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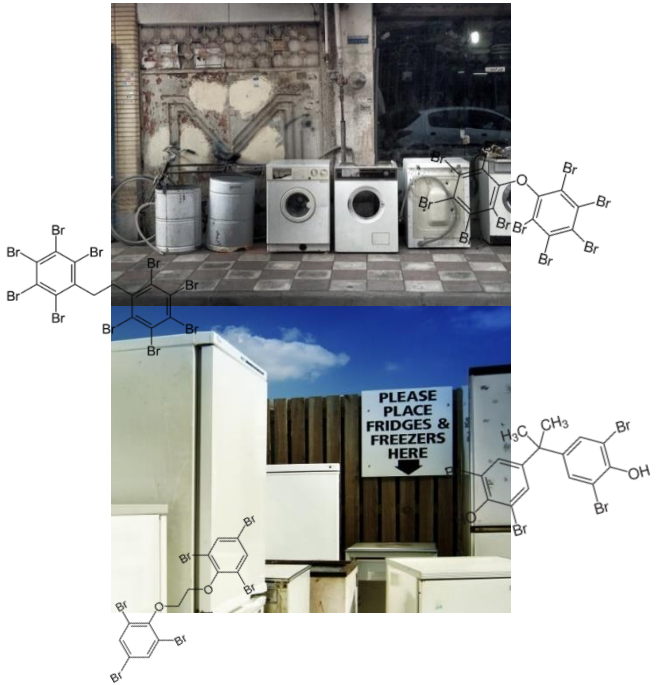
Brominated flame retardants in plastics from LHA & CFA

Results of 2018 sampling & testing study

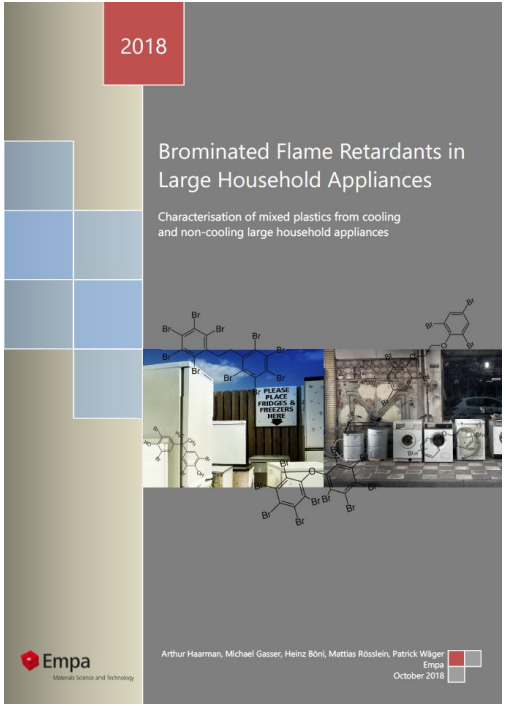


Arthur Haarman, Empa (Swiss Federal Laboratories for Materials Science and Technology)

EuRIC WG WEEE meeting, 23.01.2019

Context

- EN 50625 exempts plastics from large household appliances (LHA) as well as cooling and freezing appliances (CFA) from the BFR separation requirement.
- Plastics from these streams are assumed to be "BFR-free" and can be recycled without prior separation.
- This exemption has been questioned, in particular by a French study (INERIS) in 2017. Are these plastics really clean?
- Empa was commissioned to carry out a sampling and analysis study at European level, facilitated by the WEEE Forum.
- Sampling during 25 batch tests (11 CFA, 14 LHA) in 7 countries and 19 treatment plants. Plastic fractions were sampled before BFR separation.
- Final report delivered in October 2018.



Goal & Scope

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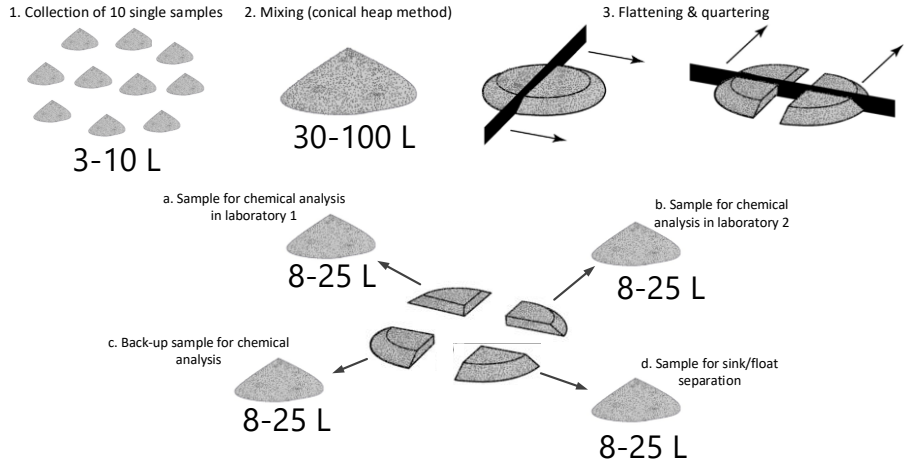
- Primary goal: provide comprehensive data on the brominated flame retardant (BFR) content in mixed plastics from CFA and LHA
- Secondary goal: assess the composition of these plastics, both in terms of polymers and additive content
- Scope:
  - Sampling in 7 countries (CH, ES, FR, GR, IT, NL, PT) and 19 treatment facilities
  - Chemical analyses (2 labs) carried out on:
    - BFRs:
      - Restricted (RoHS, POP, REACH): PBBs, PBDEs, HBCDD
      - Non-restricted but commonly found: TBBPA, DBDPE, BTBPE
    - Inorganic elements:
      - BFR tracers: Br, Sb
      - RoHS heavy metals: Cd, Cr(VI), Pb, Hg
      - Common additives (non-brominated): P, Si, Mg, Ca, Al, Ti, Cl

Methods - sampling

- Procedure based on TS 50625-3-1
- Sampling during batch tests (min. 10 t GEMF, 10-50 t GEMHF)
- Plastic fraction(s) sampled before BFR separation
- For each lot, 1 composite sample prepared from ≥10 single samples, then divided into 4 sub-samples for analysis (**a**, **b**, **c**, **d**)



Methods - chemical analyses

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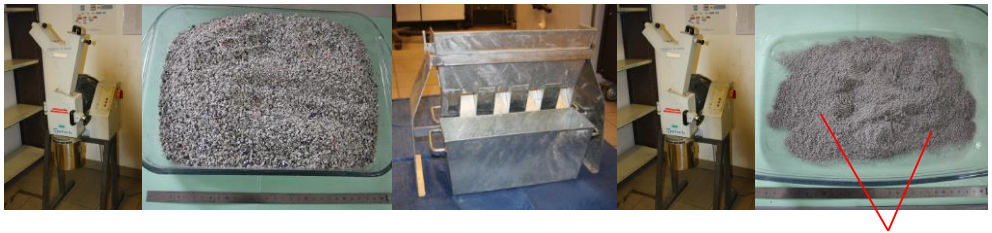
Given the considerable heterogeneity of the fractions sampled and the complexity of such chemical analyses, measures have been taken to control the quality of the sampling and analytical procedures performed:

- Analyses carried out by **2 laboratories** (main lab = "Lab 1" (FR); control lab = "Lab 2" (CH)), using analytical methods based on the same standards
- Additional analyses carried out on selected samples to assess possible sources of variability:
  1. Analysis of **reference materials** (to assess analytical accuracy)
  2. **Repeated** analyses (to assess intra-laboratory analytical precision ⇔ repeatability of analysis)
  3. Analysis of **field duplicates** (to assess field precision ⇔ reproducibility of sampling)
  4. Exchange of **laboratory duplicates** (to assess inter-laboratory analytical precision ⇔ reproducibility of analysis)

Field duplicates



Lab duplicates

Reminder: limit values (ppm) for regulated BFRs in WEEE plastics (as of 22.01.2019)

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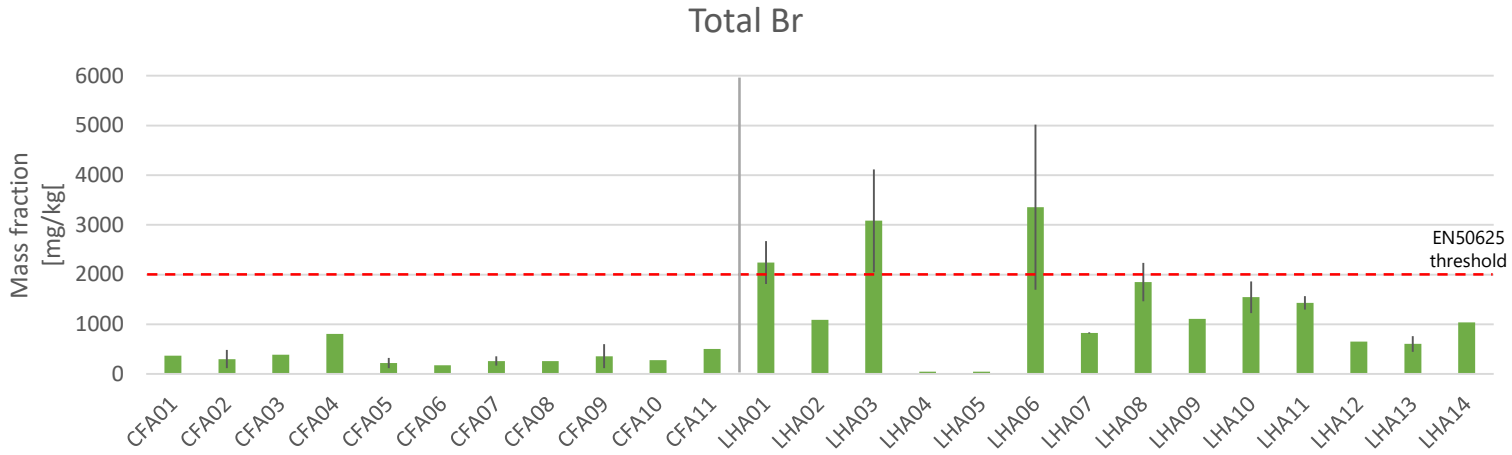
>50 ppm **hexaBB** or >1000 ppm **HBCDD** very unlikely in mixed WEEE plastics → not an issue

On the other hand, >500 ppm **ΣPBDE** is commonly found in mixed (unsorted) WEEE plastics

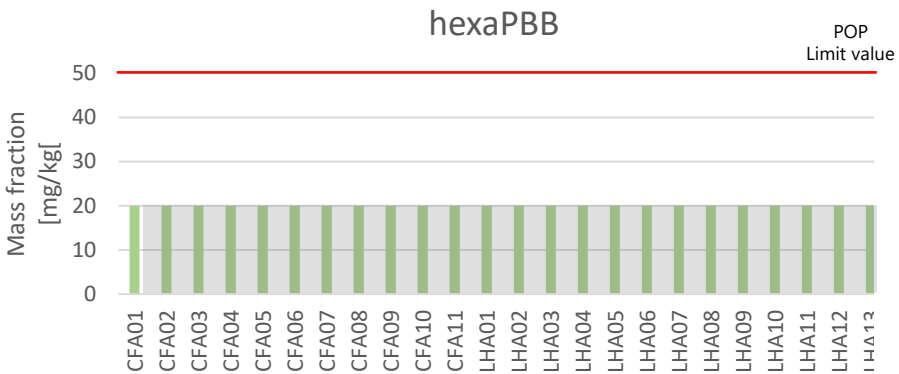
		Regulation				Standard
		POP	**WFD** (Waste Framework Directive)	**REACH**	**RoHS**	**CENELEC**
		EC 850/2004	EC 98/2008	EC 1907/2006	EU 65/2011	EN 50625-1, TS 50625-3-1
PBB	hexaBB	50	50	–	–	–
	∑PBB	–	1000	1000	1000	–
PBDE	c-pentaBDE	–	2500	–	–	–
	c-octaBDE	–	3000	–	–	–
	c-decaBDE	–	10000	1000	–	–
	ΣPBDEs	**500** (?)	–	–	1000	–
HBCDD		1000	2500	–	–	–
TBBPA		–	2500	–	–	–
Total Br		–	–	–	–	2000
Applies to WEEE plastics?		Yes	Yes	No	No	Yes (except LHA&CFA)
Consequence of an exceedance for treatment		POP content must be destroyed	Waste considered hazardous	–		BFR-rich fraction must be separated before recycling

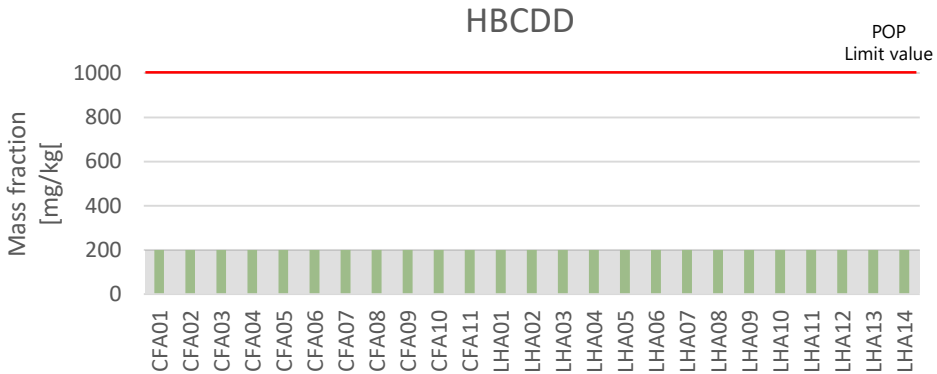
Results – total Br

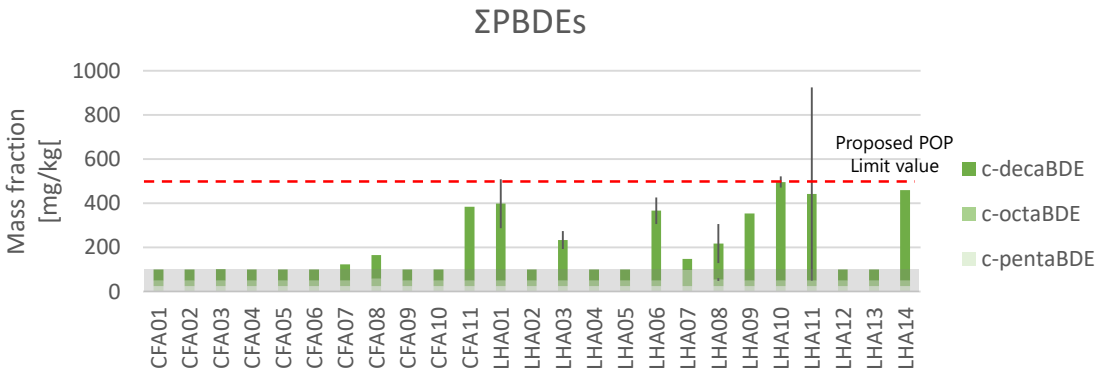


- Aggregated results (Lab 1 & 2, including additional analyses)
- Mean and standard deviation of all measurements for each batch. If no error bar: only one measurement available for the batch
- Average coefficient of variation of 33% (CV=standard deviation/average)
- 2000 ppm threshold exceeded in a several LHA samples, however this threshold does not apply to this stream according to EN 50625

Results – restricted BFRs



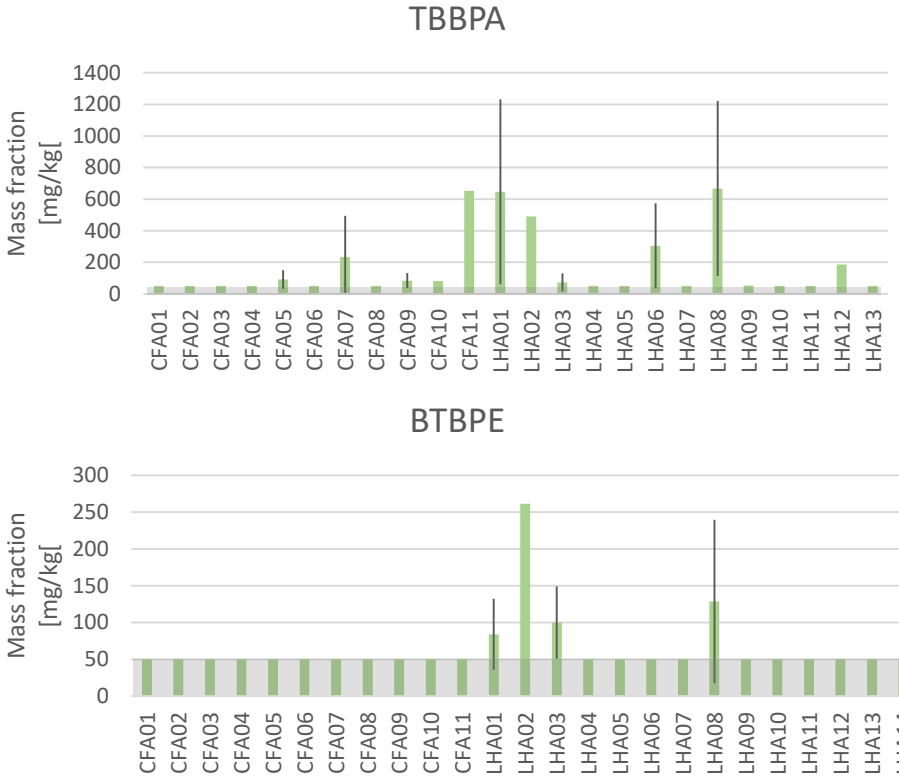


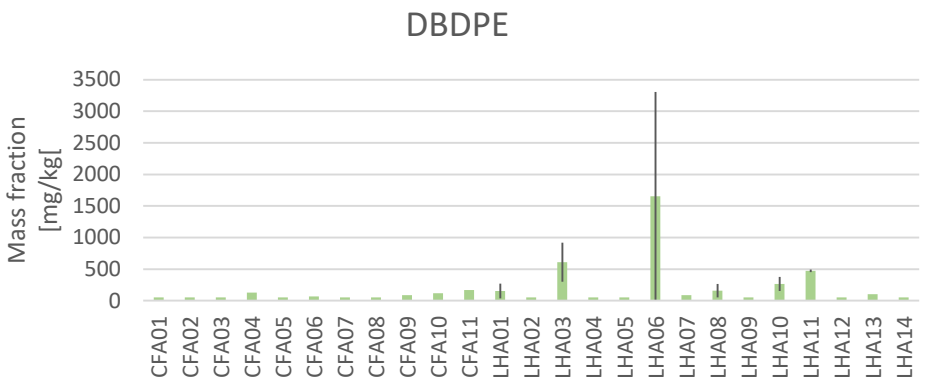


Limit of quantification

- Mean CV:
  - (hexaBB: 0%)
  - (HBCD: 0%)
  - ΣPBDEs: 40%

Results – non-restricted BFRs

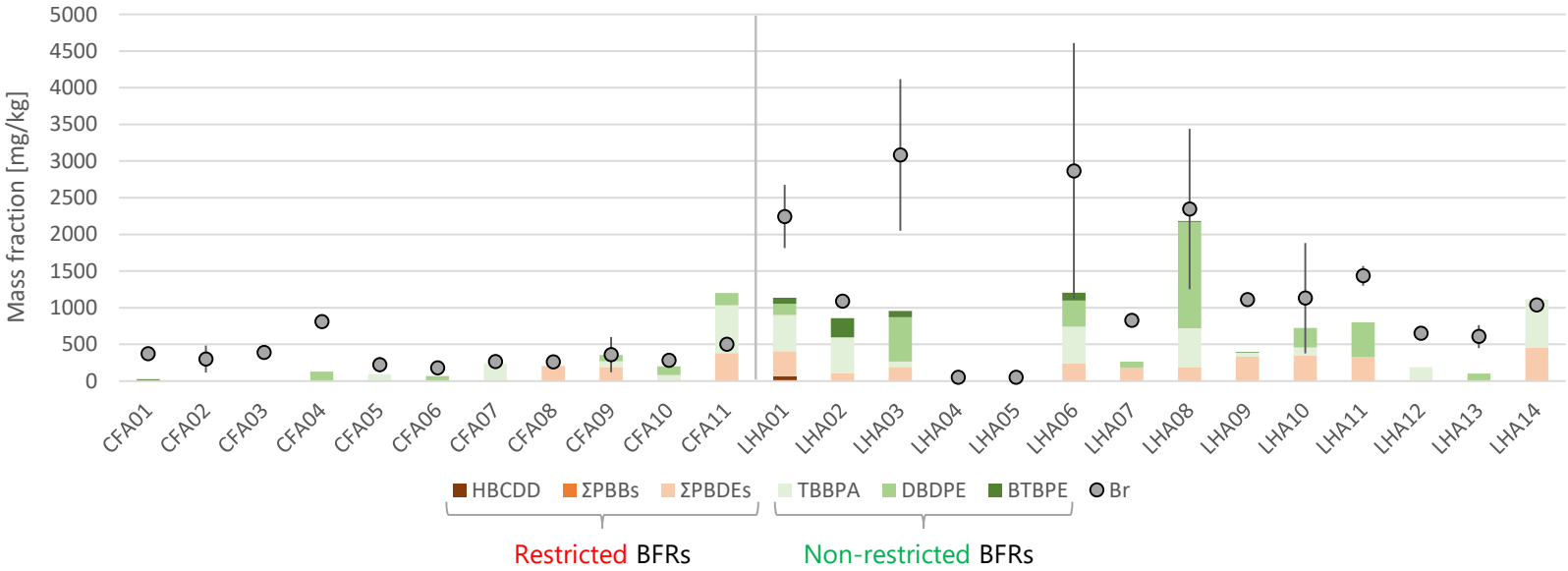




Limit of quantification

- Mean CV:
  - TBBPA: 48%
  - DBDPE: 57%
  - BTBPE: 32%

Results – BFR overview



- Large share of "unknown" bromine (Br), as typically observed in such studies
- Considerable variability (standard deviation) in measured Br & BFR levels, mainly due to heterogeneity of such materials
- ΣPBDEs <500 ppm even if Br >2000 ppm → EN50625 threshold still relevant?

Comparison with previous studies

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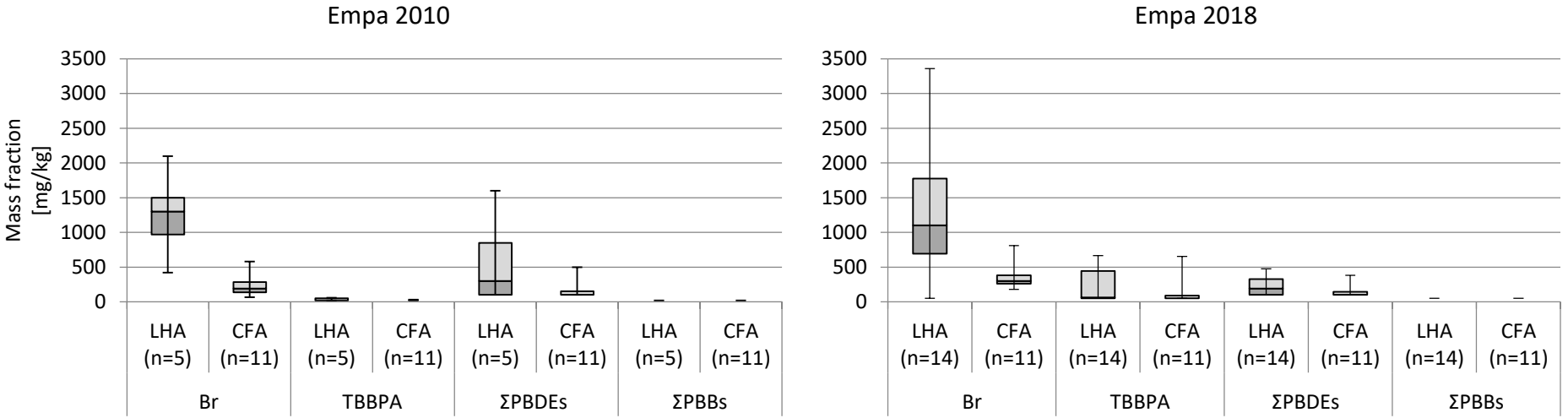


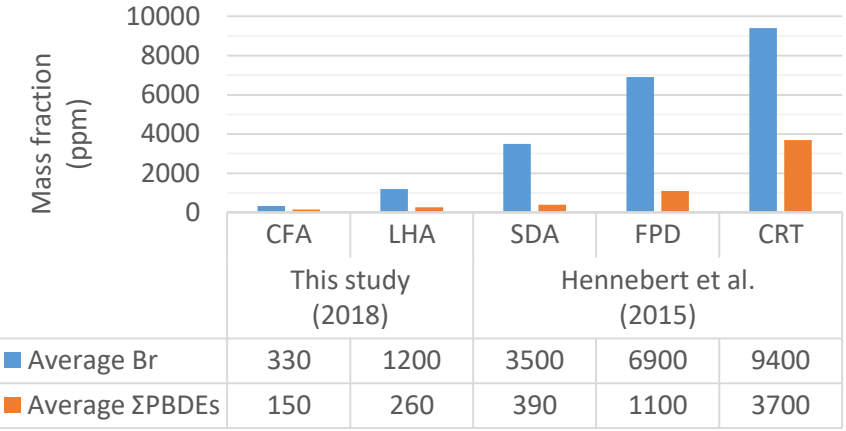
Trends:

- Slight decrease in median Br
- Decrease in PBDE levels (especially max)
- Increase in TBBPA levels

→ Phasing out of regulated BFRs and substitution by non-regulated BFRs

Discussion

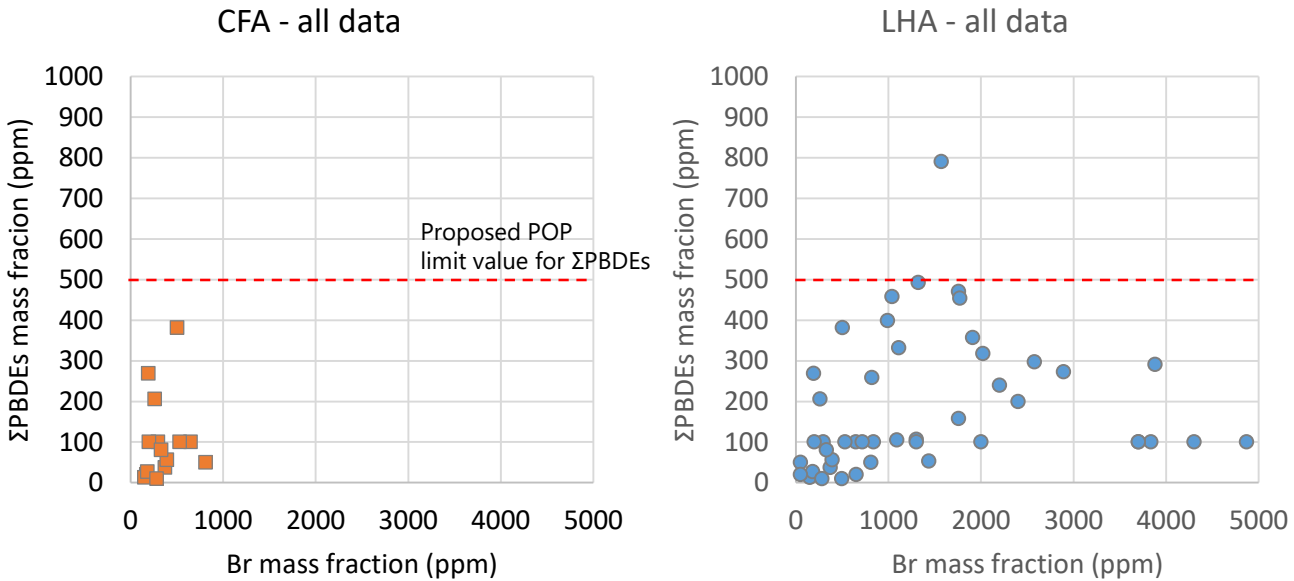
- Results confirm that BFR levels are relatively **low** in mixed plastics from **LHA**, and **very low** in those from **CFA**, compared to other WEEE streams such as screens (FPD & CRT) and small domestic appliances (SDA)
- Comparison with results of **2010 Empa study** suggest that levels of **restricted BFRs** in LHA & CFA have **decreased**, while total bromine levels remained stable, indicating **substitution** by non-regulated BFRs
- **Currently applicable** POP limit values are not exceeded in any LHA or CFA sample. However, proposed limit value of **500 ppm for ΣPBDEs** is exceeded in one LHA sample.
- **2000 ppm Br sorting threshold** exceeded in a few LHA samples, however all samples with >2000 ppm Br contain <500 ppm ΣPBDEs



Regulation/ standard	Substance	Limit value (ppm)	Number lots with **average** content above limit value		Number of lots with **maximum** content above limit value	
			LHA (n=14)	CFA (n=11)	LHA (n=14)	CFA (n=11)
POP Regulation	hexaBB	50	0	0	0	0
	HBCDD	1000	0	0	0	0
	ΣPBDEs	500 (?)	0	0	1 (7%)	0
EN 50625	Br	2000	3 (21%)	0	4 (29%)	0

Implications – BFR sorting derogation

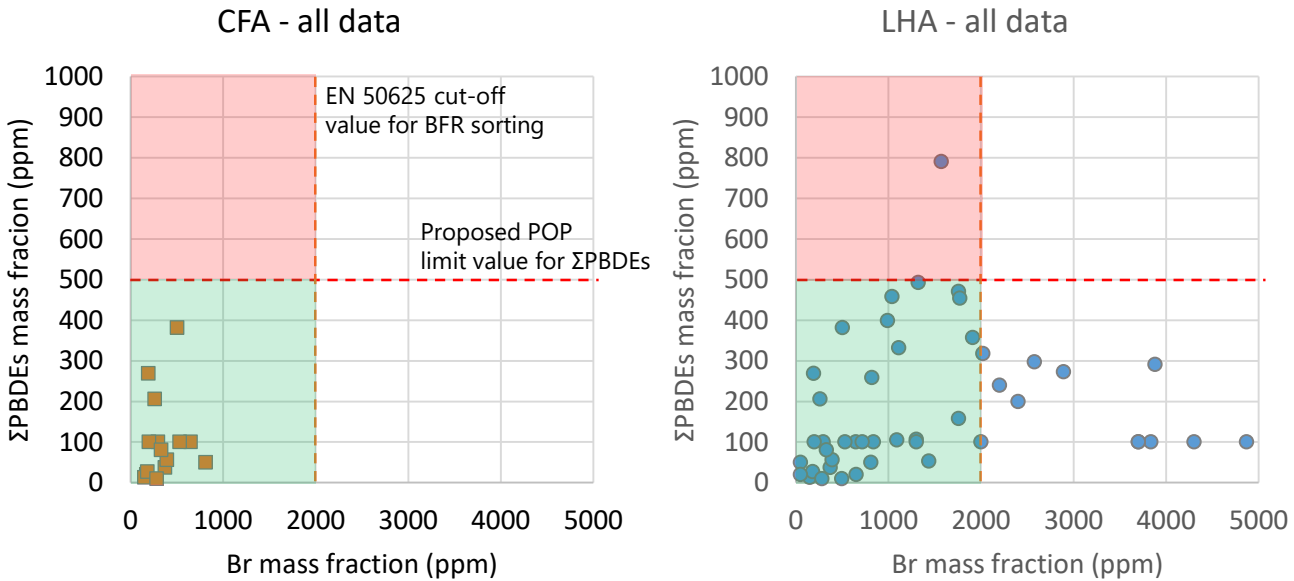
- Is the **BFR sorting exemption** for CFA and LHA plastics still relevant?
  ⇔ are BFR levels in **unsorted** fraction below limit values?



- No exceedance in unsorted CFA plastics → derogation still relevant?
- 1 exceedance in unsorted LHA plastics → derogation obsolete or outlier to be dismissed?

Implications – 2000 ppm Br threshold

- Is the **2000 ppm Br sorting threshold** still relevant?
  ⇔ are BFR levels below limit values in fractions with <2000 ppm Br?



- 1 sample with <2000 ppm Br and >500 ppm ΣPBDEs
  → 2000 ppm Br threshold obsolete or outlier to be dismissed?

Outlook

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- If 500 ppm ΣPBDEs is set as POP limit value for both wastes and regranulates, **BFR sorting of LHA plastics could become necessary** (for CFA plastics, no sorting probably OK)
- Such BFR sorting could be done:
  - Prior to mechanical processing, i.e. via manual removal of BFR hotspots such as plastic covers of printed circuit boards or transformers
  - After mechanical processing, via density separation*, XRT sorting or other methods

*Due to its low selectivity, density sorting of mixed LHA plastics **could lead to high material losses** (~70%), which could considerably **reduce recycling rates** for this category (+ **increase treatment costs**)

Next steps

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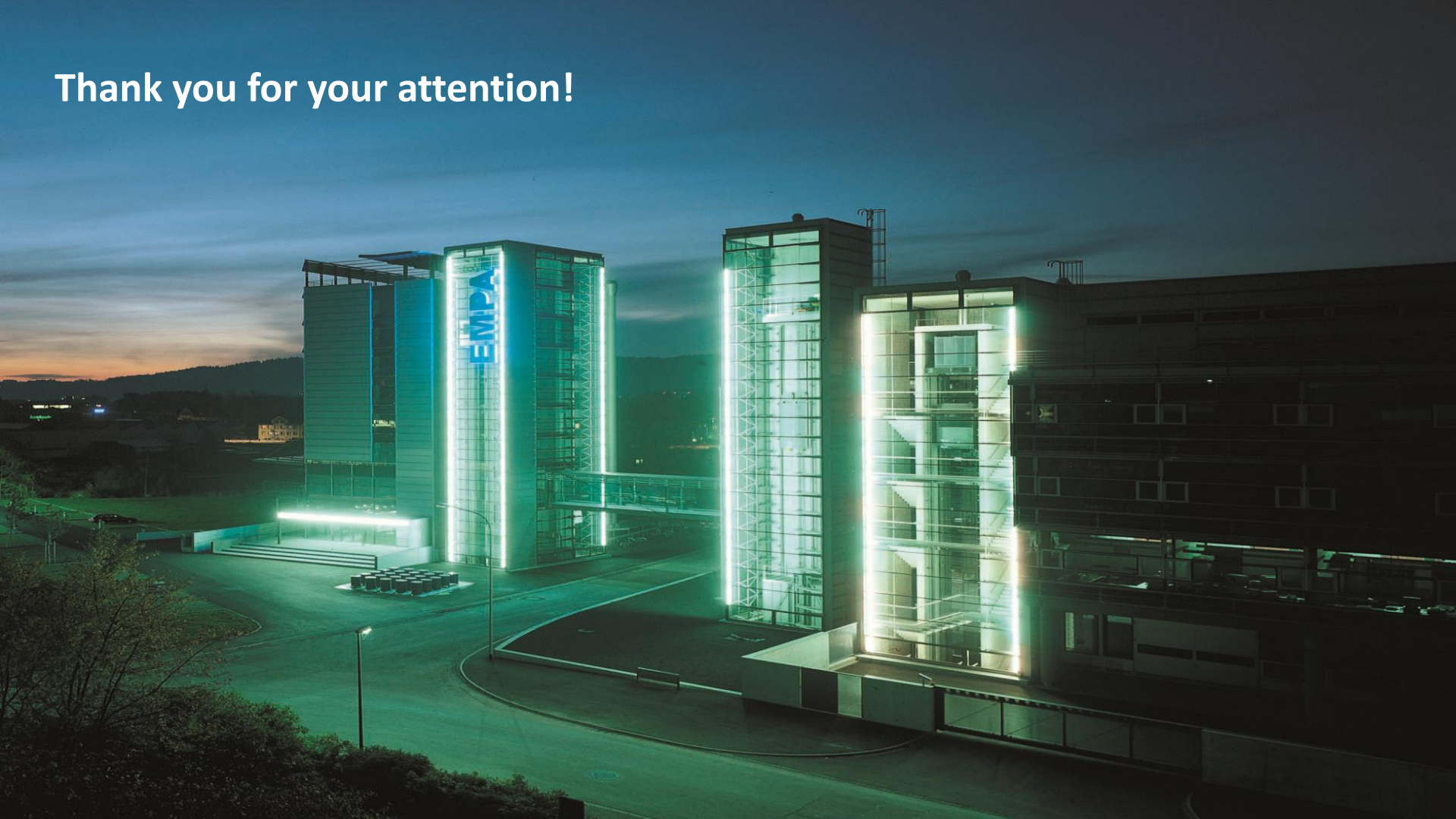
LHA&CFA study:

- Report shared (1 to 1) with various stakeholders
- Empa to submit manuscript for scientific publication in a peer-reviewed journal by March 2019
- Once scientific publication submitted, full report can be published

Other activities:

- In preparation: follow-up study (WEEE Forum/Empa) on BFRs in plastics from screens and SDA
- Ongoing: study in France (ESR/INERIS) to assess efficiency of BFR sorting technologies (and “cleanliness” of “clean” fraction)
- Ongoing: study in UK (ICER/WRc) to quantify BFR levels in various WEEE categories

Thank you for your attention!



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Annexes

BFR data review

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(Preliminary) review of BFR data (5 studies, 327 samples)

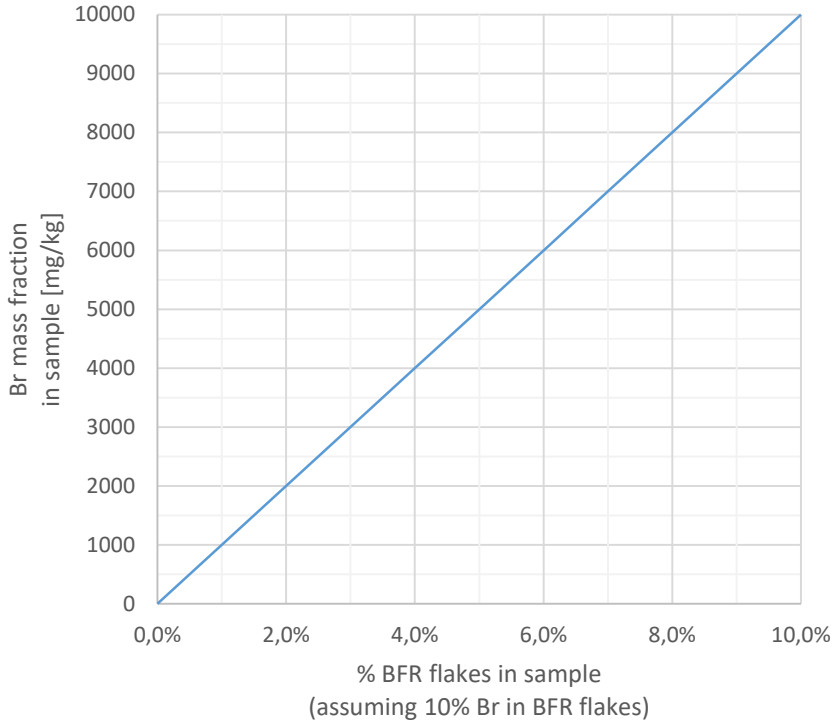
- 165 samples with <2000 ppm Br, of which 0 with >1000 ppm ΣPBDE (incl. deca).
- However, 7 of these 165 samples (4%) contain >500 ppm ΣPBDE (incl. deca)
- Considering levels measured recently (since 2014), only 2 of 135 samples (1.5%) contain <2000 ppm Br and >500 ppm ΣPBDE

Data considered so far shows that it is unlikely to have >500 ppm PBDEs in a fraction containing <2000 ppm Br. It's however not impossible → what is the admissible share of false negatives (i.e. fractions with <2000 ppm Br and >500 ppm PBDEs)?

More data and additional analyses needed to confirm validity of 2000 ppm threshold.

Especially if limit values are understood to apply on single flakes rather than mixtures of flakes.

Influence of the proportion of brominated flakes on the average content of the sample



- Considering a sample with 100 plastic particles of equal weight, an average Br content of 2000 ppm for this sample is reached if it contains 2 particles with 10% Br (typical bromine content of brominated plastics)
- According to report 65/2016 of the German Federal Ministry of the Environment*, on average 1.5% of LHA plastics are brominated. Assuming an equal weight of particles and a Br content of 10% brominated plastics, this means an average Br content of 1500 ppm

*UBA 2016 „Entwicklung von Instrumenten und Maßnahmen zur Steigerung des Einsatzes von Sekundärrohstoffen – mit Schwerpunkt Sekundärkunststoffe“ (p. 218)