<sup>1</sup> 2nd International Online Seminar about Persistent Organic Pollutants Experiences in Best Available Techniques & Best Environmental Practices

## Expert forum: Experiences in BFR-POP management

# Some Basic Information & Stockholm Convention PBDE BAT/BEP Guidance

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BFRs are contained in large material/waste flows

- Need for environmental sound management
- **BFRs (**e.g. **PBDEs, HBCD, TBBPA, DBDPE, TBP, TBB, HBBz, PolyFR)** are contained in large product/waste categories of plastic/polymers
- Plastic electrical & electronic equipment (e.g. computer, TVs);
- Plastic/upholstery in transport sector (cars/vehicles, trains, planes);
- Insulation in construction materials (presently increasing with increasing incentives for insulation of houses);
- Certain impregnated textiles, curtains, furniture, mattresses.

Link to total plastic waste management!



- (B)FR impacted plastic as risk for environmental pollution<sup>3</sup> In addition to BFR/POPs stock/waste, the plastic/polymer sectors:
- Are a major fuel for open waste burning & release (POPs, UPOPs, PM)
- A source of land based plastic pollution;
- A major source of marine litter and contamination of the Sea.

Distribution of European (EU28+NO/CH) plastics converter demand by segment 2016



Source: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

# Brominated flame retardants & POPs in products and related waste & recycling challenge



POPs: HBCDD, Penta/Octa/DecaBDE, HBB

- Electrical devices (e.g. computer, cables) ending up in E-waste Recycling/treatment WEEE plastic.
- Transport sector (plastic, textile and upholstery in cars, trains, air plane)<sup>Brm</sup> Recycling/treatment of plastic/polymers.
- Insulation in construction materials (EPS/XPS, PUR, PIR increasing with GHG incentives for insulation of buildings); Recycling/treatment of insulation/others.
- Textiles/furniture (Clothes, curtains, carpet, US: kids sleep wear, mattress ticking; PUR) Recycling/treatment of textiles; PUR.



### Plastic share and volume in WEEE categories

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- The average plastic share in WEEE is approximately 20%.
- WEEE by 2019 is ca. 50 million t/a including **10 mio t/a WEEE plastic**.

WE	EE Category/Product Category	Plastic share [in % by weight]	Annual plastic flow [in t/year]		
1	Large household w/o cooling appliances	19%	500'500		
1	Cooling and freezing appliances	28%	473'100		
2	Small household appliances	37%	369'400		
3	ICT equipment w/o screens	42%	317'600		
3	Computer screens (CRT and flat)	20%	156'100		
4	Consumer equipment w/o screens	24%	180'900		
4	TV screens (CRT and flat)	20%	200'100		
5	Lighting equipment – Lamps	3%	7'300		
6	Electrical and electronic tools	11%	37'800		

FR Industry state that the annual recycling potential for FR plastics is roughly **2.7 million** tonnes, equaling a business potential of about 8 billion and a potential CO2 reduction of up to 8 million tonnes (EFRA, 2013; Plastic News, 2013).

10	Automatic dispensers	20%	3'500
	Total amount	Average of 20%	2'266'100

Estimation of the total plastic quantities in European WEEE for the year 2008. Printed wiring boards and cables are not included. (Source: Wäger et al. 2010)

### Moving towards more circular WEEE plastic management

#### Procurement

#### Processing





- Growing supply
- Land-filled/Incinerated
  - Self-replenishing
  - Sustainable and growing supply



- Mechanical 'mining' process
  - ➡
  - •< 10% of energy
- <10% of water consumption
- Save about 1-3 tons CO2/ton



- "Green" products
- Virgin-like quality possible
  - More sustainable business
    - PCR plastics

Back to plastic for EEE!



Chris Slijkhuis (2018) Presentation, Dioxin 2018; 26-31 August, Krakow, Poland

Toxic plastic additives challenging circular economy' EU Circular Economy Strategy (Roadmap 04/2015). UNIDO and GEF stresses the need for global circular economy.



Bonnet (ARC+) Circular Economy, saving resources, creating jobs, Green Week Brussels June 2014

For moving to a (more) Circular Economy, hazardous chemicals need to be controlled and phased out by non-toxic alternatives.

## PBDE/BFR contamination of recycled plastic!

- High levels of PBDE & PBDD/F in recycled plastic in sensitive uses!
- Risks to human health demonstrated.
- Challenge to control recycling in developing & emerging economies.
- Challenge with low POPs limit 50 ppm PBDE would stop recycling.



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

- $\Rightarrow$  Need of a better life cycle management and control!
- ⇒ Important that the listing of PBDEs/HBCD result in global attention & addressing the problem by controlling & improving plastic recycling!

BFR exposure from recycling – kitchen tools

- Brominated PBDEs in kitchen tools are "extracted" in hot cooking oil within 15 minutes.
- Low brominated PBDEs are extracted with high efficiency already within 3 cookings. The higher brominated PBDEs are slower extracted and partly debrominated to lower PBDEs.



Kuang et al. (2017) Science Total Env, 610-611:1138-1146.

### PBDEs listed as POP in Stockholm Convention 2009 got an exemption for recycling – BAT/BEP need

- When PBDEs were listed 2009 an recycling exemption was included.
- The allowance of reuse and recycling of articles containing PBDEs resulted in the need to define BAT/BEP to carry out recycling and the final disposal in an environmentally sound manner (ESM).
- The objective of this guidance document is to assist Parties in developing strategies for complying with the Convention obligations related to the recycling and waste disposal of articles containing POP-PBDEs, and implementing the recommendations of the COP.
- Technologies are evaluated and defined which can be considered as BAT/BEP to manage these material streams in an ESM and would be used for developing action plans and to prioritize areas for the management of POP-PBDE containing material flows.
- Labor intensive separation techniques possibly applied in developing countries are not described in the guidance yet.



UNEP (2017) Guidance on BAT/BEP relevant to the PBDEs listed under the Stockholm Convention on POPs (Draft) http://www.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/7730/Default.aspx

## Chapter 4 Guidance. Specific BAT/BEP: POP-PBDE/bromine- containing plastic in WEEE



- Considering waste hierarchy, the BAT/BEP guidance stresses: A) Reuse/repair of electrical and electronic equipment (EEE)
- Reuse & repair of EEE is the preferred option for EoL management.
  Reuse extends the life span, safes energy for the manufacturing and lowers the environmental impacts of mining for raw materials.
- **B)** Recovery of materials from waste EEE (WEEE)
- The Stockholm Convention BAT/BEP guidance stresses the recycling and recovery of WEEE plastic considering the waste hierarchy and the elimination of PBDEs in the WEEE plastic.
- Listing of DecaBDE without recycling exemption ⇒ separation needed.
- The SC BAT/BEP guidance gives an overview on the separation techniques.
- C) Thermal recovery in cement plants, metal industry and waste-to-energy plants

UNEP (2017) Guidance on BAT/BEP relevant to the PBDEs listed under the Stockholm Convention on POPs (Draft) http://www.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/7730/Default.aspx

### Recycling/separation of POP-PBDE/bromine containing polymers in WEEE

- The recovery of metals is the key driver of WEEE recycling!
- Current WEEE recycling facilities are often not optimized for separation of PBDE/bromine containing polymers. In the EU, separation capacity for BFR plastic <30% although separation of BFR plastic is a requirement of the EU WEEE Directive.

Rubbe

PVC 1%

POM

PE

2.4%

 The complex mixture of plastic in WEEE is difficult to separate and industry has tight specifications for materials and additives resulting in low recycling rates of plastic
 PC-AE from WEEE. However there are major plastic types as target plastic (ABS, ABS-PC, HIPS, and PP). (Acrylonitrile butadiene styrene; High Impact Polystyrene; PolyPropylene)



% Wood

Other Non-Plastic

HIPS

27%

### Production of plastic for recycling from WEEE including separation of PBDE/bromine

		Contaminant																
		ABS	EP	SdIH	PA	PBT	PC	PE	PET	PMMA	POM	ЬР	Sd	PUR	PVC	SAN	PC+ABS	PC+PBT
	ABS	G	0	Y	R	0	G	R	0	0	0	R	R	Y	Y	R	G	Y
	EP	Y	U	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	HIPS	Y	Y	G	R	R	R	R	R	R	R	R	0	R	R	R	R	R
	PA	R	R	0	G	0	R	R	0	R	R	R	0	0	R	R	R	R
	PBT	0	R	R	0	G	G	R	R	R	R	R	R	0	R	R	0	G
	PC	G	0	0	R	G	G	R	G	G	R	R	R	0	0	G	G	G
	PE	R	R	R	R	R	R	G	R	R	R	G	R	R	R	R	R	R
stic	PET	0	R	0	0	R	G	R	G	R	R	R	0	0	R	R	0	R
Main plastic	PMMA	0	R	0	R	R	G	R	Y	G	0	R	0	0	G	G	G	R
Mair	POM	R	R	R	R	0	R	R	R	R	G	R	R	R	R	R	R	R
	PP	R	R	R	R	R	R	0	R	R	R	G	R	R	R	R	R	R
	PS (HI)	R	R	0	R	R	R	R	R	R	R	R	G	R	R	R	R	R
	PUR	Y	R	0	Y	0	0	0	0	0	0	0	0	G	Y	0	0	0
	PVC	Y	R	R	R	R	R	R	R	G	R	R	R	0	G	G	0	R
	SAN	G	0	R	R	R	G	R	R	G	R	R	R	Y	G	G	G	0
	PC+ABS	G	0	G	R	G	G	R	Y	G	R	R	G	Y	0	G	G	G
	PC+PBT	G	0	R	0	G	G	R	Y	R	R	R	R	0	R	G	G	G

Limited compatibility of • most plastics already at low concentrations.

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 Therefore a good separation is needed.

Source: Haarmann & Gasser (2017)



Reasonable compatibility (properties stay good only if contamination <5%)

0 Limited compatibility (properties stay good only if contamination <2%)

G Good compatibility (properties stay good even if >5% contamination)

Y

R Bad compatibility (properties are bad even if contamination =1%)

### Production of plastic for recycling from WEEE <sup>14</sup> including separation of PBDE/bromine

- A stepwise separation of WEEE plastic is needed for transformation into valuable plastic-for-recycling. Numbers of separation steps vary depending on process combinations used. Not one step!!
- The overall cost for separation steps and technologies need to be covered by the final revenues from the products.



# Separation and upgrading steps in the recycling of (WEEE) plastic: Combination of technologies

- None of the individual techniques described has the ability to separate mixed plastic from WEEE to ensure that the plastic is separated into marketable polymer fractions and that, at the same time, POP-BFR-containing plastics are separated.
- Therefore, combinations of the techniques need to be used in practice.
- Also combination of technique does not achieves 100% separation, leading to residual PBDEs in the "bromine-free" fraction:
- In the case of handheld sorting this is due to errors by the operatives.
  For automated systems, the sorting efficiency with blowing bars has its limits and the purity of sorted fractions is normally below 95%.
- The economic feasibility of process combinations may significantly vary in different countries. Local costs and revenues need to be calculated for the different combinations of technologies.



# Separation and upgrading steps in the recycling of (WEEE) plastic: Combination of technologies

Full scale plants to separate PBDE/bromine-containing polymers CONVENTION

WEEE input (country)	Separation techniques	Polymers Separated	Quality of separated polymers	PBDE/BFR Elimination (RoHS compliant)	Developme nt Stage*	Reference
Mixed plastic from WEEE (Austria, China)	Not disclosed	Low-BFR types of ABS, HIPS and PP	Good (Customer specified)	Yes; BFR rich fraction incinerated	Industrial scale	MBA Polymers (2012) and MGG Polymers (2018)
Small EEE, White goods (Switzerland)	Includes XRT	BFR and PVC free polymers	Good	Yes	Industrial scale	RUAG Technology (2012)
WEEE plastics (UK)	Undisclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	Morton (2007)
WEEE plastics (Austria, Germany)	Undisclosed (incl. S/F and Electrostatic)	Low-BFR types of PP, ABS, HIPS	Good	Yes	Industrial scale	Bage Plastics GmbH (2012, 2020)
WEEE plastics (Netherlands)	Undisclosed (incl. S/F and Electrostatic)	Low-BFR types of PP, ABS, HIPS	Good	Yes	Industrial scale	CloseWEEE (2017) Coolrec
WEEE plastics (Sweden)	Undisclosed (incl. S/F&Electrostatic)	Low-BFR types of PP, ABS, HIPS	Good	Yes	Industrial scale	NONTOX (2020)
WEEE plastics (Galea)	Undisclosed (incl. S/F & Electrostatic)	Low-BFR types of PP, ABS, HIPS	Good	Yes	Industrial scale	NONTOX (2020)
Mixed plastic from WEEE (Germany)	Successive Grinding & XRT	BFR and PVC free polymers	Not yet approved	Yes	Industrial scale	ReToVal GmbH (2018)

UNEP (2020) Guidance on BAT/BEP relevant to the PBDEs listed under the Stockholm Convention on POPs (Draft)

### Separation/upgrading steps in the recycling of " (WEEE) plastic India: Combination of technologies

- Informal recyclers developed separation of plastic with simple tools.
- With these methods 10,000ds of tonnes of WEEE plastic is separated.



### Situation India – high plastic recovery without control\*

- Swiss institutes (EMPA, WRF; Sustainable Recycling Industries SRI) had a project on assessment of WEEE plastic management in India.
- WEEE plastic is normally recycled without separation of the BFRs.
- If BFRs fraction is separated then for producing high BFR fractions for use in FR-plastic applications (V0; V1). But high load of POP-BFRs!

Haarman & Gasser (2016) Managing hazardous additives in WEEE plastic from the Indian informal sector. Report Sustainable Recycling Industries June 2016



- The remaining plastic waste from processing WEEE plastic is sold to brick kilns as fuel. No study on related releases and contamination.
- Another current practice is the use of **plastic in pyrolysis facilities**.
- Assessment need all countries: Material & substance flow analysis of plastics in waste management and final treatments and releases.

### Monitoring Dioxin in eggs around boilers burning plastic

- The burning of plastic waste in boilers of tofu factories in Indonesia is poisoning the food chain with Dioxin (PCDD/PCDFs)
- The Internat. POPs Elimination Network (IPEN) found, in an East Java village, that dioxin TEQ in free range chicken eggs around the boilers are 70 times above the level allowed by European standards. (In Asia only eggs at Agent Orange contaminated sites in Vietnam were higher (90 times above EU level)).







Plastic waste is dumped in communities by paper and plastic recycling importers.

We tested free-range chicken eggs from two communities in Indonesia where imported plastic wates are used for fuel or burned at waste dumps and found high levels of very hazardous chemical induding flavine, polyhein (PCB), polyheinisted diplengi testers (PBBCa), cherc chain chalariasted garaffins (SCCP) and perfluorooctane sulfonate (PFOS). All these substances are regulated globally under the Stockholm Convention.

https://www.bbc.com/news/science-environment-50392807 https://ipen.org/news/plastic-waste-poisons-indonesia%E2%80%99s-food-chain

### Energy recovery of bromine/chlorine containing waste

- POP-BFRs are mainly used in materials with high calorific value (WEEEplastics, car-SR, PS-foams EPS/XPS, PUR foam, (synthetic)textiles etc.).
- One option for the recovery of such materials is to utilize the energy present in the material. This is also a recommendation of Stockholm Convention BAT/BEP guidance & Basel Convention technical guidelines.
- The thermal treatment of BFR-containing wastes (EPS/XPS, ASR and WEEE) is a challenge for thermal facilities because of the high halogen (and heavy metal) content. Treated EPS/XPS contain 0.5 to 3% Br and XPS ca. 8% HFCs. The bromine content of WEEE plastic fractions were 1.7 5.2% and chlorine content 0.1 and 4.4% (Schlummer et al., 2007).
- $\Rightarrow$  Special care needed for treatment. EU require the use of hazardous waste incinerators for wastes with a halogen content above 1%.



- Challenges of developing countries with waste incinerators<sup>1</sup> Are incinerators a solution for ESM of waste from WEEE plastic recycling? BAT/BEP waste incinerators can destroy PBDEs/BFRs in plastic/polymers! Important challenges associated with incineration in developing countries:
- Capital investment and operating costs of BAT incinerators are high;
- Increase in waste treatment cost may incentivize waste generators to seek alternatives to incineration, which is good if the alternative is for recycling, but not if it ends up in uncontrolled dumping or burning;
- There is a minimum requirement to the lower calorific value (7 MJ/kg). In low to middle income countries it may be a challenge to achieve this;
- Skilled staff is required for the operation and maintenance of the facility;
- The NIMBY syndrome also exists for WtE. Source: ISWA Guidelines: Waste to Energy in Low and Middle Income countries. August, 2013
- The uptake of Waste-to-Energy (WtE) in India was not successful and the majority of plants have failed to sustain operations. As of 2012, only eight WtE plants had been installed in India. In 2017, only one WtE plant incinerating just MSW remained in operation (Nixon et al. 2017 Sustain. Energy Technol. Assess. 21, 23-32).
- Challenges to manage residues/ashes resulting in releases (Petrlik & Bell 2017). https://ipen.org/sites/default/files/documents/ipen-toxic-fly-ash-in-food-v1\_4a-en-web.pdf

### Specific challenges with BFRs in thermal treatment<sup>2</sup>

1) The treatment of BFR-waste has a risk for Dioxin/UPOP formation

- BFRs are often aromatic compounds and therefore PBDD/PBDF precursors with the associated formation potential.
  Weber & Kuch (2003) Environment International 29, 699-710<sup>Brm-Carbon</sup>
- The presence of BFRs can reduce combustion quality with increased formation of products of incomplete combustion.
- Increased halogen content and the presence of heavy metals are key factors triggering Dioxin/UPOP formation.

2) The redox potential of bromine is similar to oxygen. Therefore bromine can partly be present as **elemental bromine** and need to be removed.

	Fluorine	Chlorine	Bromine	lodine
Standard Redox potential	+2.87	+1.36	+1.09	+0.54
(Redox potential O <sub>2</sub> +1.23)				

3) HBr is a stronger acid compared to HCI and is partly present as elemental bromine (Redox). This leads to an overall **higher corrosion**.

# Chlorine/bromine in plastic & challenges in cement kilns

- **Chlorine and Bromine** (present in some large plastic/polymer waste fraction (construction, e-waste, car-shredder):
- Risk/problem of clogging of the kiln: Limit of 300 g/t total clinker input restrict the use of alternative fuel (AFR) with chlorine/bromine. The Cl/Br input via AFR must be limited; e.g. not more than 0.5 % in plastic or solvent. Option of chlorine bypass.
- Increase risk of dioxin formation (can be controlled) and corrosion.
- The fate of bromine in cement kilns is not documented. Risk of release of brominated ODS or elemental bromine?.
- Assessment/research needed for large scale use of BFR containing plastic/polymer waste in cement kiln..

### The Chlorine(Bromine?) Problem



### Some Conclusions

- Important to control the recycling of WEEE plastic into sensitive uses such as toys and food contact materials.
- Two low POPs limit are currently in Basel Guidelines: 1000 mg/kg and 50 mg/kg. The latter would be a considerable challenge to reach in recycling.
- The separation of WEEE plastic by experienced informal sector in India can result in separated plastic types for the market. Further sink-float treatment produce "BFR free" and "BFR rich" fractions. Both are used.
- Technologies are available and in use to separate POP-BFRs from WEEE plastic and produce low POP-BFR plastic for recycling.
- Thermal treatment of WEEE plastic in non-BAT facilities result in environmental pollution and is a risk for contamination of food & humans.
- WEEE plastic can be thermally recovered in incinerators & cement kilns.
- Challenges of developing countries to operate BAT waste incinerators.
- Lack of projects of co-incineration of the waste WEEE plastic fraction.
- PBDEs are only one of hazardous chemicals in WEEE plastic. Other additives need to be considered for worker and consumer exposure.

### Food for thought: What (B)FRs were and are used?<sup>26</sup> and are they safe for recycling?

- ➢ More than 70 BFRs known (Fisk et al 2003) Many are Br-aromatics.
- Some are polymers with low release risk. But many are additives.
- What is their toxicity/risk and future policy implication? Risk of PFRs?



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

# Thank you for your attention ! Questions?"

### **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: www.saicm.org/ FAO: www.fao.org/ WHO: www.who.int/
- POPs phase out & alternatives http://poppub.bcrc.cn/
- OECD: http://www.oecd.org/chemicalsafety/
- Science: www.ipcp.ch; http://greensciencepolicy.org/
- NGO: www.ipen.org; www.chemsec.org; www.ihpa.info; www.ban.org Better-world-links: http://www.betterworldlinks.org/

