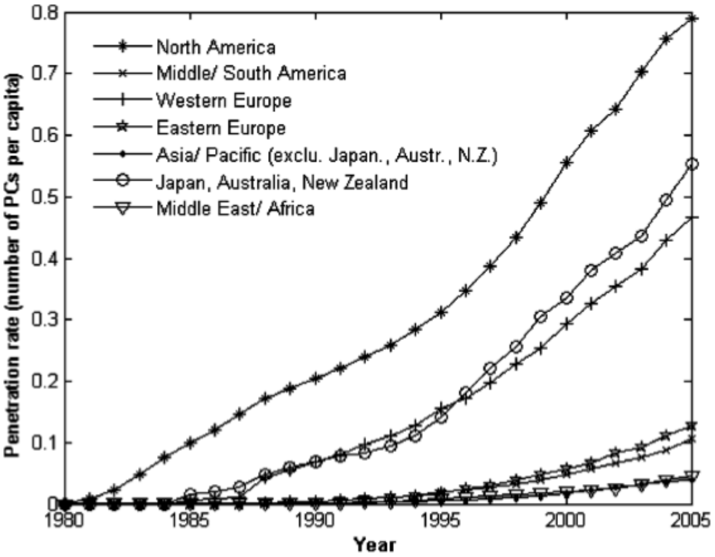


Figure 95: Historical computer penetration rate in different regions worldwide (Yu et al. 2010b)

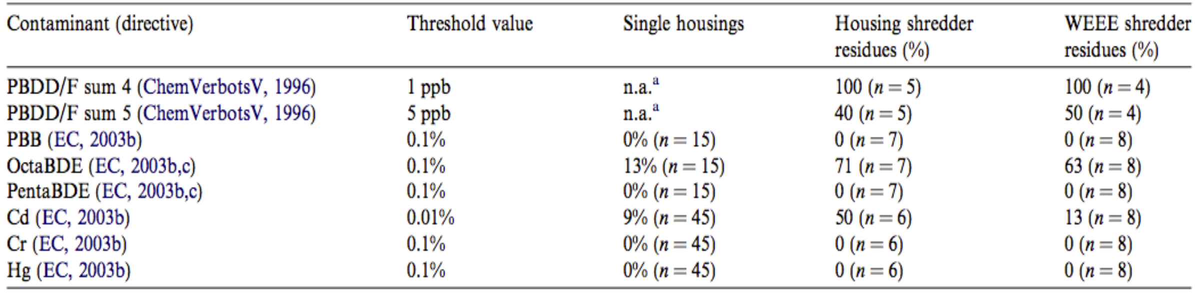
North America was well ahead of the rest of the world in the early uptake of computers and the usage of personal computers in the US grew rapidly over the period of usage of OctaBDE – although usage in computers will largely have been replaced by other BFRs and, increasingly, non-halogenated flame retardants over this period and this should have had a significant impact on current and remaining stocks. Importantly only Japan, Australia, New Zealand and Western Europe, where penetration grew at similar rates from the period 1985-2005, were major consumers over the period of highest use of OctaBDE from 1985-early 2000. Consequently it can be anticipated, consistently with the information known about production and use, that the major stocks of OctaBDE are likely to have been mainly in North America with much smaller stocks in Europe and Japan with relatively little usage of OctaBDE in the rest of the world.

The BSEF market demand data provided in Figure 9 (above) shows that in 2003 market demand for OctaBDE was split with just less than 40% each being used by America and Asia, about 16% in Europe and less than 5% in the rest of the world. It can reasonably be anticipated that most of the OctaBDE usage in Asia was exported to America and to Europe in computer and office equipment housings.

The situation with Octa BDE is likely to be similar for PentaBDE in relation to Europe with the majority of stocks now having reached the end of their useful lives. These wastes have been treated through the existing waste management infrastructure and, in the case of the ABS plastics, most have been consigned to landfill but with substantial exports for recovery in primitive recycling systems.

The fall in OctaBDE levels can be seen in results from 2007 when Schlummer detected PBDE in 40% of E-waste housing samples containing BFRs (Schlummer et al. 2007) – with higher levels in shredder residues, about 70% of which exceeded 0.1% of OctaBDE. Just two samples (out of 15) of housings exceeded 0.1% OctaBDE (and no samples exceeded 0.1% of PentaBDE). It is notable, however, that in spite of the relatively low levels of OctaBDE all samples exceeded the threshold levels of PBDD/DF for the German Dioxin Ordinance (for more details see Appendix 2 (g)):

Table 65: Percentage of samples exceeding German and European threshold values (based on the number of measurements given in brackets) (Schlummer et al. 2007).

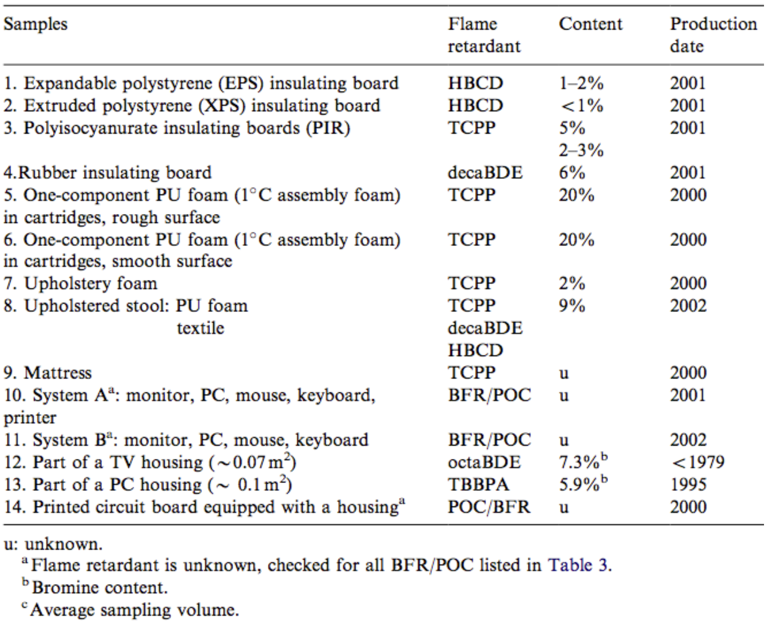


Contaminant (directive)	Threshold value	Single housings	Housing shredder residues (%)	WEEE shredder residues (%)
PBDD/F sum 4 (ChemVerbotsV, 1996)	1 ppb	n.a.[a]	100 ($n = 5$)	100 ($n = 4$)
PBDD/F sum 5 (ChemVerbotsV, 1996)	5 ppb	n.a.[a]	40 ($n = 5$)	50 ($n = 4$)
PBB (EC, 2003b)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
OctaBDE (EC, 2003b,c)	0.1%	13% ($n = 15$)	71 ($n = 7$)	63 ($n = 8$)
PentaBDE (EC, 2003b,c)	0.1%	0% ($n = 15$)	0 ($n = 7$)	0 ($n = 8$)
Cd (EC, 2003b)	0.01%	9% ($n = 45$)	50 ($n = 6$)	13 ($n = 8$)
Cr (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)
Hg (EC, 2003b)	0.1%	0% ($n = 45$)	0 ($n = 6$)	0 ($n = 8$)

By comparison Riess et al. (Riess et al. 2000) had reported PBDE in 78% of all BFR-containing housing samples in 2000 indicating a decline of total PBDE use and prevalence since the year 2000. These samples of 78% falling to 40% both include all PBDE including DecaBDE. Had only the OctaBDE in the polymers been taken into account then the fall would most likely have been steeper

It is notable that when Kemmlein sampled a range of consumer products containing PU foam in Germany in 2003 no PentaBDE was found – and OctaBDE was only present in a very old television casing (Kemmlein et al. 2003b):

Table 66: German Product Samples(Kemmlein et al. 2003b)



Samples	Flame retardant	Content	Production date
1. Expandable polystyrene (EPS) insulating board	HBCD	1–2%	2001
2. Extruded polystyrene (XPS) insulating board	HBCD	<1%	2001
3. Polyisocyanurate insulating boards (PIR)	TCPP	5% 2–3%	2001
4.Rubber insulating board	decaBDE	6%	2001
5. One-component PU foam (1°C assembly foam) in cartridges, rough surface	TCPP	20%	2000
6. One-component PU foam (1°C assembly foam) in cartridges, smooth surface	TCPP	20%	2000
7. Upholstery foam	TCPP	2%	2000
8. Upholstered stool: PU foam textile	TCPP decaBDE HBCD	9%	2002
9. Mattress	TCPP	u	2000
10. System A[a]: monitor, PC, mouse, keyboard, printer	BFR/POC	u	2001
11. System B[a]: monitor, PC, mouse, keyboard	BFR/POC	u	2002
12. Part of a TV housing (~0.07 m^2)	octaBDE	7.3%[b]	<1979
13. Part of a PC housing (~ 0.1 m^2)	TBBPA	5.9%[b]	1995
14. Printed circuit board equipped with a housing[a]	POC/BFR	u	2000

u: unknown.

[a] Flame retardant is unknown, checked for all BFR/POC listed in Table 3.

[b] Bromine content.

[c] Average sampling volume.

The information on actual usage of the POP-BDE in the US is very limited. Even in California, the State with the highest usage of the POP-BDE, the Department of Toxic Substances Control complains that the "*scant information on amounts of PBDE used in California, and the ensuing need to use assumptions, are a major limitation*" on the preparation of an accurate substance flow analysis (Petreas & Oros 2009). The consequences were that it was not possible for them to estimate the standing stock of PBDE-containing products (home and auto furnishings, electronics, etc.) that are in use at present and which will become wastes in the near future. They were also unable to estimate the PBDE in imported products compared with exported products and wastes.

The usage in the United States does appear to have reduced very significantly after 2003. This has not, however, necessarily translated at this point into throughput of all the POP-BDE-contaminated articles to waste management streams as might be expected from the limited life expectancy of the electronic items in which OctaBDE was most used. Americans own nearly 3 billion electronic products according to USEPA (USEPA 2008f). USEPA estimate that of those which reached the end of their life in 2003-5 nearly half are put into storage or re-use (see figure below). In 2005 alone, approximately 460 million units were put into storage and/or reuse:

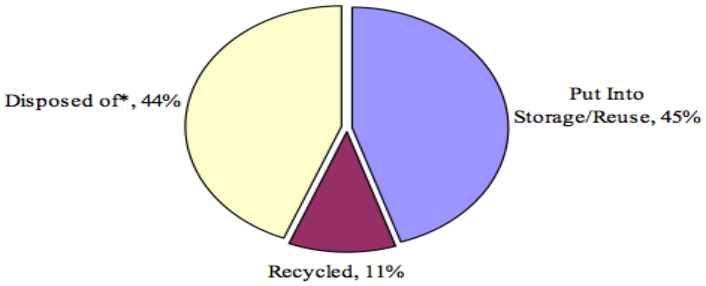
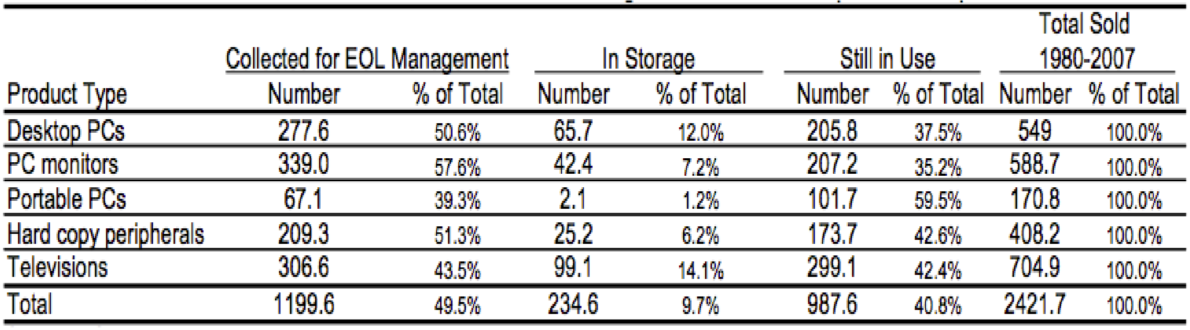


Figure 96: Electronic Products Recycled, Disposed, or Going into Storage/Reuse 2003 - 2005 (% by weight)(USEPA 2008f)

Of those which are disposed the majority (at least 81%)[95] are landfilled and of those recycled (at least for TVs and monitors)[96] more than 75% are exported (USEPA 2008f).

A 2009 review by Saphores et al. (Saphores et al. 2009) examined the number of small and large e-waste items stored by US households. The model suggests that each US household has, on average, 4.1 small and 2.4 large e-waste items in storage. The authors comment that these numbers are almost certainly under-estimates of the true e-waste count. This is because it is time consuming for a household to precisely inventory every obsolete e-waste item and secondly the surveyors relied on a narrow definition of e-waste that excluded large appliances such as refrigerators and washing machines. This does, however, mean that the results are probably more relvant to e-waste items potentially containing POP-BDE. Extrapolating the results to the whole of the United States indicates that there are more than 747 million items including at least 470 million small and 277 million large e-waste items stored by US households. This is considerably more than the EPA estimate of 180.3 million items in storage by 2005 (USEPA 2007, USEPA 2008a), although their estimate is based on a smaller range of products (printers, desktop and laptop computers, monitors, peripherals, as well as televisions). The EPA estimates of articles in storage has risen to 235 million by 2007[97]. By weight[98] Desktop PCs account for c. 24% of stored e-waste and TVs 34-52% (USEPA 2008f):

Table 67: Estimated Number of Units in Various Stages of Use as of 2007 (million units) (USEPA 2007, USEPA 2008a)



	Collected for EOL Management		In Storage		Still in Use		Total Sold 1980-2007	
Product Type	Number	% of Total	Number	% of Total	Number	% of Total	Number	% of Total
Desktop PCs	277.6	50.6%	65.7	12.0%	205.8	37.5%	549	100.0%
PC monitors	339.0	57.6%	42.4	7.2%	207.2	35.2%	588.7	100.0%
Portable PCs	67.1	39.3%	2.1	1.2%	101.7	59.5%	170.8	100.0%
Hard copy peripherals	209.3	51.3%	25.2	6.2%	173.7	42.6%	408.2	100.0%
Televisions	306.6	43.5%	99.1	14.1%	299.1	42.4%	704.9	100.0%
Total	1199.6	49.5%	234.6	9.7%	987.6	40.8%	2421.7	100.0%

In essence therefore, the USEPA estimates as of 2007 were that electronic products manufactured over the period from 1980-2007 could be divided into three categories reflecting the stages of their lifecycle:

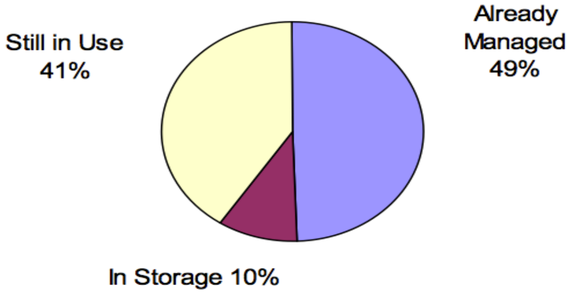


Figure 97: Stages of Life Cycle: Electronic Products 2007 (USEPA 2007, USEPA 2008a)

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[95] According to EPA data, about 19 percent of all MSW discards goes to waste-to-energy processes. Within that 19 percent, however, it is possible that computer monitors or televisions with CRTs are not being combusted, but rather are being removed on the tipping floor and sent to landfills (unless there is a ban on CRT disposal in landfills). Waste-to-energy operators would be inclined to remove these items because the glass is not combustible and because of concerns about the resulting lead in the ash from the CRT glass. Non-CRT computer equipment may not be removed because it contains plastic, which is combustible (USEPA 2008a).

[96] The EPA reports had difficulties establishing total levels of exports but provided some data for TVs and CRT monitors figures showing 2% exports for resale; 61% exports for refurbishing/remanufacturing; 14% to glass factories abroad 12% was plastics and metals some markets for which are abroad. The report comments that industry experts interviewed for project said that about 30% of material destined for remanufacturing abroad is not technically suitable for remanufacturing and has to be recycled or disposed. The recycling or disposal of unsuitable units occurs abroad (USEPA 2008a).

[97] http://www.epa.gov/epawaste/conserve/materials/ecycling/manage.htm

[98] Note these percentages differ from the table which is by number rather than weight.

The Saphores study suggests that ‘in storage’ backlog of e-waste in the US may be much larger than the 10% assessed by USEPA (Saphores et al. 2009). UNEP goes further and says (without citation) that in the USA some “*researchers estimate that three-quarters of all computers ever sold in the USA remain stockpiled, awaiting re-use, recycling or disposal*” (UNEP et al. 2005). Whilst the quantity in storage is certainly large it seems unlikely to be as large as suggested by UNEP based on the more detailed studies by Saphores and USEPA.

When the limited results from Petreas (Petreas & Oros 2009) are combined with the US inventory some indication of the likely stocks can be obtained:

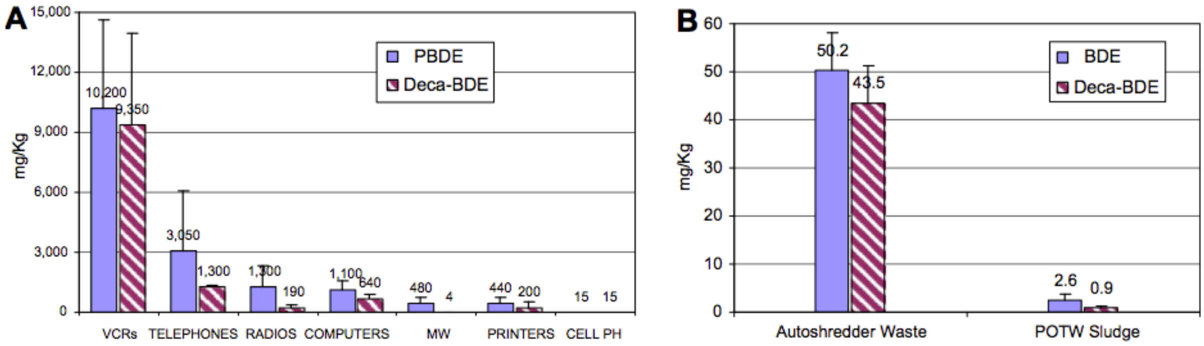

Figure 98: Concentrations of PBDE and BDE-209 in e-waste (A) and autoshredder waste and POTW sludge (B) (Petreas & Oros 2009)

Unfortunately, however, Petreas did not distinguish between the POP-BDE but she showed that computers, on average, contained 460 mg/kg of POP-BDE, telephones 1,750 mg/kg, VCRs 850 mg/kg and printers 220 mg/kg.

If an average concentration of say 750 mg/kg for total POP-BDE is applied to the e-waste production in the USA over the period from 1975 to 2004 (which equates to approximately 46,335,000 tonnes) then these electronic articles would have contained a total of 34,750 tonnes of (mainly) OctaBDE representing approximately one third of the total usage assessed in Appendix 2 of this report. Using the USEPA estimates on life cycle stages then a first approximation would indicate that approximately 50% (c. 17,000 tonnes) of this has already been managed in waste of which c.13,600 tonnes has either been landfilled or exported. Approximately 3,475 tonnes is in homes awaiting disposal and 14,250 tonnes was in articles in use in 2007.

It is clearly necessary to deal with the backlog of accumulated e-waste by ensuring that POP-BDE are captured and safely managed so far as possible. Saphores therefore recommends developing the recycling infrastructure, publicising information about how to recycle e-waste, and organizing staggered recycling campaigns for selected types of e-waste products (such as printers, for example) to avoid recycling overloads (Saphores et al. 2009).

One major transition which is likely to have a significant impact on the generation of obsolete TVs in many countries is the switch from analogue to digital broadcasting[99]. Although TVs are not a major user of OctaBDE there will certainly be some POP-BDE in the obsolete televisions and steps could be taken to ensure this is handled appropriately:

- In the United States, high-power over-the-air broadcasts are solely in digital format since 11th June 2009.
- In Japan, the switch to digital is scheduled to happen on the 24th July 2011.
- In Canada, it is scheduled to happen on 31st August 2011.
- China is scheduled to switch in 2015.
- In the United Kingdom, the digital switchover has different times for each part of the country; however, the whole of the UK will be digital by 2012.

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[99] Dates for switches are from http://en.wikipedia.org/wiki/Digital_television

- Brazil switched to digital on 2nd December 2007 in major cities and it is estimated it will take seven years for completion of the process to cover all the Brazilian territory.
- In Poland the switching to digital started in September 2009 and should be completed by July 2013.
- Croatia will cease all analogue transmissions in October 2010.
- In Australia, analogue television is gradually been phased out region by region. It started with on the 30th June, 2010 and will be completely phased out in all cities and towns by 31st December 2013.

The most recent information produced for the US comes from the USEPA exposure assessment for PBDE published in May 2010 (USEPA 2010). The assessment included some modelling of mass flows of PBDE and the outcome was an annual balance:

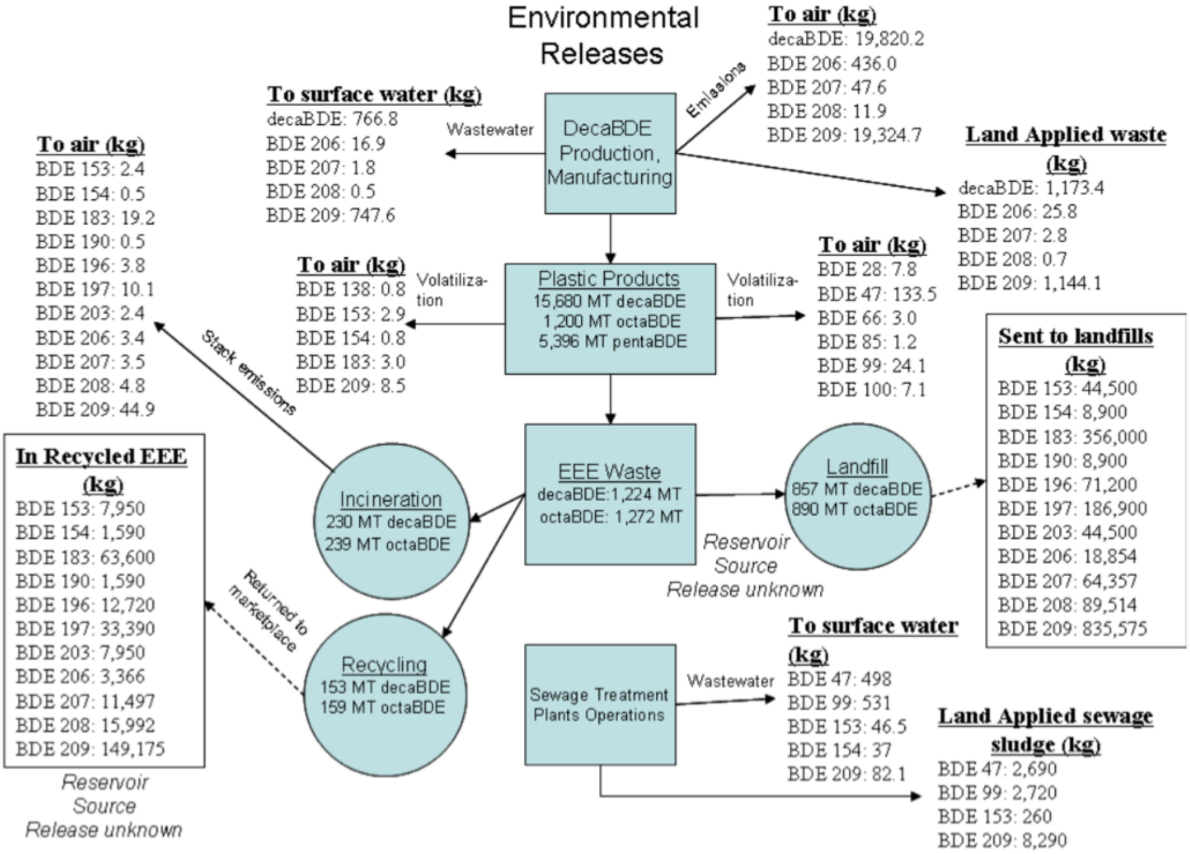

Figure 99: Summary of a generalized annual life cycle of PBDE in the United States: production, use, disposal, recycling, and sewage treatment (USEPA 2010).

The mass flow is based on 2005 but does not clarify why >1,000 tonnes of OctaBDE is still in new products when Penta and OctaBDE formulations were voluntarily withdrawn from the U.S. marketplace by their manufacturers at the end of 2004. It is also based largely on European data because, the text says "*U.S. EEE waste has yet to be adequately characterized for PBDE content*".

Whilst PentaBDE is not specifically listed on the mass flows there are some data on some components – but not enough to draw any conclusions about mass flow (and none for the main congeners in recycling, for example).

For OctaBDE, however, they show that of the 1,200 tonnes in products 890 tonnes are landfilled; 239 tonnes incinerated and 159 tonnes are recycled. This totals 1,288 tonnes and it is not clear whether the intention is to include some debromination from DecaBDE or whether it is an error in the model.

Assuming that the balance is approximately correct then it would mean that 69% has been landfilled; 19% incinerated and 12.3% recycled.

Future Developments

It is a chastening thought that the problems identified earlier in this report relating to contamination of the environment and damage to human health through the inappropriate recycling of e-waste have already become so severe. Given the relatively long period to obsolescence of computers the majority of those used and disposed of to date have come from the US with Europe following closely behind. More recently sales of personal computers in Asia have increased extremely rapidly – from less than 20 million units in 2000 to more than 65 million units in 2008. There was a doubling of sales between 2005 and 2007 (Yu et al. 2010b):

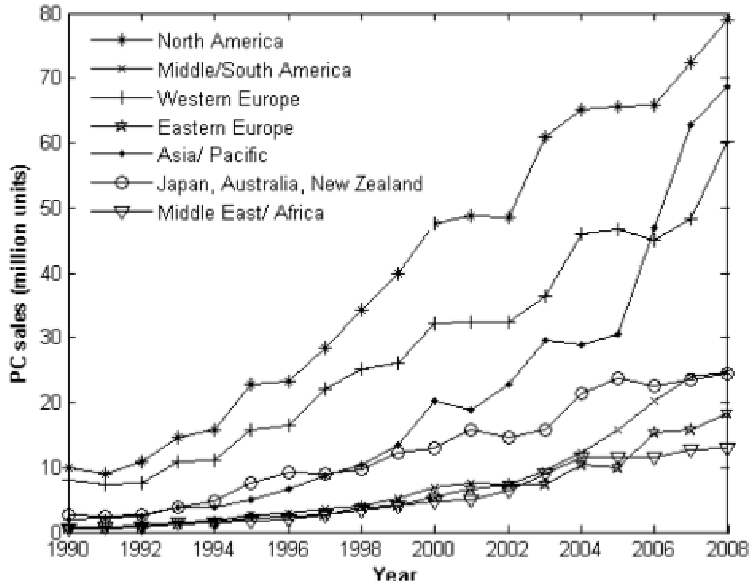

Figure 100: Historical PC sales in different regions worldwide (Yu et al. 2010b)

Very little is known about the chemicals used in the production of these computers. It is not known whether PentaBDE has been used in circuit boards or OctaBDE has been used in the casings, for example. The graph below shows that by about 2017 the number of waste computers from developing/transition countries are expected to exceed those from developed countries. The implications in terms of the potential for widespread pollution and harm are alarming given the limited capacity to safely manage e-waste in most Asian countries.

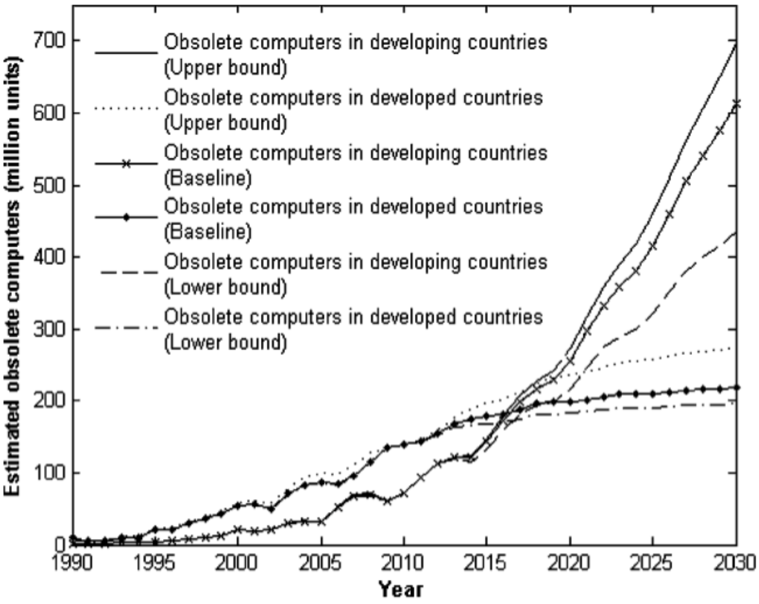

Figure 101: Forecasting of generation of obsolete computers in developed and developing/transition world (Yu et al. 2010b)

Appendix 5 (b): Information on the potential trade volume of recycled articles containing PBDE, including from developed to developing countries;

There is no doubt that global trade in products (re-cycled or new) and wastes can and has resulted in rapid and wholesale movement of PBDE (Hale et al. 2006). Historically, for example, it is estimated that more than 70% of the PentaBDE imported into Europe was incorporated as a flame retardant in finished goods as discussed in Appendix 2 (Risk & Policy Analysts Limited 2000).

The current trend is now strongly in the opposite direction with exports from Europe, Japan, Canada, Australia and the USA particularly to China, India, Africa and Southeast Asia.

The large scale export of wastes likely to be contaminated by POP-BDE make calculations remaining stocks and in ultimate sinks such as landfill sites even more problematic.

E-waste is now being transported in massive quantities around the world and particularly to developing countries. UNEP estimates that approximately 80% of computer E-waste is being exported to Asia and that in the early years of this decade 90% of these exports have been sent to China. The UNEP Bulletin recognises that sometimes "*illegal export is phrased as or hidden under the umbrella of charity ("computers for the poor") or as recycling*" (UNEP et al. 2005).

Figure 102:E-waste exports to China and India (UNEP et al. 2005) (original sources: The World Bank, World Development Indicators 2004, The Electronic Waste Guide, Basel Action Network, Silicon Valley Toxic Coalition, Toxic Link India, SCOPE (Pakistan), Greenpeace China, 2002)

China has made significant investments in domestic electronics recycling systems however despite official bans on importation of e-waste since recent publications by specialists in China indicate that the trade continues much as before (Yu et al. 2010b). The formal systems are small (with only 16,000 employees vs 690,000 in the informal sector in 2007) have failed to collect sufficient equipment because the informal sector offers superior economic incentives to those disposing of products (Yu et al. 2010a). The e-waste trade has expanded from China to include other countries in South East Asia, India and Africa.

Recently the German UBA and German Federal Ministry for Environment, Nature Conservation and Nuclear Safety (BMU) published a report confirming that more than 155,000 tonnes of what is "*sometimes hazardous electronic waste*" are exported annually from Germany to non-European destinations. These exports includes c. 50,000 tonnes of PC and television monitors.

The press release[100] says these "*often contain metals as well as flame-retardant bromide compounds such as hazardous polybrominated diphenyl ether (PentaBDE) (sic)*[101]. *Even defective appliances are often re-classified as "functional", then usually shipped to Asia and Africa where they are only rarely recycled ecologically*".

A similar quantity of exports, 160,000 tpa from the UK was estimated in a report for the Environment Agency (ICER 2004).

Even higher proportions of wastes appear to be exported from the US. Schut wrote that "*because of the FR issue*" plastics from e-waste have found applications mainly in China (Schut 2007). While there is no hard data available he adds that "*probably 99% of U.S. e-plastic is now baled and shipped to China to be recycled there because separation is so labor-intensive*"(Schut 2007).

The extent and geographical spread of the export trade makes it extremely difficult to track. The UK Environment Agency report said, for example:

"The following quote from a USA-based broker is interesting:

> *"We export to every major country in the world. We regularly ship to Pakistan, India, Sri Lanka, Egypt, Iran, Bangladesh, Azerbaijan, Vietnam, Jordan, Iraq, Saudi Arabia, Kuwait, Syria, Germany, Spain, France, Bulgaria, Italy, Belgium, Italy, Russia, Portugal, Romania, Ukraine, Poland, Canada, Hong Kong, Bolivia, Venezuela, Colombia, Peru, Chile, Nigeria, and Ghana. We currently export over 10,000 computers and monitors each month."(ICER 2004)"*

The geographical range of exports is one problem. Another is that many of the exports are unofficial – in this case the authors commented:
"Given the destinations and the fact that the company buys 'untested', these are clearly grey market exports" (ICER 2004).

Yu (Yu et al. 2010b) helpfully highlights the primary drivers of international trade in end-of-life electronics. One driver is the reuse market. Demand for computers is high worldwide but many in the developing/transition world are still unable to afford new equipment. This demand combined with low labour cost for refurbishing lead to a large electronics reuse market in developing countries.

For electrical and electronic goods the question of when end-of-(first)-life arises is not a straightforward one. Modern computers in developed countries tend to be used for an average of approximately four years as discussed above and this is much shorter than the potential operating or useful life. Operating computers and office equipment are therefore often re-used by others after the first user has finished with them – sometimes after minor repair and cleaning. At this stage it may be argued that the articles are not wastes in any case and so there are no restrictions on equipment, even if it contains POP-BDE being re-used in this way. Some are also exported at this point – sometimes as aid but often with some value for re-use or recovery.

Different countries take different positions on the importation of used electrical and electronic articles and examples include (Yu et al. 2010b):

- Thailand requires that the imported used electronics should not be more than three years old.
- The Philippines requires prior notification and consent before used electronics enter the country.
- Indonesia has banned the import of used TVs, radios, and other second-hand equipment.
- India is relatively liberal, and allows used computers up to 10 years old to enter the country as donations.

Some other countries such including Peru allow imports of e-waste. It is notable that Kahhat showed that at least 87-88% of imported end-of-life computers were bought for a price higher than the calculated recovery values and thus, he confidently stated, went to reuse as opposed to recycling in Peru (Kahhat & Williams 2009).

The second driver for exports is material recycling. A used desktop PC for example contains materials worth U.S.$16-18 (Kahhat & Williams 2009). Low wages, high demand for raw materials, and poor environmental controls in the developing world result in recycling running a net profit. High wages and low demand for used

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[100] http://www.umweltbundesamt.de/uba-info-presse-e/2010/pe10-012_export_of_waste_electrical_and_electronic_equipment_weee_plenty_of_gold_and_poison_too.htm

[101] The UBA press release included the eror in the acronym – "*polybrominated diphenyl ether (PentaBDE)". Clearly it should have been PBDE or the description should have been "pentabrominated diphenyl ether".*

electronics in developed countries imply that electronics collection and recycling runs a net cost estimated at U.S.$5-40 per computer (Kahhat et al. 2008c). Electronics collection recycling policies in the developed world therefore require a financing mechanisms such as recycling fees paid by consumers or by making manufacturers financially responsible (Kahhat et al. 2008c). There is a thus financial motivation for collectors in developed countries to export to the developing world.

Having found significantly higher chromosome aberration rates in e-waste workers in China Liu et al (Liu et al. 2008) recommended "*it is urgent for the government to prohibit the E-waste import and its processing in outdated ways*". They called for urgent further research and warned that "*the pollutants not only damage the individual genetic material or interfere with the expression of genetic material to induce cancer but may also be vertically transmitted through reproductive cells to cause infertility, spontaneous abortion, teratogenic effects, barriers to growth and development, or other problems*". Concluding "*all the data available*" provide a "*compelling case for immediate action in both countries to address workplace health and safety and waste management. In order to best protect public health and the environment, state policy makers must be willing to fundamentally redesign our approach to E-waste management*" (Liu et al. 2008).

Circuit Boards

Kahhat (Kahhat & Williams 2009) found that some circuit boards are exported to European smelters from Peru which shows that this route is apparently competitive with informal recycling. He suggested that further research is needed to understand this flow and to understand why in China and India informal (and highly polluting) recycling of circuit boards is prevalent (Kahhat & Williams 2009).

Plastics Trade

Most of the demand for waste plastics now comes from emerging economies in Asia – and particularly China where lower labour and energy costs provide a competitive advantage to reprocessors and manufacturers. There is also an enormous demand for competitively priced raw materials.

The main trading blocks for plastics waste exports and the markets are:

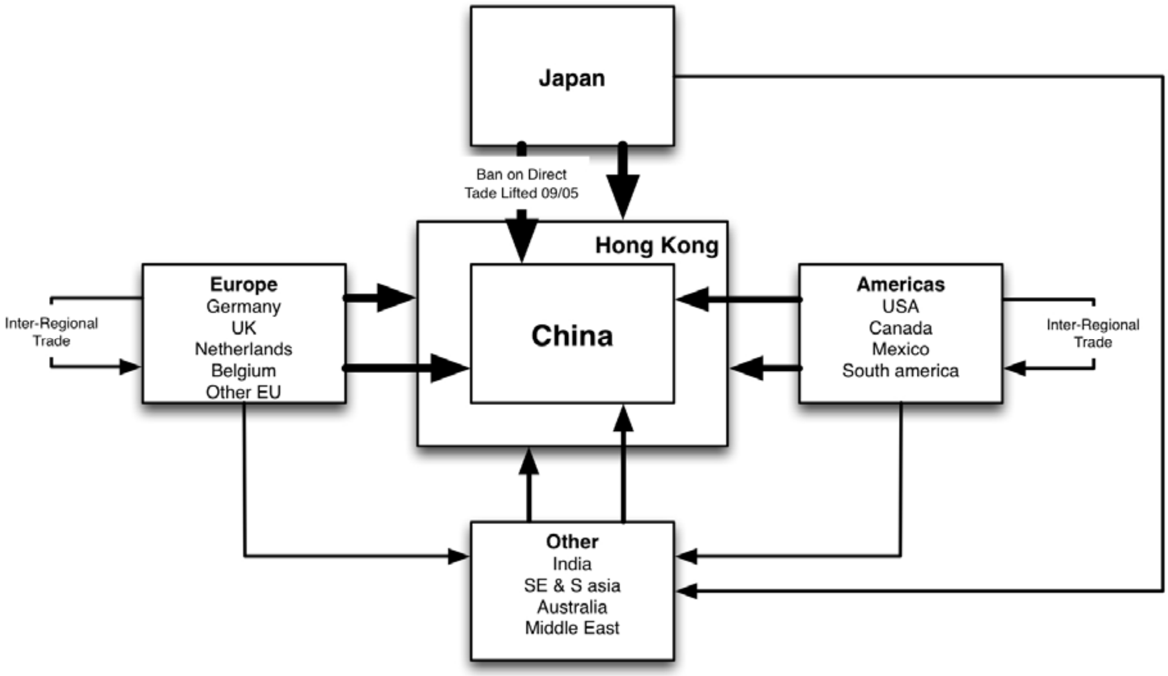

Figure 103: The global trade in recovered plastics (adapted from WRAP (WRAP 2006a))

Over 70% of globally traded recovered plastics are used by China with most trade passing through Hong Kong (which is a special administrative region of the People's Republic of China. It has a high degree of autonomy and the attraction of less stringent customs regulations and faster clearance than mainland China (WRAP

2009)). The trade in waste plastics encompasses a range of different polymers, applications and material qualities – from post-production scrap and unused inventory, through processed and semi-finished secondary plastics to unprocessed post-consumer material. The proportion of trade from each major partner is:

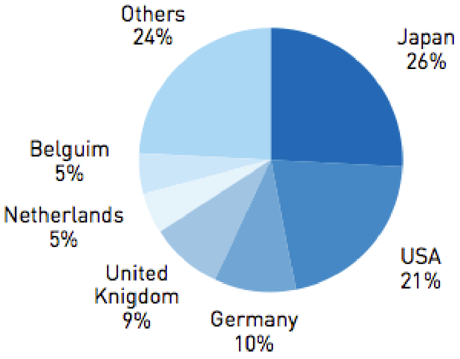

Figure 104: World exports of recovered plastics to China including Hong Kong - UNComtrade (WRAP 2009)

The trade in recovered plastics is facilitated by the comparatively low cost of container freight to China, a consequence of the imbalance of trade on the routes between China and its major markets in Europe, North America and Japan. Freight costs to other potential markets, such as India with lower levels of trade and smaller trade imbalance can be several times higher.

Low labour costs in South East Asia enable mixed plastics waste to be sorted at very low cost prior to reprocessing. Some of these mixed or lower grade plastics (including post consumer packaging and plastics from shredder waste) would not normally be recycled in Europe. The authors emphasised that it "*is imperative that these mixed plastics are sufficiently pretreated to make their export … legal*". This is clearly an important consideration – but one that is often not met – notably in relation to BFR-contaminated plastics where it is unlikely that the receiving countries will have adequate facilities to properly treat PBDE wastes (WRAP 2006a). There is little information about how effectively mixed plastics are sorted on arrival in China – or whether they are simply used for making recycled plastics with low quality specifications.

The supply chain in China, claims Berman (Berman & Swani 2010) is characterised by "*cost pressures and quality fade, multiple levels of outsourcing often involving small producers, a large number of counterfeit goods, Chinese cleverness at evading detection, and poor product safety surveillance by both the Chinese and U.S. governments*". Examples given in the paper in support of these claims include a study of products recalled by the Consumer Product Safety Commission[102] in 2007 which found that imports from China were recalled twice as often as products made elsewhere (Berman & Swani 2010). Another report states that every one of the 24 toys recalled in the first 6 months of 2007 was made in China (Lipton & Barboza 2007). Chinese goods now account for 60% of product recalls in the U.S. (Lipton & Barboza 2007). There are also indications (based, for example, on the matching antimony levels) that leaded electronic solders from e-waste and lead battery wastes in China are being used to manufacture cheap jewelry for children (Weidenhamer & Clement 2007a)(Weidenhamer & Clement 2007b).

These failings cannot be attributed to low legal standards in China. In the case of lead, for example, Chinese regulations are more strict than those set in the United States but there is still an enormous problem arising from the use of cheaper, brighter lead paints in Chinese toys. Weidenhamer says there were 79 individual recalls of toys and other products for lead paint contamination in the US alone in 2007 (Weidenhamer 2009). These recalls affected almost 14.5 million items with an additional 48 product recalls affecting more than 4 million items through to October 2008. All of the affected products were imported, with 113 of the 127 recalls being for products coming from China (Weidenhamer 2009).

The problem is rather the enforcement of existing laws (Barboza 2007). The New York Times quotes Chen Tao, sales manager at the Chenghai Guangxin Plastic Toys Factory as saying that regulators were essentially absent at this plant. He added "*There is a national standard on the lead level in toys. But no one really enforces it. Factories can pick whatever paint they want*". Lead is relatively easy to analyse, there are established standards and the import market is watched fairly carefully. The POP-BDE are much more difficult to analyse, there are

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[102] http://www.cpsc.gov/

few standards in any articles and levels in toys are almost completely unregulated. The specifications for plastics are generally low and the market is very competitive. In these circumstances there was always a strong suspicion that POP-BDE-contaminated plastics were likely to used for toys. This has been confirmed by the findings of Chen (Chen et al. 2009b).

Given the particular analytical difficulties and the lack of capacity (and motivation) for analysis in developing countries treating recyclate it is unlikely that POP-BDE have ever been controlled particularly effectively in recyclate within most transition/developing countries. There is little or no real control over the products which have been, and are still being, manufactured using polymers contaminated with POP-BDE. It is very likely that they will have been used, at least occasionally, for applications with far greater potential for exposure than the original applications. This could certainly include ABS water pipes, toys and food packaging/contact materials (plates, cups and crockery). Unfortunately it has not been possible to provide better indication of the quantities which may involved in the absence of any data from the authorities in China – or from the major exporters to China about the levels of POP-BDE in the wastes and polymers which have been exported.

Appendix 5 (c): An assessment of the costs and benefits of removing or maintaining the exemption on recycling articles containing PBDE;

Assessment of the costs and benefits has been carried out in the context of the UNEP advice published on this issue[103] together with the discussions in the teleconference held on 7th July 2010.

UNEP says that cost-benefit analysis (CBA) can be a useful tool for highlighting the potential costs and benefits of a proposed decision and its alternatives. However, there are many limitations that are relevant and need to be recognised. Those highlighted by UNEP include:

- Benefits often can be more difficult to quantify than costs.
- Cost-benefit analysis is inexact.
- Cost-benefit analysis often includes subjective assumptions regarding non-economic values.
- Shared benefits can be underestimated.
- Institutional bias and conflict.
- Limited capacity.
- Cost-benefit analysis does not always yield robust numbers.
- The more narrow analysis of weighing the costs that are directly accrued versus the shared benefits can lead to what is famously known as the Tragedy of the Commons.
- UNEP also notes that experience in a number of Western countries shows that — even where there are a surfeit of PhD economists — estimates of economic impacts of regulation on business often far exceed the actual costs.

For these reasons the results of any cost-benefit analysis need to be assessed carefully and may not be robust. While the process usually highlights the various qualitative costs and benefits, the process of assessing the actual quantitative values can be quite contentious.

UNEP also comments that underlying legal authority may not allow direct consideration of economic cost or set protection at extremely high levels regardless of costs. Particularly where a hazardous or extremely dangerous material or public harm may be at issue, the relevant statutory authority may require regulations based on addressing public harm without an explicit consideration of economic cost. A pertinent example is given where regulations may set very high protective levels, such as for exposure of children to pesticides, that may be more protective than science and costs might ordinarily warrant, but are supported by a precautionary approach.

The conclusion reached by UNEP was that as a result of these limitations – and reflected in the discussions in the teleconference - was that countries "*may wish to use cost-benefit analysis carefully*".

The limitations of comprehensive quantification are demonstrated by the small number of pollutants for which the Clean Air For Europe programme has been able to ascribe values in spite of enormous research efforts over many years:

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[103] Limitations of Cost-Benefit Analysis: http://www.unep.org/dec/onlinemanual/Enforcement/NationalLawsRegulations/Resource/tabid/777/Default.aspx

Effect	Impact quantified and valued	Impact only quantified	Qualitative assessment	Comments
Health				
Primary PM, NO_3 and SO_4 aerosols				
acute – mortality, morbidity	✓	✓		Care taken to avoid double counting with chronic effects
chronic – mortality, morbidity	✓	✓		
infant mortality	✓	✓		
Ozone				Less clear linkage between O_3 and mortality than for PM_{10}
acute – mortality	✓	✓		
chronic – mortality			✓	No information on possible chronic effects
acute – morbidity	✓	✓		
chronic – morbidity			✓	
Direct effects of SO_2			✓	Limited importance to CAFE
Direct effects of VOCs			✓	Lack of data on speciation, etc.
Direct effects of NO_2			✓	Lack of clear information of effects at ambient levels
Social impacts			✓	Limited data availability
Altruistic effects			✓	Reliable valuation data unavailable
Agricultural production				
Direct effects of SO_2 and NO_x			✓	Negligible according to past work
Direct effects of O_3 on crop yield	✓	✓		
Indirect effects on livestock			✓	
N deposition as crop fertiliser			✓	Negligible according to past work
Visible damage to marketed produce		✓	✓	
Interactions between pollutants, with pests and pathogens, climate…			✓	Exposure-response data unavailable
Acidification/liming			✓	Negligible according to past work
Materials				
SO_2/acid effects on utilitarian buildings	✓	✓		
Effects on cultural assets, steel in re-inforced concrete			✓	Lack of stock at risk inventory and valuation data
PM and building soiling	✓	✓		
Effects of O_3 on paint, rubber	✓	✓		
Ecosystems				
Effects on biodiversity, forest production, etc. from excess O_3 exposure		✓	✓	Valuation of ecological impacts is currently too uncertain
Effects on biodiversity, etc., from excess N deposition		✓	✓	Valuation of ecological impacts is currently too uncertain
Effects on biodiversity, etc., from excess acid deposition		✓	✓	Valuation of ecological impacts is currently too uncertain
Visibility: Change in visual range			✓	Impact of little concern in Europe.
Change in greenhouse gas emissions		✓	✓	Valuation too uncertain
Macroeconomic effects	✓	✓		Addressed using the GEM-E3 model
Drinking water supply and quality	✓		✓	Limited data availability

Table 68: Effects of the CAFE pollutants, and the extent of assessment (AEA Technology plc 2005)

The results presented in this Appendix should therefore not be seen as a formal cost benefit analysis, particularly in the light of the significant uncertainties. The review is intended to be indicative of some of the likely health and other socio-economic considerations as a guide to policy determination in this context.

Expsoure Thresholds

The POPRC has considered the toxicological issues in some detail as part of the preparation for the listing of the POP-BDE previously made it clear that "*it is not the task of the POPRC to set a regulatory level, for construction of which resort would need to be made a wider range of data*" (Stockholm Convention 2007d). The enormous volumes of detailed toxicological data required to establish such levels are beyond the scope of this already broad-ranging review. Instead the levels established by regulatory authorities and risk assessments in the literature (thus taking into account the inevitable time delays between the reporting of events in scientific journals to the implementation of regulatory controls) have been reviewed and an assessment is made of the levels they have established in relation to the consideration of present and future risks.

Reference Values

JECFA

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) last considered the available data on PBDE in 2005 (WHO & FAO 2005) and said that at that time the data were not adequate for allocating a safety reference value. Nevertheless, the JECFA stated from limited toxicity data that for the more toxic lower-brominated PBDE congeners, adverse effects would be unlikely to occur in rodents at dose of less than approximately 100 µg/kg bw/day and that:

"The current estimates of dietary intake were approximately 0.004 µg/kg bw per day, while intake by breastfeeding infants could be up to 0.1 µg/kg bw per day for the sum of all measured PBDE congeners, including the less toxic ones. In consequence, there appeared to be a large MOE for a non-genotoxic compound which, despite the inadequacy of the data on toxicity and intake, gave reassurance that intakes of PBDE are not likely to be a significant health concern. The Committee noted that, as with related bioaccumulative persistent contaminants (PCBs, dioxins), a more appropriate dose-metric for interspecies comparison of risk would be a measure of the internal dose. For the majority of PBDE studied, however, the data from experimental animals or on concentrations in human tissue were insufficient to allow a comparison with external dose."

The Committee commented that it "*recognized the preliminary nature of the data on concentrations of polybrominated diphenyl ethers (PBDE) in food and human milk, which adds considerable uncertainty to the intake estimates*" [104].

U.S. EPA

The U.S. EPA established a much lower chronic ''*oral reference dose*'' (Oral RfD) of 2 µg/kg bw/day for cPentaBDE and 3 µg/kg bw/day for cOctaBDe in January 1990.

The oral RfD is an estimate of the daily exposure of a person to a contaminant that is likely to be without appreciable risk of a deleterious non-carcinogenic effect during a lifetime.

The U.S. EPA has subsequently established RfDs for chronic exposure to:

Congener/ mixture	*RfD µg/kg bw/day*	*Uncertainty factor*	*Basis of departure point*
***cPentaBDE*[105]**	2	1,000[106]	No-observed-adverse-effect-level (NOAEL) for Induction of hepatic enzymes (Carlson 1980)
***cOctaBDe*[107]**	3	1,000[108]	NOAEL for induction of hepatic enzymes in experimental animals (Carlson 1980)
***47*[109]**	0.1	3,000[110]	Benchmark dose lower confidence limit (BMDL) for neurobehavioural effects (Eriksson et al. 2001b, USEPA 2006c, USEPA 2008e)
***99*[111]**	0.1	3,000[112]	BMDL for neurobehavioral effects (Viberg et al. 2004a, USEPA 2006b, USEPA 2008c)

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[104] http://apps.who.int/ipsc/database/evaluations/chemical.aspx?chemID=5294

[105] http://www.epa.gov/iris/subst/0184.htm (Viewed 1st June 2010)

[106] The uncertainty factor of 1000 was applied to the NOAEL reported by Carlson of 2.51 mg/kg/day and reflects 10 for intraspecies variability and 10 for interspecies variability to the toxicity in lieu of specific data together with10 for extrapolation of a subchronic effect level to its chronic equivalent.

[107] http://www.epa.gov/iris/subst/0180.htm (Viewed 1st June 2010)

[108] The uncertainty factor of 1000 was applied to the NOAEL reported by Carlson of 1.77 mg/kg/day and reflects 10 for both intraspecies and interspecies variability to the toxicity of this chemical in lieu of specific data, and 10 for extrapolation of a subchronic effect level to its chronic equivalent

[109] http://www.epa.gov/IRIS/subst/1010.htm (viewed 1st June 2010)

[110] A total uncertainty factor (UF) of 3,000 was applied to the BMDL of 0.35 mg/kg derived by Eriksson: 10 for extrapolating animal data to humans (inter-species variability), 10 for susceptible human subpopulation (inter-human variability), 3 for extrapolating from a single-dose duration to a chronic exposure duration and 10 to account for a deficient database.

[111] http://www.epa.gov/IRIS/subst/1008.htm (viewed 1st June 2010)

Congener/ mixture	*RfD µg/kg bw/day*	*Uncertainty factor*	*Basis of departure point*
153[113]	0.2	3,000[114]	NOAEL for neurobehavioral effects (Viberg et al. 2003a, USEPA 2006b, USEPA 2008d)
209[115]	7[116]	300	NOAEL for neurobehavioral effects (Viberg et al. 2003b, USEPA 2006a, USEPA 2008b)

Table 69: USEPA references doses for PBDE

The RfD of 7 µg/kg bw/day for DecaBDE was not an uncontroversial conclusion – the American Chemistry Council claimed that the reference level is "*three orders of magnitude lower than the best available science supports*" (Trager 2008a).

An oral RfD of 4 mg/kg-day was calculated by Hardy, the Senior Toxicology Advisor to the Albemarle Corporation, using a composite uncertainty factor of 30, which consisted of 10 for intra-species uncertainty, 3 for interspecies uncertainty (i.e., 3 for toxicodynamics x 1 for toxicokinetics) and 1 for deficiencies with the database (Hardy et al. 2009).

Uncertainty in Toxicological Literature and Current Standards.

The USEPA and JECFA recommendations are not, on their own, a satisfactory basis for the assessment of human risks associated with exposure from PBDE – not least because regulatory standards inevitably lag behind the latest research. In this case, however, the toxicological database from which the recommendations are drawn is surprisingly small in relation to the extent of the use of PBDE.

Suvorov and Takser examined on line-databases to compare the reports of toxicity experiments in animals for PCB and PBDE. They found that reports on PCB continued to rise despite PCB ban in 1976 in the USA and 1970's in most PCB-producing countries. There was a peak in the number of publications in 1984 and another in 1994. The first wave of interest, they suggested, was presumably "*triggered by current exposures and observed toxic effects*" whilst the second "*was consecutive to emerging results from long-term epidemiological studies on the general population*".

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[112] A total uncertainty factor (UF) of 3,000 was applied to the BMDL of 0.29 mg/kg derived by Viberg: 10 for extrapolating animal data to humans (inter-species variability), 10 for susceptible human subpopulation (inter-human variability), 3 for extrapolating from a single-dose duration to a chronic exposure duration and 10 to account for a deficient database.

[113] http://www.epa.gov/IRIS/subst/1009.htm (Viewed 1st June 2010)

[114] A total uncertainty factor (UF) of 3,000 was applied to the NOAEL of 0.45 mg/kg identified in the Viberg et al. (2003) study: 10 for extrapolating animal data to humans, 10 for susceptible human subpopulation, 3 for extrapolating from a single dose to a lifetime exposure duration and 10 to account for a deficient database.

[115] http://www.epa.gov/IRIS/subst/0035.htm (viewed 1st June 2010)

[116] This is not an uncontroversial conclusion – the American Chemistry Council claimed that the reference level is "*three orders of magnitude lower than the best available science supports*" (Trager 2008b)

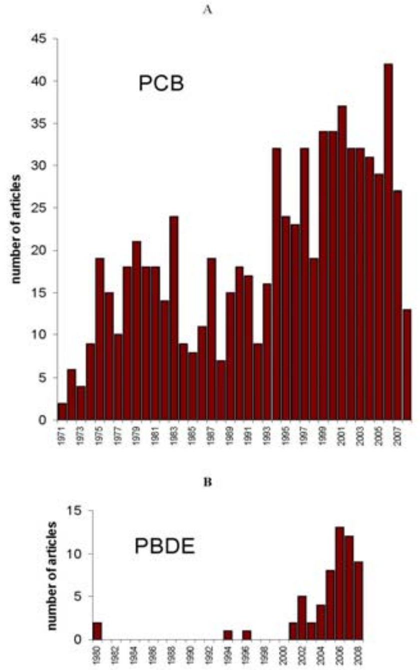


Figure 105: Temporal distribution of studies addressing PCB (A) and PBDE (B) toxicity in experiments with animal models (Suvorov & Takser 2008).

The library for PBDE is much smaller as can be seen in the figure above. The two oldest experimental studies on PBDE found through the PubMed search were published several years after the PCB ban in 1980 (Carlson 1980). This 1980 work by Carlsson is still the basis of the USEPA RfD for cPenta- and cOctaBDE as shown in the table above.

In spite of these reports on the toxic effects of PBDE - and of the known structural similarity of PBDE and PCB, there were only two further publications between 1980 and 2001 – one in 1994 and another in 1996. More interest has been shown in PBDE since 2001 but the number of research papers published is still lower than for PCB. It can reasonably be anticipated therefore that the toxicology of PBDE is still at relatively early stage and is not particularly well characterised. This is confirmed by the breakdown of the toxicity addressed in experiments with animal models in the figure below showing that some important areas (most notably cancer) have not yet been addressed at all. The development of research on epidemiology of PBDE is only recently producing results and these data are not yet reflected in the regulatory standards described in the previous section.

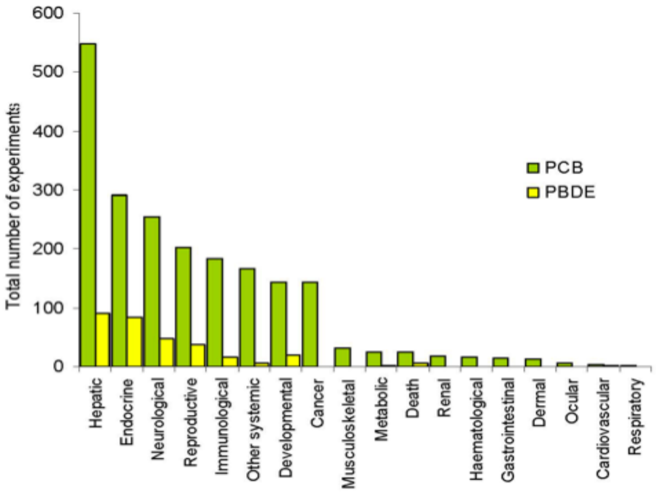


Figure 106: Distribution of endpoints of PCB and PBDE toxicity addressed in experiments with animal models (Suvorov & Takser 2008)

Suvorov et al. conclude that their analysis of the history of animal studies "*shows that the hindsight offered by PCB experimental history had little impact on experimental toxicology and future investigations into PBDE*". Furthermore the studies on PBDE "*display the same flaws as their PCB counterparts, indicating that lessons were not drawn from the history of PCB*" *(Suvorov & Takser 2008).*

A key omission highlighted by the conclusions from Suvorov is that most toxic effects in experimental studies are obtained at levels of exposure several orders of magnitude higher than exposure levels of the general population thus preventing direct transfer of animal results to human studies. There is, it was suggested, a need for toxic-substances testing with doses relevant to human exposures and measurement of internal dose *(Suvorov & Takser 2008).*

Talsness et al. (Talsness et al. 2008), as summarised by Wei (Wei et al. 2010), reported that exposure to low doses of BDE-47 (140 µg/kg body weight) caused an increase in ovarian weight in experimental rats "*but high doses (700 µg/kg) had no significant effect*".

They suggested that the data indicates endocrine disruption following *in utero* and lactational exposure to environmentally relevant doses of PBDE-47 and the doses used in the study would result in "*an approximate maternal body burden within or just above the range of concentrations reported in human adipose tissue samples collected in New York City*" (based on levels from Johnson-Restrepo (Johnson-Restrepo et al. 2005)). Their conclusions included a warning that the "*developing embryo, fetus, and neonate are highly susceptible to exogenous insults, and the magnitude of the current maternal body burden of PBDEs may be of concern for human health*" (Talsness et al. 2008). The more recent results from Herbstman, discussed below, strengthen these concerns (Herbstman et al. 2010a).

Wei comments "*toxicological studies at doses higher than environmental exposure levels might contribute little to the understanding of ecotoxic and health risks associated with PBDE*". It follows that "*toxicological studies at environmentally relevant doses are essential*" (Wei et al.). In the absence of a sound database of toxicological studies at environmentally relevant concentrations then a precautionary approach is appropriate – particularly in relation to impacts supported by epidemiological evidence of harm at current levels of environmental and human contamination.

Other Assessments of exposures, health effects and thresholds:

Netherlands:

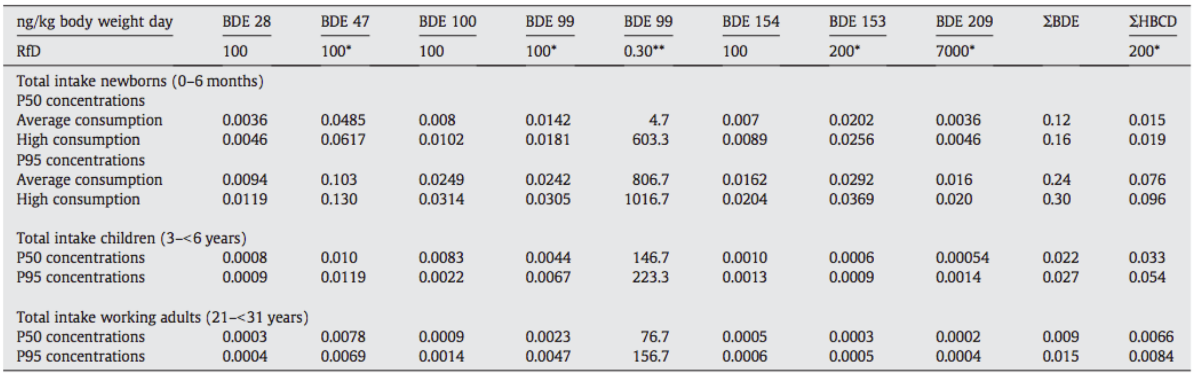
Bakker and fellow Researchers National Institute for Public Health and the Environment (RIVM) in the Netherlands have recently derived a "*no adverse effect level*" ('NAEL') for BDE-99 of 0.23– 0.30 ng/kg bw/day (Bakker et al. 2008). This was based on gestational exposure to BDE-99 which caused significant decreases in spermatid numbers and daily sperm production in adult rat offspring. After a single dose of 60 µg/kg bw on the sixth day of gestation male offspring had a reduction in daily sperm production of approximately 30% compared with controls. Whilst approximately 50% of controls had a second ejaculation, only 39% and 21% of the males from the 60 µg PBDE and 300 µg PBDE groups, respectively, achieved a second ejaculation (Kuriyama et al. 2005).

The current 99th percentile level for intake of BDE-99, based on dietary intakes, in the Netherlands is 0.24 ng/kg bw/day (median 0.11 ng/kg bw/day) which is described as "*borderline to the exposure which is considered as the benchmark for this toxic effect*". The exposure levels in the US, however, are more than ten times higher than in the Netherlands.

Belgium:

Roosens modelled the exposure of the Flemish population to brominated flame retardants (Roosens et al. 2010) and compared the results from the calculations with the US RfDs as well as to the RfD (actually a NAEL, as above) derived by Bakker (Bakker et al. 2008):

Table 70: Ratios between calculated exposure dose published RfD values (RI values).



ng/kg body weight day	BDE 28	BDE 47	BDE 100	BDE 99	BDE 99	BDE 154	BDE 153	BDE 209	ΣBDE	ΣHBCD
RfD	100	100*	100	100*	0.30**	100	200*	7000*		200*
Total intake newborns (0–6 months)										
P50 concentrations										
Average consumption	0.0036	0.0485	0.008	0.0142	4.7	0.007	0.0202	0.0036	0.12	0.015
High consumption	0.0046	0.0617	0.0102	0.0181	603.3	0.0089	0.0256	0.0046	0.16	0.019
P95 concentrations										
Average consumption	0.0094	0.103	0.0249	0.0242	806.7	0.0162	0.0292	0.016	0.24	0.076
High consumption	0.0119	0.130	0.0314	0.0305	1016.7	0.0204	0.0369	0.020	0.30	0.096
Total intake children (3–<6 years)										
P50 concentrations	0.0008	0.010	0.0083	0.0044	146.7	0.0010	0.0006	0.00054	0.022	0.033
P95 concentrations	0.0009	0.0119	0.0022	0.0067	223.3	0.0013	0.0009	0.0014	0.027	0.054
Total intake working adults (21–<31 years)										
P50 concentrations	0.0003	0.0078	0.0009	0.0023	76.7	0.0005	0.0003	0.0002	0.009	0.0066
P95 concentrations	0.0004	0.0069	0.0014	0.0047	156.7	0.0006	0.0005	0.0004	0.015	0.0084

*RI = 1 indicates possible health risk, ΣBDE = Σ5BDE (BDE 47, 100, 99, 153 and 154) and BDE 209, * indicating the EPA RfD values and ** indicating the RfD value by Bakker et al. (Bakker et al. 2008).*

The highest ratio between calculated exposure dose and the published USEPA RfD value (RI value) was found to be 0.04 (0.0369) for exposure to BDE153 of babies. Meaning total exposure equals c4% of the RfD dose. The combined total for children of the 5 lower BDE was 3% of the RfD and up to 30% for high consumption babies.

Roosens concluded that based on limited available toxicological information "*it is difficult to assess the immediate health risk for the age groups. Yet, due to high RI values for exposure through human milk combined with uncertainty involving RfD values, possible additive effects between congeners and missing RfD values for several congeners, monitoring of newborn exposure to BFRs is advised*".

"*Special attention*" was, however, given to BDE 99, for which Bakker et al. (above). (Bakker et al. 2008) established "*a new and much more stringent health-based limit value (HBLV) value between 0.23 and 0.30 ng/kg bw day*". Calculating RI-ratios based on this data, all age groups are exposed to BDE 99 above the tolerable level.

Adult exposure of BDE-99 has recently been estimated by USEPA (USEPA 2010) as 1.94 ng/kg bw/day and this clearly exceeds the NAEL.

Scandinavia:

A study by Main associated human milk (but not placenta) PBDE levels with an increased incidence of cryptorchidism in newborn Scandinavian boys (Main et al. 2007). This is an effect which is consistent with the animal data (Stoker et al. 2004, Stoker et al. 2005)(Lilienthal et al. 2006)(Kuriyama et al. 2005) and is clearly relevant at current background levels in Europe.

EU:

In the EU PentaBDE risk assessment (European Chemicals Bureau 2001), published in 2001, it was concluded "*there is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already*". The reason for this was that:

"The current use pattern provided by Industry is that pentaBDPE is only used in polyurethane foam and that consumers do not come into direct contact with these foams. The foam is only used in enclosed uses and therefore it is concluded that consumer exposure is negligible.
Since it is concluded that exposure to consumers from pentaBDPE-containing foams is negligible, then it follows that the risk to consumers is also negligible".

This conclusion must be seen as being wrong in the light of the now strong evidence linking PentaBDE-containing foams with, particularly, dust and thus to human exposure. Allen et al., as noted above, showed that XRF readings on household items were highly correlated with GC/MS measured bromine and PBDE levels in furnishings and electronic devices (R = 0.93) (Allen et al. 2008b). Imm et al. took this further by measuring bromine concentrations on the surfaces of many household items for a cohort in Wisconsin and then measuring the PBDE in blood of residents who lived in the homes they studied. They found that the bromine content in the participant's sleeping pillow (*p*-value = 0.005) and primary vehicle seat cushion (*p*-value = 0.03) were the strongest predictors of PBDE blood concentrations (Imm et al. 2009).

Any possible inference on potential risk for adverse nervous system effects in humans exposed to PBDE in utero, or neonatally through breast milk or household dust, needs to be extrapolated from animal data. By using a standard approach of dividing NOEL values for the appropriate safety factors, Reference doses (RfDs) of 92-660 ng/kg/day can be calculated (Costa & Giordano 2007a). These values are in the actual range of infant exposure in the U.S. through breast milk at >300 ng/kg/day (Schecter et al. 2006) and close to the levels of toddler exposure through (moderate) household dust and the diet at 50 ng/kg/day (Lorber 2008). Comparison of body burden across species leads to similar conclusions, i.e. levels in animals shown to cause adverse developmental behavioural effects are in the same range of high human exposures (Costa & Giordano 2007b).

Recent Literature on Toxic Responses:

A wide range of toxic responses are demonstrated by PBDE including:

- thyroid hormone perturbation and similar Ah-receptor-dependent responses (Hallgren & Darnerud 2002, Zhou et al. 2002, Kuriyama et al. 2004a, Stoker et al. 2004),
- hepatic CYP 1A1 enzyme induction (Peters et al. 2004), and
- impaired spermatogenesis (Kuriyama et al. 2005).

Major gaps in the possible impacts include data on possible carcinogenicity. Data is also lacking for human health studies, and particularly in relation to the timing of exposure, as in the case of the nursing infant and relative to the more sensitive health endpoints relevant to an infant's and toddler's exposure (Jones-Otazo et al. 2005). There is "*almost no information on possible developmental adverse effects in humans from PBDE exposure*" (Costa et al. 2008). It is these developmental effects which appear to be amongst the most sensitive impacts at low levels of exposure. Recent work includes:

Table 71: Developmental neurotoxicity of PBDE based on animal studies

Exposure	PBDE	Behavioural effects	Reference
Pre-natal	BDE-47, -99	Hyperactivity	(Kuriyama et al. 2005), (Kuriyama et al. 2004b)
Post-natal	BDE-47, -99, -153, -183, -203, -206, -209, DE-71	Hyperactivity, decreased habituation, impaired learning	(Rice et al. 2007), (Eriksson et al. 2001b), (Viberg et al. 2003a), (Viberg et al. 2003b), (Viberg et al. 2004a), (Viberg et al. 2006), (Viberg et al. 2007), (Dufault et al. 2005)
Pre- and post-natal	BDE-99	Hyperactivity	(Branchi et al. 2002), (Branchi et al. 2005)

Table 72: No Observed Effect level (NOEL) and Lowest Observed Effect Level (LOEL) after oral administration of BDE-99 congener or C-PentaBDE formulations (after (Stockholm Convention 2006)).

PentaBDE	***Duration***	***Dose***	***NOEL mg/kg/ day***	***LOEL mg/kg/ day***	***Endpoint***	***Species***	***Reference***
BDE-99	s.d	0.8 or 12.0 mg/kg	n.d.	0.8	Neurotoxicity Behaviour, motor activity level and learning	mouse	Eriksson et al. 2001
BDE-99	s.d	0.6, 6, or 30 mg/kg	n.d.	0.6	Developmental- and neurotoxicity Behaviour -hypoactive	mouse	Branchi et al. 2002
BDE-99	s.d	0.4, 0.8, 4.0, 8.0, or 16 mg/kg	0.4	0.8	Developmental- and neurotoxicity Behaviour	mouse	Viberg et al. 2004 Sand et al. 2004
BDE-99	s.d.	0,06 and 0,3 mg/kg to pregnant female	n.d.	0.06	Developmental- and neurotoxicity Behaviour (increased activity)	rat, F1 gen.	Kuriyama et al. 2005

PentaBDE	***Duration***	***Dose***	***NOEL mg/kg/ day***	***LOEL mg/kg/ day***	***Endpoint***	***Species***	***Reference***
BDE-99	s.d.	0,06 and 0,3 mg/kg to pregnant female	0.06	0.3	Reduced testis size and number of sperms	rat, F1 gen.	Kuriyama et al. 2005
Penta mix ***DE-71***	30 d	0.01, 0.05, 0.1, 0.5, or 1.0 mg/kg/day	1	n.d.	Growth, food intake, haematology, histopathology Clinical chemistry	rat	Great lakes Chemical Corporation 1985
Penta mix ***DE-71***	30 d	0, 3, 30, or 60 mg/kg/day	3	30	Liver weight, puberty, reproduction, liver enzymes, T_4-reduction	Male rat	Stoker et al. 2004
Penta mix ***DE-71***	30 d	0, 3, 30, or 60 mg/kg/day	n.d.	3	T_4-reduction	Female rat	Stoker et al. 2004
Penta mix ***DE-71***	35 d	0, 1, 10 or 30 mg/kg/day	1	10	T_4-reduction Liver enzymes	pregnant rat	Zhou et al. 2002, Zhou et al. 2001
Penta ***mix*** ***DE-71***	90 d	0-0.44 mg/kg/day	n.d.	0.44	Liver enzymes	rat	Carlson 1980
Penta mix ***DE-71***	90 d	0, 2,10, or 100 mg/kg/day	0-2	2-10	Hepatocyto-megali Tyreoidea hyperplasi	rat	Great lakes Chemical Corporation 1984

n.d. = not defined, s.d. = single dose

Gaps in the data include a need for epidemiological studies in humans to determine whether body burden of PBDE may be associated with adverse effects, particularly neurobehavioral development and reproductive effects (Costa & Giordano 2007b, Costa et al. 2008).

Also, information on potential mechanisms of PBDE toxicity is still limited (He et al. 2009). Mechanistic studies would provide important information for a better assessment of the likelihood of PBDE adverse health effects, would define the toxicity of individual congeners, and would indicate whether interactions among PBDE congeners and between PBDE and other environmental pollutants, e.g. PCBs may occur (Eriksson et al. 2001b) (Costa & Giordano 2007b, Costa et al. 2008).

Comments in the literature have indicated that a suitable reference exposure level for total PBDE may well be at or below the current exposures for infants and possibly other age groups as well (Jones-Otazo et al. 2005)(Muir 2003).

Jones-Otazo points out that the "*average*" infant exposure at 280 ng/kg bw/day is less than 10 times lower than the RfD for the PentaBDE mixture that is based on hepatotoxicity and not on developmental or neurological endpoints (Jones-Otazo et al. 2005). However, maximum infant and toddler exposures could be >4,100 and 1,485 ng/ kg bw/day, respectively, which are above and close to the RfD for PentaBDE (Jones-Otazo et al. 2005).

Muir notes that the fetus and neonate are very sensitive and vulnerable development phases, while current environmental levels may still offer a margin of safety for the mean exposure to PBDE from food the increasing concentration in human mother's milk "*is driving the alarm and concern*"(Muir 2003).

Neurodevelopmental Effects:

Evidence from rodent studies suggests that perinatal exposure to PBDE may cause behavioural problems, permanent aberrations in spontaneous behaviour, motor activity and processes associated with learning and memory /cognitive behaviour - possibly worsening with age – and continuing, sometimes increasing, into adulthood (Eriksson et al. 2001b)(Eriksson et al. 2001a)(Rice et al. 2007)(Viberg et al. 2003a, Viberg et al. 2003b, Viberg et al. 2004a, Viberg et al. 2004b, Viberg et al. 2006, Viberg et al. 2008a, Viberg et al. 2008b)(Viberg et al. 2003a, Gee & Moser 2008)(He et al. 2009)(Costa & Giordano 2007b)(Dufault et al. 2005)(Eriksson et al. 2002).

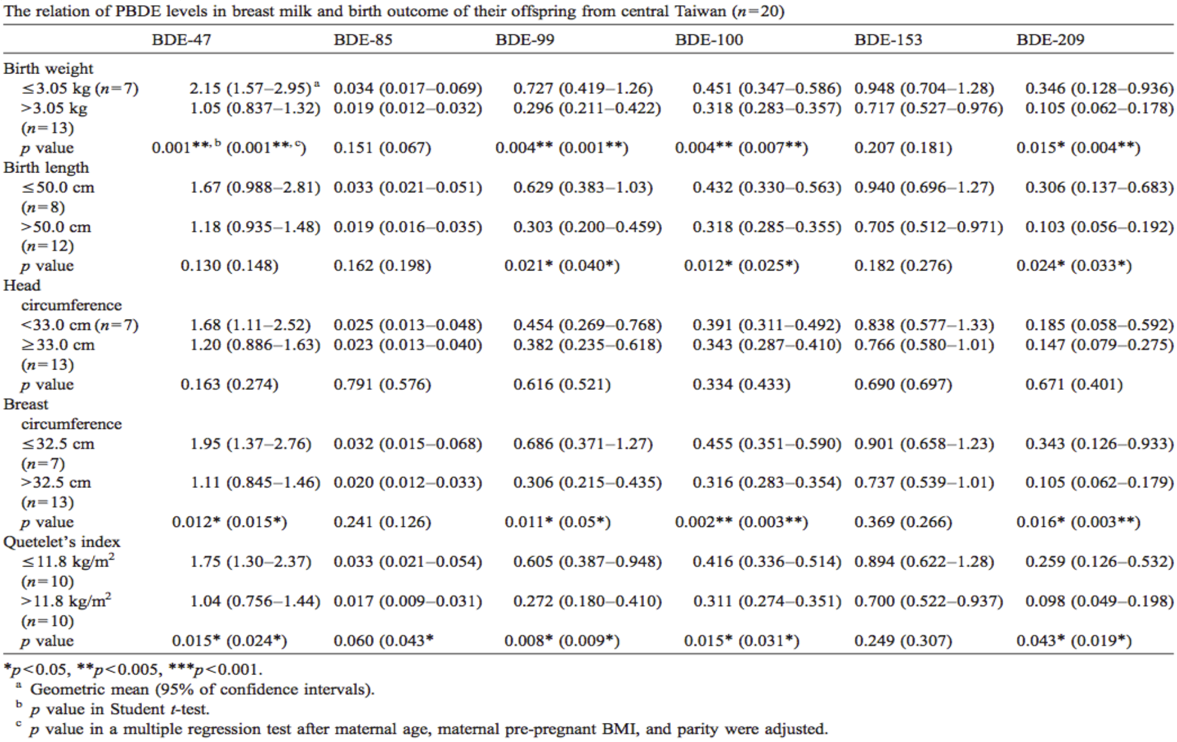
There is no NOEL for neurodevelopmental effects established for PBDE but Muir comments that PBDE are "*shown to cause neurodevelopmental deficits in doses on the same molar basis as ortho- and co-planar PCBs*" (Eriksson et al. 2001b). There are also now a number of very recent studies which are starting to find similar effects to the developmental and fertility effects reported in animals in human populations at current levels of contamination.

Harley studied a group of 223 pregnant women living in a low-income, predominantly Mexican-immigrant community in California and found that Increasing levels of BDE-47, -99, -100, -153 and the sum of these 4 congeners were all associated with longer time to pregnancy after controlling for known confounders including pesticide exposure and smoking(Harley et al. 2010).

Harley notes that because exposure to BDE is so ubiquitous in industrialised countries "*even small decreases in fecundability may have wide-reaching public health impacts*". Interestingly he adds that *"[A]nalysis of house dust from homes of low-income children in our study region has found the highest reported levels of PBDE to date (Quiros L, unpublished observations), suggesting that the next generation of Californians may be more extensively exposed*".

In a small (n=20) study by Chao in Taiwan, elevated PBDE levels in breast milk were correlated with lower birth weight and length, lower head and chest circumference, and decreased body mass (*Quetelet's)* index (Chao et al. 2007). They found that increased PBDE levels in breast milk were related with adverse birth outcome, particularly for the congeners of BDE-47, BDE-99, BDE-100, and BDE-209 after adjustments for maternal age, pre-pregnant BMI, and parity and concluded that in utero exposure to low doses of PBDE may result in lower birth weight and shorter birth length.

Table 73: The relation of PBDE levels in breast milk and birth outcome of their offspring from central Taiwan (Chao et al. 2007)



The relation of PBDE levels in breast milk and birth outcome of their offspring from central Taiwan ($n=20$)

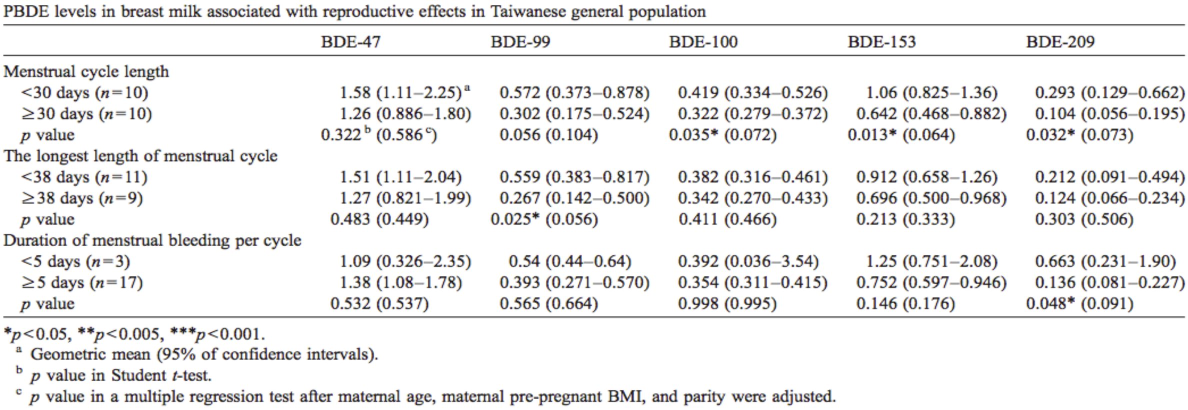
	BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	BDE-209
Birth weight						
≤3.05 kg ($n=7$)	2.15 (1.57–2.95)[a]	0.034 (0.017–0.069)	0.727 (0.419–1.26)	0.451 (0.347–0.586)	0.948 (0.704–1.28)	0.346 (0.128–0.936)
>3.05 kg ($n=13$)	1.05 (0.837–1.32)	0.019 (0.012–0.032)	0.296 (0.211–0.422)	0.318 (0.283–0.357)	0.717 (0.527–0.976)	0.105 (0.062–0.178)
p value	0.001**,[b] (0.001**,[c])	0.151 (0.067)	0.004** (0.001**)	0.004** (0.007**)	0.207 (0.181)	0.015* (0.004**)
Birth length						
≤50.0 cm ($n=8$)	1.67 (0.988–2.81)	0.033 (0.021–0.051)	0.629 (0.383–1.03)	0.432 (0.330–0.563)	0.940 (0.696–1.27)	0.306 (0.137–0.683)
>50.0 cm ($n=12$)	1.18 (0.935–1.48)	0.019 (0.016–0.035)	0.303 (0.200–0.459)	0.318 (0.285–0.355)	0.705 (0.512–0.971)	0.103 (0.056–0.192)
p value	0.130 (0.148)	0.162 (0.198)	0.021* (0.040*)	0.012* (0.025*)	0.182 (0.276)	0.024* (0.033*)
Head circumference						
<33.0 cm ($n=7$)	1.68 (1.11–2.52)	0.025 (0.013–0.048)	0.454 (0.269–0.768)	0.391 (0.311–0.492)	0.838 (0.577–1.33)	0.185 (0.058–0.592)
≥33.0 cm ($n=13$)	1.20 (0.886–1.63)	0.023 (0.013–0.040)	0.382 (0.235–0.618)	0.343 (0.287–0.410)	0.766 (0.580–1.01)	0.147 (0.079–0.275)
p value	0.163 (0.274)	0.791 (0.576)	0.616 (0.521)	0.334 (0.433)	0.690 (0.697)	0.671 (0.401)
Breast circumference						
≤32.5 cm ($n=7$)	1.95 (1.37–2.76)	0.032 (0.015–0.068)	0.686 (0.371–1.27)	0.455 (0.351–0.590)	0.901 (0.658–1.23)	0.343 (0.126–0.933)
>32.5 cm ($n=13$)	1.11 (0.845–1.46)	0.020 (0.012–0.033)	0.306 (0.215–0.435)	0.316 (0.283–0.354)	0.737 (0.539–1.01)	0.105 (0.062–0.179)
p value	0.012* (0.015*)	0.241 (0.126)	0.011* (0.05*)	0.002** (0.003**)	0.369 (0.266)	0.016* (0.003**)
Quetelet's index						
≤11.8 kg/m² ($n=10$)	1.75 (1.30–2.37)	0.033 (0.021–0.054)	0.605 (0.387–0.948)	0.416 (0.336–0.514)	0.894 (0.622–1.28)	0.259 (0.126–0.532)
>11.8 kg/m² ($n=10$)	1.04 (0.756–1.44)	0.017 (0.009–0.031)	0.272 (0.180–0.410)	0.311 (0.274–0.351)	0.700 (0.522–0.937)	0.098 (0.049–0.198)
p value	0.015* (0.024*)	0.060 (0.043*	0.008* (0.009*)	0.015* (0.031*)	0.249 (0.307)	0.043* (0.019*)

*$p<0.05$, **$p<0.005$, ***$p<0.001$.

[a] Geometric mean (95% of confidence intervals).

[b] p value in Student t-test.

[c] p value in a multiple regression test after maternal age, maternal pre-pregnant BMI, and parity were adjusted.



PBDE levels in breast milk associated with reproductive effects in Taiwanese general population

	BDE-47	BDE-99	BDE-100	BDE-153	BDE-209
Menstrual cycle length					
<30 days ($n=10$)	1.58 (1.11–2.25)[a]	0.572 (0.373–0.878)	0.419 (0.334–0.526)	1.06 (0.825–1.36)	0.293 (0.129–0.662)
≥30 days ($n=10$)	1.26 (0.886–1.80)	0.302 (0.175–0.524)	0.322 (0.279–0.372)	0.642 (0.468–0.882)	0.104 (0.056–0.195)
p value	0.322[b] (0.586[c])	0.056 (0.104)	0.035* (0.072)	0.013* (0.064)	0.032* (0.073)
The longest length of menstrual cycle					
<38 days ($n=11$)	1.51 (1.11–2.04)	0.559 (0.383–0.817)	0.382 (0.316–0.461)	0.912 (0.658–1.26)	0.212 (0.091–0.494)
≥38 days ($n=9$)	1.27 (0.821–1.99)	0.267 (0.142–0.500)	0.342 (0.270–0.433)	0.696 (0.500–0.968)	0.124 (0.066–0.234)
p value	0.483 (0.449)	0.025* (0.056)	0.411 (0.466)	0.213 (0.333)	0.303 (0.506)
Duration of menstrual bleeding per cycle					
<5 days ($n=3$)	1.09 (0.326–2.35)	0.54 (0.44–0.64)	0.392 (0.036–3.54)	1.25 (0.751–2.08)	0.663 (0.231–1.90)
≥5 days ($n=17$)	1.38 (1.08–1.78)	0.393 (0.271–0.570)	0.354 (0.311–0.415)	0.752 (0.597–0.946)	0.136 (0.081–0.227)
p value	0.532 (0.537)	0.565 (0.664)	0.998 (0.995)	0.146 (0.176)	0.048* (0.091)

*$p<0.05$, **$p<0.005$, ***$p<0.001$.

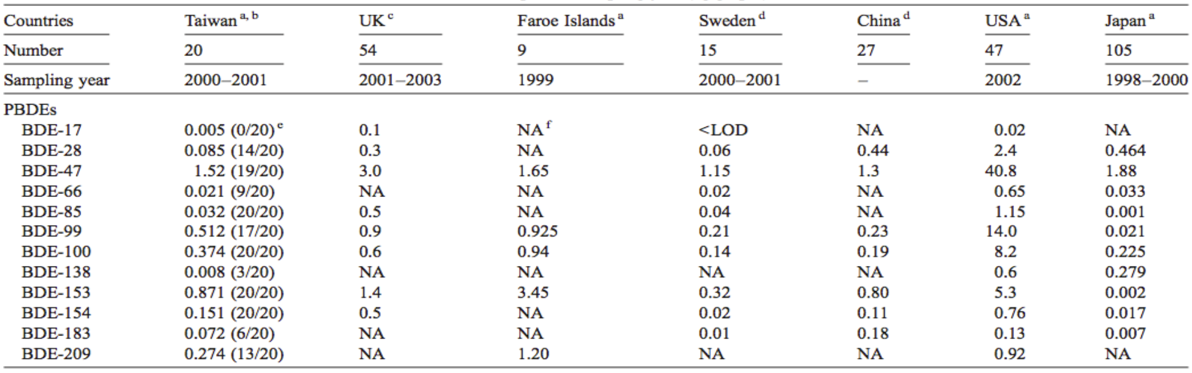
[a] Geometric mean (95% of confidence intervals).

[b] p value in Student t-test.

[c] p value in a multiple regression test after maternal age, maternal pre-pregnant BMI, and parity were adjusted.

The levels in this study were much lower than the exposures found in the US by Schecter (Schecter et al. 2003), for example:

Table 74: Current data of PBDE in breast milk from various countries with comparable sampling year (ng/g lipid) (Chao et al. 2007)



Countries	Taiwan[a, b]	UK[c]	Faroe Islands[a]	Sweden[d]	China[d]	USA[a]	Japan[a]
Number	20	54	9	15	27	47	105
Sampling year	2000–2001	2001–2003	1999	2000–2001	–	2002	1998–2000
PBDEs							
BDE-17	0.005 (0/20)[e]	0.1	NA[f]	<LOD	NA	0.02	NA
BDE-28	0.085 (14/20)	0.3	NA	0.06	0.44	2.4	0.464
BDE-47	1.52 (19/20)	3.0	1.65	1.15	1.3	40.8	1.88
BDE-66	0.021 (9/20)	NA	NA	0.02	NA	0.65	0.033
BDE-85	0.032 (20/20)	0.5	NA	0.04	NA	1.15	0.001
BDE-99	0.512 (17/20)	0.9	0.925	0.21	0.23	14.0	0.021
BDE-100	0.374 (20/20)	0.6	0.94	0.14	0.19	8.2	0.225
BDE-138	0.008 (3/20)	NA	NA	NA	NA	0.6	0.279
BDE-153	0.871 (20/20)	1.4	3.45	0.32	0.80	5.3	0.002
BDE-154	0.151 (20/20)	0.5	NA	0.02	0.11	0.76	0.017
BDE-183	0.072 (6/20)	NA	NA	0.01	0.18	0.13	0.007
BDE-209	0.274 (13/20)	NA	1.20	NA	NA	0.92	NA

a) Arithmetic mean. b) (Chao et al. 2007) central Taiwan. c)Geometric mean. d) Median. e)(Number of measurements higher than LOD/total detected number). f)NA means not analyzed.

The extreme lower estimated daily intake of PBDE for a breastfed infant was evaluated as 20.6 ng/kg bw/day in the Chao study, compared to 280 ng/kg bw/day average calculated in the Canadian study by Jones-Otazo (Jones-Otazo et al. 2005).

Roze examined prenatal exposure to flame retardants in relation to influences on motor, cognitive, and behavioural performance in healthy Dutch children at 5–6 years of age. This study is believed to be the first to investigate the influence of background exposure of PBDE on developmental outcome in healthy children at school age(Roze et al. 2009).

Prenatal background exposure to PBDE correlated (both positively and negatively) with neuro-psychological functioning in these children.

Roze concluded "*PBDE, used extensively worldwide, correlated with motor performance, attention, visual perception, and behavior, and we found the same results for OH-PCBs. We believe that unrelenting efforts should be made to find safe alternatives for these compounds*" (Roze et al. 2009).

Most recently a longitudinal cohort study by Herbstman et al. monitored the development of more than 150 U.S. children over 6 years and associates prenatal exposure to higher concentrations of PBDE flame retardants with lower scores on tests of neurodevelopment (Herbstman et al. 2010a). This demonstrates a disturbing consistency with the rodent studies.

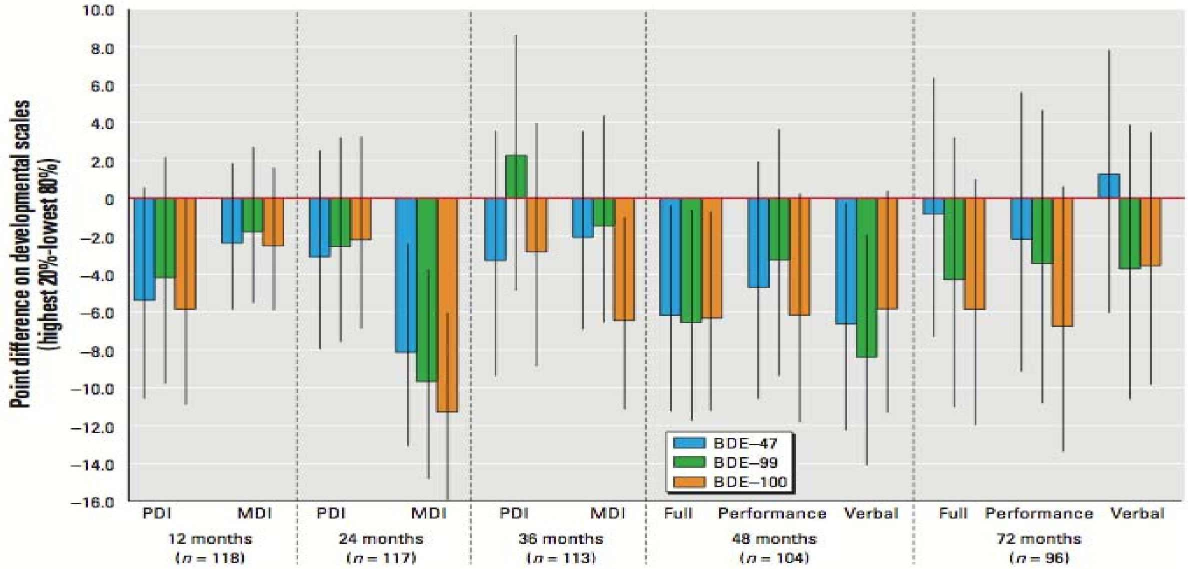


Figure 107: Difference in mean developmental score (and 95% confidence interval around the mean) comparing individuals in the highest quintile (20%) of exposure with those in the lower 80% of BDE 47, 99, and 100 (Herbstman et al. 2010a).

The mothers of the children in the study were pregnant at the time of the World Trade Centre (WTC) attacks in 2001 and gave birth at a hospital within 2 miles of the WTC site. The women were recruited for a study on the effects of exposure to compounds in dust from the decimated towers. PBDE were measured in the cord blood of 210 infants, and 152 of these children later participated in at least one round of neurodevelopmental testing conducted at 1, 2, 3, 4, and 6 years of age.

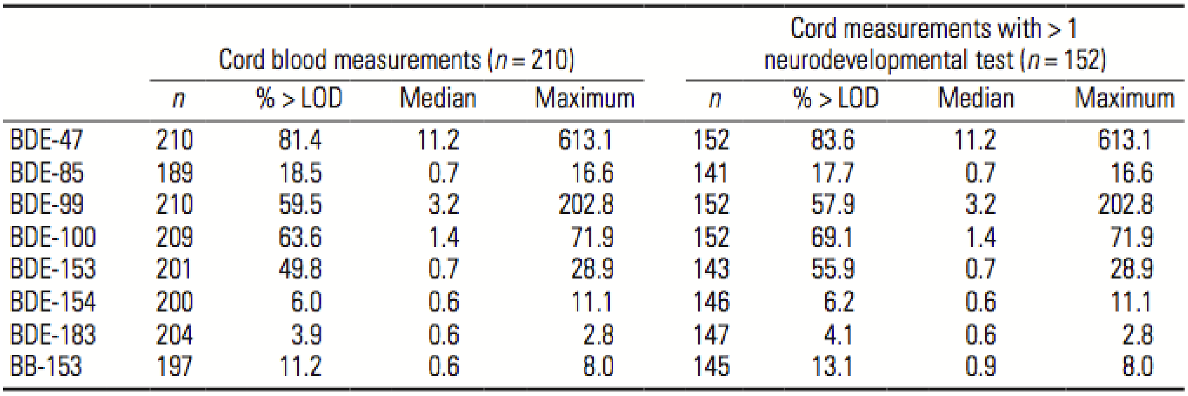
The children with higher levels of exposures consistently had, on average, lower developmental scores at each time point compared with less-exposed children; the association was particularly evident at 4 years. The researchers were not able to evaluate associations with developmental delay because few children had developmental scores low enough to meet the criterion for this outcome. However, in many cases average test scores in children with exposures in the highest 20% were 5–11 points lower than average scores for less-exposed children.

Although some evidence suggests the PBDE exposure seen in the children could be related to the WTC attack, the authors say "*it is certain*" that sources other than the WTC contributed to the PBDE levels in the infants' cord blood. The levels observed in these children were, however, similar to those reported in other U.S. populations and consequently it is likely that the effects observed will be widespread.

The authors say these findings are consistent with reports of hyperactivity and learning and memory deficits in experiments with mice exposed neonatally to PBDE.

A recent laboratory study using human cells (Schreiber et al. 2010) suggests BDE may interfere with thyroid hormones critical for normal brain development. The authors point out that additional studies exploring associations between BDE exposure and developmental effects are under way. In the meantime, they say "*identifying opportunities to reduce people's exposure to these compounds should be a priority*".

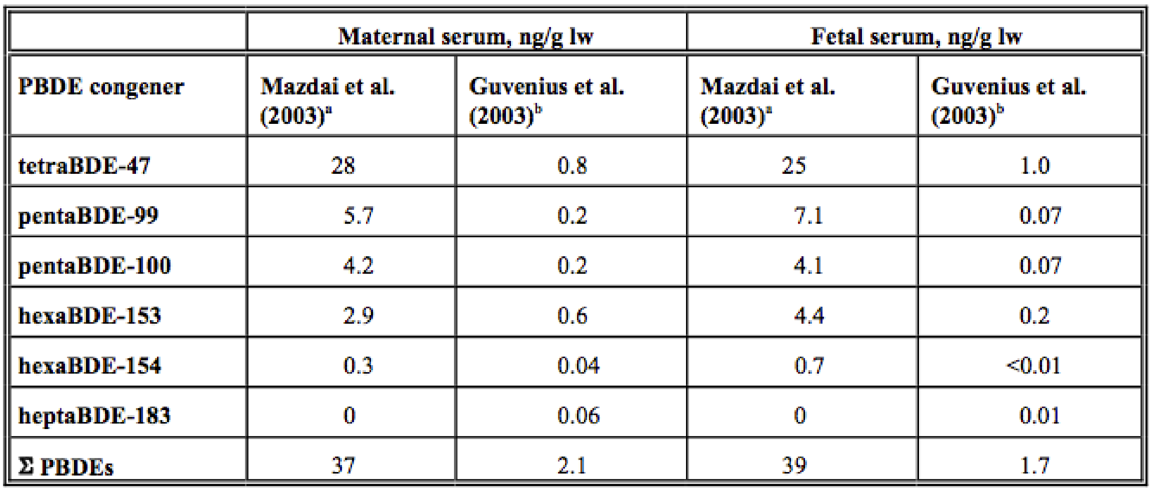
Table 75: Concentrations (ng/g lipid) of PBDE and BB-153 in cord blood (Herbstman et al. 2010a)



	Cord blood measurements (*n* = 210)				Cord measurements with > 1 neurodevelopmental test (*n* = 152)			
	n	% > LOD	Median	Maximum	*n*	% > LOD	Median	Maximum
BDE-47	210	81.4	11.2	613.1	152	83.6	11.2	613.1
BDE-85	189	18.5	0.7	16.6	141	17.7	0.7	16.6
BDE-99	210	59.5	3.2	202.8	152	57.9	3.2	202.8
BDE-100	209	63.6	1.4	71.9	152	69.1	1.4	71.9
BDE-153	201	49.8	0.7	28.9	143	55.9	0.7	28.9
BDE-154	200	6.0	0.6	11.1	146	6.2	0.6	11.1
BDE-183	204	3.9	0.6	2.8	147	4.1	0.6	2.8
BB-153	197	11.2	0.6	8.0	145	13.1	0.9	8.0

The median levels in the Herbstman study were lower than earlier results from the US by Mazdai (Mazdai et al. 2003) but significantly higher than values in Europe (compared here with data from Meironyté Guvenius for Sweden (Guvenius et al. 2003)) (USEPA 2008e):

Table 76: Median PBDE congener concentrations in maternal and fetal sera in the United States and Sweden (USEPA 2008e)



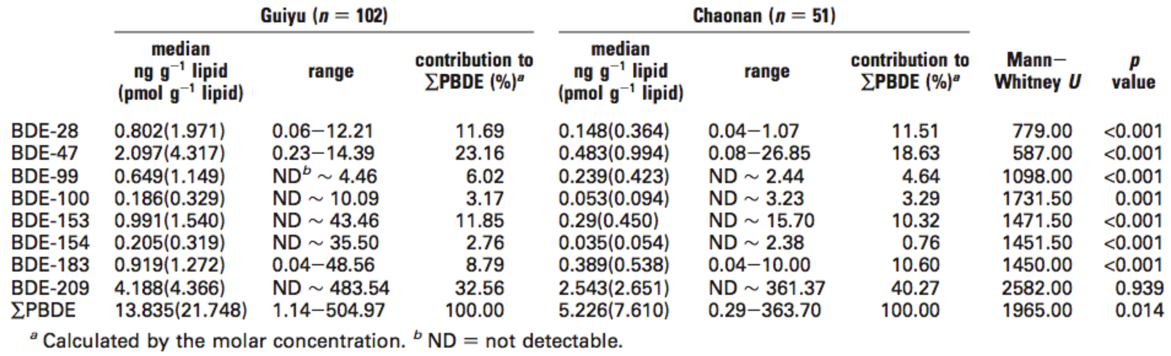
	Maternal serum, ng/g lw		**Fetal serum, ng/g lw**	
PBDE congener	**Mazdai et al. (2003)[a]**	**Guvenius et al. (2003)[b]**	**Mazdai et al. (2003)[a]**	**Guvenius et al. (2003)[b]**
tetraBDE-47	28	0.8	25	1.0
pentaBDE-99	5.7	0.2	7.1	0.07
pentaBDE-100	4.2	0.2	4.1	0.07
hexaBDE-153	2.9	0.6	4.4	0.2
hexaBDE-154	0.3	0.04	0.7	<0.01
heptaBDE-183	0	0.06	0	0.01
Σ PBDEs	37	2.1	39	1.7

It is notable that BDE-47 was the most abundant of all congeners and that the comparable median concentrations found in maternal and cord blood plasma indicate that it passes easily through the placenta. The USEPA Toxicological Review of Tetrabromodiphenyl Ether (BDE-47) warned that since the fetus and infants "*are exposed to BDE-47 via maternal/cord blood and human milk, such exposure may constitute a health risk for adverse neurodevelopmental effects in these population groups*" (USEPA 2008e).

A more recent review of levels in umbilical cord serum (Frederiksen et al. 2010a) reported that, in line with the general picture of the geographical differences of human PBDE exposure, the levels in Europe (Antignac et al. 2009)(Guvenius et al. 2003)(Meijer et al. 2008) consistently tend to be approximately one order of magnitude lower than in the United States (Herbstman et al. 2007a)(Mazdai et al. 2003).

It is interesting, although surprising, that Wu reported lower cord blood levels in e-waste in Guiyu seem lower than the US levels (Wu et al. 2010):

Table 77: Median PBDE Levels and Contribution to ∑PBDE in Umbilical Cord Blood from Guiyu and Chaonan (Wu et al. 2010).



	Guiyu (n = 102)			Chaonan (n = 51)				
	median ng g^{-1} lipid (pmol g^{-1} lipid)	range	contribution to ∑PBDE (%)[a]	median ng g^{-1} lipid (pmol g^{-1} lipid)	range	contribution to ∑PBDE (%)[a]	Mann–Whitney U	p value
BDE-28	0.802(1.971)	0.06–12.21	11.69	0.148(0.364)	0.04–1.07	11.51	779.00	<0.001
BDE-47	2.097(4.317)	0.23–14.39	23.16	0.483(0.994)	0.08–26.85	18.63	587.00	<0.001
BDE-99	0.649(1.149)	ND[b] ~ 4.46	6.02	0.239(0.423)	ND ~ 2.44	4.64	1098.00	<0.001
BDE-100	0.186(0.329)	ND ~ 10.09	3.17	0.053(0.094)	ND ~ 3.23	3.29	1731.50	0.001
BDE-153	0.991(1.540)	ND ~ 43.46	11.85	0.29(0.450)	ND ~ 15.70	10.32	1471.50	<0.001
BDE-154	0.205(0.319)	ND ~ 35.50	2.76	0.035(0.054)	ND ~ 2.38	0.76	1451.50	<0.001
BDE-183	0.919(1.272)	0.04–48.56	8.79	0.389(0.538)	0.04–10.00	10.60	1450.00	<0.001
BDE-209	4.188(4.366)	ND ~ 483.54	32.56	2.543(2.651)	ND ~ 361.37	40.27	2582.00	0.939
∑PBDE	13.835(21.748)	1.14–504.97	100.00	5.226(7.610)	0.29–363.70	100.00	1965.00	0.014

[a] Calculated by the molar concentration. [b] ND = not detectable.

These data are hard to reconcile with other studies which have found levels of PBDE in human milk in e-waste recycling areas in China as high as those in the US (Leung et al. 2010).

Synergism with PCB

One concern, which has received relatively little attention in the literature, is the issue of synergism of PBDE with PCBs. This could be particularly important in relation to neurotoxicity.

Tagliaferri demonstrated that the interactions between BDE-47 and BDE-99 in an in vitro model varied along the concentrations of both PBDE, and could be synergistic or antagonistic (Tagliaferri et al. 2010).

Tagliaferri observed the interactions by assessing cell viability or oxidative stress as end-points, and suggested a role for the latter in PBDE induced effect on neurons. The finding that a simultaneous co-exposure to BDE-47 and BDE-99 could induce synergistic neurotoxic effects, in particular at low concentrations of BDE-47 is, he said "*of particular interest from a toxicological point of view. Indeed, humans are exposed to mixtures of PBDEs, most notably tetra- and penta-BDEs, such as BDE-47 and BDE-99*".

He (He et al. 2009) confirmed that PBDE-47 has neurotoxic effects and can induce SH-SY5Y cells apoptosis via three classical apoptosis pathways. Furthermore it can interact with PCB-153 to enhance neurotoxicity.

Earlier work by Eriksson (Eriksson et al. 2006) found interactions between PCB-52 and PBDE-99 and noted that neurobehavioral defects were seen to worsen with age in mice neonatally exposed to these compounds.

He (He et al. 2009) "*could not conclude with certainty whether this phenomenon exists between PBDEs and PCB*" and whether the interaction is additive or synergistic- although *"the interaction appeared to be synergistic within the dose range that induces neurotoxicity"*. They concluded that *"further research with PBDEs and PCBs is of vital importance, as the levels of PBDEs are increasing in biological and environmental elements and because of the high background level of PCBs already existing in the environment"*.

The Most Vulnerable Groups

The groups assessed to be most at risk if exposed to elevated levels as a consequence of recycling of POP-BDE include:

- Workers – especially in low-technology E-waste operations in developing/transition countries (mainly exposed to OctaBDE from WEEE plastic)
- Workers in manufacturing/ recycling/ installing foam products (exposed to PentaBDE).
- Toddlers and breast-fed infants – especially in California and those parts of the USA where body burdens are already high. In these scenarios recycled products are likely to supplement those existing high levels of exposure.
- Workers in smelters processing printed circuit boards (possibly exposed to PBDE from PWB and OctaBDE from WEEE plastic and related PBDD/DF release)
- General population and biota worldwide (PBDE from multiple sources and PBDD/DF from food and dust)

The best data for a solid assessment stem from a study addressing a cohort related to a relevant large group vulnerable to exposures from recycled articles containing PBDE in relation to the recent epidemiological evidence from Herbstman and others (Herbstman et al. 2010b):

- Women of child-bearing age and those who are pregnant in relation to neurodevelopmental impacts on the fetus.

An assessment is therefore made for this group based on the most sensitive outcomes in the current literature. This is considered to be a valid approach on the grounds that if a general group of the wider population are exposed at levels causing harm then it follows that those who are more exposed through occupational exposure are likely to be more heavily impacted. Any financial assessment based on a general group therefore involves a high degree of conservatism compared with damages to the most exposed sectors. For other exposure scenarios the knowledgebase is, in any case, too small to do a reasonable cost assessment.

The likely exposures associated with recycling of POP-BDE, at least in the worst case, are similar to those levels already reported from existing uses. The size of the population affected should, however, reduce over time as stocks of POP-BDE move from products and into sinks. Future release from landfills and the contamination of the surrounding including human exposure will still need to be considered – particularly where containment systems break down such as by flooding, erosion, excavation or other developments.

Worker Exposure

Whilst Robinson warned that "*E-waste may affect the whole of humanity*" (Robinson 2009) it is clear that there will be some groups, especially those involved in low-tech recycling who are likely to be more exposed to direct than others. A schematic derived from that paper illustrates some of the exposure routes:

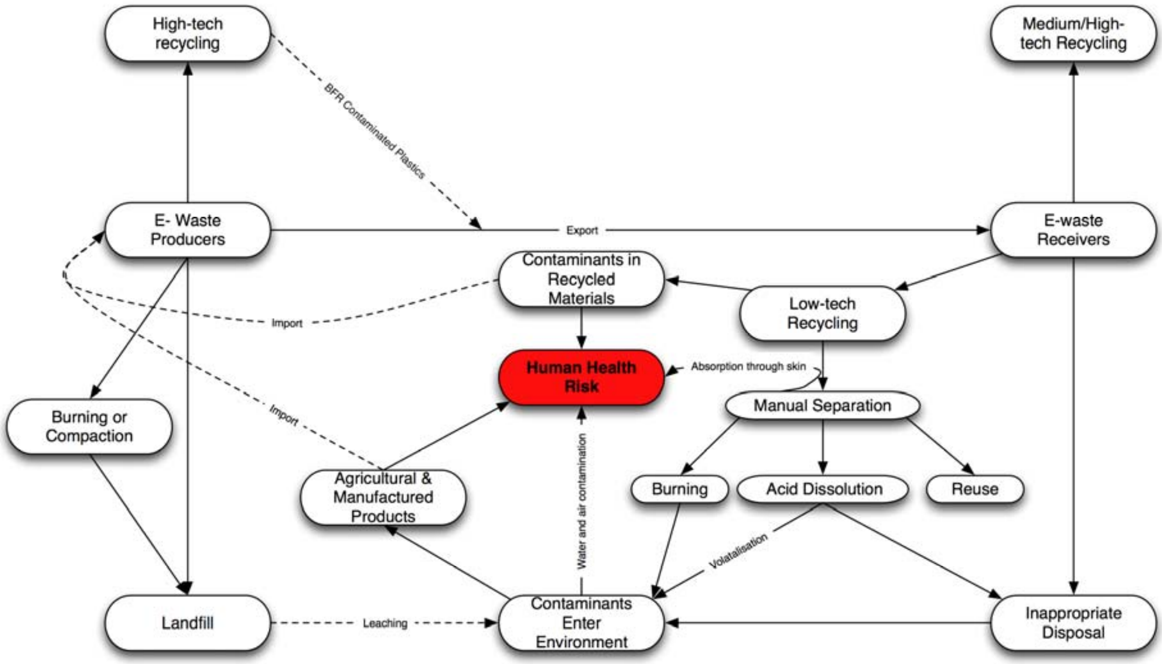


Figure 108: Fluxes of contaminants associated with E-waste from producers to receivers and ultimately to humans (adapted from (Robinson 2009))

E-waste producers tend, in general, to be exposed much less directly (by contamination from recycled products or from imported food).

The exposure of workers from recycling of POP-BDE can to be distinguished into two main groups:

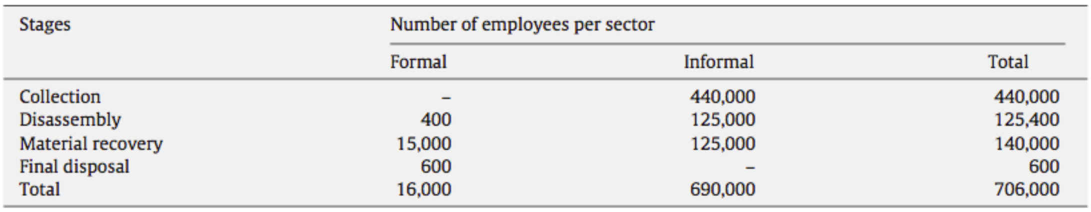
Low technology dismantlers/recyclers: workers in low technology operations in developing/transition countries where there is likely to be little protective equipment and be high exposure from open-burning or smouldering operations. Operations of non-BAT smelters and other non-BAT secondary metal industries processing PBDE-containing materials are likely to give similar levels of exposure but worker exposures in these industries is not reported in the current literature.

Workers in industrial countries: workers involved in recycling and recovery operations in industrial countries such as foam-recyclers and those who work with or install recycled articles potentially containing POP-BDE such as carpet fitters, particularly in the US, who are likely to be regularly exposed to rebond material.

The first group can include the families of workers as the family home can also be the workshop thus children and infants can be highly exposed. Similarly the third group above, pregnant women and women of child-bearing age are likely to be part of the workforce in these situations.

Whilst the best characterised exposures for this scenario tend to come from China because of the history of large volumes of waste being reprocessed there the exposures are likely to be typical of other sites in the many other countries where e-waste is recycled in similar ways – now that e-waste is being more heavily regulated in China it is hoped that the exposures will fall. In Guiyu, for example, there are more than 6,000 small-scale family-run workshops which represent 60% to 80% of the families in the town. Approximately 160,000 workers are involved in the business of e-waste dismantling and recycling most without any protective measures. Approximately 1.7 million tons of e-waste are dismantled annually at this site according to a 2007 local government report (Wu et al. 2010).

The estimated total employment in the informal e-waste sector in China was reported as 690,000 workers in 2007 approximately 250,000 of whom were working in disassembly or materials recovery:



Stages	Number of employees per sector		
	Formal	Informal	Total
Collection	–	440,000	440,000
Disassembly	400	125,000	125,400
Material recovery	15,000	125,000	140,000
Final disposal	600	–	600
Total	16,000	690,000	706,000

Figure 109: Estimated employment in the Chinese e-waste recycling industry (Duan and Eugster (2007) quoted in (Yu et al. 2010a)).

Leung et al. (Leung et al. 2006) conducted a detailed study of the Guiyu area to quantify the pollution levels generated from e-waste, and to identify their sources. They found PBDE levels up to 1,169 ng/g dwt in soils near the recycling areas. This was 10–60 times higher than PBDE contamination reported at other locations in the world. In 2007 this study was extended (Leung et al. 2007) to surface soils and combustion residue in the Guiyu area. They found total PBDE concentrations were highest in the combustion residue of plastic chips and cables collected from a residential area (33,000–97,400 ng/g, dry wt); in soils from an acid leaching site (2,720–4,250 ng/g, dry wt); and a printer roller dump site (593–2,890 ng/g, dry wt). The authors also found that DecaBDE was the dominant congener (35–82%) among the study site but did not seek to identify other additive BFR known to be present in e-waste.

More recently Leung et al (Leung et al. 2010) found high PBDE body burden in a group of childbearing-aged women at an e-waste recycling area in China and assessed the possible health risks imposed to infants. The study provided evidence that primitive e-waste recycling in China leads to high PBDE body burdens in local residents and can potentially threaten the health of infants. The estimated intake of PBDE of 6-month-old breastfed infants living at the e-waste site was 572±839 ng/kg body wt/day, which was 57 times higher than that of infants from the reference site (10.1±4.60 ng/kg body wt/day). Moreover, the maximum calculated value (2,240 ng/kg body wt/day) exceeded the chronic oral reference dose for penta-BDE (2,000 ng/kg/day) of US EPA (Leung et al. 2010).

There are already reports that exposure to PBDE in e-waste recycling areas have impacts on birth outcomes including higher levels of stillbirth, low birth weight, and premature delivery (Wu et al. 2010)

For workers in non-BAT copper smelters and other non-BAT metal industries in developing/transition countries processing PBDE-containing materials only stack emissions of PBDE and PBDD/DF have been published (Du et al. 2010)(Wang et al. 2009a)(Du et al.) but no data have been reported on human exposure or contamination levels.

Workers in industrial countries:

Stapleton (Stapleton et al. 2008) compared PBDE congener patterns among the three groups (foam recyclers, carpet layers and background population) to determine if there were any apparent differences that may be reflective of differential exposure. Differences in levels but not in patterns were apparent. The congener patterns in all groups were broadly similar to patterns observed in previous studies both in North America and in Europe. The POPs PBDE levels in foam recyclers and carpet layers were approximately an order of magnitude higher compared to related US background population (having already high levels).

Table 78: Concentrations of PBDE Congeners and PBB 153 Measured in Serum Collected from Workers and Control Groups (Median and Concentration Ranges are presented in ng/g Lipid; Values represent measurements Made by the CDC Laboratory) (Stapleton et al. 2008)

	foam workers (*n* = 12)		carpet layers (*n* = 3)		control group(*n*=5)	
compound	**median**	**range**	**median**	**range**	**median**	**range**
BDE-17	<0.4	<0.4 – 1.5	<0.5	<0.5 – 0.6	<0.4	<0.4 – 5.1
BDE-28	3.2	1.0 – 22.3	4.6	3.7 – 9.4	0.8	<0.4 – 150
BDE-47	77.8	19.5 – 540	100	73.9 – 151	7.9	<2.1 – 4640
BDE-66	0.95	<0.5 – 4.9	1.2	1.1 – 1.4	0.7	<0.5 – 42.6
BDE-99	26.1	5.8 – 185	23.5	19.1 – 26.6	3.1	<1.1 – 1200
BDE-100	20.5	5.8 – 136	18.3	13.2 – 20.0	2.0	<0.4 – 572
BDE-153	33.1	8.8 – 107	22.0	11.2 – 30.6	2.9	1.0 – 200
BDE-154	3.3	0.9 – 17.1	1.6	1.6 – 2.7	0.7	<0.4 – 69.7
BDE-183	0.5	<0.4 – 1.5	<0.4	<0.4	0.9	<0.4 – 2.1
ΣBDEs	160	67 – 973	178	125 – 241	19.3	1 – 7003
PBB-153	2.9	0.8 – 7.6	3.7	1.8 – 7.9	1.9	1.2 – 6.6
CB-153	25.8	3.6 – 62.4	47.4	11.8 – 57.7	37.7	4.5 – 54.7

The tetrabrominated congener, BDE-47, was the largest contributor to the PBDE composition in all samples except one individual from the control group. This one individual had the lowest concentration of ΣPBDE, 1 ng/g lipid, and only BDE 153 was measurable above detection limits. Among the remaining samples, the contribution of the individual congeners decreased in the following order: BDE-47 > BDE- 99 = BDE-153 > BDE-100 > BDE-28 > BDE-66 = BDE-154 (Stapleton et al. 2008).

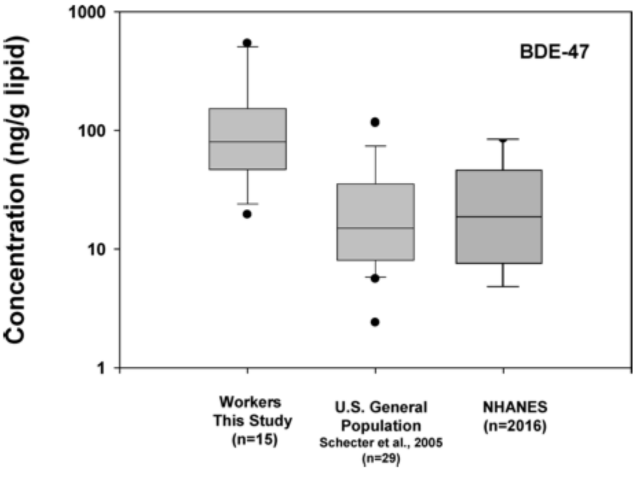


Figure 110: Box-plot of BDE-47 concentrations (ng/g lipid) measured in workers in compared to the general population as measured by Schecter et al. and the NHANES report (Stapleton et al. 2008).
The lower, middle, and upper lines of the box represents the 25th, 50th, and 75th percentile values, whereas the lower and upper bars represent the 10th and 90th percentiles, respectively. Values below the 10th and above the 90th percentiles are plotted as circles; values outside this range are not plotted for the NHANES data.

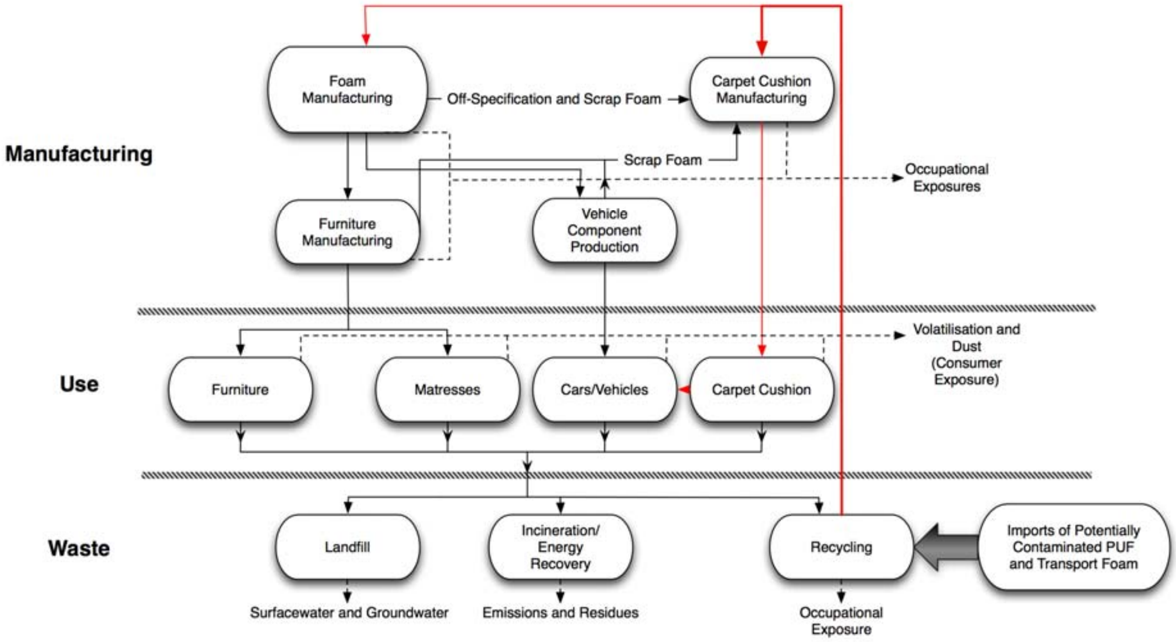


Figure 111: Simplified Life Cycle for PUR foam with recycling to carpet cushion (adapted from (USEPA 2005).

Sjodin measured serum levels of PBDE in a group of computer dismantlers at 26 ng/g, compared to 3.3 ng/g in a reference group of hospital cleaners (Sjődin et al. 1999).

The exposures of workers are generally higher than those of the wider population

Relevant Literature:

The literature was reviewed to establish what similar or relevant work had been undertaken in relation to flame retardants which might be used to inform the current review.

The current literature is rather limited and the most relevant assessments included:

1. A study by Simonson in 2006 described as a "*Cost Benefit Analysis Model for Fire Safety Methodology and TV (DecaBDE) Case Study*" and sponsored by the Bromine Industry (BSEF) (Simonson et al. 2006b, Simonson et al. 2006a).
2. An Impact Assessment for the European Parliament on the effect of amendments relating to, inter alia, the feasibility of substitution of halogenated flame retardants in the Commission Recasting Proposal on RoHS (Restriction on the use of certain hazardous substances in electrical and electronic equipment) (Lilico et al. 2010).
3. A declaration by Dr Brian Roach, an environmental policy analyst at Tufts University, to the US Bankruptcy Court in the Chapter 11 Bankruptcy proceedings against Chemtura addressing the health costs associated with IQ changes associated with BDE usage (Roach 2010).

In the first two cases the assessments are related to other BFRs and are framed in the context of the costs/benefits of fire protection in the case of the Simonson study and of substitution in the case of that by Lilico. The Lilico study was, in any case, a qualitative review in relation to the BFRs. Both have been subjected to robust criticism (see (Muir 2007)and (Evans 2010) (which points out an error of costing showing the results overestimate substitution costs which should be zero, instead of €24 billion!). Neither can be considered a good basis for consideration here. The third study is more relevant, dealing with POP-BDE specifically and based on recent research. It is therefore examined in more detail below.

Damage Costs Associated with Neurodevelopmental Impacts of PentaBDE use in California

The final assessment, by Roach (Roach 2010), is the only example specific to the POP-BDE (PentaBDE in that case) and is based upon the recently published results from Herbstman et al. relating to neurodevelopmental impacts (Herbstman et al. 2010a).

The Herbstman study was based on a cohort of mothers who were pregnant in New York during the 11th September 2001 terrorist attacks, which may have resulted in elevated exposure to PentaBDE relative to typical pregnancies. However, the paper notes that the median cord PBDE concentration in their sample from New York was actually lower than the median concentration from mothers in other parts of the USA such as Baltimore (Herbstman et al. 2007b). Zota et al. note that levels of BDE-47 were approximately twice as high in California (mean=36.2 ng/g lipid) when compared to the rest of the U.S. (mean=19.5 ng/g lipid) (Zota et al. 2008). Based on the analysis of Herbstman et al. this would imply an IQ decrease of about 1.3 to 1.9 points in California. The Herbstman study indicates that prenatal exposure to high levels of PentaBDE may reduce IQ levels by as much as 5 points. Specifically, each ln-unit change in BDE-47 levels resulted in a decrease in IQ scores of 2.1 to 3.1 points. Roach conservatively concluded that exposure to PentaBDE at the levels typically found in California will reduce average IQ scores by one point compared to the exposure levels found in other parts of the U.S.

The outcome quantified in this case, reduced IQ, has been studied in some detail and there have been a number of economic analyses which have estimated the financial damages associated with this effect:

- The EPA's comprehensive analysis of the Clean Air Act's costs and benefits included an estimate of the loss of lifetime earnings associated with a reduction in IQ levels due to lead exposure. The report concluded that the present value damages of each lost IQ point were approximately $3,000 based on a 5% discount rate (USEPA 1997). It should be noted that they also assessed that this increased to $42,000/point when the IQ was less than 70 so assuming just $3,000 on a population scale assessment would give a very conservative outcome as it underestimates the high cost losses at the lower end of the distribution.
- A recent analysis by Grosse et al. estimates that the economic benefit per additional IQ point from reduced lead exposure is $12,700 to $17,200 per individual in 2000 dollars (Grosse et al. 2002).
- Heinzerling and Ackerman note that analyses of damages per lost IQ point per individual as a result of lead exposure range from $1,500 to $9,000.

Roach considered that it was reasonable to assume that the damages for an IQ reduction due to lead exposure are applicable to an IQ reduction due to PentaBDE exposure, given that the impact, a reduction in lifetime earnings, would be the same. Based on the above studies, he assumed a conservative estimate of the present value per lost IQ point of $5,000 per individual.

Although not mentioned by Roach it is noted that the more recent values for IQ loss are significantly higher than those used in the declaration:

A paper by Pizzol et al. (Pizzol et al. 2010) valued the loss of one IQ-point for a Danish citizen at a much higher value of 18,918 Euros (2006 prices). For sensitivity Pizzol also calculated the results with a discount rate of 1.4%, (as in the Stern report (Stern 2006)) and obtained a value of 37,069 Euros (2006 prices) for each IQ-point loss.

Spadaro and Rabl(Spadaro & Rabl 2008)propose a value of 18,000 USD/IQ point lost for the U.S. When applied in other countries this is adjusted in proportion to per capita GDP, adjusted for purchase power parity. Based on extrapolations in NEEDS[117] a value of 8,600 Euro/IQ point lost has been used as an average for Europe.

Roach assumed that once the California market had become saturated with household items containing PentaBDE then:

- nearly all individuals were exposed.
- a 20-year exposure period from the early 1980s until 2003 when pentaBDE was removed from the market (although exposure clearly continued beyond 2003).
- the number of children born each year in California has historically been about 550,000

Thus a preliminary estimate of the economic damages in California as a result of pentaBDE exposure would be: 550,000 exposed individuals per year, multiplied by 20 years of exposure, multiplied by $5,000 damages per IQ point lost per individual.

He thus calculated the resulting economic damages would be $55 billion.

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[117] http://www.needs-project.org/

These damages would be higher if the IQ reduction from average PentaBDE exposure in California was greater than one point (as seems likely based on the exposures). Conversely, if the average IQ reduction was less than one point, the resulting damages would be less.

Roach also noted that if the average IQ reduction from pentaBDE exposure in California was only about 1/20 of a point then the costs of damage would still be $3 billion.

This analysis only includes damages to children born in California, and excludes other human health damages or ecosystem damages. While further analysis is clearly needed to provide a more accurate estimate of damages, these results suggest that actual damages are likely to be much higher than estimated.

If these results are applies to the health costs associated with recycling then a first order approximation would be based on applying a factor to the health costs for the proportion of POP-BDE which is recycled back into uses.

Petreas assessed that about 10% of the POP-BDE used in the USA were in California (Petreas & Oros 2009). For Penta BDE with a total production of c. 100,000 tonnes then it could be assumed that 10,000 tonnes of PentaBDE was responsible for the conservatively calculated damages of $ 55 billion – i.e $ 5,500,000/tonne.

Other factors confound this – such as if the exposure is likely to be increased by the use of carpet padding with a higher exposure risk for toddlers than the original application, for example. The most appropriate basis in these circumstances where there is great uncertainty about the exposure routes in the light of the paucity of information on recycling volumes from parties and observers is to proceed in line with the UNEP guidance on a qualitative basis rather than to attempt to apply what is likely to be a spurious degree of precision to a quantitative cost-benefit assessment.

Costs

The discussions in the POPRC in relation to both PentaBDE and OctaBDE were based on the assumption that the final listing would be in the same format as the original POPs list and thus including the new POPs in recycled products would be banned. The limited cost benefit assessments were undertaken on the same basis and concluded that the "*the overall consequence of a full global phase-out is most likely to be positive*".

The Risk Management Profile for OctaBDE said:

"Given the conclusions of the Risk Profile (UNEP 2007) for C-OctaBDE, its widespread global occurrence in biota and in humans, action taken or underway to phase it out in developed and developing countries and the increased demand for alternatives to C-OctaBDE, the overall consequence of a full global phase-out is most likely to be positive. Overall, the cost for developed countries of a phase out of C-OctaBDE should be small, as discussed above. However, specialized waste management and disposal related to C-OctaBDE (stockpiles and articles) could be costly for some countries and financial and technical assistance to developing countries should be considered to address this aspect as required".

The small costs assumed by POPRC are reflected in the competitiveness of the technologies which remove BFRs from polymer discussed in Appendix 3.

Another indication of costs in the case of PentaBDE and rebond could be obtained from the market for recycled foam. Given the long-established use of foam for rebond there is a surprising lack of information about the scale of the usage (and the levels of contamination). USEPA were unable to provide any details and the only data found for this indicated that in 2002 the rebond industry used 376,000 tonnes of scrap polyurethane foam and that of this approximately 23,000 tonnes came from post-consumer waste (Zia et al. 2007). There is no indication of how much of this post consumer waste contained PentaBDE but if it is conservatively assumed that this all contained PentaBDE at the maximum likely loading of c.5% this would represent 1,150 tonnes of PentaBDE being recycled. Historically flexible foam prices have ranged from c.25 to 35 cents/lb (International Sleep Products Association 2004). The current price of post consumer foam is reported to be very depressed at around 10 cents/lb indicating a total value of this market of between about $5 -15 million. In practice only a part of this is likely to be foam that has been treated with PentaBDE.

On this assessment the market is very small – and there are many alternative treatments available to reduce any economic impacts.

On the other hand if 1,150 tonnes of PentaBDE is being recycled then the first order approximation of damages associated with that usage would be in the region of $ 6 billion. Even if it was assumed that only 10% of the recycled foam contains PentaBDE then the damage costs would be 40 to 120 times greater than the value of the lost market if recycling of foam containing POP-BDE was to be stopped.

The impact on the industry should actually be much lower than the cost of all the post-consumer foam used in rebond. A low cost approach for the PUR foam recycling industry to avoid the contamination of their product by POP-BDE would be to screen and separate contaminated foams by the handheld screening methods discussed above and in Appendix 3.

However for WEEE recycling in developing/transition countries (the prevailing practice of WEEE plastic recycling) contaminating sensitive plastic streams (children toys or household goods) and generating contaminated megasites including PBDE and PBDD/DF pollution can not be justified from economic considerations. The assessment of the contaminated sites and associated remediation costs would need to include other pollutants like heavy metals from WEEE and is beyond the scope of this study. However the contamination of PBDE, PBDD/DF and PXDD/DF in soil and atmosphere and associated exposures and PBDE levels in human milk (PBDD/DF and PXDD/DF were not measured) demonstrate that PBDE are relevant contaminants at these sites.

For the assessment of the treatment of PWB in smelters data of PBDE and PBDD/DF contamination in workers and releases of PBDE and PBDD/DF into the environment and associated damages and human exposure. These data will be plant specific. As noted in the BAT/BEP section, BAT for these facilities need first to be defined after measuring release levels.

Appendix 5 (d): The effect of maintaining and removing the exemption on the needs of developing countries and countries with economies in transition

It is necessary to give consideration of the particular needs of developing countries and countries with economies in transition in the event that the option to recycle is:

(a) Removed - the exemption on recycling articles containing PBDE is removed; and,

(b) Maintained - the recycling exemption is maintained;

The actual difference in waste flows in either case is likely to be very small in relation to total flows – particularly given the relatively cheap availability of handheld equipment which allows sorting in the producing countries.

Considering first the removal of the option.

Recycling Option removed i.e. no recycling of products containing POP-BDE is allowed:

Considering the compiled PBDE inventory information it seems likely that for developing countries imported flows of materials for recycling would only be affected to a minimal extent. Most transition/developing countries do not have large stocks of POP-BDE in their own countries and it could reasonably be expected that in the event the recycling option was removed the exporting industrialised countries would take appropriate steps to sort and, where appropriate, to treat articles containing POP-BDE before export. Developing/transition countries can therefore require the materials sent for recycling (WEEE plastic, polyurethane foam, textiles) and goods for reuse (vehicles, electronic goods, textiles, furniture) exported from developed countries are PBDE free (or, at least, below the low POPs content level). The Basel Convention obviously has a key role in ensuring that there is no export of POP-BDE-contaminated materials.

Positive features:

- If recycling options are removed, the developed countries would need to better monitor their exports. Developing countries can require that the import of goods for recycling plastic and other are below the ‘low POPs’ content level.
- Recycling markets are protected against the risks of a consumer backlash to contamination of recycled articles by POPs. Ensuring that recycled materials are not contaminated by POPs is extremely important for the development and maintenance of markets for recycled materials.
- Some screening efforts directed towards PBDE in recycling and material flow (WEEE, WEEE plastic, PUF in mattresses furniture) will lead to more sustainable management of these flows.
- Addressing the presence of PBDE in consumer goods and screening and the phasing out of contaminated consumer goods used in daily life such as PBDE-containing furniture and mattresses is an important awareness raising tool which can result in much better protection of the consumer. Communicating and highlighting that materials used in daily life can contain hazardous POPs can become one of the best tools for raising the awareness of the public and politicians and for educating consumers about the implications of their purchasing choices. This can help with the development of more sustainable consumption. It can also be use for awareness raising of producers/exporters to care more on the content of chemicals in consumer goods leading to more sustainable production by associated requirements of producers/importers to the supply chain.
- Critically addressing PBDE in materials can help to promote the benefits of extended producer responsibility programmes and encourage countries to take legal steps in this direction. These programmes lead to an increased protection of consumers and to more sustainable production which also benefits industry.
- The greater restrictions on PBDE phase-out should lead industry (BFR industry, polymer industry, electronics industry) to consider whole life cycle assessments more carefully in future for the use of BFRs or other flame retardants.

Negative features:

- Some uncertainty remains on the options available for the recycling of all the plastic fractions from WEEE and so more material is likely to need disposal.
- It seems that for some WEEE plastic fraction levels can exceed limits set e.g. in the EU.
- If a country has received polyurethane foam from production in the US such materials would need to be screened for PBDE content and possibly phased out. This would however result in lower exposure of workers and the public.

Recycling option maintained – recycling of POP-BDE is allowed:

Positive features:

- Business as usual with little change in regulatory approach.
- Less screening efforts required for materials which may containing POP-BDE. However screening will still be required for some markets and, increasingly, for large risk adverse customers (major retailers etc) who will act unilaterally to avoid POP-BDE-contaminated products.

Negative features:

- Higher risk that POP-BDE-contaminated materials and POP-BDE-contaminated goods being exported from developed to developing/transition countries where reclamation and recycling can have serious health and environmental impacts.
- The potential consumer backlash to contamination of sensitive items like toys with POPs could severely affect the markets for all recycled products with highly damaging impacts on the future credibility of recycled materials. This in turn can increase the demand for virgin products and severely damage the recycling economies
- Higher exposure to PBDE-containing materials or goods imported to the country with increasingly obvious health and environmental damage.
- Low incentive to search for PBDE-containing materials in the country to phase out which is likely to result in higher generation of PBDD/DF through inappropriate waste management and open burning.
- Lower incentives to develop monitoring and possibly research on PBDE and generally brominated flame retarded material flow in the countries.
- The recycling of POPs sets a precedent that may be attractive in future cases for proposed POPs. Developed/transition countries are invariably the recipients of large quantities of contaminated materials from industrial countries and yet have little or no capacity to even analyse and certainly not to treat these chemicals when they become wastes. Future protection of developed/transition countries would be reduced if future recycling of future POPs is allowed or if the credibility of the Stockholm Convention is undermined by failing to protect human health and the environment.

Appendix 5 (e): Recommendations on the long-term environmental desirability of the recycling of articles containing PBDE;

The response from parties and observers to the secretariat included only one response, from Canada, confirming likely recycling of POP-BDE. This relates to two manufacturers who "*believe their rebonded foam carpet cushion may contain Penta and OctaBDE*". The Canadian submission added that "*more information is not forthcoming until analysis of this product can be performed*". Although there was no response from the USA it is known also that there are Rebond manufacturers using foam containing PentaBDE.

Although not identified by parties or observers, other waste streams which it is believed are likely to include recycling of materials containing POP-BDE are the recycling of ABS plastics and other polymers mainly from computer and office equipment housings.

Metals are also recycled from printed circuit boards (PWBs) but in this case the POP-BDE are almost certainly destroyed if BAT smelters are used.

No indication was given by any of the parties or observers of the scale of likely recycling operations or the economic value of such operations. Estimates in this review are that the value of recycling POP-BDE is very low – especially compared with the scale of health and environmental damage. It is noted that:

i. The recycling of plastics and polymers is generally desirable but it has become clear that little or no attention has been paid to the risks associated with contamination of the recyclates – even in those countries with restrictions such as in Europe. This is reflected in the paucity of information supplied by parties to the secretariat.

ii. The need to eliminate toxics including PBDE therefore becomes increasingly important and necessary in the light of the lack of effective control over the contamination of the plastic wastes recycling streams – it is clear that even sensitive uses such as children's toys are being contaminated with PBDE.

iii. Separation is possible, not particularly expensive and can further be implemented

iv. PBDE in PUR foam need to be phased out to protect consumer and workers. Foam can be screened and separated with Br-screening technologies and other foam further be recycled.

v. The recovery of PWB in smelters is undoubtedly useful from a material recycling perspective but releases of PBDE and PBDD/DF need to be further assessed – even for those plants currently considered to represent BAT. These facilities are currently processing tens of thousands of tons of wastes containing PBDE and other precursors of PBDD/DF. BAT standards such as the requirements of afterburner configurations and air pollution control devices need to be defined in Stockholm Convention BAT/BEP guidance.

vi. Other thermal recovery technologies (other secondary metal industries, cement kilns, feedstock recycling technologies) used for recycling/recovery or destruction need to be further assessed and operation conditions for the treatment of PBDE-containing materials need to be defined in Stockholm Convention BAT/BEP guidance.

There is a serious risk to the long-term credibility of recycling if consumers associate recycled products with POP contamination. This could have a profoundly damaging impact on the recycling industries, not only for polymers but, by association with the implications of low-regulation and poor quality control, for other materials. This in turn could have a major impact on the demand for virgin materials at a time when it is crucial that recycling should be promoted – not least as a tool to reduce the impacts of climate change. Nicholas Stern (Stern 2009) wrote:

"*Recycling is already making a major contribution to keeping down emissions. Indeed, its scale is so little appreciated that it might be described as one of the 'best kept secrets' in energy and climate change....New technologies for separating out forms of waste could also have a great impact.*"

The strong recommendation from the authors of this review is that the recycling of articles containing PBDE (where the articles are not first treated and the PBDE removed) should be stopped as soon as possible. Failure to do so will result in larger quantities of PBDE becoming dispersed into matrices from which recovery is not technically and economically feasible. The issues at stake include the ability of the Stockholm Convention to achieve it's principal objective and the credibility of recycling with consumers – risking vital resources at a time when conservation is crucial.

These conclusions are consistent with responses from other parties. A report commissioned by the New Zealand Ministry of the Environment says (Geo & Hydro – K8 Ltd 2010) that the high levels of BDE in house dust provide "*a case against recycling BDE-containing polymers*".

They warn:

"Despite the low levels of commercial Penta BDE imported and used in manufacturing the natural breakdown of commercial Deca BDE could lead to a future rise in presence of the lower-brominated compounds which are more soluble, more bio-accumulative and more toxic. Recycling will keep these articles in our environment 'forever' if the recycling is 100%, or in an ever more diluted form if less than 100% effective and should therefore be avoided".

And conclude:

"It is not recommended to recycle plastics which are suspect of containing BDE. An efficient recycling system extends the lifetime of BDE in our environment and would prolong our exposure to BDE. A total bromine screening system for polymers eligible for recycling would reduce our exposure to BDE, while maximising the volume of recyclable polymers".

Similarly the Swedish response says (Retegan et al. 2010):

"Since the general request from the Swedish market is for BFR-free products, and halogen-free alternative flame retardants are now emerging, the industry in Sweden has little interest in recycled plastics containing BFRs: consequently there is no interest in an exemption from the ban of penta- and octa-BDE for materials recycling of these plastics".

The findings of the April 2010 report for the Swedish Environmental Protection Agency were (Retegan et al. 2010):

- *In Sweden, the recycling industry separates WEEE plastics containing BFRs from other WEEE plastics. The former fraction is incinerated in Sweden at authorised plants. The latter fraction is exported to Asia for materials recycling.*
- *The recycling industry in Sweden has no intent or plans to subject BFR-containing plastics to materials recycling. The use of BFRs and EEE products containing BFRs is expected to decrease in Sweden.*
- *From a Swedish perspective, there is no industrial interest for an exemption from the listing of octa- and penta-BDE for materials recycling of plastics containing PBDE.*

Furthermore the previous consideration of the POP-BDE by POPRC was all on the basis that the commercial mixtures would be listed for elimination. The Conference of the Parties accepted that the POP-BDE have the properties of POPs and it is difficult to reconcile the continued use of these chemicals in recyclate with the intentions of the Convention especially as the evidence of health effects at current levels hardens as dicussed in Appendix 5 (c).

Appendix 5 (f): Recommendations for the elimination of PBDE from the waste stream.

The complete elimination of PBDE from the waste stream is undoubtedly an extremely challenging task.

The comparison with open-uses of PCBs is an instructive one. The main open applications of PCBs, as sealants in buildings, are relatively straightforward to address compared to the wider ranging and more dispersed uses of PBDE. Few parties have even included these open PCB uses in their National Implementation plans and inventories, still less managed to address them in practice. Norway, Sweden, Finland, Switzerland and with a less systematic approach also Germany are really the only parties who have made any serious attempts to decontaminate existing buildings. In the case of PBDE the limited responses to the questionnaire from the Secretariat and the near absence of any information on inventory indicates how far there is to go with PBDE. Furthermore it is more important to act promptly in the case of PBDE for several reasons.

- Exposure to PBDE is generally more direct – and in the cases of the most heavily affected individuals is through dust and particles released from PBDE-containing furniture, carpets, mattresses etc. rather than through the food chain (at least in the first instance). Delaying action at this stage may lead to renewed exposure in the future through foodchain routes as discussed in Appendix 2.
- The PBDE tend to be in articles with a shorter life than e.g. the PCB sealants in buildings or transformers in operation. Once PBDE articles have been committed to the waste/recycling streams then there is currently a high chance that at least some, and possibly most, of the PBDE will end up in a course of treatment associated with high emissions in particular after export to developing/transition countries where simple technologies are applied leading to PBDE releases and a significant risk of the formation of PBDD/DF and probable contamination of sensitive plastic streams such as children toys or other household goods. But even current recycling practice in developed countries like the US and Canada where PUR foam can be taken from relatively isolated uses and recycled into carpet padding can lead to large increases in exposure risk for particularly vulnerable babies and toddlers.
- When POP-BDE are used in recycling, future recovery is likely to be extremely difficult as the concentrations are generally diluted and the difficulties of identification of contaminated articles are increased enormously. Furthermore the likely consumers of much of the contaminated lower grade plastics containing POP-BDE will be in other developing/transition countries where final disposal is more likely to involve open burning for fuel or on landfill sites. It is noted, for example, that even UNEP is encouraging the burning of plastic waste which will be likely to include low quality imported plastic items in slum cookers in Kibera, Kenya:

Photograph 4: UNEP sponsored slum cooker – Kibera, Kenya[118]

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[118] *www.unep.org/cpi/briefs/2007Aug31.doc*

The designers are reported to be "trying to reduce the foul-smelling smoke"

- PBDE still in stocks in developed countries can best be detected in the recycling flow in these countries due to developed technologies to detect PBDE/BFR-containing materials and be phased out in this using the recovery options described in Appendices 3 and 4. It is very unlikely that such a phase-out will be feasible after export of PBDE-containing materials to developing/transition countries due to the lack of appropriate monitoring/screening capacity in these countries. Also appropriate thermal recovery facilities and destruction facilities are not available in developing/transition countries as can be seen from the large challenges, negative experience and high costs of managing PCBs or POPs pesticides in these countries.
- Further disposal of PBDE to landfills need to be avoided since PBDE deposited in landfills are slowly leaching into the environment resulting in the contamination of associated surface waters, sediments and fish (Oliaei et al. 2010) and contamination of nearby communities or informal waste pickers on landfills. The lessons learned from PCBs (having similar physico-chemical properties and POPs properties) as currently documented in a national screening of PCB contamination of fish in Swiss rivers and associated contamination from deposited PCBs in landfills (Zennegg et al. 2010) might lead to a change of approach to landfill in the future.

If the majority of POP-BDE could be treated using BAT-BEP recycling and disposal with extraction and destruction of the PBDE/BFR in the case of recycling then it is just possible that near elimination could be achieved (apart from those stocks already residing in landfill sites and which have already escaped into the environment). Any scenario which involves informal recycling/recovery operations as currently structured, however, is almost certain to fail.

Any serious attempt at elimination therefore requires that exports of POP-BDE-contaminated articles to developing/transition countries for recovery must be controlled much more rigorously than has previously been the case. Yu (Yu et al. 2010b) proposed that for trade control policies to mitigate the environmental impacts of informal recycling two conditions must be met:

Firstly - that such trade policies must be effectively enforced. There are clearly governance challenges to implementing trade controls, as demonstrated by repeated failures in practice. The import to China of e-waste has been banned for nearly a decade but is reported to continue largely as it did before policies were implemented (Chisholm & Bu 2007)(Li et al. 2008c, Xing et al. 2009, Zennegg et al. 2009, Wu et al. 2010). Only 60% of e-waste is recycled under existing national systems in Europe, and despite an export ban, it is thought that the remaining 40% is exported to Asia or Africa (United Nations University 2008).

Secondly – a vital condition for trade bans to work effectively is that they must cut off the supply of e-waste to informal recyclers. This effectiveness is predicated on the assumption that the main source of e-waste is imports from the developed world. This has been tried in China but has not succeeded to-date because the informal recyclers have consistently undercut the formal establishments (Yu et al. 2010b).

The challenge of POPs PBDE elimination is enormously increased by, as seems increasingly likely, DecaBDE debromination to the POP-BDE and partly convertion to PBDF (taking place even during the application phase and in non-BAT thermal end-of-life treatments). The consequence of this is that rather than being faced with the task of eliminating around 200,000 of POP-BDE the total reservoir would be increased to nearly 1.5 million tonnes. Furthermore production is still continuing and the uses of DecaBDE are significantly more distributed. There are also far more products in which DecaBDE has been recycled.

In summary, therefore, PBDE should be eliminated where possible and reasonable from a socio-economic and technological perspective to avoid further contamination of material recycling flows and of products from recycling and to reduce to a minimum any further contamination of humans and the environment.

I) Articles containing PBDE destined for recycling

Nearly all the stocks of PBDE are contained in articles in storage or use in industrial countries. Current approaches to waste management mean there is a high probability of export of a large proportion of these stocks to developing/transition countries for recycling.

a) PBDE in WEEE

A large proportion of WEEE containing PBDE are sent to developing/transition countries for recycling or reuse. This often results in contamination of workers and the environment from the primitive recycling methods used (see Appendix 3(c) and 5 (c)). To tackle this problem a range of international initiatives are currently underway including programmes under the Basel Convention. This is also a priority area for SAICM. The future Stockholm Convention activities should be harmonised with the ongoing activities of the Basel Convention and SAICM in this sector for establishing ESM of this waste stream.

b) PBDE in plastic from WEEE recycling

Separation technologies for BFR-containing plastic are operating in full scale. After separation of BFR and non-BFR, the BFR-containing fraction can be destroyed or the PBDE/BFR be removed from the polymer such as by the Creasolv process. This allows the cleaned resin fraction to be recycled and the high bromine fraction recovered.

If the PBDE/BFR-containing plastic fraction is to be destroyed/thermally recovered this has to be done in appropriate facilities taking care that the destruction process does not release PBDE or form and release PBDD/DF.

For several regions POP-BDE content is expected to be very low. In many cases these are likely to be below thresholds of regulatory concern (depending on the levels established by the Stockholm and Basel Conventions for a low-POPs level) and appropriate screening may show that levels of contamination do not present barriers to recycling in these countries.

c) PBDE-containing polyurethane foam

Simple handheld equipment can be used to screen the bromine content of post-consumer PUF used in recycling schemes for carpet padding and similar applications particularly in North America. This allows the easy sorting of bromine-containing PUF and the elimination of POP-BDE in recycled foams. To avoid releases in the long-term, any PUF identified as being contaminated should not be landfilled. BAT facilities should be used for destruction/thermal treatment taking care that the destruction process does not release PBDE or form and release PBDD/DF.

d) Printed wired board (PWB)

Printed wired board (PWB) should only be treated in BAT smelters with after burner. The gap analysis indicates that the details of the specification of the after burner (temperature and residence time) needs further investigation and assessment.

Alternative recycling approaches using mechanical recycling and separation of plastic and bromine have been developed at a laboratory scale. Demand is increasing for such technologies and the development should be continued to pilot or full scale and integrated with treatment in smelters[119].

II) PBDE articles destined for waste treatment

Even in industrial countries, a large proportion of articles containing PBDE are normally landfilled. This practice, as noted above, is not sustainable when releases are assessed over a long-term perspective.

a) Automotive shredder residues (ASR)

In addition to PBDE, ASR contains other toxic chemicals and elements including heavy metals and PCBs which need appropriate treatment.

b) PBDE in building insulation

Some countries (e.g. Switzerland, Germany but possibly others) have used PBDE in rigid PUR foam and other materials in longer life application in construction. Considering that HBCD is under consideration for listing as a POP this waste fraction might become increasingly important for POPs management. It is therefore important to consider the co-benefits of treatment of construction wastes.

III) Articles containing PBDE currently in use

The main human exposure route is considered indoor exposure. Possibly or most probably PUF in old furniture, mattresses, carpet padding, textiles (curtains etc.) etc. Therefore it should be evaluated if it would be wise to promote phase out e.g. PBDE-containing furniture.

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[119] The precious metals would ultimately be recovered in smelters. Therefore this process is not a competition for smelters but is a pre-treatment step which has the potential to increase recovery and reduce emissions.

IV) Articles containing PBDE destined for re-use

Some PBDE-containing articles are possibly reused. This includes, for example, second-hand cars, electronics and furniture. This seems in particular relevant for the US marked and for exports of goods for reuse from the US (vehicles, furniture containing PUF, electronics). It might be considered whether cars or electronics for export could be screened and, if free of PBDE, issued with appropriate certification allowing export.

Appendix 6: Knowledge Gaps and Confounders

The terms of reference included the identification of knowledge gaps as Item 3 (f) in relation to the assessment of possible health and environmental impacts of recycling articles containing PBDE. It has become clear during the course of the research that there are relevant knowledge gaps in relation to many of the other issues addressed in the terms of reference. These have been included in this section which thus sits more comfortably at the end of the substantive Appendices rather than in the middle where a reader may be particularly confused to read about knowledge gaps relating to sections of the work which had not yet been read.

The final fate of DecaBDE and the scale of debromination to POP-BDE is one of the largest uncertainties and knowledge gaps that has been found during this study and this has been addressed in more detail in Appendix 6 (b).

The gaps found during the review and described in Appendix6 (a) include:

- Gaps relating to the production, use and substance flow of materials:
    - Production data PentaBDE and OctaBDE
    - Data on application of PentaBDE and OctaBDE
    - Recycling flows and end-of-life of PBDE-containing materials
- Appropriateness of current RfD values
- Some key health aspects, including genotoxicity and testing at doses relevant to human exposures, have not been addressed yet.
- Occupational exposure and levels in workers from BAT and non-BAT treatments (material recycling schemes, metal industries, feedstock recycling)
- There are often very high outliers in exposure studies, and sources of contamination in humans with extreme PBDE levels have not been established yet. This is an urgent issue considering the levels of contamination which may, when aggregated, affect hundreds of thousands of people including sensitive children/toddlers.
- Hydroxy and Methoxy PBDE (health relevance, formation extent)
- Analysis and screening of PBDE and Bromine in articles
- Separation and sorting technologies
- Manual pre-separation quality with and without instrumental detectors
- Technology for automatic separation of PBDE/BFR-containing plastic
- Metal plants (destruction efficiency, PBDE and PBDD/DF release)
- Incineration (releases from non-BAT incinerators; corrosion at high Br input, grate sifting management)
- Cement kiln (PBDE wastes processed, feeding points for PBDE waste fractions, destruction efficiency, PBDE and PBDD/DF release, accumulation of Br in kiln)
- Thermal recovery and feed stock recycling technologies
- Extent and fate in pyrolysis and gasification of materials containing or possibly containing PBDE for feedstock recycling (and waste destruction)
- PBDD/DF and PXDD/DF
    - Total release of PBDD/DF conversion in the life cycle of PBDE
    - Respective share of PBDD/DF in the environment, food and humans from POPs BDE, DecaBDE, other BFRs and other processes.
    - Source of high levels of PBDF in Japanese housedust
    - Sources of high share of PBDD/DF in UK food (30%) and
    - Time trend of PBDD/DF
- Respective share of PBDD/DF in the environment, food and humans from POPs BDE, DecaBDE, other BFRs and other processes.
- Relevance of debromination of DecaBDE (see below in dedicated section)
- Long term fate of PBDE in landfills.
- Climate change (effect on debromination; fate of draught and large scale fires)

Knowledge gaps which possibly could be addressed by the science community were communicated at four major scientific meetings. Conference papers have been submitted and accepted at BFR2010: The Fifth International Conference on Brominated Flame Retardants (Kyoto, Japan); the UK POPs Conference (Birmingham, UK); the SETAC Asia Pacific meeting (Guangzhou, China) and the Dioxin2010. The abstracts are included in the supporting Annex 1.

Appendix 6 (b) is titled also with ‘Confounders’ as the issue of DecaBDE and the potential for debromination is such an important one that it could dramatically change many of the tentative conclusions in this report in relation to mass flows, emission levels and remaining stocks. Appendix 6 (b) therefore includes a substantive section on the science relating to debromination. This was an issue considered by POPRC during the process of reviewing the POP-BDE – most notably in a review prepared by Professor Ian Rae in 2008 (Stockholm Convention 2008b). This concluded:

"*New results will no doubt continue to appear in refereed literature and these will need to be assessed by the POPRC as they appear*"

It is therefore hoped that Appendix (b) will provide some assistance with that process.

Debromination is an important mechanism for the ultimate degradation of PBDE. Key issues are the degradation pathways and rates for the lower-brominated congeners constituting the commercial mixtures of PentaBDE and OctaBDE balanced against the impacts arising from the debromination of the higher brominated PBDE (OctaBDE, NonaBDE and DecaBDE). DecaBDE and NonaBDE are reported to contribute nearly 70% of the composition of some c-OctaBDE mixtures such as Bromkal 79-8DE (see Appendix 2). The much larger stock of highly brominated PBDE stem from commercial DecaBDE of which well over one million tonnes has been produced as noted above.

In the Appendix consideration is therefore given to the possible contribution to the POP-BDE from the much larger reservoir of the higher brominated PBDE with emphasis on DecaBDE – the stock of which continues to increase in most of the world.

The finding in recent scientific literature and the feedback from the scientific meetings attended as part of this work is that the evidence for debromination of DecaBDE as an important pathway is getting much stronger each year. The general view of the wider scientific community is no longer "*if*" debromination is happening - and is environmentally relevant – but rather "*how quickly*" it is happening and what the finer details of the metabolites and pathways are.

A range of knowledge gaps exist in respect to debromination of DecaBDE (and Hepta/OctaBDE)

- Details on time scale of debromination in different media (e.g. in landfills, sediments, soils, atmosphere, biota).
- The dimension of debromination and related POPsBDE formation
- The formation of other degradation products (PBDD/DF, hydroxyl-PBDE, methoxyBDE, other degradation products)
- Conditions where complete debromination can be achieved (in technical processes and in natural environments)

Appendix 6 (a): Knowledge Gaps

This Section details the knowledge gaps identified during the course of preparing this review.

Gaps relating to the production, use and substance flow of materials:

To understand and model the flow of PBDE, a dynamic substance flow analysis To understand and model the flow of PBDE, a dynamic substance flow analysis should be performed on global scale. Such dynamic substance flow analysis of BFRs have been developed on national scale (Morf et al. 2002). The European Environmental agency has acknowledged that the systematic approach to substance flow analysis has significant benefits and can be applied in practice (EEA 2007). These substance flow analyses are the preferred approach to quantifying flows and current stocks of substances. They are also a good foundation for the development of robust life cycle assessments (EEA 2007).

On an international scale there are significant information gaps to be overcome in relation to the development of a dynamic substance flow analysis for the POP-BDE.

Production data PentaBDE and OctaBDE

Data Gaps exists in the PentaBDE and OctaBDE inventory of the US, Israel and EU producers.

No data have been found (or supplied by parties) in relation to historic PentaBDE and OctaBDE production in China or other countries potentially active in relation to the commercial production/use of BFRs such as Korea, Ukraine, Russia and India.

Data on application of PentaBDE and OctaBDE

Quantitative data on application is scarce.

The substance flow analysis of Morf et al in 2002 and 2008 (Morf et al. 2002) contains some details.

During the consultancy work contacts with the bromine industry were developed and the industry indicated a willingness to support further implementation work related to PentaBDE and OctaBDE (Hofland 2010b).

Further information will almost certainly be needed from those industrial sectors having applied PBDE (in relation to plastic, PUF and textiles).

Recycling flows and end-of-life of PBDE-containing materials

There is some data on PBDE-containing materials at the end-of-life. In both Europe and the US, where this still continues, a large proportion (probably around 80%) ends up in landfill site (Alcock et al. 2003)(Morf et al. 2003)(Petreas & Oros 2009). A few countries have destroyed, thermally recovered or feedstock recycled a larger share but even Switzerland, with a historic policy of incineration, has large landfill stocks (Morf et al. 2007).

a) WEEE plastic has been recycled for a number of years with little or no record keeping:

A large part of WEEE and separated plastic from WEEE are exported e.g. from Europe. While some data on PBDE content in end-of-life products is available (generated due to WEEE and RoHS legal requirements), detailed data on total export are available to some extent. There are limited or no data from other regions.

b) PUF: PUF is recycled to some extent as carpet padding for the North American market. Although the issue has been reviewed in some detail as part of this report the actual extent of recycling of treated foams is not known (and USEPA, when asked, had no data on this). Zia says that in 2002 the rebond industry used 376,000 tonnes of scrap polyurethane foam and that of this approximately 23,000 tonnes came from post-consumer waste (Zia et al. 2007). There is no indication of how much of this post consumer waste contained PentaBDE but if it is conservatively assumed that it all contained PentaBDE at the maximum likely loading of c.5% this would represent 1,150 tonnes of PentaBDE being recycled. In reality the actual quantity is likely to be significantly less than this as not all post-consumer foam will have been treated. There is no indication, however, of whether 2002 is representative of other years and how usage might have changed. Whilst it is thought that this recycling has mainly taken place in the United States and Canada the extent of any recycling of PUF for similar uses in other regions is probably only small but total quantities involved are unknown.

c) Textiles: Some PBDE/BFR-treated textiles has been used in transport but there is little data on the commercial mixtures involved, the levels of usage or the greographical distribution of use. Some PBDE-containing textiles might be recycled Textiles. The export of cars, commercial vehicles, 'planes and trains to developing countries might provide a significant transfer of POP-BDE but it is currently not possible to quantify the extent of this movement. Better data is needed on levels of POP-BDE in textiles and their use in vehicles.

d) Automotive shredder residues: Few data exist on PBDE content in automotive shredder residues. However this is an important global waste category which needs to be controlled in respect to UPOPs (Stockholm Convention 2007b) and PBDE (and other toxics) release. Better evaluation is needed of the PBDE content and fate (particularly in relation to metallurgical processes such as electric arc furnaces and secondary aluminium plants. But also the use in cement kilns need further assessment. Also a wider analysis of the actual levels of leaching from landfills in the light of the concerns raised by Danon-Schaffer and Oliaei (Danon-Schaffer 2010) Oliaei and other studies (see Appendix 3 (c)) and more systematic studies in respect to waste deposited and releases in leachates need to be performed.

Further detailed inventory work and substance flow analysis might usefully be co-ordinated by an UN organization in cooperation with experienced research institutions. The participation of all stakeholders, including manufacturers and producers of goods containing PBDE would be essential if some of the serious deficiencies in the current database are to be filled effectively. Incoming data on PBDE in products, recycled products and end-of-life products generated in the countries could be included in such a compilation.

Analysis and screening of PBDE and Bromine in articles

The standard GC/MS analysis for PBDE is expensive and time consuming and can not be used for broad screening of articles as required in recycling schemes.

There are rapid analysis methods for PBDE available on the market (see Appendix 4 (a)). However there is no detailed reporting on the accuracy of these methods on quantification of PBDE in materials as these methods have not been thoroughly assessed for their accuracy. It is important to establish:

- What is the accuracy of the rapid screening methods for PBDE?
- What are key parameters upon which the accuracy depends?
- Early GC analysis of DecaBDE was difficult because of debromination of DecaBDE and the higher brominated compounds during the analysis - are the analyses of TetraBDE to HeptaBDE by the rapid screening technologies similarly affected by debromination during the analysis of DecaBDE (and NonaBDE and OctaBDE) ? If so, then to what extent?
- Whether the time for rapid analysis can be reduced from 15 to 30 minutes per sample as this is normally too long for practical applications in recycling.
- What are the options to use online monitoring technologies, such as those developed for online monitoring for PCDD/DF and other chlorinated aromatic compounds, to monitor PBDE in materials?

POP-BDE are most probably in relative low levels in the waste/recycling flow of most developing countries. There is however no monitoring and therefore large knowledge gaps. Here monitoring programs involving clever screening of a combination of bromine screening and PBDE measurement with GC/MS (or other appropriate method) are urgently needed to establish the scale of the stocks in developing countries and to establish whether POP-BDE are still adding to those stocks through imports of contaminated recycled plastics.

Separation and sorting technologies:

In the past it has been mainly plastic from television and computers which have been separated (BFR and non-BFR) in those countries with established recycling and waste management infrastructure (mainly EU). Recently also mixed plastic is separated in some facilities. Only a few data are available on the PBDE content of the resulting polymer fractions. Systematic data for the different separation technologies and combinations of technologies should be generated.

Manual pre-separation with and without instrumental detectors

Sweden indicated that they utilised manual separation based on experience of pre-separating staff and based on manuals for pre-separation. It would be useful to confirm how effective these manual separation techniques are in other countries and what level of sorting errors might be anticipated if they were applied more widely (and to other waste streams apart from TV/ monitor housings).

Several methods of instrumental detection of bromine have been developed. Three of these methods are applied in practice for separation of BFR-containing WEEE plastic (Sliding spark spectroscopy, XRF and XRT)

- What are the practical experiences of sliding spark spectroscopy for separation of BFR-containing plastic in industrial countries and in developing/transition countries? Are there specific limitations in practice?
- What is the practical experience of the combination of sliding spark spectroscopy and NIR technology to separate BFR and plastic type? Are there specific limitations in practice?
- What is the practical experience of XRF technologies for separation of BFR-containing plastic in industrial countries and in developing/transition countries? Are there specific limitations in practice?

From measurement principle these technologies should be usable for other materials than WEEE plastic, including PUF, therefore it would be interesting to:

- Confirm the options and limitations of these technologies for other BFR-containing materials including PUF for carpet padding.

Technology for automatic separation of PBDE/BFR-containing plastic

XRT separation is applied in full scale to separate BFR (and PVC) plastic in at least two sorting facilities in Europe. This report contains data on the separation quality for one sorting facility which demonstrates a high sorting efficiency.

It would be useful to further evaluate

- What are the long-term experiences with XRT technology to separate BFR-containing plastics?
- What are the experiences with different WEEE waste types (the data in this report comes from small electrical appliances and white goods)?
- Which plant size is necessary to justify the relatively high investment in this costly technology (approximately € 400,000)?

Thermal recovery and feed stock recycling technologies:

Dummler reported that the formation of PBDD/DF (in a municipal waste incinerator) is "*greatly enhanced*" by the presence of antimony (III) oxide when burning DecaBDE (Dumler et al. 1990). As antimony is typically used as a synergist with the POP-BDE commercial mixtures it is important to confirm the effects of antimony on the generation of dioxins and furans in practical situations in all thermal treatments. Similarly the implications for ash and residue disposal – not least because antimony is chemically and toxicologically close to arsenic and often partitions to bottom ashes in incinerators (Paoletti et al. 2001).

Metal plants

Recent studies have reported releases of PBDE and PBDD/DF from metal industries (copper smelters, electric arc furnaces, sinter plants, secondary aluminium industry) revealing that also PBDE/BFR-containing materials are entering these facilities (Du et al. 2010)(Du et al.)(Du et al. 2009)(Odabasi et al. 2009)(Wang et al. 2010c).

Copper smelters

Although a quantity of PBDE/BFR-containing materials go into copper smelters, no comprehensive monitoring studies appear to have been performed (or, at least, published) regarding PBDE, PBDD/DF and PXDD/DF releases. To properly evaluate the environmental and health impacts of options including these technologies monitoring data is required in respect to

- The release (air, solids, water) of PBDE, PBDD/DF and PXDD/DF during processing of PBDE/BFR-containing PWB or PBDE-containing WEEE plastic.
- The body burdens of PBDE and PBDD/DF in workers at copper smelters treating PWB and WEEE plastic
- What are the requirements for afterburners (residence time and temperature)?
- What level of air pollution control technology is necessary to ensure that PWB can be safely processed with acceptably low emissions of PBDE and PBDD/DF?

Electric arc furnace (EAF)

The following knowledge gaps exist:

- What type and amount of PBDE-containing wastes are entering EAF furnaces?
- What is the destruction efficiency for PBDE materials in EAF for different technology levels?
- What level of technology is necessary to ensure PBDE-containing waste can be treated in an EAF with acceptable emission levels?

Primary steel plant (blast furnace, coke plant, sinter plant)

Recent studies on PBDE and PBDD/DF emissions sinter in plants in Taiwan demonstrate their presence and releases from this industry (Du et al. 2010)(Du et al.)(Wang et al. 2010c). Plastic is used in the primary steel industry either directly in the blast furnace to substitute coke or in the coking plant as a substitute for coal in the production of coke (Japan National Institute for Environmental Studies 2010)(European Commission 2009) which might be the PBDE and PBDD/DF sources in the mentioned studies but no input assessment has been performed in these studies.

The following knowledge gaps exist:

- What are the sources of PBDE and PBDD/DF release from sinter plants?
- What are the destruction rates if PBDE-containing materials are added in the primary steel industry (coke plants, blast furnace)[120]?
- How representative are the emissions reported to date?
- What levels of bromine, and in what form, are released from coke plant and blast furnace when PBDE/BFR-containing plastic (or other materials) is added?
- What is the substance flow of PBDE/BFR in primary steel industry when PBDE/BFR materials are recovered in coke plants or blast furnace?
- What level of technology is necessary to allow the safe treatment of PBDE-containing waste by the primary steel industry?

Secondary aluminium industry

The following knowledge gaps exist:

- What type and amount of PBDE-containing wastes are entering secondary aluminium smelters?
- What is the destruction efficiency for PBDE materials in secondary aluminium industry for different technology levels?
- What level of technology is necessary is necessary to allow the safe treatment of PBDE-containing waste in a secondary aluminium smelter?

Antimony plants recycling WEEE plastic

There are no published reports on monitoring of PBDE and PBDD/DF during Antimony recovery of WEEE plastic.

The following knowledge gaps exist:

- Extent of WEEE plastic use for Antimony recovery?
- What are the PBDE destruction rates and the levels of PBDE and PBDD/DF releases in Antimony smelters when WEEE plastic is recycled?
- What level of technology is necessary to allow the safe treatment of PBDE-containing waste in Antimony smelters?

Incineration

The following knowledge gaps exist for treatment of PBDE-containing waste in incinerators

- More extensive reporting of the levels of PBDE and PBDD/DE in bottom ashes are needed with known levels of PBDE input materials.
- Practice of management of grate siftings.
- The influence of bromine levels on the production of chlorinated UPOPs (including PCDD/DF) and other products of incomplete combustion.
- Levels of corrosion in the boiler section when high load of PBDE/BFR-containing wastes are processed e.g. for recovery of bromine and the associated economic benefits and drawbacks.
- PBDE-containing household waste can enter non-BAT incinerators. The extent of PBDE and PBDD/PBDF release from non-BAT incinerators have not been reported.
- The European Scientific Committee on Toxicity Ecotoxicity and the Environment warned in relation to the incineration of PBDE (DecaBDE in this case) that "*Incineration of such material may also form PBDD/Fs, and also dioxins and furans containing both chlorine and bromine. The latter may even decrease the amount of PCDD/Fs in the emissions, compounds measured for compliance with specific permits*" (Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) 2002). It is important to establish whether the lower emissions of chlorinated dioxins may mask overall higher

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[120] The addition of PBDE containing materials directly to sinter plants have not been reported and seems not appropriate considering the relative slow increasing temperature gradient and the high gas volumes, which could be expected to lead to desorption and release rather than to destruction.

emissions of brominated dioxins given that no regulatory regime regularly monitors PBDD/DF emissions from incinerators.

Cement kiln

Cement kilns are considered by the Bromine and Cement industries as a possible energy recovery option for plastic waste containing PBDE/BFRs like WEEE plastic (Tange & Drohmann 2005) or automotive shredder residues. However no study has yet been published on the destruction efficiency of PBDE/BFR-containing waste in cement kilns which provides data on the monitoring of releases of PBDE and PBDD/DF.

The following knowledge gaps exist:

- Which PBDE-containing wastes have been and are being processed in cement kilns (and how do these relate to BAT/BEP and the e.g. Holcim positive/negative lists)?
- If PBDE-containing wastes have been (are being) introduced to cement kilns, at which feeding points are they introduced in practice?
    - Whether and what PBDE-containing waste is fed into cement kilns at the hot (burner) end – and what the options and limitations are.
    - Release of PBDE, PBDD/DF and PXDD/DF, if PBDE-contaminated waste is fed into the kiln at the cold end of the kiln. And what requirements on the technology is necessary?
- The clinker cooler has been suggested as offering conditions conducive to the formation of PCDD/DF (Kikuchi et al. 2006). Monitoring of PBDE, PBDD/DF and PXDD/DF should therefore include levels of these compounds before and after the clinker cooler for operations where PBDE/BFR-containing materials are fed.
- The long-term effect of feeding PBDE/BFR-containing materials on the operation of cement kilns and emissions by, for example, possible accumulation of alkali-bromide slag around the pre-heater or lower cyclones. Long term monitoring of PBDE and PBDD/DF releases.

Pyrolysis and gasification of materials containing or possibly containing PBDE for feedstock recycling and waste destruction

While a range of laboratory and pilot plant studies have been performed for feedstock recycling of PBDE/BFR-containing materials (e.g. plastics from electronics, Printed circuit boards) it is not clear if and in which scale full scale processes have been established utilizing PBDE-containing materials to produce e.g. alternative fuels. Ukraine mention in their questionnaire response that "*there is medium scale recycling of plastics and mineral oil regeneration*".

Considering the results from laboratory thermolysis (Thoma et al. 1987b)(Dumler et al. 1990)(Zacharewski et al. 1988)(Luijk & Govers 1992)etc., it is clear that elevated concentrations of PBDD/DF can be expected from pyrolysis processes when PBDE are present in the waste. Therefore for feedstock recycling via pyrolysis/gasification of PBDE-containing waste the formation of PBDD/DF needs to be considered and depending on the chlorine content also the formation of brominated-chlorinated PXDD/DF have to be considered (Weber & Kuch 2003).

The following knowledge gaps exist:

- The extent of the use of pyrolysis and gasification for the treatment of PBDE-containing wastes is unclear. There are very few data on operational emissions of PBDD/DF and related releases from such operations
- The total amount of PBDE waste entering pyrolysis and gasification processes and the fate of the products to enable effective Destruction Efficiencies to be calculated
- The level of debromination of DecaBDE to POP-BDE is likely to be high in such operations and should be quantified.
- Dependence of PBDD/DF formation and debromination on the reaction conditions and to what extent this can be overcome by applying appropriate temperatures and residence time or appropriate post-treatment technologies (e.g. prolysis/gasification in combination with a high temperature incineration (Boerrigter 2001) or a high-temperature melting step.

Relevance of PBDD/PBDF conversion in the life cycle of PBDE

PBDE can be (partly) converted to PBDD/DF in all treatment processes (thermal and non thermal). Additionally PBDD/DF were already included in commercial PBDE products (and therefore PBDE-treated materials) and are formed during the life time of products.

Appendix 2 (g) describes PBDD/DF formation throughout the life-cycle of PBDE. For some treatment practice PBDD/DF levels can be estimated in tons scale (contamination levels of PBDE from production (Hanari et al. 2006b) or from open burning operations in primitive e-waste recycling (Zennegg et al. 2009). For some sources like the metal industries or pyrolysis processes the data available do not allow reliable estimates to be made.

The following knowledge gaps exist:

- Which processes contribute to significant releases of PBDD/DF release and assessment of total PBDD/DF generation?
- PBDD/DF contribution from PBDE conversion to the total global PBDD/DF burden - and the balance of PBDE and the contribution from other brominated organics and bromine-containing processes contribute to this contamination.
- Levels and temporal trends of PBDD/DF contamination in the environment, food chain and humans.

PBDF provides the main contribution to dioxin-like compounds in Japanese house dust. A detailed assessment on the source of this PBDF contamination has not been established but the high PBDF to PBDD ratio strongly suggests that a PBDF precursor like PBDE or PBB is likely to be responsible. It therefore needs to be clarified

- To what extent are PentaBDE and OctaBDE responsible for this PBDF contamination?
- To what extent is the degradation of DecaBDE responsible for this PBDF contamination?
- Are other BFRs responsible for this PBDF contamination?

Also PBDD/DF levels in UK food is high (approximately 30% of total TEQ) and levels in human milk (Kotz et al. 2005) and human tissue have relevant TEQ contribution from brominated PBDD/DF.

It needs to be clarified

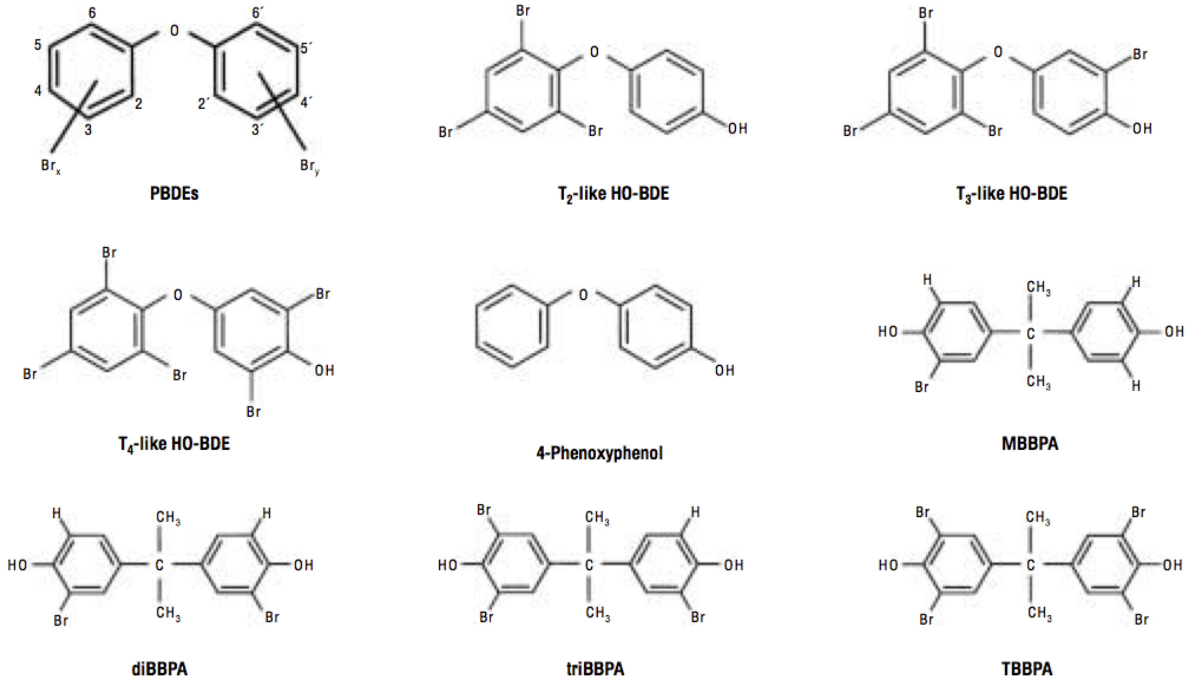
- To what extent are PentaBDE and OctaBDE are responsible for this PBDD/DF contamination?
- To what extent is the degradation of DecaBDE responsible for this PBDD/DF contamination?
- Are other BFRs or processes with high bromine levels responsible for the PBDD/DF contamination?

For chlorinated PCDD/DF precursors (e.g. Chlorophenols and Hydroxydiphenylether) it is known that PCDD/DF can be formed from the ppm through to the percent range from enzymatic reactions or metabolism (Ballschmitter & Bacher 1996)(Öberg & Rappe 1992)(Huwe et al. 2000). Such formation has not been assessed for PBDE. However it has been found that PBDE are metabolised in biota and humans to hydroxyl-PBDE (brominated phenoxyphenols). Therefore it needs to be clarified

- If the hydroxyl-PBDE (brominated phenoxyphenols) - formed from PBDE in the metabolism of biota and humans – are they further transformed into PBDD or PBDF (as shown with high conversation rates for chlorinated hydroxyl-PCDE (chlorinated phenoxyphenols) in cows (Huwe et al. 2000))
- Are PBDE transformed in the environment to PBDD/DF during other biological degradation processes?

Hydroxy and Methoxy PBDE

Hydroxylated metabolites of PBDE have a close structural resemblance to the thyroid hormones triiodothyronine (T3) and to thyroxin (T4) (Meerts et al. 2001)(Meerts et al. 1998):



PBDEs

T_2-like HO-BDE

T_3-like HO-BDE

T_4-like HO-BDE

4-Phenoxyphenol

MBBPA

diBBPA

triBBPA

TBBPA

Figure 112: Structure of PBDE, the three hydroxylated PBDE, 4-phenoxyphenol, and the differently brominated bisphenol A analogs. The hydrogens have been omitted for clarity (Meerts et al. 2001).

De Wit (de Wit et al.) commented that laboratory studies support the formation of some OH-PBDE from parent PBDE via metabolism. If this was an exposure route in practice then it would clearly be appropriate to consider these metabolites as part of a risk assessment. Dinegeman (Dingemans et al. 2010) noted that the hydroxylated metabolites of PBDE, which were recently found to bioaccumulate in humans (Athanasiadou et al. 2008, Qiu et al. 2009b) and which either from man-made PBDE or of natural origin, are currently not taken into account in regulatory human risk assessment. Dingemans group presented results revealing a structure–activity relationship for metabolites of PBDE (more shielding of the OH group reduces the potency of OH-PBDE) and suggesting that oxidative metabolism should be included in human risk assessment of persistent organic pollutants (Dingemans et al. 2010).

The methoxy and hydroxyl derivates have potentially toxic properties by interaction with the thyroid-hormone-transporting protein, thyroxine (Mörck et al. 2003)(Sandholm et al. 2003)(Marchesini et al. 2008). Recent studies (Dingemans et al. 2008)(Qiu et al. 2009a) suggest that some of the toxic effects of PBDE might be due to their HO metabolites. Li et al examined the hormonal activity of hydroxylated PBDE and reported that for the 18 HO-PBDE tested each exhibited significantly higher thyroid hormone activities than did PBDE (Li et al. 2010a).

Hydroxylated (OH-PBDE) and methoxylated PBDE (MeO-PBDE) had also previously been reported in samples of surface waters (Ueno et al. 2008), sewage effluents (Hua et al. 2005), marine organisms (Kelly et al. 2008, Malmvärn et al. 2008) and in blood from wildlife (Hakk & Letcher 2003).

There are indications that some of these compounds may be produced by algae and sponges as natural products. Thus, concludes de Wit, the presence of OH-PBDE may be due to uptake and metabolism of PBDE and/or the accumulation of naturally-occurring compounds (Hakk & Letcher 2003, Malmvärn et al. 2008)(Malmberg et al. 2005)(Malmvärn et al. 2005)(Marsh et al. 2006). The MeO-PBDE, such as 6-MeO-BDE-47 and 2'-MeO-BDE-68, have been shown to be of natural origin (Teuten et al. 2005).

The conclusion in the PentBDE Risk Profile was that it "*would seem that the origin of these substances can be natural, anthropogenic or both*" (Stockholm Convention 2006). It seems most likely that they can arise from both sources but further clarification is necessary to establish the balance in particular circumstances. Exposure from anthropogenic BDE-related sources is in any case likely to be additional to any intake from natural souces -probably mainly via seafood. Methoxy and Hydroxy BDE are thus another concern which should be considered in relation to the risks associated with recycling of articles containing POP-BDE.

Relevance of debromination of DecaBDE in technical processes

The relevance of debromination of DecaBDE to Tetra- to HeptaBDE POPs in technical processes have been most clearly demonstrated from laboratory pyrolysis experiments the. In this case the pyrolysis of DecaBDE-containing HIPS at 500ºC generated mainly mono to pentabrominated PBDE (Hall & Williams 2008) thus highlighting significant debromination of DecaBDE take place under pyrolysis conditions. Therefore for all pyrolysis and gasification processes the fate of debromination of DecaBDE to POP-BDE needs to be considered and assessed for feedstock recycling of PBDE.

Following knowledge gaps exist:

- In which technical processes is DecaBDE debrominated to POP-BDE?
- What parameters (e.g. temperature, oxygen content and residence) are necessary in these processes for a complete debromination or destruction of DecaBDE?
- What levels of PBDF are formed during debromination of DecaBDE?
- What levels of hydroxyBDE are formed during degradation/debromination of DecaBDE?

Climate change

Climate change can have significant impacts on the risks and exposure scenarios associated with POP-BDE. This is mainly due to increased photolysis – with higher levels of POP-BDE generation from the photolytic degradation of DecaBDE together with higher levels of photolytic degradation of the POP-BDE (both existing stocks and any newly formed POPs). These knowledge gaps are discussed in Appendix 4 (e).

Another consideration, about which there is significant uncertainty, is the possibiity of an increasing incidence of fire events due to Climate Change with subsequent increases in production of brominated furans from combustion of POP-BDE in open burning conditions In the past years large accidental fires triggered by drought due to climate change have occurred. In these fire event whole villages or city districts were affected e.g. in Australia or California with hundreds of houses and cars burned. In these fires tonnes of electrical equipment and BFR-treated goods have been burned. The associated releases of PBDE and PBDD/PBDF were likely to be enormous but do not appear to have been monitored (or at least the results have not been reported). Since climate change will inevitably lead to more drought and large-scale fire events the increase POPs releases from this source should be further evaluated.

Appendix 6 (b): The Potential Significance of Debromination and related knowledged Gaps

This section reviews the issue of debromination. During the course of preparing this report it has become increasingly obvious that a major knowledge gap relates to the potential significance of debromination. This is so fundamental to the assessments given the potential to ‘recharge’ the POP-BDE from the much greater stock of DecaBDE that rather than simply include this in the knowledge gaps (Appendix 6 (a)) it is considered more appropriate to provide more background about the issue in a discreet section.

Debromination is an important mechanism for the ultimate degradation of PBDE. Key issues are the degradation pathways and rates for the lower-brominated congeners constituting the commercial mixtures of PentaBDE and OctaBDE balanced against the impacts arising from the debromination of the higher brominated PBDE (OctaBDE, NonaBDE and DecaBDE). DecaBDE and NonaBDE are reported to contribute nearly 70% of the composition of some c-OctaBDE mixtures such as Bromkal 79-8DE (see Appendix 2). The much larger stock of highly brominated PBDE stem from commercial DecaBDE of which well over one million tonnes has been produced as described earlier in Appendix 2.

In this Appendix consideration is therefore given to the possible contribution to the POP-BDE from the much larger reservoir of the higher brominated PBDE with emphasis on DecaBDE – the stock of which continues to increase in most of the world.

The finding in recent scientific literature and the feedback from the scientific meetings attended as part of this work is that the evidence for debromination of DecaBDE as an important pathway is getting much stronger each year. The general view of the wider scientific community is no longer “*if*” debromination is happening - and is environmentally relevant – but rather “*how quickly*” it is happening and what the finer details of the metabolites and pathways are.

Ross et al, (Ross et al. 2009) for example, summarise the general viewpoint and the consequences:

“Deca formulation, BDE-209, provide as ready a source of Penta- and Octa-like congeners to aquatic biota as do Penta- and Octa-containing products in homes, businesses and landfills” (Ross et al. 2009).

Through its breakdown products, Ross argues, DecaBDE is therefore a source of those very PBDE congener mixtures that face restrictions around the world and this is illustrated by the bold arrows from Deca congener oval in the figure:

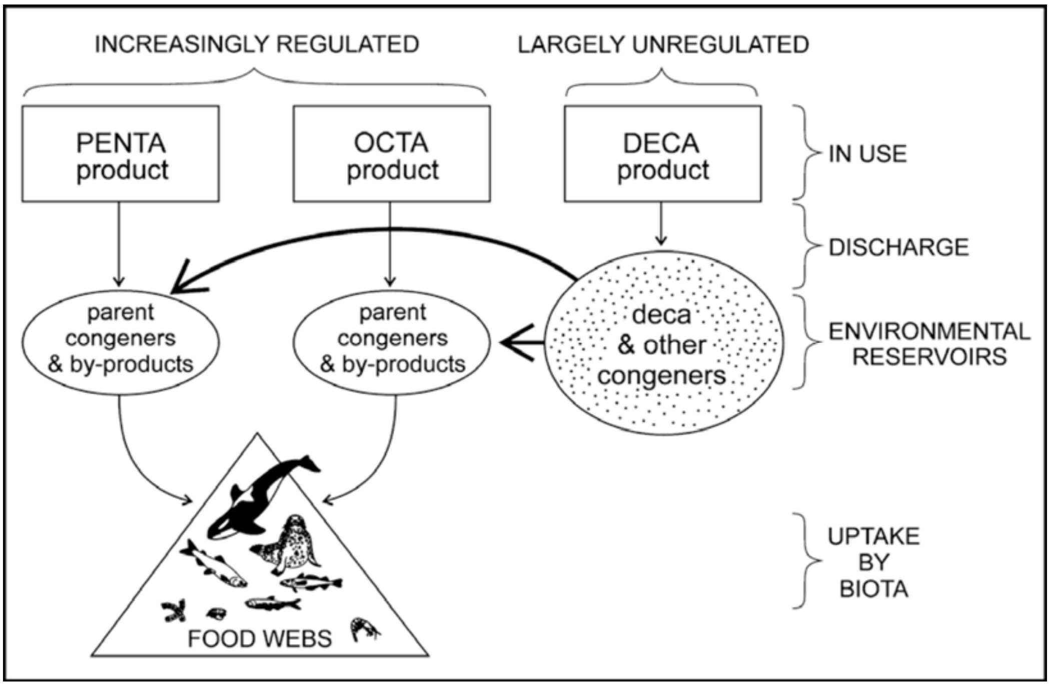


Figure 113: Relationship between PentaBDE, OctaBDE and DecaBDE in terms of regulations and environmental reservoirs (Ross et al. 2009).

They conclude that should the discharge of PBDE not be reduced, then the experience with PCBs over the last 40 years "*suggests that these largely unregulated flame retardants will continue to cycle through the environment and biota for decades or even centuries*"(Ross et al. 2009).

The evidence increasingly indicates that debromination takes place in environmentally relevant circumstances and, whilst the rates investigated to date appear relatively slow, this will lead to the formation of POP-BDE. Debromination of DecaBDE therefore has potentially profound implications for the management of the stocks of POPs HeptaBDE and the lower POPs BDE homologues in the future.

DecaBDE bans and restrictions

DecaBDE has been one of the most widely used brominated flame retardants worldwide but there have been an increasing number of bans and restrictions on the use of this flame retardant. In December 2009, the USEPA announced a phase-out of the production and use of DecaBDE in the USA. The consequences are that production, importation, and sales of DecaBDE for most uses in the United States must end by the end of December 2012 with all uses to end a year later (USEPA 2010).

In Europe the use of DecaBDE in electrical and electronic equipment was banned from 1st July 2006 by Directive 2002/95/EC on the "*restriction of the use of certain hazardous substances in electrical and electronic equipment*". As approximately 80 percent of the use of DecaBDE has been in electrical and electronic equipment this was major threat to the marketing of the chemical and subsequent use was then allowed by the European Commission. Denmark and the European Parliament filed a lawsuit before the European Court of Justice challenging this decision of the Commission. The German Federal Environment Agency[121] and others supported the case brought by Denmark.

Judgment was handed down by the European Court of Justice on 1st April 2008 in favour of Denmark and the European Parliament. The decision fully supported the position of both claimants, who demanded that the environmentally less harmful alternatives which are available for use have to be taken into account.

There are large reservoirs of DecaBDE in products still in use, in end-of-life treatment, in landfills and in the environment.

Scientific and regulatory developments relevant to debromination:

Over the past decade, much research energy has been directed to the question of whether debomination is a) environmentally relevant and b) a source of the lower-brominated congeners. Reviews in both the US and Europe since 2000 have generally been getting stronger in their conclusions.

In 2001, for example, ILS wrote that there was evidence for the debromination of highly brominated diphenyl ethers to lower-brominated diphenyl ethers. There are indications that metabolic debromination may occur in fish. Debromination due to photodegradation has been shown in many experiments involving DecaBDE.

Photohydroxylation is the expected route of transformation and the resulting hydroxylated products would then be degraded rapidly due to increased UV absorption. The half-life of decabromodiphenyl ether (BDE-209) in sand exposed to UV radiation and sunlight was between 12 and 37 hours, with lower PBDE and other compounds (not specified) detected after UV radiation (Integrated Laboratory Systems 2001). During debromination under UV or sunlight high PBDF levels have been formed (Kajiwara et al. 2008, Kajiwara & Takigami 2010)(Hagberg et al. 2006)(Watanabe & Tatsukawa 1987).

The European Union's Expert Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) was even less equivocal. In their 2002 review of Bis(pentabromophenyl)ether (DecaBDE) carried out as part of the evaluation and control of the risks of existing substances the Committee wrote (Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) 2002):

"The conclusion of the CSTEE is that the present data indicate that lower-brominated congeners are formed during photolysis in the environment".

The committee noted that even eight years ago there was field work supporting this conclusion (albeit unpublished):

"*These results have also been confirmed in soil fertilised with sewage sludge (B. Jansson, unpublished results) where the same pattern as in the photolysis experiments with D[eca]BDE was found*".

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[121] http://www.umweltbundesamt.de/produkte-e/flammschutzmittel/decabromdiphenylether.htm

The Final Draft of the May 2004 Risk Assessment of DecaBDE for the European Union by the UK Environment Agency was more cautious than the expert committee:

"*the formation of PBT/vPvB [Persistent, Bioaccumulative, and Toxic / very Persistent, very Bioaccumulative] substances in the environment as a result of degradation [of decaBDE] is a possibility that cannot be quantified based on current knowledge*."

The latest version of this review, described below, is much stronger than this early version.

Later in 2004 the Agency for Toxic Substances and Disease Registry backed off further and suggested that "*DecaBDE seems to be largely resistant to environmental degradation*" (ATSDR 2004).

This continued:

"*However, there is very little information on the environmental degradation of decaBDE and the data that exist are controversial*"

POPRC

The 2006 Risk profile on PentaBDE[122] said:

"The authors draw attention to the potential for conversion of higher congeners in the environment to more toxic congeners with fewer bromine substituents. Further studies particularly environmental monitoring studies focussing on congeners for which the primary source is likely to be debromination reactions, are required to clarify the role of debromination in determining the final mix of PBDE congeners in the environment"(Stockholm Convention 2006).

By 2007 the OctaBDE Risk profile[123] contained somewhat stronger indications of debromination:

"The number of scientific papers demonstrating debromination of Octa to DecaBDE to other PBDEs is continuously increasing; this is critical for the assessment as would (sic) indicate that the supposed low bioaccumulation potential could be in reality the consequence of metabolism to bioaccumulative PBDEs. A quantitative estimation cannot be presented yet, but the debromination process has been already reported for aquatic organisms, mammals and birds. This is an active research field, and new results will need to be assessed by the POPRC as they appear in refereed literature" (Stockholm Convention 2007d).

A comprehensive but concise review of the literature on reductive debromination upto early 2008 was prepared by Professor Ian Rae[124] (Stockholm Convention 2008b). This concluded:

"The degradation of PBDEs in the environment and biota is a key issue as higher congeners may be converted to lower, and possibly more toxic, congeners. This possibility has been demonstrated for debromination of DecaBDE and several commercial-OctaBDE components but the biodegradation reactions are slow. The extent to which different PBDEs can be degraded under various conditions, the role of metabolism in addressing the bioaccumulation potential, and the identity of all lower congeners that may be produced, is an active research field".

The conclusions continued:

"*New results will no doubt continue to appear in refereed literature and these will need to be assessed by the POPRC as they appear*" so that their significance for the presence of POPs in the environment can be assessed. Although historic production of Penta and OctaBDEs are obviously important it has become increasingly clear during the course of this review that one of the most critical future issue in terms of the reservoirs of these POPs is likely to be the contribution made by the debromination of DecaBDE.

The POPRC web site[125] on the nine new POPs includes a box commenting on the possibility of debromination saying:

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[122] UNEP/POPS/POPRC.2/17/Add.1

[123] UNEP/POPS/POPRC.3/20/Add.6

[124] UNEP/POPS/POPRC.4/INF/12

Debromination and precursors

Polybromodiphenyl ethers can be subject to debromination, i.e. the replacement of bromine on the aromatic ring with hydrogen.

Higher bromodiphenyl ether congeners may be converted to lower, and possibly more toxic, congeners. The higher congeners might therefore be precursors to the tetraBDE, pentaBDE, hexaBDE, or heptaBDE.

The Bromine industry perspective

The bromine industry has been consistently sceptical about debromination of DecaBDE.

It was originally argued that the congeners found in the environment were the result of historic emissions that have ceased. PentaBDE was used for off-shore oil drilling on a trial basis in the early 1990s, said Marcia Hardy, an environmental chemist at Albemarle Corp., in Baton Rouge, LA. Until the late 1980s, it was also used as a hydraulic fluid by the coal mining industry in Germany (Renner 2000).

Hardy noted also that sediment samples from the Mersey River in England contain deca-BDE, tetra-BDE, and penta-BDE, but no other congeners. "*If deca-BDE is breaking down, then why does it degrade down to a few specific congeners and then just stop?*" she asked. If DecaBDE were being degraded, all of the intermediate congeners would be expected, she said (Renner 2000).

The Bromine industry maintained a dismissive view about whether debromination during the early 2000's saying, for example, that "*it is far-fetched to speculate that the Deca product is degrading to lower-brominated congeners*" (Betts 2002)). More recently the argument appears to have changed to accept that debromination occurs in certain circumstances but to maintain that these are not environmentally relevant and should not be considered by POPRC. BSEF wrote, for example, that "*issues of debromination, PCB like effects and dioxin/dibenzofurans are not supported by the evidence and should not be used to justify action on c-OctaBDE or any of its components*" (BSEF 2007a)).

BSEF (Bromine Science and Environment Forum 2008) also says:

Since the adoption of the Risk Profile at the third meeting of the Persistent Organic Pollutants Review Committee in November 2007, the Background document for POPRC Members and Observers on Reductive Debromination of Bromo-aromatics' by Professor Ian Rae was distributed in April 2008;

· this paper states that "The extent to which different PBDEs can be degraded under various conditions, the role of metabolism in addressing the bioaccumulation potential, and the identity of all lower congeners that may be produced, is an active research field" and therefore latest scientific data do not indicate the need of including the environmental and health relevance of de-bromination.

It is not clear why an issue being "*an active research field*" precludes appropriate action being taken at this stage. It could be said, for example, that aspects of PCBs are still "*an active research field*" as witnessed by a current special issue of ES&T on PCB, other jounal articles and the number of papers and posters submitted to the annual Dioxin conference. Ongoing "*active research*" has, quite rightly, not prevented regulatory activity.

The issues raised in this appendix were discussed with representatives of the Bromine industry at a meeting in Holland as part of this project in an effort to clarify the current position of the industry in relation to:

a) Debromination of DecaBDE and the contribution, if any, that it is considered this may make to the New POPs
b) Debromination of the relevant congeners of Penta and OctaBDE
c) The formation of PBDD/DF during photolysis and debromination and the contribution the industry considers this may make, if any, to the risks

The reply from the Bromine Industry (Hofland 2010b) was that:

Decision COP.4/SC-4/14 Listing of hexabromodiphenyl ether and heptabromodiphenyl ether was clearly based on the nomination and assessment of the commercial OctaBDE product itself and its relevant congeners. Therefore, by definition the debromination products of DecaBDE are not components of commercial OctaBDE. As such, it is therefore outside of the scope of the current work, which we understand to

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[125] http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx (viewed 6th June 2010)

be related to the management of commercial PentaBDE and commercial OctaBDE. The need for future discussion of DecaBDE as a "POP pre-cursor" was mentioned during a previous POPRC meeting and we anticipate that the Chair of POPRC will follow up at the appropriate time. Until then we believe the charge to POPRC by the COP is to deal with managing the production, use and recycling of the newly listed components of c-PentaBDE and c-OctaBDE.

It was noted above and in Appendix 2 that some c-OctaBDE consists of upto about 20% NonaBDE and 50% DecaBDE and therefore considerations about recycling must inevitably address the implications of these homologues in terms of emissions and exposure even though they are not listed as Stockholm POPs. Furthermore the 2007 c-OctaBDE Risk profile[126] says:

"...the commercial [OctaBDE] product is a mixture of components with different properties and profiles, which may also be released to the environment due to its presence as components of other PBDE commercial products and also produced in the environment by debromination of commercial DecaBDE." (Stockholm Convention 2007d).

It continues:

"The number of scientific papers demonstrating debromination of Octa to DecaBDE to other PBDEs is continuously increasing; this is critical for the assessment as would (sic) indicate that the supposed low bioaccumulation potential could be in reality the consequence of metabolism to bioaccumulative PBDEs. A quantitative estimation cannot be presented yet, but the debromination process has been already reported for aquatic organisms, mammals and birds. This is an active research field, and new results will need to be assessed by the POPRC as they appear in refereed literature" (Stockholm Convention 2007d).

A reply was therefore sent suggesting that it seems logical that it is the congeners which together constitute the commercial mixtures that the Convention of the Parties to the Stockholm Convention agreed have the qualities of POPs and has therefore determined to list in Annex A of the Convention. The consultants interpretation of this would be that in order to ensure the objectives of the Convention then it is sensible to consider these compounds as Stockholm POPs irrespective of whether the source was a commercial mixture (certainly the major source); as a by-product of another production process; or as a metabolite or degradation product of another BFR like Deca.

Clarification was sought in relation to the logic of the Bromine Industry's apparent argument that a chemical which has qualities which justify listing as a POP should be treated differently in circumstances based purely on the source of the arising rather than any consideration of the health or environmental impact (which are, by definition, identical to those of a listed POP).

The Bromine industry interpretation also raises some difficult practical issues about which clarifcation was also sought. One is how is it realistically possible to distinguish between a HeptaBDE congener arising from commercial OctaDE and the same congener from a biotic metabolism or photolytic debromination of Deca ?

It is noted some Parties seem to go further than this in relation to their perception of the relevance of Deca. The response from Austria, for example, to Question II-A-3 of the Questionnaire from the Secretariat, details the concentrations of articles recycled as the sum of Tri, Tetra, Penta, Hexa, Hepta, Octa and Deca BDE)[127].

Finally it is noted that the final draft Risk Management Evaluation for OctBDE[128] provided what seems like a straightforward way of clarifying this issue and removing any ambiguity:

"The components of c-OctaBDE are also unintentionally formed through debromination of higher substituted congeners, including commercial decabromodiphenyl ether (c-DecaBDE). Control measures that address c-DecaBDE would be an appropriate measure to prevent further formation of c-OctaBDE and other BDE congeners in the environment. This could be accomplished by also listing c-OctaBDE in Annex C of the Stockholm Convention".

When a chemical has already been listed in Annex A it should be relatively straightforward matter to extend that listing to Annex C.

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[126] UNEP/POPS/POPRC.3/20/Add.6

[127] Nona is omitted, perhaps because it is generally low

[128] UNEP/POPS/POPRC.4/6

No reply has been received from the Bromine industry in relation to the requests for clarification of their position at the time of finalising this draft of the report.

Recent scientific developments

It is not useful to repeat here the literature review on reductive debromination prepared by Professor Ian Rae[129] (Stockholm Convention 2008b) and copies are available from the POPRC website. Key papers in relation to debromination to the lower-brominated congeners are summarised in Table 79 but much more research has been published since this was originally complied in 2006[130].

Table 79: PBDE congeners identified in commercial mixtures and in debromination studies (adapted from (Stapleton 2006a)

Substitution	***Congener***	***PentaBDE***	***OctaBDE***	***DecaBDE***	***Formed by Debromination***	***Reference***
2,4,4'-tribromo	BDE 28	X			X	(Bezares-Cruz et al. 2004, Keum & Li 2005)
2,2',4,4'-tetrabromo	BDE 47	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)(Soderstrom et al. 2004)
2,2',4,5'-tetrabromo	BDE 49	X			X	(Bezares-Cruz et al. 2004)
2,3',4,4'-tetrabromo	BDE 66	X			X	(Keum & Li 2005)
2,2'3,4,4'-pentabromo	BDE 85	X			X	(Bezares-Cruz et al. 2004)(Ahn et al. 2006a)
2,2',4,4',5-pentabromo	BDE 99	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)(Soderstrom et al. 2004)
2,2',4,4',6-pentabromo	BDE 100	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)
2,2',3,4,4',5'-hexabromo	BDE 138	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)
2,2',4,4',5,5'-hexabromo	BDE 153	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)(Soderstrom et al. 2004)
2,2',4,4',5,6'-hexabromo	BDE 154	X			X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)(Soderstrom et al. 2004)(Ahn et al. 2006a)(Stapleton et al. 2004a)(Stapleton et al. 2006)
2,2',4,4',6,6'-hexabromo	BDE 155	X			X	(Stapleton et al. 2006)(Stapleton et al. 2004a)
2,2',3,4,4',5',6-heptabromo	BDE 183	X	X		X	(Bezares-Cruz et al. 2004)(Keum & Li 2005)(Soderstrom et al. 2004)
2,2',3,4,4',6,6'-heptabromo	BDE 184				X	(Stapleton et al. 2006)
2,2',3,3',4,4',5,6'-octabromo	BDE 196		X		X	(Bezares-Cruz et al. 2004)(Ahn et al. 2006a)(Gerecke et al. 2005)

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[129] UNEP/POPS/POPRC.4/INF/12

[130] See, for example: (Fang et al. 2008, Grause et al. 2008, Kajiwara et al. 2008, Kohler et al. 2008b, Robrock et al. 2008, Schenker et al. 2008, Shaw et al. 2008, Stapleton 2008, Stapleton & Dodder 2008, Sun et al. 2008, Tokarz et al. 2008, Zhao et al. 2008, Abdallah et al. 2009, Brandsma et al. 2009, Christiansson et al. 2009, Davis & Stapleton 2009, Kemi 2009, Liu et al. 2009, Luo et al. 2009a, Luo et al. 2009b, Onwudili & Williams 2009, Park et al. 2009, Segev et al. 2009, Shih & Wang 2009, Webster et al. 2009, Yogui & Sericano 2009, Bendig & Vetter 2010, Haglund 2010, Haglund et al. 2010, Huang et al. 2010, Noyes et al. 2010, Wang et al. 2010a)

Substitution	*Congener*	*PentaBDE*	*OctaBDE*	*DecaBDE*	*Formed by Debromination*	*Reference*
2,2',3,3',4,4',6,6'-octabromo	BDE 197		X		X	(Bezares-Cruz et al. 2004)(Ahn et al. 2006a)(Gerecke et al. 2005)
2,2',3,3',4,5',6,6'-octabromo	BDE 201				X	(Stapleton et al. 2006)
2,2',3,3',5,5',6,6'-octabromo	BDE 202				X	(Stapleton et al. 2006)
2,2',3,3',4,5,5',6-octabromo	BDE 203		X	X	X	(Gerecke et al. 2005)
2,2',3,3',4,4',5,5',6-nonabromo	BDE 206		X	X	X	(Bezares-Cruz et al. 2004)(Soderstrom et al. 2004)(Ahn et al. 2006a)
2,2',3,3',4,4',5,6,6'-nonabromo	BDE 207		X	X	X	(Bezares-Cruz et al. 2004)(Soderstrom et al. 2004)(Ahn et al. 2006a)(Gerecke et al. 2005)
2,2',3,3',4,5,5',6,6'-non abromo	BDE 208		X	X	X	(Bezares-Cruz et al. 2004)(Soderstrom et al. 2004)(Ahn et al. 2006a)(Gerecke et al. 2005)
2,2',3,3',4,4',5,5',6,6'-decabromo	BDE 209		X	X	X	

The POPRC covers the period upto early 2008 very well. It is noted, however, that even in the review the relevance of certain papers is perhaps under-stated. Professor Rae wrote, for example:

"Van den Steen et al. (2007) used silastic implants to expose European starlings (Sturnus vulgaris) to deca-BDE (BDE-209) and found octa- (BDE-196, BDE-197) and nonaBDE (BDE-206, BDE-207, BDE-208) in muscle and liver in addition to deca-BDE, resulting in the first indications of debromination in birds."

The implications are that whilst debromination may be taking place it is not known to be producting POP-BDE. Van den Steen had actually gone further than implied in the summary to POPRC, however, and the original paper says:

"The present study, in accordance with previous studies (Kierkegaard et al., 1999; Morck et al., 2003; Stapleton et al., 2004), suggested that BDE 209 can be debrominated to congeners that are also present in the penta- and octaBDE commercial mixtures, which are no longer allowed for use due to their potential toxicity (Darnerud, 2003)". (underlining emphasis added)

The lower-brominated congeners of concern included Hexa- (BDE 153) and heptaBDE (BDE 183) as can be seen on the profiles from the original paper:

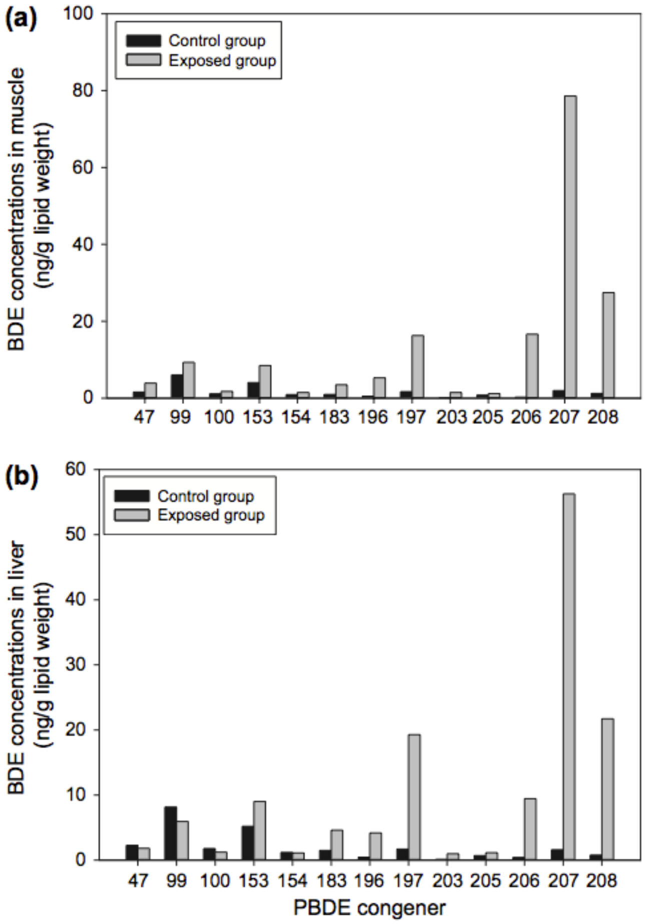

Figure 114: Profiles of PBDE congeners in (a) muscle and (b) liver (ng/g lw) after implantation with BDE 209 (Van den Steen et al. 2007).

The largest differences, of course, are clearly in the Nona and OctaBDE but over time Van den Steen added:

"Thus, phasing out the penta- and octaBDE commercial mixtures could be insufficient to restrict the potential risk of lower-brominated congeners. These results are a great cause of concern considering the large amounts of deca-BDE that are worldwide used (BSEF, 2003)".

Key papers in relation to debromination to the lower-brominated congeners are summarised in table but much has happened since[131].

The UK Environment Agency has recently published an update of the risk assessment reports for decabromodiphenyl ether (DecaBDE) produced under the EU Existing Substances Regulation (Brooke et al. 2009). The update includes literature reviews for publications of major significance through to May 2009 and this shows the science on debromination has become more firm since the earlier versions.

The Environment Agency review now says "*there is strong evidence from both laboratory and field data that metabolism of decaBDE to nonaBDEs, octaBDEs and probably heptaBDEs occurs in a number of species*" (Brooke et al. 2009).

The section concludes:

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[131] See, for example: (Fang et al. 2008, Grause et al. 2008, Kajiwara et al. 2008, Kohler et al. 2008b, Robrock et al. 2008, Schenker et al. 2008, Shaw et al. 2008, Stapleton 2008, Stapleton & Dodder 2008, Sun et al. 2008, Tokarz et al. 2008, Zhao et al. 2008, Abdallah et al. 2009, Brandsma et al. 2009, Christiansson et al. 2009, Davis & Stapleton 2009, Kemi 2009, Liu et al. 2009, Luo et al. 2009a, Luo et al. 2009b, Onwudili & Williams 2009, Park et al. 2009, Segev et al. 2009, Shih & Wang 2009, Webster et al. 2009, Yogui & Sericano 2009, Bendig & Vetter 2010, Haglund 2010, Haglund et al. 2010, Huang et al. 2010, Noyes et al. 2010, Wang et al. 2010a)

"*The persistence of decaBDE is such that the formation of even small quantities of hazardous substances in percentage terms is undesirable, since the actual amounts may become significant over long time frames. Whilst the strongest evidence is for the formation of nona- to octaBDE congeners (some of which appear to be both very persistent and toxic – see Appendix 1), there is now fresh evidence that hexa- and even pentaBDEs (which clearly have PBT/vPvB properties) may be formed (for example the Tokarz et al. (2008) study and the finding of BDE-126 in the conclusion (i) monitoring programme)"* (Brooke et al. 2009).

The monitoring programme conclusion is a report by Leslie et al. (Leslie et al. 2008) and the UK report says this reference relates to levels of BDE-126 (a pentabromodiphenyl ether). This finding is important the Environment Agency report says "*because, although the levels are low, it potentially indicates that debromination of decaBDE to lower-brominated congeners is occurring in the environment (and it is only one of a number of such substances that could be formed)*" (Brooke et al. 2009). The abiotic formation of BDE-126 from DecaBDE is clearly of relevance to the stocks of the PentaBDE and the recycling and treatment processes that are being considered by this review. The consultants therefore attempted to obtain a copy of the report by Leslie (Leslie et al. 2008) to confirm the details of their results. Unfortunately the industry refused to provide a copy saying that it related to DecaBDE and was therefore not relevant being outside the scope of this review.

Brooke (Brooke et al. 2009) suggested that it should also be noted that "*new manufacturers may be producing products that are not as pure as those made by the main European suppliers*". For example, Chen et al. (Chen et al. 2007) reported that the OctaBDE and NonaBDE content of two commercial decabromodiphenyl ether products from China was in the range 8.2 to 10.4 per cent. Chen suggests that European DecaBDE, whilst variable over time, could have been expected to be around 97% pure (Chen et al. 2007). In practice, however, European commercial mixtures have varied enormously as described earlier and have also been reported to contain high levels of contamination of PBB and PBDD/DF as described in Appendix 2.

Penta -, Hexa- and Hepta- BDE may also be formed in some fish species (Stapleton et al. 2004a)(Stapleton et al. 2006)(Kierkegaard et al. 1999). The yield of these metabolites is generally low (typically <5 per cent of the dosed DecaBDE in the various studies), but several studies indicate that other, as yet unidentified metabolites, may also be formed. For example, Huwe (Huwe & Smith 2007) found that whilst there was a low level of reductive debromination to (mainly) Octa and Nona BDE around 45 per cent of the DecaBDE dose in rats after 21 days exposure had been converted to unknown metabolites – probably hydroxylated derivatives of PBDE. This would be consistent with the work of Mörck (Mörck et al. 2003) which showed that 30% of a single carbon 14 traced BDE-209 dose was excreted in feces as parent compound, while the remainder was converted to bound residues and hydroxylated metabolites by the rats with a very small level of reductive debromination.

Huwe also dosed of rats with low levels of c-PentaBDE (Huwe et al. 2007). Calculated bioavailabilities ranged from 95% for the tetra-BDE (BDE-47) to 88% for a hexa-BDE (BDE-154) (where parent compound excreted in the feces were regarded as the unavailable portion of the dose). The authors commented that "*no evidence of debromination to lower-brominated compounds*" was suggested from the data. However a large percentage of the dose (40–60%) was not recovered indicating that metabolic transformations may have occurred in the rats. A number of hydroxylated metabolites were qualitatively identified in the faeces and carcass by GC–MS and this seems to be the most likely metabolic pathway for the lower-brominated POP-BDE (Huwe et al. 2007).

Debromination pathways:

Whilst it is beyond the scope of this review to examine the debromination kinetics in detail it is useful to summarise the consequences and, briefly, the likely pathways and mechanisms proposed in the recent literature. Together these show that there is compelling evidence that debromination in environmentally relevant circumstances is an important consideration for the future burdens of POP-BDE.

To assess the importance of the DecaBDE for concentrations of the lower-brominated com- pounds Schenker (Schenker et al. 2008) modelled debromination applying the averages of measured degradation rate constants and extrapolating to degradation rate of PBDE in gas phase and sorbed to aerosols. There are significant uncertainties in the calculations still and Schenker says results "*have to be considered preliminary*" but the calculations indicate that about 50% of the Hepta- and Hexa-BDE homologues in the temperate atmospheric environment originate from the Deca-BDE mixture. For the lower- brominated compounds, 13% of the penta- and only 2.5% of the Tetra-BDE homologues in the environment originate from the Deca-BDE mixture.

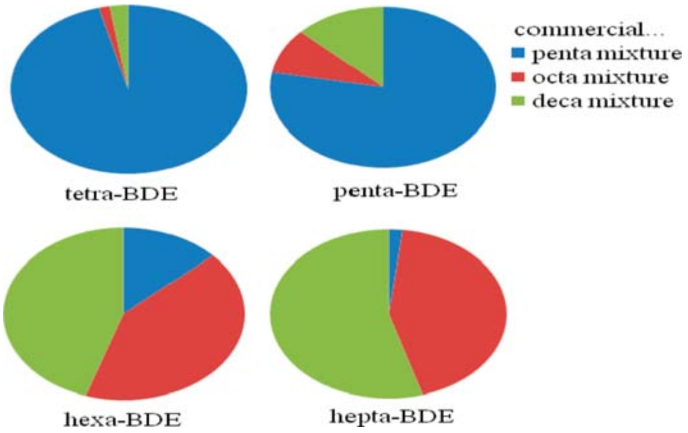

Figure 115: Contribution of the three commercial PBDE mixtures to levels of different PBDE homologues in temperate atmosphere in 2005 (Schenker et al. 2008).

Schenker considers that emission and debromination of the c-OctaBDE mixture is responsible for another 11% of the PentaBDE and 2% of TetraBDE homologues (a concern which was raised in the c-OctaBDE Risk profile[132] (Stockholm Convention 2007d)).

The consequence of these conclusions is that the reduction of environmental levels of (particularly) HexaBDE and HeptaBDE will be extremely difficult whilst the very large reservoirs of DecaBDE remain because the lower-brominated POP-BDE will be constantly regenerated from the debromination of the DecaBDE. Deca-BDE even contributes to 3-20% of penta-BDE levels in the atmospheric environment. Thus is is likely that the importance of DecaBDE as a source of PentaBDE will increase, and PentaBDE will remain in the environment, albeit in lower concentrations than today. If DecaBDE use was to increase in the future due to an increasing demand in countries with economies in transition then levels of PentaBDE (and the other POP-BDE) would be likely decrease even more slowly. Schenker suggests reducing open burnings of waste might be an efficient measure to reduce current levels of DecaBDE in the environment because a majority of DecaBDE originates from this process(Schenker et al. 2008):

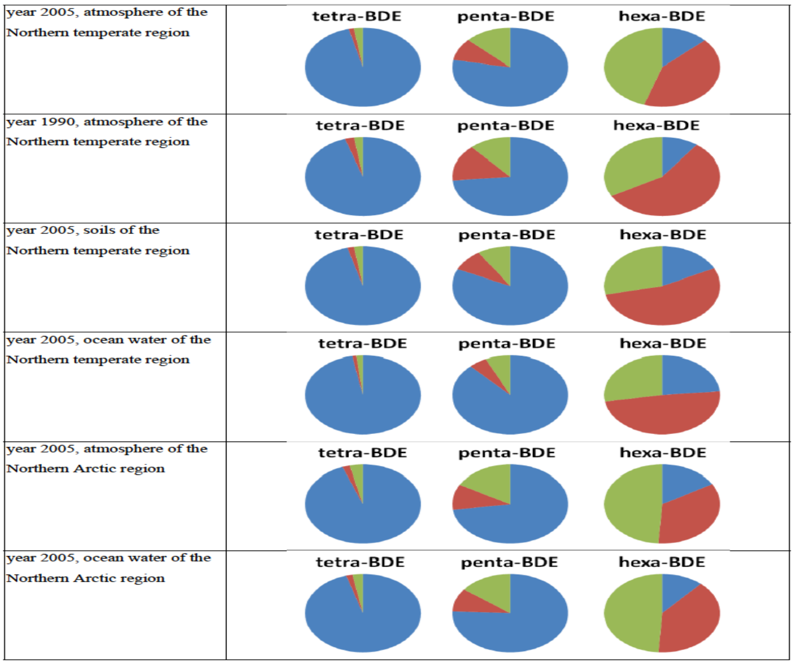

Figure 116: Contribution of the commercial penta- (blue), octa- (red), and deca-BDE (green) mixtures to levels of tetra-, penta-, and hexa-BDE in various compartments of the environment (Schenker et al. 2008).

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[132] UNEP/POPS/POPRC.3/20/Add.6

Zhang et al suggested likely pathways for debromination into relevant POPs congeners (Zhang et al. 2010a)[133]:

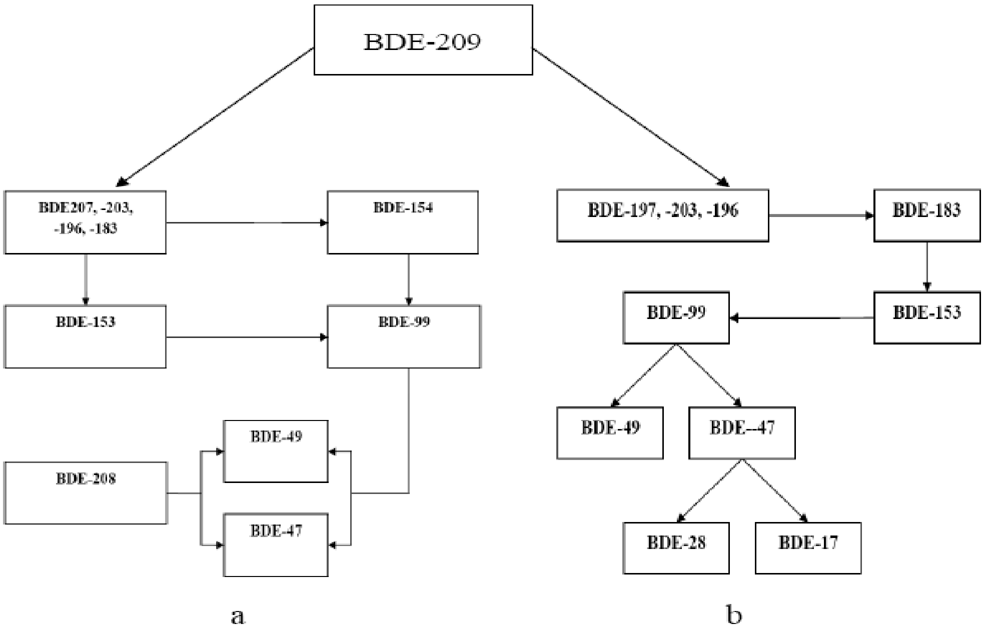

Figure 117: Schematic showing the possible pathways for debromination of highly brominated PBDE to BDE-49 (Zhang et al. 2010a)

through:

(a) anaerobic bacteria based on the study of He et al. (He et al. 2006) and

(b) through anaerobic microbe from the study of Robrock et al. (Robrock et al. 2008).

In a study by Kim et al.(Kim et al. 2009) BDE were selected for the hybrid treatment by the combination of two kinds of treatment methods; a reductive debromination by nano scaled zero valent iron (nZVI) and a biological oxidation by Sphingomonas sp. PH-07. Debromination of DecaBDE by nZVI resulted in debrominated products such as nona- to mono-BDE after 15 days reaction. Following the anaerobic debromination process, reaction mixture was aerobically treated with Sphingomonas sp. PH-07 strain for an additional 4 days. During bacterial treatment, low brominated diphenyl ethers were further biologically transformed to bromophenols and other prospective metabolites in the experiment. The authors suggested that this combination methodology could also give an insight to develop a remediation strategy of highly halogenated environmental pollutants in contaminated sites. Whilst not suggested as an environmentally relevant degradation mechanism it demonstrates how different degradation mechanisms can enhance each other as in the other studies reported in this section.

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[133] in the supplementary information

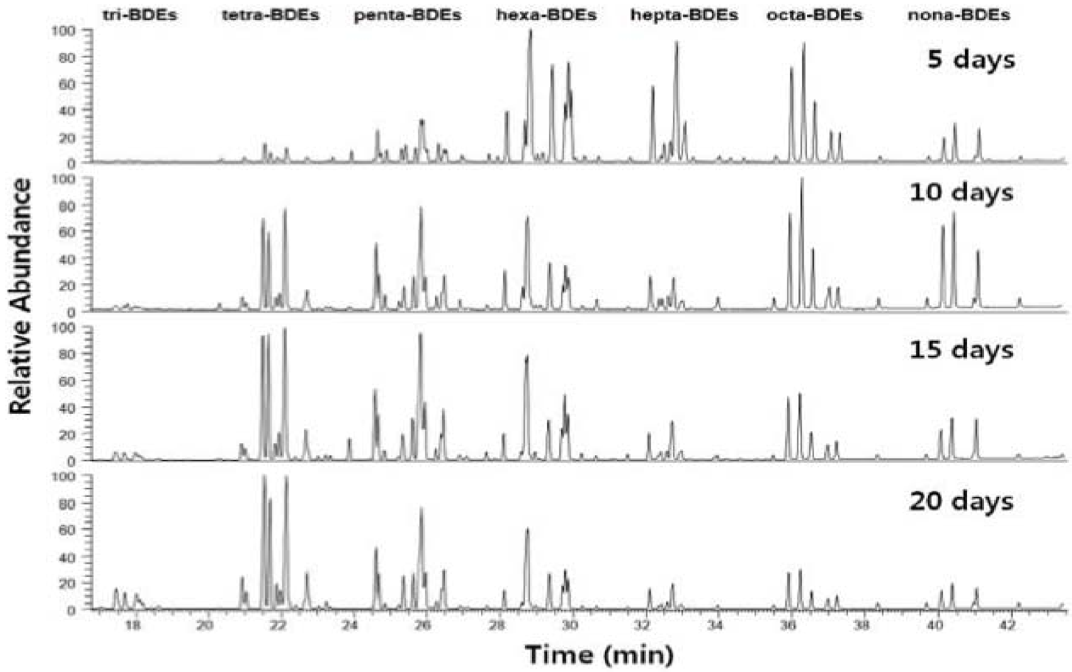


Figure 118: GC/MS chromatograms of deca-BDE-treated with nZVI. Peaks of debrominated BDE were grouped into tri- to nona-BDE (Kim et al. 2009).

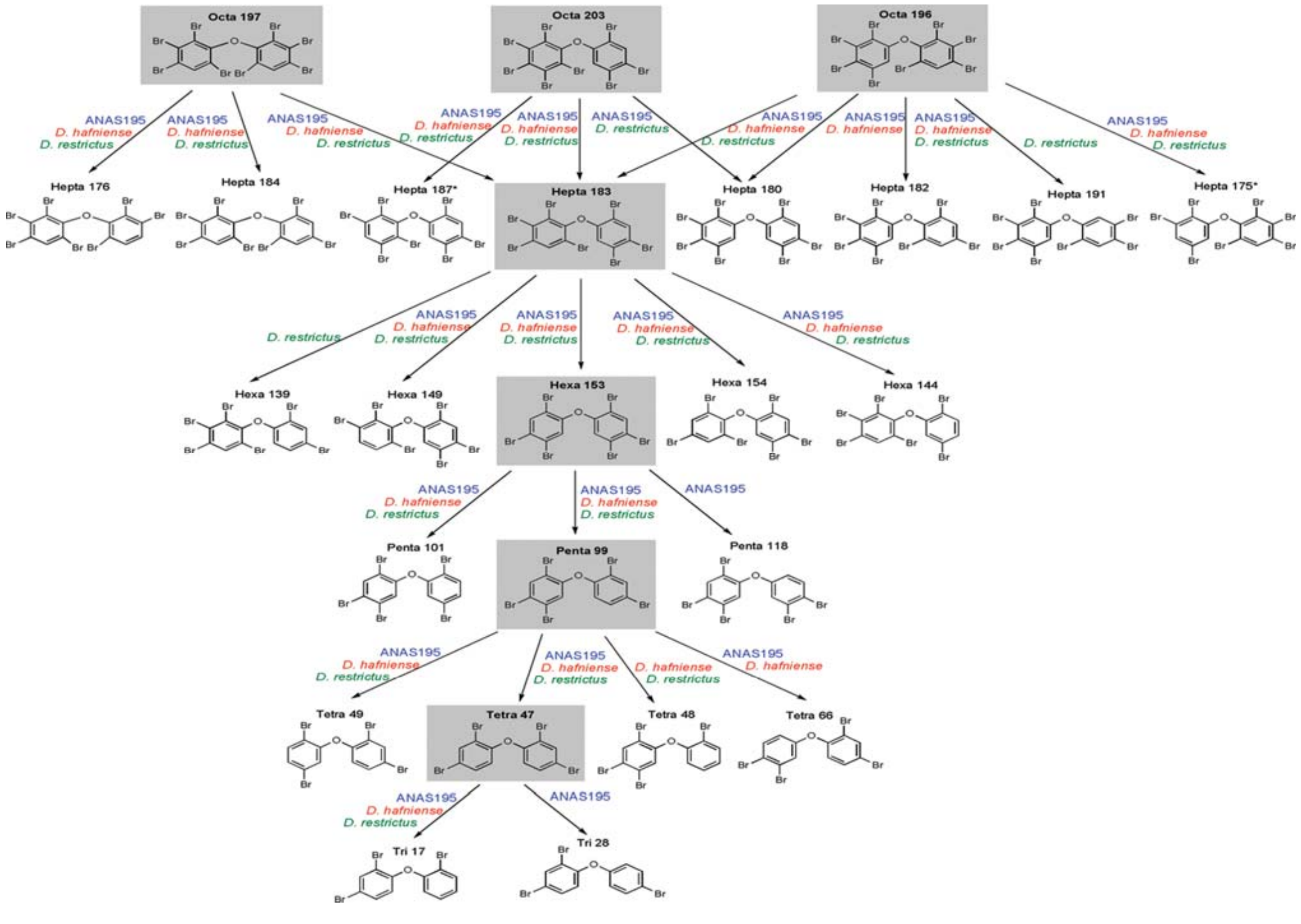


Figure 119:Suggested PBDE debromination pathway (Robrock, Korytar et al. 2008)
Asterisk (*) indicates congener that is presumptively identified due to lack of available standards.

Robrock et al. (Robrock et al. 2008) also summarised PBDE debromination pathway for all congeners tested. Highlighted molecules are those that were applied as initial substrate. The cultures that produced each congener are listed by the reaction arrows.

They conclude that the similarity of debromination pathways exhibited by the three very different bacterial cultures analysed in their study suggests that pathways for PBDE debromination are conserved across some species and genera (Robrock et al. 2008).

An alternative pathway was derived by USEPA (USEPA 2008b) from Huwe (Huwe & Smith 2007) Sandholm (Sandholm et al. 2003) and Morck (Mörck et al. 2003). Sandholm indicated that reductive debromination may be the first step in the metabolic pathway of DecaBDE, followed by oxidation to form phenolic metabolites. It was also suggested that the hydroxy/methoxy metabolites were probably formed via an arene oxide hydrolysed to a dihydrodiol and further rearomatized followed by a methylation reaction:

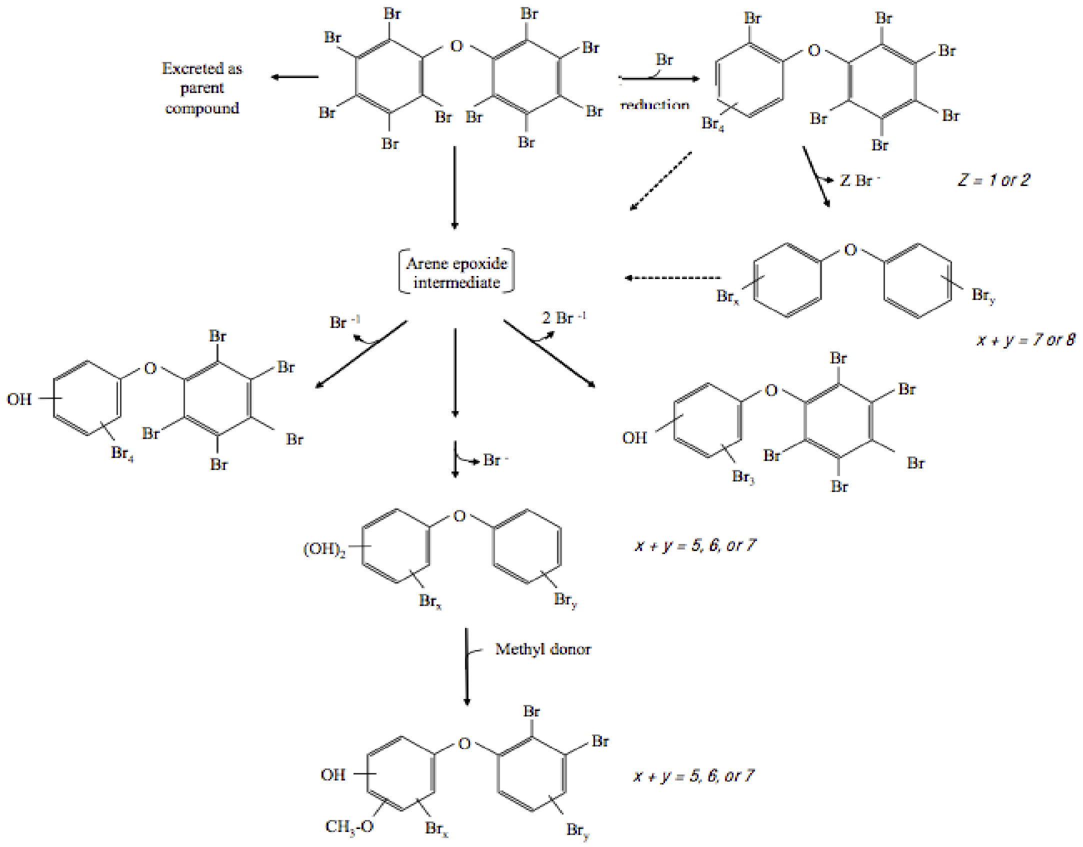


Figure 120: Alternative PBDE debromination pathway derived by USEPA (USEPA 2008b) from Huwe (Huwe & Smith 2007) Sandholm (Sandholm et al. 2003) and Morck (Mörck et al. 2003)

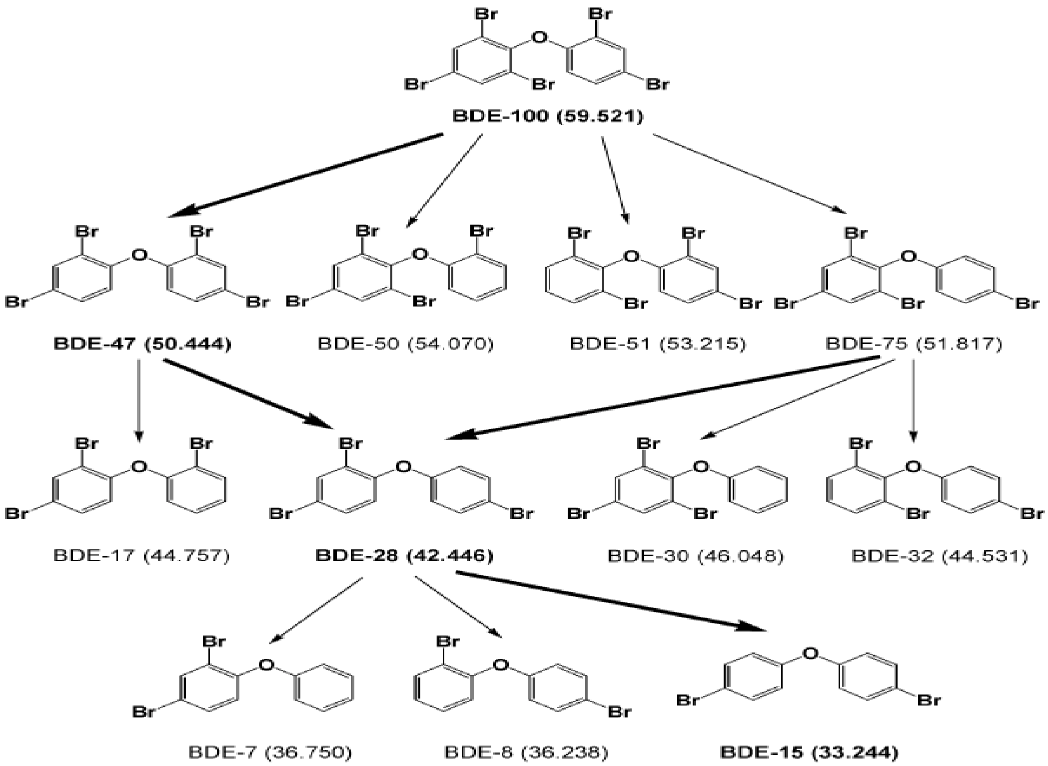


Figure 121: Proposed debromination pathways of BDE 100, 75, 47, and 28 (Keum & Li 2005).

Proposed debromination pathways of BDE 100, 75, 47, and 28. Numbers in parentheses are heats of formation in kilocalories per mole, calculated by AM1 semiempirical force field; thick lines indicate the most favourable pathways according to the difference in heats of formation between parent and product BDE. (Keum & Li 2005)

USEPA noted that debromination of DecaBDE (as reported by Huwe and Smith) differs from that for the tetra-, penta-, and hexaBDE congeners, where there is no evidence for debromination in the absence of hydroxylation (USEPA 2008b). The related knowledge gaps associated with hydroxy (and methoxy) BDE are raised in the previous section of this appendix.

Debromination of PBDE in thermal processes

In developed countries, a large proportion of the material containing the POP-BDE together with DecaBDE are ultimately thermally treated by incineration or in metal plants, cement plants and pyrolysis/gasification systems. Debromination reactions are generally observed during thermal degradation of polybrominated aromatic compounds above 400/500°C (Striebich et al. 1991)(Luijk & Govers 1992, Luijk et al. 1992)(Hall et al. 2008). However various factors can lower the on-set temperature of the debromination/hydrogenation reaction including the presence of metals and metal oxides a wide range of which have been found to be active in the dehalogenation reactions of aromatic compounds (Weber et al. 2002a). Depending on the metal/metal oxides used the onset of dehalogenation reaction is around 120°C (Hagenmaier et al. 1987)(Wiesmuller 1992) and for active dehalogenation catalysts (Palladium/Fe base) or for alkali metals dehalogenation can take place at room temperature (Grittini et al. 1995). In addition, metal oxides also may catalyse the elimination of HBr/Br_2 in the condensation step to form PBDF by, for example, the formation of SbO_xBr_y (Dumler et al. 1990).

The presence of a polymer matrix serves as hydrogen donor during thermal degradation shifting the homologue pattern to lower-brominated congeners and enhancing PBDF formation significantly (Dumler et al. 1990). In this respect, Luijk et al. (Luijk & Govers 1992, Luijk et al. 1992) reported on a debromination of DecaDBE already in the polymer melting phase and the abstraction of hydrogens from the polymer backbone.

The presence of water is a second factor increasing the formation rate of PBDFs from decaBDE (Zier et al. 1990)(Lenoir et al. 1994). This observation can be explained by a positive effect of water on dehalogenation/hydrogenation reactions. Such an influence of water on dehalogenation/hydrogenation of chlorinated aromatics has been reported for the dechlorination of PCDD/DF (Hagenmaier et al. 1987).

It has to be emphasised that the dehalogenation of PBDE in thermal processes increases the formation of PBDF and that this can increase the overall toxicity and hazard associated with resulting mixtures and thus needs to be taken into account for all thermal processes(Weber & Kuch 2003).

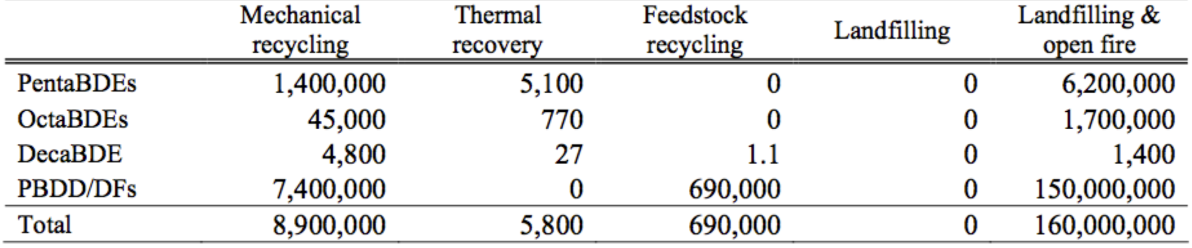
The complete thermal dehalogenation of halogenated polyaromatic compounds utilized in the destruction/decontamination of organohalogens at a technical scale[134] needs specific reaction condition: a) oxygen deficiency b) temperature above 300ºC c) extended reaction time (depending of temperature, heat transfer and catalytic activity of the matrix) (Trumpf et al. 1998)(Weber et al. 2002b). In technical processes like pyrolysis for feedstock recycling or gasification of waste plastic the reaction time is rather short which can lead to incomplete debromination. At a pyrolysis experiment of DecaBDE introduced in a polymer matrix to a fluidized bed reactor DecaBDE were dehalogenated to MonoBDE to PentaBDE (Hall et al. 2008). The lower-brominated BDE were the most abundant (Hall et al. 2008). The study demonstrates that the full range of lower PBDE can be formed from DecaBDE under pyrolysis conditions and that 500°C with a relatively short residence time[135] is not sufficient for a full debromination of DecaBDE.

Also in incineration processes during transient conditions a higher contribution of Di- through to TetraBDE congeners suggests that debromination likely occurs at some point of the disturbed combustion (Wyrzykowska et al. 2008). This demonstrates that debromination also occurs in BAT incineration during transient conditions. Since non-BAT incineration have frequently disturbed combustions debromination will be more critical in these facilities operated mostly in developing/transition countries. Therefore debromination of DecaBDE needs to be considered in incineration and pyrolysis/gasification conditions. Also in different secondary metal industries receiving PBDE-containing materials for material or energy recovery (copper smelters, electric arc furnaces, secondary aluminium, antimony smelters) pyrolysis/gasification conditions are most likely present and need to be considered as Is the case for all reductive destruction technologies (Weber 2007).

Zelinsky reported that after an accidental fires in a private residences a plastic TV-case which had been treated with DecaBDE contained 5 % PentaBDE (together with extremely high levels of PBDD/DF as discussed in Appendix 3 (c) (vi)).

Similarly Hirai carried out a life cycle assessment of TV cabinet back covers treated with commercial DecaBDE and calculated the associated damage costs and human health impacts (Hirai et al. 2008). This included consideration of the exposures to OctaBDE, PentaBDE and PBDD/DF in this study caused by impurities or thermal breakdown compounds of commercial DecaBDE. Emissions of PBDE and PBDD/DF from various recycling and disposal alternatives were addressed and these are shown in the table below (Hirai et al. 2008).

Table 80: Characterization results for human health impact by scenarios and chemicals. Unit: Yen (Hirai et al. 2008)



	Mechanical recycling	Thermal recovery	Feedstock recycling	Landfilling	Landfilling & open fire
PentaBDEs	1,400,000	5,100	0	0	6,200,000
OctaBDEs	45,000	770	0	0	1,700,000
DecaBDE	4,800	27	1.1	0	1,400
PBDD/DFs	7,400,000	0	690,000	0	150,000,000
Total	8,900,000	5,800	690,000	0	160,000,000

Among the five scenarios by far the highest damage cost was estimated in "*landfilling and open fire*", followed by "*mechanical recycling*" and "*feedstock recycling*". Among the four compounds, the highest human health impact was caused by PBDD/DF followed by PentaBDE and OctaBDE (all from DecaBDE degradation). The health impacts caused by PBDD/DF were about 1,000 to 100,000 times higher than those by DecaBDE. The health impacts caused by PentaBDE were about 20 to 60 times higher than those by DecaBDE.

Due to the relevance of the debromination/hydrogenation reaction for the debromination/transformation of DecaBDE to diphenylether, POP-BDE, hydroxyBDE and PBDD/DF such work is essential to gain a better

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[134] A major technical application is the dechlorination of PCDD/PCDF on fly ashes (Trumpf et al. 1998, Weber et al. 2002b).

[135] The residence times were not reported in the study but were determined by evaporation of the pyrolysis oil from the fluidised bed reactor.

understanding of these processes, together with any associated human and environmental risk, in respect to recovery and recycling technologies. This issues relating to PBDD/DF was considered in more detail Appendix 2(g).

Debromination in Environmental Reports:

There are an increasing number of reviews and reports where debromination is proposed as an explanation for the apparently anomalous mis-match between environmental or biotic congener profiles and the original compositions of the commercial mixtures. The weight of evidence associated with the literature is that debromination of higher brominated congeners to POP-BDE is occurring in environmentally relevant situations. A few recent examples include:

"*Moreover, BDE-209 is probably a source material for lower-brominated products, i.e. hexa-BDE- 154, that are more readily accumulated and to a greater extend and with a greater degree of persistency*". (Eljarrat et al. 2007)

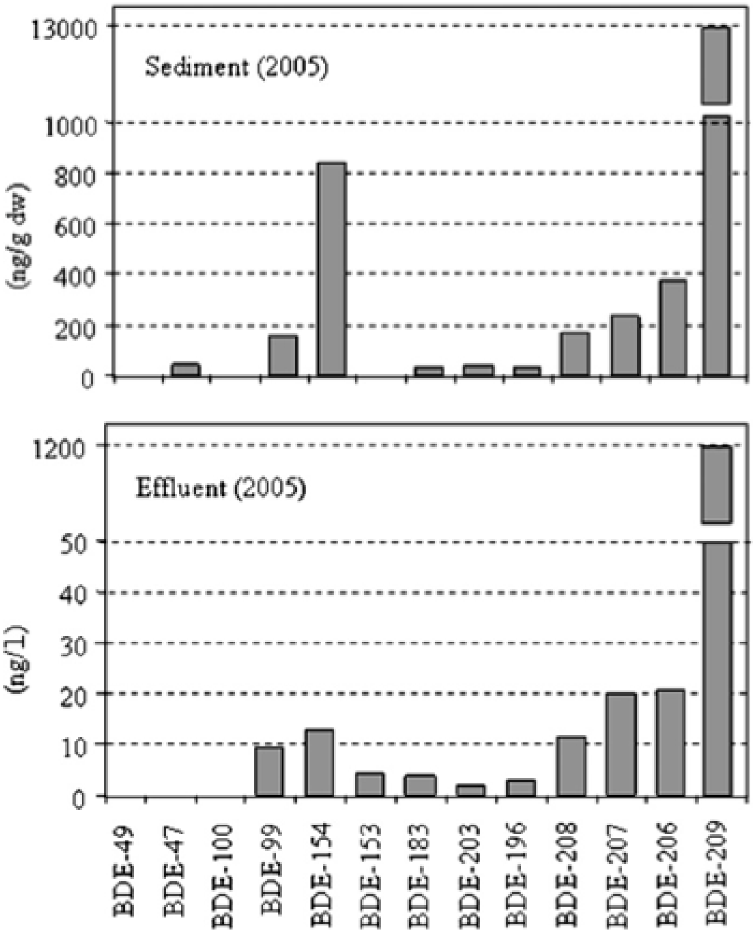

Figure 122: Comparison of congener patterns obtained from the sediment sample collected 5 m downstream of the effluent discharge, and the effluent sample collected at the discharge to the river (Eljarrat et al. 2007)

"*chromatograms showed some peaks probably related to brominated compounds…. that were not present in either the penta-BDE or octa-BDE formula but were identified as octa- and nona-BDEs on the basis of retention times found in the literature.*

Although traces of octa- and nona-BDEs (such as BDE-206, -207, and -208) are detectable in octa- and deca-BDE technical products, the relatively high abundances of octa- and nona-BDE congeners in our sediment samples ... could not be entirely attributed to the technical mixtures. Deca-BDE technical mixtures purchased *from the chemical market in Guangzhou were analyzed in the present study, and only BDE-209 was detectable. All these point to the possibility of debromination of BDE-209 in the aquatic environment.*

Clearly, further research should be conducted to thoroughly understand the degradation mechanism and fate of this compound in the PRD region, because transformation of even a small portion of BDE-209 into lower-brominated PBDEs in sediments could result in serious environmental consequences for many years to come" (Mai et al. 2005).

"*The BDEs 49 and 66 comprised 4–16% of total PBDEs in finless porpoises, which seems to be associated with debromination of higher BDEs*" (Park et al.)

"*several other higher brominated congeners (BDE-197, -206 and -207) were also present in human milk of the present study which in part was due to the possible debromination processes of BDE-209 as also observed in laboratory studies".* (Malarvannan et al. 2009)

The May 2010 USEPA PBDE exposure assessment (USEPA 2010) says:

"Evidence suggests that BDE 209 can be degraded by ultraviolet light (i.e., photolysis) to form lower-brominated BDEs, and this may be an important degradation pathway in the environment"

And:

"*Even with both the penta and octa formulations having been withdrawn from the U.S. market, past use and possible debromination of higher-brominated congeners (e.g., BDE 209) by photolytic or biological mechanisms to form lower-brominated congeners might result in the continued presence of lower-brominated congeners in humans and the environment.*"

Petreas considered that debromination may have significantly influenced the material flow assessment of PBDE in California. He commented that as the unaccounted PBDE consist of mostly BDE-209 this "*may be an indication of debromination, i.e., the original amount of BDE-209 was reduced along the way (by weathering and debromination) resulting in a smaller amount of BDE-209 at the time of its disposal. Correspondingly, more BDE-209 would reside in dust, having escaped from the original products. Indeed, vacuum cleaner dust has proportionately more highly brominated congeners*" (Petreas & Oros 2009).

The report commissioned by the New Zealand Ministry of the Environment as part of the POPRC review process also warned of the dangers associated with debromination of DecaBDE (Geo & Hydro – K8 Ltd 2010):

"*….with the high levels of Deca-BDE found in house dust as was shown above, even if the breakdown occurs slowly or to a small degree, Deca could nevertheless be an important source of exposure to the more toxic and bio-accumulative forms of the PBDEs*" (Geo & Hydro – K8 Ltd 2010).

The high levels of BDE-209 and total PBDE present in peregrine falcon eggs provided an opportunity to measure and examine the metabolic fate of the higher-brominated PBDE (hepta-, octa-, nona-BDE), and to compare patterns of these congeners with those found in PBDE commercial mixtures as well as environmental matrices (sludge, sediment, dusts). Holden et al. found differences between peregrine eggs and commercial mixtures: BDE-184 (hepta-BDE) and BDE-202 (octa-BDE) were not in the commercial mixtures but were found present in peregrine eggs. They also found higher percentages of BDE-207 and -208 (nona-BDE) in the eggs. BDE-207 is the major nona-BDE in peregrine eggs and other biota, while BDE-206 is the major nona-BDE in environmental matrices. They concluded that these "*clear differences between eggs/biota and commercial mixtures in patterns of higher-brominated BDEs offer compelling evidence for the biological debromination of BDE-209*" (Holden et al. 2008a).

Jiang et al examined the occurrence of PBDE in fish and shellfish downstream from electronic-waste recycling plants in China (Jiang et al. 2010). It was notable that the lower-brominated congeners were detected at relatively high concentrations in all species in spite of the PentaBDE levels from the e-waste being found at relatively low levels. The authors concluded that their analysis suggested that the "*primary source of PBDEs appeared to be from the debromination of high brominated PBDE*" (Jiang et al. 2010).

Ma suggested that "*BDE 209 is more readily debrominated to lower BDE congeners under the changes of pressure and temperature used during the low-tech recycling operations, so the composition of some BDE congeners were altered in e-wastes themselves*" during the processing. They found significant correlation among various PBDE congeners in matrices collected from the e-waste facility which supported a common source (Ma et al. 2009).

Other literature sources:

There is an extensive literature relevant to the issue of debromination and a bibliography for those interested in more details would include: (Buser 1988, Yamaguchi et al. 1988, Li & David 1990, Luijk et al. 1992, Morris et al. 1992, Chatkittikunwong & Creaser 1994, van de Plassche et al. 1994, WHO & IPCS 1994, WHO IPCS 1994, Monserrate & Häggblom 1997, Bedard & Van Dort 1998, Kierkegaard et al. 1999, Renner 2000, Hamm et al. 2001, Betts 2002, Blazsó et al. 2002, Risk & Policy Analysts Limited (RPA) for DEFRA 2002, Risk Policy Analysts Limited 2002, Scientific Committee on Toxicity 2002, Scientific Committee on Toxicity Ecotoxicity and the Environment (CSTEE) 2002, Zhang et al. 2002, Ahn et al. 2003, Bhaskar et al. 2003, European Chemicals Bureau 2003a, European Chemicals Bureau 2003b, Hakk & Letcher 2003, Hornung et al. 2003, Rayne et al. 2003, Uddin et al. 2003, Weber & Kuch 2003, Barontini et al. 2004, Bhaskar et al. 2004, Brebu et al. 2004, Eriksson et al. 2004, Farrar et al. 2004, Soderstrom et al. 2004, Stapleton et al. 2004a, Stapleton et al. 2004b, Tomy et al. 2004, Balabanovich et al. 2005, Betts 2005, Bonin et al. 2005, Cupples et al. 2005, Gerecke et al. 2005, Keum & Li 2005, Mai et al. 2005, Rupp & Metzger 2005, Sanchez-Prado et al. 2005, Sellstrom et al. 2005, Ahn et al. 2006a, Ahn et al. 2006b, Arbeli et al. 2006, Blazsó & Czégény 2006, Brebu et al. 2006, Brebu & Sakata 2006, Christiansson et al. 2006, Hagberg et al. 2006, Hale et al. 2006, He et al. 2006, Kierkegaard et al. 2006, Niu et al. 2006, Olsman et al. 2006, Sanchez-Prado et al. 2006, Stapleton 2006a, Stapleton & Dodder 2006, Stapleton 2006b, Stapleton et al. 2006, Streets et al. 2006, Teuten et al. 2006, Thuresson et al. 2006b, Tollback et al. 2006, Viberg et al. 2006, Benedict et al. 2007, Eljarrat et al. 2007, Grabda et al. 2007, Guo et al. 2007, Hanif et al. 2007, Hull et al. 2007, Huwe & Smith 2007, La Guardia et al. 2007, Lam et al. 2007, Li et al. 2007a, Patterson et al. 2007, Persistent Organic Pollutants Review Committee 2007, Pirard & Pauw 2007, Qiu et al. 2007, Rice et al. 2007, Riu et al. 2007, Van den Steen et al. 2007, Verreault et al. 2007, von der Recke & Vetter 2007, Wang et al. 2007, Allen et al. 2008a, Fang et al. 2008, Grause et al. 2008, Harju et al. 2008, Holden et al. 2008a, Holden et al. 2008b, Kajiwara et al. 2008, Kohler et al. 2008a, Kohler et al. 2008b, Li et al. 2008a, Robrock et al. 2008, Schenker et al. 2008, Shaw et al. 2008, Stapleton 2008, Stapleton & Dodder 2008, Stockholm Convention 2008b, Stockholm Convention 2008a, Sun et al. 2008, Tokarz et al. 2008, Vetter et al. 2008, Zhao et al. 2008, Abdallah et al. 2009, Brandsma et al. 2009, Browne et al. 2009, Christiansson et al. 2009, Davis & Stapleton 2009, Heimstad et al. 2009, Hirai et al. 2009, Kemi 2009, Kim et al. 2009, Liu et al. 2009, Luo et al. 2009a, Luo et al. 2009b, Onwudili & Williams 2009, Park et al. 2009, Rayne & Forest 2009, Segev et al. 2009, Shih & Wang 2009, Stapleton & Davis 2009, Stockholm Convention 2009a, Webster et al. 2009, Wyrzykowska et al. 2009, Xie et al. 2009, Yogui & Sericano 2009, Bendig & Vetter 2010, BSEF 2010, Danon-Schaffer & Mahecha-Botero 2010, Frederiksen et al. 2010b, Haglund 2010, Haglund et al. 2010, Huang et al. 2010, Jiang et al. 2010, Kajiwara & Takigami 2010, McKernan et al. 2010, Noyes et al. 2010, Park et al. 2010, Shih & Tai 2010, Wang et al. 2010a)

Annexes

Annex 1: Abstracts for Scientific Meetings

Annex 1a): Conference paper accepted at The Fifth International Conference on Brominated Flame Retardants April 2010 (Kyoto, Japan);

New POPs – The unique challenge of controlling PBDE under the Stockholm Convention

Roland Weber[1], Alan Watson[2], Tom Webster[3]

[1] POPs Environmental Consulting, Göppingen, Germany

[2] Public Interest Consultants, Swansea, Wales, UK.

[3] Boston University School of Public Health, Boston, Massachusetts, USA

Introduction

In May 2009 certain congeners contained in commercial pentabromodiphenyl ether[136] ('PentaBDE') and octabromodiphenyl ethers[137] ('OctaBDE') were added to Annex A of the Stockholm Convention[138] by the fourth Conference of the Parties in Geneva. As a consequence of this these chemicals are officially recognised as persistent organic pollutants ('POPs') and may no longer be produced. Furthermore Article 6 of the Convention requires that wastes containing POPs be managed in a manner protective of human health and the environment (Stockholm Convention 2001). The new listing therefore requires each party of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of persistent organic pollutants (POPs) from stockpiles and wastes.[139]

The listing of these PBDE[140], unlike the original Stockholm POPs, includes specific exemptions allowing for recycling and the use in articles of recycled materials containing these chemicals (Textbox 1) (Stockholm Convention 2009d). This exemption generated significant discussion about whether it could be considered to be consistent with the principal objective[141] of the Stockholm Convention which is to protect human health and the environment from persistent organic pollutants. Recycling of POPs inevitably increases the possibilities of generating new environmental and health risks. The possibility to include POPs in recycled products lead to exposure in the recycling stage (and future recycling cycles) and even generates the possibility that the 'second life' exposure may be greater than in previous uses. The long-term implications of allowing POPs to be released in what is likely to be an uncontrolled fashion also raises serious questions about whether the exemptions compromise the objectives of the Convention. The Persistent Organic Pollutants Review Committee was therefore requested to make recommendations to the Conference of the Parties to address the above concerns.

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136 The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

137 The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether. .

138 Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether and SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.

139 Article 6 of the Stockholm Convention.

140 For the purpose of the technical report, "PBDE" refers to certain congeners contained in commercial octabromodiphenyl and pentabromodiphenyl ethers as listed in decisions SC-4/14 and SC-4/18.

[141] Article 1 of the Stockholm Convention

These recommendations will be based on information gathered from Parties and observers, and informed by a technical report provided by external consultants.

The objective of this article is to highlight:

- the special issues that arise in relation to PBDE and the Stockholm Convention – including the extent of the PBDE contamination problem.
- the areas where it will be necessary to do additional work, to review the knowledge gaps and to suggest how the science community could contribute to solving the problems.

Exemptions for the recycling of articles

Decision SC-4/18 included specific exemption for use in articles in accordance with the following provisions:

1. A Party may allow recycling of articles that contain or may contain tetrabromodiphenyl ether and pentabromodiphenyl ether, and the use and final disposal of articles manufactured from recycled materials that contain or may contain tetrabromodiphenyl ether and pentabromodiphenyl ether, provided that:
    - (a) The recycling and final disposal is carried out in an environmentally sound manner and does not lead to recovery of tetrabromodiphenyl ether and pentabromodiphenyl ether for the purpose of their reuse;
    - (b) The Party does not allow this exemption to lead to the export of articles containing levels/concentrations of tetrabromodiphenyl ether and pentabromodiphenyl ether that exceed those permitted to be sold within the territory of the Party; and
    - (c) The Party has notified the Secretariat of its intention to make use of this exemption.

At its sixth ordinary meeting and at every second ordinary meeting thereafter the Conference of the Parties shall evaluate the progress that Parties made towards achieving their ultimate objective of elimination of tetrabromodiphenyl ether and pentabromodiphenyl ether contained in articles and review the continued need for this specific exemption. This specific exemption shall in any case expire at the latest in 2030.

Decision SC-4/14 has substantially identical provisions in respect of hexabromodiphenyl ether and heptabromodiphenyl ether.

Textbox 1: Specific exemption for the recycling of articles containing TetraBDE to OctaBDE based on Stockholm Convention Decision SC-4/14 (Stockholm Convention 2009c) and SC-4/18 (Stockholm Convention 2009d).

Discussion

As there is no longer any (known) production of commercial PentaBDE or OctaBDE the main challenges relate to the identification and treatment of existing stockpiles.

While the product types in which PBDE have been used are (largely) known details of the extent of current and likely future recycling flows are less well quantified. A particular difficulty has been the lack of information about the historic production of PentaBDE and OctaBDE and quantified details of their respective uses. This is especially important for the United States and for China where large tonnages of PentaBDE and OctaBDE have been produced and used until recently. Products and wastes containing PBDE include certain plastic fractions and foams, used electronics and electronic waste and other second-hand goods including cars, busses, trucks, planes, carpets and textiles, etc. from these countries need to be evaluated for their PBDE contamination particularly when they are exported or recycled.

To get a better understanding of the overall impact of PBDE in recycling schemes, the Conference of the Parties requested the Stockholm Convention Secretariat to collect the following information on brominated diphenyl ethers found in articles from Parties and observers[142] (Stockholm Convention 2009b):

(a) Types and quantities of articles containing brominated diphenyl ethers, including concentrations of those substances in the articles, including recycled articles;

(b) Types of articles recycled, the extent of recycling, the types of articles produced from recycling, the options for the environmental management of recycling operations and releases or potential releases resulting from recycling operations;

(c) Cost-effectiveness of different management options;

(d) Options for environmentally sound disposal;

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[142] Pursuant to paragraphs 1–4 of the annex to decision SC-4/19.

(e) Methods for identifying the presence and levels of brominated diphenyl ethers in articles;

(f) Identification of remediation methods for contaminated sites as listed in subparagraph 1 (e) of Article 6 of the Convention;

(g) Any other related information.

For this process a questionnaire was developed to gather relevant information on these issues and sent to Stockholm Convention parties and observers.

Parties were sent a copy of the questionnaire on 20th November 2009 have been requested to provide responses and information by and interim deadline of 10th April with final information to be submitted by 1st July 2010. The information will then be compiled in a report along with other relevant information on

- Assessment of the possible health and environmental impacts of recycling articles containing brominated diphenyl ethers
- Identification of the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers
- Review of the long-term environmental desirability of the recycling of articles containing brominated diphenyl ethers

It will also be necessary to assess unintentionally produced organic pollutants such as brominated dioxins and furans (Hamm et al. 2001, Tasaki et al. 2004a, Hirai et al. 2008) as part of this review.

In cases where treatments include recycling consideration has to be given to the risks associated with the release into products of PBDE-containing materials throughout the entire lifecycle of those products. This includes an assessment of possible exposure to workers involved in reprocessing, users of recycled materials and the range of exposures which arise from the end-of-life of the recycled materials. Consideration needs to be given to the possibility of labeling such materials to avoid inadvertent contamination in the future. Industries treating material which may be contaminated by PBDE (metal smelters, incinerators or cement kilns etc.) need to be alerted to the hazardous nature of the materials and guidance needs to be prepared to ensure that wastes are treated using environmentally sound methods.

One important issue which needs to be clarified is the level of PBDE contamination above which a material should be regulated by the Stockholm Convention. This question is crucial for several issues which have to be addressed for the SC implementation. For PCB and (POPs Pesticides) the current provisional low POPs limit recommended by the Open Ended Working Group of the Basel Convention (Basel Convention 2004) and which is being used pending the determination of a methodology to establish final levels is 50 ppm (and for PCDD/PCDF the limit is 15 µg TEQ/kg).

No low POPs content has yet been developed for PBDE. One existing limit for PBDE in goods is that defined by the European RoHS regulation for electrical and electronic equipment and currently at 0.1% for PentaBDE, OctaBDE and DecaBDE (Cusack & Perrett). When comparing this limit with the limit for e.g. PCB the limits seems too high and it seems likely that a lower ‘low POPs’ limit will need to be defined for PBDE.

Furthermore whilst brominated dioxins and furans may be responsible for much of the health and environmental risk associated with the use of PBDE (Hirai et al. 2008) no limits have been defined for PBDD/DF yet. Indeed they are not yet Stockholm POPs and are not currently being considered by the POP Review Committee. Only the German law on chemical (German Federal Ministry of Justice 2003) has defined a limit for PBDD/PBDF in products (table 1).

Compound classes	Compounds	Limits
Class I	2,3,7,8-TBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PBDD, 1,2,3,7,8-PBDF	Sum class I < 1 µg/kg
Class II	1,2,3,7,8-PBDF, 1,2,3,6,7,8-HBDD, 1,2,3,7,8,9-HBDD, 1,2,3,4,7,8-HBDD	Sum (I + II) < 5 µg/kg

Table 1: Limit value for polybrominated dibenzodioxins and dibenzofurans in materials according the German regulation for chemicals (German Federal Ministry of Justice 2003).

Low POPs limits for PBDE (and PBDD/PBDF) should be derived based on risk assessment and considerations for minimization of releases of POPs. The process should involve or better be guided by scientific discussions and assessments and be based on scientific criteria. In the development of a low POPs content of PBDE the scientific POPs community should therefore be an important stakeholder.

In addition there would be further research issues in the context of PBDE which might be taken up by the global POPs research community:

- Screening on contamination levels of PBDE and other critical pollutants in the recycling flow and their human exposure, final sink and phase out options
- A global substance flow analysis for PBDE and other critical pollutants
- Further data on (human) toxicity for PBDE and related risk assessment

The case of PBDE is another example of where inadequate evaluation of a halogenated chemical prior to large scale production and use has resulted in global pollution. Residual contamination of a wide range of product streams and the difficult challenges, and high economic costs, are now apparent in relation to the recyclability of several waste streams. These chemicals even impact on the recycling of other non-contaminated products in the plastics waste stream. It is clear that chemicals used now and in future for flame retardancy need a much more rigorous evaluation over their whole life cycle. In this respect a report for the European Commission on the extension of the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Groß et al. 2008) proposed the phase out all brominated and chlorinated flame retardants along with PVC and heavy metals in electric and electronic consumer to protect consumers and to facilitate easier and safer recycling at the end-of-life stage (European Commission 2010).

In addition to the evaluation required for REACH, the science community could critically evaluate currently used and emerging flame retardants to bridge the knowledge gap for these bulk chemicals which are in daily products with direct exposure to consumers. This assessment should include considerations on interaction of chemicals in chemical mixtures having in mind the increasing range of BFRs and other PBTs which are included in products but which are not adequately considered by REACH (Rudén & Hansson 2009). This approach should help to avoid repeating the mistakes of the recent past.

If independent science assists a better understanding of the hazards associated with these compounds and results in increased substitution by more benign chemicals, then PBDE could serve as examples of the benefits of the phase-out of halogenated chemicals from use in consumer products. More positive application and integration of the principles of substitution and precaution would not only guarantee reduced life cycle costs and improved recycling with associated economic benefits but would also reduce risks of damage to health and the environment over the whole life cycle of a product. This would be an important contribution to sustainable production and consumption.

References

Annex 1b): Conference paper presented at the UK POPs Conference 20th-21st April 2010 (Birmingham, UK);

Now Penta and Octa BDE are Stockholm POPs the recycling challenges begin – another reason to Phase out Hazardous Chemicals from Products

Weber[1] R, Watson A[2], Webster T[3]

[1] POPs Environmental Consulting, Göppingen, Germany

[2] Public Interest Consultants, Swansea, Wales, UK.

[3] Boston University School of Public Health, Boston, Massachusetts, USA

PBDE is another example of where inadequate evaluation of a halogenated chemical prior to large scale production has resulted in global pollution. In May 2009 certain congeners contained in commercial PentaBDE[143] and OctaBDE[144] were added in the POPs list of the Stockholm Convention[145]. As there is no longer any (known) production the main challenges is the identification and treatment of existing stockpiles and waste containing PBDE. Here the Stockholm Convention requires each party to take appropriate measures to reduce or eliminate releases of POPs.[146] The listing of PBDE[147] includes, however, specific exemptions allowing for recycling and use in articles of recycled materials containing these chemicals. Recycling of POPs inevitably increases new environmental and health risks. This exemption generated significant discussion about whether it could be considered to be consistent with the principal objective[148] of the Stockholm Convention (protection of human health and the environment from POPs). Residual contamination of a wide range of product streams is now a practical and policy challenges and high economic costs are apparent in relation to the recyclability of several waste streams. This highlights from health and economic perspective that chemicals used for flame retardancy need a more rigorous evaluation over their whole life cycle.

In this respect a report for the European Commission on extension of the RoHS Directive has proposed the phase out of all brominated and chlorinated flame retardants in electric and electronic consumer products to protect consumers and to facilitate easier and safe recycling.

The PBDE dilemma has a range of research issues which might be taken up by the global POPs research community and include inter alia:

- The discussion and determination of low POPs content for PBDE & PBDD/PBDF in products
- Improvement of the risk assessment scenario of end-of-life stage of consumer products
- Screening on contamination levels of PBDE and other critical pollutants in the recycling flow and their human exposure, final sink and phase out options

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[143] The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

[144] The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether. .

[145] Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether and SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.

[146] Article 6 of the Stockholm Convention.

[147] For the purpose of the technical report, “PBDE” refers to certain congeners contained in commercial octabromodiphenyl and pentabromodiphenyl ethers as listed in decisions SC-4/14 and SC-4/18.

[148] Article 1 of the Stockholm Convention

- A global substance flow analysis for PBDE and other critical pollutants
- Further data on (human) toxicity for PBDE and related risk assessment

The case of PBDE is another example of where inadequate evaluation of a halogenated chemical prior to large scale production and use has resulted in global pollution. Residual contamination of a wide range of product streams and the difficult challenges, and high economic costs, are now apparent in relation to the recyclability of several waste streams. These chemicals even impact on the recycling of other non-contaminated products in the plastics waste stream. It is clear that chemicals used now and in future for flame retardancy need a much more rigorous evaluation over their whole life cycle. In this respect a report for the European Commission on the extension of the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Groß et al. 2008) proposed the phase out all brominated and chlorinated flame retardants along with PVC and heavy metals in electric and electronic consumer to protect consumers and to facilitate easier and safer recycling at the end-of-life stage (European Commission 2010).

In addition to the evaluation required for REACH, the science community could critically evaluate currently used and emerging flame retardants to bridge the knowledge gap for these bulk chemicals which are in daily products with direct exposure to consumers. This assessment should include considerations on interaction of chemicals in chemical mixtures having in mind the increasing range of BFRs and other PBTs which are included in products but which are not adequately considered by REACH (Rudén & Hansson 2009). This approach should help to avoid repeating the mistakes of the recent past.

If independent science assists a better understanding of the hazards associated with these compounds and results in increased substitution by more benign chemicals, then PBDE could serve as examples of the benefits of the phase-out of halogenated chemicals from use in consumer products. More positive application and integration of the principles of substitution and precaution would not only guarantee reduced life cycle costs and improved recycling with associated economic benefits but would also reduce risks of damage to health and the environment over the whole life cycle of a product. This would be an important contribution to sustainable production and consumption.

Annex 1c): Conference paper accepted at the SETAC Asia Pacific meeting June 2010 (Guangzhou, China).

PBDE as New POPs in the Stockholm Convention Reveal Challenge of Recycling – One More Call to Phase out Hazardous Chemicals from Products

Weber[1] R, Watson A[2], Webster T*[3]

[1] POPs Environmental Consulting, Göppingen, Germany

[2] Public Interest Consultants, Swansea, Wales, UK.

[3] Boston University School of Public Health, Boston, Massachusetts, USA

PBDE is another example of where inadequate evaluation of a halogenated chemical prior to large scale production has resulted in global pollution. In May 2009 certain congeners contained in commercial PentaBDE[149] and OctaBDE[150] were added in the POPs list of the Stockholm Convention[151]. As there is no

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[149] The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

[150] The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether

longer any (known) production the main challenges is the identification and treatment of existing stockpiles and waste containing PBDE. Here the Stockholm Convention requires each party to take appropriate measures to reduce or eliminate releases of POPs.[152] The listing of PBDE[153] includes, however, specific exemptions allowing for recycling and use in articles of recycled materials containing these chemicals. Recycling of POPs inevitably increases new environmental and health risks. This exemption generated significant discussion about whether it could be considered to be consistent with the principal objective[154] of the Stockholm Convention (protection of human health and the environment from POPs). Residual contamination of a wide range of product streams is now a practical and policy challenges and high economic costs are apparent in relation to the recyclability of several waste streams. This highlights from health and economic perspective that chemicals used for flame retardancy need a more rigorous evaluation over their whole life cycle. In this respect a report for the European Commission on extension of the RoHS Directive has proposed the phase out of all brominated and chlorinated flame retardants in electric and electronic consumer products to protect consumers and to facilitate easier and safe recycling. The presentation details these policy issues.

Annex 1d):) Conference paper accepted for Dioxin 2010.

PBDE AS “NEW POPs” – CHALLENGES AND KNOWLEDGE GAPS OF CONTROLLING PBDE UNDER THE STOCKHOLM CONVENTION

Weber R[1], Watson A[2], Webster T[3]

[1] POPs Environmental Consulting, Göppingen, Germany, [2] Public Interest Consultants, Swansea, Wales, UK.

[3] Boston University School of Public Health, Boston, Massachusetts, USA

Introduction

Pentabromodiphenyl ether (‘PentaBDE’) and certain congeners of octabromodiphenyl ethers[155] (‘OctaBDE’) were added to Annex A of the Stockholm Convention by the fourth Conference of the Parties in Geneva (05/2009)[1,2]. Therefore these chemicals are officially recognised as persistent organic pollutants (‘POPs’) and may no longer be produced. Furthermore Article 6 of the Convention requires that wastes containing POPs be managed in a manner protective of human health and the environment[3]. The new listing therefore requires each of the 170 parties of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of PBDE[156] from stockpiles and wastes.

The listing of these PBDE, unlike the original Stockholm POPs, includes specific exemptions allowing for recycling and the use in articles of recycled materials containing these chemicals (Textbox 1)[1,2](Stockholm Convention 2009d). This exemption generated significant discussion about whether it could be considered to be consistent with the principal objective of the Stockholm Convention which is to protect human health and the environment from persistent organic pollutants. Recycling of POPs inevitably increases the possibilities of

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(BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether. .

151 Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether and SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.

152 Article 6 of the Stockholm Convention.

153 For the purpose of the technical report, “PBDE” refers to certain congeners contained in commercial octabromodiphenyl and pentabromodiphenyl ethers as listed in decisions SC-4/14 and SC-4/18.

154 Article 1 of the Stockholm Convention

[155] The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether

156 For the purpose of the technical report, “PBDE” refers to certain congeners contained in commercial octabromodiphenyl and pentabromodiphenyl ethers as listed in decisions SC-4/14 and SC-4/18.

generating new environmental and health risks. The possibility to include POPs in recycled products lead to exposure in the recycling stage (and future recycling cycles) and even generates the possibility that the 'second life' exposure may be greater than in previous uses. The long-term implications of allowing POPs to be released in what is likely to be an uncontrolled fashion also raises serious questions about whether the exemptions compromise the objectives of the Convention. The Persistent Organic Pollutants Review Committee was therefore requested to make recommendations to the Conference of the Parties to address the above concerns. These recommendations will be based on information gathered from Parties and observers, and informed by a technical report provided by external consultants.

The objective of this article is to highlight the special issues that arise in relation to PBDE and the Stockholm Convention – including the extent of the PBDE contamination problem. Further the article wants to draw attention to areas where it will be necessary to do additional work, to review the knowledge gaps and to suggest how the science community could contribute to solving the problems.

Discussion

As there is no longer any (known) production of commercial PentaBDE or OctaBDE the main challenges relate to the identification and treatment of existing stockpiles.

While the product types in which PBDE have been used are (largely) known details of the extent of current and likely future recycling flows are less well quantified. A particular difficulty has been the lack of information about the historic production of PentaBDE and OctaBDE and quantified details of their respective uses. This is especially important for the United States and for China where large tonnages of PentaBDE and OctaBDE have been produced and used until recently. Products and wastes containing PBDE include certain plastic fractions and foams, used electronics and electronic waste and other second-hand goods including cars, busses, trucks, planes, carpets and textiles, etc. from these countries need to be evaluated for their PBDE contamination particularly when they are exported or recycled.

Exemptions for the recycling of articles

Decision SC-4/18 included specific exemption for use in articles in accordance with the following provisions:

1. A Party may allow recycling of articles that contain or may contain tetrabromodiphenyl ether and pentabromodiphenyl ether, and the use and final disposal of articles manufactured from recycled materials that contain or may contain tetrabromodiphenyl ether and pentabromodiphenyl ether, provided that:

(a) The recycling and final disposal is carried out in an environmentally sound manner and does not lead to recovery of tetrabromodiphenyl ether and pentabromodiphenyl ether for the purpose of their reuse;

(b) The Party does not allow this exemption to lead to the export of articles containing levels/concentrations of tetrabromodiphenyl ether and pentabromodiphenyl ether that exceed those permitted to be sold within the territory of the Party; and

(c) The Party has notified the Secretariat of its intention to make use of this exemption.

At its sixth ordinary meeting and at every second ordinary meeting thereafter the Conference of the Parties shall evaluate the progress that Parties made towards achieving their ultimate objective of elimination of tetrabromodiphenyl ether and pentabromodiphenyl ether contained in articles and review the continued need for this specific exemption. This specific exemption shall in any case expire at the latest in 2030.

Decision SC-4/14 has substantially identical provisions in respect of HxBDE and HeptaBDE.

Textbox 1: Specific exemption for the recycling of articles containing TetraBDE to HeptBDE based on Stockholm Convention Decision SC-4/14[1] and SC-4/18[2].

To get a better understanding of the overall impact of PBDE in recycling schemes, the Conference of the Parties requested the Stockholm Convention Secretariat to collect the following information on brominated diphenyl ethers found in articles from Parties and observers (Stockholm Convention 2009b):

(a) Types and quantities of articles containing brominated diphenyl ethers, including concentrations of those substances in the articles, including recycled articles;

(b) Types of articles recycled, the extent of recycling, the types of articles produced from recycling, the options for the environmental management of recycling operations and releases or potential releases resulting from recycling operations;

(c) Cost-effectiveness of different management options;

(d) Options for environmentally sound disposal;

(e) Methods for identifying the presence and levels of brominated diphenyl ethers in articles;

(f) Identification of remediation methods for contaminated sites as listed in subparagraph 1 (e) of Article 6 of the Convention;

(g) Any other related information.

For this process a questionnaire was developed to gather relevant information on these issues and sent to Stockholm Convention parties and observers. Parties were sent a copy of the questionnaire on 20th November 2009 have been requested to provide responses and information by and interim deadline of 10th April with final information to be submitted by 1st July 2010. The information will then be compiled in a report along with other relevant information on

Assessment of the possible health and environmental impacts of recycling articles containing brominated diphenyl ethers

Identification of the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers

Review of the long-term environmental desirability of the recycling of articles containing brominated diphenyl ethers

It will also be necessary to assess unintentionally produced organic pollutants such as polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) as part of this review.

In cases where treatments include recycling, consideration has to be given to the risks associated with the release into products of PBDE-containing materials throughout the entire lifecycle of those products. This includes an assessment of possible exposure to workers involved in reprocessing, users of recycled materials and the range of exposures which arise from the end-of-life of the recycled materials. Consideration needs to be given to the possibility of labeling such materials to avoid inadvertent contamination in the future. Industries treating material which may be contaminated by PBDE (metal smelters, incinerators, cement kilns, pyrolysis for plastic feedstock recycling etc.) need to be alerted to the hazardous nature of the materials and guidance needs to be prepared to ensure that wastes are treated using environmentally sound methods.

One important issue which needs to be clarified is the level of PBDE contamination above which a material should be regulated by the Stockholm Convention. This question is crucial for several issues which have to be addressed for the SC implementation. For PCB and (POPs Pesticides) the current provisional low POPs limit recommended by the Open Ended Working Group of the Basel Convention[5](Basel Convention 2004) and which is being used pending the determination of a methodology to establish final levels is 50 ppm (and for PCDD/PCDF the limit is 15 µg TEQ/kg).

No low POPs content has yet been developed for PBDE. One existing limit for PBDE in goods is that defined by the European RoHS regulation for electrical and electronic equipment and currently at 0.1% for PentaBDE, OctaBDE and DecaBDE[6]. When comparing this limit with the limit for e.g. PCB the limits seems rather high and it seems likely that a lower ‘low POPs’ limit will need to be defined for PBDE.

Furthermore whilst PBDD/PBDF may be responsible for much of the health and environmental risk associated with the use of PBDE[7] no TEF value or limits have been defined for PBDD/DF yet. Indeed they are not yet Stockholm POPs and are not currently being considered by the POP Reviewing Committee. Only the German law on chemical[8] has defined a limit for PBDD/PBDF in products (table 1).

Compd class	Compounds	Limits
Class I	2,3,7,8-TBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PBDD, 1,2,3,7,8-PBDF	Sum class I < 1 µg/kg
Class II	1,2,3,7,8-PBDF, 1,2,3,6,7,8-HBDD, 1,2,3,7,8,9-HBDD, 1,2,3,4,7,8-HBDD	Sum (I + II) < 5 µg/kg

Table 1: Limit value for PBDD/DF in materials according the German regulation for chemicals.[8]

Low POPs limits for PBDE (and PBDD/DF) should be derived based on risk assessment and considerations for minimization of releases of POPs. The process should involve or better be guided by scientific discussions and assessments and be based on scientific criteria. In the development of a low POPs content of PBDE the scientific POPs community should therefore be an important stakeholder.

In addition there would be further research issues in the context of PBDE which might be taken up by the global POPs research community:

Screening on contamination levels of PBDE and other critical pollutants (e.g. HBCD, PFOS, PFCs) in the recycling flow and recycled products and related human exposure, final sink and phase out options.

PBDE (other BFR) release and PBDD/PBDE formation and releases from treatment of materials containing PBDE (other BFRs) in end-of-life stage (metal smelters, other metal industries, cement kilns, pyrolysis of plastic for feedstock recycling, etc.). Measurements should include assessment of PBDE (BFR) input to estimate destruction efficiencies and assessment of options and limitations.

Fate of debromination of DecaBDE to POPs PBDE in these technical processes, in landfills, the environment and in biota. The assessment of DecaBDE degradation should include other degradation products including OH-PBDE, PBDD/PBDF and further degradation products.

PBDE (BFR) contaminated sites from production, application and end-of-life treatment.

Global substance flow analysis of PBDE (and other critical BFRs).

Further data on toxicity for PBDE and related risk assessment.

External cost estimates/calculations of harm caused by PBDE to humans and biota.

Life Cycle Assessment of PBDE alternatives (other flame retardants and alternative technogies).

The case of PBDE is another example of where inadequate evaluation of a halogenated chemical prior to large scale production and use has resulted in global pollution. Residual contamination of a wide range of product streams and the difficult challenges, and high economic costs, are now apparent in relation to the recyclability of several waste streams. These chemicals even impact on the recycling of other non-contaminated products in the plastics waste stream. It is clear that chemicals used now and in future for flame retardancy need a much more rigorous evaluation over their whole life cycle. In this respect a report for the European Commission on the extension of the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment9 proposed the phase out all brominated and chlorinated flame retardants along with PVC and heavy metals in electric and electronic consumer goods to protect consumers and to facilitate easier and safer recycling at the end-of-life stage.[10]

In addition to the evaluation required for REACH, the science community could critically evaluate currently used and emerging flame retardants to bridge the knowledge gap for these bulk chemicals which are in daily products with direct exposure to consumers. This assessment should include considerations on interaction of chemicals in chemical mixtures having in mind the increasing range of BFRs and other PBTs which are included in products but which are not adequately considered by REACH.[11] This approach should help to avoid repeating the mistakes of the recent past.

If independent science assists a better understanding of the hazards associated with these compounds and results in increased substitution by more benign chemicals, then PBDE could serve as examples of the benefits of the phase-out of halogenated chemicals from use in consumer products. More positive application and integration of the principles of substitution and precaution would not only guarantee reduced life cycle costs and improved recycling with associated economic benefits but would also reduce risks of damage to health and the environment over the whole life cycle of a product. This would be an important contribution to sustainable production and consumption.

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Annex 2 – Responses to Questionnaire:

Questionnaires from parties

Parties were asked to supplement the information collected by the consultants with country specific details in a detailed questionnaire from the Secretariat. This included a request for:

(a) Types and quantities of articles containing brominated diphenyl ethers, including concentrations of those substances in the articles, including recycled articles;

(b) Types of articles recycled, the extent of recycling, the types of articles produced from recycling, the options for the environmental management of recycling operations and releases or potential releases resulting from recycling operations;

(c) Cost-effectiveness of different management options;

(d) Options for environmentally sound disposal;

(e) Methods for identifying the presence and levels of brominated diphenyl ethers in articles;

(f) Identification of remediation methods for contaminated sites as listed in subparagraph 1 (e) of Article 6 of the Convention;

(g) Any other related information.

The final deadline for submission was 1st July 2010. By the date of this draft responses had been received from 26 parties and these are summarised in the table below.
The replies indicated that most parties hold very little information about uses or stocks of POP-BDE. Only a small proportion of responses contained even limited detailed data inventory of articles containing POP-PBDE for Part B.

Table 81: Summary responses to Response to Stockholm Convention Secretariat's Questionnaire for submission of information on New POPs in accordance with SC-4/19
Copies of submissions are available from:
http://chm.pops.int/Programmes/NewPOPs/InformationrequestdecisionSC419/NewPOPsInformationdecisionSC419/tabid/712/language/en-US/Default.aspx

Country	*Date of Submission*	*Contact Details*	*General Information Section A*	*Detailed information Section B*
Algeria	17th June 2010	Mme Dalila BOUDJEMAA Directrice Générale de l'Environnement et du Développement Durable Adresse : Rue des quatre canons Alger Algérie Tel. 0021321432804 e-mail : d_boudjemaa[at]hotmail.com	Confirms no information is available	No Data
Austria	19th May 2010	Federal Ministry of Agriculture, Forestry, Environment and Water Management Stubenbastei 5 A- 1010 Vienna Tel: +41 1 515 22-	Completed a helpful and detailed response with data relating to all BDE including Deca – particularly for the output from the MBA recycling plant.	No data in terms of quantities but Commented that the existence of BDE-containing equipment is unlikely due to the limited lifetime
Bulgaria	7th April 2010	Ms.TSVETANKA DIMCHEVA National Focal Point, BULGARIA MINISTRY OF ENVIRONMENT AND WATER, 67, W. Gladstone Street 1000, Sofia, Tel:+359 2 940 6261 e-mail:dimcheva[at]moew.government.bg	Completed confirming that there was no production in Bulgria and no data on recycling but that the EU regulatory framework applies and that the process of collecting information on commercial pentaBDE and octaBDE in articles from interested state institution, the industry and waste management companies is underway.	No Data
Canada	30th April 2010	No Contact Details Given	Confirms that there is some recycling of POP-BDE to rebonded foam carpet cushion but no details are known of the quantities or congeners. There are no emissions data for the e-waste smelter operating in Canda and there is no data regarding disposal of foam or other non e-waste products containing Penta or OctaBDE	No Data

Country	*Date of Submission*	*Contact Details*	*General Information Section A*	*Detailed information Section B*
Côte d'Ivoire	25th May 2010	Mr.Zadi Dakouri Raphaël Ministère de l'Environnement, des Eaux et Forêts 20 BP 650 Abidjan 20 ; 00225 0617 2799	Completed confirming that it is not known whether there was any manufacturing but that there is no data on stocks or recycling.	No Data
Czech Republic	11th May 2010	Dr. Karel Bláha, +420 267 181 111; karel_blaha[at]env.cz Prof. Dr. Ivan Holoubek, +420 549 491 475; holoubek[at]recetox.muni.cz	Confirms that it not known if the Czech Republic ever manufactured articles containing cPentaBDE or cOctaBDE. There is no information on articles containing POP-BDE and there is no information on new articles produced from recycled products containaing POP-BDE but there are "probably none".	No Data
Estonia	6th April 2010	Reet Pruul, chief specialist, Narva road 7a, Tallinn, Estonia +372 6260 731 reet.pruul[at]envir.ee	Completed confirming that Penta and OctaBDE were never manufactured; that there is no data on stocks or recycling.	No Data
Germany	7th April 2010	Dr. Steffi Richter, Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany telephone: 0049-340-2103-3275 e-mail: steffi.richter[at]uba.de	Completed confirming that goods containing Penta and Octa BDE were manufactured in Germany but that there is no information on articles in use. "Electronic+Electric devices are only allowed to be recycled after separation of BDE-containing fractions/parts (there is no recycling of BDE-containing parts/polymers)" This is subject to the 0.1% RoHS threshold.	No Data
Honduras	30th April 2010	Centro de Estudios y Control de Contaminantes CESCCO, Bo. Morazán frente a estación de Bomberos, tel:231-1006/239-0954, cescco.serna[at]gmail.com	Completed confirming that there is no manufacturing information and no data stocks or recycling (although potential articles were highlighted as pipes or building materials). Treatments of waste water and agricultural plastics are listed as environmental management of recycling	No Data
Japan	1st July 2010	Ms Mayuka Ishida Global Environment Division, International Cooperation Bureau, Ministry of Foreign Affairs E-mail: mayuka.ishida[at]mofa.go.jp	No information was available	No Data

Country	Date of Submission	Contact Details	General Information Section A	Detailed information Section B
Korea	1st July 2010	Ms. Lee Jee-Yoon/Director Chemicals Management Division/Ministry of Environment Jeeyoon[at]korea.kr +82-2-2110-7963	Confirmed that Korea has manufactured goods containing Penta or OctaBDE but no details were available. Recycling of electronic & electric devices is only allowed, if the concentration of Penta- and OctaBDE in EEE Product is below the threshold of 0.1 %	No Data
Mauritius	April 2010	Ramchurn SEENAUTH, Environment Officer Ministry of Environment &NDU St Georges Street Port Louis MAURITIUS Tel : (230) 2133058 E-mail:rseenauth[at]mail.gov.mu	Completed confirming that there was no manufacturing and no data on stocks or recycling	No Data
Moldova	1st July 2010	Liudmila Marduhaeva, Ministry of Environment 9, Cosmonautilor St., MD-2005 Chisinau, Republic of Moldova Tel.: +(373 22) 20 45 26 Fax: +(373 22) 22 62 54 / 22 68 58 E-mail: Liudmila[at]moldovapops.md	Moldova confirms that no articles containing PentaBDE or OctaBDE were manufactured in the country There is no any information about articles containing commercial pentaBDE and OctaBDE that are recycled in the Republic of Moldova. The response says these “need to be inventoried”. Provisions on POPs waste / stockpiles management, including polybrominated diphenyl ethers and included in the new draft Law on waste	No Data
Monaco	18th December 2009	DIRECTION DE L’ENVIRONNEMENT 3, avenue de FONTVIEILLE 98000 MONACO TEL. :+ 377 98 98 46 80 FAX : + 377 92 05 28 91 Email : environnement@gouv.mc	No information	No Data
Mozambique	15th April 2010	Dr. Joseph Gungunhana, Avenue Acordo de Lusaka 2115, Maputo , Mozambique Jgungunhana[at]yahoo.com.br	Confirms that there has never been manufacture of articles containing POP-BDE in Mozambique and that there is no data on articles containing POP-BDE	Suggests 40 kg/year usage of BDE-153 and 152 (?) and small quantities of BDE-175 (?)

Country	*Date of Submission*	*Contact Details*	*General Information Section A*	*Detailed information Section B*
The Netherlands	1st July 2010	Mr. J.K. Kwisthout P.O. Box 30945, 2500 GX Den Haag, The Netherlands +31 703394726 JanKarel.Kwisthout[at]minvrom.nl	Confirms articles containing POP-BDE have been manufactured in The Netherlands. NO information is available about recycled articles which may contain POP-BDE. Suggests that the Netherlands consumption of OctaBDE was 600-800 tonnes/year (1990)	No Data but suggests temporal range from 1970-2001
New Zealand	24th June 2010 Report followed: 25th June 2010	Howard Ellis Senior Analyst, Environmental Protection Directorate (04) 439 7437 d/l; howard.ellis[at]mfe.govt.nz Ministry for the Environment PO Box 10362, Environment House, 23 Kate Sheppard Place, Wellington 6143, New Zealand	Completed confirming that goods containing Penta and Octa BDE were manufactured in New Zealand and that information on articles in use was under preparation. Most polymers are currently shredded for export or are landfilled in New Zealand	Submitted a report : Investigation of brominated flame retardants present in articles being used, recycled and disposed of in New Zealand.
Norway	1st July 2010	Eli Vike, Climate and Pollution Agency, P.O.Box 8100, N-0032 Oslo, Tel. +47 22 57 34 00 eli.vike[at]klif.no	Confirms that Norway has manufactured articles containing POP-BDE but that there is no information on articles containing BDE. An enforcement strategy is in place to identify articles. Waste containing more than 0.25% of pentaBDE or octaBDE is defined as hazardous waste and has to be treated according to the regulation on hazardous waste. The export hazardous waste for recycling is not allowed. Production, import, export and use of pentaBDE and octaBDE in articles were prohibited from 01.07.2004.	Between 1997 and 2003 75 kg/year was used for textiles. No further details are given.
Romania	19th May 2010	Mihaela CIOBANU, Adviser Pollution Control and Impact Assessment Directorate Ministry of Environment and Forests 12 Libertății Blvd. 5 District Bucharest, Romania	Completed confirming that it is not known whether there was any manufacturing but that there is no data on stocks or recycling.	No Data
Serbia	28th June 2010	SERBIA SERBIAN CHEMICALS AGENCY, 1, Omladinskih brigada Street 11070, Belgrade, Serbia Ms.TATJANA MARKOV MILINKOVIC National	It is not known whether Serbia ever manufactured articles containing PentaBDE or OctaBDE and there is no data available on articles containing the POP-BDE. The EU legal framework	No Data

Country	*Date of Submission*	*Contact Details*	*General Information Section A*	*Detailed information Section B*
		Official Contact Point Tel:+381 11 228 3367 e-mail: tatjana.m.milinkovic@ekoplan.gov.rs	and 0.1% limit applies	
Sierra Leone	28th April 2010	Sierra Leone Environment Protection Agency 3rd Floor, Youyi Building, Freetown, Sierra Leone. Email: ebaimba@yahoo.com Tel: +23276653065	Confirms Sierra Leone never manufactured articles containing PentaBDE or OctaBDE and there is no data available on articles in use containing the POP-BDE. As there are no recycling plants in the Country and so no POP-BDE are recycled into articles.	No Data
Slovenia	30th June 2010	Ms. Vesna Ternifi, Chemicals Office of the Republic of Slovenia, Ajdovščina 4, SI-1000 Ljubljana, Slovenia;Tel: +386 1 478 6283, Fax: +386 1 478 6266; vesna.ternifi[at]gov.si MSc. Barbara Štravs Grilc, Environmental Agency of the Republic of Slovenia, Vojkova 1b, 1000 Ljubljana, Slovenia; tel.:+386 (0)1 478 4156; barbara.stravs-grilc[at]gov.si	No information on production, use or levels in articles. Confirms that Slovenia uses the EU regulatory framework and POPs Regulations	No Data
Sweden	15th April 2010	Maria Nyholm SWEDISH ENVIRONMENTAL PROTECTION AGENCY Implementation and Enforcement Department OFFICE: Valhallavägen 195, Stockholm POSTAL: SE-106 48 Stockholm, Sweden TEL: + 46 8 698 16 95, FAX: + 46 8 20 29 25	Completed confirming that goods containing Penta and Octa BDE were manufactured in Sweden but that there is no information on articles in use. Listed ordinances for management and details of Swedish recycling operations including Boliden smelter.	No data on quantities – time periods for use noted as 1970s to 2001
Switzerland	1st July 2010	Bettina Hitzfeld Federal Office for the Environment 3003 Bern, Switzerland +41 31 32 31768 bettina.hitzfeld[at]bafu.admin.ch	Completed confirming most of the articles containing pentaBDE or octaBDE that have been put on the market in Switzerland before the ban in 2005 were imported. The proportion of such articles that have been manufactured in Switzerland is not known. A market survey carried out in Switzerland in 2008	End of 1990s: < 500 t pentaBDE < 680 t octaBDE

Country	Date of Submission	Contact Details	General Information Section A	Detailed information Section B
			concluded that no articles containing commercial pentaBDE and only very few that contain commercial octaBDE are on the market. All material from recycling processes containing pentaBDE and octaBDE is either disposed of by thermal destruction in waste incinerations plants equipped with state-of-the-art emission control technology in Switzerland or exported under the supervision of the Federal Office for the Environment to a specialized enterprise who recovers bromine-free polymers by a physical separation process.	
Trinidad and Tobago	19th March 2010	Office of the Permanent Secretary Ministry of Planning, Housing and the Environment, 44-46 South Quay Port of Spain Trinidad West Indies	Completed confirming that there is no data on production, stocks or recycling	No Data
Ukraine	9th April 2010	Ministry of Environmental Protection Department of Environmental Safety 35, Urytskogo Str., 03035 Kyiv Tel./Fax: +38 (044) 206-31-65 e-mail: waste[at]menr.gov.ua / sukhorebra[at]ukrpost.ua	Completed confirming that there was no production and no data stocks or recycling (although there is medium scale recycling of plastics and mineral oil regeneration – description to follow)	No Data
United States of America	9th April 2010	Amy Breedlove of USEPA confirmed by email that no information was being submitted on PBDE.		

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