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**Persistent Organic Pollutants Review Committee**

**Sixth meeting**

Geneva, 11–15 October 2010

Item 4 (a) of the provisional agenda\*

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

**Work programmes on new persistent organic pollutants as  
adopted by the Conference of the Parties**

**Note by the Secretariat**

1. Having amended the Stockholm Convention by decisions SC-4/10–SC-4/18 to list nine new chemicals in Annexes A, B and C to the Convention, the Conference of the Parties decided to undertake a work programme to provide guidance to parties on how best to restrict and eliminate brominated diphenyl ethers, perfluorooctane sulfonic acid (PFOS) and its salts, perfluorooctane sulfonyl fluoride (PFOSF) and the other newly listed chemicals.

2. In accordance with the elements of a work programme contained in the annex to decision SC-4/19, the Secretariat gathered information from parties and observers, pursuant to paragraphs 1–4 of the annex to decision SC-4/19, on brominated diphenyl ethers found in articles, PFOS, its salts, PFOSF and other chemicals listed at the fourth meeting of the Conference of the Parties. The submissions received by the deadline of July 2010 are summarized in document UNEP/POPS/POPRC.6/INF/6.

3. Based on the terms of reference developed by the Persistent Organic Pollutants Review Committee at its fifth meeting and adopted in decision POPRC-5/1, a draft technical paper has been prepared and is set out in the annex to the present note. A supporting document and a compilation of comments and responses in relation to the paper can be found in documents UNEP/POPS/POPRC.6/INF/10 and UNEP/POPS/POPRC.6/INF/7, respectively. The draft technical paper has not been formally edited by the Secretariat.

**Possible action by the Committee**

4. The Committee may wish:
- (a) To review the information provided by parties and observers and in the draft technical paper;
  - (b) To identify potential gaps in such information and to recommend how to fill those gaps;

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

- (c) To adopt the draft technical paper with any amendments that it deems appropriate;
- (d) To prepare reports for the Conference of the Parties at its fifth meeting on the information provided and to develop recommendations on the elimination of brominated diphenyl ethers from the waste stream and on risk reduction for PFOS, its salts and PFOSF.

**Annex**

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

**DRAFT**

**August 2010**

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## 1. Introduction

1. This is the executive summary of a report on the implications of recycling articles containing commercial Pentabromodiphenyl ether and Octabromodiphenyl ether (POP-BDE). It has been commissioned by the Secretariat of the Stockholm Convention at the request of the Persistent Organic Pollutants Review Committee (POPRC). The executive summary is supported by six Appendices and two Annexes containing the detailed technical discussions and comprehensive referencing of the issues summarised here.

2. The objectives of the technical review are:

- a) To assess the possible health and environmental impacts of recycling articles containing brominated diphenyl ethers;
- b) To review the long-term environmental desirability of the recycling of articles containing brominated diphenyl ethers;
- c) To identify the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers.
- d) The study has considered the implications for developed and developing countries and countries with economies in transition.

3. The report reviews and assesses the environmental and health risks associated with recycling articles containing the POP-BDE. It also makes recommendations as to the long-term desirability of these exemptions.

### Abstract

4. In May 2009 certain congeners contained in commercial Pentabromodiphenyl ether (PentaBDE<sup>1</sup>) and Octabromodiphenyl ether (OctaBDE) were listed in Annex A of the Stockholm Convention which prohibits production, use, import, and export. As there is no longer any known production the main challenge is the identification and treatment of existing stockpiles and wastes. Article 6 of the Stockholm Convention requires each Party to develop and implement strategies to identify existing POPs stockpiles, and to develop strategies for identifying products in use that contain or are contaminated with POPs and POPs-containing wastes. Disposal operations that would allow for the potential recovery, recycling, reclamation or reuse of the POPs content of the waste have been strictly prohibited subject to concentrations being above the respective 'low POPs' limit when environmentally sound management was required. However, the listing of commercial PentaBDE and OctaBDE includes a specific exemption allowing for recycling of articles that contain these substances and the use and final disposal of articles manufactured from recycled materials that contain or may contain these substances. Recycling of articles containing POPs inevitably increases releases of POPs which can result in environmental and health risks. The recycling 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 POPs.

5. The contamination of a wide range of product streams is now a practical and policy challenge that is likely to be exacerbated by recycling. Recent studies have revealed that plastic from waste electrical and electronic equipment (WEEE) containing PBDE is largely uncontrolled and is found in many recycled products (children's toys, household goods, video tape casings and electronics).

6. PentaBDE was mainly used in North America for the treatment of polyurethane foams (PUF) – with extensive applications in mattresses and furniture, followed by vehicles in terms of total volumes. The main recycling route, rebonding to carpet padding, is shown to expose recycling workers and carpet installers along with hundreds of thousands or even millions of consumers. Dust ingestion is the main uptake route of PBDE for more highly exposed individuals. The incorporation of PentaBDE in carpet cushion which generates the highest levels of dust in the zones where children are playing is therefore of particular concern. It is notable that dust release increases as carpet ages thus exposing the children of poorer families more heavily – an exposure reflected in the published literature. An indicative assessment of the health costs associated with PUF recycling shows that total damages can be estimated at close to \$USD 6 billion/year. The commercial value of the North American rebond market, by contrast, is estimated to be less than \$USD 15 million/year.

7. The standard analytical methods for the measurement of PBDE (GC/MS) and the more rapid pyrolysis-GC/MS method are much too slow to be used in operational screening and separation of PBDE-containing materials in recycling plants. Currently the only realistic methods for separation of PBDE-contaminated materials in recycling

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<sup>1</sup> PentaBDE and OctaBDE refer to the commercial mixtures in this review and the associated appendices. When reference is made to the congeners listed in the Stockholm Convention these are described as the POP-BDE. Where reference is made specifically to particular homolog groups the lower case is used as 'tribDE to pentaBDE'.

plants are the various rapid screening technologies which allow detection of bromine. These hand-held and automated systems are currently in use in some full-scale European WEEE recycling plants.

8. There are a number of promising technologies capable of recovering bromine from the polymers and thus allowing the safe recycling or recovery of feedstock. These include techniques for recovering materials for recycling, for recycling feedstock - as either fuel or for manufacturing use, the pyrolysis of polymers with bromine recovery, recovery of bromine in incinerators, and separation of PBDE/BFR from plastic. However, the lack of any real market incentive to remove PBDE/BFRs from end-of-life articles is possibly the reason that they appear to remain at the laboratory/pilot stage. No information was available on any full-scale operation.

9. During the assessment key knowledge gaps were found for technologies used or suggested for energy recovery or end-of-life treatment of PBDE-containing waste streams. The uncertainties are often great and currently do not allow a final conclusion and recommendation on the appropriateness of any technology for treatment of materials containing POP-BDE. In particular it is noted that there have been no studies performed or published on PBDE and PBDD/DF release from cement kilns although PBDE-containing waste streams are already used as alternative fuels. For a range of metal industries (primary and secondary iron industry, copper and aluminium smelters) PBDE and PBDD/DF releases have been reported in the literature. No investigations have assessed the composition of the input materials, however, and so it is not possible to model the mass balances or to calculate destruction efficiencies. In dedicated tests for treatment of PBDE/BFR containing printed wire boards in smelters only PCDD/DF levels have been reported. There are no data on releases of PBDE/BFRs and PBDD/DF and mixed brominated-chlorinated PXDD/DF in the public domain.

10. For key technologies used or proposed for treatment of PBDE/BFR containing waste, further assessments are therefore urgently needed in order to provide a robust evidence base for firm recommendations on the appropriateness of treating PBDE/BFR containing waste in these facilities. Such evidence would also assist with decisions relating to the establishment of BAT for the furnace design, flue gas treatment and the associated protection of workers and the environment. This in turn would permit the currently available treatment and disposal options to be evaluated more robustly. At present the assessments are inevitably somewhat speculative.

11. Significant amounts of PBDD/DF are formed and released during the entire lifecycle of PBDE and PBDE are considered to make a key contribution to total quantity of PBDD/DF released into the environment. PBDD/DF has already become an important contributor to the dioxin-like toxicity in house dust and food - the major human exposure pathways for POPs. Furthermore exposure to these compounds via human milk already exceeds the WHO daily intake levels if equivalence is assumed for toxicity with the chlorinated congeners. This is not necessarily a conservative assumption as the PBDD/DF are in some cases significantly more toxic than their chlorinated counterparts.

12. The only report of a life-cycle assessment on management of a PBDE contaminated waste stream shows that the impacts of PBDD/DF are by far the most significant contributor to total health impacts for recycling and feedstock recycling scenarios. When the life cycle scenario includes landfill and open burning the damages associated with PBDD/DF are about fifteen times greater than the total health impacts attributable to all the PBDE. It is clear therefore that emissions of PBDD/DF are highly relevant pollutants in relation to the recycling and end-of-life treatment of PBDE-containing articles. Any assessment which does not properly take these emissions into account is likely to be fundamentally flawed and would therefore be unreliable as a guide to informing policy decisions.

13. However despite the obvious relevance of the formation of PBDD/DF (and increasingly also of PXDD/DF) for the management, recycling and destruction of PBDE these compound classes have been largely ignored (not measured or reported) in previous discussions about the existing end of life treatments. The sole exception is perhaps BAT incineration. In this case it has been shown that enormous levels of PBDD/DF, PXDD/DF and PCDD/DF were formed in the primary combustion zone when high levels of WEEE waste were added. Most of these unintentionally formed POPs (UPOPs) were successfully destroyed in the secondary combustion zone. In another study PBDE and PBDD/DF have been discovered in bottom ash, probably as a result of mixing contaminated grate-siftings with the bottom ash. These studies demonstrate that treating PBDE-containing waste in non-BAT incinerators will lead to high dioxin releases. It follows that it is important to confirm the effectiveness of destruction conditions for PBDE and PBDD/DF in other thermal treatment technologies. All discharges also need to be effectively monitored to ensure that solid residues do not lead to releases of PBDE or PBDD/DF. Finally it is important to introduce adequate controls to ensure that PBDE or PBDD/DF are not inadvertently released into the environment. Precautions should be taken, for example, to ensure that contaminated grate siftings from incinerators are not combined with bottom ash and then used for construction or similar purposes.

14. Landfilling has been, and still is, the most widely used disposal practice for articles containing PBDE. However there is growing evidence that PBDE in articles deposited in landfills are slowly released in leachates and into the atmosphere with further contamination of ground and surface water and sediments and soil. The toxicity of the PBDE mixtures can be substantially increased by debromination of the higher brominated PBDE (which are normally present in much higher concentrations) to the more toxic lower brominated congeners by the anaerobic processes in the landfill site. When the persistence of PBDE in landfills is compared with the limited life-time of the engineered protection and

management systems in landfills it can be seen that the landfilling of PBDE-containing articles can not be considered as a safe or sustainable solution, and that it is inconsistent with the obligations of the Stockholm Convention.

15. This study found a number of major knowledge gaps which need to be addressed. Information needed to fill these gaps includes:

- a) Comprehensive data for a global substance flow analysis.
- b) Improvement of risk assessment scenarios and particularly better information on the emissions and exposures during the end-of-life stage (recycling, recovery and disposal) of consumer products.
- c) Contribution of PBDE to global PBDD/DF pollution compared to other BFRs and potential further sources.
- d) Appropriate low POPs content limits for PBDE and PBDD/DF in products.
- e) Contamination levels of PBDE and other critical pollutants in the recycling flow and their human exposure, final sink and phase out options.
- f) Additional data on human and environmental toxicity of PBDE relevant to the assessment of hazards and risks.

16. Efforts have been made to encourage research to fill some of these gaps by raising them in a number of papers presented to the global POPs research community at major scientific meetings during the course of this year.

17. This report, together with the review by POPRC which resulted in the listing of the POP-BDE in the Stockholm Convention, demonstrates that PBDE are another example of where inadequate evaluation of a halogenated chemical prior to large scale production and use resulted in global contamination by POPs (and probably also PBDD/DF) requiring global action to reduce the damage caused by further pollution. The PBDE in the current stocks and recycling flow is contributing to further contamination at levels which the evidence presented in this report indicates are causing harm to human health and the environment. The reduction of further damage requires strict control of these flows and the cessation of recycling. With the harm caused by the use of PBDE and with the threats to important recycling flows it has become obvious that chemicals used now and in the future for flame-retardancy need a much more rigorous evaluation over their whole life-cycle. This should include recycling and end-of-life scenarios so that flame-retarding strategies become an integrated part of sustainable production and can thus be considered to contribute to sustainable consumption in future.

## 2. Background and purpose of the Technical Report

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

18. 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<sup>2</sup> certain congeners contained in commercial pentabromodiphenyl ether<sup>3</sup> and octabromodiphenyl ethers<sup>4</sup>. 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.

### 2 (b): Descriptions of terms used:

19. 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*".

20. Descriptions of the following terms: "*article*", "*recovery*", "*recycling*", "*reclamation*", "*direct reuse*" and "*other disposal operations*", have been requested as part of this review.

<sup>2</sup> **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.**

<sup>3</sup> 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.

<sup>4</sup> 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.

21. The Stockholm Convention does not define these terms. Nor does the Convention 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*”.

22. 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.

23. The key definitions proposed are therefore:

**“Disposal operations”**

24. Disposal is defined by Article 2 (4) of the Basel Convention as: “*any operation specified in Annex IV to this Convention*”.

25. 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.

26. 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*”.

27. This issue was discussed in a teleconference on 7<sup>th</sup> 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”**

28. It is proposed that the definition of “*Article*” should be the taken from that in the European REACH<sup>5</sup> Regulations (Article 3 (3)) (European Parliament and Council 2006) which is: “*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”**

29. 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)

30. 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*”

31. 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”**

32. It would follow 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.

33. It is noted that the revised version (2008/98/EC) of the European Waste Framework Directive to the EU<sup>6</sup> will define incineration facilities with an efficiency above a certain threshold to as recovery operations (*RI – use principally as a fuel or other means of to generate energy*) rather than the current definition of disposal operations (*D10 –*

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<sup>5</sup> “**Registration, Evaluation, Authorisation and Restriction of Chemicals**”

<sup>6</sup> Certain parts of which are now in effect but which must be transposed by Member States in full by 12th December 2010.

*Incineration on Land*). The Basel Convention lists incineration as D10 – Incineration on Land – i.e. a waste disposal operation.

**“Reclamation”**

34. 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<sup>7</sup> than for waste management. ISWA (International Solid Waste Association (ISWA) 1992) helpfully define reclamation for waste management as: *The process of collecting and segregating wastes for reuse.*

35. 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”**

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

37. 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.

38. 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.

**2 (c): The structure and contents of the report**

39. The contents and numbering of the Sections of this summary reflect the appendices which support them:

**Section 1: Executive Summary**

**Section 2: Background and purpose**

- 2 (a): The decisions by the Conference of the Parties and the Persistent Organic Pollutants Review Committee and the rationale for the report;
- 2 (b): Proposed definitions
- 2 (c): The structure of the report
- 2 (d): The methodology used to obtain data
- 2 (e): Production, Use, and Stocks of PentaBDE and OctaBDE
- 2 (f): Environmental and Human Levels of PBDE
- 2 (g): Unintentionally formed Brominated Dioxins and Furans

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

- 3 (a): Re-Use and Secondary Recycling Operations
- 3 (b): Tertiary Recycling Operations
- 3 (c): Energy Recovery and end-of-Life Options
- 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

**Section 4: Identification of the best available techniques and best environmental practices for the recycling of articles containing brominated diphenyl ethers**

- 4 (a): Current methods to identify articles/recycled articles containing PBDE
- 4 (b): Separation of articles containing PBDE from other components

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<sup>7</sup> “Restoring land to the natural state after destruction associated with some economic activity” (Wyman 2007)

4 (c): The assessment of BAT Technologies for recycling PBDE-containing articles considering exposures from recycling and disposal options

4 (d): Identify capacity of developing/transition countries to implement BAT/BEP

4 (e): Regulatory approaches and strategies used to support the implementation of BAT/BEP

**Section 5: Review of the long-term environmental desirability of the recycling of articles containing PBDE**

5 (a): Penta and Octa BDE stocks and implications for levels in recycling and recycle

5 (b): Information on the potential trade volume of recycled articles containing PBDE, including from developed to developing countries;

5 (c): An assessment of the costs and benefits of removing or maintaining the exemption on recycling articles containing PBDE;

5 (d): The effect of maintaining and removing the exemption on the needs of developing countries and countries with economies in transition

**Section 6: Knowledge gaps and confounders**

6 (a): Knowledge gaps

6 (b): The potential significance of debromination

40. The related Appendices detail the issues and include comprehensive referencing to sources and a bibliography containing the full-text references compiled for the project library.

**2 (d): Methodology used to obtain data and presentation of data**

41. There is now a very large literature on PBDE and it is estimated that the library is increasing by the publication of an additional five to ten papers each week (Brooke 2009).

42. 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 with full collections of the papers to the International Conferences on Brominated Flame Retardants for 2000, 2004, 2007 and 2010 and the International Dioxin Conferences (published as ‘Organohalogen Compounds’) for each year from 1990 to date. Search terms included combinations of the CAS numbers, names and synonyms of PentaBDE and OctaBDE together with the technologies of interest.

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

44. A combination of citation databases (Sente, Papers and EndNote) were used for indexing and together with “DevonThink Pro Office” data-mining software, for searching, classifying and linking documents, peer reviewed papers, web sites and grey literature.

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

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

46. Analysis by the authors of data collected during this review indicates that total production of all PBDE from 1970 to 2005 was between 1,300,000 and 1,500,000 tonnes broken down as:

**Table 1: Estimated total production of PBDE commercial mixtures 1970 to 2005 (derived by the authors from (Schenker 2008, Li 2010)).**

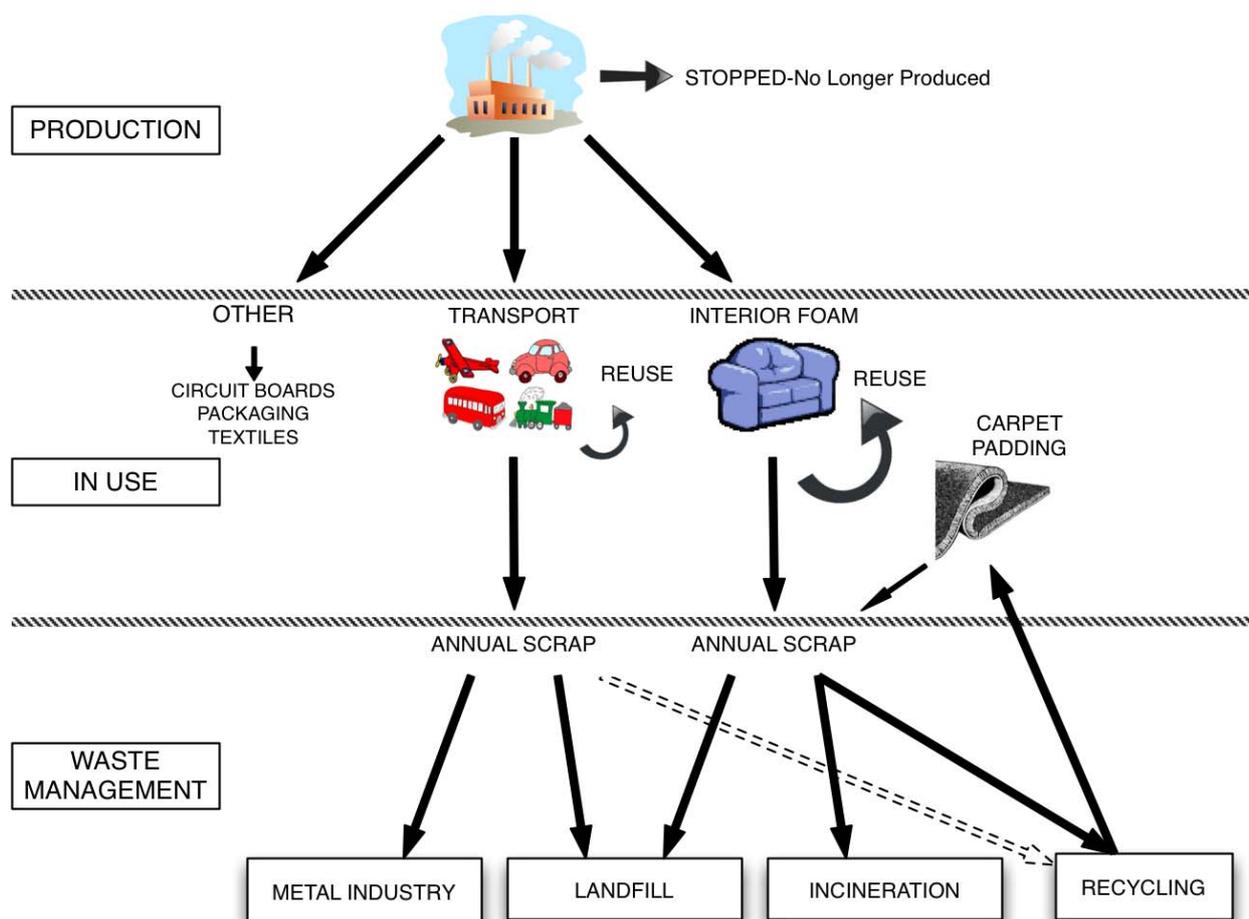
<b>Commercial Mixture</b>	<b>Tonnes</b>
<b>DecaBDE</b>	1,100,000 to 1,250,000
<b>OctaBDE</b>	102,700 to 118,500
<b>PentaBDE</b>	91,000 to 105,000

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

**PentaBDE:**

48. It is considered that largest use of PentaBDE (90-95%) was the treatment of polyurethane foam and that about 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 about 95% by 2000.

49. Balancing the evidence available indicates furniture being a larger user of PentaBDE in both Europe and the US rather than transport. An approximate distribution of known production of 36% in cars, 60% in furniture with a 4% residual in other articles is considered to be reasonable and is generally consistent with analytical data for different waste streams.



**Figure 1: Schematic diagram of the life cycle of PentaBDE (adapted from Alcock (Alcock 2003)).**

50. The ‘other’ uses are estimated to account for 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 the EU) 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.

51. The POPRC Risk Profile for PentaBDE listed global production of PUR foam as only 150,000 tonnes/year:

**Table 2: 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)**

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

52. 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). It is therefore assumed, although the text does not say so, that this was intended to represent the total quantity of PUR foam that has been treated with PentaBDE<sup>8</sup>.

53. The dosing rate assumption in the Risk Profile 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 2003). The automotive industry has also indicated that 4% would be the most realistic figure for PUR foam in cars (Risk & Policy Analysts Limited 2000).

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

**Table 3: Usage of PentaBDE in PUR Foam (Cambell 2010)**

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

55. The consequences of these loadings being much lower than had previously been assumed is that the total quantity of foams treated with PentaBDE is several times larger, that the current consumer exposures arise from lower levels of PentaBDE and that the potential for bromine recovery is much less likely to be a realistic prospect. The table in the Risk Profile has therefore been revised based on an average loading of 4%:

**Table 4: Revised assessment of the total tonnage of PentaBDE treated PUR foam**

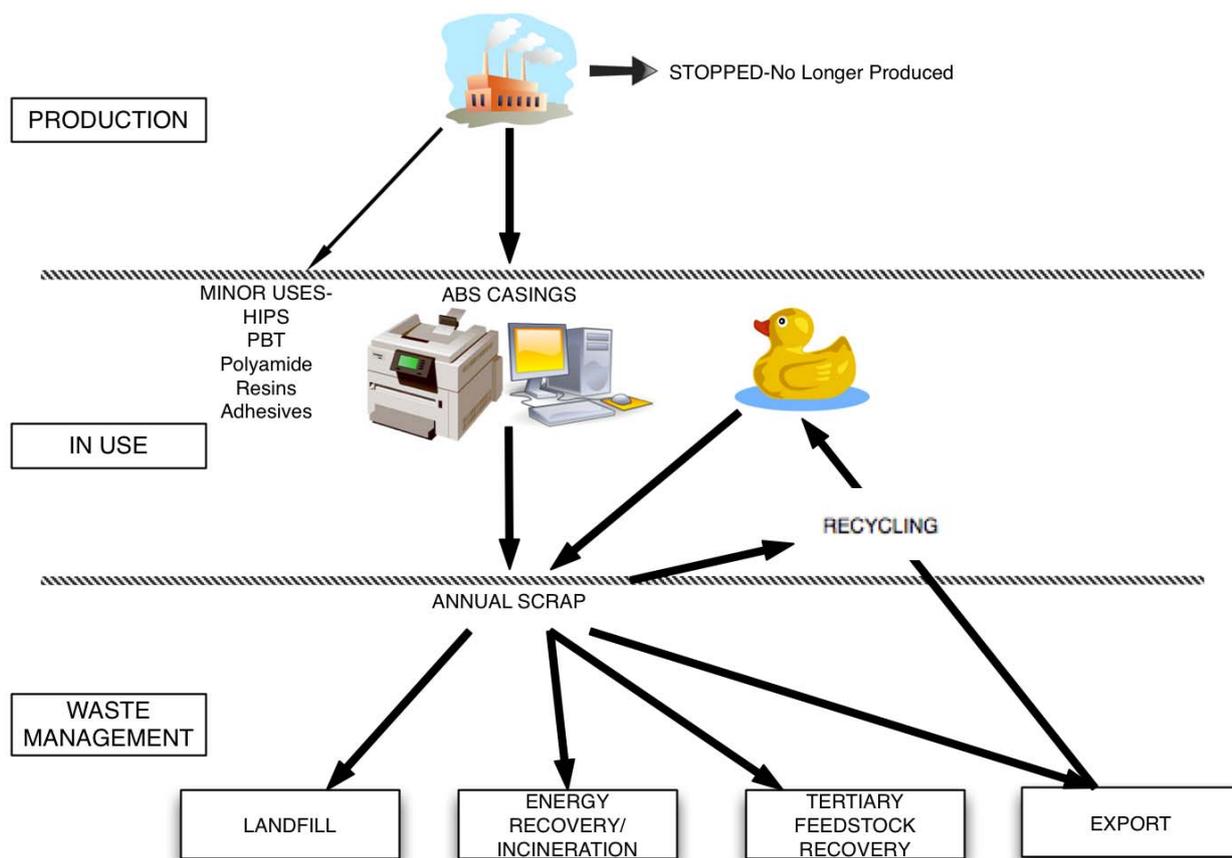
<i>Region</i>	<i>PentaBDE treated PUR foam production tpa</i>	<i>Quantity of PentaBDE tpa</i>
<b>US</b>	175,000	7000
<b>Europe</b>	25,000	1,000
<b>Total</b>	<b>200,000</b>	<b>8,000</b>

56. The lifespan of the main articles containing PentaBDE are estimated to be 10 years for furniture and c.12 years for cars. The consequence is that as European use peaked in the mid 1990s and had almost stopped by 2000 most articles containing POP-BDE have likely already become waste and have been treated by the existing waste management infrastructure. Most materials containing PentaBDE in Europe have probably been landfilled, incinerated or exported. The evidence indicates that only low concentrations are now being found in the waste stream in this region.

### **OctaBDE**

57. The assessment indicates that the large majority of the use of OctaBDE was for ABS plastics, and possibly some HIPS, used in electronic equipment. Minor uses are dispersed and poorly characterised and will largely be captured by the existing waste streams handling circuit boards and shredder residues.

<sup>8</sup> There is evidently an error in the Risk Profile table, however, as PentaBDE production has never risen as high as 15,000 tonnes/year (and certainly not 27,000 tonnes/year). Maximum annual production has always been less than 10,000 tonnes and normally less than 5,000 tonnes.



*Figure 2: 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).*

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

58. Human and environmental levels in developed countries 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. The key literature is summarised in the Appendices 3 and 5(c).

59. 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.

60. 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 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.

61. 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).

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

62. Brominated dioxins and furans have been shown to have toxicities similar to, and in some cases greater than<sup>9</sup>, their chlorinated counterparts in human cell lines and mammalian species and assay tests (Mennear 1994, Behnisch

<sup>9</sup> It is particularly notable that 2,3-Dibromo-7,8-dichlorodibenzo-p-dioxin and 2,3,7,8-T<sub>4</sub>BDD are shown to elicit up to 2.5 times the toxic response of 2,3,7,8-TCDD – often though to be the most toxic anthropogenic chemical.

2003, Birnbaum 2003, Olsman 2007, Matsuda 2010). Compelling evidence has accumulated over the past twenty years or so that brominated flame-retardants, and especially PBDE, are a major source of toxic tri- to octa-brominated dioxin and furan contamination. There is an extensive literature on this as discussed in Appendix 5. The peer-reviewed and grey literature clearly shows that consideration of the generation, emissions and impacts of PBDD/DF are relevant considerations in relation to the manufacture/processing, recycling and disposal of products containing, or contaminated with, PBDE and related compounds. PBDD/DF contamination has been reported in humans (Choi 2003, Kotz 2005, Ericson Jogsten 2010) and in biota (Ashizuka 2008, Fernandes 2008). There are relevant concentration for the average population in human milk (Kotz 2005), food (Rose 2010), and house dust (Suzuki 2006, Takigami 2008, Franzblau 2009, Ma 2009, Suzuki 2010).

63. PBDD/DF are present as contaminants in commercial PBDE (and therefore all products containing PBDE) and are additionally formed throughout the whole lifecycle of PBDE (Appendices 2 (g), 3 (b) and (c)). Some major processes where PBDD/DF can be formed and released include:

- a) blending of PBDE to polymers (PBDD/DF in PBDE product and formation);
- b) formation/release during textile finishing with PBDE;
- c) formation/release in/from articles in use containing PBDE;
- d) formation/release during recycling of plastic articles containing PBDE;
- e) formation/release during accidental fires of articles containing PBDE; and
- f) formation/release during the combustion of waste containing PBDE (in facilities, open burning scenarios and simple recycling operations);

64. The total generation of PBDD/DF from all type of PBDE are at a scale of tons per year (Zennegg 2009) and therefore of the same order or even larger than the total inventory of PCDD/DF.

### 3. Operations to recycle and recover articles containing POP-BDE and an Assessment of their possible health and environmental impacts

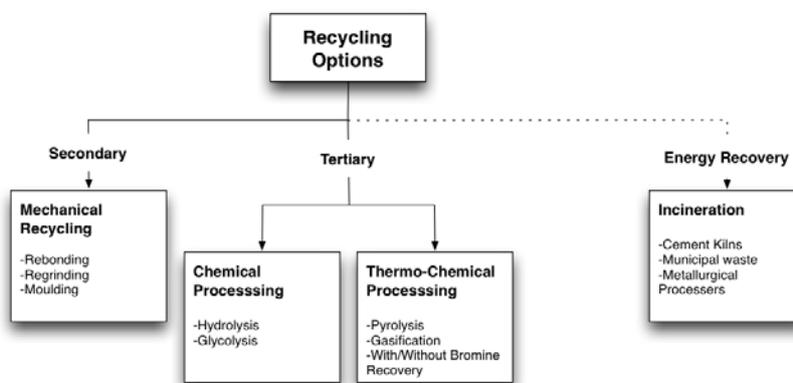


Figure 3: Recycling options for polymers containing BFRs and particularly PUR foams.

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

##### 3 (a) (I): Direct re-use

65. Direct re-use relating to POP-BDE is most relevant to furniture, mattresses and cars. For cars the sales and exports of second hand cars and to a more limited relevance of car-parts have to be considered. There is minor reuse of other PBDE-containing materials (see Appendix 3).

##### 3 (a) (II): Material recycling/Secondary recycling

###### Plastic

66. PBDE/BFR-containing plastic (mainly) from WEEE is often recycled to other plastic materials by blending with virgin polymer materials. Due to the mix of polymer types the WEEE plastic is typically down-cycled to products in applications with less material demanding properties. Screening of plastic products has revealed that even sensitive uses like children toys (Chen 2009, 2010a) along with household goods (Chen 2010c) and video tapes (Hirai 2007a) are

contaminated with PBDE and other BFRs. There is no evidence that the flow of plastics recovered from WEEE and containing PBDE is properly controlled in recycling operations.

### *Polyurethane foam (PUF)*

67. PUF from mattresses, furniture, transport and possibly other sources are recycled. The main use is in the production of carpet cushions for use in homes and offices (Eaves 2004). Other uses of rebond include transport applications such as school bus seats (USEPA 1996) and floor mats for gymnasia (Zia 2007).

### *Other materials*

68. Other materials which may contain POP-BDE are also recycled. These include textiles, rigid PUR foam and other polymers used for construction. Total usage in these application is likely to have been relatively small (<5,000 tonnes) and it has not been possible to quantify the levels or distribution of POP-BDE in these application and the quantities recycled are unknown.

## **3 (b): Tertiary Recycling Operations**

69. 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).

70. The monomers may then repolymerised and the regenerated or reconstituted polymer can be 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

71. Feedstock recycling and thermal recovery of energy in thermal processes include:

- a) Pyrolysis of PBDE/BFR containing materials (to oil, chemicals)
- b) Plastic recovery in primary steel industry (where the plastics act as a reducing agent)
- c) Hydrolysis and glycolysis processes

72. The extent of tertiary recycling in practice is unclear and needs further investigation.

## **3 (c): End-of-life Options**

73. Most metallurgical processes fall into the category of end-of-life treatments rather than recovery operations in relation to treatment of POP-BDE. Whilst metals are recovered for recycling the polymer to which the POP-BDE had been added is not recovered. Instead it is used for the recovery of energy. Alternatively it may have been introduced to the process incidentally due to a failure to separate PBDE-containing materials from the metals being recovered. An example would be where scrap cars were compacted for recovery in secondary steel industry without first removing all the PBDE-containing polymers). The presence, and recovery, of the metal in these cases is due to the mixing processes, usually shredding or compacting, used in disassembly rather than to any specific use of POP-BDE in metal components. This allocation is slightly more ambiguous when considering material and energy recovery in smelters used for tens of thousands of tonnes of PWB, some containing PentaBDE in the resin, as BFR containing plastic is often added to the process.

74. Options for energy recovery of plastics containing PBDE (or just the recovery of metals incidentally mixed with BDE-containing plastics) include:

- a) Electric arc furnaces for iron scrap recycling
- b) Secondary aluminium
- c) Antimony recovery from PBDE/BFR plastics containing antimony
- d) Energy recovery from PBDE/BFR containing high calorific waste in cement kilns
- e) Energy recovery and, in theory at least, bromine recovery from PBDE/BFR containing materials in incinerators

75. There is evidence showing PBDE and PBDD/DF releases from several of these operations - in particular metal industries (Du 2009, Odabasi 2009, Du 2010, Wang 2010). There remain large knowledge gaps for all these technologies in respect of the total extent of PBDE containing materials processed and the corresponding PBDE and PBDD/DF releases. There is very little data on the possible associated contamination of workers. This is true both for

BAT facilities and for facilities operated in developing/transition countries and releases and associated occupational exposure need to be assessed for both.

76. A large proportion of PBDE containing waste has been deposited and is still deposited in landfill and dump sites. Over the past 8 years a range of studies have been published revealing the release of PBDE from landfills into leachates, ground water and surrounding soils (Oliaei 2002, Osako 2004, Odusanya 2009, Danon-Schaffer 2010a, Danon-Schaffer 2010b, Oliaei 2010). The options and limits of landfilling PBDE containing waste need to be reflected considering the long-term fate of releases.

77. The suitability of landfill as a final sink for POP-BDEs is to a large extent dependent on the timescale over which an assessment is made. Longer timescales also increase the uncertainty of transitions in the waste stream within the landfill site by anaerobic debromination processes (Danon-Schaffer 2010b). Thus the hazards of the PBDE mixture steadily increases over time whilst the 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 1995, Allen 2001, Simon 2004).

78. 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.

### **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**

#### **3 (d) (I): Direct re-use**

79. Direct re-use of articles containing PBDE results in further releases similar to those in first uses and continues human exposure. As protective covers wear and, for example, PentaBDE-containing foam is exposed there may be significant increases in releases and exposures.

#### **3 (d) (II): Material recycling/Secondary recycling**

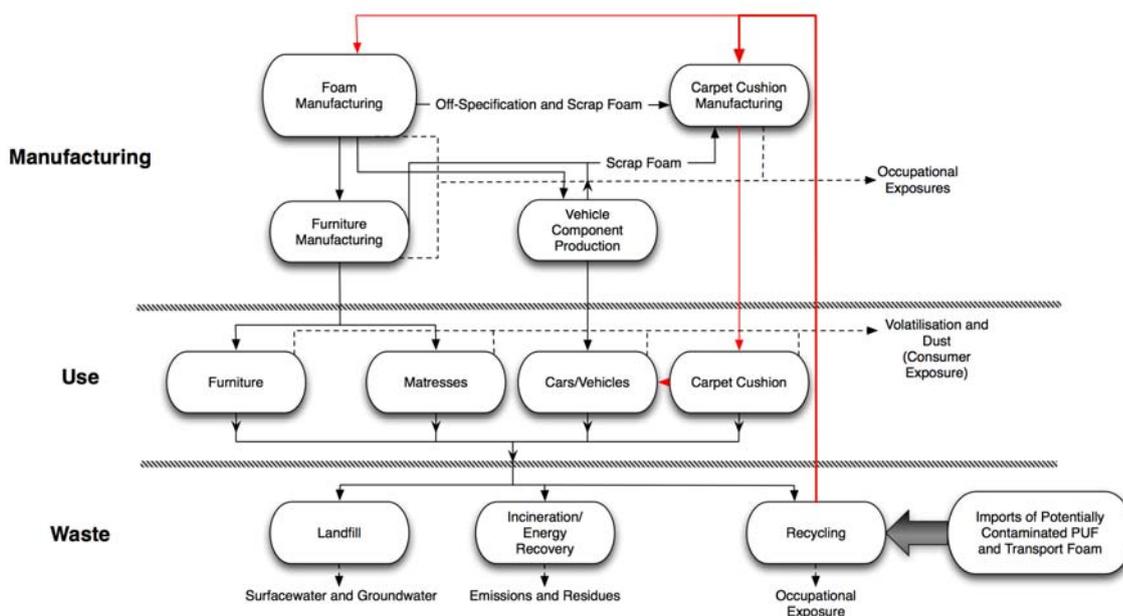
80. There are key concerns in relation to recycled articles containing POP-BDE specifically relating to PentaBDE in carpet padding and OctaBDE in recycled plastics, particularly those used for sensitive uses including toys.

#### ***Recycling of PUF***

81. In North America both post-consumer PUF and production off-cuts have been recycled into carpet cushion (‘rebond’) for many years as illustrated in Figure 4. This recycling route is relatively rare outside of the USA and Canada<sup>10</sup>.

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10 The reply from Canada to the questionnaire was the only response confirming the 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*”



**Figure 4: Simplified materials flow of foam and recycling routes (marked in red) to carpet cushions (adapted from (USEPA 2005)).**

82. 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 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 and subsequently re-introduced into homes and offices where exposure continues along with any releases to the environment which occur when the padding becomes waste.

83. USEPA has published a detailed assessment on the re-suspension of particulate matter from carpets in relation to pesticides but which is relevant here also (RTI International 2007). This shows that walking on medium carpet re-suspended almost 2% of the particulate matter (PM) between 1 and 10  $\mu\text{m}$  available on the carpet fibres, but up to 40% could be re-suspended under conditions more representative of children playing. The consequences of increased exposure of toddlers and children playing close to the floor is obvious and is consistent with the much higher levels of PBDE reported in children compared with adults (Fischer 2006, Toms 2009, Lunder 2010). The much higher emission factors of older carpets might, at least in part, help explain the higher body burdens of children reported from low income families (Zota 2010). These families are likely to use older furniture and mattresses, possibly bought refurbished as well as older carpets.

84. 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”). Recycling of PUF containing PBDE results in continued releases of PBDE, and subsequent environmental and human exposure.

### **Recycling of PBDE-containing Plastics**

85. Knowledge is far more limited about the recycling of OctaBDE treated plastics into alternative plastic products. There are, however, an increasing number of examples in the literature where it is clear that PBDE have been included in recycled plastics for sensitive uses including toys. The report commissioned by the New Zealand Ministry of the Environment (Geo & Hydro – K8 Ltd 2010) as part of the POPRC review process also reported the authors interpretation „that during the manufacture of these goods or of the polymers to make these goods some recycled polymers have been blended with virgin polymers”.

86. 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.

87. Chen et al. very recently published data on children's exposure together with a risk assessment for BFRs in children's toys in South China (Chen 2009, 2010a). A critical response was made by the industry (Banasik 2010) to which Chen responded (Chen 2010b). Chen found that PBDE were the predominant BFRs in the toys 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 of 0.1%. The highest exposures were assessed to be children aged 3-18 months mouthing toys with a total PBDE exposure of 8.9 ng/kg bw/day. The exposure levels were significantly below the current “oral reference doses” (Oral RfD) established by USEPA. However EPA’s confidence in the reference dose is low. For PentaBDE and OctaBDE the RfD was established in 1990 and more recent research shows that health effects are found at, or close to, background levels (as described in Appendix 5 (c)). Chen therefore concluded that the exposures “are of special concern because of the relatively higher exposures observed for young children”.

#### **4. Identification of the best available techniques and best environmental practices for the recycling of articles containing PBDE**

##### **4 (a): Current methods to identify articles/recycled articles containing PBDE**

##### **4 (a) (I): Analysis of PBDE in articles and other matrices**

88. 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 1998, Rieß 2000, Covaci 2003, Kemmlein 2005, International Electrotechnical Commission 2008). 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 2003, Covaci 2007). However since brominated flame retardants can overlap with retention times in the gas chromatograph (Vetter 2008) detectors like ECD, FID and UV have some uncertainty and need experience in the interpretation of chromatograms. An International Standard IEC 62321 Ed.1 (International Electrotechnical Commission 2008) has been developed for Electrotechnical products. The Determination of PBDE (monoBDE to decaBDE) in polymers by GC-MS is described in Annex A of IEC 62321 - including extraction, analysis and quality assurance.

89. An alternative method to screen PBDE/BFRs in plastic without extraction and clean-up is pyrolysis of pulverised plastic coupled directly with gas chromatography and mass spectroscopic detection (py-GC/MS) (Danzer 1997, Rieß 2000, Paul 2010). The pyrolysis GC/MS method has been developed to a commercially available application (Shimadzu 2010) and has been found robust and reliable after optimizing parameters and establishing fingerprints for the different commercial PBDEs and BFRs (Paul 2010).

90. A measurement method for PBDE for Stockholm Convention purposes would need to focus on the  $\Sigma$ tetraBDE to heptaBDE with less emphasis on octaBDE to decaBDE. 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.

91. Standard commercial GC/MS analysis of PBDE in plastic and other materials is widely available in developed countries. This is largely because of the demand that has arisen over the past few years due to the requirement of RoHS compliance and other national laws. The commercial GC/MS analysis of brominated flame retardants is, however, still relatively expensive. The price in Europe for PBDE analysis starts from approximately \$USD 180 per sample.

##### **Considerations for developing countries:**

92. 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 detailed in Appendix 4 (a). It is evident, therefore, that the establishment of specific PBDE analysis capacity in developing and transition countries will need significant efforts and resources directed towards capacity building.

93. Experience on 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.

94. The evidence available indicates that most developing countries probably have relatively low stocks of wastes containing POP-BDE. There are likely, however, to be some significant hot-spots - especially related to imports of WEEE from industrialised countries for recycling or re-use. To assess quantities of POP-BDE containing materials in developing countries representative sampling and analysis of key waste/recycling streams should be undertaken to determine the level of contamination by relevant amounts of POP-BDE. Obviously such sampling should focus on the streams most likely to be impacted, including e-wastes and shredder residues.

##### **4 (a) (II): Monitoring of PBDE in articles for separation in recycling and waste flow**

95. The key challenge is the screening of PBDE for separation of PBDE-containing articles. For this purpose Standard GC/MS methods or GC methods with other detectors but also the rapid screening methods (e.g. Pyrolysis-

GC/MS) are far too slow for practical application in recycling or waste treatment plants (see Appendix 4). Currently the only practical method for screening and separation of PBDE-containing materials is the separation of all BFR-containing materials by online screening of the bromine content.

96. Three technologies for bromine screening are applicable in practice (see Appendix 4):

- A) Sliding Spark Spectra analysis (SSS) (hand held method)
- B) X-ray Fluorescence (XRF) (hand held method<sup>11</sup>);
- C) X-ray Transmission (XRT) (for automated separation plants)

**Table 5: Comparison of the hand held methods for separation of BFR and non-BFR containing plastic (Adapted from WRAP 2006).**

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 fluorescence 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 known peaks at Br and Cl wavelength to estimate % concentration.
Weight approx	1.7 kilos	0.75 kilo (gun)
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	Relatively slow – 15 to 30 seconds	Fast – 1 second
Price	Approx. \$USD 40-50,000	Approx. \$USD 6,000
Operator Skill level required	Technical operator to interpret results	Factory operator with basic training

**4 (b): Separation of articles containing PBDE from other components**

**4 (b) (I): Separation of articles containing PBDE from other components**

97. The online detection and separation of articles containing PBDE (plastic, foam, textiles etc.) from other materials is currently not feasible due to the relatively slow analytical methods described above combined with the difficulties in automating a system to handle the heterogeneous mix of components which need to be sorted in most systems. The only currently feasible approach is the separation of materials containing any brominated flame retardants from non-BFR treated material<sup>12</sup> with the bromine screening methods detailed in section 4 (a) i.e. XRF, SSS and XRT. XRT is only used in automated systems and due to the relative high cost (approx. 400,000 EURO) is only be used in large WEEE separation plants. XRF and SSS are hand held methods and cannot be installed in automated systems suitable for the matrices in which the POP-BDE are commonly found. All three approaches are already applied in some full-scale operational facilities mainly in Europe (see Table 6 below). Additionally manual separation based on workers’ experience is used in some countries such as Sweden. Sink and float technologies can be used to separate, to some extent at least, those more dense fractions of WEEE plastics containing PBDE/BFR.

98. The separation of PBDE/BFR-containing plastics needs to be effectively integrated with the technologies used for separation of plastics for polymer material recycling (see Appendix 4) as these are really the main economic driving force of a WEEE recycling plant.

99. These separation techniques have currently mainly been established for plastics from electronic waste. However the technologies seem to be appropriate for other articles containing PBDE homogeneously distributed in the article (e.g. PUF in mattresses, transport or furniture; textiles). The methods would need however further testing and possibly adjustments to be used in practice for other key applications of PBDE-containing articles. This presents economic

<sup>11</sup> At least one supplier provides an XRF configured as an automated sorter – this is likely to be more relevant to more homogeneous metal scrap than to the applications for WEEE plastics or PUF. See <<http://www.innovx.com/en/products/qxr/overview>>

<sup>12</sup> There are a range of other practical reasons to separate BFR and non-BFR materials. These are listed in Appendix 4.

challenges as the separation of other articles for recycling is less economically attractive compared with the high specification plastics used in WEEE.

100. While the hand held technologies (XRF, SSS) for separation have in developed countries the disadvantage of being expensive due to high wages, these technologies might be favourable for developing/transition countries where there are lower wages for staff. A combination of SSS and NIR in a single device which is able to screen for Bromine and also for the plastic type might be applicable here to separate plastics into clean polymer fractions with correspondingly high market value.

#### **4 (b) (II): Remove PBDE from articles containing PBDE**

101. Some technologies have been developed to separate PBDE/BFRs or bromine from materials.

- a) CreaSolv® process to dissolve plastic and recover plastic resin and BFR fraction (pilot scale) (Schlummer 2010).
- b) Haloclean pyrolysis of BFR containing plastic with separation step bromine (pilot scale) (Hornung and Seifert 2008).
- c) Mechanical recycling of printed circuit boards including separation step of BFRs for Bromine recovery (laboratory scale) (Kolbe 2010).
- d) Incineration with bromine recovery (Tange 2004).

102. All these technologies have been tested at a pilot or laboratory scale. Some, including the CreaSolv® processes, appear to be ready for full-scale application. They would, however, need further assessment before any firm recommendation can be given to the technologies. Any assessment should also address the issue of the practical level of separation of BFR/Bromine from materials containing BFR considering the current high price of Bromine (c. \$USD 2,500/tonne) together with the future markets for such bromine and the contribution relied upon from this in relation to the economics of the process.

#### **4 (c): The Assessment of BAT Technologies for recycling PBDE-containing articles considering exposures from recycling and disposal options**

103. Key material flows used in material recycling streams containing PBDE are assessed to be ABS plastic from WEEE, polyurethane foams (mattresses, furniture, transport), textiles and printed circuit boards.

#### **4 (c) (I): Plastic containing PBDE**

104. Recent studies have shown that PBDE-containing plastics have been used to produce articles for which no flame-retardancy is required including children's toys, household goods and video tapes (Hirai 2007a, Chen 2009, 2010a, Chen 2010c). This shows that the flows of PBDE/BFR-containing plastics for recycling are not well controlled and that these plastics are being mixed with the non-flame retarded plastic streams in the recycling operations.

105. 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 POP-BDE-containing materials into uses where 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 appear to be 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 countries as described below.

106. 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/BFRs by the Creasolv process (see Table 6) for example. From the remaining highly PBDE/BFR enriched fraction bromine could be recycled. This could be an attractive option given the current high prices for bromine depending on the efficiency of the recovery process.

107. 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 2006).

108. 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 Table 6 and Appendix 3), both types of facility need further assessment before any final recommendation can be given. Several non-combustion technologies have been used for treatment and destruction of other POPs, including liquid PCBs (Danish Environmental Protection Agency 2004, McDowall 2004, Weber 2007, Zinoviev 2007). The authors are not, however, aware of any commercial operations of these technologies for the treatment of solid polymer matrices. Currently, therefore, the only tested and commercially operating technology for treating the high PBDE/BFR fraction is BAT incineration (Stockholm Convention 2007a). Depending upon the plant configuration this gives the additional possibility of recovering bromine. BAT Incineration is available mainly in industrial countries but even in some of these countries (e.g. Canada, Australia, Ireland), incineration is not the favoured waste treatment option for a variety of socio-economic reasons including problems of public acceptability, government policy, high cost, waste hierarchy considerations and loss of resources as well as ash management and disposal difficulties.

109. Feedstock recycling to produce by pyrolysis technologies fuel has been suggested as another option (Hornung 2003, Zia 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.

**Table 6: Operational Industrial Scale and Pilot Scale WEEE separation technologies and their potential to separate PBDE-containing plastic**  
**Operational Industrial Scale WEEE separation technologies and their potential to separate PBDE-containing plastic:**

WEEE input	Separation techniques	Plastics 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	BFR and PVC free polymers	Good	Yes	Industrial scale	(Gerig 2010)
Small electronic equipment (Germany)	Smasher → NIR → NIR → XRT	Low-BFR types of ABS and HIPS	Not reported yet.	low Br levels	Industrial and pilot scale	(Krämer 2010)
WEEE plastics (UK)	Undisclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	(Morton 2007)
WEEE plastics (Germany)	Undisclosed (incl. S/F and Electrostatic)	Low-BFR types of PP, ABS and HIPS	Undisclosed	Undisclosed	Industrial scale	(Schlummer 2010)
TV and computer casings (Sweden)	Manual, not disclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	(Retegan 2010)

**Operational Pilot Scale WEEE separation technologies and their potential to separate PBDE-containing plastic:**

TV and monitor housings (Germany)	Dismantling → S/F	Low-BFR types of ABS, HIPS and ABS-HIPS-Mix	Good	Yes	Pilot scale	(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 2006a)
TV housings (UK)	Dismantling → BFR rich fraction → CreaSolv®	Low-BFR types of HIPS-ABS-Mix	Good	Yes	Pilot scale	(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)
Monitor housings (Germany)	Dismantling → NIR → S/F	Low-BFR types of ABS, HIPS and PC/ABS	Good	Yes	Pilot scale	(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)

Table 7: Assessment of different treatment scenarios

Scenario (Material)	Applied in practice	Waste Hierarchy	Economics **	BFR Removal/ Destruction	PBDD/DF	Worker Exposure	Consumer Exposure
Rebonding (PUF)	Green	Green	Orange	Red	Yellow	Red	Red
Regrinding (Polymer)	Green	Green	Orange	Red	Yellow	Red	Red
Moulding (Polymer)	Green	Green	Orange	Red	Orange	Red	Red
Creasolv (Polymer)	Yellow	Green	Yellow	Green	Green	Yellow	Green
Hydrolysis	Orange	Yellow	Orange	Orange	Green	Yellow	Green
Glycolysis	Orange	Yellow	Orange	Orange	Yellow	Yellow	Green
Pyrolysis for fuel/feed	Yellow	Yellow	Orange	Orange	Red	Orange	Yellow
Pyrolysis/ Gasification	Green	Orange	Yellow	Yellow	Orange	Yellow	Green
Blast Furnace (Polymer)	Green	Orange	Green	Green	Yellow	Yellow	Green
Copper Smelters (PWB)	Green	Orange	Green	Green	Red	Orange	Green
Antimony Smelter	Green	Orange	Yellow	Green	Red	Orange	Green
Electric Arc*	Orange	Orange	Yellow	Green	Red	Orange	Green
Secondary Aluminium*	Orange	Orange	Yellow	Green	Red	Orange	Green
Cement Kilns (All)	Green	Orange	Yellow	Green	Yellow	Yellow	Green
HW/MW Incineration (All)	Green	Orange	Red	Green	Orange	Yellow	Green
Landfill (All)	Green	Red	Yellow	Red	Orange	Orange	Orange
Open Burning (All)**	Green	Red	Red	Red	Red	Red	Red

\* 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

**Scoring:**

-  Positive – e.g. low emissions/ environmental/ health impacts
-  Uncertain - probably OK
-  Uncertain - possibly negative
-  Negative – high emissions/ environmental/ health impacts

110. An alternative approach, further down the waste hierarchy, is energy recovery of the entire WEEE plastic fraction in primary steel industry. The steel industry is present in all regions (although not necessarily in each country) and subject to appropriate (BAT) technology being available might provide an option for treatment around the world. Hirai (Hirai 2007b) 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%<sup>13</sup> (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 and more information is required before this approach can be fully evaluated.

#### **4 (c) (II): PUF containing PBDE**

111. 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).

112. For PBDE-containing PUF no technology has been developed yet for separation of PBDE/BFR to reuse the polymer.

113. 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 leads to large logistic challenges for transport and therefore can only be treated relatively locally. The low density also (probably) does not allow the use in blast furnaces.

#### **4 (c) (III): Textiles containing PBDE**

114. 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 textiles. Textiles containing PBDE could be separated and thermally treated with the same considerations mentioned in (II) above.

#### **4 (c) (IV): Printed circuit/wire board (PWB) containing PBDE**

115. 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.

116. 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 and more information is required before this approach can be fully evaluated.

#### **4 (d): Identify the capacity of developing countries and countries with economies in transition to implement BAT/BEP**

##### **4 (d) (I): Material recycling of PBDE-containing articles**

117. Currently plastics 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 streams (see above and Annex 4a). As mentioned above and described in Annex 4 several technologies are used in developed countries (Annex 4f).

##### ***Recycling of plastic including detection of PBDE/BFR***

##### ***Manual separation of PBDE/BFR-containing plastic***

118. 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 contains BFR materials. However it is not clear how much of the non-marked plastic contains PBDE/BFRs.

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<sup>13</sup> 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 by the steel industry.

#### ***Separation by means of instrumental PBDE/BFR screening***

119. 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 SSS technology seems favourable for developing/transition countries. Such handheld SSS equipment is available combined with NIR spectrometer for the identification of plastic type (the cost is then c. \$USD 25,000) and could be used for producing clean polymer fractions with associated market value. The options should be further assessed.

#### ***Recycling of plastic into non-sensitive uses without determining of PBDE/BFR content***

120. There might be other applications where concentrations of PBDE/BFR are very low or in uses which do not constitute an immediate threat to humans and the environment. Important considerations when recycling PBDE/BFR plastics into these less sensitive uses are the end-of-life considerations including the risks of open burning, the need for environmentally sound management, and other obligations arising under Article 6 of the Stockholm Convention. This is a challenge for developing/transition countries when considering their limited waste management, regulatory and analytical capacities. It also presents long-term risks of contamination of sensitive uses in any future recycling.

#### ***Material recovery of PBDE-containing PUF***

121. 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 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**

122. 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 2009, Odabasi 2009, Du 2010, Wang 2010). Many developing/transition countries have some of these facilities and therefore possible releases.

123. It is currently not clear whether metal industries in developing countries are appropriate to treat waste containing PBDE due to the lower average technology levels than in industrial countries. More importantly, there are large knowledge gaps in this respect in developed countries (see Appendix 3, Appendix 4d).

124. Since there are still considerable knowledge gaps for the different metal industries in developed countries (copper smelters, electric arc furnaces, secondary aluminium, antimony smelters) no recommendation can be given to these technologies for developing/transition countries at this stage.

#### **4 (d) (III): Feedstock recycling and thermal recovery of energy in thermal processes**

##### ***Energy recovery (and bromine recovery) from PBDE/BFR containing materials in incinerators***

125. Only BAT incinerators should be used to treat PBDE-containing materials and municipal waste incinerators are limited to low bromine levels for regulatory, corrosion and economic reasons. The construction of BAT incinerators in developing/transition countries is, however, questionable considering the high cost of waste treatment (normally well above \$USD 100/tonne) (World Bank 2005, Brunner 2007). Therefore general municipal waste incineration is unlikely to be a feasible option for treatment of PBDE-containing waste in developing countries either now or in the future.

126. Currently there is also no dedicated hazardous waste incineration capacity in most developing countries. Proposals to develop dedicated hazardous waste treatment capacity in developing countries, whether incineration or other non-thermal technologies, are inevitably very expensive. Consideration should be given to extended producer responsibility obligations and projects might be funded by stakeholders (producers, importers, vendors and users) as the local populations are unlikely to be able to afford the high costs.

##### ***Energy recovery from PBDE/BFR containing waste in cement kilns***

127. Cement kilns are increasingly used in waste management schemes also in developing/transition countries for energy and material recovery (Holcim 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 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 should be considered for waste management. 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 by-pass stack, and including sampling for PBDD/DF, should always be carried out before any POP-BDE waste is considered for routine disposal.

#### ***Pyrolysis and gasification of PBDE/BFR containing polymers/articles***

128. No recommendation can currently be given for using pyrolysis or gasification of PBDE-containing materials for developing/transition countries due to the lack of documented full scale experiences even in industrial countries (see Appendix 3b).

#### **4 (e): Regulatory approaches and strategies used to support the implementation of BAT/BEP and control of PBDE**

129. Article 6(2)(c) requires the Stockholm Conference of the Parties to cooperate closely with the Basel Convention to work to define the low persistent organic pollutant ('low POPs') content referred to in Article 6(1)(d)(ii) of the Stockholm Convention. The Basel Convention provides an international regulatory framework which is already addressing global WEEE management and is, in any case, a key consideration for this PBDE flow. PBDE flows should be regulated by Stockholm Convention requirements (Articles 2, 3, and 6) and the Basel Convention framework after a 'low POPs' content for PBDE has been established. This will presumably include either an updating of the general technical guidelines or the preparation of new regulatory guidance by the Basel Convention.

130. BAT/BEP for POPs waste is addressed by the Stockholm Convention process. Existing BAT/BEP considerations for UPOPs control already address some issues relating to PBDE in certain facilities (e.g. waste management, furnace qualities, flue gas treatment technologies). Some sections are likely to require updating, however, to address specific issues for PBDE treatment (e.g. afterburner in copper smelter with specifications, autoshreeder residue recovery, PBDD/DF related issues etc.). If the BAT/BEP guidance is updated to consider PBDE (and other new POPs) the waste management section could then address crucial waste streams relevant for management PBDE articles. Additional sections for technologies could explicitly be added in the BAT/BEP guide (e.g. feedstock recycling for fuel production).

131. The European WEEE directive covers POP-BDE and DecaBDE in WEEE and includes recycling goals. A similar approach incorporating Stockholm Convention requirements might be considered by other regions. The implementation in respect to PBDE is certainly challenging when the scale of recent exports of WEEE are considered.

132. The establishment of appropriate emission and low POPs content limits for PBDE and PBDD/DF might be considered as part of this process.

133. Guidance and recommendations should also be developed for the role of sustainable landfilling<sup>14</sup> considering the long-term perspective of contaminants and engineering/management measures.

134. China has already strengthened regulation on the import of WEEE and polymer fraction but faces major challenges in relation to the effective regulation of the informal sector and their undercutting of the higher standards which are desired. Formal trial projects have usually failed to collect sufficient e-waste, mainly because informal recyclers pay consumers for their e-waste and pilot projects do not (Yu 2010). Changes in economic incentives are clearly required to complement the new regulations.

#### **5: Review of the long-term environmental desirability of the recycling of articles containing PBDE**

##### **5 (a): Penta and Octa BDE Stocks and implications for levels in recycling and recycle<sup>15</sup>**

135. At least 85% of PentaBDE use was in North America – as was the majority of recycling of products containing PentaBDE. Most of the remaining PentaBDE was used in Europe but there is a significant knowledge gap for production and use in China.

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<sup>14</sup> Sustainable landfilling as a final sink of deposits should consider a time perspective of 10,000 years (Brunner 2004)

<sup>15</sup> The authors are aware that the term 'recyclate' is not universally known. It is, however, a convenient label for "*the products resulting from recycling*". The UK Government's Waste Resources Action Programme provides a helpful definition as: "*Recycled material that will be used to form new products. This material will normally have undergone some form of treatment e.g. plastic pellets, produced from collected plastic bottles, to be re-used as a new product.*" <<http://aggregain.wrap.org.uk/terminology/recyclate.html>>

136. For Europe combined effects of the relatively smaller amounts used together with the earlier phase out dates and lack of recycling and relatively short product life for articles using PentaBDE mean that the peak of the PentaBDE being delivered to waste in the EU should have been in the period 2005-7. Only relatively low levels of residual PentaBDE should now be included in wastes being delivered for disposal in the EU. 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 PentaBDE 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.

137. It appears likely, therefore, that in the case of Europe 80%-95% of the PentaBDE 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.

138. In North America the limited data available indicate that most of the PentaBDE has been used in relatively short life products – mainly furniture and mattresses with a life of around 10 years. Some has therefore now reached the end-of-life stage but a significant proportion of the foam has been recovered and recycled into carpet cushion. Environ indicated that “*carpet padding likely contains 3-5% flame retardant similar to that for cushion FPUF*” (ENVIRON 2003). Dust samples from automobiles in the US showed the six highest levels of BDE-47 and BDE 99 reported were all in cars which were made in or after 2004 and the three highest levels were from cars manufactured in the USA (Lagalante 2009) This seems likely to be a consequence of the use of rebond containing PentaBDE in new cars.

139. There are some grounds for optimism about the phase out of use of PentaBDE in furniture in the US reflecting the experience in Europe. Heather Stapleton sampled a range of foam-containing furniture to establish the flame retardants used as replacements for PentaBDE (Stapleton 2009). She found TDCPP and TPP in >96% of dust samples at concentrations 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 (0.5%). This sample was collected from a futon which was (probably) purchased prior to 2004. The relatively low level of PentaBDE found in this futon was below the loading at which it would be applied as a flame retardant. This indicates that the presence of the PentaBDE may have been due to PentaBDE-containing foam having been recycled as padding for the futon.

140. 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 intentional usage of OctaBDE in the rest of the world. More recently exports from the US have been reducing the stock as described in Section 5 (b).

141. BSEF market demand data (see Appendix 2) indicates 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 other countries (particularly, given the relatively limited usage rates at that time in other regions) to America and to Europe in computer and office equipment housings.

142. The situation with OctaBDE is assessed 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 basic, and often very polluting, recycling systems. From a limited numbers of studies, the OctaBDE levels in EU mixed WEEE seems below or around the RoHS limit of 0.1% and the BFR rich fractions after separation steps seems above the RoHS level.

143. The flame retardants tetrabromobisphenol A (‘TBBPA’) and 1,2-bis(tribromophenoxy)-ethane (TBPE) were increasingly used as a replacement for OctaBDE as flame retardants for ABS through the 1990s (Schlummer 2007).

144. The largest uncertainties by far lie in the US stocks of OctaBDE – particularly old electrical equipment which is often held in storage for several years before disposal or export.

**5 (b): Information on the potential trade volume of recycled articles containing PBDE, including from developed to developing countries;**

145. There is no doubt that global trade in products (re-cycled or new) and wastes can and have resulted in rapid and wholesale movement of PBDE (Hale 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 (Risk & Policy Analysts Limited 2000).

146. The current trend is now strongly in the opposite direction with exports from Europe, Japan, Canada, Australia and the USA going mainly to China, India, Southeast Asia and Africa.

147. Over 70% of globally traded recovered plastics are used by China with most trade passing through Hong Kong. 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 US and Japan are the major exporters of plastics to China and in each case this includes large proportion of PBDE-containing WEEE plastics.

148. 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 be 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

**5 (c): An assessment of the costs and benefits of removing or maintaining the exemption on recycling articles containing PBDE**

149. 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 2007b). 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. For key articles that are recycled (PUF, WEE, PWB) concerns on main recycling path are addressed.

150. The groups considered to be most at risk if exposed to POP-BDE as a consequence of recycling include:

- a) Workers in low-technology E-waste operations.
- b) Those living in areas of developing/transition countries where intensive low-technology E-waste operations are carried out.
- c) Workers in manufacturing/ recycling/ installing foam products (exposed to PentaBDE).
- d) Toddlers and breast-fed infants – especially in countries or localities where body burdens are already high. In these scenarios recycled products are likely to supplement those existing high levels of exposure.
- e) Workers in smelters processing printed circuit boards (possibly exposed to PBDE from PWB, OctaBDE from WEEE plastic, and related PBDD/DF releases)
- f) Women of child-bearing age and those who are pregnant in relation to neurodevelopmental impacts on the fetus.

151. 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 2010).

152. 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.

153. 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.

154. Using the USEPA RfDs, which were established in 1990, gives a generally reassuring perspective of current exposures –although RfDs are approached by breast fed infants and some toddlers on high dust intake assumptions and by a few highly exposed outliers amongst adults. It is more prudent however, particularly given the low confidence levels that EPA expresses in these RfDs, to give consideration to the more recent epidemiology and science that has emerged in the last twenty years. This indicates that population scale effects in humans are consistent with the longer standing research relating to neurodevelopmental impacts from animal experiments.

155. The NOAEL derived by RIVM is exceeded by current exposures even in the EU – and very significantly in the USA thus indicating that current exposures need to be reduced. Consideration is given in Appendix 5 to the approximate health costs associated with exposures to POP-BDE in recycled foam as the exposure scenario with the best, though still limited, data. Conservative assumptions indicate that current costs of health damage for California alone exceed \$USD 55 billion. Current levels of rebound recycling based on flows from Zia (Zia 2007) could be responsible for damages valued at approximately \$USD 6 billion/year assuming a total of 1,150 tonnes of PentaBDE is being recycled. 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 the recycling of foam containing POP-BDE was to be stopped.

156. The impact on the industry should actually be much lower than the cost of all the post-consumer foam used in rebound. 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 using the handheld screening methods discussed above and in Appendix 3.

157. 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 large contaminated sites including PBDE and PBDD/DF pollution cannot 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.

158. For the assessment of the treatment of PWB in smelters, data on PBDE and PBDD/DF contamination in workers and releases of PBDE and PBDD/DF into the environment and associated damages and human exposure is needed. These data will be plant specific. As noted above BAT requirements for these facilities need first to be defined after assessing 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**

159. It is necessary to give consideration to 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;

#### **Recycling option removed i.e. no recycling of articles containing POP-BDE is allowed:**

160. 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-BDEs in their own countries. If the recycling option was removed, Parties would be obliged to comply with provisions of Articles 3 and 6 which govern production, use, import, and export of POPs and wastes containing POPs including products and articles. Parties would be obligated to dispose of wastes containing POP-BDE (including products and articles) so that the POPs content of the waste is destroyed or irreversibly transformed and no longer exhibits POPs characteristics or by other means if this is not the environmentally preferred option or if the POPs content of the waste is low. Export of materials containing POP-BDE would only be allowed for environmentally sound disposal.

#### **Positive aspects:**

- a) Reduced human and environmental exposure to POP-BDE from recycled articles.
- b) Reduced possibility of exporting POP-BDE to countries that do not have the infrastructure to handle these types of wastes.

- c) Recycling markets would be 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.
- d) 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.
- e) 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 as outlined in Article 10. This can help with the development of more sustainable consumption. It can also be use for awareness-raising of producers/exporters to care more about the content of chemicals in consumer goods leading to more sustainable production by associated requirements of producers/importers to the supply chain.
- f) 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.
- g) The greater restrictions on PBDE phase-out should stimulate innovation and lead the relevant industries (chemical industry, polymer industry, electronics industry) to consider whole life cycle assessments more carefully in future when selecting flame retardant alternatives.

***Negative aspects:***

- a) Resources and technical capacity are required to conduct an inventory and assessment of POP-BDE in wastes.
- b) Some uncertainty remains on recycling of whole plastic fractions from WEEE and so more material is likely to need sorting and disposal.
- c) Resources and technical capacity needed for environmentally sound management of POP-BDE that ensure the POPs content of the waste is destroyed or irreversibly transformed.
- d) 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 articles containing POP-BDE is allowed:**

***Positive aspect:***

- a) Business as usual with little change in regulatory approach.
- b) Less screening would be required for some materials which may contain 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 aspect:***

- a) 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.
- b) 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
- c) Higher exposure to PBDE-containing materials or goods produced or imported to the country with increasingly obvious health and environmental damage.
- d) 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.

- e) Lower incentives to develop monitoring and possibly research on PBDE and generally brominated flame retarded material flow in the countries.
- f) The recycling of POPs sets a precedent that may be attractive in future cases for proposed POPs. Developing/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 developing/transition countries would be reduced if 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.

#### **5 (e): Recommendations on the long-term environmental desirability of the recycling of articles containing PBDE**

161. The response from parties and observers to the secretariat included only one response, from Canada, confirming likely recycling of PBDE. 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.

162. Although not identified by parties or observers, other waste streams which it is believed are likely to include recycling of materials containing PBDE are the recycling of ABS plastics and other polymers, mainly from computer and office equipment housings.

163. Metals are also recycled from printed circuit boards (PWBs) but in this case the POP-BDE certainly largely destroyed if BAT smelters are used. However, BAT standards need to be developed for these facilities and releases of PBDE and PBDD/DF need to be further assessed.

164. 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 articles containing PBDE is very low – especially compared with the scale of health and environmental damage. It is noted that:

- a) 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.
- b) 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.
- c) Separation is possible, not particularly expensive, and can be implemented quickly and relatively easily.
- d) PBDE in PUR foam needs to be phased out to protect consumer and workers. Foam can be screened and separated with Br-screening technologies and other the non-BFR containing foam can then be recycled.
- e) The recovery of metals from PWB in smelters is undoubtedly useful from a material recycling perspective but the ancillary 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.
- f) 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.

165. 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:

166. “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.”

167. 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 its principal objective and the credibility of recycling with consumers – risking vital resources at a time when conservation is crucial.

168. Finally it must be noted that the concentrations of POP-BDE in first use articles are at levels where their identification, at least on the basis of bromine content, is straightforward using relatively cheap techniques. If the concentrations of POP-BDE are diluted by recycling then their subsequent identification for collection and treatment becomes much more difficult, the identification of the waste streams likely to be contaminated becomes more challenging – and much larger volumes of material would then have to be treated. In practical terms, therefore, if recycling of articles containing POP-BDE is allowed then future recovery of these POPs is likely to be much more difficult and may be impossible. In these circumstances widespread human and environmental contamination would be inevitable.

#### **5 (f): Recommendations for the elimination of PBDE**

169. POP-BDE should be eliminated as outlined in Articles 3 and 6 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.

#### **5 (f) (I): Articles containing PBDE destined for recycling**

170. Most stocks of PBDE are contained in articles developed 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.

#### ***PBDE in WEEE***

171. 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 Basel Convention and SAICM activities should be harmonised with ongoing activities of the Stockholm Convention to ensure ESM of this waste stream.

#### ***PBDE in plastic from WEEE recycling***

172. Separation technologies for BFR containing plastic are operating at a commercial 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.

173. 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 do not release PBDE or form and release PBDD/DF.

174. For several regions POP-BDE content is expected to be very low but this requires confirmation with some inventory and assessment studies.

#### ***PBDE-containing polyurethane foam***

175. 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, the 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.

#### ***Printed wired board (PWB)***

176. Printed wired board (PWB) should only be treated in BAT smelters with after burner. Note that the gap analysis indicates that the details of the specification of the after burner (temperature and residence time) as well as emissions of PBDD/DF needs further investigation and assessment.

177. 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<sup>16</sup>.

#### **5 (f) (II): PBDE articles destined for waste treatment**

178. 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.

#### ***Automotive shredder residues (ASR)***

179. In addition to PBDE, ASR contains other toxic chemicals and elements including heavy metals and PCBs which need appropriate treatment (Stockholm Convention).

#### ***PBDE in building insulation***

180. 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.

#### **5 (f) (III): Articles containing PBDE currently in use**

181. 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.

#### **5 (f) (IV): Articles containing PBDE destined for re-use**

182. 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 market and for exports of goods for reuse from the US (vehicles, furniture containing PUF, electronics). Consideration might be given to whether cars or electronics for export could be screened and, if free of PBDE, issued with appropriate certification allowing export.

## **6. Knowledge Gaps and Confounders**

### **6 (a): Knowledge Gaps**

183. A detailed list of knowledge gaps are listed and detailed in Appendix 6. The gaps found during the review and described in the Appendix include:

- a) Gaps relating to the production, use and substance flow of materials:
- b) Production data PentaBDE and OctaBDE
- c) Data on application of PentaBDE and OctaBDE
- d) Recycling flows and end-of-life of PBDE-containing materials
- e) Appropriateness of current RfD values
- f) Some key health aspects, including genotoxicity and testing at doses relevant to human exposures, have not been addressed yet.
- g) Occupational exposure and levels in workers from BAT and non-BAT treatments (material recycling schemes, metal industries, feedstock recycling)
- h) 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.
- i) Hydroxy and Methoxy PBDE (health relevance, formation extent)
- j) Analysis and screening of PBDE and Bromine in articles

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<sup>16</sup> 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.

- k) Separation and sorting technologies
- l) Manual pre-separation quality with and without instrumental detectors
- m) Technology for automatic separation of PBDE/BFR containing plastic
- n) The extent of tertiary recycling in practice is unclear and needs further investigation.
- o) Metal plants (destruction efficiency, PBDE and PBDD/DF release)
- p) Incineration (releases from non-BAT incinerators; corrosion at high Br input, grate sifting management)
- q) Cement kiln (PBDE wastes processed, feeding points for PBDE waste fractions, destruction efficiency, PBDE and PBDD/DF release, accumulation of Br in kiln)
- r) Thermal recovery and feed stock recycling technologies
- s) Extent and fate in pyrolysis and gasification of materials containing or possibly containing PBDE for feedstock recycling (and waste destruction)
- t) The applicability of bromine stripping technologies and their affordability and practicality on requires further assessment.
- u) PBDD/DF and PXDD/DF
- v) Total release of PBDD/DF conversion in the life cycle of PBDE
- w) Respective share of PBDD/DF in the environment, food and humans from POPs BDE, DecaBDE, other BFRs and other processes.
- x) Source of high levels of PBDF in Japanese housedust
- y) Sources of high share of PBDD/DF in UK food (30%) and
- z) Time trend of PBDD/DF
- aa) Respective share of PBDD/DF in the environment, food and humans from POPs BDE, DecaBDE, other BFRs and other processes.
- bb) Relevance of debromination of DecaBDE (see below in dedicated section)
- cc) Long term fate of PBDE in landfills.
- dd) Climate change (effect on debromination; increased drought and more large scale fires; leaching from landfill)

184. 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 Dioxin 2010. The abstracts are included in the supporting Annex 1.

#### **6 (b): Unintentionally formed POP-BDE from Debromination and related knowledge gap**

185. 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.

186. Appendix 6 (b) 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 2008) which 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*”.

187. 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*”.

188. 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 2009) which confirms “*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 2009).

189. The section concludes: “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, 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 2009).

190. Modelling by Schenker (Schenker 2008) indicated that even by 2005 commercial DecaBDE appeared to be making a much larger contribution to atmospheric concentrations of heptaBDE and hexaBDE than commercial PentaBDE and a similar contribution to that made by commercial OctaBDE (Schenker 2008) (see Appendix 6). Since production was stopped in 2004 the contribution made by PentaBDE and OctaBDE to POP-BDEs has been decreasing and it follows that the contribution from DecaBDE will increase further in the future. Therefore - although the authors accept that there are uncertainties associated with their calculations - attempting to manage POP-BDEs without giving proper considerations to the contribution to POP-BDE arising from the debromination of DecaBDE is not a sensible approach.

191. 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). NonaBDE and decaBDE are reported to contribute nearly 70% of the composition of some c-OctaBDE mixtures such as Bromkal 79-8DE. The much larger stock of highly brominated PBDEs stem from commercial DecaBDE of which well over one million tonnes has been produced as noted above (Table 1).

192. In Appendix 6(b) consideration is therefore given to the possible contribution to the POP-BDE from this much larger reservoir of the higher brominated PBDEs with emphasis on DecaBDE. As production and use of DecaBDE continues in much of the world the associated problems being stored up for the future continue to grow.

193. The finding in the scientific literature over the past decade (summarised in Appendix 6(b)) together with information and feedback from the scientific meetings attended as part of this work confirms that the evidence for debromination of DecaBDE as an important pathway is getting much stronger year by year. The general consensus view of the wider scientific community is now no longer “*if*” environmentally relevant debromination is happening - but rather “*how quickly*” it is happening and what the finer details of the metabolites and debromination pathways in different circumstances are.

194. Furthermore in thermal processes proposed or used for feedstock recycling (pyrolysis, gasification) or used for end-of-life treatment highly brominated PBDE are certainly debrominated to lower brominated PBDE including POPs. The pyrolysis of DecaBDE containing HIPS at 500°C, for example, generated mainly mono to pentabrominated BDE (Hall 2008). The study shows that significant debromination of DecaBDE to lower brominated PBDE take place under pyrolysis conditions. For all pyrolysis and gasification processes the fate of debromination of DecaBDE to POP-BDE need to be considered and assessed for feedstock recycling of PBDE.

195. A range of knowledge gaps exist in respect to debromination of DecaBDE (and also for OctaBDE)

- a) Details on time scale of debromination in different media (e.g. in landfills, sediments, soils, atmosphere, biota).
- b) The dimension of debromination and related POPs-BDE formation
- c) The formation of other degradation products (PBDD/DF, hydroxyl-PBDE, methoxyBDE, other degradation products)
- d) Conditions where complete debromination can be achieved (in technical processes and in natural environments)

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