Workshop on sound management of PBDEs and phasing-out opportunities in Sri Lanka

Held on 27th November 2015 @ Water,s Edge, Battaramulla, Sri Lanka

Organized by

Ministry of Environment & Renewable Energy

In Collaboration with

Basel Convention Regional Centre for Asia and the Pacific (BCRC), Stockholm Convention Regional Centre for Capacity-Building and the Transfer of Technology in Asia and the Pacific (SCRCAP), China

And

South Asia Co-operative Environment Programme (SACEP)

Introduction

Project on Sub regional Action Plan (Asia) for Polybrominated diphenyl ethers (PBDEs) management and reduction was developed by Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific (SCRCAP)/Basel Convention Regional Centre for Asia and the Pacific (BCRC, China) together with Cambodia, Laos, Mongolia, Pakistan, Sri Lanka to access pollution characteristics of PBDEs in main waste recycling sectors, to reduce the risks caused by PBDEs through a demonstration of application of Best Available Techniques (BAT)/Best Available Practice (BEP) in selected sectors and propose a regional pollution control strategy and national frameworks in Asia.

The workshop on Sound Management of PBDEs and phasing-out opportunities in Sri Lanka was one of the key activities of the above project in addition to the report prepared on "National Summary Report on Present Status of PBDEs Management". The workshop is jointly organized by BCRC/ China, Ministry of Mahaweli Development and Environment and SACEP. The financial support for the workshop is provided by BCRC/China through UNEP /GEF. The total project cost is USD 3,950,000 and co- financing is USD 11,800,000.

PBDEs are organic chemical compounds, which were and partly are extensively used as flame retardants in products such as electronic equipment, plastic housings, textiles and polyurethane applications. They are one of the most hazardous industrial Persistent Organic Pollutants (POPs) identified by the Stockholm Convention (SC). Hexabromodiphenyl ether and heptabromodiphenyl ether, Tetrabromodiphenyl ether and pentabromodiphenyl ether are considered as PBDEs under the SC. Sri Lanka being a party to the SC, for which the amendments have entered into force on 2012 has the obligation to ensure sound management of the PBDEs. The Ministry of Mahaweli Development & Environment, the National Focal Point of the SC in Sri Lanka is implementing the project while eligible for USD 440,000 under the project and the co-financing is USD 1,420,000. This in-kind contribution which calculated as Co-financing is from Ministry of Mahaweli Development & Environment and other related stakeholders including staff time, coordination, office, equipments, etc. The project will be started in year 2016 and project period is 3 years.

Objective of the Workshop

The one day workshop to gather the background information and creating awareness among the stakeholders on "Sound Management of PBDEs and phasing-out opportunities in Sri Lanka" was held on 27th November 2015 at the Water's Edge Hotel, Battaramulla, Sri Lanka in collaboration with Basel Conventional regional Centre for Asia and the Pacific (BCRC), Stockholm Convention Regional Centre for Capacity-Building and the Transfer of Technology in Asia and the Pacific (SCRCAP) - China and South Asia Co-operative Environment Programme (SACEP) and an international POPs expert from Germany. About 30 government officers/individuals were participated at the workshop representing key stakeholder institutions. The Agenda (Annex I) of the workshop and list of the participants (Annex II) are attached.

Summary of the Work Shop

The workshop was started with the Welcome Remarks by Mr. Anura Jayatilake, Director, Air Resource Management and International Relation /Ministry of Mahaweli Development and Environment.

Mr. Jayatilake was introduced the country overview of the POPs and chemical management and importance of having an environmental sound management of PBDEs in the country. He further explained about the POPs, their special features, adverse impacts and the present and future activities to control POPs by the Ministry as the focal point of Stockholm Convention to Sri Lanka. The presentation is attached in Annex III

On behalf of the BCRC/China, Ms. Fang LIU, Technical Assistant was made the Welcome Remarks and explained the objective of the workshop is to find out the phasing out opportunities of PDBEs in Sri Lanka. She also explained about the participating countries of the project, resource allocation and Regional Corporation.

At the end of the opening session, self introduction of the participants were made and participants gave a brief introduction of them and their institutes.

Technical Session was started with the presentation made by Ms. Fang LIU, Technical Assistant, BCRC/China. Introduction of PBDEs, their properties, risk, use, and end of life were presented and she explained that production and use of PBDEs have to be eliminated by Parties subject to the exemptions allowed by the Convention. Products and articles containing PBDEs include; electronic equipments and wastes, interior foam and carpet padding, interiors in transportation, and drilling and construction materials. Due to the complexity and magnitude of usage of the PBDEs, eliminating them represents a challenge for many Parties. Through the presentation she explained the chemical and physical nature of PBDEs, production and usage and their risk to human health. The presentation is attached in Annex IV

Dr. Roland Weber, International POPs Consultant, UNIDO was made couple of presentations on "Guidance for the inventory of PBDEs listed under the Stockholm Convention- a tiered approach", "Introduction to draft Guidance on Sampling and Analysis of POPs in Products and Articles", "Case studies on PBDE and HBCD monitoring in articles, products and waste" and Alternatives to PBDEs and substitution approaches. He is working in the POPs management and have involved in Review and Updated of National Implementation Plans (NIP) of POPs in many countries including Sri Lanka. He stressed the importance of Environmental Sound Management of PBDEs while presenting several case studies of the different countries. He showed that immediate action to be taken for the management of PBDEs. The presentations are attached in Annex V

Thereafter, Ms. Fang LIU, BCRC/China was made couple of presentations on "E-waste Management including E-waste plastic in China" and "Testing of PBDE samples and Challenge of PBDE analysis". The presentation was based on the studied done by BCRC/China. China is one of the best examples of Environment Sound Management of e-waste in the region. Also Ms. Fang also

explained about the duties and responsible of BCRC with regards to e-waste and PBDEs management. The presentations are attached in Annex VI

Prof. Ajith De Alwis, Head-Faculty of Chemical & Process Engineering, University of Moratuwa and PBDEs Expert of the NIP update project was made a presentation on "Present Status of PBDESs Management in Sri Lanka". The presentation was based on the inventory preparation of the NIP project and study conducted under the regional project on PBDES management. Prof. Ajith explained that the production of PBDE in Sri Lanka is effectively zero. Even though PBDEs are considered to be no longer produced, the main challenge for their elimination is the identification of existing stockpiles and articles containing PBDEs and their disposal at end-of-life according to the presentation. Mainly there are two types of material flows of PBDEs; electrical and electronic equipment (EEE) and related waste (WEEE) and transport sector and end-of-life vehicles (ELV). In order to phase out of PBDEs in Sri Lanka, an environmental Sound Management of PBDEs is essential and management actions are to be taken soon. The presentation made by Prof. Ajith is attached in Annex VII

During the Questions and Answers session, participants were allowed to raise questions and clarifications from the respective presenters. Finally, all the participants of the workshop were shown their interest to support the upcoming project on PBDEs.

The way forward and closing remarks of the workshop were made by Mr. S M Werahera, Assistant Director, Air Resource Management & International Relations, Ministry of Mahaweli Development & Environment by conveying special thank to the Dr. Roland Weber, International POPs Consultant, Ms. Fang LIU, Technical Assistant from BCRC/China, Director General, SACEP and the Ministry staff. He further mentioned that under the NIP, there are many management actions have identified and those actions can implement together with the PBDEs management project activities. According to him, there are several upcoming projects related to chemical and waste management that are interconnected and therefore a single approach can be taken to implement them in the country.

Annex I

Workshop on Sound Management of PBDEs and Phasing-out Opportunities in Sri Lanka
27th November 2015 at Water's Edge Hotel, Battaramulla

Organized by:
Air Resource Management & International Relations, Ministry of Mahaweli Development & Environment
In Collaboration with,
Basel Convention Regional Centre for Asia and the Pacific (BCRC)/ Stockholm Convention Regional Centre for Capacity-Building and the Transfer of Technology in Asia and the Pacific (SCRCAP), China
And
South Asia Co-operative Environment Programme (SACEP), Sri Lanka

PROVISIONAL AGENDA

TIME	TOPIC	PRESENTER
09.00 – 09.30am	**Registration of Participants**	
Session I: Introduction and Objectives of the workshop		
09.30 -09.40am	**Welcome & Opening Remarks**	*Secretary/Additional Secretary, Ministry of Mahaweli Development & Environment*
09.40 -9.50 am	**Objectives of the Workshop**	**Ms. Fang LIU, Technical Assistant** *Basel Convention Regional Centre for Asia and the Pacific (BCRC)/Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific (SCRCAP), China*
09.50 - 10.00am	**Introduction of Participants**	*ALL*
10.00 –10.15 am	**POPs Management In Sri Lanka**	**Mr. Anura Jayatilake,** *Director, Air Resource Management & International Relations, Ministry of Mahaweli Development & Environment*
10.15 -10.30am	***Tea/Coffee Break***	
Session 2: Introduction of Polybrominateddiphenyl ethers (PBDEs)		
10.30 -10.50 am	Introduction of PBDEs (properties, risk, use & end of life)	**Ms. Fang LIU, Technical Assistant** *BCRC/SCRCAP, China*
10.50-11.05 am	Questions and Answers	**ALL**
Session 3: Inventory of PBDEs		
11.05–11.25 am	Guidance for the inventory of PBDEs listed under the Stockholm Convention- a tiered inventory approach	**Dr. Roland Weber** *International Expert on POPs*
11.25 -11.40 am	Questions and Answers	**ALL**

Session 4: Monitoring of PBDEs in articles: case studies		
11.40 - 12.00pm	Introduction to Guidance on monitoring on new listed POPs in articles (with special emphasis on PBDEs)	**Dr. Roland Weber** *International Expert on POPs*
12.00 12.10 pm	Questions and Answers	**ALL**
12.10 - 12.45 pm	Presentations on case studies	**Dr. Roland Weber** *International Expert on POPs*
12.45 - 1.00 pm	Questions and Answers	**ALL**
1.00 - 2.00 pm	***Lunch***	
Session 5: Articles containing PBDEs identify and analysis		
2.00 - 2.20 pm	E-waste Management including E-waste plastic in China	**Ms. Fang LIU** *Technical Assistant* *BCRC/SCRCAP, China*
2.20 - 2.40 pm	Testing of PBDE samples and Challenge of PBDE analysis	**Ms. Fang LIU** *Technical Assistant* *BCRC/SCRCAP, China*
2.40 - 2.55 pm	Questions and Answers	**ALL**
2.55 - 3.10 pm	***Tea/Coffee Break***	
Session 6: Alternatives and substitution approach		
3.10 - 3.40 pm	Alternatives to PBDEs and substitution approaches	**Dr. Roland Weber** *International Expert on POPs*
3.40 - 3.50 pm	Questions and Answers	**ALL**
3.50 – 4.10 pm	Present Status of PBDESs Management In Sri Lanka	**Prof. Ajith De Alwis** *PBDEs Expert/NIP project* *Head-Faculty of Chemical & Process Engineering, University of Moratuwa*
4.10 - 4.15 pm	Questions and Answers	**ALL**
4.15 - 4.25 pm	Way Forward	**Mr. S M Werahera**, *Assistant Director, Air Resource Management & International Relations, Ministry of Mahaweli Development & Environment*
04.25 pm	**Close of Programme**	

Annex II

Workshop on Sound management of PBDEs and phasing-out opportunities in Sri Lanka
27th November 2015 at Waters Edge, Battaramulla

Organized by:
Air Resource Management & International Relations, Ministry of Mahaweli Development & Environment
In Collaboration with,
Basel Convention Regional Centre for Asia and the Pacific (BCRC)/ Stockholm Convention Regional Centre for Capacity-Building and the Transfer of Technology in Asia and the Pacific (SCRCAP), China
***And** South Asia Co-operative Environment Programme (SACEP), Sri Lanka*

List of Participants

No	Name	Designation	Institute	Telephone	Fax	E mail
1	Mr. Gamini Gamage	Addl. Secretary (E&P)	Ministry of Mahaweli Development & Environment, 82, Sampathpaya, Battaramulla	011-2875327	0112879834	gaminigamage@yahoo.co.uk
2	Mr. Anura Jayatilake	Director, ARM & IR		011-2888248	011-2888248	lasith@slt.lk
3	Ms. Deepa Liyanage Director	Sustainable Environment Division		011-2877286	011-2861726	
4	Mr. S. M. Werahara	Assistant Director/ ARM & IR		011 2888248	011-2888248	smwerahera@yahoo.com
5	Ms. Vindya Hewawasam	RA		011-2888248	011-2888248	eeconga@yahoo.com
6	Ms. Chandima S N. Mohettige Programme Assistant	Sustainable Development Division		011-2883456	011-2865452	Snm_2014@yahoo.com
7	Ms. Kasunhari Pathirage	DO		011-2888248	011-2888248	
8	Dr. Roland Webber	International Expert on POPs	Germany	+49-7171-189809		roland.weber10@gmail.com
9	Ms. Fang Liu	Technical Assistant	BCRC/ SCRCAP, China	+89-13810987672		

10	Ms. Jacintha S Tisera	Administrative Officer	South Asia Co-operative Environmental Programmed (SACEP), 69/4, Maya Avenue, Col 6	0718-188658	0112872605	Jacintha.tissera@sacep.org
11	U.K.Rathnadeera	Senior Programme Officer		0716-436307	0112-589369	Rathnadeera.uk@sacep.org
12	Prof. Ajith De Alwis PBDE Expert	Head-Faculty of Chemical & Process Engineering	University of Moratuwa, Katubedda, Moratuwa	077-7342476		ajith@uom.lk
13	Mr. Asitha Senavirathne	Addl. Secretary	Ministry of Industrial Development, P O Box: 570, 73/1, Galle Rd, Col 03	011-2447224	0112333341	asithakumara@gmail.com
14	Ms. Hasini Lakdarani	Assistant Director	Ministry of Transport & Civil Aviation,No 1, D R Wijewardena Mw,Col 10	011-2687105 011-2669307 011-2682952	011-2684 930 011-2689 454	info@transport.gov.lk
15	Ms. Sujeewa Fernando	EMO	Ministry of Health, Sawsiripaya, Baddegama WimalawansaThero Mw, Colombo 11	0714-439218		sujeewaf@gmail.com
16	Ms. Dushanthi Ranpatige	Research Engineer	Industrial Technology Institute, Head Office, 363, Baudhaloka Mw, Col 07	0714434773		ranpatige@iti.lk
17	Ms. D.M. Hasanthie S Disanayaka	Research Engineer		0714433422		
18	Mr. Keerthini Suraweera	Senior Deputy Director	Sri Lanka Standards Institution, 17 Victoria Place ,Elvitigala Mawatha, Col 08	011 2671573 011-2671567-72 011-2671575	11 2671579	
19	Ms. I.N. Weerasekara	Assistant Controller	Import and Export Control Department,No: 75 1/3, 1st Floor, Hemas Building, York Street,P.O. Box - 559 Colombo 01	011-2324386 011-2326774	112-328486	imexport@sltnet.lk
20	Mr. Sajith Fernando	Assistant Director	Department of National Planning, The Secretariat, 1st Floor, Colombo 1	011-2484500 011-2484600 076-6815790	011-2445065	

21	Ms. Wilka Ranasinghe	Senior Environmental Officer	Central Environment Authority, 104, Parisara Piyasa, Robert Gunawardena Mw, Battaramulla	0714934191		Wilka.wayanthi@gmail.com
22		Production Manager	Damro Co. (Pvt) Ltd, 361, Salgastennawatta, Kandy Rd, Nittambuwa.	033-2285339	033-2285449	
23	Mr. Inu Devin Gamage	Brand Manager	Abans PLC, 498, Galle Road, Colombo 03	011 2 376000 0112-565265	011 2-263300	
24	Ms. A.K.M.Priyanvada	Assistant Director	Construction Industrial Development Authority (CIDA), "Savsiripaya", 123, Wijerama Mw, Col.07	0777348325	0112-699738	mpriyanvada1973@gmail.com
25	Ms. Nisansala Ranundeniya	RECP Technologist	National Cleaner Production Centre, 66/1, Devala Road Nugegoda.	011-2822272/3	0112-822274	Nsranvndeniya@gmail.com
26	Mr. Rashanka Gunarathna	Business Development	Green Link (Pvt) Ltd 20/1 A, Moragasmulla Road Rajagiriya	0714 066 455 071 6305184, 0115 661 731	0714-200555	rashanka.greenlink.lk
27	Mr. Oshada Werasingahe	Business Development	Green Link (Pvt) Ltd 20/1 A, Moragasmulla road Rajagiriya	0115 661 731,		
Supporting Staff						
30	Mr. Kasun Dewapriya	KKS	Ministry of Mahaweli Development & Environment, 82, Sampathpaya, Battaramulla	011-2888248		eeconga@yahoo.com
31	Ms. Dilhani Maheshika	Trainee		011-2888248		eeconga@yahoo.com
32	Mr. R. Thilakarathna	Driver		011-2888248		eeconga@yahoo.com

Annex III

POPs Management in Sri Lanka

Mr. Anura Jayatilake
Director
Air Resource Management & International Relations
Ministry of Mahaweli Development & Environment

Stockholm Convention on Persistent Organic Pollutants (POPs)

Objective:
To protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in the fatty tissue of humans and wildlife.

- Date of Adoption: 22.05.2001
- Date of Entry into Force: 17.05.2004
- Date of Ratification by Sri Lanka: 22.12. 2005
- Date of Entry into force in Sri Lanka: 22.12.2005
- Number of Countries which have ratified the Convention: 179
- National Focal Point: Ministry of Mahaweli Development & Environment
- Competent Authority:
  - *Pesticides*-Registrar of Pesticides (ROP)
  - *Industrial Chemicals*: Central Environment Authority (CEA)

What are the POPs?

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes

Special Features of POPs

- Persist in the environment for long periods
- Capable of long-range transport
- Bioaccumulation in human and animal tissues
- Biomagnify in food chains
- Potentially significant impacts on human health and the environment.
- Grass hopper effect and cocktail effect

Adverse impacts of POPs

Exposure to POPs can cause serious health problems including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease and even diminished intelligence

The initial 12 POPs

Annex A (Elimination)

●Aldrin ●Chlordane ●Dieldrin ●Endrin
●Heptachlor ●Mirex ●Toxaphene ▲PCBs
●/▲Hexachlorobenzene

Annex B (Restriction)

●DDT

Annex C (Unintentional production)

■Dioxin ■Furan ■Hexachlorobenzene ■PCBs

●*Pesticides* ▲*Industrial chemicals* ■*By-products*

POPs are coming under 3 Annexes

- Annex A: Parties must take measures to eliminate the production and use of the chemicals listed under Annex A. Specific exemptions for use or production are listed in the Annex and apply only to Parties that register for them. (Elimination)
- Annex B: Parties must take measures to restrict the production and use of the chemicals listed under Annex B in light of any applicable acceptable purposes and/or specific exemptions listed in the Annex. (Restriction)
- Annex C: Parties must take measures to reduce the unintentional releases of chemicals listed under Annex C with the goal of continuing minimization and, where feasible, ultimate elimination. (Unintentional production)

Nine new POPs

Alpha hexabromocyclododecane Beta hexabromocyclododecane Gamma hexabromocyclododecane	A	Production: Use:
Chlordecone	A	Production: Use:
Hexabromobiphenyl	A	Production: Use:
Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether)	A	Production: Use: Articles in accordance with the provisions of Part IV of Annex A
Lindane	A	Production: Use: Human health pharmaceutical for control of head lice and scabies as second line treatment
Pentachlorobenzene (PeCB)	A and C	Production: Use:
Perfluorooctane sulfonic acid and its salts, perfluorooctane sulfonyl fluoride	B	Production for the use below: Use: Acceptable purposes and specific exemptions in accordance with Part III of Annex B
Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether)	A	Production: Use: In accordance with the provisions of Part IV of Annex A

●*Pesticides* ▲*Industrial chemicals* ■*By-products*

Activities conducted to implement the convention at country level:

- Ministry Submitted the 1st National Implementation Plan (NIP) in 2006 and now in the process of making the 2nd NIP
- Development of Harmonized System (HS) codes for prioritized POPs Chemicals in collaboration with Department of Customs
- Capacity building of stakeholder institutions for the formulation of national inventories
- Development and update the of the National Inventories for PCBs, Unintentional POPs and Pesticides identifying existing situation of the country and future trends
- Development of PFOS and PBDEs inventories
- Public awareness on POPs including school children
- Information Exchange & submitting National Status to Stockholm Convention

Cont....

- Development and publication of awareness materials on POPs and related health impacts (Videos, Exhibition models, Leaflets, Posters, CDs)
- Participation for National & International meeting/ workshops/ seminars/ trainings/ COPs in relation to POPs management
- In collaboration with the Basel and Stockholm Coordination Centre for Asia and the Pacific, China (BCRC) and three other Asian countries (Cambodia, Lao PDR, Pakistan) have completed the regional project on Capacity Strengthening and Information Exchange on PCBs Management in Selected Asia Countries to strengthen the national institutional capacity on PCBs elimination and management at regional level.

Cont....

- Control of Pesticides Act No. 33 of 1980 - Regulation of imports, restriction and ban of pesticides through registration and gazette notification. All POPs pesticides have banned.
- Imports and Exports (Control) Act No. 1 of 1969 – Regulation of import of industrial chemicals including POPs chemicals. Government Extraordinary Gazette No. 1813/14 of 05.06.2013 of the import and Export Control banned PCBs
- Technical Advisory Committee Meeting for the management of industrial Chemicals on Implementation of the Rotterdam Convention in Sri Lanka
- Establishment of a National Coordinating Committee for the implementation of the Basel Convention in Sri Lanka, Basel, Stockholm, Rotterdam Conventions and SAICM related issues are discussed at the meeting.
- Study on Socio – Economic related to proposed EPR system on Control E-waste to control associated POPs.
- Program with pesticide industries for management of big plastic containers to minimize the possible mismanagement activities including burning (This program is scheduled to be extended to farmers too).

Present & Future Activities

- Project on Enabling Activities to Review and Update the National Implementation Plan under the Stockholm Convention for Persistent Organic Pollutants (GEF/UNIDO) -On going
- Project on Environmentally Sound Management and Disposal of PCBs Wastes and PCB Contaminated Equipment in Sri Lanka (GEF/UNIDO) - On going
- Project on Sub Regional Action Plan (Asia) for PBDEs Management and Reduction (GEF/BCRC, China). Participating countries are Cambodia, Lao PDR, Mongolia, Pakistan and Sri Lanka -GEF CEO approved
- Preparation of list of products and HS Code for the issuing a new gazette through Import and Export Control Department.
- Banning and minimizing the use of plastic bags to reduce their effects on environment through illegal dumping and burning.

Thank You

For further information:

Air Resource Management & International Relations
Ministry of Mahaweli Development & Environment
980/4 A, Wickramasinghe Place
Ethul Kotte
Tel/ Fax : 011-2888248
Email: eeconga@yahoo.com

Annex IV

Introduction to PBDEs

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

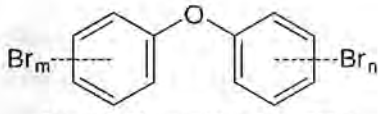
27th Nov. 2015

Contents

01 Structural characteristics and properties

Structural characteristics

- Polybrominated diphenyl ethers or PBDEs, (see figure below) are a group of industrial aromatic organobromine chemicals that have been used since the 1970s as additive flame retardants in a wide range of — mainly — consumer products.



Structure of polybrominated diphenyl ethers (PBDEs)

Structural characteristics

- They are structurally similar to the PCBs and other polyhalogenated compounds, consisting of two halogenated aromatic rings.
- PBDEs are classified according to the average number of bromine atoms in the molecule: Mono-, di-, tri-, Tetra-, penta-, Hexa-, hepta-, Octa-, Nona-, and Decabromodiphenyl ethers.
- The family of PBDEs consists of 209 possible substances, which are called congeners (PBDE = $C_{12}H_{(10-x)}Br_xO$ (x = 1, 2, ..., 10 = m + n)).
- Higher brominated PBDEs average more than 5 bromine atoms per molecule, accordingly, lower brominated PBDEs average 1-5 bromine atoms. The most hazardous congeners are tetra- to heptabrominated PBDEs because they can best bioaccumulate.

Properties

- The boiling point of PBDEs is between 310 and 425° C and their vapor pressure is low at room temperature. PBDEs are lipophilic, and their solubility in water is low, especially for the higher brominated compounds.
- As persistent organic pollutants (POPs), PBDEs resist degradation and tend to bioaccumulate in living tissues. Hence, elevated concentrations of PBDEs are being detected worldwide in various environmental matrices, both in urban and remote areas alike.

02 Production and use of PBDEs

Production of PBDEs

- Commercial PBDEs are synthesized by bromination of diphenyl ethers under conditions resulting in mixtures of brominated diphenyl ethers. The commercial products predominantly consist of Penta-, Octa-, and Decabromodiphenyl ethers.
- The composition of commercial brominated diphenyl ethers is given in Table below.

Production of PBDEs

- Commercial-PentaBDE (c-PentaBDE) is produced mainly in Israel, Japan, the United States, the European Union and China*(UNEP 2010)*. Production ceased in the European Union in 1997. It is assumed that since the late 1990s PentaBDE has been produced in decreasing quantities, and that production ended in 2004*(UNEP 2010b)*.

- *UNEP 2010a: Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/2)*
- *UNEP 2010b: Supporting document for technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/6)*

Production of PBDEs

- Commercial-OctaBDE (c-OctaBDE) has been produced in the Netherlands, France, the United States, Japan, the United Kingdom and Israel. Production stopped in the European Union, the United States and the Pacific Rim in 2004, and there is no information indicating that it is being produced in developing countries*(BSEF 2007)*.

- *BSEF 2007: Bromine Science and Environment Forum. Annex E response*

Production of PBDEs

- A compilation of PBDEs production data, prepared for the POPs Reviewing Committee of the Stockholm Convention, estimated the total production of all PBDEs from 1970 to 2005 as between 1.3 million and 1.5 million tonnes(UNEP 2010a). The total amounts of c-PentaBDE and c-OctaBDE used globally were estimated at around 100,000 tonnes each. The production of c-DecaBDE, which is not listed as POPs, was estimated at over 1.1 million tonnes until 2005. While the production of POPs c-PentaBDE and c-OctaBDE ended in 2004, the production of DecaBDE continues. Since 2005, the production of DecaBDE has been about 100,000 tons in the world, this figure has remained at approximately the same level for many years.

Use of PBDEs

- The major manufacturing sectors that have used PBDEs are *(SSC et al. 2015)*:
- Organobromine industry;
- Electrical and electronics industry;
- Transportation industry;
- Furniture industry;
- Textiles and carpet industry;
- Construction industry;

Since PBDEs are present in these end of life material flows they ender different recycling schemes and are relevant for the recycling industry

SSC, UNEP, UNIDO, UNITAR, UN (2015): Guidance on best available techniques and best environmental practices for the recycling and disposal of wastes containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants. (Draft)

Uses of PBDEs

- Electrical and electronics industry;

Computer and TV casings (mainly CRTs), cold resistant separators in refrigerators, casings, and other parts in electrical and electronic appliances are made of ABS, HIPS, or PBT, which may contain PBDEs.

- Transportation industry;

Most present-day PBDEs are used in the transportation in conveyor belts; rubber pipes for insulation; and the textile coatings of seating in automotive, aircraft, and trains.

- Furniture industry;

PBDEs have also been applied to back coatings and impregnation for carpets, as well as furniture coating in homes and office buildings, and PBDEs are added into polyamide polymers as coating for furniture.

Use of PBDEs

- Textiles and carpet industry;

Fabrics; curtain; carpet; coating, ect.

- Construction industry;

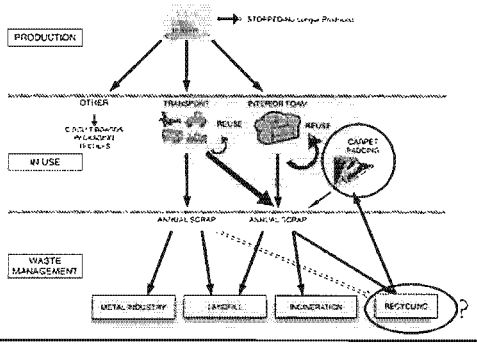
PBDEs are incorporated into potentially flammable construction materials to slow down and/or inhibit combustion. Polyurethane foam containing PBDEs is also used for sound insulation.

Former uses of c-PentaBDE

- It is considered that between 90% and 95% of the use of c-PentaBDE was for the treatment of PUR foam. These foams were mainly used in automotive and upholstery applications. Minor uses included textiles, printed circuit boards, insulation foam, cable sheets, conveyer belts, lacquers and possibly drilling oils. (UNEP, 2007)

UNEP. 2007. Report of the Persistent Organic Pollutants Review committee on the work of its third meeting – addendum. Risk management evaluation on commercial pentabromodiphenylether. UNEP/POPS/POPRC.3/20/Add1

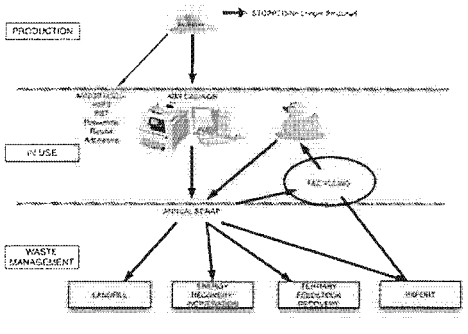
Material flow c-PentaBDE containing articles



Former uses of c-OctaBDE

- The main former use of c-OctaBDE was in acrylonitrile-butadiene-styrene (ABS) polymers, accounting for about 95% of c-OctaBDE supplied in the EU. The treated ABS was mainly used for housings/casings of EEE, particularly for cathode ray tube (CRT) housings and office equipment such as copying machines and business printers. Other minor uses were high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers. Although the majority of these polymers were used in electronics, there was also some use in the transport sector.
- Other minor uses found in literature include nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, unsaturated polyesters, adhesives and coatings. (UNEP 2010 a,b)

Material flow c-OctaBDE containing articles



Uses of ~~DecaBDE~~

- DecaBDE is widely used in rubber, plastics, fibers and other materials as additive flame retardant.
- DecaBDE is now acknowledged as POP by the POP Reviewing Committe and will be recommended to be listed at the next Stockholm Convention Conference of Parties.

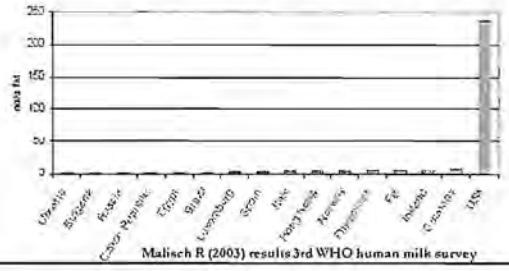
03 Risks associated with PBDEs

Risks associated with PBDEs

- The persistence of PBDE components in the environment is well documented. The only relevant degradation pathways identified until now are photolysis, anaerobic degradation and metabolism in biota, acting through debromination and producing other BDE which may have higher toxicity and bioaccumulation potential.
- Main routes of human exposure to PBDEs include indoor exposure by e.g. ingestion of (house) dust, inhalation of PBDE-contaminated air and possibly skin contact. Also food intake cause additional PBDE exposure. Furthermore occupational exposure is relevant.
- Moreover, PBDEs were all detectable in the collected human tissue samples, such as placentas, umbilical cord blood, breast milk, blood and serum, hair, kidney, liver, and lung; some researches showed significant statistical differences between the human in the exposed areas and control areas, which showed that they had entered the subjects' bodies through the environment and dietary exposure.

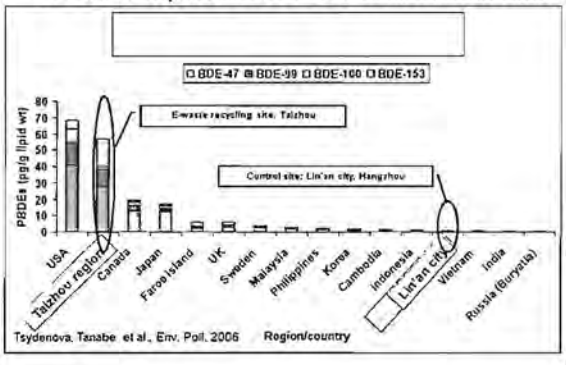
Use and human exposure of POP-PBDEs

- PBDE human milk levels from 3rd WHO study for the different regions show high levels in USA.
- Largest use of POP-PBDE in North America with specific flammability standards for e.g. furniture and transport.



Malisch R (2003) results 3rd WHO human milk survey

Global comparison of PBDEs in human milk



Tsydenova, Tanabe et al., Env. Poll. 2006 Region/country

PBDEs in human milk

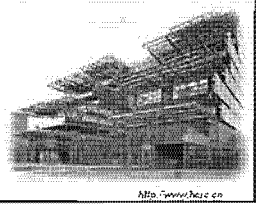
- According to Xing et al. (2009), residents living near an e-waste recycling area in Taizhou had higher concentrations of PBDEs in breast milk (with a value of 59.3 ng/g lipid wt) than those at other sites (Leung et al., 2010)
- Compared with the e-waste recycling sites, breast milk samples from 19 provinces in China (non-e-waste-recycling sites) had low levels of PBDEs (mean: 1.49 ng/g lipid wt, ranging from 0.56 to 3.5 ng/g lipid wt) (Ni et al., 2013).

References: Q. Song, J. Li / Environment International 65 (2014) 52–93

Risks associated with PBDEs

- Health risk of PBDEs: cryptorchidism, organohalogen compounds present in the serum of pregnant women would transfer over the placenta to the infants, diabetes, and highest exposure individual scored five less IQ points, etc.
- The risks associated with individual POPs have been assessed by the Persistent Organic Pollutants Review Committee (POPRC). The risk profiles on c-PentaBDE (UNEP/POPS/POPRC.2/17/Add.1) and c-OctaBDE (UNEP/POPS/POPRC.2/17/Add.4), and the risk management evaluation documents for c-PentaBDE (UNEP/POPS/POPRC.3/20/Add.1) and c-OctaBDE (UNEP/POPS/POPRC.4/15/Add.1), can be viewed and downloaded at *www.pops.int*.

04 PBDEs end of life



PBDEs end of life

- Energy/material recovery from POP-PBDE-containing materials

Plastic wastes which contain polybrominated diphenyl ethers (PBDE) should be excluded from material recycling because of the possibility of emitting dioxins and furans. Instead such plastic wastes should be treated in feedstock recycling facilities or in controlled incinerators recovering energy. *The Technical Guidelines for the Identification and Environmentally Sound Management of Plastic Wastes and for their Disposal" (Basel Convention, 2002)*

Cement kilns are increasingly used in waste management schemes in both industrial and developing countries. Major POP-PBDE-containing materials like WEEE plastic, ASR and potentially other POP-PBDE/BFR-containing materials are also partly treated. Since cement kilns can only take a limited amount of chlorine/bromine particular care has to be taken on input amount.

PBDEs end of life

- Disposal of POP-PBDE-containing materials to landfills
- Most developing countries do not have established recycling schemes to separate POP-PBDEs from large material flows such as end-of-life vehicles, WEEE plastics, furniture and mattresses. Nor do they have the capacity, human or financial resources, for sophisticated waste management practices, treatment and disposal options.
- Therefore in many developing countries a high proportion of wastes is still disposed of to landfills and open dump sites, sometimes with open burning, which has severe negative impacts on human health and the environment.
- This situation needs to be urgently improved for a better environmentally sound management of this waste and for a better recovery of materials from e-waste and other PBDE containing materials.

THANKS

Contacts:

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific
Add: Sino-Italian Environmental and Energy Building, Tsinghua University
Tel: 86 10 62794351 Fax: 86 10 62772048
Email:

Annex V

Workshop on Sound Management of PBDEs and Phasing-out Opportunities in Developing Parties
27. November 2015, Colombo, Sri Lanka

Guidance for the inventory of PBDEs listed under the Stockholm Convention - a tiered approach

Dr. Roland Weber
POPs Environmental Consulting, Germany
roland.weber10@web.de

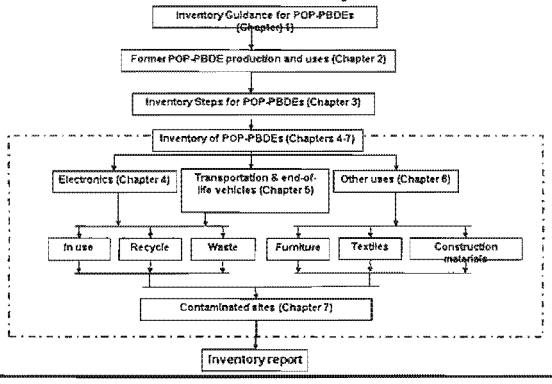
Why to develop a POP(-PBDE) Inventory ?

- POP inventories are the basis for prioritization, action plan development and for deciding on management strategies.
- It allows the assessment whether the current country situation meets the SC requirements and where not.
- It provide a basis for the reporting obligations.
- Helps to identify information gaps for prioritization and action plan development.
- To identify the need for further financial/technical support.

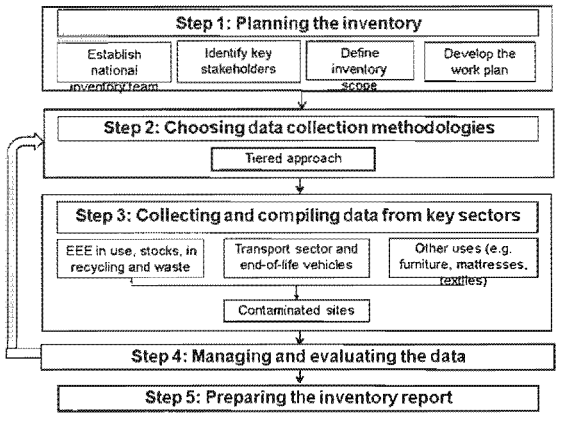
POP-PBDE Inventory Guidance

- Guide to identify/quantify articles containing POP-PBDEs in import/export, use, stockpiles, recycling and wastes;
- Provide guidance to estimate missing information required to complete the inventory;
- Give information for prioritization in POP-PBDE action plan;

Content/Structure of POP-PBDE Inventory Guidance



STEPS TO CONDUCT A POP-PBDE INVENTORY



Step 1 – Planning of the Inventory

1. National inventory team:

- Multi-stakeholder inventory team with necessary competences and access to relevant inventory information for the different sectors.
- This team would comprise government ministries (chemicals and waste management), customs, private sectors, NGOs, research (working on POPs and resource/waste management and possibly material flows).

2. Identification of key stakeholders

- For the different sectors key stakeholders need to be contacted to get access to the necessary information in the different sectors.
- Depending on the needs and availability, stakeholders could become inventory team members or just support with data/information.

Step 1 – Planning of the Inventory

3. Objectives and scope :
- Setting objectives of the inventory and decide on scope considering the national circumstances
- Use outcomes of initial assessment for scope setting
- Consider availability/need of resources and capacity

4. Development of workplan:
- For the different inventory sectors
- Setting time frame
- Allocation of resources for planned activities

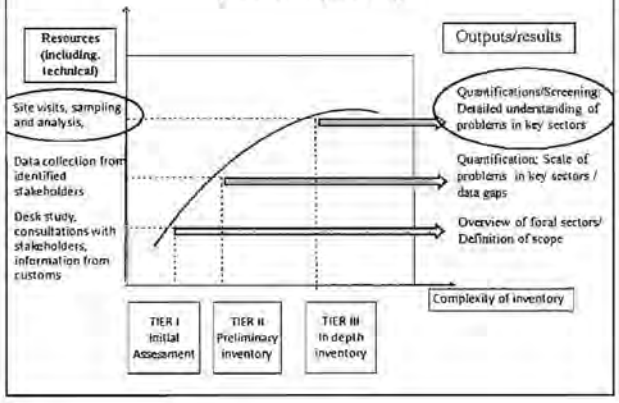
EEE and WEEE | Transport Sector | Other former Uses | Contaminated sites

Step 1 – Planning of the Inventory Development of the workplan(s)

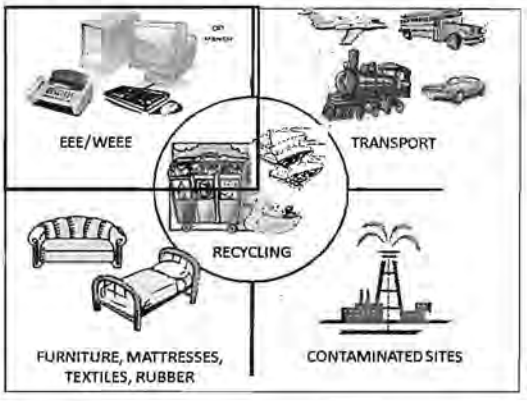
The core inventory teams are expected to develop a work plan for the inventories, which can be discussed with the stakeholders. Elements of a workplan include:
- Identification of the sectors and inventory strategy;
- Methodologies to be used (in inventory guidance);
- Activities needed and assignments;
- Resources allocation including responsibilities and budget;
- Timeline and milestones.

The inventory team may need to augment and revise the work plan as the inventory proceeds.

Step 2 – Choosing Methodology for data collection (Tiered approach)



Step 3 – Collecting and compiling data from sectors

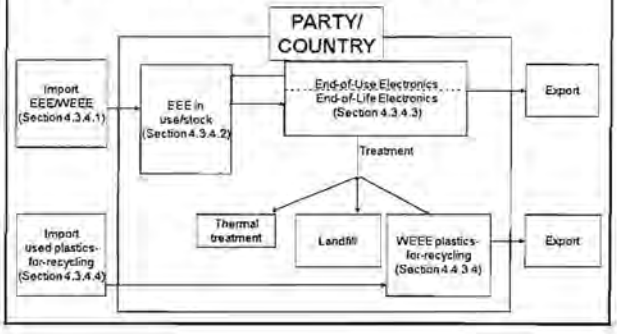


Inventory EEE and WEEE

The inventory of POP-PBDEs EEE/WEEE should address:
- Imported (second-hand) EEE and WEEE
- EEE stocks (in use and stored)
- EEE entering the waste stream (WEEE).
- Recycling of WEEE polymers (own/imported polymer)

POP-PBDE inventory plastics in EEE/WEEE

Inventory considers relevant life cycle stages for data compilation of POP-PBDEs in plastic of EEE/WEEE



13

EEE and WEEE
Development of an in-depth inventory

- c-OctaBDE in CRT devices can be calculated as follows:

  $M_{PBDE(i)} = M_{EEE(j)} * \%(Polymer) * Conc\ PBDE(i)/Polymer$

- Information is needed about the amount of (W)EEE in the country, the share of the relevant polymers in different (W)EEE categories and the content of POP-PBDEs in those polymers.
- Adopt of a three step approach:
  1. Inventory of stocks and flows of EEE/WEEE in the country.
  2. The estimation of the polymer fraction in relevant EEE and WEEE containing POP-PBDEs.
  3. Estimation of POP-PBDEs content in the polymer fraction.

14

POP-PBDE content in the polymer fraction

- The data for c-OctaBDE content in WEEE polymers fractions are derived from a study in 2010 in Europe in different countries

Category/Article		Total PBDE f_{PBDE} [in kg/tonne]		
		Minimum	Maximum	Mean
3	ICT equipment without monitors	0.05	0.4	0.225
4	Consumer equipment without monitors	-	-	0.15
3	CRT monitors	0.14	10.6	2.54
4	CRT-TVs	0.05	3.54	0.87

Source: Wäger et al. (2010) RoHS Substances in Mixed Plastics from Waste Electrical and Electronic Equipment. Final Report.

- Restriction of Hazardous Substance (RoHS) Regulation EU is 1000 ppm PBDE (1 kg/tonne). Also suggested as provisional Basel Convention low POPs content for waste.

15

PBDEs measured in WEEE plastics (EU 2010)

		Penta BDE	Octa BDE	Deca BDE	Deca BB
	Cooling and freezing appliances (all plastics, except foams)			ABS HIPS,PP	
	Vacuum cleaners w/o hoses			ABS HIPS	
	Small appliances for high temperature applications			ABS HIPS PP	
	CRT monitors		[illegible]	[illegible]	
	Flat screen monitors				
	Printers			ABS HIPS	
	CRT TVs		ABS	[illegible]	

(Source: Wäger et al. 2010; Wäger et al. 2012)

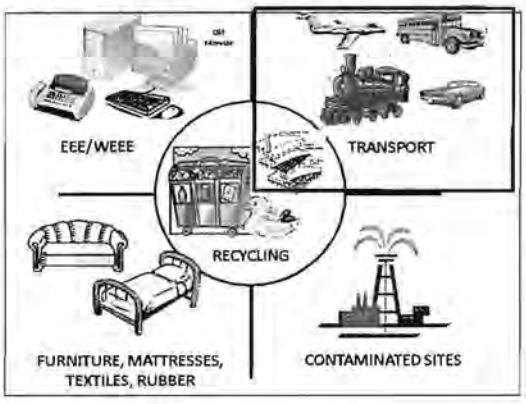
16

POP-PBDE content in the polymer fraction

- Are the data representative for other regions?
- Study on E-waste plastic in Nigeria.
- Same order of magnitude in CRT casings (total 382 casings were sampled and screened and analysed for PBDE).
- In the Nigerian study the CRT casings from TVs had higher values (0.69%) than the TV CRTs in EU study (0.1%) (Nigeria has very old TVs in stocks). Opposite with computer CRTs (0.1 versus 0.25%).
- Therefore there are some regional differences in the PBDE content. However the concentration range seems the same.
- On the long term the average concentration of c-OctaBDE (and c-PentaBDE) will decrease along with the phase out of c-OctaBDE, Therefore on the long term these impact factors will change and will need an update.
- However c-DecaBDE will be listed in the conventions and by this the values of PBDEs listed in the Convention will increase considerably.

17

Step 3 – Collecting and compiling data from sectors



18

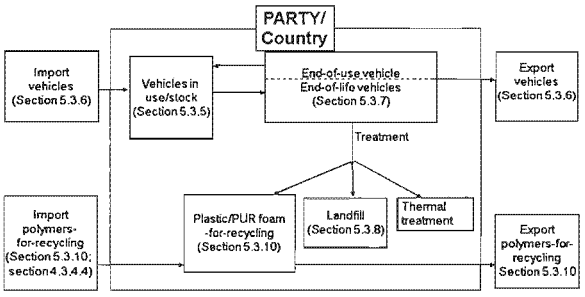
Transport Sector

- Large material flows of goods and waste:
  - Cars, busses, trucks, trains, planes, ships
- End-of-life management:
  - Recovery of materials and of managing pollutants.
- POP-PBDEs in transport:
  - C-PentaBDE: major use in flexible PUR foams (seating; head rests; car ceilings, back-coating of textiles).
  - C-OctaBDE: Minor use in plastics parts (dashboards; door panels, steering wheels; bumpers).

19

POP-PBDE inventory polymers in vehicles

The inventory considers relevant life cycle stages for data compilation of POP-PBDEs in polymers of the transport sector



20

SC Guidance formula used for calculating POP-PBDEs in vehicles

The following basic formula from the *POP-PBDE Inventory Guidance* is used to calculate the POP-PBDEs content of vehicles for the different categories (cars/trucks or busses) in the live cycle stages:

Amount of POP-PBDEs$_{\text{Vehicle category}}$ =

Number of vehicles$_{\text{category}}$ (manufactured 1975 to 2004) x amount POP-PBDEs$_{\text{category}}$ x F_{regional}

Where:

- ***Number of vehicles*$_{\text{category}}$ is the number of vehicles (manufactured 1975-2004) present in a category (car, bus or truck) calculated for the different life cycle stages.**
- ***Amount POP-PBDEs*$_{\text{category}}$ is the amount of POP-PBDEs in a individual car, truck or bus treated with POP-PBDEs**
- ***F*$_{\text{regional}}$ The regional factor of percentage of POP-PBDE impacted vehicles produced in a region (1975s to 2004)**

21

SC Guidance formula used for calculating POP-PBDEs in vehicles

Only cars produced between 1975 and 2004 are considered.

The regional factors are based on a small set of data:

For the US the total use of c-PBDE in PUR foam is published and the levels in treated flame retarded PUR foam is known. Based on this the impact factor of these cars was estimated to 0.5 (1 out of 2 cars treated with PentaBDE).

For Europe measurements of Automotive Shredder Residues exist (time around 2000). Based on this the impact factor were calculated: that approx. 1 of 20 cars where treated with c-PentaBDE (regional factor of 0.05).

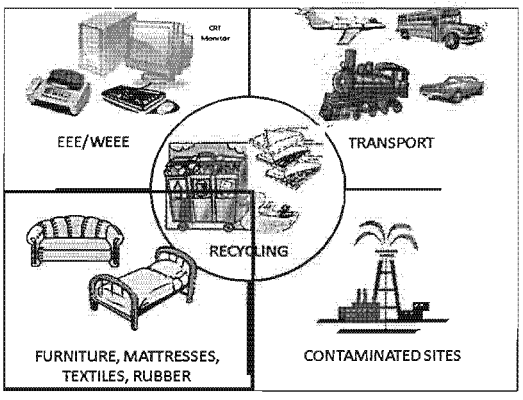
It is known that Europe and Japan phased out c-PentaBDE in the 1990s. Therefore for both regions the impact factor of 0.05 is considered.

For other regions no data of PBDE use existed. The same low/moderate emission factor (0.05) as for Europe/Japan are suggested by the guidance.

More data are needed for vehicles. Best would be monitorings of large sets of EoL vehicles with XRF and then confirmation analysis (with information on producer, year and production origin) for better factors.

22

Step 3 – Collecting and compiling data from sectors

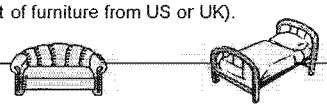


23

PBDE inventory in other (former) uses

Other use sectors of POP-PBDEs (furniture, mattresses, textiles, construction materials, rubber, and drilling operation) are thought to be of minor relevance for most countries due to:

- Relative low overall use volumes of POP-PBDEs in most of these other application (except furniture for which a large share of c-PentaBDEs was used in PUR foam);
- Lack of flammability standards in most countries for these use areas (only a few countries had flammability standards e.g. for furniture in US and UK);
- Limited export of such flame retarded second hand articles from countries with flammability standards and related stocks (e.g. export of furniture from US or UK).



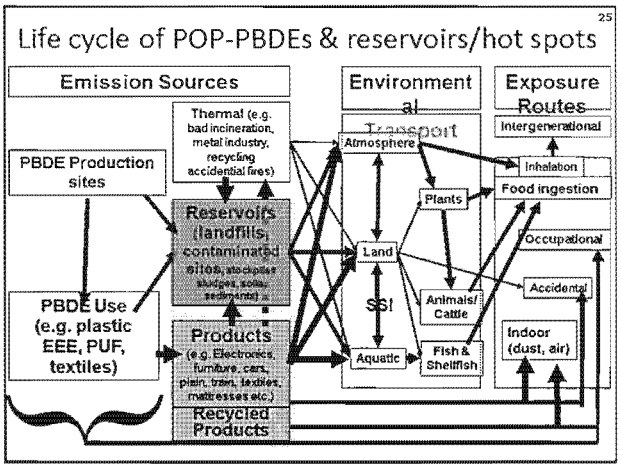
24

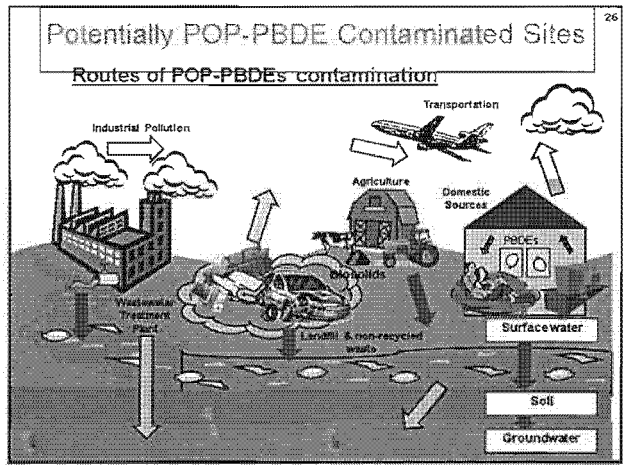
PBDE inventory in other (former) uses

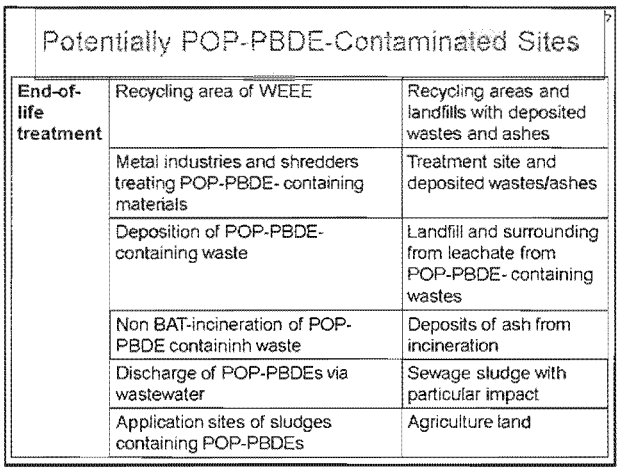
- **Furniture/mattresses:** Countries with certain flammability standards or imports from these countries.
- **Textile:** Limited volume of c-PentaBDE has been used in textiles. Considering that Hexabromocyclododecane (HBCD) is/was used in textiles the sector will become relevant.
- **Construction** (rigid PUR foam): Minor use of c-PentaBDE. For the inventory construction companies could be interviewed on former use of POP-PBDEs in rigid PUR foam. (Considering that the main use of HBCDD is in insulation (XPS and EPS) the sector will become more POPs relevant.

✓Guidance: If countries consider establishing an inventory for some of these uses it is advised to seek data on % of impacted materials in the region or apply Br-screening.

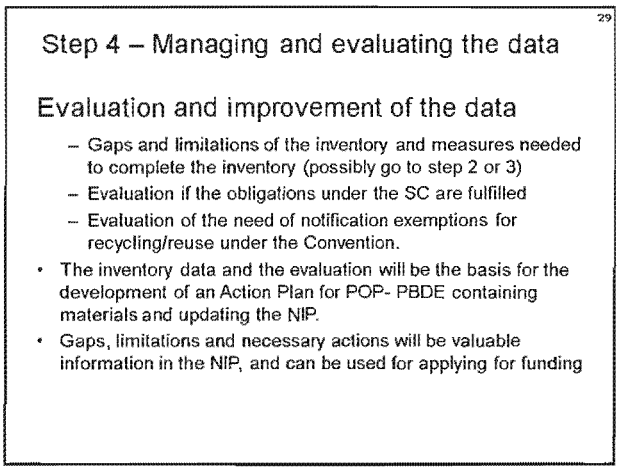
Therefore for these former (regional) PBDE uses monitoring/analysis is needed for a useful estimate.

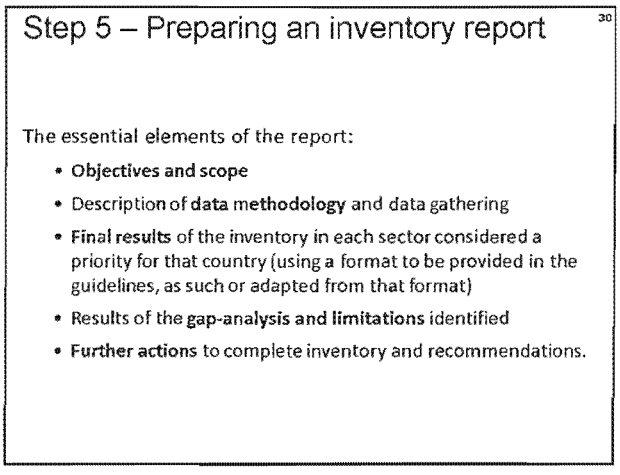






End-of-life treatment	Recycling area of WEEE	Recycling areas and landfills with deposited wastes and ashes
	Metal industries and shredders treating POP-PBDE- containing materials	Treatment site and deposited wastes/ashes
	Deposition of POP-PBDE-containing waste	Landfill and surrounding from leachate from POP-PBDE- containing wastes
	Non BAT-incineration of POP-PBDE containinh waste	Deposits of ash from incineration
	Discharge of POP-PBDEs via wastewater	Sewage sludge with particular impact
	Application sites of sludges containing POP-PBDEs	Agriculture land





31

Step 4 – Managing and evaluating the data

Data management

- Assessment what information to use for reporting
- Inventory data would be managed in a database (waste database; contaminated site database)
- Data of EEE/WEEE and transport are valuable for the (waste) management of these material flows.
- Data shared with other (governmental) institutions.

32

Annexes to POP-PBDE Inventory Guidance

Annex in inventory

- SC-4/18: Listing of tetrabromodiphenyl and pentabromodiphenyl ether
- SC-4/14 Listing of hexabromodiphenyl and heptabromodiphenyl ether
- List of EEE/WEEE inventories from developing countries (with web-links)
- Questionaire for gathering information on EEE/WEEE
- Questionaire for gathering information on transport sector

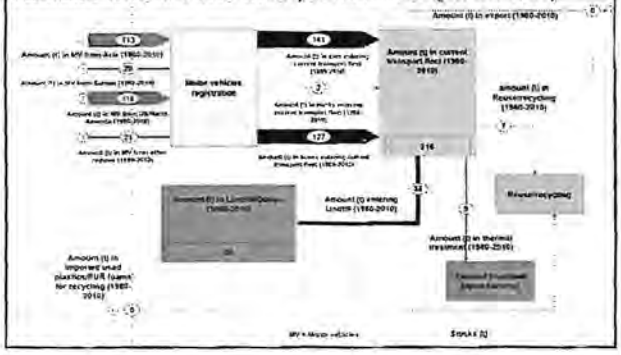
In Annex or otherwise available on UNIDO/Secretariat website

- Case study on inventory of PBDEs in electrical and electronic equipment (EEE) and related waste (WEEE)
- Case study on PBDE in the Transport Sector

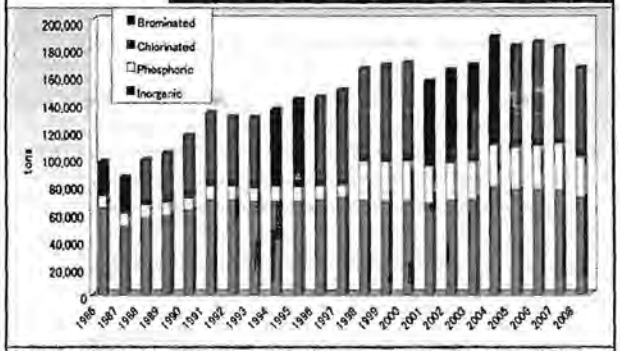
33

POP-PBDE inventory transport sector Nigeria

In a pilot project in Nigeria POP-PBDE inventories and material & substance flows have been developed for vehicles (1980 to 2010).



Trends in the annual consumption of Flame Retardants in Japan (1986~2008)

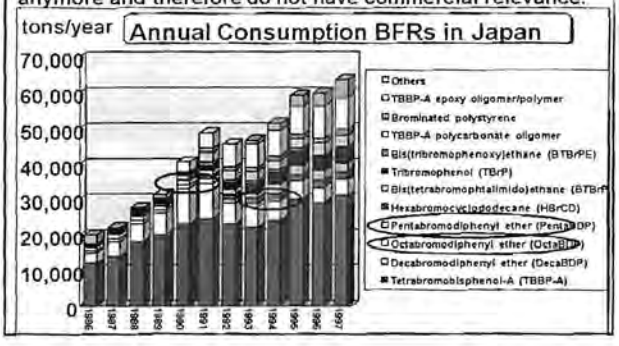


Source: I. Watanabe, 5th International Symposium on Brominated Flame Retardants, April 7.-9. 2010, Kyoto Japan

35

Stockholm Convention POPs - From "Dead" to "Live" Chemicals

Most current Stockholm Convention POPs are not produced anymore and therefore do not have commercial relevance.



ASSESSING POP-PBDEs and BFRs IN E-WASTE POLYMERS IN NIGERIA

[1]Department of Chemistry, Faculty of Science, University of Ibadan, Nigeria;
Smoku U.K.[1], Babayemi J.O.[1], Yosibanjo O.[1], Schlummer M.[3], Schlegel M.[4], Weber R.[5]
[2]Basel Convention Coordinating Centre for Training & Technology Transfer for the African Region, University of Ibadan, Nigeria;
[3]Fraunhofer-Institute for Process Engineering and Packaging, 85354 Freising, Germany, [4]Empa Technology and Society Lab, 9014 St. Gallen, Switzerland;
[5]POPs Environmental Consulting, Ulmenstra[illegible] Göppingen, Germany

UNIVERSITY OF IBADAN

This study is a collaborative research between Stockholm Convention Secretariat, Geneva; the Basel Regional Coordinating Centre for Africa; Fraunhofer Institute Freising, Germany; EMPA Switzerland and the University of Ibadan.

South-North Cooperation of monitoring POP-PBDEs in E-waste plastic in Nigeria

37

- 5 samples out of the 159 Television samples analysed had c-OctaBDE and related POP-PBDEs with concentration ranging from 0.1% to 29.00% with an average concentration for all 159 TV samples of 0.69% c-OctaBDE.
- 3 samples out of the 224 computer CRT sample screened for BFRs had c-OctaBDE with concentration ranging from 0.87% to 5.09% with an average concentration recalculated to total polymers of the 224 computer CRTs was 0.05% (See Table 1)

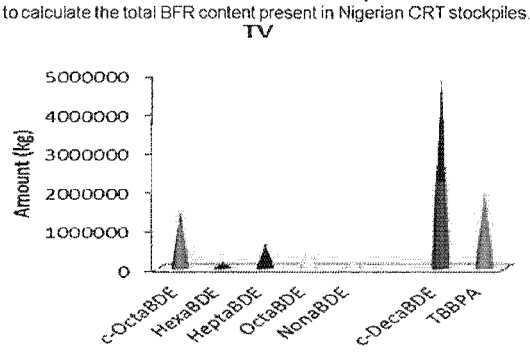
TV and PC CRTs where OctaBDE have been detected

SAMPLE Type	Conc. of c-OctaBDE (%)	Country (production)	Brand	Year of manufacture
TV CRT	29.00	U.K	ITT Consumer Color TV	1986
TV CRT	6.41	Germany	Saba Color TV	1986
TV CRT	0.10	China	Anitech Color TV	1989
TV CRT	0.66	Germany	Saba Color TV	1983
TV CRT	5.93	Germany	Saba Color TV	1988
PC CRT	5.09	U.S.A	Compaq	2003
PC CRT	0.95	U.S.A	IBM	2005
PC CRT	0.87	China	Compaq	2003

POP-PBDEs and BFR inventory Nigeria (TV-CRTs)

38

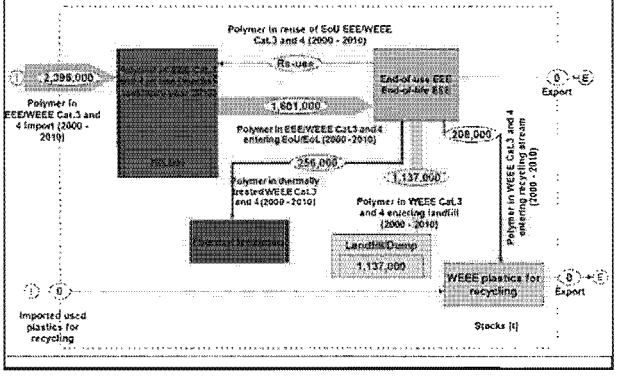
- Based on WEEE/EEE inventory of Nigeria and using the methodology of the Stockholm Convention POP-PBDE Inventory Guidance we were able to calculate the total BFR content present in Nigerian CRT stockpiles.



Material Flow of WEEE plastic in Nigeria

39

- Stocks and flow of WEEE plastic in Nigeria (2000 to 2010; stock 2010)

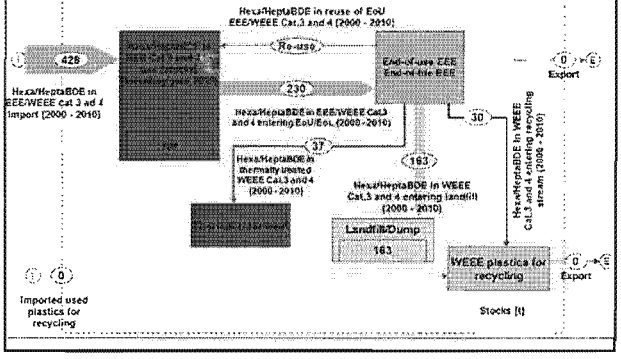


Substance Flow of WEEE plastic in Nigeria

40

- Total WEEE plastic material flow in Nigeria (2000 to 2010)

With impact factors from POP-PBDE guidance



Inventory team – working group organisation

41

Inventory team POP-PBDE in polymers of transport sector

- Polymers in vehicles is a component of an inventory of transport sector
- Multi-stakeholder inventory team with necessary competences and access to relevant inventory information.
  - Task team leader POP-PBDE in polymers transport (inventory transport sector)
  - Ministry of transport or other ministry responsible for transport sector;
  - Ministry responsible for waste management;
  - Association of importers and exporters of cars and other vehicles;
  - Retailers of vehicles (in particular, second-hand vehicles);
  - Association and/or main stakeholders of scrap recycling;
  - Association and/or main stakeholders of polymer recycling;
  - University groups working on material flows or transport issues;
  - NGOs working on transport; NGOs working on POPs;
  - Other relevant stakeholders in the country .

EEE and WEEE Preliminary inventory – Cathode Ray Tube (CRT)

42

- c-OctaBDE in CRT devices can be calculated:

  $M_{PBDE(i)}$ = No CRTs/capita (Region) x population x M_{PBDE}/CRT
- CRTs/capita (Region) is compiled in the guidance
- CRT monitors (TVs and PC monitors) are expected to contain more than 50% of the total POP-PBDE present in EEE, these data give an estimate of the major portion of POP-PBDEs in the EEE/WEEE sector in the country.

EEE and WEEE Preliminary inventory – Cathode Ray Tube (CRT)

- $M_{PBDE(i)}$ = No CRTs/capita (Region) x population x M_{PBDE}/CRT
- CRTs/capita (Region) is compiled in the guidance

Table 4-1: Total and per capita amounts of CRT (TVs and personal computer (PC) monitors) in different regions and countries. The average weight of a CRT device used in this table is 25 kg.

Country/Region	Total weight (10^3 tonnes)	Total number (million units)	Population (million)	CRT weight/person (kg/capita)	No. of CRTs /person (units/capita)	Source
Asian average (including Australasia)	36'226	649	3'906	4.1	0.17	Gregory, 2009
North American average	14'623	585	529	27.6	1.11	Gregory ,2009
LAC - average	5'189	207	572	9.1	0.36	Gregory, 2009
Benin	17.4	0.7	6.7	2.6	0.08	Basel Convention, 2011
Côte d'Ivoire	78.0	3.1	20.8	3.75	0.15	
Ghana, 2010	117	4.68	24.2	4.6	0.19	Green Advocacy & Empa, 2011
Nigeria, 2010	670	26.8	154.7	4.33	0.17	BOCG-Nigeria et al., 2011
Colombia, 2006/2009	343	13.7	46	7.46	0.3	León, 2010
Switzerland, 2008	54	2.2	7.7	7.05	0.28	BFE, 2011

Challenge: The CRT weight/person change over time

Workshop on Sound Management of PBDEs and Phasing-out Opportunities in Developing Parties
27. November 2015, Colombo, Sri Lanka

Introduction to draft "Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles"

Relevant to the substances listed in Annexes A, B and C to the Stockholm Convention on Persistent Organic Pollutants in 2009 and 2011

Dr. Roland Weber
POPs Environmental Consulting, Germany
roland.weber10@web.de

Guidance provided by the monitoring document

The document provides guidance on monitoring (sampling, screening and analysis) of the POPs content in articles and products in use and in the recycling streams for those POPs listed in 2009 and 2011.

Guidance is provided:

- On articles and products possibly containing the POPs listed in 2009 and 2011;
- To develop strategies for monitoring of POPs in articles/products and recycling streams;
- On inventory development aspects such as determining emission/impact factors;
- Might be used for import control and possible monitoring at customs or at consumer protection level;
- Possibly useful for the assessment of human exposure through articles in use and through recycled materials.

Guidance on screening of newly listed POPs in products and articles (Draft)

1.3 Types of articles and products:

- Major articles, products and other material, which may contain POPs listed in 2009 and 2011 (Annex 1).
- A list of potentially POP-PBDE containing articles and materials are listed in Annex 1-B.
- If a study on the presence of POP-PBDE containing materials is planned this list can be assessed for possible relevant samples for the country.

- Process of updating for listed 2013 chemical (HBCD).
- Future update for listed 2015 chemicals (PCP/PCA; PCN)

Step by step approach for monitoring PBDE in articles and products

The monitoring guidance has a step by step approach to monitor POPs in articles and products and these steps are elaborated for the major POPs groups.

Step by step approach for monitoring PBDE in articles and products

Step 1: Survey of products and articles possibly containing POP-PBDEs

- Before collecting samples, a survey would be conducted to preliminarily determine target presence of consumer products in use and in re-use that might contain POP-PBDE.
- Also material flows known to possibly contain POP-PBDE and further used in recycling (e.g. plastic from WEEE recycling or polyurethane (PUR) foam from different end-of-life products) would be targeted considering the need to register for exemptions for POP-PBDE in recycling.
- Stakeholders for the different use groups might be contacted for support and input and possibly for providing samples. Relevant stakeholders to be contacted for the different use categories are listed in Annex 1-B.

Guidance on screening of newly listed POPs in products and articles (Draft) –

Annex 1-B lists .

Step by step approach for monitoring PBDE in articles and products

7

Step 2: Sample collection

- Sampling campaigns might be conducted by research institutions possibly in collaboration with the ministry or other competent authorities or directly with the industry or waste management facilities.
- Samples can also be collected e.g. by the customs at the import or by competent authorities such as factory control or consumer protection authorities and related institutions.
- For the major POP-PBDE contaminated material flow "WEEE plastic" a detailed sampling methodology and a sampling protocol has been developed and is described in detail in Wäger et al. (2010) in Annex 1 and Annex 2. This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants for processing of WEEE.
- An approach of sampling of single EEE for screening of POP-PBDE in e.g. Cathode Ray Tube casings of TV and PC is shortly described in Annex 4.

Step by step approach for monitoring PBDE in articles and products

8

Step 3: Screening in the field or laboratory

- Sample articles can be screened for the presence of bromine in the field or in laboratory with more sensitive instrument. So the field monitoring screening approach can already be used for sampling.
- Rapid screening methods such as pyrolysis-GC/MS can be used for a quick verifying the presence of PBDEs (and other BFRs types).
- Care has to be taken that by such methods without clean-up possibly present DecaBDE is not debrominated to POP-PBDEs, which would lead to false positive results.
- When screening methods are applied it has to be ensured that the detection limit of the screening method is more sensitive than (below) the limit required for the screening (e.g. required from a certain legislation limit).

Guidance on screening of newly listed POPs in products and articles (Draft)

9

Step 3: Screening in the field or laboratory:

- The guidance gives an introduction to screening approaches. This includes screening technologies for bromine or fluorine.
- Such screening enables relatively cheap and simple pre-selection of some article groups with regards to their possible POPs content (e.g. PUR foams for bromine as indication of POP-PBDE content, or carpets for fluorine as indication for PFOS).
- Screening helps to minimise the time and expenses (by pre-selection of samples) for confirmation analysis, which requires extraction and appropriate clean-up steps.

Screening methods for bromine as indicator

10

Step 3: Screening in the field or laboratory

A range of technologies are currently applied as screening tools for bromine in WEEE plastic in some recycling plants (see also PBDE BAT/BEP Guidelines). These technologies can also be used for screening bromine in other materials like PUR foams, textile or rubber.

Screening methods for bromine as indicator

11

Step 3: Screening in the field or laboratory – XRF screening

- The X-ray fluorescence (XRF) technology can be used for detection of bromine in polymers or other materials (detection limit 10-100 ppm).
- XRF analysis is limited to the detection of bromine/elements in the material, without any capacity to identify the type of BFR compound.
- Using handheld instruments the time requirement for a measurement is less then a minute. Precision of XRF screening measurements is limited and thus relative standard deviations of up to 30% may be obtained. Only critical when measuring levels close to the threshold.
- If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened.
- XRF is a non-destructive method and can, therefore, be used to screen articles in stores or currently in use without damaging them.
- The use of XRF instrument requires a specific instruction for the operator of handling such materials according to national guidelines.

Step by step approach for monitoring PBDE in articles and products

12

Step 4: Quantification

- Different analytical methods can be applied for the instrumental quantification of PBDEs and have been reviewed. One accredited method used for commercial analysis is described in Annex 2-A.
- Further methods are described in the listed case studies.
- The extraction and clean-up of selected samples are described.

Step by step approach for monitoring PBDE in articles and products

13

Step 4: Quantification.

- Sample preparation need to be adjusted & optimized to the materials.
- Care has to be taken that the polymers do not contaminated the instruments (MS) and GC-columns. Optimized clean-up!!!

Step by step approach for monitoring PBDE in articles and products

14

Step 4: Quantification.

- Also care need to be taken for memory effects and contamination of the laboratory. Laboratory room analyzing such materials can not be used for low contaminated samples like food or environment.
- ECD detectors are sensitive enough for the PBDE amount to detect and can be cleaned easier (heating to 350C).

Guidance on screening of newly listed POPs in products and articles (Draft)

15

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of respective articles and mention their limitations for articles/products;
- Describe some standard methodologies used by laboratories experienced in the analysis of POPs listed in 2009 and 2011 contained in certain articles and products;
- Describe case studies with links to reports where monitoring or analytical procedures for a certain matrix are described.
- For specific matrices, procedures and standards will further be developed. They could be considered during the updating of the draft monitoring guidance.

Guidance on screening of newly listed POPs in products and articles (Draft)

16

- Where possible, links are made to existing international standards for analysis of a particular POP.
- For a number of article matrices no international standards are available for sampling, extraction & clean-up.
- E.g. a standard for measuring PBDEs in EEE (International Standard IEC 62321) in respect to RoHS compliance is under development and might become available in 2013. .

Guidance on screening of newly listed POPs in products and articles (Draft)

17

Best practice case studies.

- Where available, best practice case studies for key articles/products possibly containing POPs listed in 2009 and 2011 are referenced in the respective chapters and described in Annex 3. If possible, case studies or publications were selected with reports available in the public domain and the access information provided.
- By inclusion of case studies, the guidance endeavours to provide information on already performed studies, and the approaches used.

Guidance on screening of newly listed POPs in products and articles (Draft)

18

Approach of case studies having screened new listed POPs in articles/products.

- These case studies can be assessed with the view of selecting the most appropriate approaches and methodologies (sampling and analysis) – and to add a good case study (not to repeat!).
- Some of the case studies reveal that many former applications of PFOS and PBDE are not relevant anymore e.g. in recent surveys PFOS and related substances in Europe were no more detected in coated paper (but other PFCs).
- New case studies can be added and linked. Best if they are described as a case study in the internet (as publication or in a report available in internet to be directly linked),

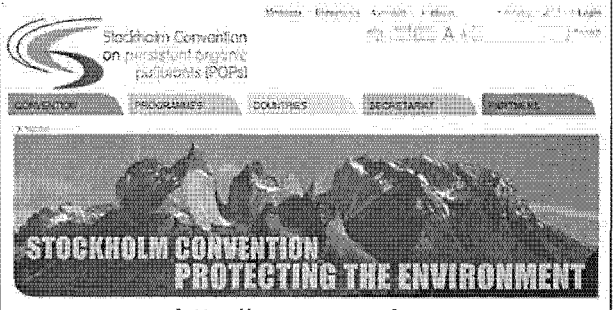
Guidance on screening of newly listed POPs in products and articles (Draft) – Approach of case studies

19

Case studies listed/linked on PFOS and related substances in articles/products.

Thank you for your attention – Questions ?

20



http://www.pops.int

ssc@pops.int

Need of further improvements of the draft guidance document

21

- The guidance document is a draft version. Suggestions for additions and modifications can be made.

What issues are missing and need improvement?

- Inclusion and update in respect to related international and national standards (e.g. China has a analytical standard for PFOS in textiles).
- Inclusion of Hexabromocyclododecane (HBCD) (draft is developed and currently assessed in the laboratory)
- Inclusion of new listed POPs (PCNs, PCP/PCA)-

Guidance on screening of newly listed POPs in products and articles (Draft)

22

1.3 Screening approaches for newly listed POPs:

- The guidance has compiled approaches for sceening of newly listed POPs in articles - PFOS

Guidance on screening of newly listed POPs in products and articles (Draft)

23

1.3 Screening approaches for newly listed POPs:

- The guidance has compiled approaches for sceening of newly listed POPs in articles - PBDE

Japan technology

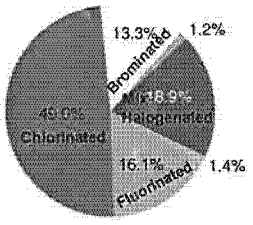
Guidance on screening of newly listed POPs in products and articles (Draft)

24

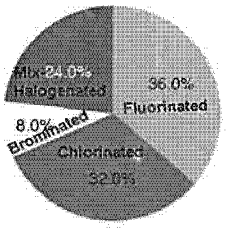
Look throught table of content of guidance and explain detail on content there.

What are the analytical future challenges? How many potential POPs in use?

574 Potential POPs



193 Chemicals "very POP" group



fluorinated
chlorinated
brominated
iodinated
several halogens
no halogens

M. Scheringer et al., (2012), Atmos. Pollut. Res. 3 DOI: 10.5094/APR.2012.044

Guidance on screening of newly listed POPs in products and articles (Draft) – Approach of case studies

26

Case studies listed/linked on POP-PBDE in articles/products.

Guidance on screening of newly listed POPs in products and articles (Draft) – Approach of case studies

27

Case studies listed/linked on PeCBz, HCB and PCDD/PCDF in articles/products.

Workshop on Sound Management of PBDEs and Phasing-out Opportunities in Developing Parties
27. November 2015, Colombo, Sri Lanka

Case studies on PBDE and HBCD monitoring in articles, products and waste

Dr. Roland Weber
POPs Environmental Consulting, Germany
roland.weber10@web.de

Challenge to (useful) monitor PBDE in articles

- Most countries have challenges to monitor new listed industrial POPs (PBDE, HBCD, PFOS) due to the lack of analytical capacity.
- Also the monitoring of new POPs in products included in plastic or other polymers has challenges in sampling, extraction and clean-up.
- If monitoring studies are conducted now in the frame of Stockholm Convention also in developing countries, there is a risk that similar monitoring studies are conducted in several countries adding no new information and wasting time/resources hardly available.
- Therefore good assessments and planning including the detailed assessment of the research already done should be conducted before a new monitoring study is conducted including literature studies. Also options on possible regional approaches or research cooperations should be considered .and options assessed.

Case study approach of Guidance on screening of newly listed POPs in products and articles

The monitoring guidance has an Annex where case studies for monitoring of POPs in articles and products where compiled and shortly described to avoid repetition and learn from former studies.

"*Types of articles and products:*

- *Where available, best practice case studies for key articles/products possibly containing POPs listed in 2009 and 2011 are referenced in the respective chapters and described in Annex 3. If possible, case studies or publications were selected with reports available in the public domain and the access information provided.*
- *By inclusion of case studies, the guidance endeavours to provide information on already performed studies, and the approaches used.*"

Case study approach of Guidance on screening of newly listed POPs in products and articles

Approach of case studies having screened new listed POPs in articles/products.

- These case studies can be assessed with the view of selecting the most appropriate approaches and methodologies (sampling and analysis) – and to add to this (not to repeat!).
- New case studies can be added to the guidance and linked. Best if they are described as a case study in the internet (as publication or in a report available in internet).
- Some of the case studies reveal that many former applications of PFOS and PBDE are not relevant anymore e.g. in recent surveys PFOS and related substances in Europe were no more detected in coated paper (but other PFCs).

Case studies shortly described in the Guidance

Case studies listed/linked on POP-PBDE in articles/products.

Case study: PBDEs/RoHS substances in WEEE plastic (EU)

Specific features of Swiss EMPA's case study on PBDE and other RoHS relevant substance screening in WEEE plastics in EU are:

- In the study a sampling methodology and a sampling protocol has been developed and is described in detail of Annex 1 and Annex 2 of EMPA study. This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants for processing of WEEE.
- The study gives a broad overview on the current POP-PBDE content of the polymer fractions of WEEE categories in Europe (which originated/s largely from imports from Asia as in other regions).
- It further gives an overview on other critical RoHS relevant pollutants in plastic which might be relevant today for other regions too.
- The developed PBDE impact factors from this study are used for the Stockholm Convention PBDE inventory guidance.

Case study: PBDEs/RoHS substances in WEEE plastic (EU)

		Penta BDE	Octa BDE	Deca BDE	Deca BB
WEEE Category	Large household appliances w/o cooling and freezing appliances			ABS PP	
	Small household appliances				
	ICT equipment without CRT- and flat screens		ABS	ABS HIPS	
	Consumer equipment without CRT- and flat screens		ABS	ABS HIPS	

not detected or at average concentrations clearly (i.e. more than an order of magnitude) below the RoHS Directive maximum concentration value (MCV) of 0.1%

average concentrations below (yellow cells) or in the vicinity (orange cells) of the RoHS MCV

average concentrations above the RoHS MCV of 0.1%

XXX: plastic type predominantly containing the substance

(Source: Wäger et al. 2010; Wäger et al. 2012)

Case study: PBDEs/RoHS substances in WEEE plastic (EU)

		Penta BDE	Octa BDE	Deca BDE	Deca BB
	Cooling and freezing appliances (all plastics, except foams)			ABS HIPS,PP	
	Vacuum cleaners w/o hoses			ABS HIPS	
	Small appliances for high temperature applications			ABS HIPS PP	
	CRT monitors		[illegible]	[illegible]	
	Flat screen monitors				
	Printers			ABS HIPS	
	CRT TVs		ABS	[illegible]	

(Source: Wäger et al. 2010; Wäger et al. 2012)

Case Study: Assessing POP-PBDEs and BFRs in CRT casing plastic in Nigeria

Sindiku OK[1], Babayemi J.O[1], Osibanjo O[1,2], Schlummer M[3], Schluep M[4], Weber R[5]

[1]Department of Chemistry, Faculty of Science, University of Ibadan, Nigeria;
[2]Basel Convention Coordinating Centre for Training & Technology Transfer for the African Region, University of Ibadan, Nigeria;
[3]Fraunhofer-Institute for Process Engineering and Packaging, 85354 Freising, Germany; [4]Empa Technology and Society Lab, 9014 St. Gallen, Switzerland;
[5]POPs Environmental Consulting, Ulmenstrasse 3, 73035 Göppingen, Germany

UNIVERSITY OF IBADAN

This study is a collaborative research between Stockholm Convention Secretariat, Geneva; the Basel Regional Coordinating Centre for Africa; Fraunhofer Institute Freising, Germany; EMPA Switzerland and the University of Ibadan.

Case Study: Assessing POP-PBDEs and BFRs in CRT casing plastic in Nigeria

Specific features of the case study on BFR screening and PBDE in WEEE plastic are:

- A sampling methodology of CRT polymers for individual electronics and for countries having no shredder plants (and where the EMPA approach is difficult to apply) have been developed.
- Bromine screening was applied and POP-PBDE content separately for the different main importing regions (North America, Asia & Europe).
- Product specific information (producer, product name & year, region of origin) on POP-PBDE/BFR content in the CRTs products specific.
- With the generated data set POP-PBDE impact factors for plastic of TV CRTs (6.9 kg c-OctaBDE/tonne TV CRT plastic) and computer CRTs (0.5 kg c-OctaBDE/tonne PC CRT plastic) in Nigerian. Based on the EEE/WEEE inventory of Nigeria these impact factors have been used for developing the POP-PBDE inventory for Nigerian EEE/WEEE.

Case Study: Assessing POP-PBDEs and BFRs in CRT casing plastic in NIGERIA

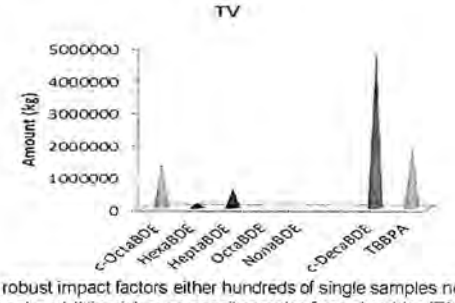
- 5 samples out of the 159 Television samples analysed had c-OctaBDE and related POP-PBDEs with concentration ranging from 0.1% to 29.00% with an average concentration for all 159 TV samples of 0.69% c-OctaBDE.
- 3 samples out of the 224 computer CRT sample screened for BFRs had c-OctaBDE with concentration ranging from 0.87% to 5.09% with an average concentration recalculated to total polymers of the 224 computer CRTs was 0.05% (See Table 1).

TV and PC CRTs where OctaBDE was detected > 0.1%

SAMPLE Type	Conc. of c-OctaBDE (%)	Country (production)	Brand	Year of manufacture
TV CRT	29.00	U.K	ITT Consumer Color TV	1986
TV CRT	6.41	Germany	Saba Color TV	1986
TV CRT	0.10	China	Anitech Color TV	1989
TV CRT	0.66	Germany	Saba Color TV	1983
TV CRT	5.93	Germany	Saba Color TV	1988
PC CRT	5.09	U.S.A	Compaq	2003
PC CRT	0.95	U.S.A	IBM	1998
PC CRT	0.87	China	Compaq	2003

POP-PBDEs and BFR inventory Nigeria (TV-CRTs)

- Based on WEEE/EEE inventory of Nigeria and the methodology of the Stockholm Convention POP-PBDE inventory guidance and the national adjusted emission factors a PBDE inventory was developed.

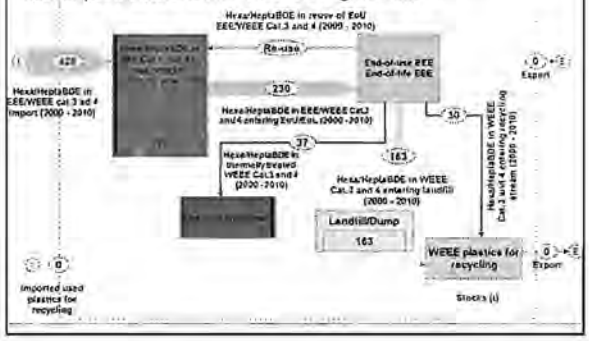


- For robust impact factors either hundreds of single samples need to be analysed (Nigeria) or composit samples from shredder (EMPA)

Case Study: Assessing POP-PBDEs and BFRs in CRT casing plastic in Nigeria

- Total POP-PBDE WEEE plastic material flow in Nigeria (2000 to 2010)

With impact factors from POP-PBDE guidance



Case Study: Assessing PBDEs and BFRs in new products on the market in Switzerland

- The Swiss competent authorities monitored in 2000 consumer products the presence of brominated flame retardants including electrical devices, building materials and lighting equipment.
- The aim of the survey was to evaluate the compliance of commercial articles with the provisions of the Swiss restrictions on BFRs: In Switzerland, the placing on the market and use of PBBs, c-PentaBDE, and c-OctaBDE as substances on its own, as well as in preparations with contents of each of these BFRs equal to or exceeding 0.1% by mass is prohibited.
- Only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.

Specific features of the case study on PBDE and other RoHS relevant substances in WEEE plastic are:

- The study is a comprehensive market survey with a three step

Case Study: Assessing PBDEs and BFRs in new products on the market in Switzerland

Specific features of the case study on PBDE and other RoHS relevant substances in WEEE plastic are:

The study is a comprehensive market survey with a three step approach to monitor brominated flame retardants in contemporary products

- Screening of BFRs in products
- Analysis of the bromine positive samples for prohibited POP-PBDEs and common used flame retardants
- Scanning of bromine positive samples where the BFR wsd not determined to screen used/new brominated flame (Zennegg et al. 2011)

Bantelmann E, Ammann A, Naf U, Tremp J. (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008, BFR 2010, April 7-9, Kyoto, Japan http://www.bfr2010.com/abstract-download/2010/90004.pdf.
Zennegg et al (2011) Identification of "Novel" Brominated flame retardants in new products of the Swiss market, Organohalogen Compd 73, 1238-1241 http://www.dioxin20xx.org/pdfs/2011/3101.pdf

Case Study: Assessing PBDEs and BFRs in new products on the market in Switzerland

The study gives an insight on BFRs used in electronic products imported to the European market. The study shows that the POP-PBDE content in current products on the Swiss (and therefore European) market is small. From the approximately 2000 samples:

- Only 2 contained c-OctaBDE above the 0.1% RoHS threshold.
- 17 samples contained DecaBDE above the RoHS threshold of 0.1%

The study further gives an overview on other critical RoHS relevant pollutants which is relevant for other regions with RoHS like legislation

The results of the third screening level of unknown BFRs in the samples by EMPA revealed that some of these samples contained e.g. hexabromobenzene or pentabromobenzene where the chlorinated analogues (HCB & PeCB) are prohibited by the Stockholm Convention.

Bantelmann E, Ammann A, Naf U, Tremp J. (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008, BFR 2010, April 7-9, Kyoto, Japan http://www.bfr2010.com/abstract-download/2010/90004.pdf.

Case Study: Assessing PBDEs and BFRs in new products on the market in Australia

- A three-tiered testing strategy comparing results from non-destructive testing (X-ray fluorescence (XRF)) (n =1714), a surface wipe test (n=137) and destructive chemical analysis (n=48) was undertaken to systematically identify BFRs in a wide range of consumer products.
- XRF rapidly identified bromine in 92% of products later confirmed to contain BFRs (rem: the 8% probably contained non extractable BFRs)
- Surface wipes of products identified tetrabromobisphenol A (TBBPA), c-octaBDE congeners and BDE-209 with relatively high accuracy (>75%) when confirmed by destructive chemical analysis.
- A relationship between the amounts of BFRs detected in surface wipes and subsequent destructive testing shows promise in predicting not only the types of BFRs present but also estimating the concentrations.

Gallen et al. (2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated FRs in plastics of consumer products. Sci Total Environ. 491-492:255-265.

Case Study: Assessing PBDEs and BFRs in children/consumer products (Washington State)

- In 2012-2013, the Washington State Department of Ecology assessed the presence of flame retardant chemicals such as PBDEs, HBCD and other flame retardants in general consumer and children's products.
- 169 products from 30 retailers in Washington State were collected 2012/13. Product types were seat cushions, mattresses, upholstered furniture for children, electronics, clothing, and baby carriers.
- The majority of samples tested (94%) did not contain PBDEs above a reporting limit of 100 ppm. Therefore manufacturers have moved from PBDEs in products available to Washington State consumers.
- Problematic alternative flame retardants were still being used.

Washington State Department of Ecology (2014) Flame Retardants in General Consumer and Children's Products. https://fortress.wa.gov/ecy/publications/publications/1404021.pdf

Case Study: Assessing PBDEs and BFRs in children/consumer products (Washington State)

- A subset of samples were tested for HBCD, TBBPA and a newer flame retardant mixture called Antiblaze® V6 (V6). All three flame retardants were found in some of the samples analyzed.
- Numerous products were found to contain chlorinated phosphate flame retardants, in particular tris(1,3-dichloro-2-propyl) phosphate (TDCPP) but also tris(2-chloroethyl) phosphate (TCEP) and tris(1-chloro-2-propyl) phosphate (TDPP), and the non-halogenated phosphate triphenyl phosphate (TPP). The majority of these samples were foam and many were children's products.
- Overall a number of samples were found to contain a flame retardant identified as a chemical of high concern to children (CHCC) above the reporting limit established in the Children' s Safe Product Act.

Washington State Department of Ecology (2014) Flame Retardants in General Consumer and Children's Products. https://fortress.wa.gov/ecy/publications/publications/1404021.pdf

Case Study: Assessing PBDEs and BFRs in plastic toys (China)

The study assessed the presence of PBDEs and other BFRs (including PBBs, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE)) in children's toys from South China.

- In all samples PBDE or other BFRs were detected.
- The median BFR concentrations in the hard plastic toys were notably higher than values in other toys. The PBDE concentrations were below the threshold limit (1000 ppm) required by the European RoHS and WEEE directives in all of the toys, except for one hard plastic toy with a total PBDE concentration of 5344 ppm.
- High OctaBDE and NonaBDE indicated debromination during production or recycling in some samples.
- The BFR profiles in the toys were consistent with the patterns of their current production and consumption in China, where PBDEs, specifically decaBDE product, were the dominant BFR, followed by the emerging DBDPE.

Chen et al (2009) Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure & Risk Assessment. Environ Sci Technol 43, 4200- 4206.

Case Study: Assessing PBDEs and BFRs in plastic toys (China)

Specific feature of the study analysing PBDEs and other BFRs in toys:

- This was the first study to examine the concentrations of PBDEs and other BFRs in toys, and the potential exposures to children.
- Revealed the broad use of recycled WEEE plastic in such sensitive use area like children toys.
- The study highlighted that because of extended periods of play, mouthing behaviour, and frequent hand-to-mouth contact, toys may pose a significant pathway of BFR exposure in children.

Chen et al (2009) Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure & Risk Assessment. Environ Sci Technol 43, 4200- 4206.

Case Study: Assessing PBDEs, HBCD, PBDD/F in polymers in vehicles (Japan)

- A total of 40 End-of-Life Vehicles (ELVs) manufactured during 1993 and 2004 were investigated at an ELV-dismantling plant in Japan. For comparison, 5 currently-used vehicles manufactured during 2008 to 2012 were also included in the study.
- Interior materials/components including dashboard, door trim panel, automotive headliner, car seat fabric, seat polyurethane foam (PUF), plastic parts of car seats, floor covering, floor mat, and soundproof material were collected from each vehicle.
- In a first step, a screening survey of bromine in each component was conducted by using a handheld XRF analyzer with RoHS/WEEE mode and analytical time was set at 30 seconds.
- The materials/components containing more than 0.1% by weight of bromine were selected for further chemical analysis.

Kajiwara Takigami et al. (2014) Brominated flame retardants and related substances in the interior materials and cabin dusts of end-of-life vehicles collected in Japan. Organohalogen Compounds 76, 1022-1025. http://www.dioxin20xx.org/pdfs/2014/1015.pdf

Case Study: Assessing PBDEs, HBCD, PBDD/F in polymers in vehicles (Japan)

- The XRF survey showed that 32 out of 515 materials/components investigated (6.2% of the total) contained > 0.1% by Bromine weight.
- These samples were further analysed for PBDEs and HBCD. Subsequent analysis by mass spectrometry confirmed that 16 samples were treated with either the technical PBDEs or HBCDs; this result indicates the use of alternative BFRs in the rest of 11 samples.
- The congener and isomer profiles of PBDEs indicated that 12 samples including 9 seat fabric samples were DecaBDE treated materials.
- Only a set of seat fabric and PUF collected from a foreign car (ELV-10) were found to be treated with the PentaBDE technical mixture.
- High HBCD contents were found in only 2 floor covering samples (none of seat fabric).
- Also PBDD/F were detected with highest levels in the PBDE samples.

Kajiwara Takigami et al. (2014) Brominated flame retardants and related substances in the interior materials and cabin dusts of end-of-life vehicles collected in Japan. Organohalogen Compounds 76, 1022-1025. http://www.dioxin20xx.org/pdfs/2014/1015.pdf

Case Study: Assessing PBDEs and BFRs in carpet rebond (different countries)

PUR foam is recycled to carpet rebond in some regions in particular North America (see Draft BAT/BEP Guidance on for the recycling and waste disposal of articles containing POP-PBDEs).

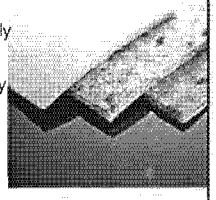
- The study was planned and performed from the International POPs Elimination Network (www.IPEN.org) (NGO working globally on POPs
- Monitoring project of POP-PBDEs in carpet rebond was performed with XRF for bromine screening and 26 samples were analysed by GC/MS.
- The study combines bromine screening methodology with confirmation analysis (as suggested in this guidance document)

DiGangi J, Strakova J, Watson A (2011) A Survey of PBDES in Recycled Carpet Padding. Organohalogen Compounds 73, 2067-2070. www.dioxin20xx.org/pdfs/2011/4511.pdf

Case Study: Assessing PBDEs and BFRs in carpet rebond (different countries)

Specific features of the IPEN case study on PBDE and screening of carpet rebond:

- The study sampled in different world regions covering industrial and developing countries. Only some samples from North America contained high PBDE levels from recycling of PBDE treated foams.
- The study addresses a product category manufactured from recycling materials possibly impacted by POP-PBDE-containing materials
- Results were published including the company names with high/low impacted products that consumers could assess company policy and possibly ask a company when purchasing similar products.



DiGangi J, Strakova J, Watson A (2011) A Survey of PBDES in Recycled Carpet Padding. Organohalogen Compounds 73, 2067-2070. www.dioxin20xx.org/pdfs/2011/4511.pdf

Case Study: Assessing HBCD in EPS/XPS packaging and food contact materials (Korea)

Monitoring of HBCD in EPS/XPS packaging & food contact materials

- Rani et al. (2014)163 determined the concentration of HBCD in 34 polystyrene products including EPS and XPS in an Asian country.
- They used high pressure liquid chromatography-tandem mass spectrometry (HPLC-MS) for determining HBCD.
- In some food related EPS articles relatively high concentration of HBCD was detected including an ice box (960,000 ng/g) and disposable tray (8430 ng/g) used in fish market. HBCD was also detected in buoy used in aquaculture (53500 ng/g),
- Overall the study showed that HBCD is/has been used to some extent in PS packaging including food packaging and that PS including HBCD is recycled to some extent including packing and other products.

Rani et al. (2014) Hexabromocyclododecane in polystyrene based consumer products: an evidence of unregulated use. Chemosphere. 110, 111-119.

Case Study: Assessing HBCD in EPS/XPS foam in buoy in aqua farms (Korea)

Monitoring of HBCD in Buoy in aquafarms and related oysters

- A Korean group detected elevated levels of HBCD in all tested buoy samples used in aquaculture farms (28-249 µg/g; median 91 µg/g). The HBCD contents showed a large variation, even within one buoy.
- To obtain preliminary information about the impact of EPS buoys on farmed oysters, the concentration levels and profiles of HBCD isomers were measured in oyster samples collected from aquaculture farms (AF) and natural coasts. Two times higher levels of HBCDs was detected in the farmed oyster compared to the wild oyster from different countries (note: different to PCB & Dioxin in fish).
- Sediment in AF had higher HBCD levels compared to other sediments.
- The study concluded that HBCDs in aquaculture buoy demonstrate an exposure path of technical EPS to food and the lack of proper control for the use of HBCDs in manufacturing polystyrene products.

Hong SH, Jang M, Rani M, Han GM, Song YK, Shim WJ. (2013). Expanded polystyrene (EPS) buoy as a possible source of hexabromocyclododecanes (HBCDs) in the marine environment. Organohalogen Compd 75, 882-885. http://www.dioxin20xx.org/pdfs/2013/3211.pdf

Case Study: Monitoring of POP-PBDE in waste streams (the Netherlands)

- A study investigated how waste materials possibly containing PBDEs are sorted, disposed of, recycled, and/or exported in the Netherlands.
- The relevant information was collected from interviews with key actors in the waste sector and from reports and scientific literature.
- For both End-of-Life vehicles (ELVs) and waste electrical and electronic equipment (WEEE) there are national organizations coordinating the collection and processing.
- These waste flows are relatively well documented. Many companies are involved in collection and the first processing, while only a few companies perform the separation of plastics containing POP-PBDE.
- Only part of these separated plastics can be traced to companies producing recycled plastics which are ready to use in new products. In which new products these plastics are subsequently used is harder to trace, as most of this production is not done in the Netherlands.

Leslie H.A, Leonards PEG, Brandsma SH Jonkers N (2013) POP STREAM POP-BDE waste streams in the Netherlands: analysis and inventory. (available at the Basel Convention Website). .

Case Study: Monitoring of POP-PBDE in waste streams (the Netherlands)

- Sampling of materials for PBDE analysis was performed in waste products, in shredded materials and in new products.
- The focus of waste sampling was on plastic waste products which were likely to contain POP-PBDEs, such as the automotive and electronic waste stream materials (especially PUR & ABS).
- Samples were taken of new plastic products sold in Netherlands (toys and household/office items), and manufactured with recycled plastic.
- A cost-effective, fast 'direct probe' screening method that has been applied to quickly determine the presence of POP-PBDEs. The method can be used to screen samples for POP-PBDEs.
- In general, POP-PBDEs were found in very few single automotive parts (when found, the car part was from the USA) or WEEE items.
- Seats of American cars were shown to be a POP-PBDE hot spot in the ELV sector, with up to 25,000 µg/g in PUR foam of a Pontiac car seat (mostly c-PentaBDE congeners).

Leslie H.A, Leonards PEG, Brandsma SH Jonkers N (2013) POP STREAM POP-BDE waste streams in the Netherlands: analysis and inventory. (available at the Basel Convention Website). .

Case Study: Assessing PBDEs and FRs in PUR foam baby products (United States)

PUR foam samples collected from 101 commonly used US baby products were monitored for POP-PBDEs and other flame retardants (Stapleton et al. 2011). From these products:

- Five samples contained POP-PBDE congeners commonly associated with c-PentaBDE, suggesting that such products are still in-use in sensitive use areas although production of c-PentaBDE is considered to have stopped in 2004.
- 80% of the PUR foam baby products contained an identifiable flame retardant additive, and all but one of these was either chlorinated or brominated compounds.
- The most common flame retardant detected was tris(1,3-dichloroisopropyl) phosphate (TDCPP; detection frequency 36%), followed by polybrominated aromatic compounds typically found in the Firemaster550 commercial mixture (detection frequency 17%).

Stapleton et al (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. Env. Sci. Technol. 45. 5323-5331 http://pubs.acs.org/doi/abs/10.1021/es2007462

Case Study: Assessing PBDEs and FRs in PUR foam baby products (United States)

PUR foam samples collected from 101 commonly used US baby products were monitored for POP-PBDEs and other flame retardants (Stapleton et al. 2011)124. From these products:

- Five samples contained POP-PBDE congeners commonly associated with c-PentaBDE, suggesting that such products are still in-use in sensitive use areas although production of c-PentaBDE is considered to have stopped in 2004 .
- 80% of the PUR foam baby products contained an identifiable flame retardant additive, and all but one of these was either chlorinated or brominated compounds.
- The most common flame retardant detected was tris(1,3-dichloroisopropyl) phosphate (TDCPP; detection frequency 36%), followed by polybrominated aromatic compounds typically found in the Firemaster550 commercial mixture (detection frequency 17%).

Stapleton et al (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. Env. Sci. Technol. 45. 5323-5331 http://pubs.acs.org/doi/abs/10.1021/es2007462

Case Study: Assessing PBDEs and FRs in PUR foam baby products (United States)

Specific features of the study on PBDE and FR in PUR baby products:

- The study combined bromine screening methodology with confirmation. A significant correlation was observed for bromine with quantitative analysis of BFRs; however, there was no significant relationship observed for chlorine and CFRs.
- For the first time a wide range of PUR baby products were sampled, screened and analysed for POP-PBDEs and other flame retardants.
- Based on exposure estimates, the study predict that infants may receive greater exposure to TDCPP from these products compared to the average child or adult from upholstered furniture, all of which are higher than acceptable daily intake levels of TDCPP set by the US Consumer Product Safety Commission.
- The study revealed that flammability standard in a country can result in high levels of flame retardant in sensitive products with critical exposure to vulnerable groups like infants. New study 2015 on PFRs

Stapleton et al (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. Env. Sci. Technol. 45. 5323-5331 http://pubs.acs.org/doi/abs/10.1021/es2007462

PBDE/BFR contamination of recycled plastic?

- What is the flow of PBDE/BFR in recycled materials? What articles are contaminated? What are risks to human and the environment?

PBDE in carpet padding (DiGangi et al, OHC , 2011) *PBDE in children toys China (Chen et al, ES&T 43, 4200, 2009)* *PBDE in thermo-cup Samsonek & Puype (2013) Food Add. & Contam.*

⇒ The recycling flow of PBDE/BFR containing plastic seems largely uncontrolled. Need a better life cycle management & control!

⇒ Increased screening of sensitive products and complain to producers and governments might result in pressure. Normally no regulation? 1000 ppm PBDE for sensitive products seems too high

Conclusions

- A range of monitoring studies gave already a good insight in contamination of different products, recling materials and waste.
- The Stockholm Convention POP-BFRs are still present in a range of products from recycled materials (at deluted lower POP-BFR level) and in products in use and end of life. With relevance to exposure.
- If a study is conducted it is advised that first the available monitoring studies are evaluated and then the study outline is developed considering the available information.
- There are much unknowns in respect to PBDE use e.g. in the transport sector but also in products produced from recycled materials and more (systematic) studies should be conducted here.

Conclusions

- Several of the alternative flame retardants detected in baby, children and other consumer products are of high concern and are present in US studies at levels above health concern.
- Therefore it is recommended that studies assessing POP-BFRs should also monitor other BFRs, CFRs and PFRs of concern.
- New studies should add pieces to the puzzle what FRs are used for what products and in which recycling flow and what are the risks.

Thank you for your attention !

More Information

Basel Convention: www.basel.int
Rotterdam Convention: www.pic.int
Stockholm Convention: http://chm.pops.int/
Montreal Protocol/Vienna Convention: http://ozone.unep.org
SAICM: http://www.saicm.org/
POPs phase out & alternatives http://poppub.bcrc.cn/
OECD/IOMC: http://www.oecd.org/chemicalsafety/
Science: www.ipcp.ch; http://greensciencepolicy.org/
NGO: www.ban.org; www.ipen.org; www.ihpa.info; www.chemsec.org
Better-world-links: http://www.betterworldlinks.org/

Guidance on screening of newly listed POPs in products and articles (Draft) –

Annex 1-B lists .

Step by step approach for monitoring PBDE in articles and products

Step 1: Survey of products and articles possibly containing POP-PBDEs

- Before collecting samples, a survey can be conducted to preliminarily determine target presence of consumer products in use and in re-use that might contain POP-PBDE.
- Also some material flows known to possibly contain POP-PBDE and further used in recycling (e.g. plastic from WEEE recycling or polyurethane (PUR) foam from different end-of-life products) would be targeted considering the need to register for exemptions for POP-PBDE in recycling.
- Stakeholders for the different use groups might be contacted for support and input and possibly for providing samples. Relevant stakeholders to be contacted for the different use categories are listed in Annex 1-B.

Step by step approach for monitoring PBDE in articles and products

Step 2: Sample collection

- Samples can then be collected e.g. by the customs at the import or by competent authorities such as factory control or consumer protection authorities and related institutions.
- Sampling campaigns might also be conducted by research institutions possibly in collaboration with the ministry or other competent authorities or directly with the industry or waste management facilities.
- Following criteria and information can be used by the stakeholders:
- a) The article or the material is listed in Annex 1-B and contains brominated flame retardants (e.g. the plastic of a computer is labelled as containing brominated flame retardants)
- b) The article or the material is listed in Annex 1-B and bromine is being detected by a screening method (see section 3.)
- For the major POP-PBDE contaminated material flow WEEE plastic a detailed sampling methodology and a sampling protocol has been developed and is described in detail in Wager et al. (2010) in Annex 1

Step by step approach for monitoring PBDE in articles and products

Step 3: Screening in the field or laboratory

- Sample articles can be screened for the presence of bromine also in the laboratory where a more sensitive method might be available compared to the mobile equipments used in the field.
- Rapid screening methods such as pyrolysis-GC/MS can be used for verifying the presence of PBDEs (and other BFRs types).
- Care has to be taken that by such methods without clean-up possibly present DecaBDE is not debrominated to POP-PBDEs, which would lead to false positive results.
- When screening methods are applied it has to be ensured that the detection limit of the screening method is more sensitive than (below) the limit required for the screening (e g. required from a certain legislation limit).

Screening methods for bromine as indicator

Step 3: Screening in the field or laboratory

The screening of bromine can be a simple, rapid and cost-effective method for pre-selection steps of samples to determine which samples to select for the more complex and expensive confirmation analysis.

A range of technologies are currently applied as screening tools for bromine in WEEE plastic in some recycling plants (see also PBDE BAT/BEP Guidelines). These technologies can also be used for screening bromine in other materials like PUR foams, textile or rubber.

Screening methods for bromine as indicator

Step 3: Screening in the field or laboratory – XRF screening

- The X-ray fluorescence (XRF) technology can be used for detection of bromine in polymers and other materials with a detection limit for bromine of 10 to 100 ppm.
- XRF analysis is limited to the detection of bromine in the material, without any capacity to identify the type of BFR compound.
- Using handheld instruments the time requirement for a measurement is less then a minute. Precision of XRF screening measurements is limited and thus relative standard deviations of up to 30% may be obtained. However, this is only critical when measuring levels very close to a given threshold.
- If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened.
- XRF is a non-destructive method and can, therefore, be used to screen articles in stores or currently in use without damaging them-
- The use of XRF instrument requires a specific instruction for the operator of handling such materials according to national guidelines.

Step by step approach for monitoring PBDE in articles and products

Step 4: Quantification

- Different analytical methods can be applied for the instrumental quantification of PBDEs and have been reviewed. One accredited method used for commercial analysis is described in Annex 2-A.
- Further methods are described in the listed case studies.
- The extraction and clean-up of selected samples are described.

Step by step approach for monitoring PBDE in articles and products

Step 4: Quantification.

The sample preparation need

Step by step approach for monitoring PBDE in articles and products

Step 4: Quantification.

The sample preparation need

Guidance on screening of newly listed POPs in products and articles (Draft)

1.3 Types of articles and products:

- The guidance gives an introduction to screening approaches. This includes screening technologies for bromine or fluorine.
- Such screening enables relatively cheap and simple pre-selection of some article groups with regards to their possible POPs content (e.g. PUR foams for bromine as indication of POP-PBDE content, or carpets for fluorine as indication for PFOS).
- Screening helps to minimise the time and expenses (by pre-selection of samples) for confirmation analysis, which requires extraction and appropriate clean-up steps.

Guidance on screening of newly listed POPs in products and articles (Draft)

- Screening helps to minimise the time and expenses (by pre-selection of samples) for confirmation analysis, which requires extraction and appropriate clean-up steps.
- For final confirmation or quantification by instrumental analysis basic information is provided, including examples of instrumental setting.
- Where available, the guidance links to case studies with analytical procedures described in detail. Available information is outlined in Annex 2.

Guidance on screening of newly listed POPs in products and articles (Draft)

1.3 Screening approaches for newly listed POPs:

- The guidance has compiled approaches for sceening of newly listed POPs in articles - PBDE

Japan technology

Guidance on screening of newly listed POPs in products and articles (Draft)

- Where possible, links are made to existing international standards for analysis of a particular POP.
- For a number of article matrices no international standards are available for sampling, extraction & clean-up.
- E.g. a standard for measuring PBDEs in EEE (International Standard IEC 62321) in respect to RoHS compliance is under development and might become available in 2013.
- An international standard for extractable PFOS in articles and its analysis has been developed (NPR-CEN/TS 15968) but has not been validated yet.
- Furthermore, no (standard) analytical procedure is available for many of the 160 listed PFOS related substances including some non-extractable PFOS precursors.

Guidance on screening of newly listed POPs in products and articles (Draft)

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of respective articles and mention their limitations for articles/products;
- Describe some standard methodologies used by laboratories experienced in the analysis of POPs listed in 2009 and 2011 contained in certain articles and products;
- Describe case studies with links to reports where monitoring or analytical procedures for a certain matrix are described.
- For specific matrices, procedures and standards will further be developed. They could be considered during the finalization and updating of this draft guidance.

Guidance on screening of newly listed POPs in products and articles (Draft)

Step by step approach of the guidance:

Guidance on screening of newly listed POPs in products and articles (Draft)

Look throught table of content of guidance and explain detail on content there.

Need of further improvements of the draft guidance document

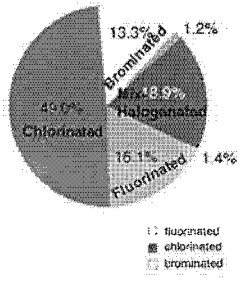
- The guidance document is a draft version. Suggestions for additions and modifications can be made.

What issues are missing and need improvement?

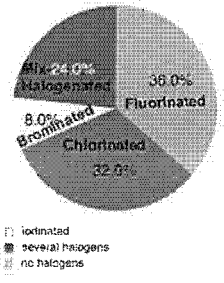
- Inclusion and update in respect to related international and national standards (e.g. China has a analytical standard for PFOS in textiles).
- Inclusion of Hexabromocyclododecane (HBCD)
- Inclusion of other upcoming POPs (e.g. PCN)

What are the analytical future challenges? How many potential POPs in use?

574 Potential POPs



193 Chemicals "very POP" group



fluorinated
chlorinated
brominated
iodinated
several halogens
no halogens

M. Scheringer et al., (2012), Atmos. Pollut. Res. 3 DOI: 10.5094/APR.2012.044

Guidance on screening of newly listed POPs in products and articles (Draft) – Approach of case studies

Case studies listed/linked on PFOS and related substances in articles/products.

Alternative Flame Retardants to Brominated Compounds

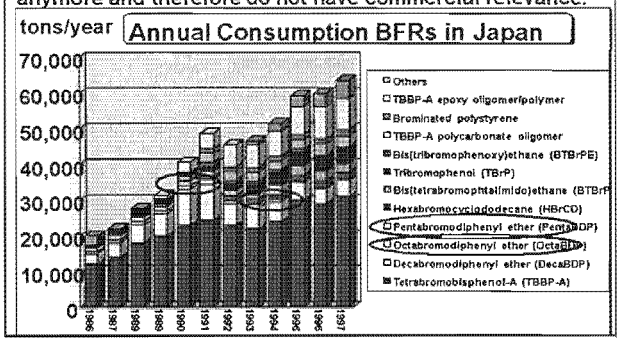
Dr. Roland Weber
POPs Environmental Consulting
roland.weber10@web.de

Content of Presentation**

- Substitution of PentaBDE and OctaBDE by BFRs
- General concern on BFRs – Activities in EU on BFRs within RoHS directive & general assessment
- Key application areas FR and alternatives
- DecaBDE/BFR and substitution approach in plastics
- DecaBDE/HBCDD and alternatives in textiles
- HBCDD and alternatives in foams
- LCA approaches for FR alternative assessment
  a) USEPA: TBBPA in Printed Circuit Boards –
  b) EU Research: LCA of alternative FR „ENFIRO".
- Recommendations/Conclusions

Stockholm Convention POPs - From "Dead" to "Live" Chemicals

Most current Stockholm Convention POPs are not produced anymore and therefore do not have commercial relevance.

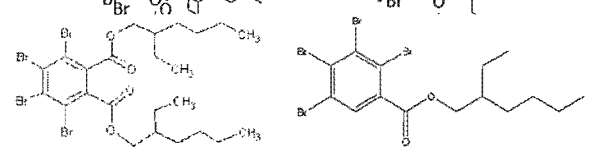


Some Major Uses of BFRs

Polymer	Content [%]	Current Substances	Former Use
Polystyrene foam	0.8–4	Brominated polystyrene	HBCDD
High impact polystyrene	11–15	DecaBDE, DBDPE; HBCDD	OctaBDE
Epoxy resin	0-10	TBBPA; reactive TBBPA	PentaBDE
Polyamides	13–16	DecaBDE;	OctaBDE
Polyolefins	5–8	DecaBDE, propylene dibromo styrene	OctaBDE
Flex. Polyurethanes	3-5	Di(2-ethylhexyl)- tetrabromophthalate (TBPH); 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB)	PentaBDE
Polyesters	8–11	Brominated polystyrene	OctaBDE
Unsaturated polyesters	13–28	TBBPA	PentaBDE
Polycarbonate	4–6	Brominated polystyrene	
Styrene copolymers	12–15	Brominated polystyrene	

Brominated Compounds in Firemaster® 550

Substitute for ~~PentaBDE~~ in flexible Polyurethane foam:

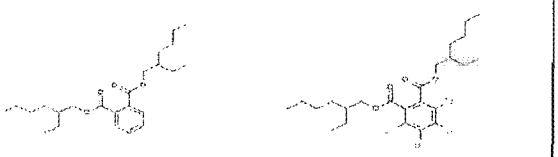


Di(2-ethylhexyl)-tetrabromophthalate (TBPH)

2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB)

PBDD/PBDF formation potential?

Firemaster 550 Component – Analog to Known Toxicant DEHP

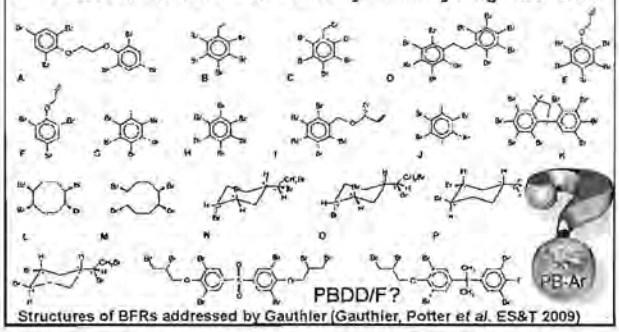


DEHP: Di (2-ethylhexyl) phthalate
- Prop 65 cancer, reproductive, developmental toxin
- Animal effects at environmental levels
- Bioaccumlates, persistent

Di (2-ethylhexyl) tetrabromophthalate
- Wide use as flame retardant
- Almost no studies !
  - (1 report – PubMed)

Other Brominated Flame Retardants - in the Market and Environment

- Approx. 75 BFR are on the market (Fisk et al 2003).
- BFR2010: Research community is analysing ~20 BFR



Structures of BFRs addressed by Gauthier (Gauthier, Potter *et al.* ES&T 2009)

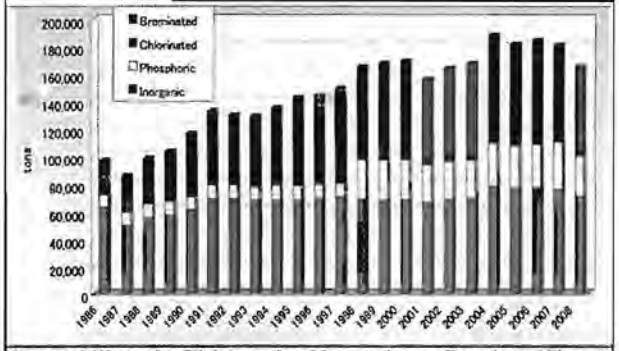
Pressure on Br Flame Retardants: Current Discussion EU on RoHS

- A report for the European Commission on the extension of the RoHS Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Groß & Bunke et al. 2008) proposes to phase out all brominated and chlorinated flame retardants and some other toxics in electric and electronic consumer goods to protect consumers and to facilitate easier and safer recycling at the end of life stage (European Commission 2010).

Will electronics go halogen free??

In the 2011 RoHS update not (yet) included. Assessment chemical by chemical (as REACH)

Trends in the annual consumption of Flame Retardants in Japan (1986~2008)



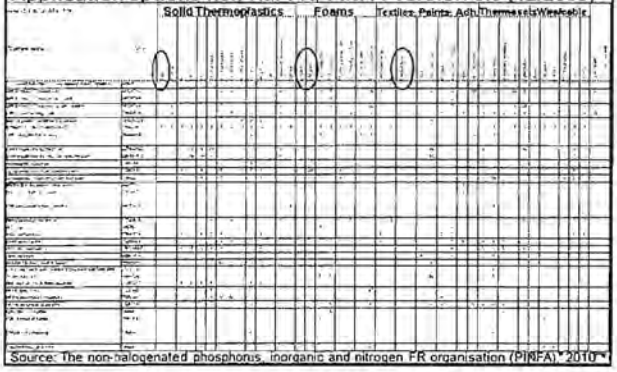
Source: I. Watanabe, 5th International Symposium on Brominated Flame Retardants, April 7 -9, 2010, Kyoto Japan

Main Materials and Application Areas for Flame Redardants

- Solid Thermoplastics (ABS, HIPS, PET, PA, PP, PE etc.)
- Thermosets (Epoxi Resin, Phenolic Resin, Acrylic resin etc.)
- Wire and Cable (PP, PVC flexible),
- Foams (EPS, XPS, PUR); Rubbers
- Textiles (Nylon, Polyester, Viscose, Cotton, others),
- Others: Paper, Wood, Paints, Adhesives

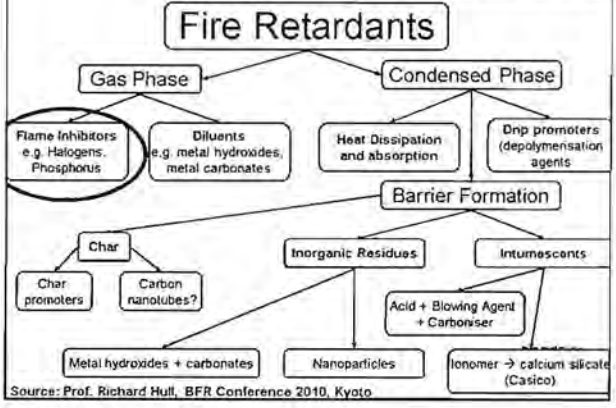
Overview Table Non-Halogenated FR In the Whole Application Range

Application options non-Hal-FR: PINFA Version 5.0 (12/2009)



Source: The non-halogenated phosphorus, inorganic and nitrogen FR organisation (PINFA) 2010

Fire Retardants - Mode of Action



Source: Prof. Richard Hull, BFR Conference 2010, Kyoto

Alternatives for Brominated Flame Retardants

Substitution can take place at three levels:

A. Flame Retardant Substitution: This approach involves identifying a drop-in chemical substitute for the BFR. It is the simplest approach because it typically does not require changes to the polymer material or to the design of the product.

B. Resin/Material Substitution: This approach involves changing the resin system, while also changing the chemical used as the flame retardant. This is a more complex approach than simple flame retardant substitution because it has a greater effect on overall product cost and performance.

C. Product Redesign: This approach involves changes to the actual product design to minimize or eliminate the need for flame retardant chemicals. Examples of product redesign include using fire barrier material, as well as separating or reducing the source of heat from the product.

Requirements for Alternatives of Candidate POPs

Overall evaluation of alternatives for substitution of BFR (in accordance Annex F)

- Equal or better flame retardancy for the product
- Equal or better performance and physical properties for the product/part
- Less risk to environment and human health
- Cost (including environmental and health costs)
- Commercial availability and accessibility of the alternative solution

DecaBDE - International Measures

- EU: DecaBDE has been restricted for electrical and electronic equipment (Directive 2002/95/EC + 2005/717/EC) but not for other uses.
- DecaBDE to be phased out from all applications in US by 2013.
  http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/deccadbe.html
- If relevant debromination to lower PBDE will be further demonstrated then DecaBDE will be SC relevant.
- Evidence for relevant PBDF formation during some application (in plastic and textile Kajiwara et al 2008, 2010) and in end of life thermal treatments.
- Direct and indirect pressure to phase out DecaBDE.

DecaBDE Main Applications

- Due to it's good performance it is used in a wide range of plastics in particular applied in electronics.
- Major use in HIPS TV casings (US 80% of total use (Lowell 2005). Other use Polyamids and Polyolefins.
- Textiles: Primary textile uses appear to be in the mattress, drapery, commercial upholstered furniture, and transportation (automotive and airplane) industries. Other niche applications of decaBDE in textiles include tents, awnings, and related fabric applications.
- Use pattern in China not known

DecaBDE Substitutes in Plastic Resin

Wide range of alternative plastic/flame retardant combination available on the market and used in former key applications of DecaBDE (e.g. Electronic enclosures) by international producers.

Cost estimate range from 0.2 % to 2.5 % of final product price.

Resin System	Flame Retardant(s)	Example Uses
HIPS/PPO	• Resorcinol bis diphenyl phosphate (RDP)	• Used throughout Europe -- roughly 20,000 metric tons in the EU TV enclosure market
PC/ABS	• Bis-phenol A diphosphate (BPADP)	• Sharp AQUOS LCD TV • Philips Electronics flat panel TV
PC	• Phosphate esters	• Apple Computer Monitor • Philips Plasma TV front housing
PLA	• Metal hydroxide	• NEC (currently in developmental products only)

Source: Lowell 2005; Danish EPA 2006

DecaBDE Substitutes in Plastic Resin

Phosphate Flame Retardants Used in Electronic Applications

Producer of Phosphor flame retardants claim that some application of Phosphor flame retardants can even be cheaper then brominated alternatives.

Flame Retardant	Acronym (s)	Applicable Resin Systems and Other Notes	Known Uses	Manufacturer Trade Name
Resorcinol bis diphenyl phosphate	RDP	• 11% phosphorus • V0 rating achieved when used in PPO/HIPS blends • Dominant flame retardant in PC/ABS and PPO/HIPS systems	• Bayer Bayblend FC ABS resin • GE Plastics PC/ABS resins • Used in Dell PC/ABS CRT Monitor	• Adeka Noburt: Fyrolflex®RDP 10 • Great Lakes: Reofos RDP
Bisphenol A diphosphate	BPADP BAPP, BDP	• Usage increasing in PC/ABS and PPO/HIPS applications • 9% phosphorus	• Dow Chemical PC/ABS 3560, used in the Sharp AQUOS LCD TV	• Great Lakes: Reofos BAPP • Albemarle NcendX P-30 • Adeka Noburt: Fyrolflex®BDP
Diphenyl cresyl phosphate	DPK	• Used in PC/ABS		
Proprietary monophosphate		• PC/ABS	• Low magnitude hydrolysis resistance	• Great Lakes: Reofos 50
Triphenyl phosphate	TPP	• Also known as triaryl phosphate • Usage shrinking in PC/ABS and PPO/HIPS applications		• Great Lakes: Reofos TPP •

Source: Lowell 2005

Substitution DecaBDE in Plastic Resin

DecaBDE Substitution Strategies for plastic used in electronics

Substance → Material → Product

- HIPS resins using decabromodiphenyl*ethane* instead of decaBDE
- HIPS and PPO blend with phosphorus-based FR
- PC/ABS blend with phosphorus-based FR
- Separation of high/low voltage
- Reduce operating voltage

Increasing innovation depth

Green Design!

Source: Öko-Institute 2003

Leading E-Companies about Eliminating DecaBDE

A large number of companies in the EE sector specifically state that they have phased out Deca-BDE in all of their products, among these, Dell, Hewlett-Packard Company (including Compaq), Sony, IBM, Ericsson, Apple, Matsushita (including Panasonic), Intel and B&O.

Some of the main driving forces for these commitments have been EU RoHS Directive, eco-labels, customer requirements (e.g. "green procurement" initiatives).

DecaBDE Substitution in Textiles: Substitute Flame Retardant

Exposure-release

For textiles a range of possible substitution approaches:

- Substitute flame retardants (evaluation of substitute!)
- Alternative fibers,
- Inherently fire resistant fibers,
- Increased use of barrier layers, laminates and nonwovens.

Substance → Material → Product

- Use other BFRs instead of decaBDE (**e.g. Decabromodiphenylethane, HBCDD**)
- Use of a phosphate type flame retardant instead of decaBDE
- Use Inherently Flame Resistant Fiber or Non-Woven Barrier Layer
- Redesign Product To Eliminate the Fire Load

Increasing innovation depth

Source: Öko-Institute 2003

BFR Substitution in Textiles: Flame Retardant Substitution

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Applications	FR Type	Characteristics
Fire Retard KX Manufacturers Chemical	100% cotton, rayon, cotton/polyester blends, other cotton/synthetic blends	Drapery, decorative fabrics	organic phosphate	• Semi-durable • Does not cause color change • 25-35% solutions padded on • [illegible] cents per pound • Used as "drop in" decaBDE replacement
Fire Retard 102-52A Manufacturers Chemical	PVA, acrylic and vinyl acrylic polymer emulsions	Backcoating Textiles	Organic phosphate	• Semi-durable • Does not cause color change in most applications
Fire Retard 66 Manufacturers Chemical	Polyester	Drapery, upholstery, automotive products, backcoatings	Phosphate ester blend	• Curing and rinsing [illegible] after application
AFLAMMIT P CONC Thor	Cotton, cellulose fibers		Organic phosphorus compound	• Durable to washing • applied using special equipment with gaseous ammonia
AFLAMMIT PE CONC Thor	Polyester		Organic phosphorus compound	• Durable halogen-free flame retardant for polyester • applied by padding
AFLAMMIT SAP Thor	Cotton, Cellulose fibers		Organic phosphorus compound	• Durable flame retardant • Applied using special equipment with gaseous ammonia
AFLAMMIT ZAL Thor	Wool		Zirconium acetate solution	• For low smoke flame retardant finishing of wool by an exhaust process (Zirpro treatment)

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Applications	FR Type	Characteristics
AFLAMMIT ZR Thor	Wool		[illegible] (ZAL)	• [illegible] AFLAMMIT ZAL for low smoke [illegible]
AFLAMMAN [illegible] Thor			[illegible] phosphorus and nitrogen [illegible]	• [illegible] flame retardant liquid form • Used [illegible] systems
AFLAMMIT [illegible] Thor			[illegible] and nitrogen [illegible]	• [illegible] flame retardant • [illegible] coating systems • Halogen free
FLAMMENTIN [illegible] Thor	cellulose for synthetic fibers		Organic [illegible] nitrogen compound	• [illegible]
FLAMMENTIN CMD Thor			[illegible]	• [illegible]
FLAMMENTIN UCR-N Thor	cellulose fibers		Inorganic phosphorus compound	• [illegible] after water soak
ANTIBLAZE CU Rhodia	polyester	backcoating applications	cyclic phosphonate ester	• Flame retardant for [illegible]
ANTIBLAZE [illegible] Rhodia	many fibers especially polyester and cottons		organic phosphonate blend	• Minimal effect on fabric hand. Durable or nondurable, depending on application
ANTIBLAZE [illegible] Rhodia	plastics, synthetics and a wide range of other uses		cyclic phosphonate ester	• Nondurable flame retardant for [illegible]
ANTIBLAZE [illegible] Rhodia	variety of fibers		Phosphonic acid	• [illegible]

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution

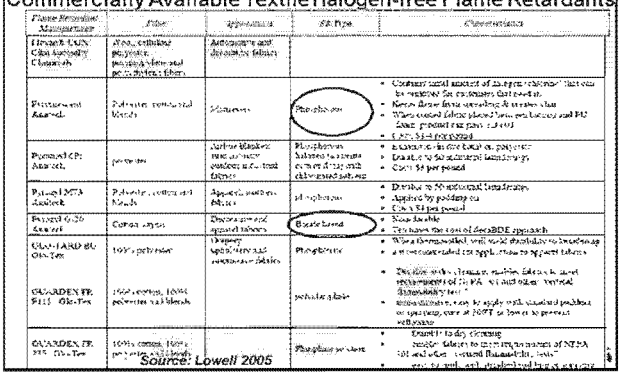
Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Applications	FR Type	Characteristics
PROBAN Rhodia	Cotton, cotton-rich fibers & blends	Protective wear, bedding, furnishings, [illegible]	Phosphorus based blend of [illegible] (THPC) & urea	• [illegible] • [illegible] • No chemical [illegible] • [illegible]
Flamestab NOR 116 Ciba Specialty Chemicals	Polyolefin		[illegible]	• Provides flame retardancy to polyolefin fibers, nonwovens and films at concentrations [illegible]
[illegible] Textile Chem	100% Polyester, acrylic			• Durable flame retardant • Halogen free • [illegible] • Used to help meet NFPA 701 • Can be applied [illegible]
Flamestab NOR [illegible] Ciba Specialty Chemicals	polypropylene		[illegible]	• Can pass NFPA 701 vertical burn test [illegible] level of UV stability • Can be made non-halogenated

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution

Commercially Available Textile Halogen-free Flame Retardants



Source: Lowell 2005

BFR Substitution in Textiles/PUR: Chlorinated Phosphorester

Flame Retardants in Baby Product Foam US

Flame Retardant in 101 samples	*# of Detects*	*(%)*
PentaBDE	*4*	*3.8 – 5.3*
ΣTBB and TBPH (Firemaster 550/600)	*17*	*.6 – 4.3*
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) or Chlorinated Tris	*36*	*0.5- 12.4*
Tris (2-chloro-ethyl) phosphate (TCEP)/"V6"	*15*	*0.02 – 6*
Tris(1-chloro-2-propyl)phosphate (TCPP)	*14*	*0.02 - .4*

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

BFR Substitution in Textiles/PUR: Chlorinated Phosphorester

TDCPP (Chlorinated Tris)

Tris (1,3-dichloroisopropyl) phosphate

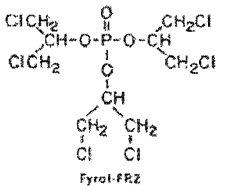
Classifued as Carcinogen (State of California 10/2011)

http://oehha.ca.gov/prop65/hazard_ident/pdf_zip/TDCPP070811.pdf

Detected in 36 Samples

Levels up to 12.4 percent or 124,000 ppm

- Car Seat (11)
- Changing Table Pad(8)
- Sleeping Wedge (6)
- Portable Mattress (3)
- Baby Walker (2)
- High Chair (2)
- Rocking Chair (1)
- Baby Carrier (1)
- Nursing Pillow (1)
- Infant Bath Sling (1)

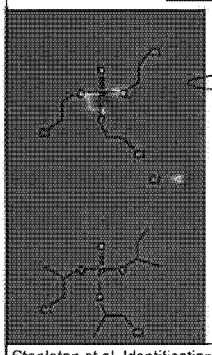


Fyrol-FR2

Tris-(1, 3-dichloro-2-propyl) phosphate

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

BFR Substitution in Textiles/PUR: Chlorinated Organophosphates



Found at lower levels. may be impurities in another chlorinated FR mixture:

Tris(2-chloroethyl)phosphate (TCEP)

- Carcinogen
- Phased out in Europe
- California Prop 65 list
- Detected in 14 Samples:
  - Nursing Pillow (9)
  - Infant Bath Sling (2)
  - Baby Carrier (1)
  - Sleeping Wedge (1)
  - Portable Crib (1)

Tris(1-chloro-2-propyl)phosphate (TCPP)

- Replaced TCEP
- Little toxicity information
- Detected in 13 Samples

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

Hexabromcyclododecane (HBCDD) - Evaluation Status

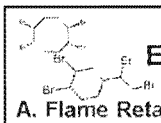
- Stockholm Convention: HBCDD is in the POP Reviewing Committee evaluation process and will be proposed for listing to COP6.
- UNECE: HBCDD evaluated for listing in protocol
- Europe (REACH): HBCDD listed as substance of very high concern for authorisation (10/2008).
- Japan: Classified HBCDD as a Type I Monitoring Chemical Substance in the Law Concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture.

Applications of HBCDD

- Primary use of HBCDD is as a flame retardant additive in expanded polystyrene (EPS) and extruded polystyrene (XPS) applications. EPS and XPS are typically used for thermal insulation foams for applications in the building and construction industry and in products.
- High impact polystyrene (HIPS) applications (electrical and electronic appliances, cables).
- Textile back-coating (upholstery furniture) in order to meet the strict fire safety standards in place e.g. in the United Kingdom and California.
- Global demand 2003: 21,900 metric tonnes (BSEF)

Q use China?

HBCDD Alternatives for use in EPS and XPS Polystyrene Insulation



A. Flame Retardant Substitutions

- There is limited data supporting non-brominated drop-in flame retardant chemical substitutes for HBCDD used in EPS and XPS applications. However, there are brominated chemicals other than HBCDD commercially available as flame retardant materials for EPS and XPS applications.
- However no data found for health/environmental evaluation

Manufacturer	Model	Properties	Applications
Albemarle	Saytex BC-48	Contains tetrabromo-cyclooctane	Expandable polystyrene (EPS)
Albemarle	Saytex BCL-462	Contains dibromoethyldibromo-cyclohexane	Expandable polystyrene (EPS)
Great Lakes Chemical	BE-51	Contains TBBPA	Expandable polystyrene (EPS)

Source: Morose 2006

HBCDD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Polyurethane and Polyisocyanurate Products.

- Most rigid foam boardstock is characterized by a high polyisocyanurate content and is usually based on lower-cost polyester polyols. These polyisocyanurate modified urethane foams are used in a variety of construction applications, and are commonly referred to as "polyiso" products.

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Polyurethane and Polyisocyanurate Products.

Key Health, Environmental and Performance Concerns:

Following flame retardant chemicals: tris monochloropropyl phosphate (TMCPP), tris chloroethyl phosphate (TCEP) and diol from tetrabromo phthalic anhydride.

- TCEP is categorized as carcinogen (e.g. listed in California)
- TMCPP is of low to moderate acute toxicity. Current assessment of neurotoxic properties.
- TDCPP & metabolites are carcinogen.

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Other Insulation Materials – inorganic materials

- **Blankets (fiber batts or rolls):** Blanket insulation is usually made of fiber glass or rock wool. Batts with special flame resistant facing are available where the insulation wil be left exposed. Fiberglass is a synthetic vitreous fiber.
- **Loose-fill:** Loose-fill insulation is typically blown into place or spray-applied by special equipment. Materials used for blown-in or spray-applied insulation include rock wool, fiber glass, cellulose, or polyurethane foam. Loose-fill cellulose insulation is commonly manufactured from recycled newsprint, cardboard, or other forms of waste paper, vermiculite or perlite (expanded naturally minerals).

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

C. Resin/Material Substitution & Production Redesign

- **When using alternative building insulation materials, the necessary flame retardancy is often provided by use of a thermal barrier.**
- **Thermal barriers are fire resistant coverings or coatings that separate the insulation material from the building interior. Thermal barriers can be used to increase the fire retardant performance for various types of insulation.**
- **Commonly used thermal barriers include: gypsum board, gypsum or cement plasters, perlite board, spray-applied cellulose, mineral fiber, or gypsum coatings, and select plywoods.**

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Key Health, Environmental and Performance Concerns:

- The fiber glass blanket/batt, loose-fill fiber glass, perlite and loose-fill rock wool have a lower R-Value than XPS boards and therefore may not be desirable for applications where high R-Value is a critical property.
- When fibers are suspended in air they can cause irritation o the eyes, nose, throat, and parts of the lung. Animal studies show that repeatedly breathing air containing synthetic vitreous fibers can lead to inflammation and fibrosis of the lung. (Agency for Toxics Substances and Disease Registry, 2004) EU: Accomplished improvement of fibres in respect to health concerns.
- Some fibres have melamine based binders (formaldehyde)

Conclusion HBCDD Substitution in Polystyrenes (EPS, XPS, HIPS)

German Environmental Agency (UBA 2008):

- No phase in flame retardant for HBCDD in polystyrene applications (XPS, EPS and HIPS).
- A range of alternative insulation materials is commercially available and can substitute HBCDD containing polystyrene in many applications.

POPRC: HBCDD list in Annex A or B

Sweden: propose to evalute if XPS/EPS would need an excemption if HBCDD would be restriced in EU.

BASF (largest producer of XPS/EPS Europe): „In a few years substitution possible."

HBCDD in Textiles - Key Contamination Source

- A wide range of alternative flame retardants (non-halogenated) and/or alternative textiles are available (see DecaBDE textile). Therefore substitution of HCBDD in textiles no issue.
- EPS/XPS producing industry (HBCDD use) (Germany): ***"The dispersive use of HBCDD in textiles is a main cause of environmental and human contamination. A second important source were releases from industrial production (e.g. Aycliffe/UK stopped 2003). These two releases mainly causes current pressure on HBCDD."***

⇒ HBCDD industry should have a vital interest to stop application in textiles and optimize releases from production to continue their core business (XPS/EPS).

Information on Socio-Economic Considerations (Annex F)

(a) Efficacy and efficiency of possible control measures in meeting risk reduction goals:
- (i) Technical feasibility; and
- (ii) Costs, including environmental and health costs;

(b) Alternatives (products and processes):
- (i) Technical feasibility;
- (ii) Costs, including environmental and health costs;
- (iii) Efficacy;
- (iv) Risk;
- (v) Availability; and (vi) Accessibility;

It is of key importance to evaluate PBT criteria for the alternatives! Important for human and environmental risk assessment but also of key impotance for the industrial producers and users (approach of REACH!).

Printed Circuit Boards: TBBPA and Alternative Fire Retardants

- A main use of TBBPA is in Epoxy resins used for PrCBs
- Currently the US EPA has a comprehensive project on "FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS" to evaluate possible alternatives to TBBPA.
- The report is divided into two parts
  - Part 1: provides an evaluation of the environmental and human health hazards associated with the manufacture and use of the FR-4 boards (UL 94 V0 compliant) and a preliminary discussion/identification of end of life issues
  - Part 2: Part two of the report will present experimental data from the investigation of the thermal breakdown of boards and the by-products formed under different combustion conditions. These data may provide further insight into end of life disposal issues

US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

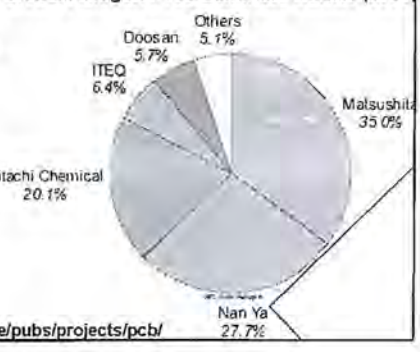
Printed Circuit Boards: TBBPA and Alternative Fire Retardants

- **Alternative flame retardant materials are used in only 3-5 percent of the current FR-4 boards. Additional alternative flame retardant materials are under development.**
- **There has been a continuous increase in the demand for halogen-free material over past few years. In 2003, global halogen-free laminate market was approx. $60 million. In 2004 this market grew to $161 million, in 2005 it reached $239 million estimated at $307 million for 2006.**

http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative Fire Retardants

- Most key laminate suppliers now include halogen-free materials in their portfolio.
- Pricing for halogen-free laminate is still higher than conventional material by at least 10 %, and often by more.



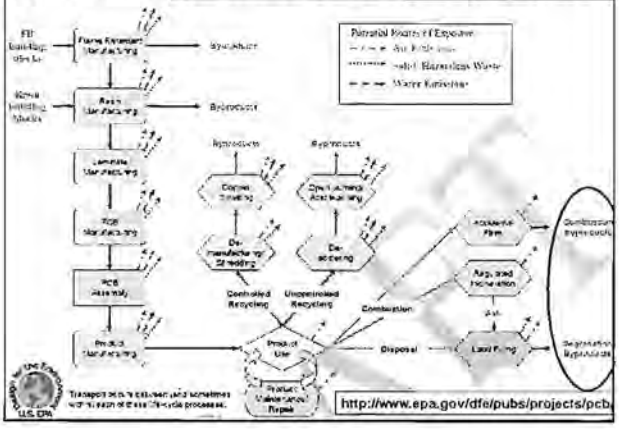
http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative Fire Retardants

- Little information exists concerning the potential environmental and human health impacts of the materials which are being developed as alternatives to those used today that are based on brominated epoxy resins.
- Environmental and human health impacts can occur throughout the life cycle of a material, from development and manufacture, through product use and finally at end of life of the material or product.

http://www.epa.gov/dfe/pubs/projects/pcb/

Exposure Pathways Considered During Life Cycle of PrCB



http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative Fire Retardants

- In addition to understanding these potential impacts associated with flame retardant chemicals, stakeholders have expressed a particular interest in understanding the combustion products that could be formed during certain end of life scenarios.

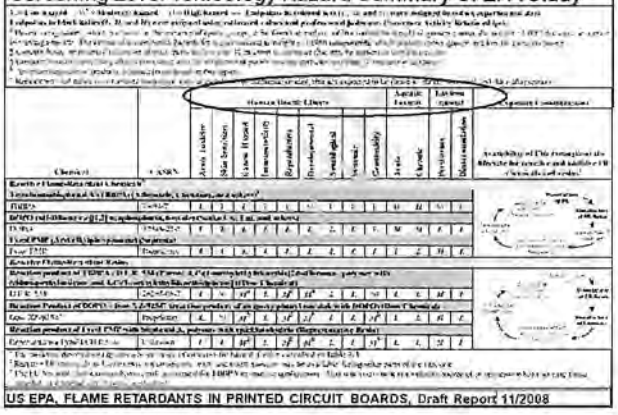
It is a challenge to do this assessment in laboratory!
Way forward: Field measurements in smelters managing PrCB. And test of simple smelting operations.

- The electronics industry is forming this partnership to develop information that will improve their understanding of the environmental and human health impacts of new and current materials that can be used to meet the fire safety requirements for circuit boards.

http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative FRs

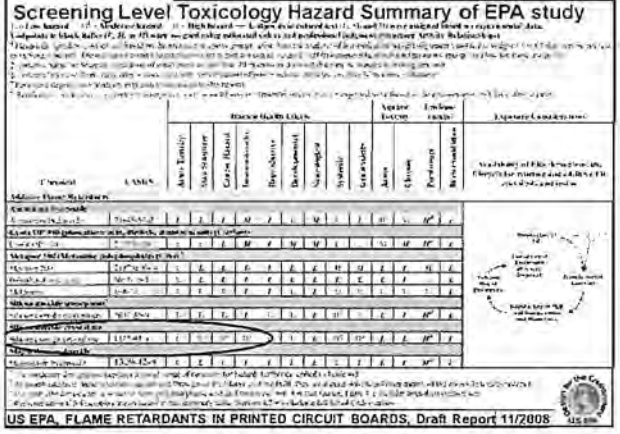
Screening Level Toxicology Hazard Summary of EPA study



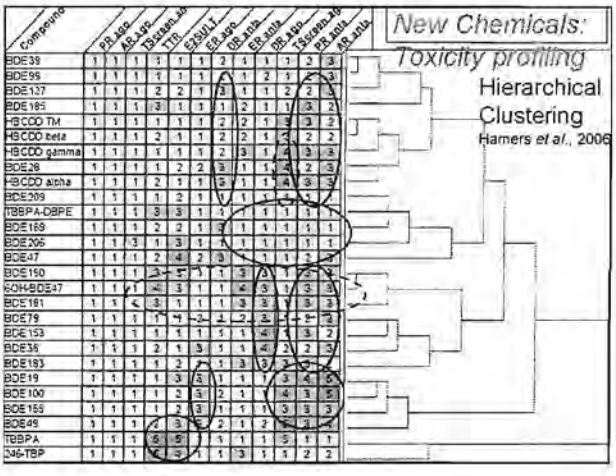
US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

Printed Circuit Boards: TBBPA and Alternative FRs

Screening Level Toxicology Hazard Summary of EPA study



US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

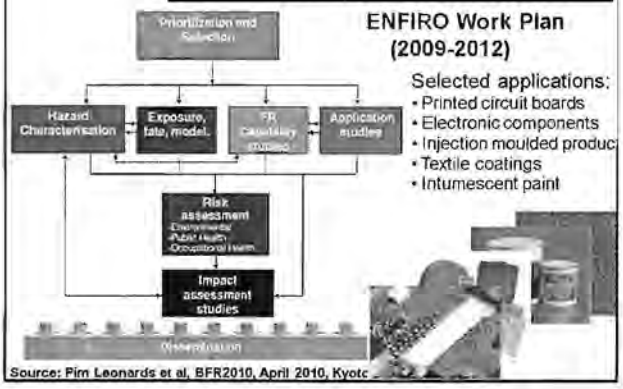


European Research Project ENFIRO: LCA of Environment-Compatible Flame Retardants

- Objective of ENFIRO: To study the substitution options for specific BFRs by a prototypical approach.
- ENFIRO offers a prototypical case study on substitution options resulting in a comprehensive dataset on the viability of production, application, and environmental safety, including a life cycle assessment (LCA)
- This will finally result in a recommendation of certain FR/product combinations. The case studies will give recommendations for industrial and governmental stakeholders.

http://www.enfiro.eu/

European Research Project ENFIRO: LCA of Environment-Compatible Flame Retardants



ENFIRO Work Plan (2009-2012)

Selected applications:
- Printed circuit boards
- Electronic components
- Injection moulded produc
- Textile coatings
- Intumescent paint

Source: Pim Leonards et al, BFR2010, April 2010, Kyotc

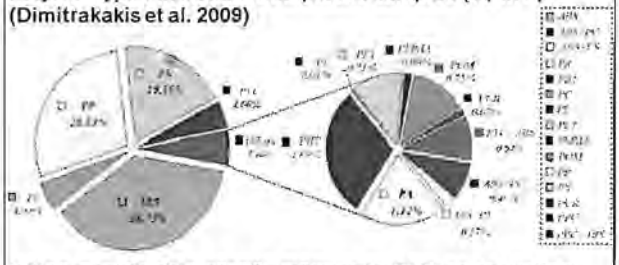
Ecological Priorities for Choice of Flame Retardants

Recommendation German Environmental Agency (2008)

1. Measures for reduction of the flame retardant in product design (use of less flammable materials, introduction of fire walls, adoption of the amount of flame retardant to the demand)
2. Inorganic flame retardants (Aluminiumhydroxid, Magnesiumhydroxid, red Phosphorus, NH3-polyphosphat).
3. Reaktive embedded, halogen free organic Nitrogen- and Phosphorus-compounds
4. Additive halogen free organic Nitrogen- and Phosphorus-compounds, non persistant, non-bioaccumulating without long-term human toxic or ecotoxic effects
5. Reactive embedded halogenated flame retardants.
6. Additive halogenated flame retardants which are non persistent, non-bioaccumulating without long-term human toxic or ecotoxic effects.

Sustainable Production: Recyclability Polymers

Polymer types in small WEEE plastic samples (%, w/w) (Dimitrakakis et al. 2009)



- Non sustainable plastic mixture in EEE as recycling challenge (can not be moulded but must be separated)!
- Stability of flame retardants & polymers in recycling

Recommendation/Conclusion

- (Organic) Chemicals need to be evaluated for their Persistence, Bioaccumulation and Toxicity before bulk production starts (concept of REACH). This is crucial to address global chemical contamination. For most FR applications alternatives to BFRs are on the market. Currently large research projects on total LCA of BFRs & alternatives in EU and US.
- Toxicological assessment of alternative needed.
- End of life/recycling performance of alternatives.
- The most sustainable chemicals („Green Chemistry") and sustainable products („Green Design") are likely to survive on the market. Several excellent Chinese research groups work on alternative flame retardants!!

Thank you for your attention!

www.pops.int www.saicm.org www.ipen.org

Assessment:
PFOA, PFXSi, PFHx
DeBDE,HBCDD,PBE
PBDD/F, HBBz, PBF
TBBPA, TBPAE,
SCCP, MCCP,
PCN, HCBD, OCS,
PCP, PCNB
PAHs, Nitro-PAH
Halogenated PAHs
PT-Pesticides,
PT-Biocides
PT-Pharmaceuticals
PT-Siloxanes
Sn-Organics
Hg, Cd, Pb et al.

Information and further Research: Contribution from Research Community

- Risk assessment of recycling scenarios and end of life treatments in industrial and developing countries considering multiple pollutants.
- Global substance flow analysis of PBDE (other critical BFRs and PBTS) in products and recycling.
- PBDE (BFR) contaminated sites from production, application and end of life treatment.
- External cost estimates/calculations of harm caused by PBDE/BFRs to humans and biota.
- Life Cycle Assessment of PBDE alternatives (other flame retardants and alternative technologies).

Study on DBDPE

- Now higher production volume then DecaBDE.
- Only few debromination studies (key question for the assessment of fate of DecaBDE).
- Analysis of Mono to NonaBDPE not available.
- What are other degradation products? (thermal, photolysis, sediments).
- What is persistence and toxicity of degradation products?

Study on Chlorinated Paraffins

- Short, medium & long chain chlorinated paraffins
- 1 million tons production (mainly China & India).
- Substance flow and LCA of CCPs
- Env./human fate of chlorinated paraffins.
- Degradation products of chlorinated paraffins (hydroxy-, carboxy-metabolites?)
- What are UPOPs in these materials?

Workshop on Sound Management of PBDEs and Phasing-out Opportunities in Developing Parties
27. November 2015, Colombo, Sri Lanka

Alternatives to PBDEs and substitution approaches

Dr. Roland Weber
POPs Environmental Consulting, Germany
roland.weber10@web.de

Content of Presentation

- Substitution of chemicals – definition and why?
- Substitution of PentaBDE and OctaBDE by BFRs
- General concern on BFRs – Activities in EU on BFRs within RoHS directive & general assessment
- Key application areas FR and alternatives
- DecaBDE and substitution approach in plastics
- The Publication on POPs Phase out and best practice studies.
- Integrating substitution and alternative assessment in the update of the National Implementation Plan.

Substitution of chemicals: Definition

- There is no standard definition of substitution
- *"... the replacement or reduction of hazardous substances in products and processes by less hazardous or non-hazardous substances, or by achieving an equivalent functionality via technological or organisiatonal measures." - Lohse/Lissner (2003)*
- *"The Principle of Substitution states that hazardous chemicals should be systematically substituted by less hazardous alternatives or preferably alternatives for which no hazards can be identified." - Greenpeace*

Substitution of chemicals: Definition

- Substitution is *"...the replacement of one substance by another with the aim of achieving a lower level of risk." - CEFIC*
- *1. The employer shall ensure that the risk from a hazardous chemical agent to the safety and health of workers at work is eliminated or reduced to a minimum. 2. In applying paragraph 1, substitution shall by preference be undertaken, whereby the employer shall avoid the use of a hazardous chemical agent by replacing it with a chemical agent or process which, under its condition of use, is not hazardous or less hazardous to workers' safety and health, as the case may be. – Directive 98/24/EC - risks related to chemical agents at work*

Some examples of substitution

- Asbestos by bio-soluble mineral fibers
- Nickel-cadmium batteries by lithium-ion batteries
- Dichloromethane as paint stripper by esters
- High volatile cleaner by low volatile cleaners
- Laboratory solvent hexane by heptane
- Lead-free soldering in the electronics industry
- Lead, chromium, mercury and nickel in the automotive manufacturing

What triggers substitution?

- Legal requirements (occupational safety, environmental protection, consumer protection)
- For more favorable safety measures - handling and storage
- For more environmentally sound disposal
- Requirements within the supply chain
- Green and innovative image as a competitive advantage

Main Materials and Application Areas for Flame Retardants

- Solid Thermoplastics (ABS, HIPS, PET, PA, PP, PE etc.)
- Thermosets (Epoxi Resin, Phenolic Resin, Acrylic resin etc.)
- Wires and Cables (PP, PVC flexible),
- Foams (EPS, XPS, PUR, PP, PE, PVC, rubbers)
- Textiles (Nylon, Polyester, Viscose, Cotton, others),
- Others: Paper, Wood, Paints, Adhesives

Requirements for Alternatives of Candidate POPs

Overall evaluation of alternatives for substitution of BFR (in accordance Annex F for risk management evaluation for the Stockholm Convention)

- Equal or better flame relardancy for the product
- Equal or better performance and physical properties for the product/part
- Cost (including environmental and health costs)
- Less risk to environment and human health
- Commercial availability and accessibiy of the alternative solution

Alternatives for PBDEs & POP Flame Retardants

Substitution can take place at three levels:

A. Flame Retardant Substitution: This approach involves identifying a drop-in chemical substitute for the BFR. It is the simplest approach because it typically does not require changes to the polymer material or to the design of the product.

B. Resin/Material Substitution: This approach involves changing the resin system, while also changing the chemical used as the flame retardant. This is a more complex approach than simple flame retardant substitution because it has a greater effect on overall product cost and performance.

C. Product Redesign: This approach involves changes to the actual product design to minimize or eliminate the need for flame retardant chemicals. Examples of product redesign include using fire barrier material, as well as separating or reducing the source of heat from the product.

POP-BFRs were often substituted by other BFRs

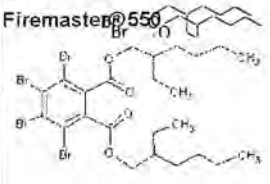
Polymer	Content [%]	POP-BFRs	Current Substances
High impact polystyrene	5–15	OctaBDE	DecaBDE, Br-polystyrene Ethane 1,2 bis(pentabromophenyl)
Epoxy resin	1-10	PentaBDE	TBBPA
Polyamides	10–16	OctaBDE	DecaBDE, Br-polystyrene
Polyolefins	5–8	OctaBDE	DecaBDE, propylene dibromo styrene
Polyurethanes	1-10	PentaBDE	Firemaster550, Br-polyols
Polyesters	8–11	OctaBDE	Brominated polystyrene
Unsaturated polyesters	13–28	PentaBDE	TBBPA
Polycarbonate	4–6		Brominated polystyrene
Textiles	12–15	PentaBDE	DecaBDE, HBCD

HBCD is listed in the Stockholm Convention and DecaBDE is suggested to be listed by the POP Reviewing Committee.

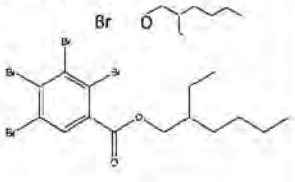
Brominated Compounds in Firemaster® 550

Major Substitute for PentaBDE in flexible polyurethane foam:

Firemaster® 550



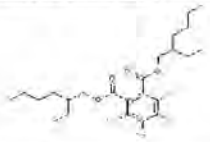
Di(2-ethylhexyl)-tetrabromophthalate (TBPH)



2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB)

PBDD/PBDF formation potential?

Firemaster 550® Component – Analogue to the known toxicant DEHP



DEHP: Di (2-ethylhexyl) phthalate

- Prop 65 cancer, reproductive, developmental toxin
- Animal effect at env. levels
- Bioaccumlates, persistent

Di (2-ethylhexyl) tetrabromophthalate

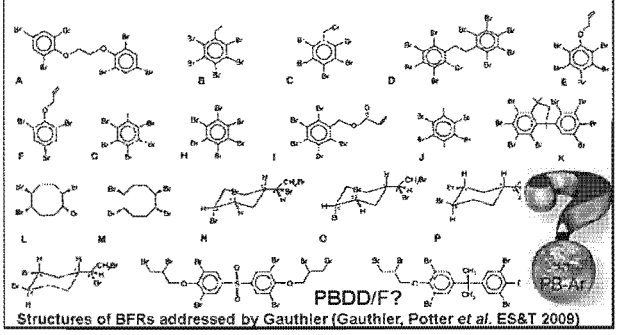
- Wide use as flame retardant
- Only few studies !

Metabolite TBMEHP, elicited maternal thyrotoxic and hepatotoxic effects and induced MNGs in the fetal testes in a rat model. In mouse NIH 3T3 L1 preadipocyte cells, TBMEHP inhibited rat hepatic microsome deiodinase activity and was an agonist for PPARs in murine FAO and NIH 3T3 L1 cells

Other Brominated Flame Retardants - on the market and partly in the environment

13

- **Approx. 75 BFR are on the market** (Fisk et al 2003).
- **BFR2010: Research community is analysing ~20 BFR**



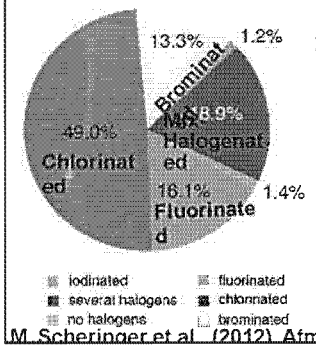
Structures of BFRs addressed by Gauthier (Gauthier, Potter *et al.* ES&T 2008)

How many potential POPs in use?

14

Assessment of approximately 100,000 chemicals in chemical database according POP criteria from REACH.

574 Potential POPs



- Chlorinated, brominated and fluorinated persistent toxic substances need to be systematically assessed.

M. Scheringer et al. (2012) Atmos. Pollut. Res. 3 DOI:

Pressure on Br Flame Retardants: Current Discussion in EU & elsewhere

15

- Concern about halogenated flame retardants.
- A report for the European Commission on the extension of the RoHS Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Groß & Bunke et al. 2008) proposes to phase out all brominated and chlorinated flame retardants in electric and electronic consumer goods to protect consumers and to facilitate easier and safer recycling at the end of life stage (European Commission 2010).
- In several EU Eco-lable drafts the restriction of BFRs were proposed.
- Several electronic producers have stopped the use of BFRs.

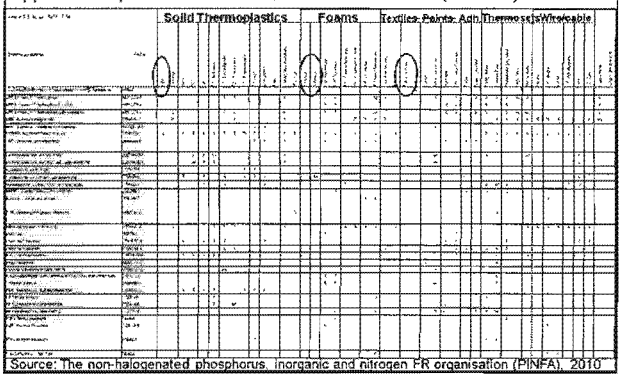
Will electronics go halogen free?

Assessment chemical by chemical (as REACH)

Overview Table Non-Halogenated FR In the Whole Application Range

16

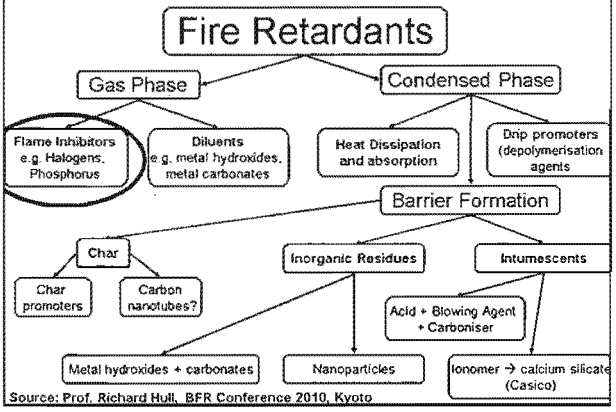
Application options non-Hal-FR; PINFA Version 5.0 (12/2009)



Source: The non-halogenated phosphorus, inorganic and nitrogen FR organisation (PINFA), 2010

Fire Retardants - Mode of Action

17

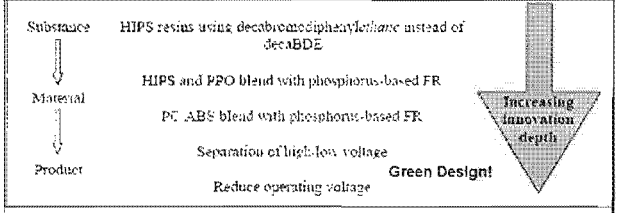


Source: Prof. Richard Hull, BFR Conference 2010, Kyoto

DecaBDE Substitution in Plastic Resin

18

DecaBDE Substitution Strategies for plastic used in electronic



Source: Öko-Institute 2003

Stockholm Convention POPs free initiative:

- A 'POPs-free initiative' has been initiated by the Secretariat of the Stockholm Convention to improve the exchange of information on alternatives/substitutes to POPs.
- Here an electronic publication "*POPs in articles and phasing-out opportunities*" has been developed compiling information on alternatives to POPs & phase out (Web-version with Basel/Stockholm Convention Regional Centre Asia & the Pacific)

http://poppub.bcrc.cn/

Stockholm Convention POPs free initiative: "POPs in articles and phasing-out opportunities" publication

- Part III of the publication includes information on alternatives to listed POPs which are still in use.
- The publication is considered to be updated for current and future new listed POPs.

http://poppub.bcrc.cn/

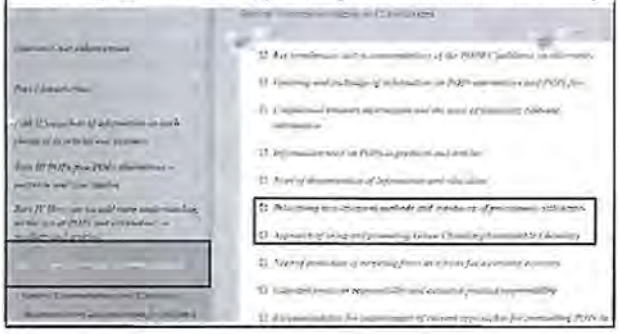
Stockholm Convention POPs free initiative: "POPs in articles an.d phasing-out opportunities" publication

- The publication contains in part IV information on tools for assessment of alternatives and case studies.
- The publication already links to SUBSPORT and to compilation of IOMC on alternative assessment.
- Inputs including country experience case studies are welcome.

http://poppub.bcrc.cn/

Stockholm Convention POPs free initiative: "POPs in articles and phasing-out opportunities" publication

Part V „Conclusions and recommendations" includes already a short section on „Approach of using/promoting Green/Sustainable Chemistry"



Case study in SUBSPORT on halogen-free cable

An alternative to PVC in wires and cables. A kind of plastic completely free from halogens, BFR´s (brominated flame retardants), PVC and plasticizers.

Abstract

Substituted substance(s)

- Polyvinyl chloride (PVC)

Alternative substance(s)

- Thermoplastic co-polyester; polymer with 1,4-butanediol and .alpha.-hydro-.omega.-hydroxypoly(oxy-1,4-butanediyl)

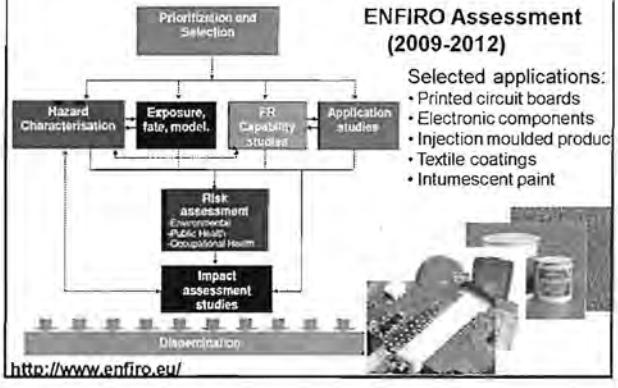
Other type of alternative

Reliability of information

Hazard assessment

http://www.subsport.eu/

European Research Project ENFIRO: LCA of Environment-Compatible Flame Retardants



ENFIRO Assessment (2009-2012)

Selected applications:

- Printed circuit boards
- Electronic components
- Injection moulded produc
- Textile coatings
- Intumescent paint

http://www.enfiro.eu/

Selection of alternatives to HBCD within the SC

- Also HBCD has been listed in the Stockholm Convention with a specific exemption for the use in insulation in construction (EPS/XPS)
- A draft inventory guidance has been developed containing a chapter on HBCD alternatives (potential alternatives; criteria for alternatives).

Action plan development within SC: Considering substitution of POPs in use

- When updating their national implementation plans, countries can include in their action plans for those chemicals which are still used for acceptable purpose and specific exemptions:
  - the assessment of alternatives
  - the phase-in of alternatives
  - the assessment of phase-in alternatives and lessions learned
- Within this frame and activities „sustainable chemistry" could be used as a tool or a guiding principle.

National Implementation Plan development within SC: Considering sustainable alternatives to POPs

Countries case: National Implementation Plan of Sudan:

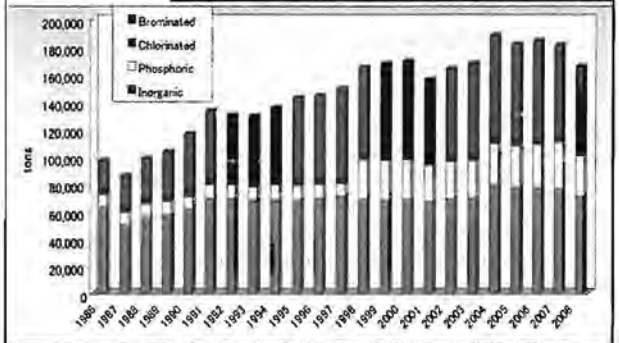
Here the implementation strategy of the Stockholm Convention is already linked to Sustainable Consumption and Production (SDGs!)

Thank you for your attention !

More Information

Basel Convention: www.basel.int
Rotterdam Convention: www.pic.int
Stockholm Convention: http://chm.pops.int/
Montreal Protocol/Vienna Convention: http://ozone.unep.org
SAICM: http://www.saicm.org/
POPs phase out & alternatives http://poppub.bcrc.cn/
OECD/IOMC: http://www.oecd.org/chemicalsafety/
Science: www.ipcp.ch; http://greensciencepolicy.org/
NGO: www.ban.org; www.ipen.org; www.ihpa.info; www.chemsec.org
Better-world-links: http://www.betterworldlinks.org/

Trends in the annual consumption of Flame Retardants in Japan (1986~2008)



Source: I. Watanabe, 5th International Symposium on Brominated Flame Retardants, April 7.-9. 2010, Kyoto Japan

DecaBDE - International Measures

- EU: DecaBDE has been restricted for electrical and electronic equipment (Directive 2002/95/EC + 2005/717/EC) but not for other uses.
- DecaBDE to be phased out from all applications in US by 2013.
  http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/deccadbe.html
- If relevant debromination to lower PBDE will be further demonstrated then DecaBDE will be SC relevant.
- Evidence for relevant PBDF formation during some application (in plastic and textile Kajiwara et al 2008, 2010) and in end of life thermal treatments.
- Direct and indirect pressure to phase out DecaBDE.

DecaBDE Main Applications

31

- Due to it's good performance it is used in a wide range of plastics in particular applied in electronics.
- Major use in HIPS TV casings (US 80% of total use (Lowell 2005). Other use Polyamids and Polyolefins.
- Textiles: Primary textile uses appear to be in the mattress, drapery, commercial upholstered furniture, and transportation (automotive and airplane) industries. Other niche applications of decaBDE in textiles include tents, awnings, and related fabric applications.
- Use pattern in China not known

DecaBDE Substitutes in Plastic Resin

32

Wide range of alternative plastic/flame retardant combination available on the market and used in former key applications of DecaBDE (e.g. Electronic enclosures) by international producers.

Cost estimate range from 0.2 % to 2.5 % of final product price.

Resin System	Flame Retardant(s)	Example Uses
HIPS/PPO	• Resorcinol bis diphenyl phosphate (RDP)	• Used throughout Europe -- roughly 20,000 metric tons in the EU TV enclosure market
PC/ABS	• Bis-phenol A diphosphate (BPADP)	• Sharp AQUOS LCD TV • Philips Electronics flat panel TV
PC	• Phosphate esters	• Apple Computer Monitor • Philips Plasma TV front housing
PLA	• Metal hydroxide	• NEC (currently in developmental products only)

Source: Lowell 2005; Danish EPA 2006

DecaBDE Substitutes in Plastic Resin

33

Phosphate Flame Retardants Used in Electronic Applications
Producer of Phosphor flame retardants claim that some application of Phosphor flame retardants can even be cheaper then brominated alternatives.

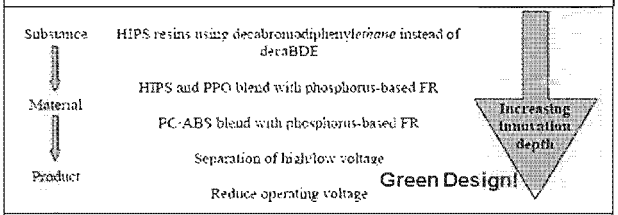
Flame Retardant	Acronym (s)	Applicable Resin Systems and Other Notes	Known uses	Manufacturer Trade Name
Resorcinol bis diphenyl phosphate	RDP	• 11% phosphorus • V0 rating achieved when used in PPO/HIPS blends. • *Dimensional stability somewhat in PC/ABS and PPO/HIPS systems*	• Bayer Bayblend PC/ABS resins • GE Plastics PC/ABS resins • Used in Dell PC/ABS CRT Monitor	• Adeka Nobel: Fyrolflex RDP 10 • Great Lakes: Reofos RDP
Bisphenol A diphosphate	BPADP, BAPP, BDP	• Usage growing in PC/ABS and PPO/HIPS applications • 9% phosphorus	• Dow Chemical PC/ABS 7560, used in the Sharp AQUOS LCD TV	• Great Lakes: Reofos BAPP • Albemarle: NcendX P-30 • Adeka Nobel: Fyrolflex BDP
Diphenyl cresyl phosphate	DPC	• Used in PC/ABS		
Proprietary monophosphate		• PC/ABS	• Low migration, hydrolysis resistant	• Great Lakes: Reofos 200
Triphenyl phosphate	TPP	• Also known as triaryl phosphate • Usage shrinking in PC/ABS and PPO/HIPS applications		• Great Lakes: Reofos TPP •

Source: Lowell 2005

Substitution DecaBDE in Plastic Resin

34

DecaBDE Substitution Strategies for plastic used in electronics



Source: Öko-Institute 2003

35

Leading E-Companies about Eliminating DecaBDE

A large number of companies in the EE sector specifically state that they have phased out Deca-BDE in all of their products, among these, Dell, Hewlett-Packard Company (including Compaq), Sony, IBM, Ericsson, Apple, Matsushita (including Panasonic), Intel and B&O.

Some of the main driving forces for these commitments have been EU RoHS Directive, eco-labels, customer requirements (e.g. "green procurement" initiatives).

DecaBDE Substitution in Textiles

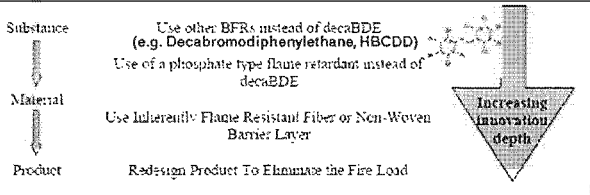
36

Exposure-release

Substitute Flame Retardant

For textiles a range of possible substitution approaches:

- Substitute flame retardants (evaluation of substitute!)
- Alternative fibers,
- Inherently fire resistant fibers,
- Increased use of barrier layers, laminates and nonwovens.



Source: Öko-Institute 2003

BFR Substitution in Textiles: Flame Retardant Substitution [37]

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Application	FR Type	Characteristics
Fire Retard NX Manufacturers Chemical	100% cotton, rayon, cotton/polyester blends, other cotton/synthetic blends	Drapery, decorative fabrics	Organic phosphate	• Semi-durable • Does not cause color change • 15-20% solution padded on • [illegible] • Used as "drop in" decaBDE replacement
Fire Retard 102-57A Manufacturers Chemical	PVA, acrylic and vinyl acrylic polymer emulsions	Backcoating Textiles	Organic phosphate	• Semi-durable • Does not cause color change in most applications
Fire Retard 6a Manufacturers Chemical	Polyester	Drapery, upholstery, nonwoven products, backcoatings	Phosphate ester blend	• Curing and rinsing req. after application
AFLAMMIT P CONC Thor	Cotton, cellulose fibers		Organic phosphorus compound	• Durable to washing • applied using special equipment with gaseous ammonia
AFLAMMIT PE CONC Thor	Polyester		Organic phosphorus compound	• Durable halogen-free flame retardant for polyester • applied by padding
AFLAMMIT SAP Thor	Cotton, Cellulose fibers		Organic phosphorus compound	• Durable flame retardant • Applied using special equipment with gaseous ammonia
AFLAMMIT ZAL Thor	Wool		Zirconium acetate solution	• For low smoke flame retardant finishing of wool by an exhaust process (Zirpro treatment)

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution [38]

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Application	FR Type	Characteristics
AFLAMMIT [illegible] Thor	Wool		[illegible] (ZAL)	• [illegible]
AFLAMMIN [illegible] Thor			Based on phosphorus and nitrogen compounds	• Intumescent flame retardant, liquid form • Used alone or in coating systems
AFLAMMIT [illegible] Thor			phosphorus and nitrogen compounds	• Intumescent flame retardant • For coating systems • Halogen free
FLAMMENTIN [illegible] Thor	cellulose for nonwoven fibers		Organic phosphorus nitrogen compound	• semi-durable
FLAMMENTIN [illegible] Thor			Phosphorus nitrogen compound	• [illegible]
FLAMMENTIN [illegible] Thor	cellulose fibers		Inorganic phosphorus compound	• [illegible]
ANTIBLAZE [illegible] Rhodia	polyester	backcoating applications	Cyclic phosphonate ester	• [illegible]
ANTIBLAZE [illegible] Rhodia	many fabrics especially polyester and cotton		Organic phosphonate blend	• Minimal effect on fabric hand. Durable or nondurable, depending on application
ANTIBLAZE [illegible] Rhodia	plastics, synthetics and a wide range of other uses		Cyclic phosphonate ester	• [illegible]
ANTIBLAZE [illegible] Rhodia	variety of fabrics		Phosphonic acid	• [illegible]

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution [39]

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Application	FR Type	Characteristics
PROBAN Rhodia	Cotton, cotton-rich fabrics & blends	Protective wear, bedding, furnishing, draperies	Phosphorus based blend of [illegible] (THPC) & urea	• [illegible] • [illegible] • [illegible] • [illegible]
Flamestab NOR 116 Ciba Specialty Chemicals	Polyolefin		[illegible]	• Provides flame retardancy to polyolefin fibers, nonwovens and films [illegible]
[illegible]	100% Polyester, acrylic			• Durable flame retardant • Halogen free • Can be incorporated in backcoatings • Used to help meet NFPA 701 • Can be applied [illegible]
Flamestab NOR 116FF Ciba Specialty Chemicals	polypropylene		1,3-Propanediamine [illegible]	• Complies NFPA 701 vertical burn as well as a level of UV stability • Can be made non-halogenated

Source: Lowell 2005

BFR Substitution in Textiles: Flame Retardant Substitution [40]

Commercially Available Textile Halogen-free Flame Retardants

Flame Retardant Manufacturer	Fiber	Application	FR Type	Characteristics
[illegible] Ciba Specialty Chemicals	Wool, cellulose, polyester, polypropylene and polyamide fibers	Automotive and decorative fabrics		
[illegible]	Polyester, cotton and blends	Mattresses	Phosphorus	• [illegible] • [illegible] • [illegible] • [illegible]
[illegible]	polyester	[illegible]	[illegible]	• [illegible] • Durable to 50 industrial launderings • [illegible]
[illegible]	Polyester, cotton and blends	Apparel, mattress fabrics	phosphorus	• Durable to 50 industrial launderings • Applied by padding on • [illegible]
[illegible]	Cotton, rayon	Decorative and apparel fabrics	Borate based	• Non-durable • [illegible]
[illegible] Glo-Tex	100% polyester	Drapery, upholstery and [illegible]	Phosphonate	• [illegible] • [illegible]
GUARDEX FR [illegible] Glo-Tex	100% cotton, 100% polyester and blends		[illegible]	• [illegible] • [illegible]
GUARDEX FR [illegible] Glo-Tex	100% cotton, 100% polyester and blends		[illegible]	• Durable to dry cleaning • [illegible] • [illegible]

Source: Lowell 2005

BFR Substitution in Textiles/PUR: Chlorinated Phosphorester [41]

Flame Retardants in Baby Product Foam US

Flame Retardant in 101 samples	*# of Detects*	*(%)*
PentaBDE	*4*	*3.8 – 5.3*
ΣTBB and TBPH (Firemaster 550/600)	*17*	*.6 – 4.3*
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) or Chlorinated Tris	*36*	*0.5 - 12.4*
Tris (2-chloro-ethyl) phosphate (TCEP)/"V6"	*15*	*0.02 – 6*
Tris(1-chloro-2-propyl)phosphate (TCPP)	*14*	*0.02 - .4*

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

BFR Substitution in Textiles/PUR: Chlorinated Phosphorester [42]

TDCPP (Chlorinated Tris)

Tris (1,3-dichloroisopropyl) phosphate

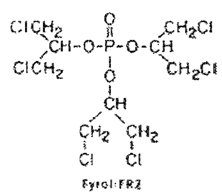
Classifued as Carcinogen (State of California 10/2011)

http://oehha.ca.gov/prop65/hazard_ident/pdf_zip/TDCPP070811.pdf

Detected in 36 Samples

Levels up to 12.4 percent or 124,000 ppm

- Car Seat (11)
- Changing Table Pad (8)
- Sleeping Wedge (6)
  Portable Mattress (3)
- Baby Walker (2)
- High Chair (2)
- Rocking Chair (1)
- Baby Carrier (1)
- Nursing Pillow (1)
- Infant Bath Sling (1)

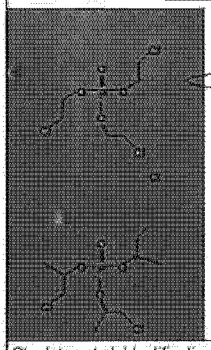


Fyrol FR2

Tris-(1, 3-dichloro-2-propyl) phosphate

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

BFR Substitution in Textiles/PUR? Chlorinated Organophosphates



Found at lower levels. may be impurities in another chlorinated FR mixture:

Tris(2-chloroethyl)phosphate (TCEP)

- Carcinogen
- Phased out in Europe
- California Prop 65 list
- Detected in 14 Samples:
  - Nursing Pillow (9)
  - Infant Bath Sling (2)
  - Baby Carrier (1)
  - Sleeping Wedge (1)
  - Portable Crib (1)

Tris(1-chloro-2-propyl)phosphate (TCPP)

- Replaced TCEP
- Little toxicity information
- Detected in 13 Samples

Stapleton et al. Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ. Sci. Technol.*, 2011, 45 (12), pp 5323–5331

Hexabromcyclododecane (HBCDD) - Evaluation Status

- Stockholm Convention: HBCDD is in the POP Reviewing Committee evaluation process and will be proposed for listing to COP6.
- UNECE: HBCDD evaluated for listing in protocol
- Europe (REACH): HBCDD listed as substance of very high concern for authorisation (10/2008).
- Japan: Classified HBCDD as a Type I Monitoring Chemical Substance in the Law Concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture.

Applications of HBCDD

- Primary use of HBCDD is as a flame retardant additive in expanded polystyrene (EPS) and extruded polystyrene (XPS) applications. EPS and XPS are typically used for thermal insulation foams for applications in the building and construction industry and in products.
- High impact polystyrene (HIPS) applications (electrical and electronic appliances, cables).
- Textile back-coating (upholstery furniture) in order to meet the strict fire safety standards in place e.g. in the United Kingdom and California.
- Global demand 2003: 21,900 metric tonnes (BSEF)

Q use China?

HBCDD Alternatives for use in EPS and XPS Polystyrene Insulation

A. Flame Retardant Substitutions

- There is limited data supporting non-brominated drop-in flame retardant chemical substitutes for HBCDD used in EPS and XPS applications. However, there are brominated chemicals other than HBCDD commercially available as flame retardant materials for EPS and XPS applications.
- However no data found for health/environmental evaluation

Manufacturer	Model	Properties	Applications
Albemarle	Saytex BC-48	Contains tetrabromo-cyclooctane	Expandable polystyrene (EPS)
Albemarle	Saytex BCL-462	Contains dibromoethyldibromo-cyclohexane	Expandable polystyrene (EPS)
Great Lakes Chemical	BE-51	Contains TBBPA	Expandable polystyrene (EPS)

Source: Morose 2006

HBCDD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Polyurethane and Polyisocyanurate Products.

- Most rigid foam boardstock is characterized by a high polyisocyanurate content and is usually based on lower-cost polyester polyols. These polyisocyanurate modified urethane foams are used in a variety of construction applications, and are commonly referred to as "polyiso" products.

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Polyurethane and Polyisocyanurate Products.

Key Health, Environmental and Performance Concerns:

Following flame retardant chemicals: tris monochloropropyl phosphate (TMCPP), tris chloroethyl phosphate (TCEP) and diol from tetrabromo phthalic anhydride.

- TCEP is categorized as carcinogen (e.g. listed in California)
- TMCPP is of low to moderate acute toxicity. Current assessment of neurotoxic properties.
- TDCPP & metabolites are carcinogen.

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Other Insulation Materials – inorganic materials

- Blankets (fiber batts or rolls): Blanket insulation is usually made of fiber glass or rock wool. Batts with special flame resistant facing are available where the insulation wil be left exposed. Fiberglass is a synthetic vitreous fiber.
- Loose-fill: Loose-fill insulation is typically blown into place or spray-applied by special equipment. Materials usec for blown-in or spray-applied insulation include rock wool, fiber glass, cellulose, or polyurethane foam. Loose-fill cellulose insulation is commonly manufactured from recycled newsprint, cardboard, or other forms of waste paper, vermiculite or perlite (expanded naturally minerals).

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

C. Resin/Material Substitution & Production Redesigr

- When using alternative building insulation materials, the necessary flame retardancy is often provided by use of a thermal barrier.
- Thermal barriers are fire resistant coverings or coatings that separate the insulation material from the building interior. Thermal barriers can be used to increase the fire retardant performance for various types of insulation.
- Commonly used thermal barriers include: gypsum board, gypsum or cement plasters, perlite board, spray-applied cellulose, mineral fiber, or gypsum coatings, and select plywoods.

HBCD Alternatives for use in EPS and XPS Polystyrene Insulation

B. Resin/Material Substitution

Key Health, Environmental and Performance Concerns:

- The fiber glass blanket/batt, loose-fill fiber glass, perlite and loose-fill rock wool have a lower R-Value than XPS boards and therefore may not be desirable for applications where high R-Value is a critical property.
- When fibers are suspended in air they can cause irritation o the eyes, nose, throat, and parts of the lung. Animal studies show that repeatedly breathing air containing synthetic vitreous fibers can lead to inflammation and fibrosis of the lung. (Agency for Toxics Substances and Disease Registry, 2004) EU: Accomplished improvement of fibres in respect to health concerns.
- Some fibres have melamine based binders (formaldehyde)

Conclusion HBCDD Substitution in Polystyrenes (EPS, XPS, HIPS)

German Environmental Agency (UBA 2008):

- No phase in flame retardant for HBCDD in polystyrene applications (XPS, EPS and HIPS).
- A range of alternative insulation materials is commercially available and can substitute HBCDD containing polystyrene in many applications.

POPRC: HBCDD list in Annex A or B

Sweden: propose to evalute if XPS/EPS would need an excemption if HBCDD would be restriced in EU.

BASF (largest producer of XPS/EPS Europe):
„In a few years substitution possible."

HBCDD in Textiles Key Contamination Source

- A wide range of alternative flame retardants (non-halogenated) and/or alternative textiles are available (see DecaBDE textile). Therefore substitution of HCBDD in textiles no issue.
- EPS/XPS producing industry (HBCDD use) (Germany): *"The dispersive use of HBCDD in textiles is a main cause of environmental and human contamination. A second important source were releases from industrial production (e.g. Aycliffe/UK stopped 2003). These two releases mainly causes current pressure on HBCDD."*

⇒ HBCDD industry should have a vital interest to stop application in textiles and optimize releases from production to continue their core business (XPS/EPS).

Information on Socio-Economic Considerations (Annex F)

(a) Efficacy and efficiency of possible control measures in meeting risk reduction goals:
- (i) Technical feasibility; and
- (ii) Costs, including environmental and health costs;

(b) Alternatives (products and processes):
- (i) Technical feasibility;
- (ii) Costs, including environmental and health costs;
- (iii) Efficacy;
- (iv) Risk;
- (v) Availability; and (vi) Accessibility;

It is of key importance to evaluate PBT criteria for the alternatives! Important for human and environmental risk assessment but also of key impotance for the industrial producers and users (approach of REACH!).

Printed Circuit Boards: TBBPA and Alternative Fire Retardants [55]

- A main use of TBBPA is in Epoxy resins used for PrCBs
- Currently the US EPA has a comprehensive project on "FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS" to evaluate possible alternatives to TBBPA.
- The report is divided into two parts
  - Part 1: provides an evaluation of the environmental and human health hazards associated with the manufacture and use of the FR-4 boards (UL 94 V0 compliant) and a preliminary discussion/identification of end of life issues
  - Part 2: Part two of the report will present experimental data from the investigation of the thermal breakdown of boards and the by-products formed under different combustion conditions. These data may provide further insight into end of life disposal issues

US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

Printed Circuit Boards: TBBPA and Alternative Fire Retardants [56]

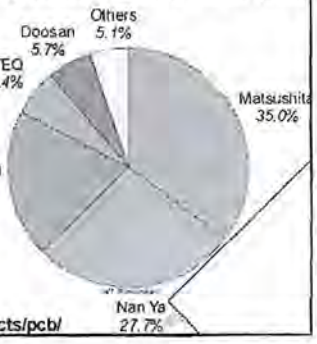
- Alternative flame retardant materials are used in only 3-5 percent of the current FR-4 boards. Additional alternative flame retardant materials are under development.
- There has been a continuous increase in the demand for halogen-free material over past few years. In 2003, global halogen-free laminate market was approx. $60 million. In 2004 this market grew to $161 million, in 2005 it reached $239 million estimated at $307 million for 2006.

http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative Fire Retardants [57]

- Most key laminate suppliers now include halogen-free materials in their portfolio.
- Pricing for halogen-free laminate is still higher than conventional material by at least 10 %, and often by more.

Global Halogen-Free Laminate Market (2006)



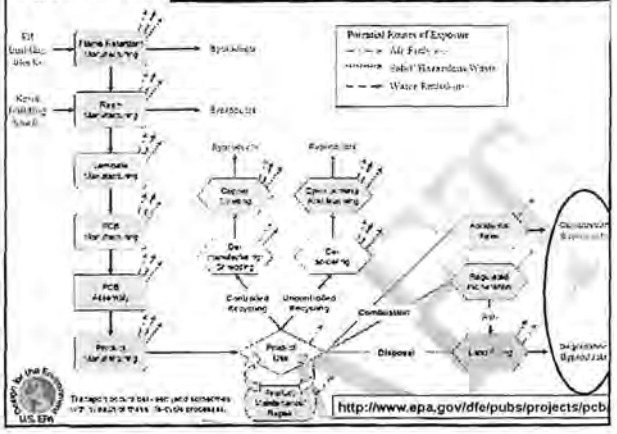
http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative Fire Retardants [58]

- Little information exists concerning the potential environmental and human health impacts of the materials which are being developed as alternatives to those used today that are based on brominated epoxy resins.
- Environmental and human health impacts can occur throughout the life cycle of a material, from development and manufacture, through product use and finally at end of life of the material or product.

http://www.epa.gov/dfe/pubs/projects/pcb/

Exposure Pathways Considered During Life Cycle of PrCB [59]



http://www.epa.gov/dfe/pubs/projects/pcb

Printed Circuit Boards: TBBPA and Alternative Fire Retardants [60]

- In addition to understanding these potential impacts associated with flame retardant chemicals, stakeholders have expressed a particular interest in understanding the combustion products that could be formed during certain end of life scenarios.

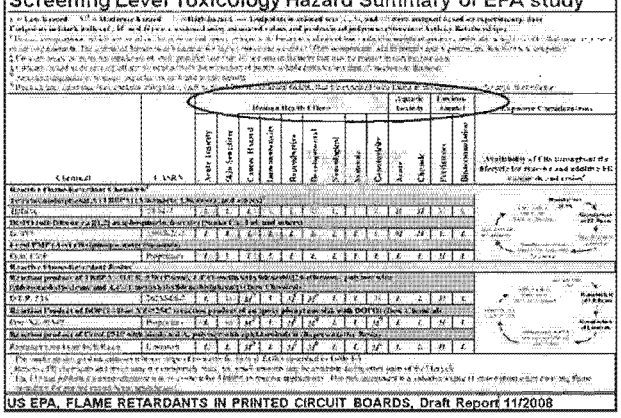
It is a challenge to do this assessment in laboratory!
Way forward: Field measurements in smelters managing PrCB. And test of simple smelting operations.

- The electronics industry is forming this partnership to develop information that will improve their understanding of the environmental and human health impacts of new and current materials that can be used to meet the fire safety requirements for circuit boards.

http://www.epa.gov/dfe/pubs/projects/pcb/

Printed Circuit Boards: TBBPA and Alternative FRs [61]

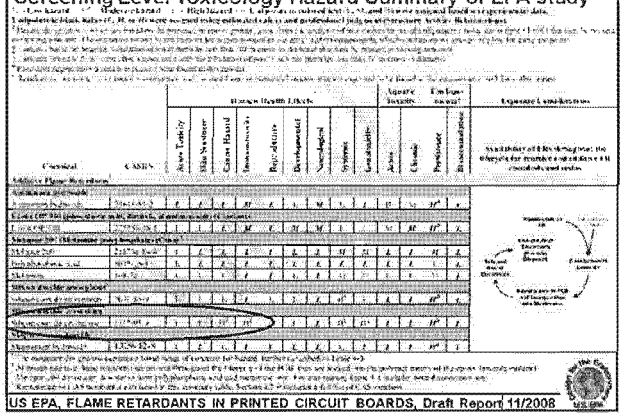
Screening Level Toxicology Hazard Summary of EPA study



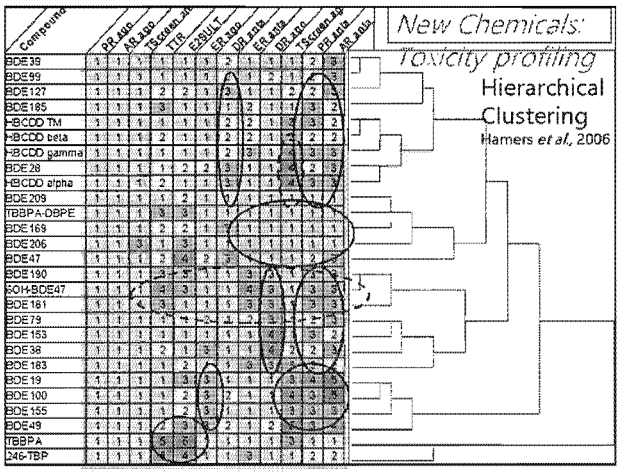
US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

Printed Circuit Boards: TBBPA and Alternative FRs [62]

Screening Level Toxicology Hazard Summary of EPA study



US EPA, FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS, Draft Report 11/2008

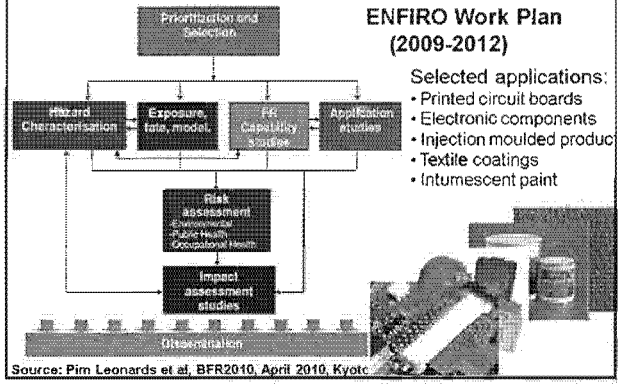


European Research Project ENFIRO: LCA of Environment-Compatible Flame Retardants

- **Objective of ENFIRO: To study the substitution options for specific BFRs by a prototypical approach.**
- **ENFIRO offers a prototypical case study on substitution options resulting in a comprehensive dataset on the viability of production, application, and environmental safety, including a life cycle assessment (LCA)**
- **This will finally result in a recommendation of certain FR/product combinations. The case studies will give recommendations for industrial and governmental stakeholders.**

http://www.enfiro.eu/

European Research Project ENFIRO: LCA of [65] Environment-Compatible Flame Retardants



Source: Pim Leonards et al, BFR2010, April 2010, Kyoto

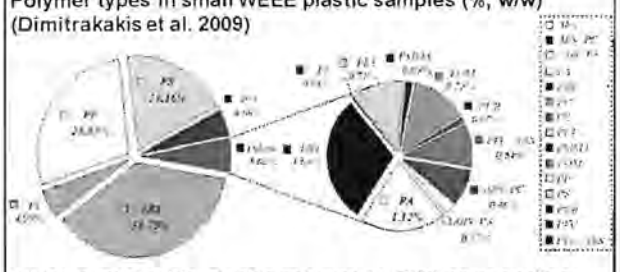
Ecological Priorities for [65] Choice of Flame Retardants

Recommendation German Environmental Agency (2008)

1. Measures for reduction of the flame retardant in product design (use of less flammable materials, introduction of fire walls, adoption of the amount of flame retardant to the demand)
2. Inorganic flame retardants (Aluminiumhydroxid, Magnesiumhydroxid, red Phosphorus, NH3-polyphosphat).
3. Reaktive embedded, halogen free organic Nitrogen- and Phosphorus-compounds
4. Additive halogen free organic Nitrogen- and Phosphorus-compounds, non persistant, non-bioaccumulating without long-term human toxic or ecotoxic effects
5. Reactive embedded halogenated flame retardants.
6. Additive halogenated flame retardants which are non persistent, non-bioaccumulating without long-term human toxic or ecotoxic effects.

Sustainable Production: Recyclability Polymers

Polymer types in small WEEE plastic samples (%, w/w)
(Dimitrakakis et al. 2009)



- Non sustainable plastic mixture in EEE as recycling challenge (can not be moulded but must be separated)!
- Stability of flame retardants & polymers in recycling

Recommendation/Conclusion

- (Organic) Chemicals need to be evaluated for their Persistence, Bioaccumulation and Toxicity before bulk production starts (concept of REACH). This is crucial to address global chemical contamination. For most FR applications alternatives to BFRs are on the market. Currently large research projects on total LCA of BFRs & alternatives in EU and US.
- Toxicological assessment of alternative needed.
- End of life/recycling performance of alternatives.
- The most sustainable chemicals („Green Chemistry") and sustainable products („Green Design") are likely to survive on the market. Several excellent Chinese research groups work on alternative flame retardants!!

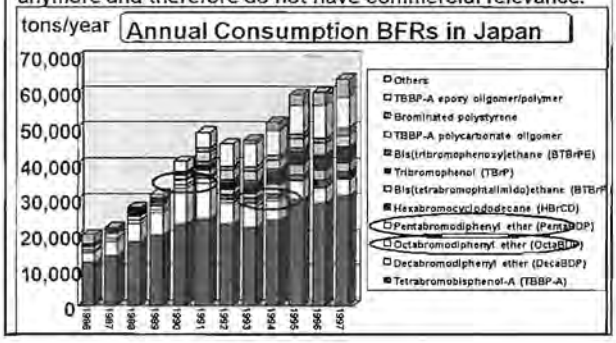
Thank you for your attention!

Assessment:
PFOA, PFXSi, PFHx
DeBDE,HBCDD,PBE
PBDD/F, HBBz, PBF
TBBPA, TBPAE,
SCCP, MCCP,
PCN, HCBD, OCS,
PCP, PCNB
PAHs, Nitro-PAH
Halogenated PAHs
PT-Pesticides,
PT-Biocides
PT-Pharmaceuticals
PT-Siloxanes
Sn-Organics
Hg, Cd, Pb et al.

www.pops.int www.saicm.org www.ipen.org
http://www.springerlink.com/content/6q10km8582605r1x/fulltext.pdf

Stockholm Convention POPs - From "Dead" to "Live" Chemicals

Most current Stockholm Convention POPs are not produced anymore and therefore do not have commercial relevance.



Information and further Research: Contribution from Research Community

- Risk assessment of recycling scenarios and end of life treatments in industrial and developing countries considering multiple pollutants.
- Global substance flow analysis of PBDE (other critical BFRs and PBTS) in products and recycling.
- PBDE (BFR) contaminated sites from production, application and end of life treatment.
- External cost estimates/calculations of harm caused by PBDE/BFRs to humans and biota.
- Life Cycle Assessment of PBDE alternatives (other flame retardants and alternative technologies).

Study on DBDPE

- Now higher production volume then DecaBDE.
- Only few debromination studies (key question for the assessment of fate of DecaBDE).
- Analysis of Mono to NonaBDPE not available.
- What are other degradation products? (thermal, photolysis, sediments).
- What is persistence and toxicity of degradation products?

Study on Chlorinated Paraffins

- Short, medium & long chain chlorinated paraffins
- 1 million tons production (mainly China & India).
- Substance flow and LCA of CCPs
- Env./human fate of chlorinated paraffins.
- Degradation products of chlorinated paraffins (hydroxy-, carboxy-metabolites?)
- What are UPOPs in these materials?

Annex VI

E-waste management including e-waste plastic in China

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

Relevant regulative action on import of e-waste

- Administrative Measures for the Import of Solid Waste (2011)
  - Catalogue for the Administration of the Import of Solid Waste (2009 version, 2015 version, Announcement No. 69/2015)

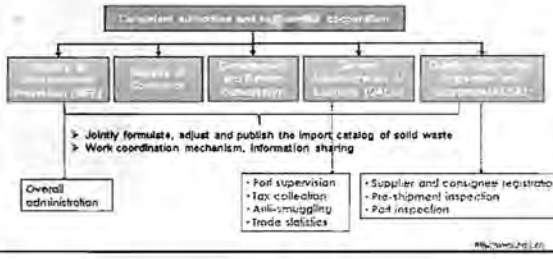
Catalog	Types of e-waste included	Types of import control
Catalog of Solid Waste Prohibited from Importation	• waste batteries • 9 types of waste mechanical and electrical products, home appliance, office appliance, etc	• Prohibited to import
Catalog of Solid Waste that Can Be Used as Raw Materials under Import Restrictions	• scrap motor • metal and electrical appliance scraps • scrap wires and cables	• Require import permit • Meet environmental standards and inspection and quarantine rules
Catalog of Solid Waste that Can Be Used as Raw Materials not under Import Restrictions (former "Automatic Import Licensing", revised on 19 Nov. 2016)	No e-waste	• Meet environmental standards and inspection and quarantine rules

Relevant regulative action on import of e-waste

Standards and rules for certain e-waste:

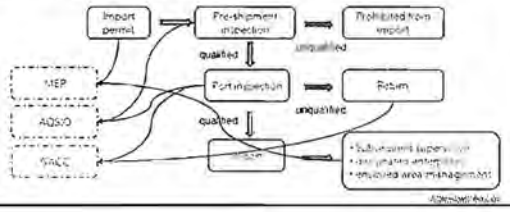
- Environmental protection control standard for imported solid wastes as raw materials – Waste electric motors (GB 16487.8—2005); Waste wires and cables (GB 16487.9—2005); Metal and electrical appliance scraps (GB 16487.10—2005)
- Rules for the inspection and quarantine of waste imported as raw material —Part 6: Scrap metal and electrical appliance (SN/T 1791.6—2006); Part 7: Scrap wires and cables (SN/T 1791.7—2006); Part 8: Scrap motor (SN/T 1791.8—2006)

Relevant regulative action on import of e-waste

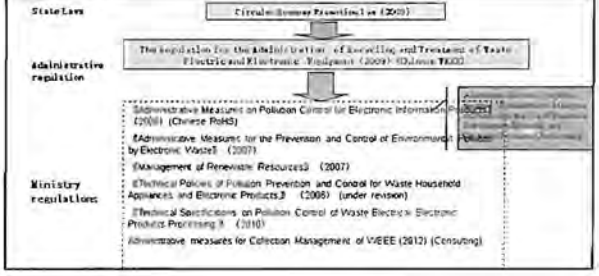


Relevant regulative action on import of e-waste

- Management procedures for the import of scrap motor, scrap metal and electrical appliance, and scrap wires and cables:



E-waste management



E-waste management

Catalogue	• 《The catalogue of disposal of Waste Electrical and Electronic Equipment (the first batch)》Sep. 2010
Plan	• 《Notice on the formation of the Development Plan of the treatment and Disposal of Waste Electrical and Electronic Products (2011-2015)》, Sep. 2010 • 《Guide on the Development Plan of the treatment and Disposal of Waste Electrical and Electronic Products》, Nov. 2010
Permit	• 《Administrative Measures on Qualification Permit of the treatment and disposal of Waste Electrical and Electronic Products》 • 《Guide on Qualification Verification and Approval on treatment Enterprises of Waste Electrical and Electronic Products》, Dec. 2010
Information System	• 《Guide on Establishment of Data Information Management System and Information Submission of treatment Enterprises of Waste Electrical and Electronic Equipment》, in Nov.2010
Fund	• 《Administrative Measures on Collection and Use for treatment Fund of Waste Electrical and Electronic Equipment》effective since July,2012 • Guide on Subsidy Approval of treatment Enterprises of Waste Electrical and Electronic Products, in Nov. 2010

E-waste collection

- The Regulation for the Administration of Recycling and Treatment of Waste Electric and Electronic Equipment (2009) (Chinese WEEE) regulates multi-channel collection system.
- The existing e-waste collection system is a mixed system with the traditional collection and collection under the national policy guidance .

E-waste collection

➢ Traditional collection

Characteristics
• Driven by interest • regional • Flexible operation • Difficult to supervise • Mainly flow to waste material collection market, small workshop and second-hand market

Individual collector | Repair store | Second-hand market

E-waste collection

- Production enterprise collection -reverse logistics
  Through the sales or repairing store, service agencies

Advantage	Disadvantage
• Big coverage of collection network • Open channels for the consumers	• No mandatory provisions and effective encouraging mechanism, low enthusiasm

- Treatment enterprise Collection

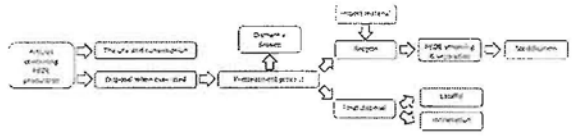
  Self-construction collection pots and recycling network, such as through telephone and online trading, to collect e-waste from residents.
  For example,
  • Beijing residents could login in the website
  ( )
  • Shanghai residents could login in the website ( ) to deal with e-waste.

Development foundation of e-waste treatment facilities

1. Included in the planning and obtaining permits
2. Best available technology and best environmental practice on e-waste recycling
   - Make full use of the abundant human resources in developing countries;
   - Consider the requirements of human health and environmental protection
3. Financial support by the Funds

E-waste treatment facilities

China experience on treatment of WEEE plastic



The material flow of articles containing PBDE

Existing separating technologies of PBDEs containing materials in China

Waste plastic mixture separation technology can be divided into two categories:

➢ Dry method
- light separation;
- electrostatic separation;
- wind power separation.

➢ Wet method
- density separation;
- sink and float separation.

Basel and Stockholm BAT/BEP guidance

Under the Convention, Best Available Techniques (BAT) are defined as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole".

Best Environmental Practices (BEP) are defined as "the application of the most appropriate combination of environmental control measures and strategies."

Basel and Stockholm BAT/BEP guidance

Practical example of successful implementation of BAT and BEP

Kitakyushu's Experience in Getting Pollution under Control

1960s Today

https://chm.pops.int/Implementation/BATandBEP/Guidance/tabid/4838/Default.aspx

BAT and BEP Guidance

Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Articles 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants

Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants

Guidance on best available techniques and best environmental practices for the recycling and waste disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs

THANKS

Contacts:

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific
Add Sino-Italian Environmental and Energy Building, Tsinghua University
Tel 86 10 62794351 Fax 86 10 62772048
Email

Testing of PBDE samples and challenge of PBDE analysis

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

27th Nov. 2015

http://www.brcs.cn

Contents

- Testing of PBDE samples
- Challenge of PBDE analysis

http://www.brcs.cn

01 Testing of PBDE samples

http://www.brcs.cn

Testing of PBDE samples

PBDE screening method

- ✓ Sliding spark spectroscopy : Is a surface screening destructive method capable to rapidly detect halogens in plastic without prior sample preparation. The scanning time takes only a few seconds. The lowest detection limit for bromine with this technology is 0.1%.
- ✓ X-ray fluorescence (XRF) : is a non-destructive method and can be used for detection of bromine in polymers and other materials with a detection limit for bromine of 10 to 100 ppm. The time requirement for a measurement when applying handheld items is less than a minute.
- ✓ Above two methods are labour intensive, but it is not a barrier in developing/transition countries with lower wages.

Testing of PBDE samples

- ✓ X-ray transmission technology (XRT) : The XRT is non-mobile equipment applied in dismantling plants to sort scrap plastic by automatically monitoring the atomic density of materials. Industrial machines sort up to 1 tonne of scrap per hour.
- ✓ Sink and float technology : Polymer types exhibit different specific weights, and therefore liquid media with appropriate densities allow for separation of different thermoplastics into density groups.
- ✓ Raman spectroscopy : is mainly implemented in an experimental stage.
- ✓ Neutron activation analysis : this technique can only be applied in laboratory, the instruments are rather expensive and of limited practicability as nuclear expertise is required.

http://www.brcs.cn

Testing of PBDE samples

Instrument of XRF-1800

http://www.brcs.cn

Testing of PBDE samples

- ✓ Gas chromatography/mass spectrum(GC/MS) , is the most popular method to analyse PBDE in plastic and environmental media.
- ✓ High performance liquid chromatography/mass spectrum(LC/MS) , is another popular method to analyse PBDE in plastic and environmental media.
- ✓ Other detection techniques , Sensitive electron ionization mass spectrometry

Testing of PBDE samples

Gas Chromatograph-Mass Spectrometer (GC/MS) analysis

Testing of PBDE samples

- Equipment

✓ A gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) is used for the analysis. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 1 000 m/z. The high-range mass is required to unambiguously identify decaBDE and nonaBDE. The use of an autosampler is strongly recommended to ensure repeatability.

✓ A column length of approximately 15 m has sufficient separation efficiency for PBB and PBDE compounds.

Testing of PBDE samples

- International Standard

International Standard IEC 62321 Ed.1 (International Electrotechnical Commission, 2008) has been developed for determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, PBDEs) in electrotechnical products. The determination of PBDEs (monoBDE to decaBDE) in polymers by gas chromatography with mass spectroscopy (GC-MS) is described in Annex A to IEC 62321, including extraction, analysis and quality assurance.

- operation staff

Operation staff need well trained.

Testing of PBDE samples

Gas Chromatograph-Mass Spectrometer (GC/MS) analysis

- The popular technique used to detect PBDEs in plastic products in China.
- There are two standard methods in China:

□ National standard method named Determination of Restricted Substances (Polybrominated biphenyls and polybrominated diphenyl ethers) in Electrical and Electronic Equipment (GB/Z21276-2007).

□ Industrial standard method named Testing Methods for Hazardous Substances in Electronic Information Products (SJ / T11365-2006).

Testing of PBDE samples

Take National standard, GB/Z21276-2007 as an example:

Testing of PBDE samples

1. Sample pretreatment

- Sample size
  samples are ground to a size less than 1 mm using the crush method
- Sample quality
  0.5-2g
- Extraction solvent
  for Soxhlet extraction, the solvent is toluene and n-propanol;
  for microwave extraction, the solvent is toluene and methanol
- Extraction time and rate
  at least 30 extraction cycles, about 6 hours

Testing of PBDE samples

- **Addition of the internal standard (IS)**

Add C13-pendaBDE, C13-octaBDE or DBOFB(4,4'-dibromoctafluorobiphenyl)

- **Calibration**

A calibration curve shall be developed for quantitative analysis. At least five calibration solutions shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the peak areas. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

Testing of PBDE samples

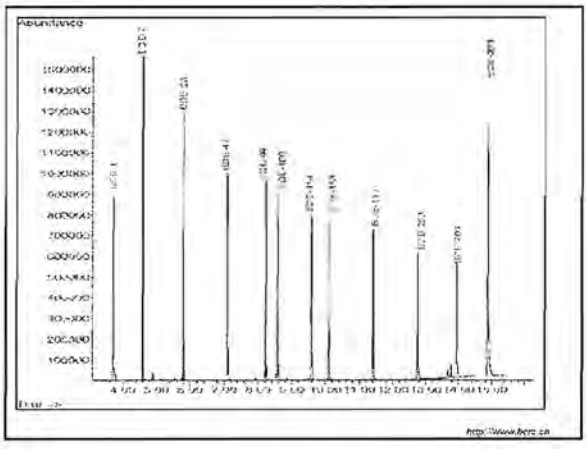
2. Equipment condition

- Gas chromatography condition
  the GC column is fused quartz capillary column length 15 m, internal diameter 0.25 mm, film thickness 0.1 μm (DB-5MS)
- Injector
  pulse without split, the temperature is 250-320° C, and the injection volume is 1-2μL
- Carrier 1.8 mL/min
- Transfer line 320° C
- Ionization method ion source temperature is 300 ° C

Testing of PBDE samples

Quality control method

- One reagent blank shall be extracted with each sequence of samples.
- One sample per sequence or one every ten samples, depending on the sample load, shall be spiked with 10 μg of each congener in the matrix spiking solution.
- A solvent blank run between each injection is recommended in order to be certain that there is no analyte carry-over from sample to sample.
- More details please see IEC62321-2008



02 Challenge of PBDE analysis

Challenge of PBDE analysis

1. Challenges of sampling

Precise sampling is a difficulty. Take a discarded computer as an example. There are many plastic parts in a computer, such as shells, cables, fans, plug and so on. It is difficult to identify which parts of plastic contain PBDEs or some other brominated compounds by visual detection.

Challenge of PBDE analysis

2. Challenges of sample pretreatment
   - Because different types of plastics have distinct characteristics, the crushing methods should change according to the sample
   - Different types of plastics need different solvents, which need many research work to select proper solvent for different plastics.
   - Many extracting solvents can dissolve the polymer which increase the solution viscosity and jam the injector
   - Long time for pretreatment

Challenge of PBDE analysis

3. Can not be used on site
4. Cost is high(include maintainance cost, operation cost, investment cost, standard sample cost etc.)
5. Etc.

THANKS

Contacts:

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific
Add: Sino-Italian Environmental and Energy Building, Tsinghua University
Tel: 86 10 62794351 Fax: 86 10 62772048
Email:

Objectives of the workshop on sound management of PBDEs and phasing-out opportunities in Sri Lanka

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

Objectives

Workshop on sound management of PBDEs and phasing-out opportunities in Sri Lanka

- A part of a project "Support developing Parties to phase-out industrial Persistent Organic Pollutants"
- Facilitate the understanding of national situations regarding industrial POPs, in particular the brominated diphenyl ethers (POP-PBDEs) in one typical usage area and containing articles, while promoting the environmental sound management of them in the target Asian countries
- An opportunity to find the regional need for POPs management

Objectives

- To promote the information platform and share the outcomes and experiences, including lessons learned.
- To create a communication channel for advanced experience on international POPs.
- To explore possibilities to develop a regional strategy to promote environmentally sound POPs management.
- To explore potential collaboration in the future.

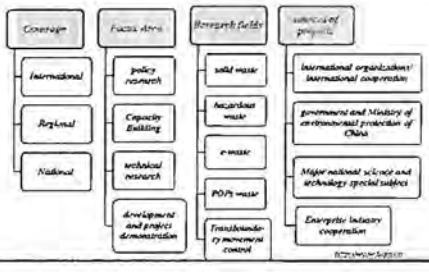
Basel Convention Regional Centre for Asia and the Pacific

Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

Functions and Roles

Function	• Training , Information • Awareness Raising, Consulting • Technology Transfer
Regional Role	• To assist the developing countries to implement BC and SC in Asia and the Pacific through all kinds of activities.

Main Fields



General introduction

- Until now over 180 projects has been completed or being implemented by BCRC China, financed by international organizations including the Strategic Approach to International Chemicals Management (SAICM), Trust Fund (BC) and Technical Cooperation Trust Fund (BD) for the Basel Convention, bilateral cooperation finance from governments of Netherlands, Japan and other countries, finance from ministries of China including Ministry of Environmental Protection, Ministry of Science and Technology, and provincial and city Environmental Protection Agencies, and cooperation finance from industries.
- The contents involve policy studies, experiment analysis, technology research and development, project demonstrations, etc. And the research areas cover solid waste, hazardous waste, e-waste, POPs, and support for convention implementation.

E-Waste

- China Fluorescent Lamps collection and treatment demonstration project, EU-China ESP, 2013-2016
- Study on the Best Environment Practices of Producers on E-Waste Management (Case study on Mobile Phone), 2015-2016
- Assessing the Status of E-waste Recycling in Selected Countries in the Asia-Pacific Region and Facilitating the Environmentally Sound Management of E-waste, The secretariat of Basel Convention, 2014
- Study on the "The Regulations for the Administration of Recycling and Treatment of Waste Electric and Electronic Equipment "and supporting policies in China, Ministry of Environmental Protection of China, 2011-2013.
- Studying the Labour, Human Health and Environment Dimensions of the E-waste Management Sector in China, International Labour Organization, 2011
- Development of a Public-Private Partnership for E-waste Collection, the Secretariat of Basel Convention, 2010-2011.

POPs Management

Recent specific projects:

- Support developing Parties to phase-out industrial Persistent Organic Pollutants (POPs), 2014-2015
- Project on the sound management of POPs in articles and passing-out opportunities on emerging countries, 2013-2014
- Sound Management of POPs in article and phasing -out opportunities in developing countries and emerging economies, 2012-2013

Training and workshop

- ➢International
- ➢Regional
- ➢National

- ➢Hazardous waste
- ➢E-waste
- ➢POPs

- ➢More than 60 meetings
- ➢More than 3000 participants
- ➢More than 50 countries

[illegible]

The conference was organized by BCRC China , is held annually since 2005

- More than 500 delegates from 32 countries and regions of enterprises, research institute and waste management centers participated in the 2015 conference (ICWMT 10)
- Topic include e-waste, sludge, hazardous waste, industrial solid waste, contaminated sites, circular economy, POPs waste

THANKS

Contacts:

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific
Add: Shanghai Environmental and Energy Building, Tsinghua University
Tel: 86 10 62784051 Fax: 86 10 62772048
Email:

Objectives of the workshop on sound management of PBDEs and phasing-out opportunities in Sri Lanka

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

Objectives

Workshop on sound management of PBDEs and phasing-out opportunities in Sri Lanka

- A part of a project "Support developing Parties to phase-out industrial Persistent Organic Pollutants"

- Facilitate the understanding of national situations regarding industrial POPs, in particular the brominated diphenyl ethers (POP-PBDEs) in one typical usage area and containing articles, while promoting the environmental sound management of them in the target Asian countries
- An opportunity to find the regional need for POPs management.

Objectives

- To promote the information platform and share the outcomes and experiences, including lessons learned.
- To create a communication channel for advanced experience on international POPs.
- To explore possibilities to develop a regional strategy to promote environmentally sound POPs management.
- To explore potential collaboration in the future.

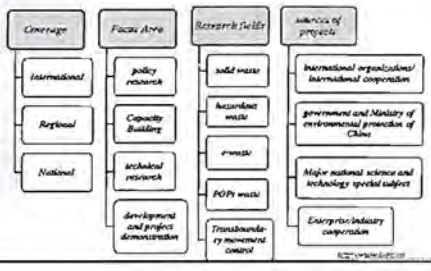
Basel Convention Regional Centre for Asia and the Pacific

Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific

Functions and Roles

Function	• Training , Information • Awareness Raising, Consulting • Technology Transfer
Regional Role	• To assist the developing countries to implement BC and SC in Asia and the Pacific through all kinds of activities.

Main Fields



General introduction

- Until now over 150 projects has been completed or being implemented by BCRC China, financed by international organizations including the Strategic Approach to International Chemicals Management (SAICM), Trust Fund (BC) and Technical Cooperation Trust Fund (BD) for the Basel Convention, bilateral cooperation finance from governments of Netherlands, Japan and other countries, finance from ministries of China including Ministry of Environmental Protection, Ministry of Science and Technology, and provincial and city Environmental Protection Agencies, and cooperation finance from industries.
- The contents involve policy studies, experiment analysis, technology research and development, project demonstrations, etc. And the research areas cover solid waste, hazardous waste, e-waste, POPs, and support for convention implementation.

E-Waste

- China Fluorescent Lamps collection and treatment demonstration project, EU-China ESP, 2013-2016
- Study on the Best Environment Practices of Producers on E-Waste Management (Case study on Mobile Phone), 2015-2016
- Assessing the Status of E-waste Recycling in Selected Countries in the Asia-Pacific Region and Facilitating the Environmentally Sound Management of E-waste, The secretariat of Basel Convention, 2014
- Study on the "The Regulations for the Administration of Recycling and Treatment of Waste Electric and Electronic Equipment "and supporting policies in China, Ministry of Environmental Protection of China, 2011-2013.
- Studying the Labour, Human Health and Environment Dimensions of the E-waste Management Sector in China, International Labour Organization, 2011
- Development of a Public-Private Partnership for E-waste Collection, the Secretariat of Basel Convention, 2010-2011.

POPs Management

Recent specific projects:

- Support developing Parties to phase-out industrial Persistent Organic Pollutants (POPs), 2014-2015
- Project on the sound management of POPs in articles and passing-out opportunities en emerging countries, 2013-2014
- Sound Management of POPs in article and phasing -out opportunities in developing countries and emerging economies, 2012-2013

Training and workshop

	➢International ➢Regional ➢National
Focus	➢Hazardous waste ➢E-waste ➢POPs
Quantity	➢More than 60 meetings ➢More than 3000 participants ➢More than 50 countries



The conference was organized by BCRC China , is held annually since 2005

- More than 500 delegates from 32 countries and regions of enterprises, research institute and waste management centers participated in the 2015 conference (ICWMT 10)
- Topic include e-waste, sludge, hazardous waste, industrial solid waste, contaminated sites, circular economy, POPs waste

THANKS

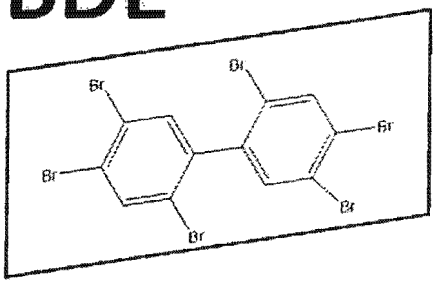
Contacts:

Basel Convention Regional Centre for Asia and the Pacific
Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific
Add: Sino-Italian Environmental and Energy Building, Tsinghua University
Tel: 86 10 62794351 Fax: 86 10 62772048
Email:

Annex VII

PBDE in Sri Lanka – Assessment and Management

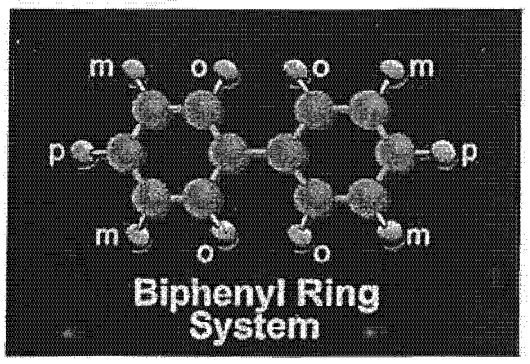
PBDE



Team PBDE

- Min of Environment
- Central Environmental Authority
- Industrial Technology Institute
- Ministry of Health
- University of Moratuwa

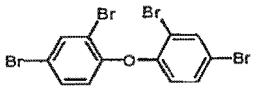
PBDE

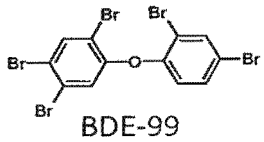


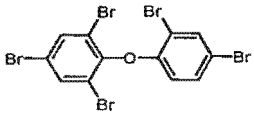
A new entrant into POPs'

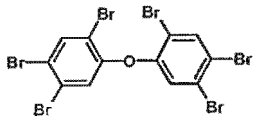
PBDE Commercial Mixtures and Major Congeners

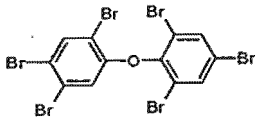
Penta


BDE-47

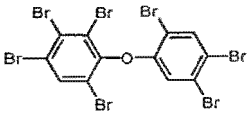

BDE-99


BDE-100

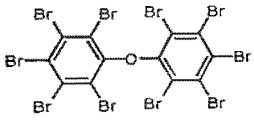

BDE-153


BDE-154

Octa

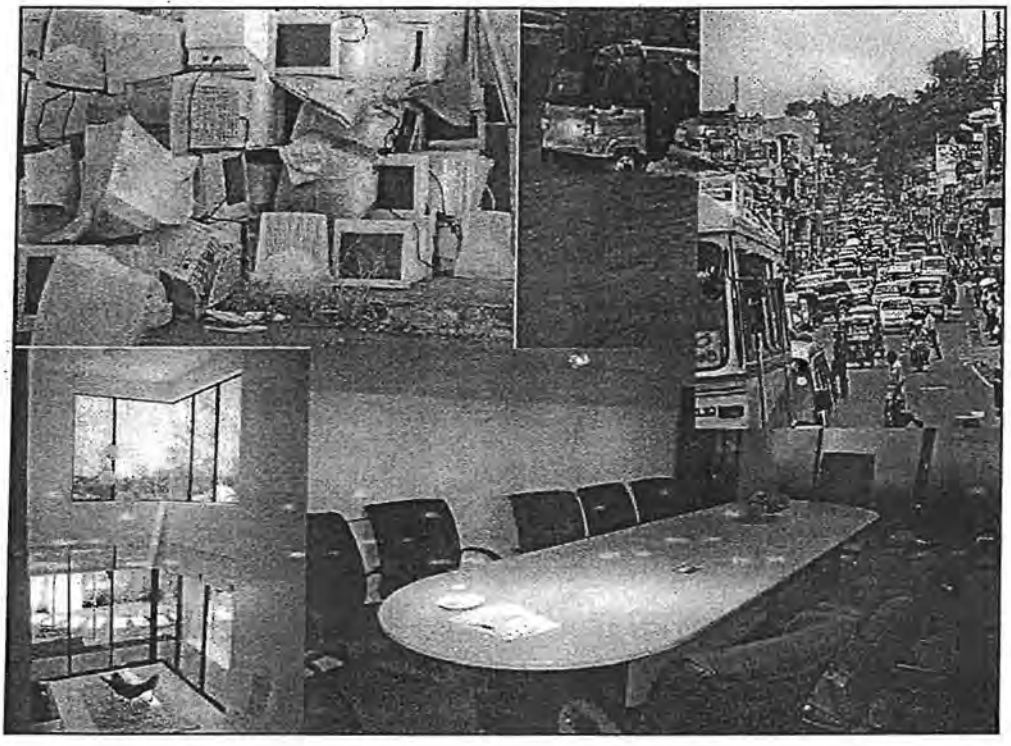

BDE-183

Deca


BDE-209

PBDE Study - Background

- National Inventory development for specific chemicals
- **Nature of Chemicals entry to Sri Lanka**
- Objective of the inventory
- **Implementation of international conventions**
- Understanding the chemicals management environment



National PBDE Inventory and Action Plan

Step by step inventory approach

Step 1: Planning the Inventory

Step 2: Choosing data collection methodologies

Step 3: Collecting and compiling data from key sectors

Step 4: Managing and evaluating the data

Step 5: Preparing the inventory report

Scope and Stakeholders

Identify key stakeholders

- Ministry of environment and ministry of industry;
- Basel Convention focal point (and stakeholders in Basel activities on e-waste) ;
- Importers and exporters of electronics ;
- Retailers of electronics and second-hand electronics;
- Recyclers of WEEE;
- Recyclers and users of polymers from WEEE;
- Research group working on EEE/WEEE
- NGOs working on WEEE/POPs ;
- Other relevant stakeholders in the country.

Define inventory scope

- Second-hand EEE imported in the inventory year and the previous years (base for estimating stocks);
- EEE stocks (in use and/or stored in the possession of consumers);
- EEE entering the waste stream, i.e. WEEE;
- WEEE plastics for recycling (from domestic WEEE and imported WEEE polymer fraction).

PBDE in EEE

Total POP-PBDEs in EEE can be calculated as:

- $M_{PBDE(i)} = M_{EEE(j)} \times f_{Polymer(k)} \times C_{PBDE(i);Polymer(k)}$

amount of POP-PBDEs (*i*) in [kg]

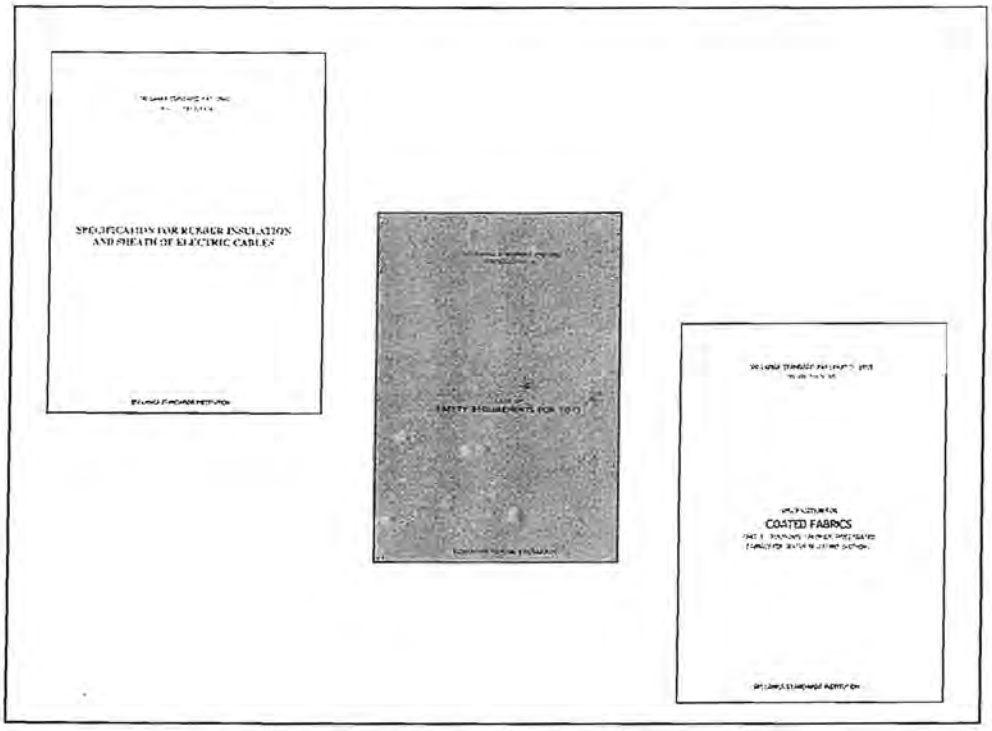
amount of EEE (*j*) in [in tonnes]

total polymer fraction in [weight-%]

content of the POP-PBDEs (*i*) in the total polymer fraction in [kg/tonne]

Information needed

- an inventory of stocks and flows of EEE/WEEE
- the share of the polymers in different EEE/WEEE categories
- the POP-PBDE content of those polymers



The amount of c-OctaBDE in stockpiled CRT computer and TV monitors during the period of 2007-2014

HS Code	$M_{EEE(j),Stockpiled}$ [tonnes]	$f_{Polymer}$ [% by weight]	$C_{c\text{-}OctaBDE,Polymer}$ [kg/tonne]	$M_{c\text{-}OctaBDE,\ Stockpiled\ EEE(j)}$ [kg]
85.28.41	5780.77	30	2.54	4404.95
85.28.49.01	1.23	30	0.87	0.32
85.28.49.09	8.85	30	0.87	2.31
85.28.49.10	17.79	30	0.87	4.64
85.28.49.90	12.03	30	0.87	3.14
The sum of POP-PBDEs (c-OctaBDE) in all stockpiled CRT computer and TV monitors				4415.36

The amount of c-OctaBDE in waste CRT computer and TV monitors for the inventory year

HS Code	$M_{EEE(j),Stockpiled}$ [tonnes]	$ls_{EEE(j)}$ [years]	$M_{WEEE(j)}$ [tonnes]	$f_{Polymer}$ [% by weight]	$C_{c\text{-}OctaBDE,Polymer}$ [kg/tonne]	$M_{c\text{-}OctaBDE,WEEE(j)}$ [kg]
85.28.41	5780.77	8	722.5963	30	2.54	550.62
85.28.49.01	1.23	8	0.15375	30	0.87	0.04
85.28.49.09	8.85	8	1.10625	30	0.87	0.29
85.28.49.10	17.79	8	2.22375	30	0.87	0.58
85.28.49.90	12.03	8	1.50375	30	0.87	0.39
The sum of POP-PBDEs (c-OctaBDE) in CRT computer and TV monitors entering the waste stream						551.92

The amount of POP-PBDEs present in EEE and WEEE

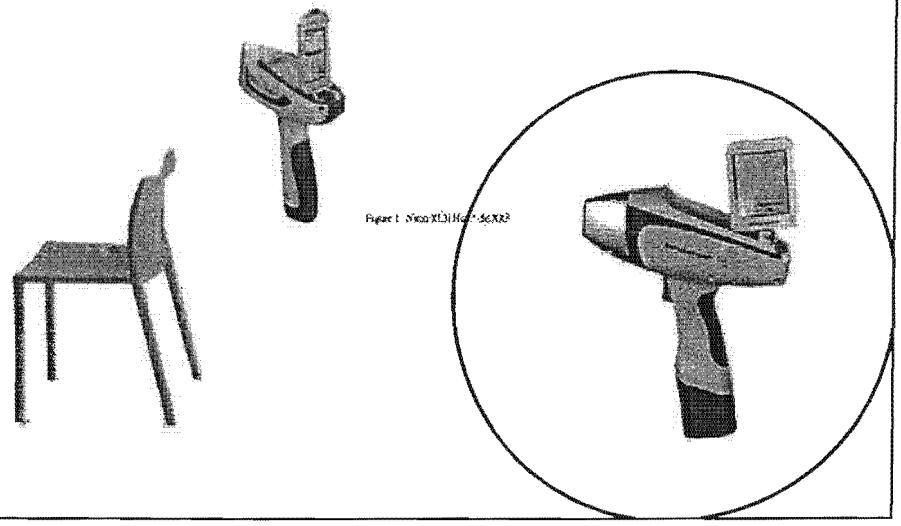
The sum of POP-PBDEs	POP-PBDEs in EEE stocks for inventory year 2014 [kg]	POP-PBDEs entering the waste stream for inventory year 2014 [kg]
c-OctaBDE	$\Sigma M_{c\text{-}OctaBDE;\ Stockpiled\ EEE(j)}$	$\Sigma M_{c\text{-}OctaBDE;WEEE(j)}$
	4415.36	551.92

Total amount of POP-PBDEs in PUR foam of vehicles in current use or sale

Vehicle category	$M_{c\text{-}PentaBDE;\ Category}$ [kg]		
	Originated from US region	Originated from other regions	Total
Motor cars	38.04	1307.92	1345.96
Busses	113.54	1819.95	1933.49
Dual purpose vehicles	3.16	1054.32	1057.49
Motor lorries	219.36	888.29	1107.65
Total	374.11	5070.48	5444.59

Moving Forward after Inventory

Suggested handheld XRF equipment
Model: Niton XL3t Handheld XRF , Manufacturer Thermo Scientific USA

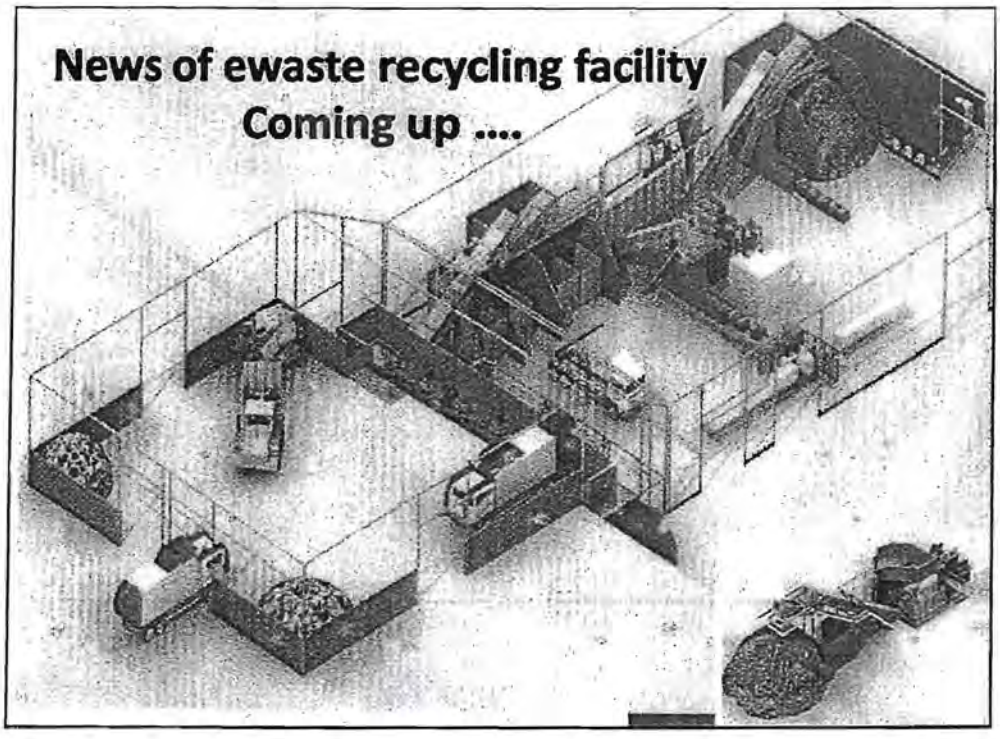


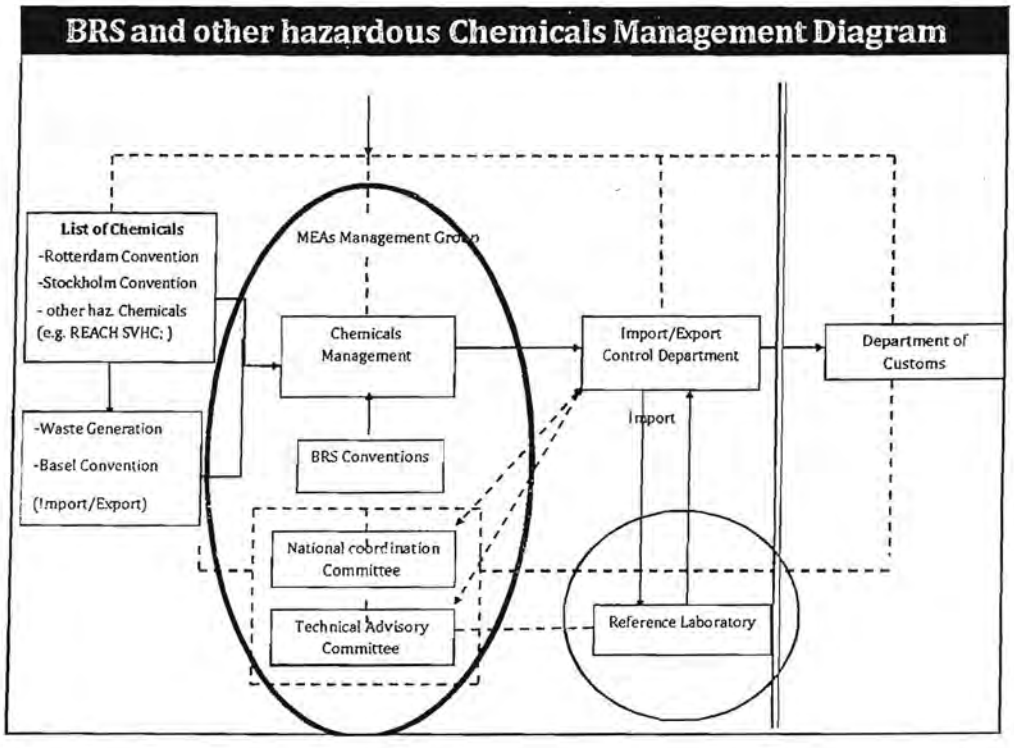
PBDEs measured in WEEE plastics (EU 2010)

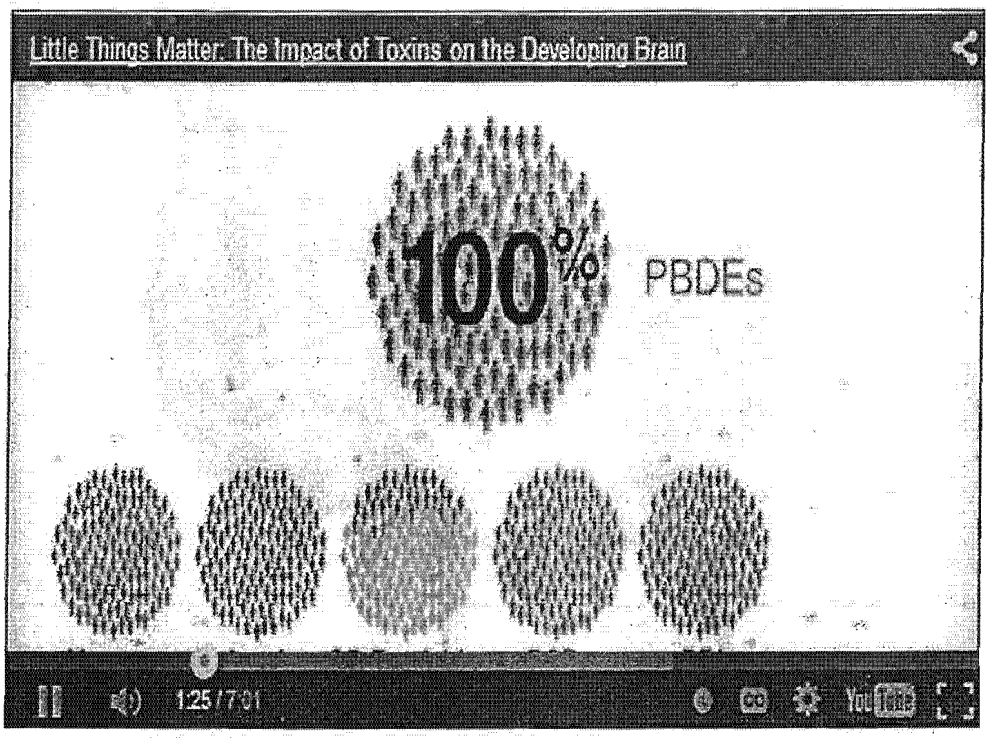
		Penta BDE	Octa BDE	Deca BDE
WEEE Category	Large household appliances w/o cooling and freezing appliances			ABS PP
	Small household appliances			
	ICT equipment without CRT- and flat screens		ABS	ABS HIPS
	Consumer equipment without CRT- and flat screens		ABS	ABS HIPS

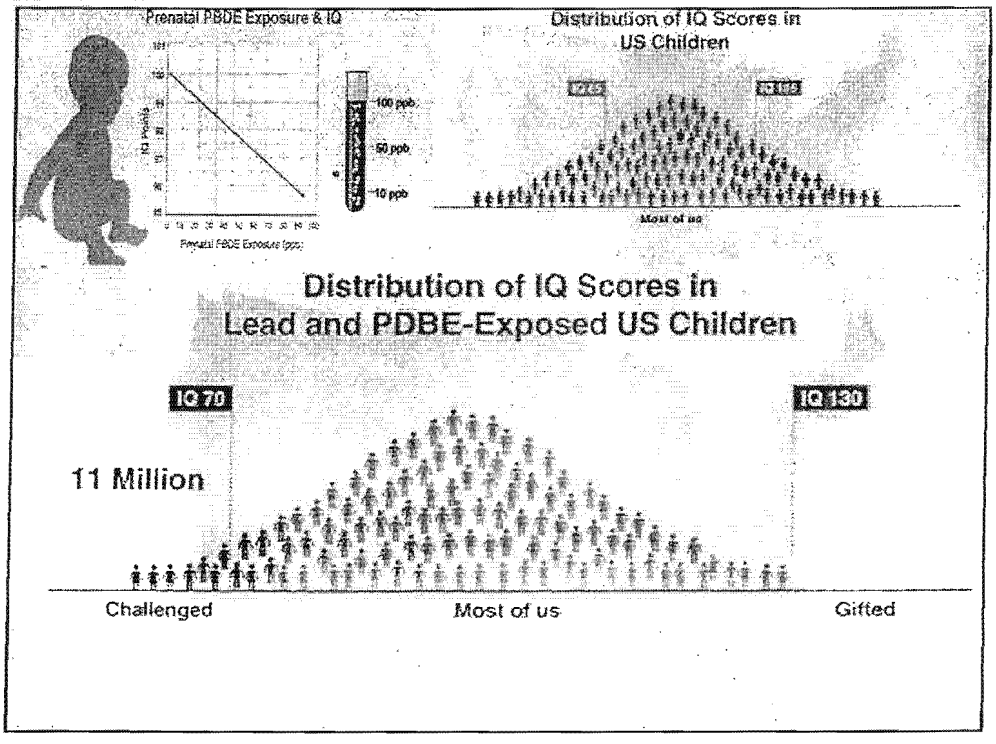
	not detected or at average concentrations clearly (i.e. more than an order of magnitude) below the RoHS Directive maximum concentration value (MCV) of 0.1%
	average concentrations below (yellow cells) or in the vicinity (orange cells) of the RoHS MCV
	average concentrations above the RoHS MCV of 0.1%
XXX:	plastic type predominantly containing the substance

(Source: Wäger et al. 2010; Wäger et al. 2012)


News of ewaste recycling facility
Coming up ....


BRS and other hazardous Chemicals Management Diagram
List of Chemicals
-Rotterdam Convention
-Stockholm Convention
- other haz. Chemicals
(e.g. REACH SVHC;)
-Waste Generation
-Basel Convention
(Import/Export)
MEAs Management Group
Chemicals Management
BRS Conventions
National coordination Committee
Technical Advisory Committee
Import/Export Control Department
Import
Reference Laboratory
Department of Customs


Little Things Matter: The Impact of Toxins on the Developing Brain
100%
PBDEs
1:25 / 7:01


Prenatal PBDE Exposure & IQ
Distribution of IQ Scores in US Children
100 ppb
50 ppb
10 ppb
Distribution of IQ Scores in
Lead and PDBE-Exposed US Children
IQ 70
IQ 130
11 Million
Challenged
Most of us
Gifted