RoHS - regulated substances in mixed plastics from Waste Electrical and Electronic Equipment

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Abstract

This paper summarizes the findings of a research study, which was commissioned by the WEEE Forum to contribute to a formulation of normative requirements with respect to depollution of WEEE. Two main questions are addressed: (i) What are the concentrations of substances regulated by the Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) in mixed plastics from selected WEEE categories and products?, and (ii) What are the implications for an environmentally sound recovery of plastics from WEEE? The study included 53 sampling campaigns for mixed plastics from WEEE. The samples were analysed with regard to flame retardants (PentaBDE, OctaBDE, DecaBDE, DecaBB) and heavy metals (cadmium, chromium, mercury and lead) regulated in the RoHS Directive. Besides these substances, other brominated flame retardants known to occur in electronics (HBCD, TBBPA) as well as the total bromine and phosphorus contents were considered. Results were evaluated with regard to the maximum concentration values defined in the Directive.

1 Introduction

The plastics share from European waste electrical and electronic equipment (WEEE) over all categories was estimated to amount to 20.6% in 2008 [1]. Currently the recovery of these plastics is of large economic interest in the trade of secondary raw materials. However plastics from WEEE are also of concern, due to their content of hazardous substances such as cadmium, lead or brominated flame retardants (see [2–5]), which on the one hand are associated with risks for health and the environment [6], [7] and on the other hand may give rise to high processing costs, depending on the disposal or recovery route chosen.

For newly marketed electrical and electronic equipment (EEE), maximum concentration values for selected heavy metals and brominated flame retardants have been defined in the Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) [8]. According to the Directive, the Member States are expected to make sure that from July 1, 2006, newly marketed EEE shall not contain any lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls or polybrominated diphenyl ethers in concentrations above defined maximum concentration values (MCVs) for homogeneous materials [9].

As a consequence, the WEEE Forum commissioned the Swiss Federal Laboratories for Materials Science and Technology (Empa) to perform a study, which provides a comprehensive empirical foundation regarding the levels of substances regulated by the RoHS Directive in mixed plastics from the treatment of the quantitatively most relevant categories defined in the European WEEE Directive [10].

In this paper we present the results of the study, which intended to provide answers to the following two key questions:

- What are the current concentrations of substances regulated by the RoHS Directive in mixed plastics from selected WEEE categories and products?
- What are the implications for an environmentally sound recovery of plastics from WEEE?

The content of this paper is directly related to the results presented in a recent publication [11], which was awarded as the Best Policy Analysis Paper 2011 in Environmental Science & Technology [12]. Here, we put more emphasis on the implications of applying flame retardants that are not regulated in the RoHS directive, and on the discussion of the results with regard to the situation outside of Europe.

2 Methodology

The sampling strategy was defined based on the results of an extensive literature review and a comprehensive expert consultation. It addressed mixed plastics stemming from the pre-treatment of the following WEEE flows:

- Mixed WEEE categories as typically processed by European WEEE recycling companies;
- WEEE categories 1, 2, 3 and 4;
- WEEE products expected to either contain particularly high levels of RoHS substances (e.g. cathode ray tubes (CRT) monitors/televisions (TVs), small appliances for high temperature applications) or especially low levels (e.g. flat screens) in their respective plastics fraction.

An overview of all WEEE input material flows considered in this study is given in Table 1.

	Code	WEEE input material flow	WEEE cat. included
Mixed WEEE categories	M1	Small appliances w/o screens (CRTs, flat screens)	2,3,4,6,7
	M2	Small household appliances, tools, toys, leisure and sports equipment	2,6,7
	M3	ICT and consumer equipment w/o screens	3,4
Single WEEE categories	C1	Large household appliances	1
	C2	Small household appliances	2
	C3	ICT equipment w/o screens	3
	C4	Consumer equipment w/o screens	4
Single product types	P11	Cooling and freezing appliances (inside lining without drawers)	1
	P12	Cooling and freezing appliances (all plastics, except foams)	1
	P22	Vacuum cleaners w/o hoses	2
	P23	M2 w/o vacuum cleaners	2
	P24	Small appliances for high temperature applications	2
	P31	CRT Monitors	3
	P32	Flat screen monitors*	3
	P33	Printers	3
	P41	CRT TVs	4

Table 1: Overview WEEE input material flows

Under consideration of the existing standards DIN EN 14899 [13], [14] and LAGA PN 98 [15], a sampling procedure was developed. According to this procedure, mixed plastics samples from maximally 20 tonnes of input WEEE material were taken under the responsibility of those 15 members of the WEEE Forum that had previously agreed to participate in the sampling campaign. Mixed plastics samples were analysed with regard to the following elements and compounds:

- Brominated flame retardants regulated by the RoHS Directive: PentaBDE, OctaBDE, DecaBDE;
- Other brominated flame retardants: HBCD; TPPBA;
- Other elements such as bromine and phosphorus.
- Heavy metals regulated by the RoHS directive: cadmium, chromium, lead and mercury;

Brominated flame retardants as well as cadmium, chromium, lead, mercury and were quantitatively analysed. A series of elements including, amongst others, bromine, cadmium, chromium, lead, mercury and phosphorus, were also semi-quantitatively analysed with X-Ray Fluorescence spectrometry. Further methodological details of the sampling procedure and the chemical analyses can be found in Wäger et al. [11].

3 Results and discussions

3.1 Brominated flame retardant concentrations

Figure 1 displays the concentration ranges for the brominated flame retardants TBBPA, PentaBDE, OctaBDE and DecaBDE in WEEE for each of the four WEEE categories. DecaBB and HBCD were not considered, because they were either only found at concentrations not exceeding 0.5 g/kg (DecaBB in CRT TVs) or not found above the detection limit at all (HBCD). For the calculation of average values, concentrations measured below detection limits were approximated with the detection limit, which corresponds to a worst case perspective.

TBBPA was detected in most samples with average concentration levels typically ranging from 1 to 10 g/kg. The highest concentrations were found in mixed plastics from CRT monitors (P31) with an average concentration of 37 g/kg and a maximum level of 63 g/kg. The lowest detected value was found in a single sample of mixed plastics from small appliances for high-temperature applications (P24), namely 0.1 g/kg DM. Mixed plastics from large household appliances (C1, P11, P12) is the only category where TBBPA was not detected. PentaBDE only could be found in a mixed plastics sample from mixed small appliances w/o CRT- and flat screens (M1) and from consumer equipment w/o CRT- and flat screens (C4) at maximum concentrations of 0.14 and 0.13 g/kg, respectively. This suggests that PentaBDE no longer occurs in mixed plastics from WEEE in relevant concentrations, a finding supported by previous studies, (see e.g. [2–5]).

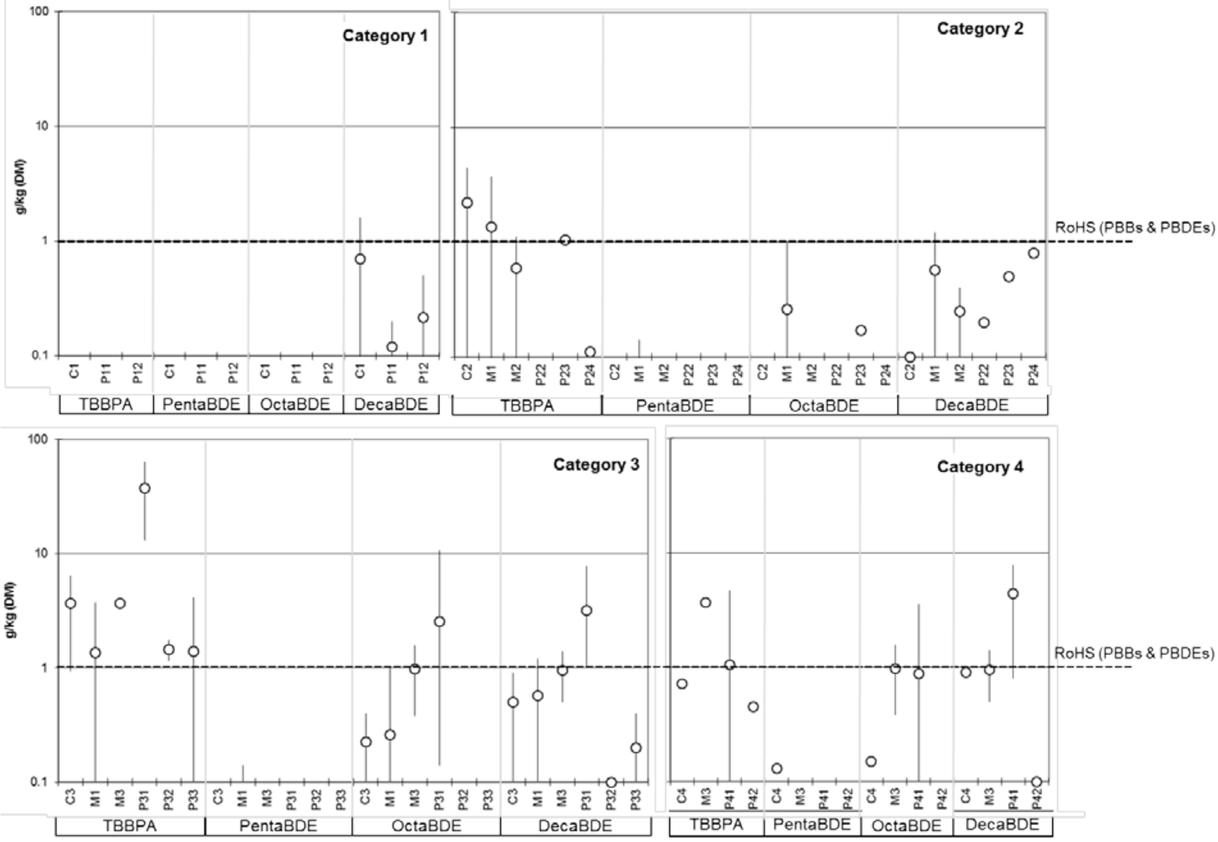

Figure 1: Concentration ranges of specific BFRs in the mixed plastics fractions, allocated to each WEEE categories 1, 2, 3 and 4 (C1: Large household appliances w/o cooling appliances {5}; C2: Small household appliances {2}; C3: ICT equipment w/o CRT- and flat screens {2}; C4: Consumer equipment w/o CRT- and flat screens {1}; M1: Small appliances w/o CRT- and flat screens {7}; M2: Small household appliances, tools, toys, leisure and sport equipment {2}; M3: ICT and consumer equipment w/o CRT- and flat screens {2}; P11: Cooling and freezing appliances (inside lining without drawers) {5}; P12: Cooling and freezing appliances (all plastics, except foams) {6}; P22: Vacuum cleaners w/o hoses {1}; P23: M2 w/o vacuum cleaners {1}; P24: Small appliances for high-temperature applications (e.g. toasters, hair dryers, curlers) {1}; P31: CRT monitors {5}; P32: Flat screens {3}; P33: Printers {3}; P41: CRT TVs {7}; P42: Flat Screen Monitors {1}). {}: number of sampling campaigns.

OctaBDE was detected at concentrations above the RoHS MCV of 1 g/kg in mixed plastics from ICT and consumer equipment w/o CRT- and flat screens (M3, average 1 g/kg, maximum 1.6 g/kg), from CRT monitors (P31, average 2.5 g/kg, maximum 10.6 g/kg) and from CRT TVs (P41, average 0.9 g/kg, maximum 3.5 g/kg). In mixed plastics from small appliances w/o CRT- and flat screens (M1), from ICT equipment w/o CRT and from flat screens (C3), OctaBDE was found in concentrations close to the RoHS MCV. In mixed plastics from consumer equipment w/o CRT- and flat screens (C4), OctaBDE was detected at levels well below the RoHS MCV (0.15 g/kg). OctaBDE was not detected in mixed plastics from large household appliances. These results correspond to those obtained in previous studies [2–4], where levels clearly above the RoHS MCV were detected in mixed plastics from CRT monitors and TV sets, and concentrations in the vicinity of the RoHS MCV in mixed plastic fractions from mixed WEEE categories. The measured average concentrations confirm typical ranges of OctaBDE concentrations in plastics from WEEE as indicated by [5]; however, these ranges might be clearly exceeded in individual mixed plastics samples from CRT monitors.

DecaBDE was measured at concentrations close to or above the RoHS MCV in almost all samples. The highest concentrations were found in mixed plastics from CRT monitors (P31, average 3.2 g/kg, maximum 7.8 g/kg) and from CRT TVs (P41, average 4.4 g/kg, maximum 7.8 g/kg). In mixed plastics from mixed small household appliances (C2) as well as from flat screen monitors and - TVs (P32 and P42), DecaBDE concentrations did not exceed the detection limit. These results correspond to those obtained in previous studies (see [2–4]) and confirm the range of DecaBDE concentrations in plastics from WEEE as indicated by [5]; however, these ranges might be clearly exceeded in individual mixed plastics samples from CRT monitors and - TVs.

The average bromine contents from total bromine measurements exceed the average bromine contents calculated from measured concentrations for the specific BFRs (HBCD, TBBPA, PentaBDE, OctaBDE, DecaBDE, DecaBB) in almost all mixed plastics addressed in this study. This suggests that these appliances also contain other BFRs (see e.g. [16]) not specifically addressed in this study. Differences between directly measured and calculated bromine contents were found to be largest for mixed plastics from WEEE categories 3 and 4.

3.2 Total phosphorus content

Phosphorus flame retardants (PFRs) such as bisphenol A bis(diphenyl phosphate) (BDP) and resorcinol bis-(diphenyl phosphate) (RDP) are typically used in ABS/polycarbonate(PC) - blends. Phosphate esters being susceptible to hydrolysis, recycling of ABS/PC containing these flame retardants may face some difficulties under conditions of heat and humidity [17]. Typically, PFRs are applied at much lower concentrations than BFRs and hence are more difficult to analyse [18]. The results of the analyses of phosphorus in WEEE plastics (see Figure 2) show that total phosphorus concentrations in the analysed plastic samples lie in the range between 1 g/kg and 35 g/kg. This range corresponds to reported amounts of PFRs typically applied in EEE plastics [17]). The highest phosphorus concentrations were found in mixed plastics from flat screens TVs (P32, average 23 g/kg, maximum 35 g/kg), CRT monitors (P32, average 7 g/kg, maximum 14 g/kg), CRT TVs (P41, average 5 g/kg, maximum 9 g/kg) and consumer equipment w/o CRT - and flat screens (C4, 5 g/kg). These findings are in line with the recent trend that PFR containing ABS/PC is substituted for ABS containing BFRs. In the case of consumer products, poly(p-phenylene oxide) (PPO) is substituted for ABS containing BFRs [19]. Below concentrations of 5 g/kg, phosphorus was detected in mixed plastics from large household appliances (C1) as well as from mixed WEEE categories M1 and M3. All other samples did not contain phosphorus above the detection limit of 0.1 g/kg.

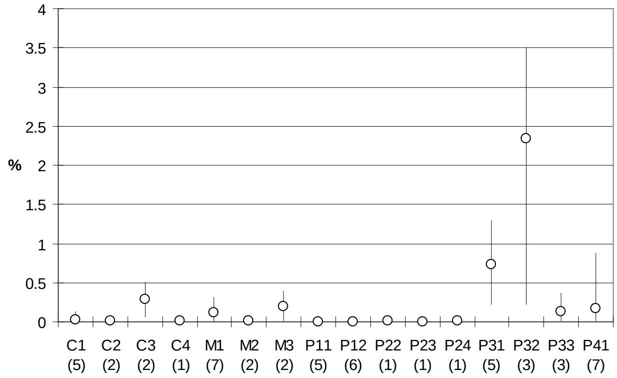

Figure 2: Concentration ranges of phosphorus in all samples (Number of samples analysed per category or product type in brackets).

3.3 Heavy metals concentrations

Lead concentrations in mixed plastics from WEEE were found to range from 12 ppm (P41) up to 7800 ppm (M1). In most samples, average lead levels were found to lie around the RoHS MCVs of 1000 ppm. The MCVs are exceeded for all mixed categories (M1 – M3) as well as for mixed plastics from ICT equipment w/o CRT- and flat screen monitors (C3) and mixed plastics from consumer equipment w/o CRT- and flat screen TVs (C4). Concentrations above the MCV were also found in one mixed plastics sample from printers (P33). In mixed plastics from WEEE categories 1 and 2 (C1 and C2), lead was found to lie in the vicinity of the RoHS MCV. Elevated lead levels in mixed plastics could be the consequence of cross contaminations from fractions such as printed wiring boards, which had not been sorted out prior to shredding [2]. This hypothesis is supported by the fact that mixed plastics samples with manual removal of the non-plastic fractions before the shredding process showed considerably lower levels of lead than mixed plastics samples without prior removal of non-plastic fractions.

Cadmium was detected in concentrations which lie close to or above the RoHS MCV of 100 ppm for cadmium in mixed plastics from small household appliances categories (C2, M2, P23). In all other mixed plastics samples the concentrations were found to lie between 2 and 62 ppm (averages: 2 – 30 ppm), with the highest concentrations in mixed plastics from TV monitors.

For some mixed plastics from WEEE category 1 to 3 devices (M2, P23), unspecified chromium was detected at concentrations near to or above the RoHS MCV defined for hexavalent chromium in all samples; in mixed plastics from WEEE category 4 devices, concentrations were lower than the MCV by at least a factor of about 2. Except for category 4 devices, our results do not allow one to exclude the possibility that the hexavalent chromium concentrations might exceed the respective RoHS MCV.

Mercury was detected in all samples at levels of at least two orders of magnitude below the corresponding RoHS MCV. This is in accordance with the findings of other studies, where mercury was not found in relevant concentrations in mixed plastics from WEEE (see. e.g. [2]).

4 Conclusions and outlook

The results of the sampling campaigns show that no mixed plastics fraction from European WEEE is completely free from substances regulated in the RoHS Directive. All the investigated mixed plastics fractions contained at least one substance regulated by the RoHS Directive in measurable amounts. This pattern can also be observed outside Europe. Especially in developing countries, which import second-hand appliances from OECD countries in large quantities [20] RoHS substances are expected to pose a challenge for the treatment of WEEE. A recent assessment of plastics from CRT monitors and TVs in Nigeria shows concentrations of brominated flame retardants in the same range as or above the levels measured in this study [21]. Also in India, a recent sampling campaign in the informal plastic recycling sector in Delhi indicates that recycled plastic fractions are often cross contaminated with brominated flame retardants by mixing plastics from WEEE with nonhazardous plastic fractions from other waste types [22]

Hence, to avoid a dissipation of hazardous substances into plastics and the environment, it is recommended that mixed plastics from WEEE are subject to a strict quality management. Plastics should be traced throughout the entire recycling chain, from the moment they are generated up to the point where they are either reintegrated into new products or properly disposed of.

In response to these results the WEEE Forum created clauses in its WEEELABEX normative requirements [23] specifying that plastic fractions containing brominated flame retardant should be removed and treated separately from other plastic fractions and in case of plastic recycling, plastic end-of-waste products should be achieved. All 41 member organisations of the WEEE Forum are required to implement the requirements in their contracts with processors. For example, the Swiss WEEE collection and recovery systems included in their technical regulations [24] that recyclers have to ensure that they either can separate RoHS regulated substances or the plastics containing these substances and dispose them of properly. The plastics fraction destined for re-use in new products have to be analyzed periodically and must comply with the RoHS Directive, unless there is clear evidence that it is not reintegrated into new EEE products. In that case, the REACH Directive [25] applies, which is less strict with regard to PBDEs, as it does not include DecaBDE and applies the limit value of 1 g/kg for PentaBDE and OctaBDE each.

On international level our study results are also in support of the development of guidance documents under the Stockholm Convention on Persistent Organic Pollutants [26]. Related to BFRs listed in Annex A, two guidance documents, for the Inventory of PBDEs and on best available techniques and best environmental practices for the recycling and disposal of articles containing PBDEs are currently established [27], [28],

Our study indicates that WEEE plastics contain brominated flame retardants which are not regulated by the RoHS Directive and hence were not specifically measured in this study. As a consequence it is suggested that further studies should be dedicated to the identification of those substances. In addition, our study indicates that phosphorus based flame retardants are applied, in particular, in WEEE category 3 and 4 appliances. Hence, investigations destined to assess the impacts of a shift to phosphorus based flame retardants with regard to inter alia recyclability and environmental impacts should be considered as well.

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