



RoHS Substances in Mixed Plastics from Waste Electrical and Electronic Equipment

Final Report

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Patrick Wäger, Mathias Schluep and Esther Müller



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Authors:

Dr. Patrick Wäger

Dr. Mathias Schluep

M. Sc. Eng. Esther Müller

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For further information please contact:

Dr. Patrick Wäger

Empa - Swiss Federal Laboratories for Materials Science and Technology

Technology & Society Laboratory

Lerchenfeldstrasse 5

CH-9014 St. Gallen

Email: patrick.waeger@empa.ch

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Summary

Since 1980, the share of plastics in electrical and electronic equipment (EEE) has continuously increased from about 14% to 18% in 1992, 22% in 2000 and estimated 23% in 2005. In 2008, the plastics share from European waste electrical and electronic equipment (WEEE) over all categories was estimated to amount to 20.6%. Assuming that the members of the WEEE Forum collected and treated about 1.5 million tons of WEEE in 2008, they salvaged or disposed of some 300'000 tons plastic waste.

The disposal and recovery of plastics from WEEE is of considerable significance, both financially/commercially and in terms of environmental implications. Amongst other things, plastics from WEEE may contain hazardous substances and can give rise to high processing costs, depending on the disposal or recovery route.

This report was commissioned by the WEEE Forum to contribute to a formulation of normative requirements with respect to depollution of WEEE. It is a sub-project of WEEELABEX, the 4-years project co-financed by the European Community (LIFE07 ENV/B/000041) that aims at producing a set of standards and procedures to verify compliance with those standards. In particular, this report intends to provide answers to the following key questions:

- 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?
- What are the implications for an environmentally sound recovery of plastics from WEEE?

The study focused on plastics from WEEE categories 1 (large household appliances), 2 (small household appliances), 3 (IT and telecommunications equipment) and 4 (consumer equipment). It partly also addressed plastics from WEEE categories 6 (electric and electronic tools) and 7 (toys, leisure and sports equipment), and excluded resins from circuit boards and plastics from cables and wires.

According to the RoHS 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 (MCV) for homogeneous materials. It is important to keep in mind that putting the focus on the RoHS Directive to evaluate plastics from WEEE with regard to their recovery potential corresponds to the application of a product-oriented perspective, which is strictly speaking only valid for specific boundary conditions (e.g. that recycled plastics is intended for use in newly marketed EEE).

Table 0-1: Maximum concentration values (MCVs) for homogeneous materials in new Electrical and Electronic Equipment (EEE) according to the RoHS Directive (amendment of August 18, 2005)

	Cd	Cr(VI)	Hg	Pb	PBBs	PBDEs ¹⁾
MCV in % by weight	0.01	0.1	0.1	0.1	0.1	0.1

1) The PBDEs include commercial pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE) and decabromodiphenyl ether (DecaBDE)

In addition, other brominated flame retardants (BFRs) known to occur in EEE (HBCD, TBBPA), the total bromine content (as an indicator allowing to estimate, if other brominated substances than the specifically analysed BFRs occur in a plastics sample), the total phosphorus content (as an indicator for the presence organophosphorus compounds) and elements such as antimony (antimony trioxide is an effective synergist for halogenated flame retardants) were analysed.

The present report consists of three parts: A first part which includes the results of a preliminary literature review originally designed to consider Swiss conditions and later adapted to the European context, a second part which presents the results of a sampling campaign including WEEE plastics, and a third part which identifies implications for WEEE plastics recovery and disposal.

Part I: Literature review

Part I of the report presents estimates of shares and amounts of plastics in European WEEE as well as approximations for plastic type shares in selected products and product types (chapter 2). After a brief introduction of the European regulatory framework related to the recovery of plastics from WEEE, hazardous substances regulated in the RoHS Directive are characterized with regard to their applications, their concentrations in WEEE plastics and expected developments regarding their occurrence in WEEE (chapter 3).

a) Plastics shares and quantities in WEEE categories and product types

The literature review has shown that data on plastics and plastic type shares in EEE and WEEE exist or may be derived from existing data. However, these data are still associated with significant uncertainties i.a. due to the limited scopes of the studies considered, data limitations and different assumptions made (e.g. regarding service lives). Despite these limitations, the quantitatively most relevant plastic types have been identified for the WEEE categories and product types in the focus of this study. These are:

- **Large household appliances w/o cooling appliances:** PP (~225'000 t/a), followed by PUR, ABS, PS and HIPS.
- **Cooling and freezing appliances:** ABS (~142'000 t/a), HIPS (~95'000 t/a) and PUR (~95'000 t/a), with PP and PVC also occurring in significant quantities.
- **Small electronic appliances:** PP (~130'000 t/a) and HIPS (~111'000 t/a), with ABS (~74'000 t/a) also occurring in significant quantities.
- **IT equipment w/o screens (CRT monitors or flat screens):** ABS (~127'000 t/a), followed by ABS/PC and HIPS.
- **CRT monitors:** ABS (~70'000 t/a), followed by HIPS (~39'000 t/a), ABS/PC and PPO/PPS.
- **Consumer equipment w/o screens (CRT monitors or flat screens):** HIPS (~100'000 t/a), followed by ABS, PPO, PPO/PS and PMMA.
- **TV sets:** HIPS (~120'000 t/a), followed by ABS (~30'000 t/a), ABS/PC, PPO and PPO/PS.

b) RoHS substances in WEEE plastics

The literature review has shown that data on RoHS substance concentrations in plastics from WEEE are available. However, these data typically focus on particular fractions such as TV set - and CRT monitor housings or unspecified WEEE shredder residues. A comprehensive overview of their occurrence in typically occurring plastic fractions from mixed WEEE categories, single WEEE categories and product types based on this data is associated with significant uncertainties.

Heavy metals in WEEE plastics

Among the elements regulated by the RoHS Directive cadmium and lead appear to pose the greatest potential problems in plastics from WEEE. In a recent study, cadmium was measured at concentrations in the range of the RoHS MCVs both in TV set – and monitor-housing shredder residues and in mixed WEEE shredder residues. The concentrations for lead have been found to lie in the range of the MCV for mixed WEEE shredder residues, which has been explained by cross contaminations from circuit boards. Unspecified chromium was measured at concentrations below the RoHS MCV for hexavalent chromium, mercury at concentrations significantly below its RoHS MCV.

On the level of plastic types, concentrations above the respective RoHS MCV are expected for cadmium, hexavalent chromium and lead in **PVC** from WEEE category 1-4 products. In **ABS** from products WEEE category 1-4 products, in particular from CRT monitors, TV sets and video appliances, the MCVs for hexavalent cadmium are expected to be exceeded. For other plastics types such as **ABS / PC** blend in WEEE category 3 and 4 products, and **PP** in category 1, 2 and 4 products, concentrations above the RoHS MCV might possibly occur.

Besides the four heavy metals regulated in the RoHS Directive, other elements such as antimony, arsenic, nickel or tin were found in plastics fractions from WEEE dismantling. For antimony, which is applied as a synergist (antimony trioxide) for BFRs, there are indications that the levels in plastics from WEEE have decreased in the past years due to a phase-out of BFRs; the same appears to be true for cadmium from cadmium-based additives. The observed reduction of chromium, lead and nickel contents in plastics from mixed WEEE shredder residues, on the other hand, points at an improved technology regarding the separation of thermoplastics from printed circuit boards.

Flame retardants in WEEE plastics

According to the literature review, PentaBDE, OctaBDE and DecaBDE appear to be the most critical flame retardants regulated by the RoHS Directive in WEEE plastics. For the five quantitatively most relevant plastic types in WEEE, Table 0-2 shows where these flame retardants possibly or most probably will occur at concentrations above the RoHS MCV for PBDEs. In **ABS**, OctaBDE and DecaBDE might exceed the MCV for PBDEs in WEEE category 1 and 2 products, whereas in **ABS** from WEEE categories 3 and 4 concentrations above the MCV for PBDEs are possible for DecaBDE and expected for OctaBDE. In **HIPS**, only DecaBDE is expected to occur in relevant concentrations, in particular in products from WEEE categories 3 and 4. In **PP**, DecaBDE might occur at concentrations above the MCV for PBDE, and in PU, PentaBDE concentrations possibly might exceed the MCV for PBDEs.

In other plastic types, DecaBDE is expected to occur at concentrations which might exceed the RoHS MCV for PBDEs in **PA** for category 1 (w/o freezing and cooling appliances), category 2 and category 3 products, and in **PC** for WEEE category 2 products, LCD-monitors as well as WEEE category 4 products. For **PS** in CRT TV sets, the MCV for PBDEs is expected to be exceeded for DecaBDE. In **PE** found in PC/servers, notebooks, printers and copiers, both OctaBDE and DecaBDE might occur at concentrations above the MCV for PBDEs.

Table 0-2: Expected occurrence of substances regulated by the RoHS Directive in the five quantitatively most relevant plastic types from WEEE categories 1 to 4 (bold text: concentrations above of RoHS MCV for PBDEs expected; plain text: Concentrations above the RoHS MCV for PBDEs possible; grey cell: no relevant amounts of plastic type in the corresponding WEEE category)

	Category 1	Category 2	Category 3	Category 4
ABS	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE
HIPS	DecaBDE	DecaBDE	DecaBDE	DecaBDE
ABS/PC			Cadmium	Cadmium
PP	Cadmium, DecaBDE	Cadmium, DecaBDE		Cadmium, DecaBDE
PUR	PentaBDE	PentaBDE		

Regarding polybrominated biphenyls, there are strong indications that if they still occur in WEEE at all, then at concentrations well below the RoHS MCV. Moreover, BFRs regulated by the Directive appear to be increasingly being substituted by other, unspecified brominated flame retardants and organophosphorus compounds. The latter are expected to occur in PC/ABS, in particular.

When processing plastics containing BFR at elevated temperatures, polybrominated dibenzo dioxins and –furans (PBDD/PBDF) can be unintentionally produced, leading to concentrations exceeding the limit values defined in the German Chemicals Ordinance. In shredders, it has to be expected that PBDD/PBDF levels increase with the energy applied, i.e. with decreasing particle size of the shredder residues.

Part II: Sampling campaign

Part II of the report presents the methodology (chapter 5) and the results (chapter 6) of the sampling campaign performed between October 2009 and February 2010 with the participation of members of the WEEE Forum. A comprehensive sampling campaign complementing the literature review was considered necessary because of the incompleteness and uncertainty of published data with regard to WEEE categories covered by European recovery and disposal companies.

Table 0-3 presents the main outcome of the sampling as discussed in detail in chapter 6. It abstains from displaying a special column for total PBDE concentrations, because these typically only exceeded the RoHS MCV for PBDEs, when the average concentration of one of the regulated single PBDE (PentaBDE, OctaBDE and DecaBDE) was above the MCV (indicated in red).

Table 0-3: Classification of measured concentrations according to the RoHS maximum concentration levels (MCVs) for lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), polybrominated diphenyl ethers (PentaBDE, OctaBDE, DecaBDE) and polybrominated biphenyls (DecaBB) in the analysed mixed WEEE categories, WEEE categories and single product types.

		Pb	Cd	Hg	Cr	Penta BDE	Octa BDE	Deca BDE	Deca BB
Mixed WEEE categories	Small appliances w/o CRT- and flat screens (M1, 7)		ABS PP				ABS	ABS HIPS,PP	
	Small household appliances, tools, toys, leisure and sports equipment (M2, 2)		ABS PP					ABS HIPS,PP	
	ICT and consumer equipment w/o CRT- and flat screens (M3, 2)		ABS ABS/PC				ABS	ABS HIPS	
WEEE categories	Large household appliances w/o cooling and freezing appliances (C1, 5)							ABS PP	
	Small household appliances (C2, 2)		ABS PP						
	ICT equipment w/o CRT - and flat screens (C3, 2)		ABS ABS/PC				ABS	ABS HIPS	
	Consumer equipment w/o CRT- and flat creens (C4, 1)		ABS ABS/PC				ABS	ABS HIPS	
Single product types	Cooling and freezing appliances (inside lining without drawers) (P11,5)		ABS PP					ABS HIPS,PP	
	Cooling and freezing appliances (all plastics, except foams) (P12, 6)		ABS PP					ABS HIPS,PP	
	Vacuum cleaners w/o hoses (P22, 1)		ABS PP					ABS HIPS	
	Small appliances for high temperature applications (P24, 1)		ABS,PP					ABS HIPS,PP	
	CRT monitors (P31,5)		ABS				ABS	ABS HIPS	
	Flat screen monitors (P32, 3)								
	Printers (P33, 3)							ABS HIPS	
	CRT TVs (P41, 7)		ABS,PP ABS/PC				ABS	ABS HIPS	

in brackets: sample code and number of sampling campaigns
w/o: without

not detected or at average concentrations clearly (i.e. more than an order of magnitude) below the RoHS MCV
average concentrations below (yellow cells) or in the vicinity (orange cells) of the RoHS MCV
average concentrations above the RoHS MCV

XXX: plastic type predominantly containing the substance (according to the literature review in chapter 3)

For the interpretation of the results it has to be considered that the measured values refer to a mixture of plastic types from single product type samples, WEEE category samples or mixed WEEE category samples. Hence, in this study RoHS substances in single plastic types were not analysed. This implies that measured concentrations could underestimate the level of RoHS substances in specific plastic types due to a dilution by products (for mixed samples) and plastic types (for all samples) with lower or not detectable RoHS substance concentrations.

Mercury, PentaBDE and DecaBB were measured at average concentrations of at least an order of magnitude below the respective MCV in all mixed plastics fractions except for consumer equipment (PentaBDE) and CRT TVs (DecaBB), where they were detected at average concentrations slightly above 0.1 g/kg. The highest DecaBB levels were found in a single CRT TV set sample at concentrations of about half of the RoHS MCV.

For mixed plastics from WEEE category 1 appliances (C1, P11, P12), the most critical brominated flame retardant appears to be DecaBDE, however with average concentrations below the RoHS MCV. According to the literature review, the occurrence of DecaBDE is a consequence of the application of ABS and PP in large household appliances w/o cooling and freezing appliances, and of ABS, HIPS and PP in cooling and freezing appliances. Whereas other BFRs were not detected in relevant average concentrations at all, lead and total chromium were found in average concentrations below their respective RoHS MCVs.

Regarding WEEE category 2 appliances, average cadmium concentrations above the RoHS MCV were found in the mixed plastics fraction from small household appliances without CRT- and flat screens (C2). In the same mixed plastics fraction, average DecaBDE concentrations did not appear to be relevant, however mixed plastics fractions from vacuum cleaners (P21) and small appliances for high temperature applications (P24) showed to contain DecaBDE at average concentrations below or in the vicinity of the RoHS MCV. In all investigated mixed plastics fractions related to WEEE category 2 appliances other RoHS regulated BFRs could not be detected at relevant concentrations; lead and chromium were found at average concentrations below their RoHS MCV.

For mixed plastics from WEEE category 3 appliances, OctaBDE and DecaBDE in CRT monitors are the hot spot regarding brominated flame retardants, with average concentrations clearly above the RoHS MCV for PBDEs. Mixed category 3 samples without CRT monitors (M1, M3 and C3) showed elevated OctaBDE - and DecaBDE concentrations, with values in the vicinity of the RoHS MCV. For printers (P33), slightly elevated DecaBDE concentrations well below the RoHS MCV were measured. Literature data indicate that ABS is the main source for elevated concentrations of OctaBDE and DecaBDE in mixed plastics from WEEE category 3 appliances, to some extent also HIPS (in CRT monitors and printers). In flat screen monitors, chromium was the only RoHS substance which could be measured in relevant concentrations, however well below the RoHS MCV for hexavalent chromium. Average lead concentrations in mixed plastics from mixed category 3 samples (M1, M3 and C3) clearly exceeded the RoHS MCV; in mixed plastics from printers they were found to be in the vicinity of the RoHS MCV. Cadmium and chromium were detected, however at concentrations well below their corresponding RoHS MCVs.

For mixed plastics from WEEE category 4 appliances, the main source of RoHS regulated BFRs were CRT TVs (P41), with average OctaBDE concentrations in the vicinity of the RoHS MCV and average DecaBDE concentrations clearly above the RoHS MCV. According to literature data, in WEEE category 4 appliances the main source for OctaBDE is ABS, and for DecaBDE either ABS or HIPS. The mixed plastics fraction from mixed WEEE category 4 without CRT screens (C4) showed average levels of DecaBDE in the vicinity of the RoHS MCV and OctaBDE concentrations well below the RoHS MCV. In the same fraction, average lead concentrations exceeded the RoHS MCV.

TBBPA was detected in most samples, with the highest concentrations in CRT monitors. HBCD could not be found in any of the samples.

The results of the analyses of the total bromine contents and antimony concentrations indicate that besides the specifically measured BFRs (PentaBDE, OctaBDE, DecaBDE, DecaBB, HBCD, TBBPA) other unspecified BFRs were present in WEEE category 2, 3 and 4 plastic samples.

The results of the analyses of phosphorus in WEEE plastics show that WEEE category 3 and 4 samples total phosphorus concentrations lie in range between 0.1 % and 3.5 % by weight, which corresponds to reported amounts of phosphorus based flame retardants (PFRs) typically applied in EEE plastics. Findings are in line with the recent trend that ABS containing BFRs is substituted with PFRs containing ABS/PC.

Part III: Conclusions, Implications and Outlook

Part III of the report allocates the mixed plastics fractions considered in the sampling campaign to four groups reflecting different degrees of 'criticality' with regard to their recovery, and derives some implications from each a product - and a waste perspective. According to the allocation there is no uncritical mixed plastics fraction, however there are two fractions which appear to be very critical (mixed plastics from CRT monitors and CRT TVs). Based on this classification, possible guidelines for a recovery of plastics out of mixed plastics fractions from WEEE treatment are proposed as a starting point for further discussions with the relevant stakeholders. With regard to the classification of mixed plastics as hazardous waste, the Swiss practice appears to be more restrictive than the European Commission Decision 2000/532EC.

List of Abbreviations

a	year
ABS	Acrylonitrile butadiene styrene
ABS/PC	Acrylonitrile butadiene styrene / polycarbonate blend
ABS/PVC	Acrylonitrile butadiene styrene / polyvinyl chloride blend
ASA	Acrylonitrile Styrene Acrylate
BB	Brominated biphenyls
BDE	Brominated diphenyl ethers
BDP	Bisphenol A bis(diphenyl phosphate)
BFR	Brominated Flame Retardant
Cd	Cadmium
Cr(VI)	Hexavalent chromium
CRT	Cathode ray tube
DecaBB	Decabromobiphenyl
DecaBDE	Decabromodiphenyl ether
DIN	Deutsche Industrienorm
DM	Dry Matter
EC	European Community
EBP	bis(pentabromophenyl)ethane
EEE	Electrical and Electronic Equipment
EP	Epoxy resin
EPS	Extruded polystyrene
EU	European Union
FOEN	Swiss Federal Office for the Environment
HBCD	Hexabromocyclododecane
HexaBDE	Hexabromodiphenyl ether
HeptaBDE	Heptabromodiphenyl ether
Hg	Mercury
HIPS	High impact polystyrene
IT	Information technology
LAGA	Länder-Arbeitsgemeinschaft Abfall
MCV	Maximum concentration value
OctaBDE	Octabromodiphenyl ether
ORRChem	Swiss Ordinance on Risk Reduction related to Chemical Products
PA	Polyamide
Pb	Lead

PBB	Polybrominated biphenyls
PBDD	Polybrominated dibenzo dioxins
PBDE	Polybrominated diphenyl ethers
PBDF	Polybrominated dibenzo furans
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCDD	Polychlorinated dibenzo dioxins
PCDF	Polychlorinated dibenzo furans
PE	Polyethylene
PentaBDE	Pentabromodiphenyl ether
PFR	Phosphorus based flame retardant
PMMA	Poly(methyl methacrylate)
ppm	parts per million (corresponds to e.g. 1 mg/kg)
PP	Polypropylene
PPE	Polyphenylene ether
POP	Persistent Organic Pollutant
PPO	Poly(<i>p</i> -phenylene oxide)
PS	Polystyrene
PUR	Polyurethane
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RDP	Resorcinol bis-(diphenyl phosphate)
RoHS	Restriction of Hazardous Substances
SAN	Styrene acrylonitrile
Sb	Antimony
TBBPA	Tetrabromobisphenol A
TBPE	1,2-bis-tribromophenoxyethan
TC	Telecommunications
TPP	Triphenyl phosphate
TV	Television
WEEE	Waste Electrical and Electronic Equipment
w/o	without

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1 Introduction

1.1 Background

Since 1980, the share of plastics in electrical and electronic equipment (EEE) has continuously increased from about 14% to 18% in 1992, 22% in 2000 and estimated 23% in 2005 (APME 2001). In 2008, the plastics share from European waste electrical and electronic equipment (WEEE) over all categories was estimated to amount to 20.6% (Huisman et al. 2008). Assuming that the members of the WEEE Forum collected and treated about 1.5 million tons of WEEE in 2008 (WEEE Forum 2009), they salvaged or disposed of some 300'000 tons plastic waste.

The disposal and recovery of plastics from WEEE is of considerable significance, both financial-ly/commercially and in terms of environmental implications. Amongst other things, plastics from WEEE may contain hazardous substances and can give rise to high processing costs, depending on the disposal or re-covery route.

In a preliminary literature review, the different plastics used in WEEE and their content of hazardous substances regulated by the RoHS Directive were identified by means of a desktop research (Wäger et al. 2008). The study gave valuable insights, but also showed that there still are considerable data gaps and un-certainties, which require additional plastic sample analyses. As a consequence, on behalf of the WEEE Fo-rum a comprehensive sampling campaign covering different WEEE categories and – product types all over Europe has been designed and carried out between October 2009 and May 2010. In the present report, se-lected outcomes of the preliminary literature review and the results of the sampling campaign are present-ed.

1.2 Goals and scope

The study presented in this report intended to give answers to the following key questions:

- What are the concentrations of substances regulated by the Directive 2002/95/EC of the European Par-liament 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?
- What are the implications for an environmentally sound recovery of plastics from WEEE?

The study focused on plastics from WEEE categories 1 (large household appliances), 2 (small household appliances), 3 (IT and telecommunications equipment) and 4 (consumer equipment). It partly also ad-dressed plastics from WEEE categories 6 (electric and electronic tools) and 7 (toys, leisure and sports equipment), and excluded resins from circuit boards and plastics from cables and wires.

According to the RoHS Directive, the Member States are expected to make sure that from July 1, 2006 new-ly marketed EEE shall not contain any lead, mercury, cadmium, hexavalent chromium, polybrominated bi-phenyls or polybrominated diphenyl ethers in concentrations above defined maximum concentration values (MCV) for homogeneous materials. It is important to keep in mind that putting the focus on the RoHS Di-

rective to evaluate plastics from WEEE with regard to their recovery potential corresponds to the application of a product-oriented perspective, which is only valid for specific boundary conditions (i.a. no dilution of the recycled plastics with other plastics and use of recycled plastics for newly marketed EEE only).

In addition, other brominated flame retardants (BFRs) known to occur in EEE (HBCD, TBBPA), the total bromine content (as an indicator allowing to estimate, if other brominated substances than the specifically analysed BFRs occur in a plastics sample), the total phosphorus content (as an indicator for the presence organophosphorus compounds) and elements such as antimony (antimony trioxide is an effective synergist for halogenated flame retardants) were analysed.

1.3 Outline of the report

The present report consists of three parts: A first part which includes the results of a preliminary literature review originally designed to consider Swiss conditions (Wäger et al. 2008, Wäger et al. 2009) and then adapted to the European context, a second part which presents the results of a WEEE plastics sampling campaign, and a third part which identifies implications for WEEE plastics recovery and disposal.

Part I of the report begins with estimations of the shares and amounts of plastics in European WEEE as well as approximations for plastic type shares in selected products and product types (chapter 2). After a brief introduction of the European regulatory framework related to the recovery of plastics from WEEE, hazardous substances regulated in the RoHS Directive are then characterized with regard to their applications, their concentrations in WEEE plastics and expected developments regarding their occurrence in WEEE (see chapter 3). Part I concludes with a synopsis summarizing main insights from the preliminary literature review (chapter 4).

Part II of the report presents the methodology (chapter 5) and the results (chapter 6) of the sampling campaign performed between October 2009 and February 2010 with the participation of members of the WEEE-Forum. A comprehensive sampling campaign complementing the literature review had been considered necessary because of the incompleteness and uncertainty of published data with regard to WEEE categories covered by European recycling and disposal companies. Part II concludes with a synopsis of the insights from the sampling campaign (chapter 7).

Part III of the report addresses the implications of the results presented in Parts I and II for recovery and disposal of WEEE plastics each from a product and a waste perspective. From a product perspective, which considers criteria defined in the RoHS Directive, the analysed plastics mixtures are tentatively allocated to recovery categories, each with different requirements regarding separation and disposal of specific plastics fractions. From a waste perspective referring to existing European waste legislation, mixed plastics fractions are identified, which according to the results of the sampling campaign would have had to be classified as hazardous waste.

Part III of the report allocates the mixed plastics fractions considered in the sampling campaign to four groups reflecting different degrees of 'criticality' with regard to their recovery, and derives some implications from each a product - and a waste perspective. In particular, possible guidelines for a recovery of plastics out of mixed plastics fractions from WEEE treatment are proposed as a starting point for further discus-

sions with the relevant stakeholders. Besides, the outcome of the application of European Union - and Swiss waste classification criteria on the investigated mixed plastics fractions are shown. The outlook concludes with some remaining open questions.

Part I: Literature Review

2 Plastics in WEEE

2.1 WEEE mass flows in Europe

A reliable data source for the amount of WEEE generated per year in Europe is the 2008 Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE) (Huisman et al. 2008), which was refined with regard to the extrapolations needed to calculate the total amount of WEEE generated in EU27 plus Norway and Switzerland in the past two years (Huisman 2010). Table 2-1 lists the amount of WEEE generated in Europe according to these studies, subdivided into the different WEEE categories. Since the focus of the present study is not only on WEEE categories but also on various single product groups (see Table 5-2 in section 5.1), the most important ones ('Cooling and freezing appliances', 'Computer screens' and 'TV screens') are reported separately in the table.

Table 2-1: Amount (in t/year) of WEEE generated in 2008 in EU27 plus Norway and Switzerland (Huisman et al. 2008, Huisman 2010)

Category		Share	Amount [t]
1	Large household appliances w/o cooling appliances	27.7%	2'624'000
1	Cooling and freezing appliances	17.7%	1'680'000
2	Small household appliances	10.64%	1'008'000
3	ICT equipment w/o screens (CRTs, flat screens)	8.0%	759'000
3	Computer screens	8.4%	791'000
4	Consumer equipment w/o screens (CRTs, flat screens)	7.8%	741'000
4	TV screens	13.2%	1'250'000
5	Lighting equipment – Lamps	2.4%	227'000
6	Electrical and electronic tools	3.5%	333'000
7	Toys, leisure and sports equipment	0.1%	10'000
8	Medical devices	0.1%	11'000
9	Monitoring and control instruments	0.2%	20'000
10	Automatic dispensers	0.2%	17'000
Total amount 2008		100%	9'472'000

It is important to mention that the total amount of 9'472'000 tonnes corresponds to WEEE generated in 2008, and not to WEEE collected and treated. Since a considerable amount of WEEE is stored or disposed of in other disposal channels, these two figures can differ significantly.

2.2 Total plastic shares and quantities in European WEEE

In Western Europe the domain of IT- and telecommunication accounted for 40% of the plastics applied in EEE, large household appliances for 33%, consumer electronics for 15% and small household appliances for 10%. Together, these product categories accounted for 97% of the plastics use in EEE. Within the IT and telecommunications category data processing appliances are the most important with a share of 29%. For cables and wires as well as for electrical installations significant amounts of plastics have also been applied (APME 2001).

Because of the differing service lives for the different product types, these shares do not reflect the actual plastics composition in WEEE. Furthermore, it has to be assumed that the plastics use for some product types is higher than the plastics consumption of the Western European industry due to imports from Asia and from the USA. Such imports appear to be more relevant for consumer electronic- and IT/telecommunications appliances than for example for large household appliances, which would change the plastics proportions for the different WEEE categories presented in Figure 2-1 (Wäger et al. 2008).

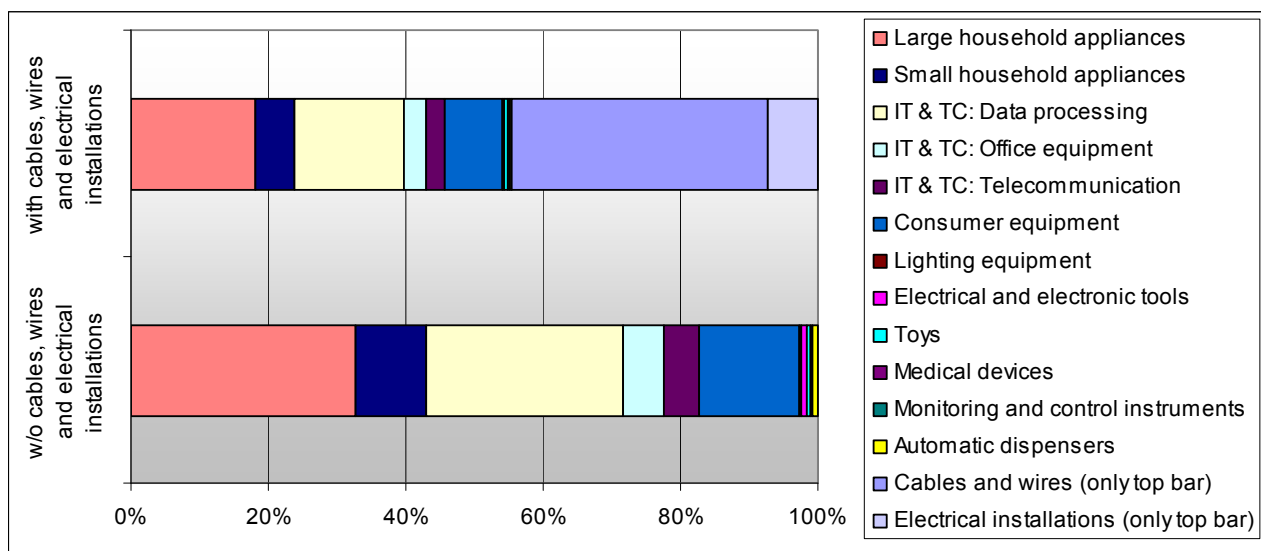


Figure 2-1: Relative plastics consumption in the EEE domain in Western Europe for the year 2000 (APME 2001)

The plastics share in European WEEE over all categories was estimated to amount to 20.6% in 2008 (Huisman et al. 2008). In new WEEE appliances, the share has continuously increased since 1980 from scarcely 14% to 18% in 1992, 22% in 2000 and estimated 23% in 2005 (APME 2001). Depending on the category or product, the plastic shares vary between 3% for medical equipment and 73% for electronic toys. Figure 2-2 shows the plastic shares for different WEEE categories and single product types.

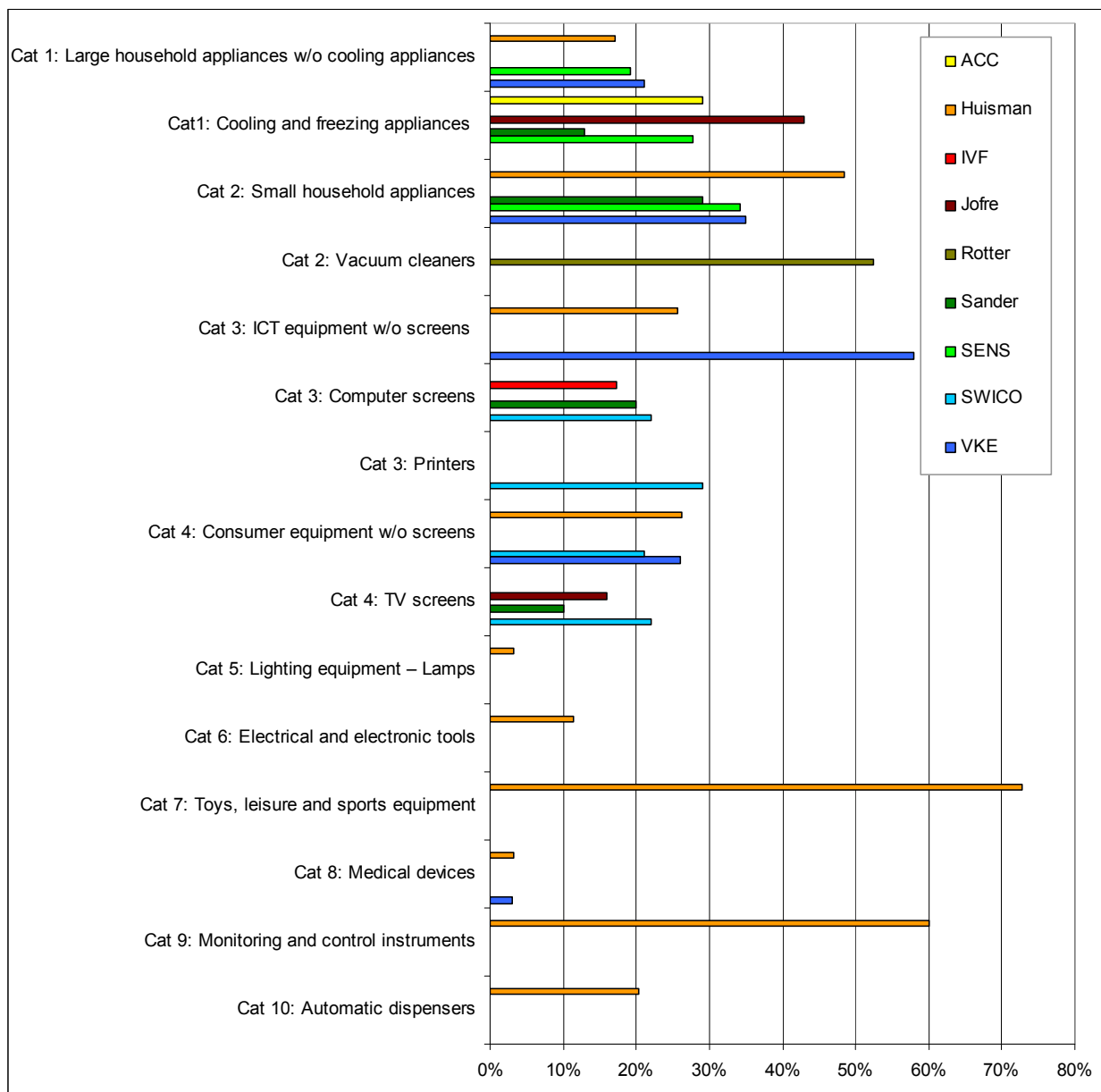


Figure 2-2: Plastic shares by weight for different WEEE categories and single product types. Printed wiring boards and cables are not included ((ACC undated), (Huisman et al. 2008), (IVF 2007), (Jofre and Morioka 2005), (Rotter et al. 2006), (Sander et al. 2004), (SENS 2008), (SWICO 2009), (VKE 2003))

For most categories with more than one reference available, plastic shares correspond quite well. The discrepancies are highest for ICT equipment w/o screens, where (Huisman et al. 2008) state a significantly lower plastic share (26 %) than (VKE 2003) (58%). This is most probably due to the fact that (VKE 2003) refers to the plastic use of new EEE appliances for telecommunication, whereas in (Huisman et al. 2008) devices for both information technologies and telecommunication were considered.

Significant deviations can also be found for cooling and freezing appliances. (Sander et al. 2004) states a plastic share of 13%, based on information of different recyclers in Germany. (Jofre and Morioka 2005) indicates a share of 43%, but only considers Japanese appliances. Data from batch experiments carried out by (SENS 2008) lie in between with 28%.

For category 5, 6, 7, 9 and 10, data only were found in (Huisman et al. 2008).

Table 2-2: Estimation of the total plastic quantities in European WEEE for the year 2008, divided into the different WEEE categories or single products. Printed wiring boards and cables are not included.

Category/Product		Plastic share [in % by weight]			Annual plastic flow [in t/year]		
		minimum	maximum	mean	minimum	maximum	mean
1	Large household appliances w/o cooling appliances	17%	21%	19%	446'600	551'000	500'500
1	Cooling and freezing appliances	13%	43%	28%	217'600	722'600	473'100
2	Small household appliances	29%	48%	37%	292'300	487'800	369'400
3	ICT equipment w/o screens	26%	58%	42%	195'100	440'100	317'600
3	Computer screens	17%	22%	20%	136'200	174'000	156'100
4	Consumer equipment w/o screens	21%	26%	24%	155'600	194'600	180'900
4	TV screens	10%	22%	16%	125'000	275'100	200'100
5	Lighting equipment – Lamps	3%	3%	3%	7'300	7'300	7'300
6	Electrical and electronic tools	11%	11%	11%	37'800	37'800	37'800
7	Toys, leisure and sports equipment	73%	73%	73%	7'600	7'600	7'600
8	Medical devices	3%	3%	3%	300	400	400
9	Monitoring and control instruments	60%	60%	60%	11'900	11'900	11'900
10	Automatic dispensers	20%	20%	20%	3'500	3'500	3'500
Total amount					1'636'900	2'913'600	2'266'100

2.3 Plastic type shares in European WEEE

According to Figure 2-3, the quantitatively most relevant plastic types in EEE appear to be ABS (incl. SAN and ASA), polystyrene (in particular HIPS) and PP. The higher shares of PVC, PE and PA for Germany ((Lindner et al. 2002) (APME 2001)) are due to the inclusion of cables and electrical installations, which were not accounted for in the Western European figures (APME 2001). Besides differences between the overall Western European and the German industry, this is also the reason for the lower share of ABS/ASA/SAN. For the interpretation of the data it should be considered that for some product types a large fraction of the products is imported from outside of Europe (in particular from Asia), which is why the plastic type shares might have to be modified.

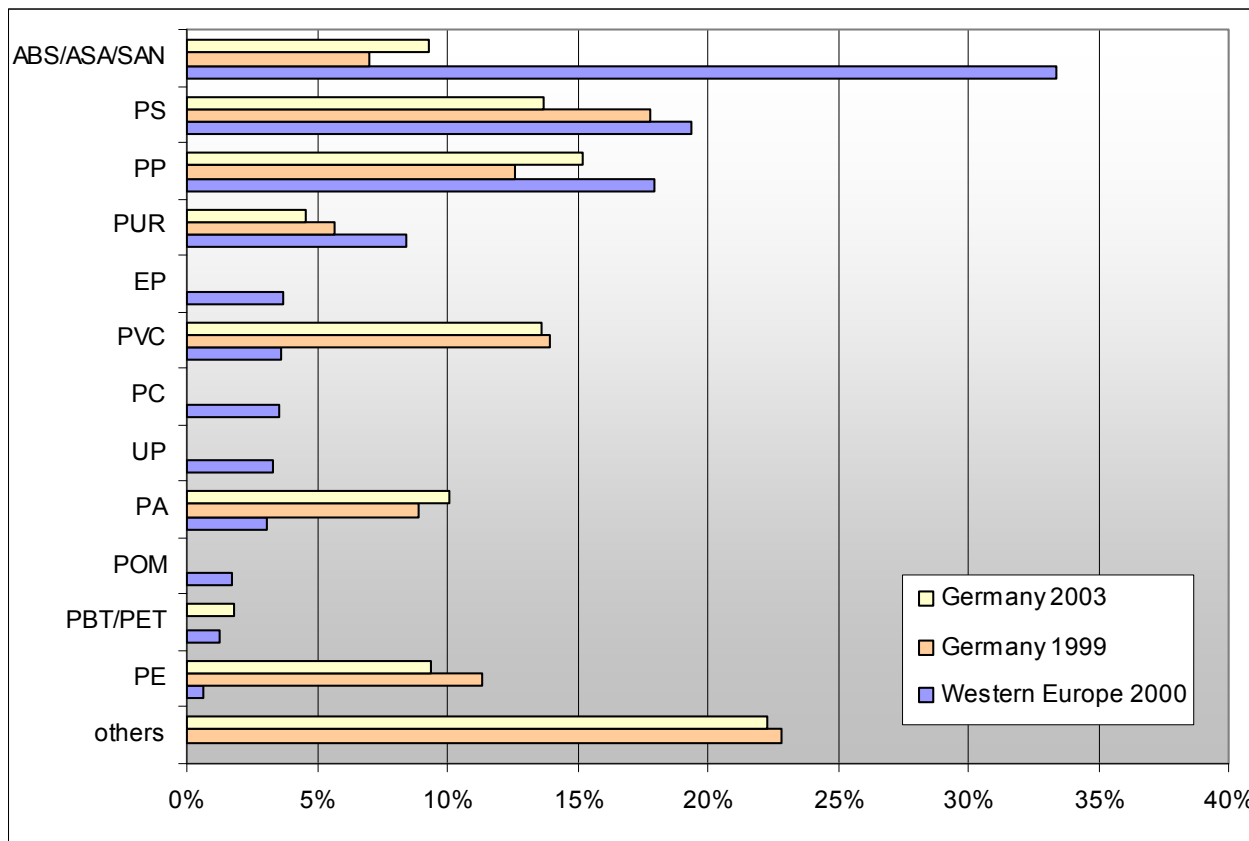


Figure 2-3: Plastic type use for EEE ((APME 2001, Lindner et al. 2002, PlasticsEurope 2004)

For Western Europe, an allocation of plastic types to product types has been published for the year 1998 (see Figure 2-4; a request for more recent data remained unanswered). Assuming typical service lives for EEE (see (Huisman et al. 2008)), these data approximately reflect the WEEE plastics composition in the year 2008 for brown goods (10 years service life for television sets, hi-fi systems and radios; 5 years for video and DVD-appliances) and for large household appliances (10 years dish washers, refrigerators, deep freezers and tumblers; 8 years for washing machines), while for small household appliances and office equipment they are considered to be too old.

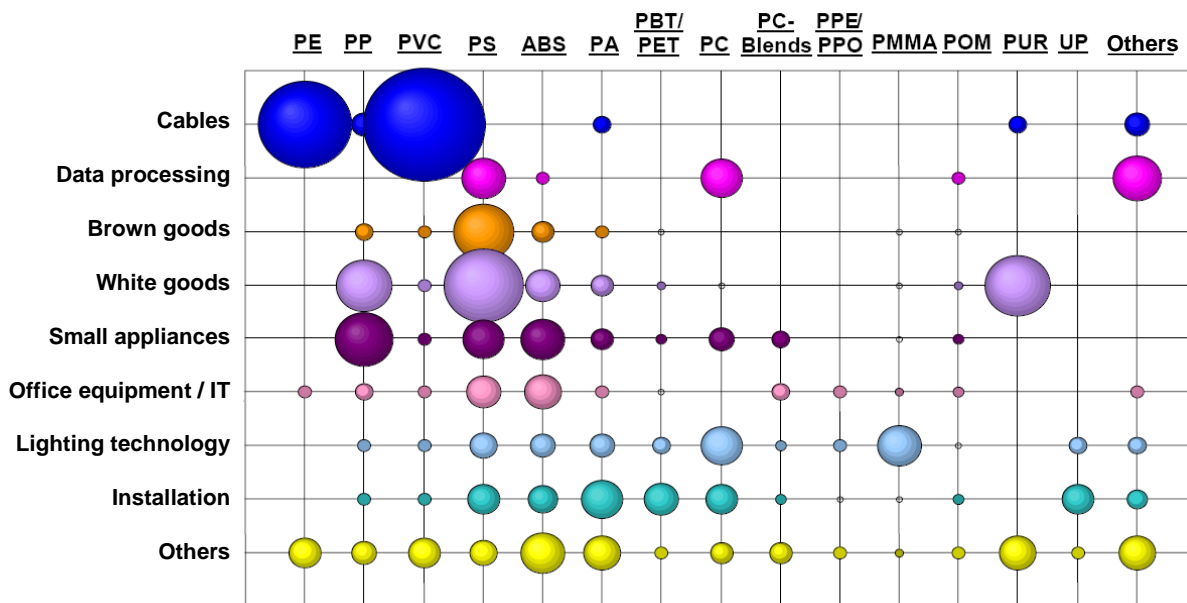


Figure 2-4: Plastics use in the Western European EE industry depending on the application (adapted from (VKE 2000))

2.3.1 IT and Telecommunication

In computers and other office devices a relatively small number of different plastics are applied. While ABS, ABS/PC and HIPS are by far the most important, plastics such as PVC and PC are of less relevance (Dufton 2003). This is quite well confirmed by available studies on the plastics composition of computer monitors, which show that ABS is most prominent with shares between 20% and 73% (see Figure 2-5). Omitting the two studies, in which a mix of PC monitors and television sets has been investigated, the lowest share of ABS reported was 32%. ABS/PC and HIPS only were found in an older study and in the two studies of mixed PC monitors and television sets, while they were not identified or separately accounted for in newer CRT- and LCD monitors. Here, the plastic types PS (19% and 20%, respectively), EPS (7% and 13%, respectively) occur in significant amounts; in LCD monitors PC (18%), PE (8%) and PMMA (7%), which were not accounted for in other studies, also could be found in relevant amounts.

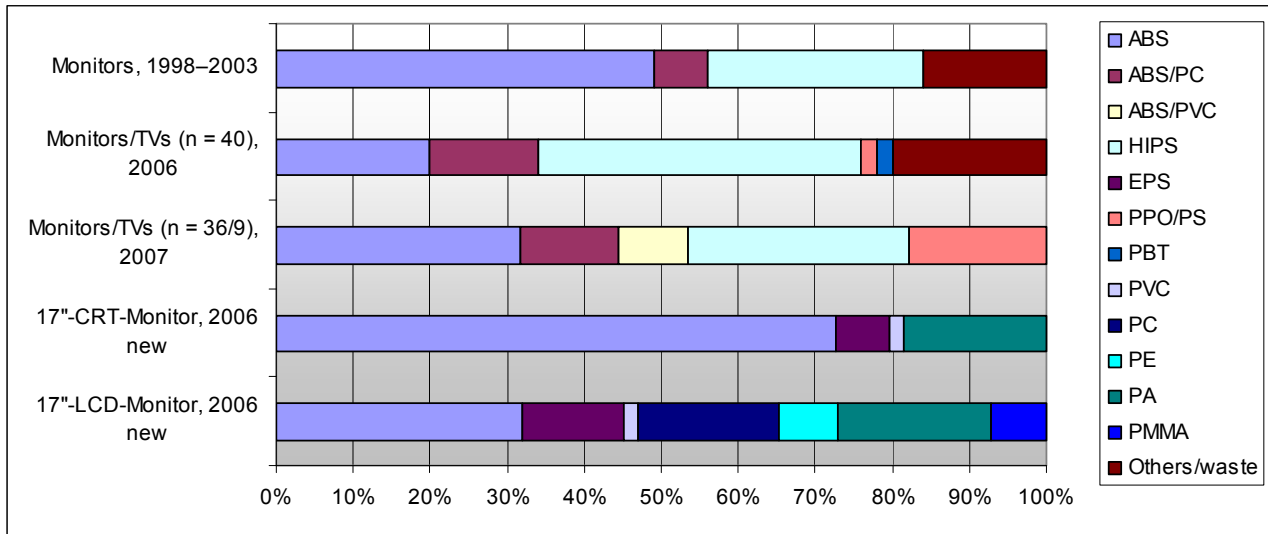


Figure 2-5: Composition of the plastics fraction in PC monitors (Rios et al. 2003, Schlummer and Maurer 2006, IVF 2007, Schlummer et al. 2007)

If new notebooks with only 17% of ABS are not considered, ABS is also the most relevant plastic type in other IT-devices, with shares of 34% to 77%. The above-mentioned observation that ABS/PC and HIPS can be found in old devices, but not in new ones, is at least partly also true for the other IT-devices. In three studies, the shares of PPO or PPO/PS lay between 17% and 36%, while these plastic types were not accounted for in the other studies. As for new monitors, great shares of PC (23% and 31%, respectively), PA (12% and 33%, respectively) and pE (22% and 5%, respectively) were found.

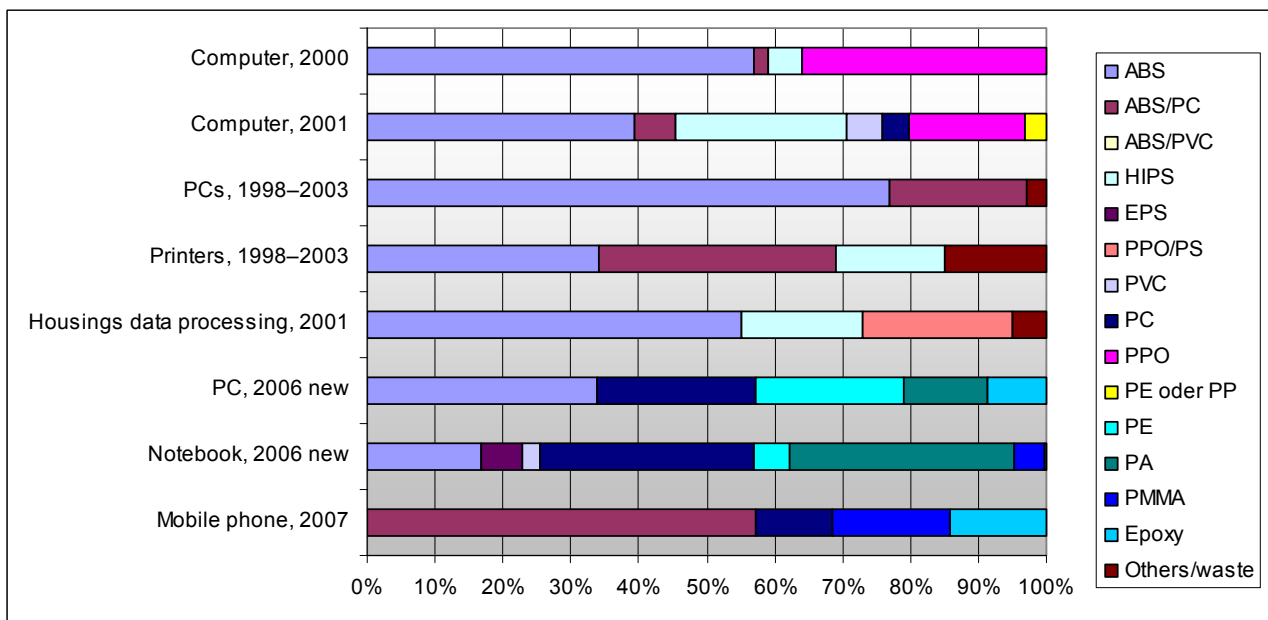


Figure 2-6: Composition of the plastics fraction in the IT- and telecommunications domain, excluding monitors (Headley Pratt Consulting 2000, MOEA 2001, Rios et al. 2003, Schlummer and Maurer 2006, IVF 2007, Müller and Griese 2007, Schlummer et al. 2007)

2.3.2 Television sets

The composition of the plastics fraction in television sets has been investigated in several studies. The reported plastics types and their shares partly show significant deviations. For PPO/PS for example, in some studies a share of 35% is reported, while in other studies the share amounts to 2%, or has not been considered. On the other hand, PPO is partly reported alone. In the study of (Jofre and Morioka 2005), the PS-share of 85% probably corresponds to HIPS (see Figure 2-7, uppermost bar). The studies of (Schlummer and Maurer 2006) and (Schlummer et al. 2007) (see Figure 2-7, lowermost two bars) are the most recent, however television sets were investigated together with computer monitors, which explains the lower shares of HIPS compared to the other studies. In the last mentioned study, HIPS has been identified in eight samples from nine (89%); for the ninth sample, plastics was not considered. Under omission of the study of (Schlummer and Maurer 2006), and of the exceptionally low share of 18% measured by (Riess et al. 2000) (see Figure 2-7, third bar from top), the amount of HIPS lies between 53% and 89%. Despite this variability and the outlier it can be concluded that HIPS is the most important plastic type in television sets. This is confirmed by a market study of (Dufton 2003), which however does not mention any figures for the share of HIPS. The second most important plastic type in television sets is ABS with a share of 2% to 43 %, depending on the study. The only other plastic types which could be found in relevant amounts were PPO/PS and PPO, respectively, and ABS/PC. According to (Dufton 2003), for ABS/PC it is to be expected that its share will increase in the future to the expense of ABS; the market share of HIPS should remain constant. In contrast, according to (Townsend 2005), ABS/PC and PPO will increase to the expense of HIPS.

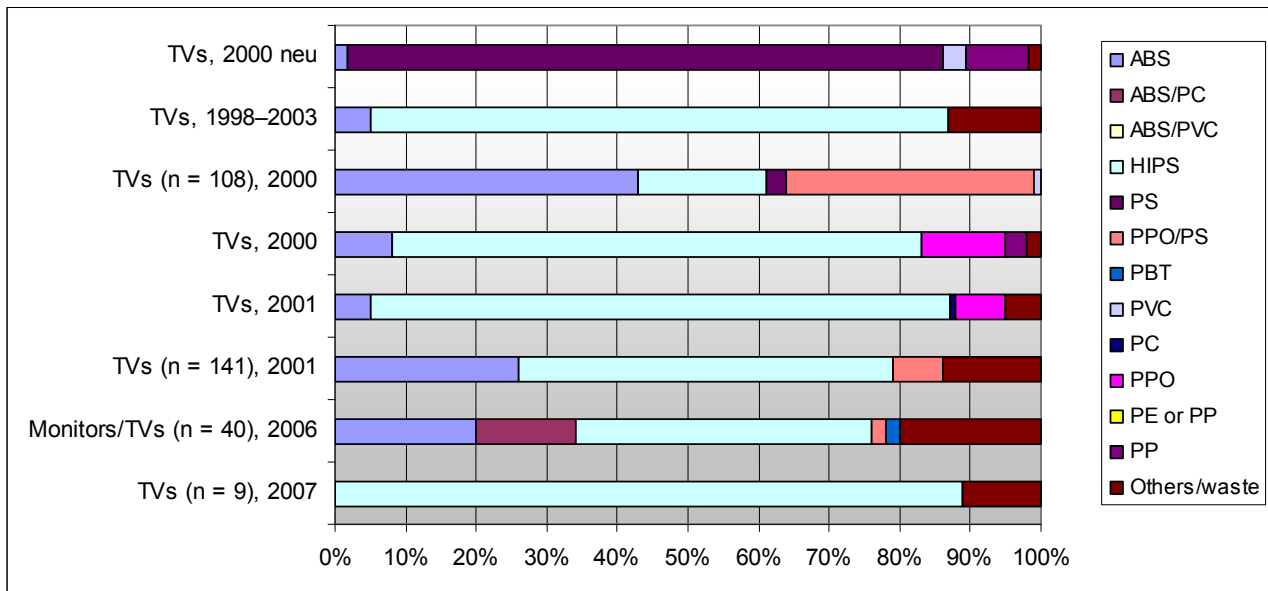


Figure 2-7: Composition of the plastics fraction in television sets (Headley Pratt Consulting 2000, Riess et al. 2000, MOEA 2001, Wolf et al. 2001, Rios et al. 2003, Jofre and Morioka 2005, Schlummer and Maurer 2006, IVF 2007, Müller and Griese 2007, Schlummer et al. 2007)

2.3.3 Consumer electronics (w/o TV sets) and small household appliances

Because the plastic shares of consumer electronics (w/o television sets) and small electric appliances are mainly investigated in combination in the available studies (e.g. as mixed fractions), they are considered together here. With a share of 48% of HIPS (see Figure 2-8), for hi-fi systems a similar picture appears as for television sets (see Figure 2-7). In a market study (Dufton 2003), HIPS was considered to be almost the only plastic type in housings of consumer electronic equipment. In contrast to television sets however, the shares of PPO (16%) and PMMA (11%) were significantly higher in hi-fi systems. For ABS, great differences between single products (5%) and mixed fractions (41%) are reported. Noticeable were the 58% of PP for the hair dryers as well as the 27% of PVC and 16% of PC for the vacuum cleaners. In two samples, SAN was accounted for separately, while in other studies it was included in the ABS share.

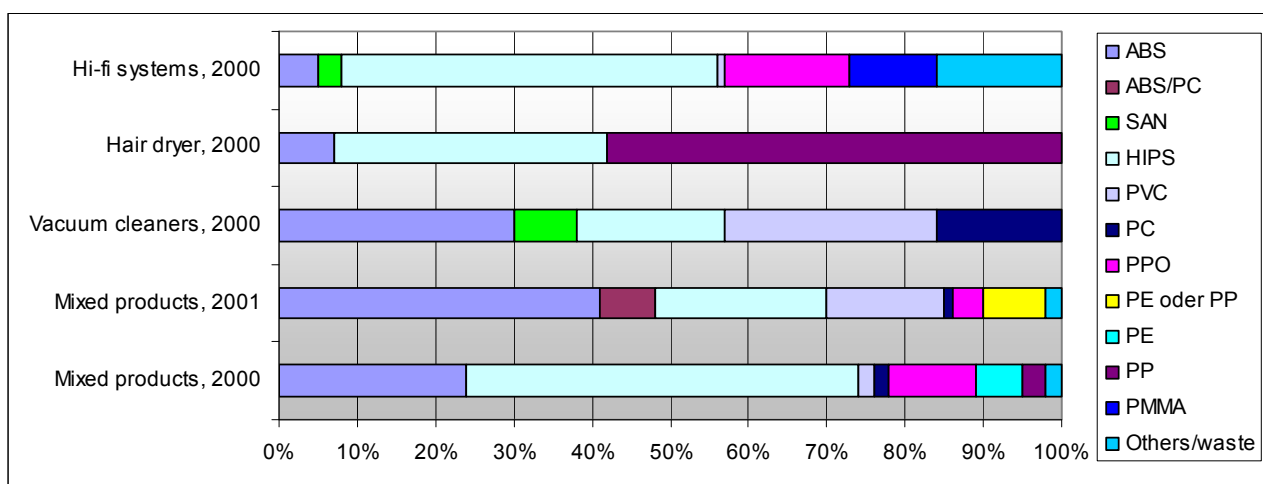


Figure 2-8: Composition of the plastics fraction in consumer electronics and small electric devices (Headley Pratt Consulting 2000, MOEA 2001)

In a study carried out in the mid of the nineties (Kaiser 1995), the plastic composition of different small electric appliances has been determined. For the housings, PP and ABS had the greatest shares for all product types. In the quantitatively less relevant small parts, ABS had the greatest share, followed by PA and PP. For the vacuum cleaners, which were by far the quantitatively most important fraction, ABS was the dominant plastic type in housing. This is also true for small parts, however to a lesser extent. In coffee machine housings, quantitatively the second most important fraction, PP was the greatest plastics fraction, accounting for curtly more than half of the total amount of plastics (see Figure 2-9). The results of this older study are well confirmed by newer studies: The share of vacuum cleaners in small household appliances, for example, is reported to correspond to about 50% (Novak 2001, Sander et al. 2004, Müller and Giegrich 2005). According to a German recycling company, for every ton of vacuum cleaners 300 kg of ABS can be recovered, and for every ton of coffee machines 400 kg of PP granulate (Jehle 2005).

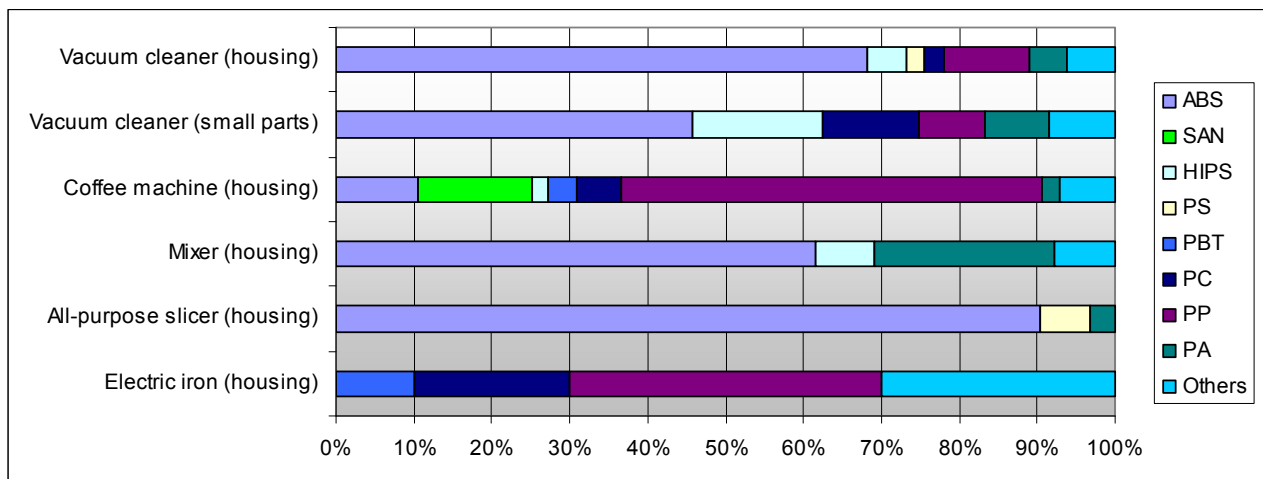


Figure 2-9: Composition of the plastics fraction in small electric appliances in the mid-nineties (Kaiser 1995)

2.3.4 Large household appliances

Plastic shares have been reported by (ACC undated) for refrigerators produced in the years 1972, 1980 and 1988; according to the authors, these refrigerators are expected to have a service life of approximately 15 – 20 years, i.e. they should be disposed of today. In (ACC undated), the share of plastics in refrigerators is reported to have increased from 16% in the year 1972 to 18% in 1980 and 21% in 1988. If fibreglass is excluded, which was no more used in 1988, the plastics shares for the years 1972 and 1980 amounted to 8% and 14%, respectively. With regard to the plastics types, an increase between 1972 and 1988 is also reported for the shares of ABS and PUR-foam, which amounted to 50% and 38%, respectively, in 1988 (see Figure 2-10; (ACC undated)). On the other hand, the share of HIPS decreased to 12% in 1988, while PS was no more applied (ACC undated). According to a German recycling company, for the inside lining almost exclusively polystyrene (not specified as PS oder HIPS) is applied (Novak 2001). In an overview of (Jofre and Morioka 2005), the share of ABS (16%) in refrigerators is significantly lower than reported in (ACC undated), whereas PS (26%) is significantly higher. As HIPS has not been accounted for separately, it is possible that parts of the categories 'PS' or 'others' correspond to HIPS. Compared to (ACC undated), two more plastics types are reported by (Jofre and Morioka 2005), namely PP (25%) and PVC (8%). In the same publication, the composition of air conditioning systems is stated to be similar to that of refrigerators. In washing machines, PP (77%) accounted for the greatest share of plastics.

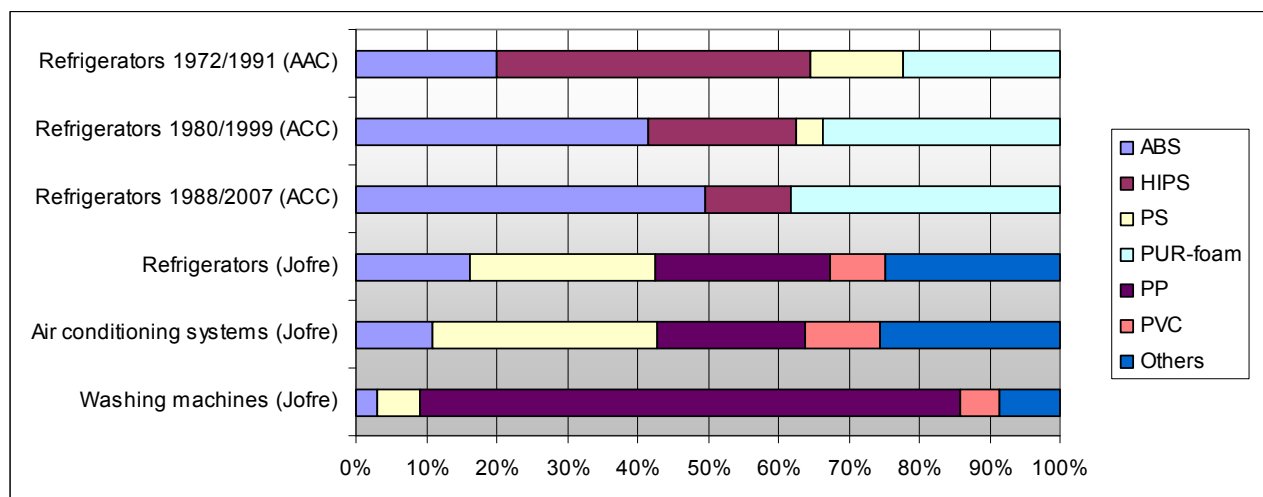


Figure 2-10: Composition of the plastics fraction in refrigerators, air conditioning systems and washing machines (Jofre and Morioka 2005, ACC undated)

2.4 Plastic type quantities in WEEE categories and product types

Based on the estimation of the total plastic quantities in European WEEE for the year 2008 (see Table 2-2), the amounts of plastics for WEEE categories and product types in the focus of this study were calculated by multiplication with the mean, minimal and maximal values for the respective plastic type shares (see section 2.3). The results, which are depicted in Figure 2-11, show that they are associated with great uncertainties.

In the category of large **household appliances w/o cooling appliances**, the most dominant plastic type appears to be PP with ~225'000 t/a, followed by PUR, ABS, PS and HIPS. In **cooling and freezing appliances**, the most dominant plastic types are ABS (~142'000 t/a), HIPS (~95'000 t/a) and PUR (~95'000 t/a); PP and PVC also occur in significant quantities.

In the category of **small electronic appliances**, the most dominant plastic types are PP (~130'000 t/a) and HIPS (~111'000 t/a), with ABS also occurring in significant quantities (~74'000 t/a).

In the category of **IT equipment w/o screens**, the most dominant plastic type is ABS (~127'000 t/a), followed by ABS/PC and HIPS. The most significant plastic type in **consumer equipment w/o screens**, by contrast, is HIPS (~100'000 t/a), followed by ABS, PPO, PPO/PS and PMMA. The shift from ABS to HIPS as the most dominant plastic type between IT w/o screens and consumer electronic w/o screens is very well reflected in the differences in plastics composition between **CRT monitors** and **TV sets**.

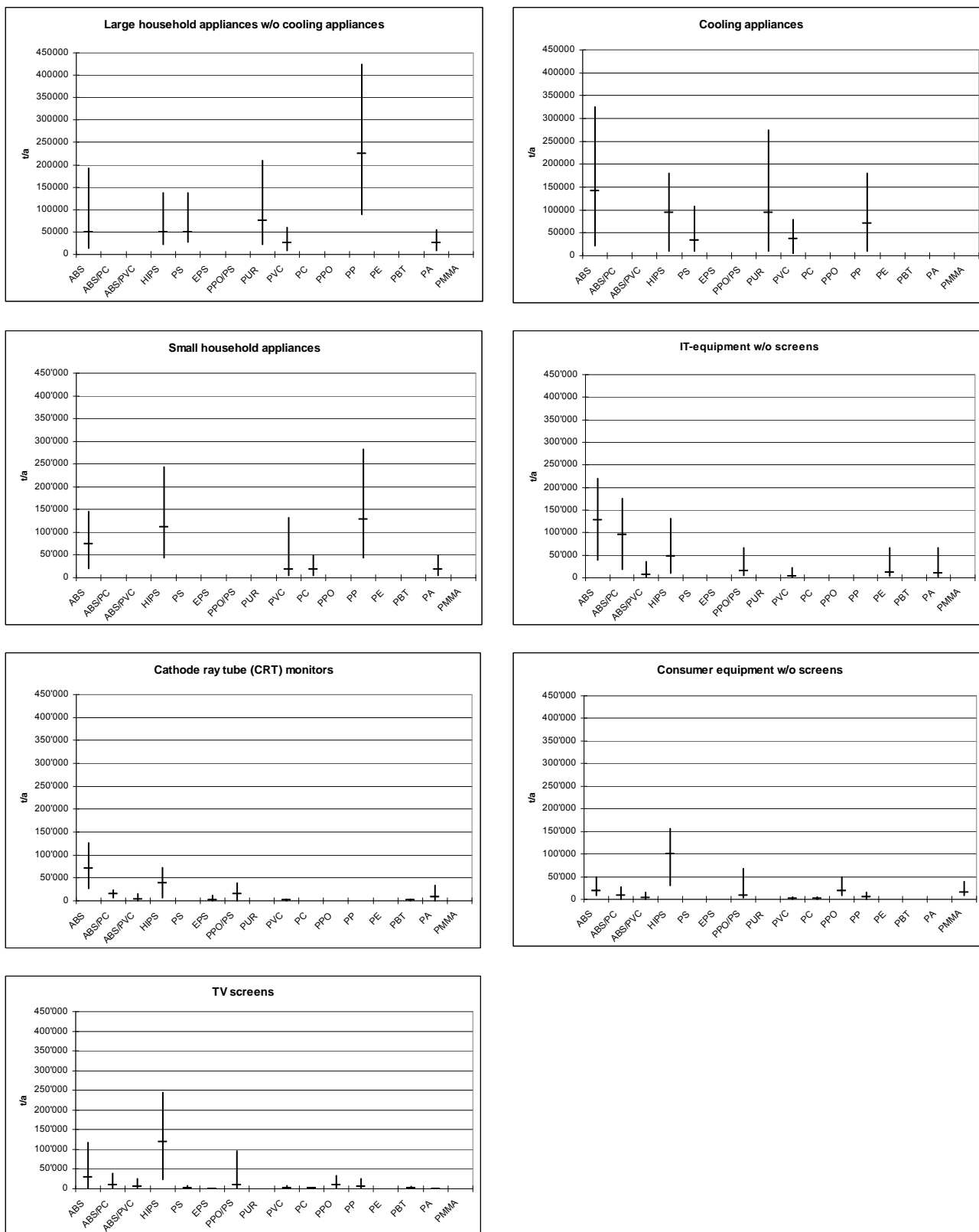


Figure 2-11: Estimated quantities of different plastic types for selected European WEEE categories and product types (minimal, maximal and mean values)

3 Hazardous substances in WEEE plastics

3.1 Regulatory framework for plastics recovery from WEEE

In the European Union, relevant regulations for the pre-processing, shipment and end-processing of plastics from WEEE include, amongst others, the WEEE Directive, the RoHS Directive, the REACH Regulations, the Commission Decision 2000/532/EC and the Waste Shipment Directives. The Stockholm Convention on Persistent Organic Pollutants (POPs) also has to be considered, because some flame retardants known to have been applied in EEE have recently been defined to be POPs.

3.1.1 The WEEE Directive

The Directive on Waste Electrical and Electronic Equipment (WEEE Directive; (EC 2003c) from January 27, 2003 aims at preventing WEEE, and where this is not possible, reusing, recycling and recovering it so as to reduce its disposal. Furthermore, the Directive seeks to improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment. Amongst others, for eight of the ten WEEE categories defined in Annex IB, the WEEE Directive sets targets for recovery and for component, material and substance reuse and recycling (Article 7.2). Compliance with these targets depends, not least, on the plastics fraction of WEEE. Plastics containing brominated flame retardants are listed in Annex II, which addresses those substances, preparations and components that have to be removed from any separately collected WEEE as a minimum.

3.1.2 The RoHS Directive

The Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic equipment (RoHS Directive; (EC 2003b) from January 27, 2003 regulates the application of hazardous substances in new EEE falling under the categories 1, 2, 3, 4, 5, 6, 7 and 10 set out in Annex IA to the WEEE Directive (and to electric light bulbs, and luminaires in households). According to the RoHS Directive, member states must ensure that from July 1, 2006, newly marketed EEE does not contain cadmium, chromium (VI), lead, mercury, polybrominated biphenyls (polyBBs) and polybrominated diphenyl ethers (polyBDEs) above defined maximum concentration values (MCVs) for homogeneous materials.

Table 3-1: Maximum concentration values (MCVs) for homogeneous materials in new Electrical and Electronic Equipment (EEE) according to the RoHS Directive (amendment of August 18, 2005)

	Cd	Cr(VI)	Hg	Pb	PBBs	PBDEs ¹⁾
MCV in % by weight	0.01	0.1	0.1	0.1	0.1	0.1

1) The PBDEs include commercial pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE) and decabromodiphenyl ether (DecaBDE)

In Switzerland, the restrictions on heavy metals and flame retardants in electrical and electronic equipment as well as their spare parts, which are defined in the Ordinance on Risk Reduction related to Chemical Products (*ORRChem*), are identical to those the RoHS Directive with regard to the nature and extent of the regulated heavy metals and flame retardants, the categories of equipment affected, exemptions from the substance bans and the time of commencement (FOEN 2010a).

The RoHS Directive is presently under revision. The recast draft of December 3, 2008 proposes, amongst others, to move the list of substances regulated by the RoHS Directive into a new Annex IV; the latter shall not include new substances. However, four substances are identified for priority assessment in view of possible future inclusion in the list of restricted substances: the flame retardant Hexabromocyclododecane (HBCD) and the plasticizers Bis(2-ethylhexyl)phthalate (DEHP), butylbenzylphthalate (BBP) and Dibutylphthalate (DBP) (Premier Farnell 2010). The German Federal Environment Agency also recommends the restriction of Tetrabromobisphenol A (TBBPA) used as an additive (German Federal Environment Agency 2009).

3.1.3 The REACH Regulation

The EU Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), which came into effect on June 1, 2007, will require the registration of 30,000 currently marketed chemicals. Much of the data needed for registration are already available thanks to risk assessments of continued production and use already undertaken in the EU. Within the authorisation, substitution by less hazardous chemicals is encouraged (Kemmllein et al. 2009).

The timing of REACH registration is based on the market volumes of the respective chemicals and, for the time being, classifies them into 'existing' and 'new' categories, depending on whether they were initially produced before or after 1981. In the long term, REACH will abolish the existing or new substance distinctions and will establish a single legislative system for the marketing of chemical substances within Europe. As such, manufacturers, importers and users need to be aware that chemicals falling within the REACH requirements must be registered before being produced, imported, or placed on the market within the EU (Kemmllein et al. 2009).

According to the timeline for REACH, following registration deadlines for the different tonnage bands will apply (Kemmllein et al. 2009):

- December 1, 2010: registration for substances supplied in amounts > 1000 t/a, > 100 t/a (substances classified dangerous), > 1 t/a (substances classified as carcinogenic, mutagenic or toxic to reproduction (CMR));
- June 1, 2013: registration for substances supplied in amounts > 100 t/a;
- after June 1, 2018: registration for substances supplied in amounts > 1 t/a.

3.1.4 Regulations related to hazardous waste classification

According to Article 2 of the Commission Decision 2000/532/EC ((EC 2000)), wastes classified as hazardous are considered to display one or more of the properties listed in Annex III to the Council Directive 91/689/ on hazardous waste (EC 1991b) and, as regards H3 to H8, H10 and H11 of that Annex, one or more of the following criteria:

- flash point ≤ 55 °C,
- one or more substances classified as very toxic at a total concentration $\geq 0,1$ %,
- one or more substances classified as toxic at a total concentration ≥ 3 %,
- one or more substances classified as harmful at a total concentration ≥ 25 %,
- one or more corrosive substances classified as R35 at a total concentration ≥ 1 %,
- one or more corrosive substances classified as R34 at a total concentration ≥ 5 %,
- one or more irritant substances classified as R41 at a total concentration ≥ 10 %,
- one or more irritant substances classified as R36, R37, R38 at a total concentration ≥ 20 %,
- one or more substances known to be carcinogenic of category 1 or 2 at a total concentration $\geq 0,1$ %,
- one or more substances toxic for reproduction of category 1 or 2 classified as R60, R61 at a total concentration $\geq 0,5$ %,
- one or more substances toxic for reproduction of category 3 classified as R62, R63 at a total concentration ≥ 5 %,
- one or more mutagenic substances of category 1 or 2 classified as R46 at a total concentration $\geq 0,1$ %,
- one or more mutagenic substances of category 3 classified as R40 at a total concentration ≥ 1 %.

In Switzerland, according to the Swiss Federal Office for the Environment (FOEN), plastics from the dismantling of WEEE with cadmium-, PentaBDE-, OctaBDE- and DecaBDE concentrations exceeding the limit values for newly marketed EEE defined in the Swiss Ordinance on Risk Reduction related to Chemical Products (ORRChem) are to be classified as hazardous waste according to the European Waste Code (EWC) 19 12 11; WEEE plastics with substance concentrations below these limit values are to be classified as waste not subject to control according to EWC 19 12 04 (FOEN 2010b, Hauser 2010). The limit values for newly marketed EEE defined in the ORRChem correspond exactly to the RoHS MCV.

3.1.5 Regulations related to waste shipment

The Regulation No 1013/2006 of the European Parliament and of the Council on Shipments of Waste (EC 2006) aims at strengthening, simplifying and specifying the procedures for controlling waste shipments to improve environmental protection. It applies to shipments of waste

- between Member States, within the Community or with transit through third countries;;
- imported into the Community from third countries;

- exported from the Community to third countries;
- in transit through the Community, on the way from and to third countries.

The Regulation defines two control procedures: the 'green listed' procedure, which applies to non-hazardous waste intended for recovery, and the notification procedure, which applies to shipments of all waste intended for disposal and hazardous waste intended for recovery. Wastes subject to notification are set out in the "Amber List" (Annex IV), while wastes subject only to information requirements are set out in the 'Green List' (Annex III); wastes for which export is prohibited are listed separately (Annex V). Regarding flame retardants addressed in the RoHS Directive, only PBB is nominatively mentioned at a threshold level of 50 ppm (waste identification code A 3180). Waste having cadmium, hexavalent chromium, lead or mercury as constituents or contaminants is also subject to notification (waste identification codes A 1020, 1030, 1040).

3.1.6 The Stockholm Convention

The Stockholm Convention, which also has been ratified by the European Union (EU), aims at reducing and eliminating production, use and release of persistent organic pollutants (POPs) (Secretariat of the Stockholm Convention 2001). In May 2009, on the occasion of the fourth Conference of the Parties in Geneva, certain congeners contained in commercial PentaBDE and OctaBDE were added to Annex A of the Stockholm Convention. As a consequence of this, these chemicals are now officially classified as POPs and may no longer be produced. Furthermore, Article 6 of the Convention requires that wastes containing POPs be managed in a manner protective of human health and the environment ((Secretariat of the Stockholm Convention 2001)). The new listing demands from each party of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of persistent organic pollutants (POPs) from stockpiles and wastes (Weber et al. 2010).

Unlike the original Stockholm POPs, the new listing includes specific exemptions allowing for recycling and the use in articles of recycled materials containing these chemicals (see Figure 2-1). This exemption generated significant discussion about whether it could be considered to be consistent with the principal objective of the Stockholm Convention which is to protect human health and the environment from persistent organic pollutants. Recycling of POPs inevitably increases the possibilities of generating new environmental and health risks (Weber et al. 2010).

To get a better understanding of the overall impact of PBDE in recycling schemes, the Conference of the Parties requested the Stockholm Convention Secretariat to collect information on brominated diphenyl ethers and to assess unintentionally produced organic pollutants such as brominated dibenzodioxins and – dibenzofurans (PBDD and PBDF). Although PBDDs and PBDFs may be responsible for much of the health and environmental risk associated with the use of PBDEs ((Hirai & Sato et al. 2008); cited in (Weber et al. 2010)), they are not classified as unintentionally Produced Organic Pollutants (uPOPs) in the Stockholm Convention and are not currently being considered by the POP Review Committee. In the EU, only the German law on chemicals (German Federal Ministry of Justice 2003) has defined limits for these substances in products (Weber et al. 2010)). The limits according to German Law are: < 1 µg/kg for the sum of class I compounds (2,3,7,8-TBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PBDD, 1,2,3,7,8-PBDF), and < 5 µg/kg for the sum of

class I and class II (1,2,3,7,8-PBDF, 1,2,3,6,7,8-HBDD, 1,2,3,7,8,9-HBDD, 1,2,3,4,7,8-HBDD) compounds (German Federal Ministry of Justice 2003).

Exemptions for the recycling of articles

Decision SC-4/18 included specific exemption for use in articles in accordance with the following provisions:

A Party may allow recycling of articles that contain or may contain TetraBDE and PentaBDE and the use and final disposal of articles manufactured from recycled materials that contain or may contain TetraBDE and PentaBDE, provided that:

- (a) The recycling and final disposal is carried out in an environmentally sound manner and does not lead to recovery of TetraBDE and PentaBDE for the purpose of their reuse;
- (b) The Party does not allow this exemption to lead to the export of articles containing levels/ concentrations of TetraBDE and PentaBDE that exceed those permitted to be sold within the territory of the Party; and
- (c) The Party has notified the Secretariat of its intention to make use of this exemption.

At its sixth ordinary meeting and at every second ordinary meeting thereafter the Conference of the Parties shall evaluate the progress that Parties made towards achieving their ultimate objective of elimination of TetraBDE and PentaBDE contained in articles and review the continued need for this specific exemption. This specific exemption shall in any case expire at the latest in 2030.

Decision SC-4/14 has substantially identical provisions in respect of HexaBDE and HeptaBDE

Figure 3-1: Specific exemption for the recycling of articles containing TetraBDE to HeptaBDE based on the Stockholm Convention Decision SC-4/14 and SC-4/18 according to (Weber et al. 2010)

Regarding PBDEs, an important issue which needs to be clarified is the level of PBDE contamination above which a material should be regulated by the Stockholm Convention (Weber et al. 2010). For PCB and POP Pesticides, the current provisional low POPs limit recommended by the Open Ended Working Group of the Basel Convention (Basel Convention 2004), which is being used pending the determination of a methodology to establish final levels, is 50 ppm (and for PCDD/PCDF the limit is 15 µg TEQ/kg). For PBDEs, no low POPs content has yet been developed. According to (Weber et al. 2010), the existing limit for PBDE in goods defined by the European RoHS regulation appears to be high compared e.g. to the limit for PCB, and it seems likely that a lower 'low POPs' limit will need to be defined for PBDE.

3.2 Characteristics and applications of RoHS substances

In the following section the substances, which are relevant according to the RoHS Directive, are briefly characterized with regard to their application in EEE, their reported concentrations in WEEE plastics, and expected developments regarding their occurrence in WEEE. The characterization is mainly based on the literature review (Wäger et al. 2008).

3.2.1 Heavy metals

3.2.1.1 Cadmium

Applications

Cadmium sulphide and cadmium sulphoselenide are utilised as bright yellow to deep red pigments in plastics (Harant 2002). Both compounds are well known for their ability to withstand high temperature and high pressure without chalking or fading, and therefore are used in applications, where high temperature or high pressure processing is required, such as ABS, PA, PC or HDPE (International Cadmium Association 2010). Another possibility for an import of cadmium into plastics, especially PVC, is the use of mixed barium- and cadmiumcarboxylates as stabilizing agents.

In a Swiss market study from 1993 (Hohl and Randegger-Vollrath 1995), the share of cadmium containing plastic samples (i.e. samples with $\geq 0.01\%$ of cadmium) was highest for PVC, where cadmium was applied as a thermally stable pigment and as a stabilising agent; for PP (9%), PE (7%), PA (6%), PC (6%) and PS (2%) the shares were lower. For EEE, the share of cadmium containing plastics was exceptionally low (2%). Cadmium could not only be found in yellow, orange, red and green plastics, i.e. plastics for which cadmium is used for pigmentation, but also in grey and white plastics ((Hohl and Randegger-Vollrath 1995)).

Concentrations in WEEE plastics

(Wolf 2001) analysed plastic samples from 35 TV set rear panels and 114 CRT monitor housing with regard to their cadmium content. They found that in 19% of the samples cadmium exceeded the RoHS MCV of 100 ppm. In 5% of the samples cadmium concentrations above the MCV of 0.01 % by weight were found; the highest cadmium concentration corresponded to a value exceeding the RoHS MCV for cadmium by a factor of 120. From the 29 plastic samples containing cadmium, 24 were ABS plastics; 5 of these samples had been taken from devices built after 1990, which all were from Asia (China, Taiwan, Korea). In an analysis of 188 TV set rear panels, computer- and printer housings, in 23% of the cases cadmium was detected (Wolf 2001). While in black plastic parts the cadmium concentrations were lower than the RoHS MCV by a factor of 2, the MCV was exceeded by a factor of 25-40 in LCD-toys and black plastics housings (Rotter et al. 2006). In a Swiss recycling plant, the average cadmium concentrations in TV set and CRT monitor housings corresponded to 0.0078% by weight (95% confidence interval: 0.0050 - 0.0106% by weight), and 0.014% by weight (confidence interval: 0.008 - 0.019% by weight) in the fine grained plastics fraction. Hence, the RoHS MCV for cadmium was partly exceeded (Morf and Taverna 2004). In a study by (Schlummer et al. 2007), the medians of the cadmium concentrations in single TV set - and CRT monitor housings, in TV set - and CRT monitor housing shredder residues and in mixed WEEE shredder residues were slightly lower than the cadmium MCV.

Trends

Within the European Union the use of cadmium-containing pigments at concentrations above 0.01 % by weight has been restricted for plastics such as PVC, PUR, PE, PP, HIPS, PBT and PET (EC 1991a). ABS and SAN were not subjected to this restriction.

Compared to earlier studies, the share of cadmium containing plastics generally decreased from 20-30 % to about 7% in 1993 (Hohl and Randegger-Vollrath 1995). (Schlummer et al. 2007) found that in 2006, in WEEE plastics a share of 9% of housings had a cadmium content of more than 0.01% mass, whereas in an earlier study from the year 2000 a share of 50% still had been found (Ernst et al. 2000). According to (Schlummer et al. 2007), this is an indication for a reduced application of cadmium as a consequence of a phase-out of cadmium-based additives.

Worldwide cadmium production for pigments decreased from 4006 t in 1980 to 2600 t in 1995 and 1600 t in 2005; worldwide cadmium production for stabilising agents decreased from 2000 t in 1980 to 1700 t in 1995 and 240 t in 2005 (International Cadmium Association, cited in (UNEP 2006)). According to (Brigden et al. 2008), who analysed the cadmium content of notebooks bought in Europe in 2006 with XRF spectrometry, no sample contained cadmium at concentrations above the detection limit of 0.01%.

3.2.1.2 Chromium (VI)

Applications

In EEE, chromium (VI) is applied as a pigment in the form of lead chromate as well as in metal coatings protecting from corrosion and abrasion. Elementary chromium (Cr(0)) is applied in metallised plastics, which are used in the electronics -, the automotive - or the sanitary sectors (Schmiemann 2000). In a Swiss market study (Hohl and Randegger-Vollrath 1995), the share of (unspecified) chromium containing products was found to be highest for PVC (20%). For PP and PE the shares were 11% and 4%, respectively, while PS did not contain any chromium. For EEE, the share of chromium containing plastics was found to be exceptionally high (16%).

Concentrations in WEEE plastics

In a study investigating 149 plastic samples (from 35 TV-housings and 114 monitor housings), (Wolf 2001) found no (unspecified) chromium in 30% of the samples. For 17% of the samples, (unspecified) chromium was measured at concentrations exceeding 0.01 % by weight; in the other samples the element appeared in trace concentrations up to 0.01% by weight (Wolf 2001). In another study considering 188 TV-housings, computer- and printer housings, (unspecified) chromium was found in 32% of the samples (Wolf 2001). In a Swiss recycling plant, the average concentrations of (unspecified) chromium in TV- and monitor housings amounted to 0.015% by weight (95% confidence interval: 0 – 0.035% by weight), and 0.095% by weight (95% confidence interval: 0.045-0.145% by weight) in the fine-grained plastic fraction (Morf and Taverna 2004). In a more recent study by (Schlummer et al. 2007), (unspecified) chromium concentrations in shredded housings and WEEE shredder residues were found to lie below the RoHS MCV for Cr(VI) by about one order of magnitude.

Trends

Compared to earlier studies, (Schlummer et al. 2007) found (unspecified) chromium contents which were lower by a factor of about four for shredded housing residues and even a factor of 20 for mixed WEEE shredder residues (Schlummer et al. 2007). According to (Schlummer et al. 2007), this is not only due to a decreasing application of chromium, but also to a better separation of circuit boards. Further improvements

in recycling technologies could lead to a further reduction of the chromium concentrations in plastic fractions.

3.2.1.3 Mercury

Applications

In EEE mercury is applied, amongst others, in batteries, thermostats, sensors, relays in switches and discharge lamps. The application of mercury in electrical switches is no more state of the art (Harant 2002). The use as a pigment in plastics was stopped many years ago; an application in plastics in the last few years is not known.

Concentrations in WEEE plastics

In a study investigating the mercury content in LCD-games, black plastics parts and – housings, as well as in circuit boards, the mercury concentrations were lower than the RoHS MCV by a factor of 5-50, for different circuit boards even by a factor of 66 to >1000 (Rotter et al. 2006). In a Swiss recycling plant, the average concentrations in TV- and monitor casings were 0.00012% by weight (95%-confidence interval: 0.00007-0.00018 % by weight), in the fine-grained plastics fraction 0.00001% by weight (95%-confidence interval: 0 – 0.000035% by weight). Hence, these concentrations were lower than the RoHS MCV by about a factor of 1000 – 10 000 (Morf and Taverna 2004). In the study of (Schlummer et al. 2007), the concentrations of mercury in the investigated casings and WEEE shredder residues were at least one magnitude lower than the RoHS MCV. According to (Brigden et al. 2008), no mercury was found above the detection limit of 0.05% by weight in notebooks analysed with XRF spectrometry. (Morf and Taverna 2004) show that in a modern recycling plant 98% of the mercury are transferred into the fraction 'hazardous waste carrier' (batteries, accumulators), and each about 1% by weight into the dust fraction and the fine grained metals fractions (Morf and Taverna 2004).

3.2.1.4 Lead

Applications

In EEE lead has been applied as a solder in printed circuit boards, in glass from cathode ray tubes (CRT), light bulbs or in electrical ceramics. Infrared remote control units can contain LED with lead selenide (Harant 2002). In plastics, lead compounds are applied as pigments and, as carboxylates, stabilizing agents. The application of lead carbonates and lead sulfates in formulations, which are intended to be used as colors, is restricted in directive 89/677/EC (EC 1989). In a Swiss market study, the share of lead containing samples (\geq 0.3% by weight) was clearly highest for PVC with 43%, and lower for PP (10%), PE (8%), PA (6%) and PS (2%). For EEE, the share of lead containing plastics was exceptionally high with 30%, which was caused by the use of lead additives in the PVC isolation of cables. Lead was not only found in yellow, orange and red plastics, which can contain lead pigments, but also in plastics of (all) other colours (Hohl and Randegger-Vollrath 1995).

Concentrations in WEEE plastics

In a study carried out by (Wolf 2001), lead could be found in about 70% of 149 investigated plastic samples (from 35 TV-casings and 114 monitor housings). Lead mostly occurred in trace concentrations (< 0.01% by weight); concentrations of more than 0.01 % by weight were found in 16% of the samples. In another study investigating 188 TV-housings, computer- and printer housings, lead was found in 32% of the samples (Wolf 2001). In a study investigating the mercury content in LCD-games, black plastics parts and –housings, the RoHS MCV of 0.1% by weight was undershot by a factor of 5-50. For different circuit boards, however, the RoHS MCV was exceeded by a factor of 6-13 (Rotter et al. 2006). The average concentration in TV- and monitor housings in a Swiss recycling plant amounted to 0.023% by weight (95% confidence interval: 0.011-0.035% by weight), in the fine grained plastics fraction to 0.12% by weight ((0.001-0.24% by weight) (Morf and Taverna 2004). Hence, the lead concentrations were clearly below the corresponding MCV of 0.01% by weight, whereas it was partly exceeded in the fine grained plastics fraction. In the study by (Schlummer et al. 2007), the RoHS MCV for lead was never exceeded for single housings and shredded housing residues (see Figure 4-1 in section 4). For shredder residues from mixed WEEE, the median curtly exceeded the MCV for lead; the highest concentration amounted to 0.25% by weight. The higher values in the fine grained plastic fraction or shredder residues from mixed EEE indicate that there might be a lead import through not separated, lead containing components such as solder or circuit boards.

Trends

In the year 2000, the European Stabiliser Producer Association (ESPA) and the European Plastic Converters (EuPC) have committed themselves to substitute lead-containing stabilizing agents until the year 2015. As interim goals, a reduction by 15% until 2005 and 50% until 2010 have been defined (Biron 2008). (Brigden et al. 2008) did not find any lead above the detection limit of 0.05% by weight in plastics from notebooks bought in Europe in the year 2006. Compared to earlier studies, a reduction of a factor two could be observed for shredder residues from housings in the lower concentration range (Schlummer et al. 2007). As for chromium (see section 3.2.1.2), this reduction has not been attributed to a lower use, but to an improved separation of the circuit boards. Technical improvements in the dismantling and sorting processes could lead to a further reduction of the lead concentrations in the plastics fractions.

3.2.2 Polybrominated flame retardants

3.2.2.1 Applications

Flame retardants are applied in plastics contained in telecommunication devices, computers, monitors, television sets and other consumer equipment as well as – to a lesser extent – in office equipment. In household appliances, only a small part of the plastics is flame-protected (see Figure 3-2). In vacuum cleaners, for example, which account for a large part of the plastics amount (see section 2.3.3), ABS is considered to be mostly flame-retardant free (Müller and Griese 2007). The share of flame-protected plastics in WEEE over all categories has been estimated to amount to about 25% (5.3 % related to the whole amount of WEEE) by (Huisman et al. 2008).

Considering all applications, in less than 1% of the polyolefines (PP and PE) flame-retardants are applied; the BFR-concentrations however, are expected to be rather elevated. In these plastic types DecaBDE is often applied, in the past partly also OctaBDE. The concentrations of BFR are also reported to be high in polystyrene and polystyrene-copolymers ((Dufton 2003, Townsend 2005). For HIPS, the application of DecaBDE and HBCD is reported to be widespread. For PA, where DecaBDE is also applied, the share of BFR is reported to correspond to 58% (Dufton 2003). In ABS, TBBPA and DecaBDE are currently applied, while OctaBDE often was used in the past. TBBPA – just like OctaBDE and DecaBDE – is used as an additive, while in circuit boards it is reactively bound to the plastics. In PVC, BFR are scarcely applied. In PUR, just as in circuit boards, PentaBDE was applied in the past ((Leisewitz and Schwarz 2001, Zweifel 2001, Troitzsch 2006).

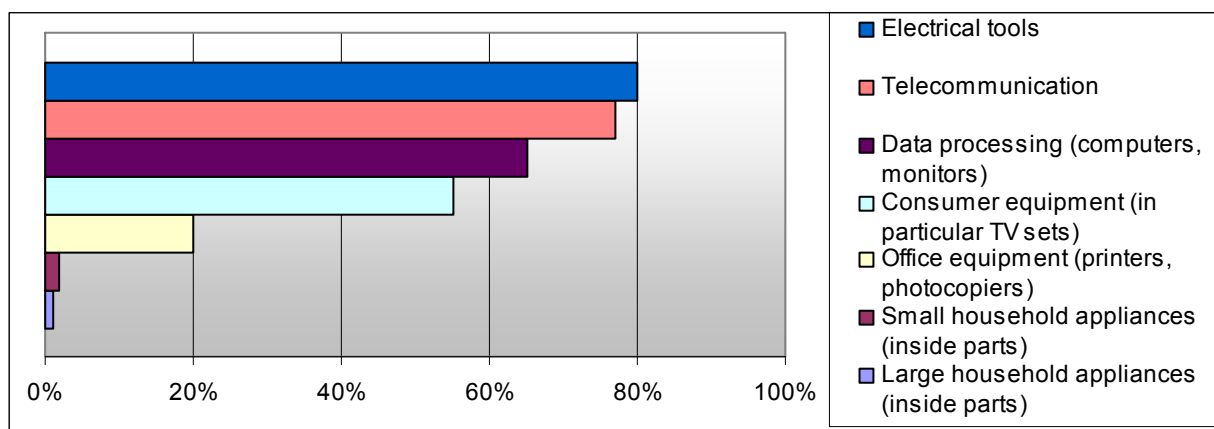


Figure 3-2: Shares of flame-protected plastics in plastics of different product categories (APME 2001, Harant 2002)

3.2.2.2 Concentrations in WEEE plastics

In a Swiss market survey, between 1999 and 2002 486 plastic components from 366 new products in the domains of office appliances, household appliances, electric devices, car manufacturing, electric materials and construction materials have been investigated with regard to BFRs (Kuhn et al. 2004). From all the investigated materials, 22% contained bromine (> 0.1% by weight), 3% DecaBDE, 1% OctaBDE, 0.4% DecaBB and each 2% TBBPA and HBCD. PentaBDE was not detected (Kuhn et al. 2004). In a recent Swiss market survey, 1359 new products from the domains of electronics/electrical engineering, consumer electronics, household appliances, lighting, office appliances and construction materials were again investigated with regard to BFR (Bantelmann 2009). 476 components out of these products, particularly often from automatic dispensers, consumer electronic devices and lighting equipment, were found to have elevated bromine concentrations (> 500 ppm). According to the further analysis of 214 samples with regard to their contents of TBBPA, HBCDA, PentaBDE (technical mixture BDE 71), OctaBDE (technical mixture BDE 79), DecaBDE and PBB, 60 samples contained these target compounds. DecaBDE was found in 11%, TBBPA in 10%, HBCD in 6%, OctaBDE in 1% and PentaBDE as well as PBB in 0% of these samples; other, unspecified brominated compounds were found in 72% of the samples. The highest contents of OctaBDE, DecaBDE, TBBPA and HBCD were detected in an emergency lamp (6% by weight), a shrinking foil (26 % by weight), a covering plate for an electro motor (16% by weight) and two samples of insulating material (2-2.4 % by weight), respectively. The study comes to the conclusion that brominated flame retardants, which are regulated in the

RoHS Directive, have been to a large extent replaced by other brominated compounds ((Bantelmann 2009, Kanton Bern 2009)). A further investigation of these other brominated compounds is presently being performed (Trempe 2010).

In the study of (Wolf 2001), where 149 plastic samples from disused EEE devices (35 TV set housings and 114 monitor housings) were investigated, about 70% of the plastics were equipped with BFR. In 45% of the samples a bromine between 6% and 10% by weight was found, 12% of the samples even had a bromine content of >10% by weight. PPO/PS did not contain any BFR.

In four out of fifteen investigated single housings TBBPA was found, while DecaBDE and OctaBDE were present in two housings. In housing shredder residues OctaBDE was found in seven samples at concentrations between 0.3% by weight and 1.4% by weight. In the mixed WEEE shredder residues seven of eight samples contained OctaBDE, the concentrations amounting to 0.08% by weight and 0.44% by weight (Schlummer et al. 2007). In an investigation of WEEE (excl. large appliances) in Switzerland, following concentrations were detected for OctaBDE in the plastics fraction: 0.75% ± 0.06% by weight in housings of TV sets and monitors, 0.77% ± 0.36% by weight in TV-housings, 0.001% ± 0.0001% by weight in circuit boards (Morf et al. 2005). In a German study, depending on the fraction (coarse or fine-grained), in WEEE shredder residues OctaBDE-concentrations between 0.03% and 0.1% by weight were measured (Mark et al. 2006). The concentrations hence clearly exceeded the RoHS MCV for housing, and were just below the MCV for mixed WEEE shredder residues. Six of seven samples of the housing shredder residues contained DecaBDE at concentrations between 0.2% and 1.7% by weight, while six of eight samples of mixed WEEE residues six of eight samples contained DecaBDE at concentrations between 0.1–0.3% by weight (Schlummer et al. 2007). For shredder residues of WEEE concentrations between 0.2% and 0.5% were measured, depending on the fraction (Mark et al. 2006). In the Swiss WEEE study of (Morf et al. 2005), DecaBDE concentrations of 0.48% ± 0.04% and 1.3% ± 0.9% by weight, respectively, were measured in housings of TV sets and monitors, as well as in TV set rear panels. While these concentrations are significantly above the RoHS MCV of 0.1%, the average concentration in circuit boards of 0.0027% ± 0.009% by weight is significantly lower (Morf et al. 2005). In contrast to OctaBDE and DecaBDE, PentaBDE was not found at concentrations above the RoHS MCV in any sample (Morf et al. 2005, Mark et al. 2006, Schlummer et al. 2007).

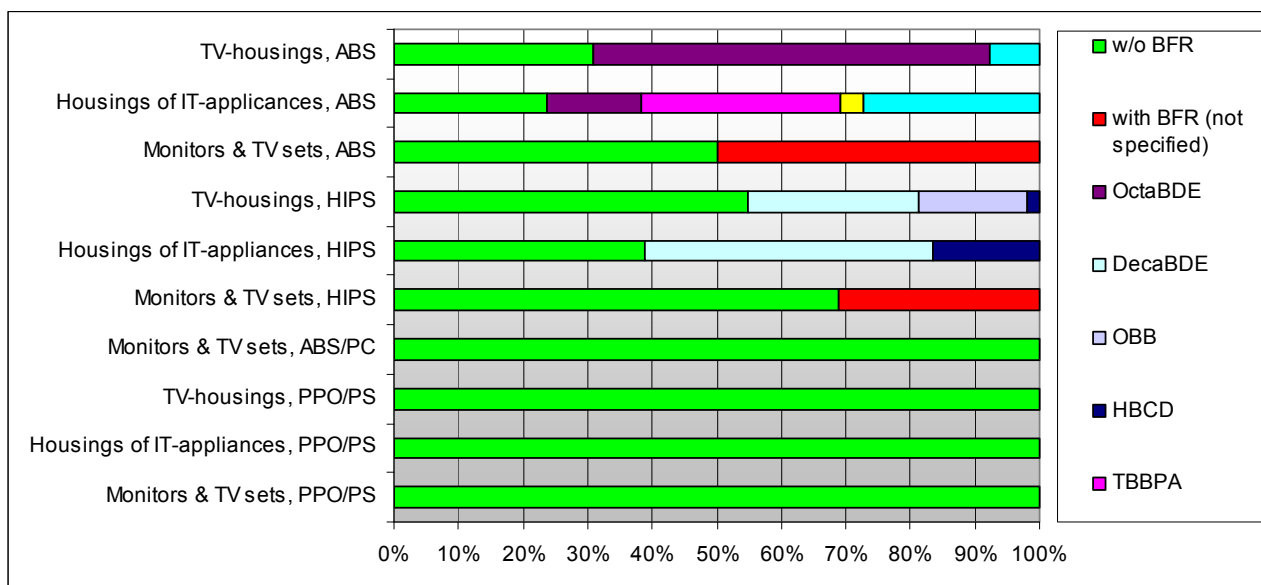


Figure 3-3: Shares of plastic types with and without BFR in EEE (Wolf 2001, Schlummer et al. 2007)

From the 456 plastic components from new products analysed in the study of (Kuhn et al. 2004) for the domains of office appliances, household appliances, electric devices, car manufacturing, electric materials and construction materials, only two were positively tested for DecaBB with concentrations of 0.002% and 0.1% by weight. The authors considered the DecaBB concentrations measured in a component from automobile construction and a component from a household appliance to be a consequence of the use of old plastics or recycled plastics (Schlummer et al. 2007) did neither find PBBs above the detection limits in 15 single TV set – and CRT monitor housings nor in housing - and mixed WEEE shredder residues. In studies carried out earlier, PBB in WEEE had still been found, e.g. by (Riess et al. 2000) in 16% of the analysed plastics samples from disused television sets and monitors, or by (Wolf 2001) in 9% of the TV rear panels (OctaBB in HIPS).

Considering that a worldwide voluntary industry commitment (VIC) on the abandonment of PBB production, export and import (with the exception of DecaBB in Europe) has been agreed upon in 1995 (Kuhn et al. 2004), these results strongly indicate that if PBBs still occur in WEEE at all, then at concentrations well below the RoHS MCV. The last DecaBB production plant in Europe was closed in 2000 (Kuhn et al. 2004).

In Table 3-2, indicative values for the occurrence of PentaBDe, OctaBDE, DecaBDE and total PBDE in groups of plastic most commonly recycled by specialized companies as reported by are (Tange and Slijkhuys 2009) summarized. The indicative values are based on measurements performed by MBA Polymers, Kematen and the Austrian Ministry of Environment.

Table 3-2: Indicative values for the occurrence of BFRs regulated by the RoHS directive in selected groups of plastic most commonly recycled by specialized companies (Tange and Slijkhuis 2009)

	PentaBDE in ppm	OctaBDE in ppm	DecaBDE in ppm	Total PBDE in ppm
TV sets and CRT monitors	< 100	500 – 3000	500 – 3000	< 10000
Refrigerators (cooling and freezing)	< 100	< 1000	< 1000	< 1000
White goods (washing machines – dryers)	< 100	<1000	< 1000	< 1000
Small domestic appliances (brown goods)	< 100	< 200	< 1000	< 2000
Office, data processing & telecommunica- tions equipment				
i. Business-to-Business returns where the plastics are manually dismantled and recycled, which have a higher than average percentage of heat generating appliances such as laser printers, copying machines, switch stations	< 100	500 – 3000	500 – 3000	< 10000
ii. Remainder of the ICT equipment (Jet printers, PC's telephones, routers, set-up boxes, ...)	< 100	< 500	< 1000	< 2000

According to (Tange and Slijkhuis 2009), PBB can no longer be found in WEEE plastic housings at levels above detection limits, as they have never been used for this purpose in the first place and because PBBs have been phased out long ago, i.e. longer than the service life of EEE.

3.2.2.3 Trends

Since the mid-nineties, the use of PentaBDE has decreased (Prevedouros et al. 2004); the same is true for OctaBDE as a consequence of its substitution by DecaBDE or TBBPA, however slightly later (Leisewitz and Schwarz 2001). Based on a comprehensive risk assessment under the Existing Substances Regulation 793/93/EEC (Hansen et al. 2001, Munn et al. 2003), the EU has prohibited the placing on the market of articles containing PentaBDE and/or OctaBDE in concentrations higher than 0.1 % by weight (for the sum of all existing Penta- and Octa-BDE congeners) in 2004 (EC 2003a).

According to data from BSEF and CEFIC, the consumption of DecaBDE in the European industry was almost constant between 1991 and 2005 ((BSEF 2003, CEFIC 2008)). Considering the EU risk assessment for PentaBDE and OctaBDE, the ban to place articles on the market containing these substances in 2004, and the pressure from consumer organisations and ecological labels such as TCO or Blue Angel, the use of DecaBDE should also have begun to decrease in the last few years. In Greenpeace's guide to greener electronics, giving up the use of BFR containing plastics is an important evaluation criterion. Many companies either already fulfil the criterion or have presented a timeline for the phase-out of BFR containing materials (see (Greenpeace 2010)).

In WEEE, a reduction of OctaBDE concentrations due to the reported decrease in its use is to be expected in the next years. For appliances with a high service life (including interim storage before disposal), however, elevated concentrations will probably still be measured for years. For DecaBDE in WEEE, on the other hand, no considerable reduction in concentration is to be expected in the short term, except for product types with a short service life. In the middle- and long-term, a significant reduction should occur due, in particular, to the RoHS Directive.

According to (Kemmlin et al. 2009), many large international electronic companies have voluntarily phased out the use of DecaBDE in their products but have not specified which flame retardants are now being used in its place. A typical replacement scheme may include the use of copolymers with halogen-free organophosphorus compounds for enclosures and other large parts (see section 3.2.3), and the use of alternative BFRs for small parts (<25 g in weight), such as connectors, switches, etc. In Table 3-3, possible alternative BFR according to (Kemmlin et al. 2009) are summarized for some quantitatively relevant plastic types occurring in products from WEEE categories 1-4.

Table 3-3: Possible alternative BFRs for some quantitatively relevant plastic types occurring in products from WEEE categories 1-4 (Kemmlin et al. 2009)

ABS	EBP; EBTPi; TBBPA; TBBPA-epichlorhydrinpolymer; TBPE; 2,4,6-tris (2,4,6-tribromophenoxy)-1,3,5 triazine; brominated epoxy oligomer
ABS/PC	EBP; EBTPi; TBBPA carbonate oligomer; TBBPA-epichlorhydrinpolymer; brominated epoxy oligomer.
HIPS	EBP; EBTPi; HBCD; 2,4,6-tris(2,4,6-tribromophenoxy) -1,3,5 triazine; brominated epoxy oligomer.
PA	EBP; EBTPi; brominated polystyrene; poly(dibromostyrene)
PE	EBP; EBTPi; TBBP-A bis(2,3-dibromopropylether).
PP	EBP; EBTPi;

EBP: 1,2-bis(pentabromophenyl)ethane; EBTPi: ethylene bistetradabromophthalimide; TBBPA: Tetrabromobisphenol A; TBPE: bis(tribromophenoxy)ethane

3.2.3 Organophosphorus flame retardants

According to (Döring and Diederichs 2007), there are especially three phosphorus based flame retardants which allow to meet criteria for polymer resins such as processability, thermal stability, mechanical properties, hydrolytic stability, recyclability and compliance with the RoHS - and WEEE Directives: triphenyl phosphate (TPP), resorcinol bis-(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP). All three phosphorus compounds can be used in PC/ABS as well as in HIPS/PPO blends. For PC/ABS blends, the required loadings depend on the ratio of PC and ABS. In commercial PC/ABS blends, where the ABS content normally does not exceed 25%, it is possible to comply with the safety standard UL 94 V0 at 8 to 15 % by weight loading in combination with a co-additive. The co-additive usually is an anti-dripping agent like polytetrafluoroethylene (PTFE), with loadings up to 5 % by weight (Döring and Diederichs 2007). HIPS/PPO blends, where typical levels of PPE used to achieve a UL 94 V0 rating are 30 to 70%, contain 10 to 20% of PTT, RDP or BDP (Döring and Diederichs 2007).

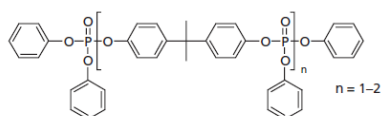
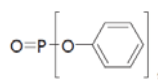
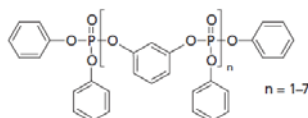
Bisphenol A bis(diphenyl phosphate) (BDP):**Triphenyl phosphate (TPP):****Resorcinol bis-(diphenyl phosphate) (RDP):**

Figure 3-4: Organophosphorus compounds used in PC/ABS and PEE/HIPS blends (Döring and Diederichs 2007)

Regarding the recyclability of PC/ABS with organophosphorus flame retardants, (Döring and Diederichs 2007) found that used at typical recycling rates (20%), all bis-phosphate flame retardants (i.e. BDP and RDP) meet industry standards with respect to the retention of flammability, the retention of impact properties and stable melt viscosity. Phosphate esters such as BDP and RDP are known to be susceptible to hydrolysis (all phosphate esters decompose to acid species especially after exposure to high heat and humidity, BDP being less susceptible but eventually showing PC polymer degradation and RDP displaying instability earlier); according to (Döring and Diederichs 2007), substantial improvements can be seen when adding stabilizers.

In the study of (Schlummer et al. 2007), which investigated 45 housings of television sets and monitors, in contrast to ABS and HIPS, no BFRs were found in ABS/PC and PPO/PS. The latter exhibited partly elevated phosphorus levels, pointing at phosphate-based flame retardants. In HIPS from television set housings, neither brominated nor phosphorus-based flame retardants were found; however, the sample size was rather small (9 samples).

3.2.4 Polybrominated dibenzodioxins and - dibenzofurans

When dismantling and recycling plastics containing brominated compounds at elevated temperatures, polybrominated dibenzo dioxins and – furans (PBDD/PBDF) might be unintentionally produced. In HIPS with DecaBDE and ABS with OctaBDE and TBPE, in particular, (Wolf 2001) found concentrations of PBDD/PBDF which exceeded the limit values defined in the German Chemicals Ordinance (German Federal Ministry of Justice 2003) (see also section 3.1.6). (Schlummer et al. 2007) measured PBDD/PBDF concentrations above these limit values in five shredded TVset - and CRT monitor housing samples and four mixed WEEE shredder residue samples.

According to (Schlummer et al. 2007), BFRs are the most likely sources of PBDDs and PBDFs at temperatures below 300 °C e.g. in shredders. Copper, which is typically found in WEEE shredder residues, acts as a catalyst for the formation of PBDDs and PBDFs (Weber and Kuch 2003). Although in a review on the formation of PBDD/PBDFs the highest PBDD/F build-up potentials have been described for PBB, OctaBDE and

former DecaBDE qualities ((Ebert and Bahadir 2003)), in their study (Schlummer et al. 2007) found no correlation between PBDD/PBDF levels and total bromine content or specific BFR levels. Rather, their results indicate that PBDD/PBDF levels increase with decreasing particle size of the shredder residues. Because particle sizes decrease with increasing duration and impact of the shredding process, (Schlummer et al. 2007) conclude that PBDD/PBDF levels increase with the energy applied by the shredders.

4 Synopsis

Plastics shares and quantities in WEEE categories and product types

The literature review has shown that data on plastics and plastic type shares in EEE and WEEE exist or may be derived from existing data. However, these data are still associated with significant uncertainties i.a. due to the limited scopes of the studies considered, data limitations and different assumptions made (e.g. regarding service lives). Despite these limitations, the quantitatively most relevant plastic types have been identified for the WEEE categories and product types in the focus of this study. These are:

- **Large household appliances w/o cooling appliances: PP** (~225'000 t/a), followed by PUR, ABS, PS and HIPS.
- **Cooling and freezing appliances:** ABS (~142'000 t/a), HIPS (~95'000 t/a) and PUR (~95'000 t/a), with PP and PVC also occurring in significant quantities.
- **Small electronic appliances:** PP (~130'000 t/a) and HIPS (~111'000 t/a), with ABS (~74'000 t/a) also occurring in significant quantities.
- IT equipment w/o screens (CRT monitors or flat screens): ABS (~127'000 t/a), followed by ABS/PC and HIPS.
- **CRT monitors:** ABS (~70'000 t/a), followed by HIPS (~39'000 t/a), ABS/PC and PPO/PPS.
- Consumer equipment w/o screens (CRT monitors or flat screens): HIPS (~100'000 t/a), followed by ABS, PPO, PPO/PS and PMMA.
- **TV sets:** HIPS (~120'000 t/a), followed by ABS (~30'000 t/a), ABS/PC, PPO and PPO/PS.

RoHS substance concentrations in WEEE plastics

The literature review has shown that data on hazardous substance concentrations in plastics from WEEE are available. However, these data typically focus on particular fractions such as TV set - and CRT monitor housings or unspecified WEEE shredder residues. A comprehensive overview of their occurrence in typically occurring plastic fractions from mixed WEEE categories, single WEEE categories and product types based on this data is associated with significant uncertainties.

Heavy metals in WEEE plastics

Among the elements regulated by the RoHS Directive cadmium and lead appear to pose the greatest potential problems in plastics from WEEE ((Schlummer et al. 2007), see Figure 4-1). In a recent study, cadmium was measured at concentrations in the range of the RoHS MCVs both in TV set – and monitor-housing shredder residues and in mixed WEEE shredder residues. The concentrations for lead have been found to lie in the in the range of the MCV for mixed WEEE shredder residues, which has been explained by cross contaminations from circuit boards. Unspecified chromium was measured at concentrations below the RoHS MCV for hexavalent chromium, mercury at concentrations significantly below its RoHS MCV.

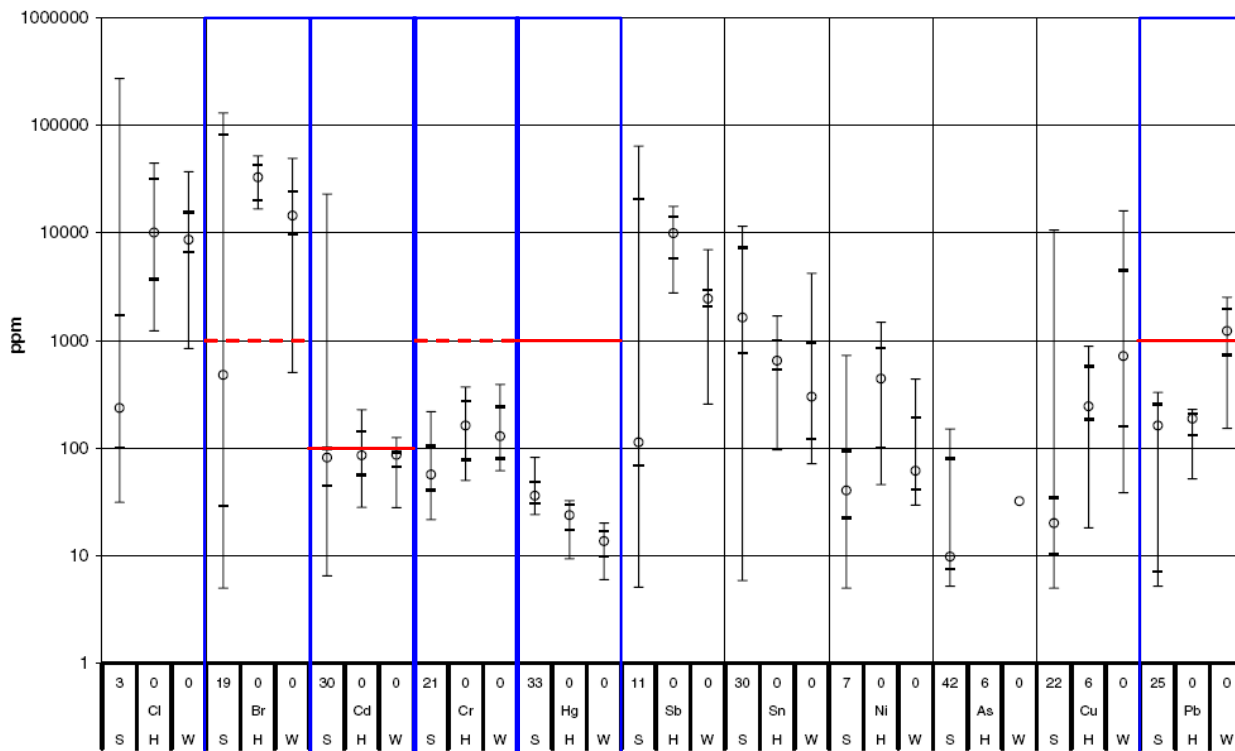


Figure 4-1: Concentration ranges for different elements in single casings (S), housing shredder residues (H) and mixed WEEE shredder residues (W), modified according to (Schlummer et al. 2007). For each element the median, minimum, maximum as well as the 25- and 75-percentiles are shown. The figures on the x-axis correspond to the number of samples below the detection limit. The MCVs of the RoHS Directive for bromine (Br) and (unspecified) chromium (Cr) are dashed, because the MCV refer to brominated flame retardants (and not bromine) and chromium (VI) (and not unspecified chromium), respectively.

On the level of plastic types, concentrations above the respective RoHS MCV are expected for cadmium, hexavalent chromium and lead in **PVC** from WEEE category 1-4 products. In **ABS** from WEEE category 1-4 products, in particular from CRT monitors, TV sets and video appliances, the MCVs for hexavalent cadmium are expected to be exceeded. For other plastics types such as **ABS / PC** blend in WEEE category 3 and 4 products, and **PP** in category 1, 2 and 4 products, concentrations above the RoHS MCV might possibly occur.

Besides the four heavy metals regulated in the RoHS Directive, other elements such as antimony, arsenic, nickel or tin were found in plastics fractions from WEEE dismantling. For antimony, which is applied as a synergist (antimony trioxide) for BFRs, there are indications that the levels in plastics from WEEE have decreased in the past years due to a phase-out of BFR; the same appears to be true for cadmium from cadmium-based additives. The observed reduction of chromium, lead and nickel contents in plastics from mixed WEEE shredder residues, on the other hand, points at an improved technology regarding the separation of thermoplastics from printed circuit boards.

Flame retardants in WEEE plastics

According to the literature review, PentaBDE, OctaBDE and DecaBDE appear to be the most critical flame retardants regulated by the RoHS Directive in WEEE plastics. For the five quantitatively most relevant plastic

types in WEEE, Table 4-1 shows where these flame retardants possibly or most probably will occur at concentrations above the RoHS MCV for PBDEs. In **ABS**, OctaBDE and DecaBDE might exceed the MCV for PBDEs in WEEE category 1 and 2 products, whereas in **ABS** from WEEE categories 3 and 4 concentrations above the MCV for PBDEs are possible for DecaBDE and expected for OctaBDE. In **HIPS**, only DecaBDE is expected to occur in relevant concentrations, in particular in products from WEEE categories 3 and 4. In **PP**, DecaBDE might occur at concentrations above the MCV for PBDE, and in PU, PentaBDE concentrations possibly might exceed the MCV for PBDEs.

Table 4-1: Expected occurrence of hazardous substances regulated by the RoHS Directive in the five quantitatively most relevant plastic types from WEEE categories 1 to 4 (bold text: concentrations above of RoHS MCV for PBDEs expected; plain text: Concentrations above the RoHS MCV for PBDEs possible; grey cell: no relevant amounts of plastic type in the corresponding WEEE category)

	Category 1	Category 2	Category 3	Category 4
ABS	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE	Cadmium, OctaBDE, DecaBDE
HIPS	DecaBDE	DecaBDE	DecaBDE	DecaBDE
ABS/PC			Cadmium	Cadmium
PP	Cadmium, DecaBDE	Cadmium, DecaBDE		Cadmium, DecaBDE
PUR	PentaBDE	PentaBDE		

In other plastic types, DecaBDE is expected to occur at concentrations which might exceed the RoHS MCV for PBDEs in **PA** for category 1 (w/o freezing and cooling appliances), category 2 and category 3 products, and in **PC** for WEEE category 2 products, LCD-monitors as well as WEEE category 4 products. For **PS** in CRT TV sets, the MCV for PBDEs is expected to be exceeded for DecaBDE. In **PE** found in PC/servers, notebooks, printers and copiers, both OctaBDE and DecaBDE might occur at concentrations above the MCV for PBDEs.

Regarding polybrominated biphenyls, there are strong indications that if they still occur in WEEE at all, then at concentrations well below the RoHS MCV. Moreover, BFRs regulated by the Directive appear to be increasingly being substituted by other, unspecified brominated flame retardants and organophosphorus compounds. The latter are expected to occur in PC/ABS, in particular.

When processing plastics containing BFR at elevated temperatures, polybrominated dibenzo dioxins and –furans (PBDD/PBDF) can be unintentionally produced, leading to concentrations exceeding the limit values defined in the German Chemicals Ordinance. In shredders, it has to be expected that PBDD/PBDF levels increase with the energy applied, i.e. with decreasing particle size of the shredder residues.

Part II: Sampling Campaign

5 Materials and methods

5.1 Plastics sampling

The sampling strategy was defined based on the results of “Part I: Literature review” and a comprehensive expert consultation. The expert consultation included various workshops with the Swiss collection and recovery systems SENS and SWICO (incl. the participation of recyclers) and the members of the WEEE Forum. Samples were defined in order to meet the following requirements:

1. Samples should represent the current recycling practice, i.e. samples should be taken from typical input streams as processed by European recyclers.
2. Separate samples should be taken from each of the WEEE categories 1-4.
3. Separate samples should be taken from WEEE product types either suspected to contain high particularly levels of RoHS substances (e.g. CRT monitors/TVs, small appliances for high temperature applications) or particularly low levels of RoHS substances (e.g. flat screens) in their respective plastics fraction.

As a result, the sampling procedure and sample types were defined as presented in Table 5-1 and in Table 5-2, respectively.

The plastics sampling campaigns were carried out according to the sampling procedure defined in a sampling manual (see Annex 1) under the responsibility of the following collection and recovery systems:

Figure 5-1: Collection and recovery systems responsible for the sampling campaigns

- Amb3E, Portugal (2 sampling campaigns)	- Envidom, Slovakia (1 sampling campaigns);
- Asekol, Czech Republic (2 sampling campaigns)	- NVMP, The Netherlands (1 sampling campaigns);
- Ecolec, Spain (2 sampling campaigns)	- Recupel , Belgium (5 sampling campaigns, including 2 product type mixtures not considered in this report);
- EcoLogic, France (8 sampling campaigns)	- SENS, Switzerland (7 sampling campaigns);
- Eco-Systèmes, France (7 sampling campaigns)	- SWICO Recycling, Switzerland (7 sampling campaigns);
- Ecotic, Spain (2 sampling campaigns)	- UFH, Austria (2 sampling campaigns).
- ElektroCoord, Hungary (2 sampling campaigns)	
- Elektrowin, Czech Republic (2 sampling campaigns)	
- Elretur, Norway (5 sampling campaigns);	

Every sampling campaign was documented on the basis of a sampling protocol template (see Annex 2). Manual and protocol were developed by Empa under consideration of DIN EN 14899 and LAGA PN 89 ((LAGA 2001, DIN EN 14899 2005, CEN 2006)). Due to the participation of many different systems and recyclers, small deviations from the sampling procedure described in the manual could not be avoided. All deviations were communicated by the responsible persons of the participating systems and considered for the interpretations of the results.

According to LAGA PN 89, for a basic volume of analysed material (in this case, WEEE) up to 30 m³ every sampling campaign should result in two laboratory samples in order to allow for a repeated analysis. For grain sizes of > 2 to < 20 mm, > 20 to > 50 mm and 50 to <120 mm, each two samples with a volume of 2 litres, 4 litres and 10 litres, respectively, are required. The two samples were obtained by combination and reduction of each four randomly selected samples of defined volumes taken from waste stream according to a specified procedure (see Annex 1).

Under consideration of the financial boundary conditions for the project, one (randomly chosen) sample was analysed for each campaign as a general rule, with repeated analyses for 9 sampling campaigns to allow for an evaluation of the uncertainties related to sampling (Table 5-2). The repeated analyses were performed for one randomly chosen sampling campaign each for the mixed WEEE categories M1 – M3, the WEEE categories C1 - C4, vacuum cleaners and small appliances for high temperature applications.

Table 5-1: Sampling procedure as defined in the sampling manual

Step	Task	Remarks	Reference
1	Define input categories / product types	<ul style="list-style-type: none"> Is defined prior to the sampling campaign by the responsible WEEE forum member in coordination with the WEEE Forum 	WEEE Forum
2	Collect input material quantity	<ul style="list-style-type: none"> Approx 20 tons for mixed WEEE categories and WEEE categories Appropriate (realistic) quantity for single product types (to be confirmed with Empa – Esther Müller) 	LAGA 2001
3	Choose the fraction to be sampled	<ul style="list-style-type: none"> One fraction only, most relevant 	System operators
4	Define sampling location	<ul style="list-style-type: none"> If possible directly from the output flow Otherwise from a container 	DIN EN 14899 2005 CEN 2006
5	Take the samples	<p>Consider guidance on</p> <ul style="list-style-type: none"> required number and size of samples and sampling period and interval 	LAGA 2001
6	Prepare the samples	<p>Consider guidance on</p> <ul style="list-style-type: none"> mixed sample preparation and sample reduction 	DIN EN 14899 2005 CEN 2006
7	Package the samples	<ul style="list-style-type: none"> Use stable package material and label the samples 	DIN EN 14899 2005 CEN 2006
8	Document the sampling procedure	<ul style="list-style-type: none"> Keep records of all required information according to the standard protocol during the entire sampling procedure Photo documentation 	LAGA 2001 DIN EN 14899 2005 CEN 2006

Table 5-2: Analysed Mixed WEEE categories, WEEE categories and single product types.

Category/Product				Number of sampling campaigns and single sample analyses	Number of repeated analyses	Number of additional washed sample analyses	Total number of analyses
Mixed WEEE categories	Cat. 2,3,4,6,7	M1	Small appliances w/o screens (CRTs, flat screens)	7	1	1	9
	Cat. 2,6,7	M2	Small household appliances, tools, toys, leisure and sports equipment	2	1	1	4
	Cat. 3,4	M3	ICT and consumer equipment w/o screens (CRTs, flat screens)	2	1	0	3
WEEE categories	Cat. 1	C1	Large household appliances	5	1	0	6
	Cat. 2	C2	Small household appliances	2	1	0	3
	Cat. 3	C3	ICT equipment w/o screens (CRTs, flat screens)	2	1	0	3
	Cat. 4	C4	Consumer equipment w/o screens (CRTs, flat screens)	1	1	0	2
Single product types	Cat. 1	P11	Cooling and freezing appliances (inside lining without drawers)	5	0	1	6
		P12	Cooling and freezing appliances (all plastics, except foams)	6	0	0	6
	Cat. 2	P22	Vacuum cleaners w/o hoses	1	1	0	2
		P23	M2 w/o vacuum cleaners	1	0	0	1
		P24	Small appliances for high temperature applications	1	1	0	2
	Cat. 3	P31	CRT Monitors	5	0	0	5
		P32	Flat screen monitors*	3	0	0	3
		P33	Printers	3	0	0	3
	Cat. 4	P41	CRT TV's	7	0	0	7
Total				53	9	3	65

* due to sampling inconsistencies the samples also include plastics from flat screen TV's

5.2 Chemical analyses

5.2.1 Sample preparation

In a first step of the sample preparation all metals except stranded copper wire and thin non-magnetic cables were removed by magnet and hand sorting, and the resulting plastic and metal fractions each

weighed. In a second step the grain size of the plastic fraction was reduced to < 0.5 mm in consecutive steps by milling and sieving with a high performance cutting mill and sieves with different mesh sizes. The grain size reduction, which varied depending on the initial grain size, typically consisted in the following three steps: Reduction to 6 mm, then 2 mm and finally 0.5 mm. After each grain size reduction step, the sample size was reduced to a representative fraction of the total sample with a riffle splitter (Bunge 1999). Finally, about 80 g of the final fraction with a grain size of <0.5 mm were ground to a particle size of <0.12 mm by an ultra centrifugal mill, under application of liquid nitrogen.

To address the question, if the elevated lead concentrations found in some samples were the consequence of a cross contamination during the shredding process or were caused by lead effectively bound to plastics, additional three samples were thoroughly washed with a Nanopure distilled water spray (Gloor 2010) in the 2 mm sieving step before being analysed.

5.2.2 Quantitative metal analyses

The quantitative analyses of cadmium, chrome, lead and mercury included a sample preparation step followed by a chemical analyses.

a) Microwave Digestion

Sample preparation was done with closed vessel microwave digestion. The procedure slightly differed for the first and second set of samples.

For most samples a two- step digestion was performed. In the first step, 0.3 g of the dried and ground sample were digested in a closed vessel with 5 ml of HNO₃ 65% and 3 ml H₂O₂ 30%. For the subsequent second digestion step, 3ml of HCl 37% were added. After digestion and cooling down (or having reached a pressure below < 10 psi), the content was transferred into a 50 ml volumetric flask. Vessel and cover were rinsed with Nanopure-water into to the volumetric flask, and the flask filled up with Nanopure-water to the mark. After shaking, the content was filtered through a folded Sartorius 1289 (d=125 mm) filter into a 200 ml PP bottle.

For a few samples from the beginning of the sampling campaign, a one-step digestion was performed. 0.5 g of the dried and ground sample were digested with 2ml of HNO₃ 65% und 6ml HCl 37% (aqua regia). After cooling down (or having reached a pressure below < 10 psi), the content was transferred to a 100 ml volumetric flask. Vessel and cover were rinsed with Nanopure-water into the volumetric flask and the flask filled up to the mark with Nanopure-water. After shaking, the content was filtered through a folded Sartorius 1289 (d=125 mm) filter into a 200 ml PP bottle.

b) Chemical analysis

Cadmium was determined by ICP-MS (inductively coupled plasma, mass spectrometry) with an Agilent 7500ce, Octopole Reaction System. Calibration was performed with cadmium isotope 111 at concentrations of 0, 1, 5 and 10 ppb.

Lead and chromium were determined by ICP-OES (inductively coupled plasma, optical emission spectrometry) with a Varian 735-ES device. The lead concentrations were measured at a wavelength of 200.353 nm, and the calibration was performed at concentrations of 0, 0.2, 1.0, 2.0 and 10 mg/kg. The chromium concentrations were measured at a wavelength of 205.560 nm, and the calibration was performed at concentrations of 0, 0.1, 0.5, 1.0 and 5.0 mg/kg.

Mercury was determined by AFS (atomic fluorescence spectrometry) with a Mercur Analytik Jena device. To do so, the mercury in the digested sample was reduced to elementary mercury with a SnCl₂-solution and the reduced mercury expelled with argon. Finally, the expelled mercury was scavenged in to a fluorescence cuvette, where the mercury content was measured at a wavelength of 254 nm. Calibration was performed at concentrations of 0, 10, 50 and 100 ng/l.

For each sample, three measurements per element were performed. According to the laboratory performing the analyses, the extended, combined uncertainty for the determination of cadmium, chromium, lead and mercury amounts to 12 – 25% ((Bachema 2007)). In the case of chromium, the standard analysis with aqua regia results in a systematic underestimation of chromium (Gloor 2010). The evaluation of the chromium content in the samples therefore refers to the results of the XRF analysis (see section 5.2.3).

5.2.3 Semiquantitative elemental analyses

A series of elements including, amongst others, antimony, bromine, cadmium, chlorine, chromium, lead, mercury and phosphorus, were semiquantitatively analysed with X-Ray Fluorescence (XRF) spectrometry. In a first step, a quantity of the dried and ground sample was introduced into a cuvette so that its bottom was fully covered with the sample and the layer thickness corresponded to about 1 cm. The cuvette was then transferred into the automatic sampler of a Spectro X-Lab device and the analyses were started by selecting the Turbo-Quant method. For each sample a single measurement was performed.

The basic calibration of the device has been performed by the equipment manufacturers (SPECTRO GmbH). The Turbo-Quant method was calibrated with many different matrices by the laboratory performing the analysis and is suitable for analyses of samples which are not of geological origin ((Gloor 2010)).

The detection limits for each of the elements analysed depended on the calibration performed. The extended, combined uncertainty for the determination of e.g. antimony, bromine, cadmium, chromium, lead, mercury and phosphorus exceed the uncertainties for samples of geological origin (12 – 25%) by a factor of 2, i.e. they amount to about 25-50% ((Bachema 2007, Gloor 2010)).

Despite higher uncertainties, a chromium analysis with XRF spectrometry is still more accurate than the standard analysis with ICP-OES (Gloor 2010).

5.2.4 Brominated flame retardants

The sorted, reduced and ground samples were extracted with a mixture of cyclohexane and acetone (1:1). The extract was diluted where necessary and the compounds derivatized, separated by gas chromatography and detected with an electron capture detector (ECD). The procedure was carried out in accordance with DIN EN 62321 (DIN EN 62321 2009). For samples with elevated BFR concentrations, repeated measurements were performed.

a) Extraction

A 100 – 500 mg sample was extracted with cyclohexane / acetone in a Soxleth extractor during 16 hours at a minimum. After extraction, the solvent was changed to toluene. As a surrogate, 4,4'-Dibromooctafluorobiphenyl (DBOBF) was applied. The internal standard was PCB 209.

b) Derivatization

The diluted extract was derivatized with trimethylsilyl N,N-dimethylcarbamate (DMCTMS) or with a mixture of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (silyl-991: BSTFA + TMCS (99:1)).

c) Chemical analysis

1 to 2 µl of the extract each were injected on a splitless injector BGB-1 10m*0.25mm*0.1µm capillary column with a GC PAL autosampler. After separation in a Trace GC Ultra (make up gas N2 5.0 30ml/min, carrier gas H2), the brominated flame retardants were detected with an ECD Ni63 and quantified using a software. As required by DIN EN 62321 ((DIN EN 62321 2009)), which is typically applied for the analysis of electro-technical products with regard to compounds regulated in the RoHS, the procedure was calibrated with the pure compounds, namely BDE-47 (2,2',4,4'-Tetrabromodiphenylether), BDE 99 (2,2',4,4',5-Pentabromodiphenylether), BDE-183 (2,2',3,4,4',5',6-Heptabromodiphenylether), BDE-197 (2,2',3,3',4,4',6',6-Octabromodiphenylether), BDE-209 (DecaBDE), DecaBB (Decabromobiphenyl), HBCD (Hexabromocyclododecane) and TBBPA (Tetrabromobisphenol-A).

To obtain the concentrations of the technical mixtures of Penta- and OctaBDE (C_{DE-71} and C_{DE-79}), which were used for the evaluation of the samples with regard to the RoHS Directive, the concentrations resulting from the calibration with the pure compounds were multiplied with factors according to following equations:

$$C_{DE-71} = (c_{BDE-47} + c_{BDE-99}) \times 1.3 \quad (1)$$

$$C_{DE-79} = (c_{BDE-183} + c_{BDE-197}) \times 1.4 \quad (2)$$

The detection limits for the different compounds were 0.02 g/kg BDE-47, BDE-99, BDE-183, BDE-197, DecaBB and TBBPA, 0.05 g/kg for DE-71 (Great Lakes, Pentas) and DE-79 (Great Lakes, Octas), 0.1 g/kg for BDE-209 and 0.2 g/kg for HBCD.

The procedure followed here slightly differs from DIN EN 62321 ((DIN EN 62321 2009)), which is typically applied for the analysis of electrotechnical products with regard to compounds regulated in the RoHS. In particular

- the samples were not extracted with toluene, because the recovery rate for TBBPA would be too low;
- the measurements were performed with an ECD and not with an MS - detector;
- the extracts were derivatized in order to be able to determine TBBPA.

According to the laboratory performing the analysis, these changes do not distort the results (Gloor 2010). The extended, combined uncertainty for the determination of brominated flame retardants with this method amounts lies between 25 and 40 % ((Bachema 2007)).

6 Results

6.1 Heavy metals

Concentration ranges for heavy metals are displayed in Figure 6-1 to Figure 6-4 for each WEEE category 1-4. The number of samples taken per category and product type is summarized in Table 5-2. A full listing of all laboratory results is presented in Annex 3. For the calculation of average values, concentrations measured below detection limits were set to the detection limit (worst case scenario).

Lead concentrations in plastics from WEEE were found to range from 12 ppm (P41 in Figure 6-4) up to 7800 ppm (M1 in Figure 6-2). In most samples, average lead levels were found to lie around the RoHS maximum concentration levels (MCV) of 1000 ppm. The MCV are exceeded for all mixed categories (M1 – M3) as well as for ICT equipment w/o CRT- and flat-screens (C3) and consumer equipment w/o CRT- and flat-screens (C4). Concentrations above the MCV were also found in one printer sample (P33). In plastics from WEEE categories C1 and C2, lead is found to lie in the vicinity of the RoHS MCV. Single product types also show concentrations close to the RoHS MCV with the exception of CRT monitors, flat screens and CRT TVs, which contain less than 100 ppm of lead. This is in partial discordance to the results of other studies, which found lead levels in CRT monitors and TVs (as well as in other consumer equipment) close to or just above the RoHS MCV ((Morf and Taverna 2004), (Schlummer et al. 2007).

It is possible that lead detected in our study could partially originate from shredding residues of metal fractions, which were not sorted out when samples were taken and prepared for the laboratory analyses. To clarify this possible cross contamination, three samples were washed and analysed a second time. This procedure revealed that in one case the lead concentration dropped significantly from 5300 to 160 ppm (M2 sample), whereas in the other two cases a clear drop of concentrations (from 1800 to 1400 ppm in an M1 sample and from 1720 to 1340 ppm in a P11 sample) could not be observed. These results suggest that lead levels, which significantly exceed the RoHS MCV, might originate from cross contamination of metal fractions in shredder residues and hence cannot be allocated to the plastic fraction only. This finding is also supported by the fact that samples with prior manual removal of the non-plastic fractions before the shredding process showed considerably lower levels of lead, than samples without prior removal of non-plastic fractions. This effect can be seen in Figure 6-3 between the samples for CRT and flat screens (P31 and P32 with lead levels around 100 ppm), where the non-plastic fractions were removed prior to shredding, and the (mixed) categories samples C3, C4, M1 and M3, where the non-plastic fractions were not removed prior to shredding. Still, our results don't allow excluding the possibility, that lead concentrations in plastics from all four categories may reach or exceed the RoHS MCV.

Cadmium was detected in concentrations which lie close to or above the RoHS MCV (100 ppm for cadmium) in small household appliances categories (C2, M2, P23). In all other samples the concentrations lie between 2 and 62 ppm (averages between 2 – 30 ppm), with the highest concentrations in TV monitors. The study of (Wolf 2001) demonstrated similar concentrations in CRT monitors and - TVs ten years ago, though with 25% of the samples clearly exceeding the RoHS MCV. The results of the sampling campaign suggest

that small household appliances are the main source for cadmium, and that compared to ten years ago the levels dropped to the level of the RoHS MCV and below.

For category 1 to 3 samples, unspecified **chromium** has been detected at concentrations near to or above (M2, P23) the RoHS MCV defined for hexavalent chromium in all samples; in category 4 samples concentrations were lower than the MCV by at least a factor of about 2.

Mercury was detected in all samples at levels of at least two orders of magnitude lower than RoHS MCV. Hence it is not expected that mercury occurs at relevant concentrations in WEEE plastics.

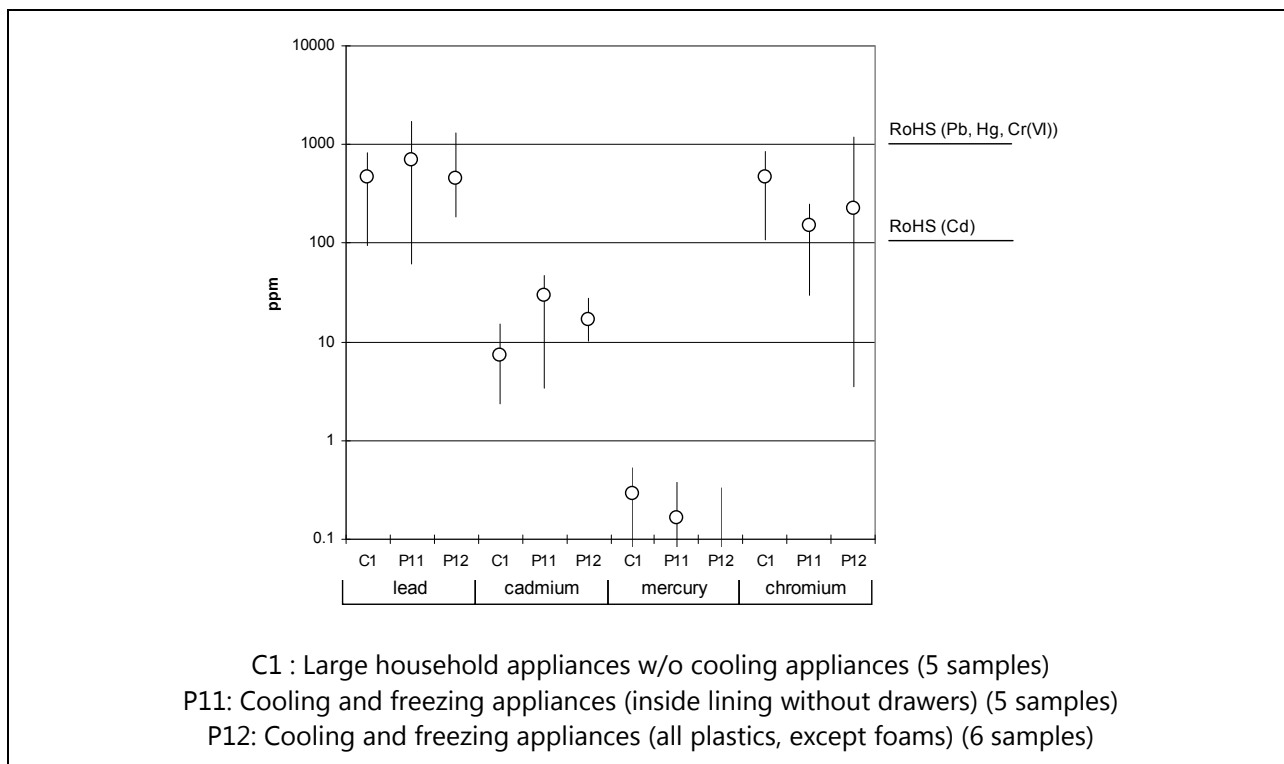


Figure 6-1: Concentration ranges of heavy metals in WEEE Category 1 samples

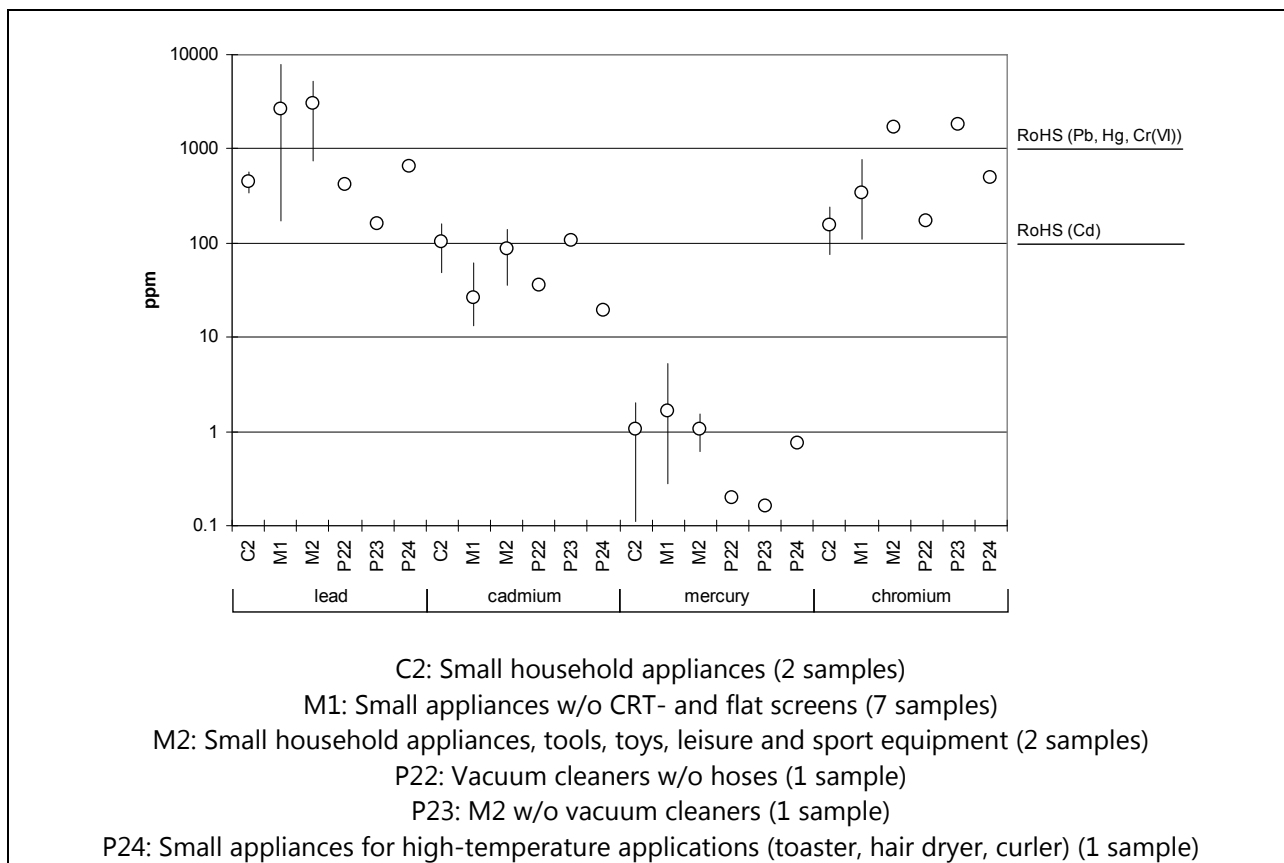


Figure 6-2: Concentration ranges of heavy metals in WEEE Category 2 samples

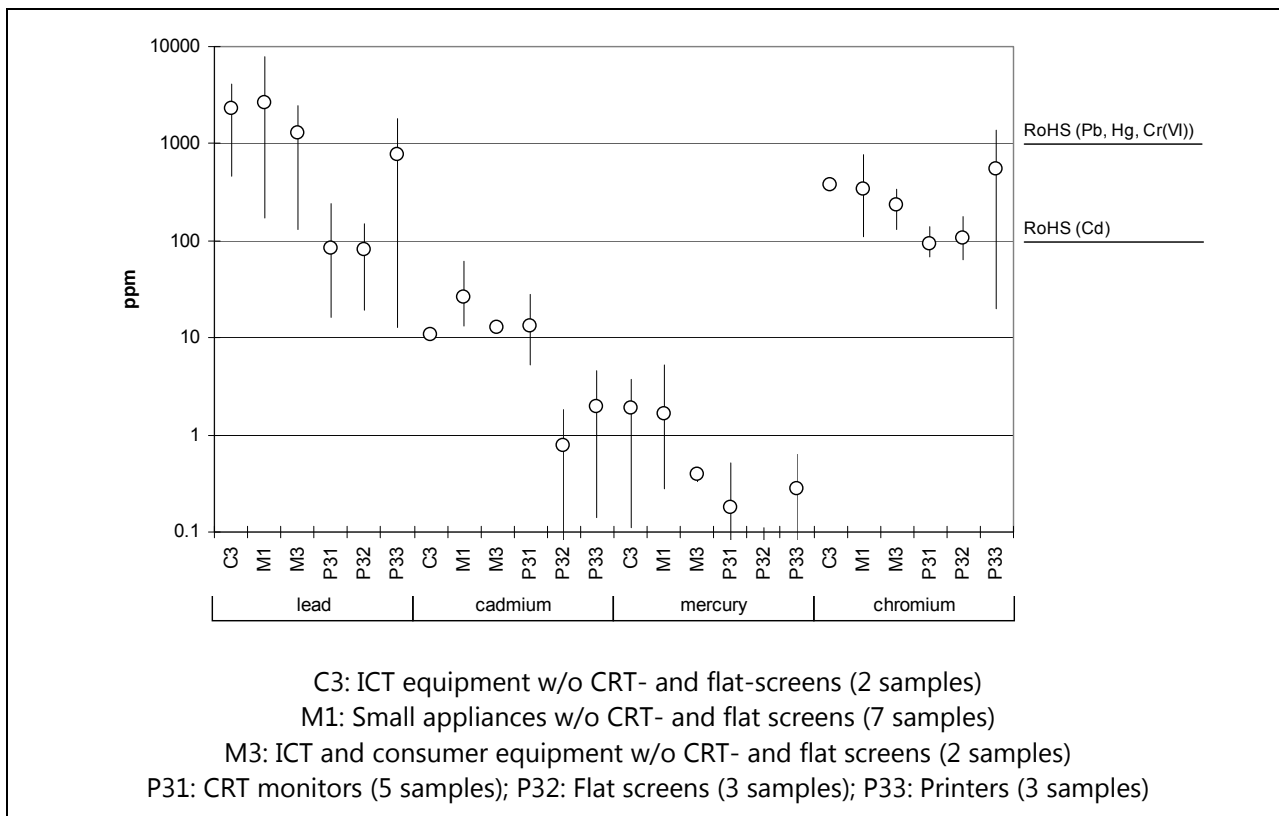


Figure 6-3: Concentration ranges of heavy metals in WEEE Category 3 samples

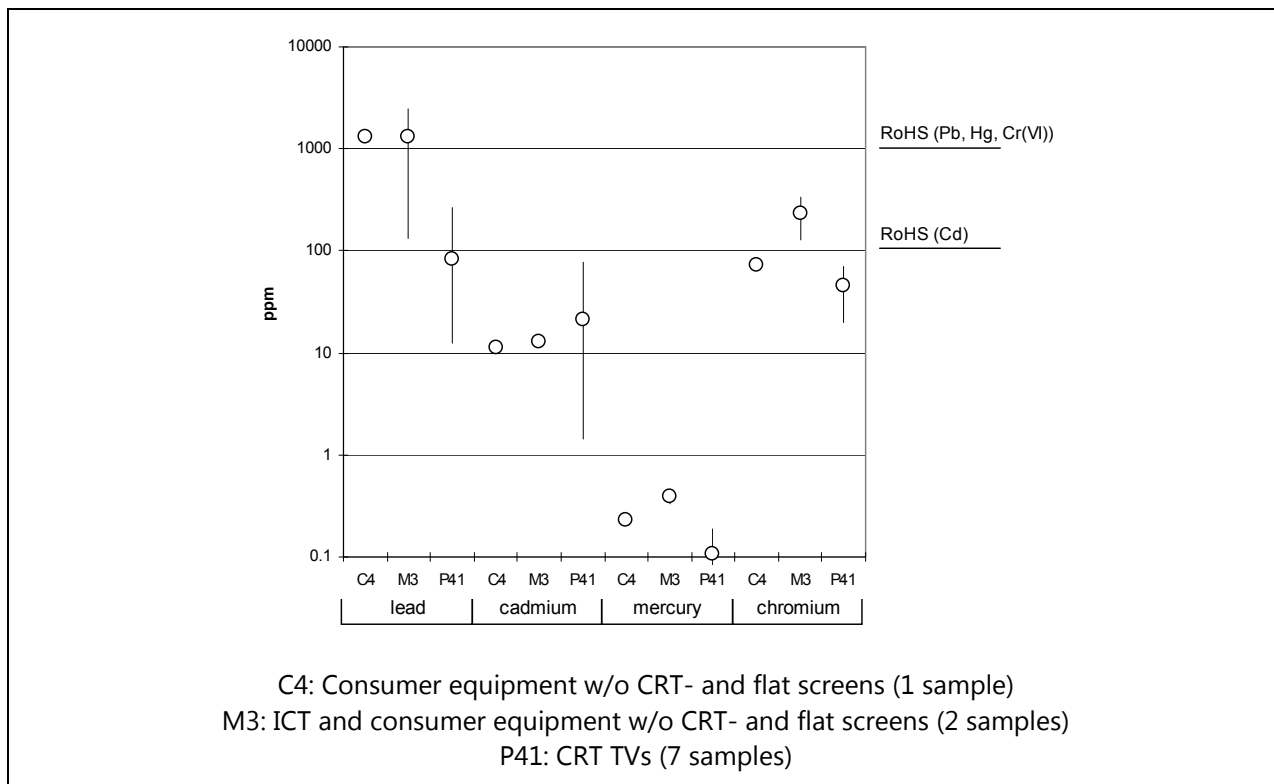


Figure 6-4: Concentration ranges of heavy metals in WEEE Category 4 samples

6.2 Flame retardants

6.2.1 Brominated flame retardants

The concentration ranges for the brominated flame retardants TBBPA, PentaBDE, OctaBDE and DecaBDE in WEEE plastics are displayed for each of the four WEEE categories in Figure 6-5 to Figure 6-8. Results for DecaBB are mentioned in the text, because it was only detected at elevated concentrations in few cases. HBCD could not be found above the detection limit at all. The number of samples taken per category and product type is summarized in Table 5-2 (see section 5.1). A full listing of all laboratory results is presented in Annex 3. For the calculation of average values, the detection limit was taken as a (worst case) approximation for the concentration of a substance found below the corresponding detection limit.

TBBPA was detected in most samples with average levels typically ranging from 1 to 10 g/kg. The highest concentrations were found in 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 small appliances for high-temperature applications (P24), namely 0.1 g/kg DM. Large household appliances (C1, P11, P12) is the only category where TBBPA was not detected. Summing up, the results suggest that TBBPA has to be expected in concentrations between 1-10 g/kg or above in plastics from WEEE categories 2 – 4, whereas there are indications that they do not occur in WEEE category 1. Considering the literature review presented in section 3.2.2, TBBPA concentrations found in category 2-4 samples are most probably a consequence of its application in ABS plastics.

PentaBDE only could be found in one mixed sample of small appliances w/o CRT- and flat screens (M1) as well as in consumer equipment w/o CRT- and flat screens (C4) at 0.1 g/kg. This suggests that PentaBDE does no more occur in plastics from WEEE at relevant concentrations, a finding which is supported by earlier studies ((Mark et al. 2006); (Morf et al. 2005); (Schlummer et al. 2007); (Tange and Slijkhuis 2009)).

OctaBDE was detected at concentrations above the RoHS MCV of 1 g/kg in 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). OctaBDE was also detected at concentrations close to the RoHS MCV in plastics from small appliances w/o CRT- and flat screens (M1), from ICT equipment w/o CRT and flat screens (C3). In 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 found in plastics from large household appliances (WEEE category 1 samples). The measured concentrations correspond to earlier studies ((Mark et al. 2006); (Morf et al. 2005); (Schlummer et al. 2007)), where levels clearly above the RoHS MCV were detected in plastics from CRT monitors and TV sets, and concentrations in the vicinity of the RoHS MCV in shredder fractions from mixed categories. Results also correspond to typical ranges found in WEEE summarized by (Tange and Slijkhuis 2009), whereas maximum concentrations found in CRT monitors from this study clearly exceed the indicative values of 500

– 3000 ppm (compare

Table 3-2). Summing up, and in accordance with other studies, the results of the sampling campaign suggest that elevated OctaBDE concentrations have to be expected in plastics from ICT equipment (with the highest levels in CRT monitors), as well as in plastics from CRT TVs. Literature data suggests that these concentrations mostly are a consequence from the application of OctaBDE in ABS plastics in the past (see chapter 3). OctaBDE at relevant concentrations is also to be expected in small appliances (from cat. 2 and 3), but most probably not in large household appliances.

DecaBDE was measured at concentrations close to or above the RoHS MCV in almost all samples. The highest concentrations were found in 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). Literature data for plastics from CRT monitors and TV sets support these findings with concentrations in a similar range ((Mark et al. 2006); (Morf et al. 2005); (Schlummer et al. 2007)). Also slightly above the RoHS MCV are concentrations in large household appliances w/o cooling appliances (C1, average 0.6 g/kg, maximum 1.6 g/kg). DecaBDE was also found in all other samples, except in plastics from the mixed samples of small household appliances (C2) and from flat screens (P32), where the DecaBDE concentrations were below the detection limit. Results correspond to the indicative values given by (Tange and Slijkhuis 2009) (Table 2-1). Our results suggest that plastics from CRT monitors and TV sets contain the most relevant concentrations of DecaBDE. According to section 3.2, DecaBDE is typically used in ABS and HIPS plastics (monitors and TV sets) as well as PP (large household appliances and in small appliances for high-temperature applications (P24)). The results of the literature review also suggest that ABS is the main source for DecaBDE found in category 2 and 3 samples, as well as in cooling & freezing appliances (see chapter 2). CRT TVs and other consumer equipment seem to be the source for DecaBDE in HIPS plastics.

DecaBB in relevant concentrations only could be found in plastics from CRT monitors (maximum 0.2 g/kg) and from CRT TVs (maximum 0.5 g/kg).

The hypothesis that plastics in vacuum cleaners (P23) and small appliances for high-temperature applications (P24) may contain high levels of BFRs regulated by the RoHS Directive could not be confirmed (see chapter 5). However, the measured total bromine content clearly exceeds the sum of bromine calculated from the specific BFR analyses (see discussion in section 0 and data in Annex 3), which suggests that these appliances contain other BFRs not specifically measured in this study.

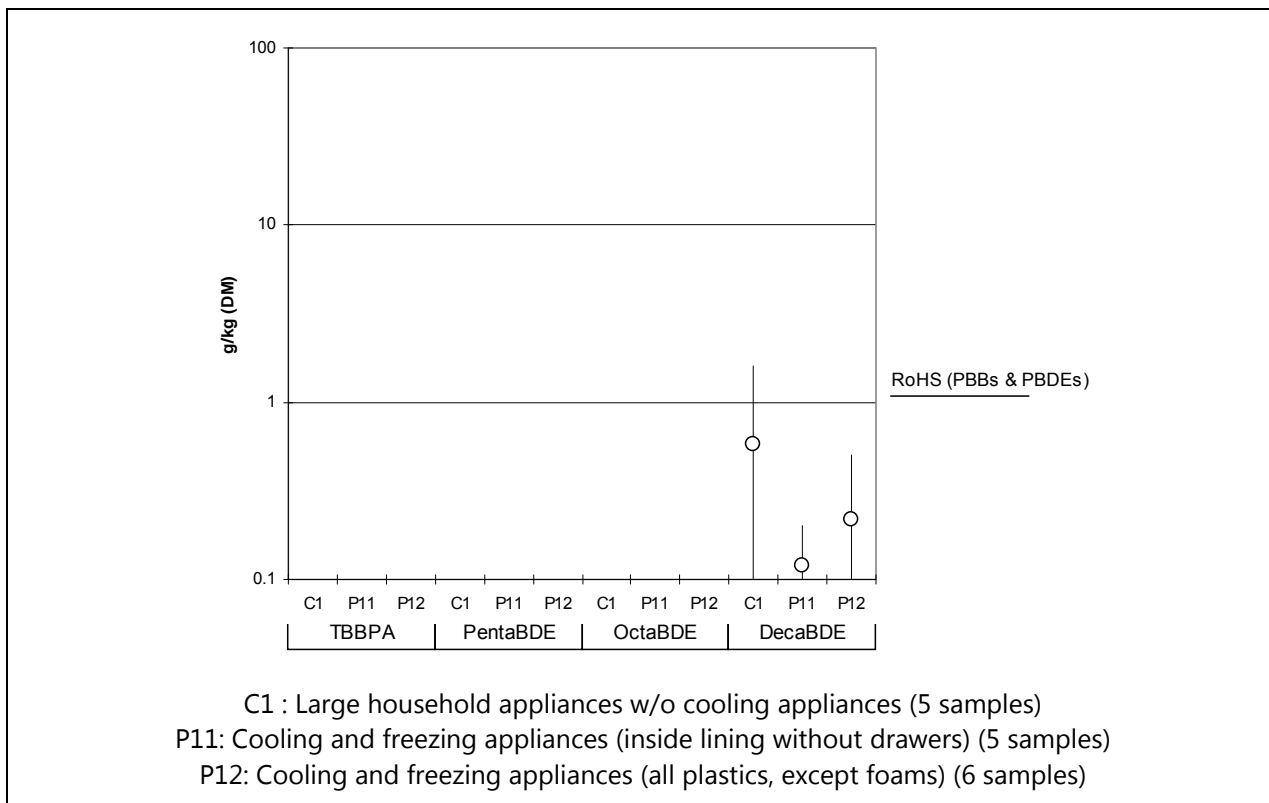


Figure 6-5: Concentration ranges of brominated flame retardants in WEEE Category 1 samples

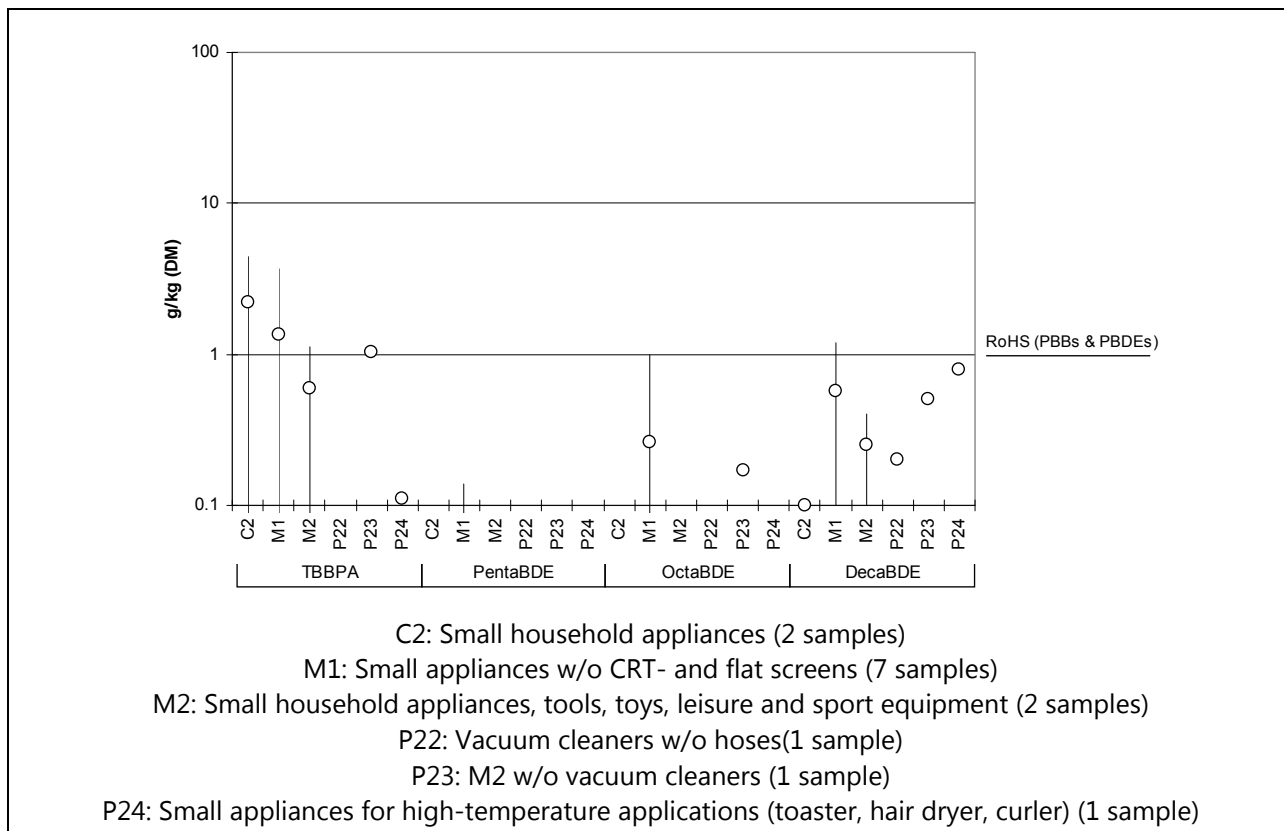


Figure 6-6: Concentration ranges of brominated flame retardants in WEEE Category 2 samples

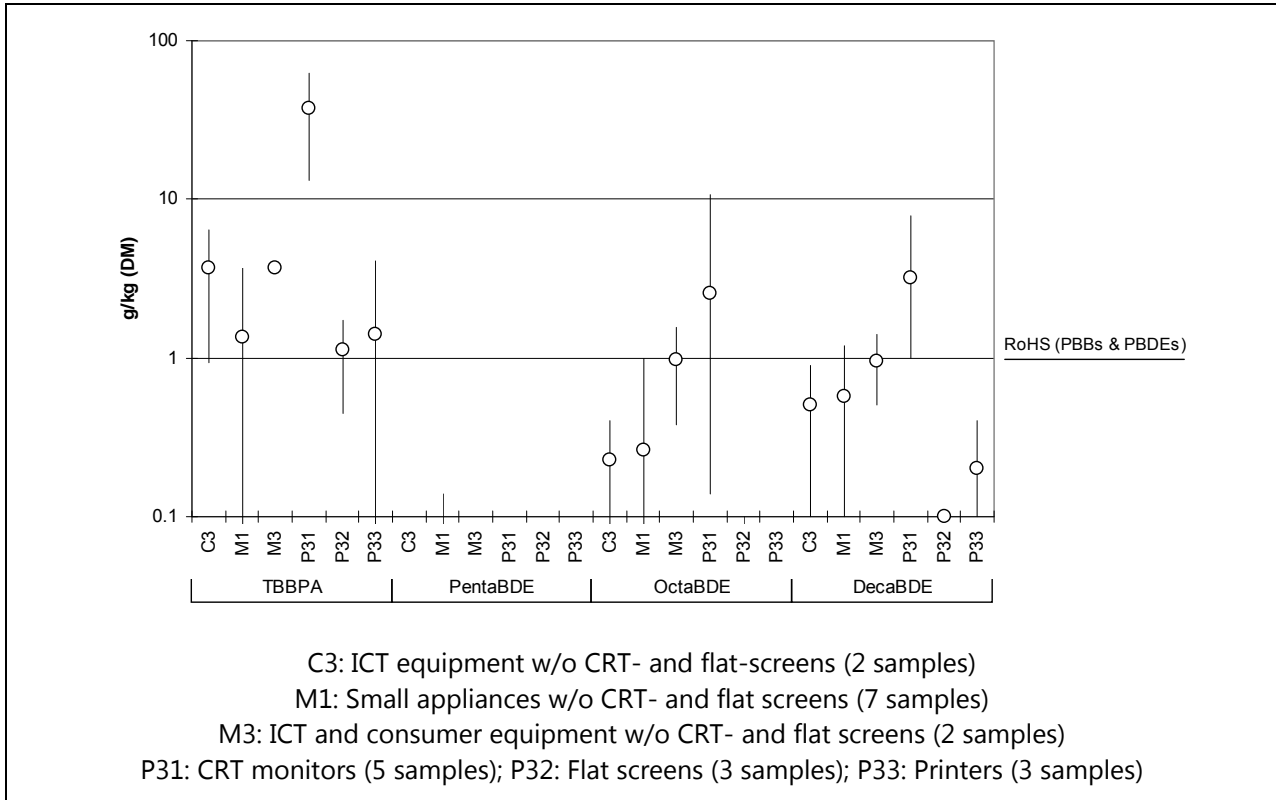


Figure 6-7: Concentration ranges of brominated flame retardants in WEEE Category 3 samples

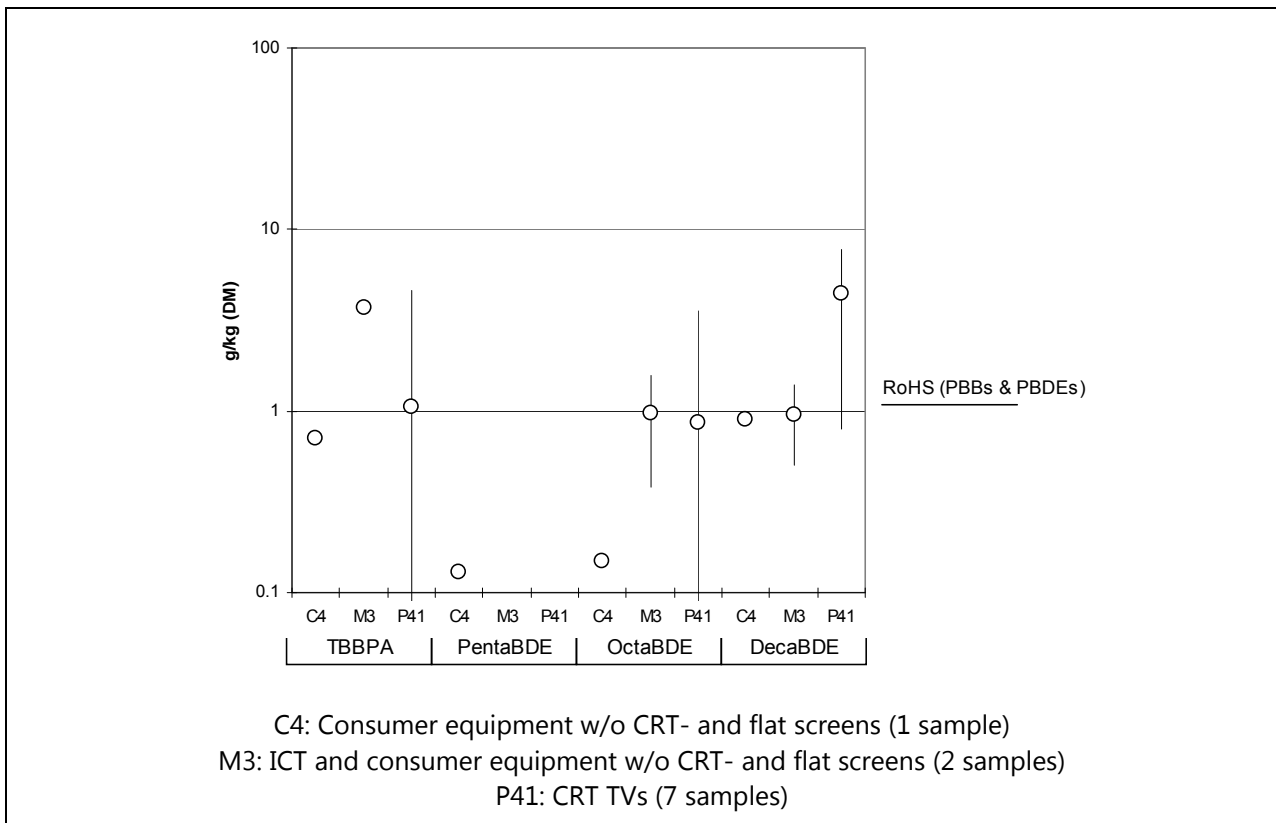


Figure 6-8: Concentration ranges of brominated flame retardants in WEEE Category 4 samples

6.2.2 Total bromine content

In order to get an indication, if other brominated substances than those specifically addressed could be present in a sample, the total bromine content was directly measured for each sample and compared to the total bromine content calculated from the results for the specifically measured brominated flame retardants. As can be seen in Figure 6-9, which displays the bromine contents by sample types (cat 1-4), the directly measured total bromine content almost always exceeds the calculated bromine content by factors ranging between 0 and 10. It can be seen that differences are the largest in cat 3 and 4 samples types as well as partially in cat 2 sample types. However any further correlation between total bromine content and different sample categories or the concentration levels of the total bromine content calculated from the results for the specifically measured brominated flame retardants cannot be seen.

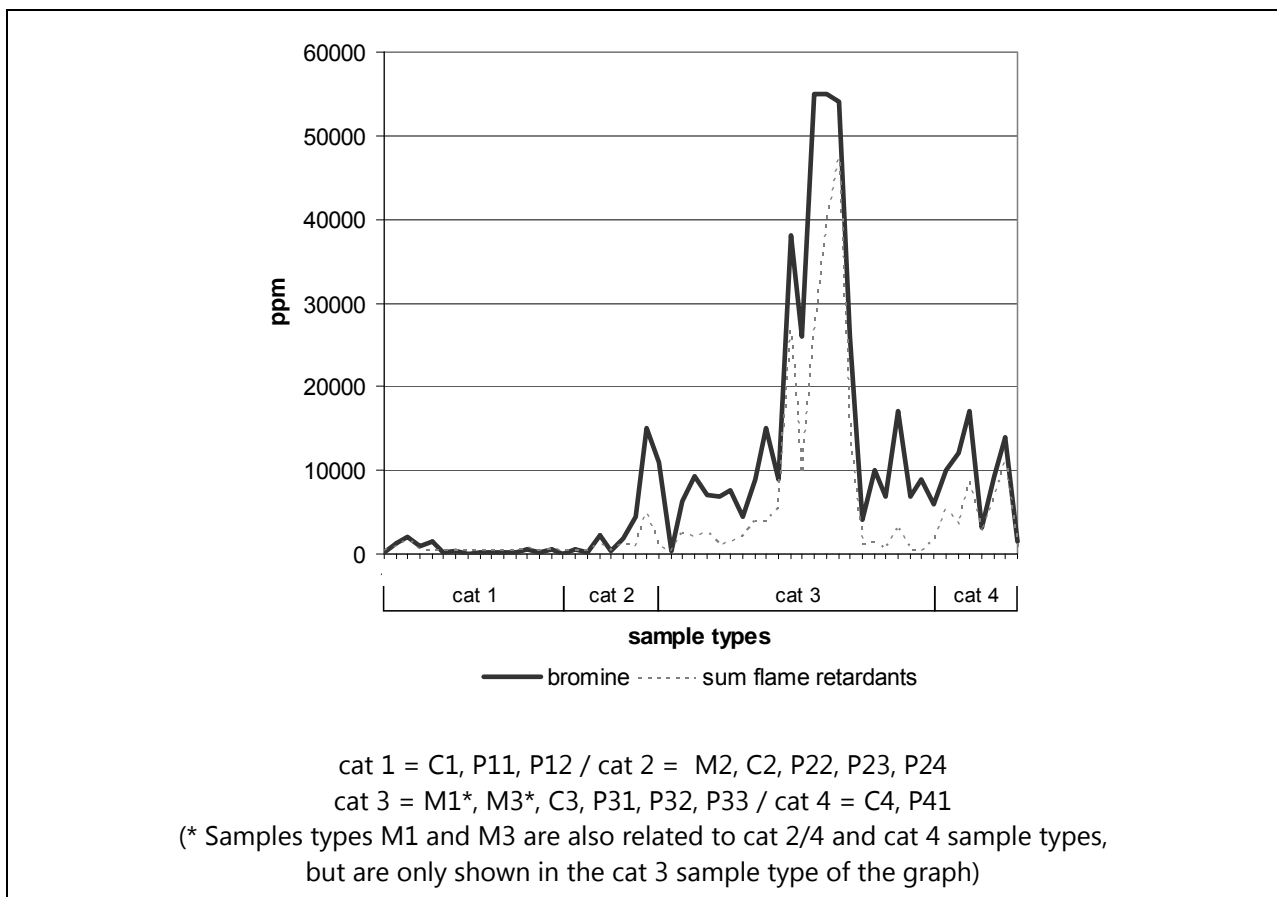


Figure 6-9: Total bromine content in comparison with the bromine content derived from the specific measurements of brominated flame retardants (TBBPA, PentaBDE, OctaBDE, DecaBDE, HBCD, DecaBB); the samples are organized by sample types (cat 1-4).

In polymers, BFRs are typically compounded with antimony trioxide. Antimony trioxide does not have flame retarding properties on its own, but is an effective synergist for halogenated flame retardants (Freeguard et al. 2006). In order to get an indication, if the non-identified brominated compounds could be flame retardants, the ratio between total antimony and total bromine concentrations was calculated for each sample (excluding samples measured below detection limit). All calculated ratios lie between 0.07 and 0.29 (data not shown; for original data consult Annex 3). This is an indication that total bromine concentrations found in the samples and consequently also bromine concentrations not related to the specifically measured brominated flame retardants are at least partly due to of an application of (other) brominated flame retardants. This finding is supported by various studies (summarized in (Chen and Wang 2009) and (Freeguard et al. 2006)), which point out that there are at least 75 different types of commercially available BFRs, of which 30-40 are or were widely used in EEE.

6.2.3 Phosphorus-based flame retardants

Phosphorus flame retardants (PFRs) such as BDP and RDP are typically used in ABS/PC-blends (see section 3.2.3); phosphate esters being susceptible to hydrolysis, recycling of ABS/PC containing these flame retardants may face some difficulties under conditions of heat and humidity ((Döring and Diederichs 2007); section 3.2.3). Typically, PFRs are applied at much lower concentrations than BFRs (References) and hence are more difficult to analyse (Tange 2010, oral communication).

The results of the analyses of phosphorus in WEEE plastics, which are depicted in Figure 6-10, show that total phosphorus concentrations in the analysed plastic samples lie in the range between 0.1 % and 3.5 %. This range corresponds to the reported amounts of PFRs typically applied in EEE plastics (Döring and Diederichs 2007), see section 3.2.3). The highest phosphorus concentrations were found in flat screens (P32, average 2.3%, maximum 3.5%), in CRT monitors (P32, average 0.7%, maximum 1.4%), in CRT TVs (P41, average 0.5%, maximum 0.9%) and in consumer equipment w/o CRT - and flat screens (C4, 0.5%). These findings are in line with the recent trend that ABS containing BFR is substituted with PFR containing ABS/PC and, for consumer products only, PPO (Dufton 2003). Below concentrations of 0.5%, phosphorus was detected in large household appliances (C1) as well as in the mixed categories M1 and M3. All other samples did not contain phosphorus above the detection limit of 0.01%.

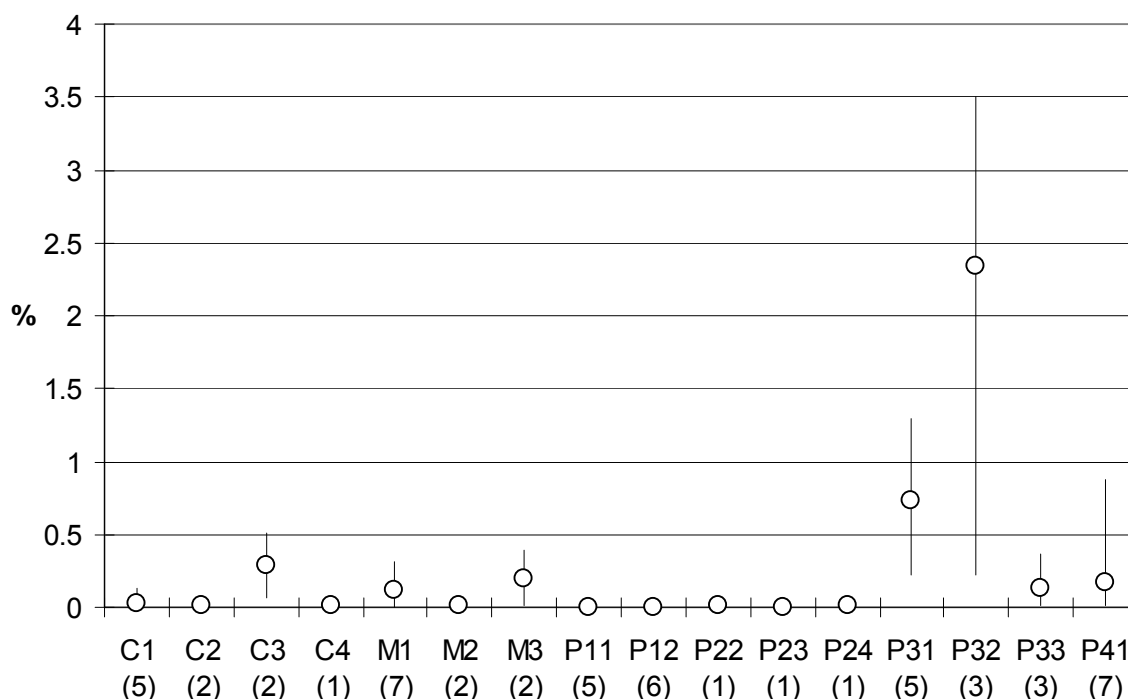


Figure 6-10: Concentration ranges of phosphorus in all samples (Number of samples analysed per category or product type in brackets).

6.3 Uncertainties

Uncertainties in the above presented results are a combination of deviations related to sampling and the combined uncertainties in chemical analysis. While uncertainties from the chemical analysis are described quantitatively in chapter 5, repeated analyses were performed for 9 samples in order to allow for a qualitative evaluation of uncertainties related to sampling. The repeated analyses are presented in Figure 6-11 for heavy metal concentrations and Figure 6-12 for brominated flame retardants concentrations.

Differences of heavy metal concentrations in separate samples from the same sampling campaign are in the range of the uncertainties related to chemical analysis for most samples. This is an indication that deviations related to sampling do not contribute to the overall uncertainty of the results. However, exceptions from this finding can be seen for mercury in the C2 sample. It is assumed that this deviation is due to inhomogeneity concerning the occurrence of mercury in the sample.

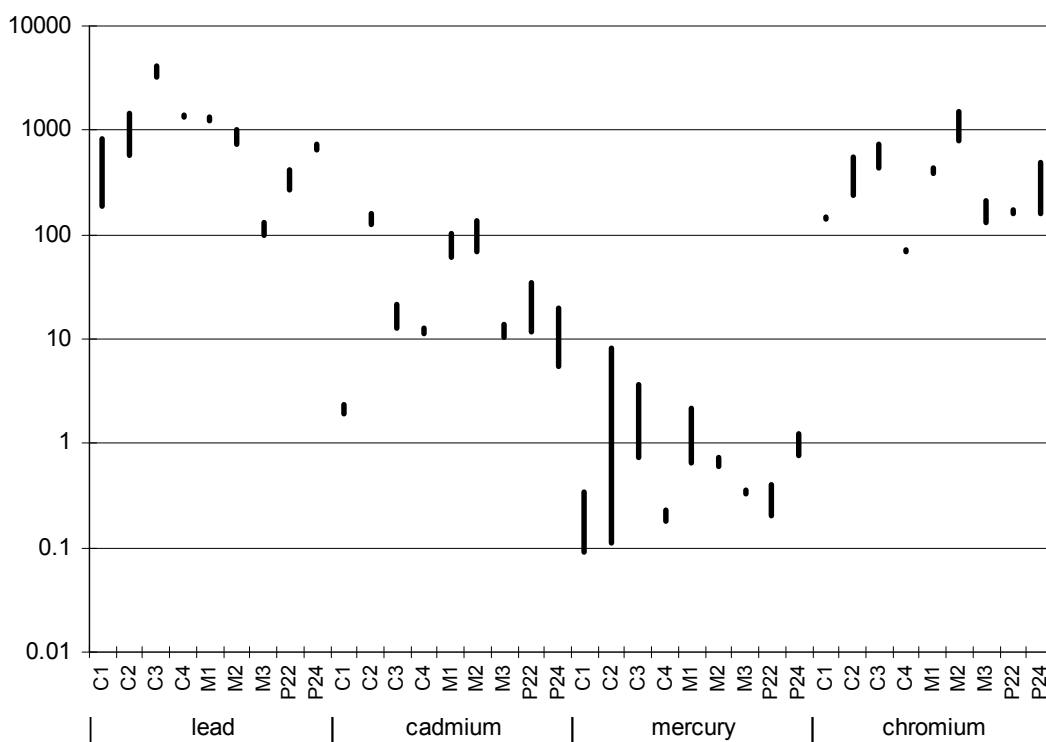


Figure 6-11: Upper and lower heavy metal concentration levels for repeated samples (visualized with a connecting line)

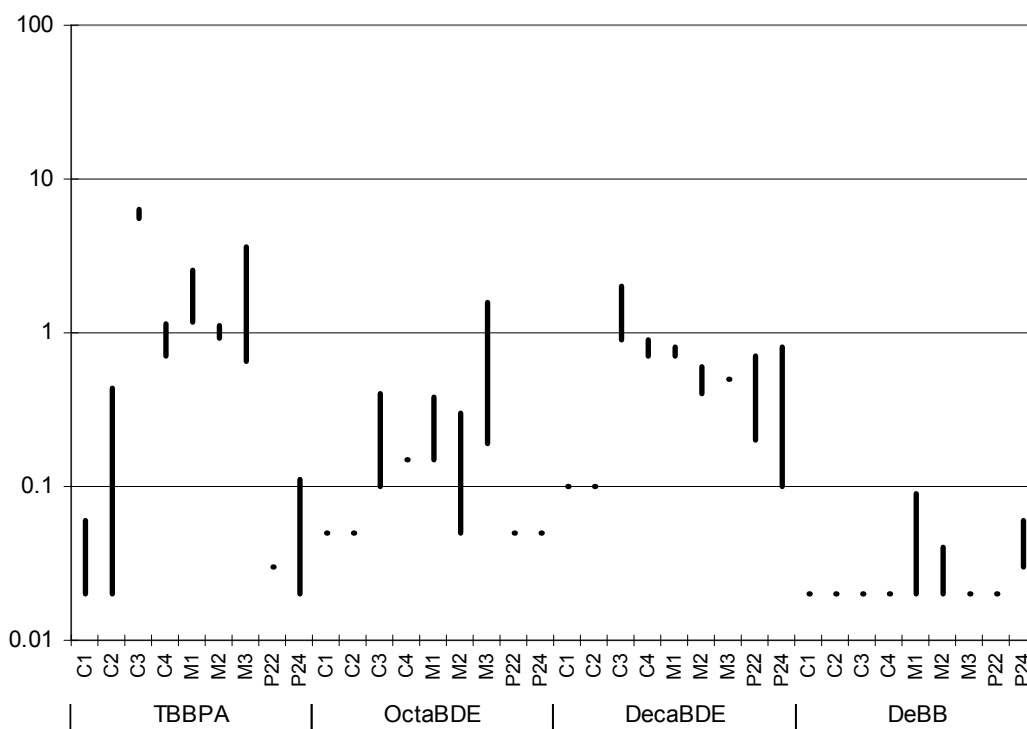


Figure 6-12: Upper and lower brominated flame retardant concentration levels for repeated samples (visualized with a connecting line)

The comparison of brominated flame retardant concentrations in separate samples from the same sampling campaign gives a less clear picture. Differences close to one order of magnitude can be observed for TBBPA (C2), OctaDBE (M2, M3) and DecaBDE (P24). For TBBPA, the differences appear in a range clearly below RoHS MCV for other compounds, hence they do not have any effect on the outcome of this study. For OctaBDE and DecaBDE, however, they occurred in the range of the RoHS MCV for the M3 and the P24 sample, respectively. This stands in contrast with a correctly performed sampling campaign in the case of these two samples, which does not give any indication for possible inhomogeneities between the repeated samples. Moreover, the repeated analysis for heavy metals, where deviations are small for the same M3 and P24 sample, indicate homogeneity between the repeated samples. Possible explanations for the deviations can only point in the direction of large differences between OctaBDE and DecaBDE concentrations in the specific appliances within the mixed samples, whereas sample preparation for the chemical analysis would have picked shredder pieces with rather low concentrations in one case and with rather high concentrations in the other case. This would be possible if the analysed shredder pieces were too large compared to the size of the shredded appliances, which could be the case in the respective M3 - and P24 samples, both containing rather small appliances..

Although the above discussion leaves some open questions, we do not expect that uncertainties in sampling and chemical analysis would hamper the validity of our results. Both the sampling procedure and chemical analysis are following common standards as described in chapter 5. Moreover, BFR concentration ranges found in this study correlated with findings in previous studies as discussed in section 6.2.1 and summarized in (Figure 6-13) for the case of CRT monitors.

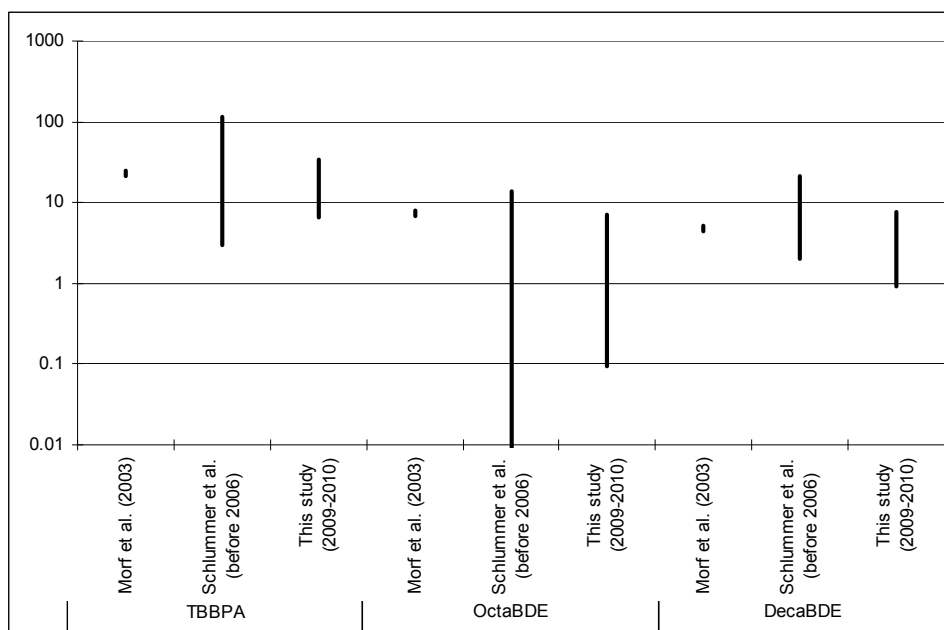


Figure 6-13: Concentration ranges of TBBPA, OctaBDE and DecaBDE in CRT monitors measured in this study and reported for other studies ((Morf et al. 2005); (Schlummer et al. 2007)); the year in brackets corresponds to the year of the sampling campaigns.

7 Synopsis

Table 7-1 presents the main outcome of the sampling as discussed in detail in chapter 6. It abstains from displaying a special column for total PBDE concentrations, because these typically only exceeded the RoHS MCV for PBDEs, when the average concentration of one of the regulated single PBDE (PentaBDE, OctaBDE and DecaBDE) was above the MCV (indicated in red).

For the interpretation of the results it has to be considered that the measured values refer to a mixture of plastic types from single product type samples, WEEE category samples or mixed WEEE category samples. Hence, in this study RoHS substances in single plastic types were not analysed. This implies that measured concentrations could underestimate the level of RoHS substances in specific plastic types due to a dilution by products (for mixed samples) and plastic types (for all samples) with lower or not detectable RoHS substance concentrations.

Mercury, PentaBDE and DecaBB were measured at average concentrations of at least an order of magnitude below the respective MCV in all mixed plastics fractions except for consumer equipment (PentaBDE) and CRT TVs (DecaBB), where they were detected at average concentrations slightly above 0.1 g/kg. The highest DecaBB levels were found in a single CRT TV set sample at concentrations of about half of the RoHS MCV.


For mixed plastics from WEEE category 1 appliances (C1, P11, P12), the most critical brominated flame retardant appears to be DecaBDE, however with average concentrations below the RoHS MCV. According to the literature review, the occurrence of DecaBDE is a consequence of the application of ABS and PP in large household appliances w/o cooling and freezing appliances, and of ABS, HIPS and PP in cooling and freezing appliances. Whereas other BFRs were not detected in relevant average concentrations at all, lead and total chromium were found in average concentrations below their respective RoHS MCVs.

Regarding WEEE category 2 appliances, average cadmium concentrations above the RoHS MCV were found in the mixed plastics fraction from small household appliances without CRT- and flat screens (C2). In the same mixed plastics fraction, average DecaBDE concentrations did not appear to be relevant, however mixed plastics fractions from vacuum cleaners (P21) and small appliances for high temperature applications (P24) showed to contain DecaBDE at average concentrations below or in the vicinity of the RoHS MCV. In all investigated mixed plastics fractions related to WEEE category 2 appliances other RoHS regulated BFRs could not be detected at relevant concentrations; lead and chromium were found at average concentrations below their RoHS MCV.

Table 7-1: Classification of measured concentrations according to the RoHS maximum concentration levels (MCVs) for lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), polybrominated diphenyl ethers (PentaBDE, OctaBDE, DecaBDE) and polybrominated biphenyls (DecaBB) in the analysed mixed WEEE categories, WEEE categories and single product types.

		Pb	Cd	Hg	Cr	Penta BDE	Octa BDE	Deca BDE	Deca BB
Mixed WEEE categories	Small appliances w/o CRT- and flat screens (M1, 7)		ABS PP				ABS	ABS HIPS,PP	
	Small household appliances, tools, toys, leisure and sports equipment (M2, 2)		ABS PP					ABS HIPS,PP	
	ICT and consumer equipment w/o CRT- and flat screens (M3, 2)		ABS ABS/PC				ABS	ABS HIPS	
WEEE categories	Large household appliances w/o cooling and freezing appliances (C1, 5)							ABS PP	
	Small household appliances (C2, 2)		ABS PP						
	ICT equipment w/o CRT - and flat screens (C3, 2)		ABS ABS/PC				ABS	ABS HIPS	
	Consumer equipment w/o CRT- and flat creens (C4, 1)		ABS ABS/PC				ABS	ABS HIPS	
Single product types	Cooling and freezing appliances (inside lining without drawers) (P11,5)		ABS PP					ABS HIPS,PP	
	Cooling and freezing appliances (all plastics, except foams) (P12, 6)		ABS PP					ABS HIPS,PP	
	Vacuum cleaners w/o hoses (P22, 1)		ABS PP					ABS HIPS	
	Small appliances for high temperature applications (P24, 1)		ABS,PP					ABS HIPS,PP	
	CRT monitors (P31,5)		ABS				ABS	ABS HIPS	
	Flat screen monitors (P32, 3)								
	Printers (P33, 3)							ABS HIPS	
	CRT TVs (P41, 7)		ABS,PP ABS/PC				ABS	ABS HIPS	

in brackets: sample code and number of sampling campaigns
w/o: without



not detected or at average concentrations clearly (i.e. more than an order of magnitude) below the RoHS MCV
average concentrations below (yellow cells) or in the vicinity (orange cells) of the RoHS MCV
average concentrations above the RoHS MCV

XXX: plastic type predominantly containing the substance (according to the literature review in chapter 3)

For mixed plastics from WEEE category 3 appliances, OctaBDE and DecaBDE in CRT monitors are the hot spot regarding brominated flame retardants, with average concentrations clearly above the RoHS MCV for PBDEs. Mixed category 3 samples without CRT monitors (M1, M3 and C3) showed elevated OctaBDE - and DecaBDE concentrations, with values in the vicinity of the RoHS MCV. For printers (P33), slightly elevated DecaBDE concentrations well below the RoHS MCV were measured. Literature data indicate that ABS is the main source for elevated concentrations of OctaBDE and DecaBDE in mixed plastics from WEEE category 3 appliances, to some extent also HIPS (in CRT monitors and printers). In flat screen monitors, chromium was the only RoHS substance which could be measured in relevant concentrations, however well below the RoHS MCV for hexavalent chromium. Average lead concentrations in mixed plastics from mixed category 3 samples (M1, M3 and C3) clearly exceeded the RoHS MCV; in mixed plastics from printers they were found to be in the vicinity of the RoHS MCV. Cadmium and chromium were detected, however at concentrations well below their corresponding RoHS MCVs.

For mixed plastics from WEEE category 4 appliances, the main source of RoHS regulated BFRs were CRT TVs (P41), with average OctaBDE concentrations in the vicinity of the RoHS MCV and average DecaBDE concentrations clearly above the RoHS MCV. According to literature data, in WEEE category 4 appliances the main source for OctaBDE is ABS, and for DecaBDE either ABS or HIPS. The mixed plastics fraction from mixed WEEE category 4 without CRT screens (C4) showed average levels of DecaBDE in the vicinity of the RoHS MCV and OctaBDE concentrations well below the RoHS MCV. In the same fraction, average lead concentrations exceeded the RoHS MCV.

TBBPA was detected in most samples, with the highest concentrations in CRT monitors. HBCD could not be found in any of the samples.

The results of the analyses of the total bromine contents and antimony concentrations indicate that besides the specifically measured BFRs (PentaBDE, OctaBDE, DecaBDE, DecaBB, HBCD, TBBPA) other unspecified BFRs were present in WEEE category 2, 3 and 4 plastic samples.

The results of the analyses of phosphorus in WEEE plastics show that WEEE category 3 and 4 samples total phosphorus concentrations lie in range between 0.1 % and 3.5 % by weight, which corresponds to reported amounts of phosphorus based flame retardants (PFRs) typically applied in EEE plastics. Findings are in line with the recent trend that ABS containing BFRs is substituted with PFRs containing ABS/PC.

Part III: Conclusions, Implications and Outlook

8 Conclusions

With the present study a comprehensive empirical foundation regarding, in particular, the levels of substances regulated by the RoHS Directive in mixed plastics from the treatment of WEEE categories 1 to 4 has been provided. For an interpretation of the results of the study, which mainly covers mixed plastics generated during the treatment of appliances from WEEE categories 1 to 4, the following limitations have to be considered, in particular:

- The study focused on substances regulated by the RoHS Directive, which were evaluated with regard to the maximum concentration values (MCV) defined in that Directive.
- For different mixed plastics fractions (e.g. mixed plastics from consumer equipment w/o CRT- and flat screens, small appliances for high temperature applications or vacuum cleaners), the number of available samples was lower than originally intended. While for other samples the findings are considered to be rather robust, the results for these mixed plastics fractions are associated with higher uncertainties.
- As an approximation for the levels of hexavalent chromium, which is one of the heavy metals regulated by the RoHS Directive, the total chromium content was measured and related to the RoHS MCV for hexavalent chromium. This corresponds to a worst case perspective.

Considering these limitations, the following indicative conclusions regarding substances regulated by the RoHS Directive can be drawn from the present study:

1. All the investigated mixed plastics fractions contained at least one substance regulated by the RoHS Directive in measurable amounts.
2. The lowest number and average concentrations of substances regulated by the RoHS Directive were found in flat screen monitors (lead).
3. Mixed plastics fractions containing high average concentrations of heavy metals (i.e. concentrations in the vicinity or above their respective MCVs) originate from the treatment of small household appliances (cadmium), ICT equipment (lead) and consumer equipment (lead).
4. Mixed plastics fractions containing high average concentrations of brominated flame retardants (i.e. concentrations in the vicinity or above the respective MCVs) originate from the treatment of small household appliances, particular small appliances for high temperature applications (DecaBDE), CRT monitors (OctaBDE and DecaBDE) and consumer equipment, in particular CRT TVs (DecaBDE).
5. There are indications, that the high average concentrations of heavy metals in several mixed plastics fractions, in particular lead, are at least partly the results of cross-contaminations from other EEE components during treatment. However, more evidence is needed.

The fractions considered in the present study may be allocated to four groups reflecting different degrees of 'criticality' with regard to their recovery:

- Group A (uncritical fractions): The average concentrations of all RoHS substances in mixed plastics are clearly (i.e. more than one order of magnitude) below the corresponding MCVs.
- Group B (less critical fractions): The average concentrations of all RoHS substances in mixed plastics are below the corresponding MCVs;
- Group C (critical fractions): The average concentrations of one or more RoHS substances are in the vicinity or above the corresponding MCVs;
- Group D (very critical fractions): The average concentrations of one or more RoHS substances are well above the corresponding MCVs.

The results of such a classification are presented in Table 8-1. In particular, it can be seen that no mixed plastics fraction could be allocated to group A, and two mixed plastics fractions can be found in group D.

Table 8-1: Classification of mixed plastic fractions from WEEE treatment with respect to their RoHS substance content

Group	Classification criteria	Origin of mixed plastics
A	<ul style="list-style-type: none"> - Average concentrations of all RoHS substances are clearly below the corresponding MCVs; 	
B	<ul style="list-style-type: none"> - Average concentrations of all RoHS substances are below the corresponding MCVs; 	<ul style="list-style-type: none"> - Cat. 1: Large household appliances w/o C&F appliances - Cat. 1: C&F appliances (except foams) - Cat. 2: Vacuum cleaners w/o hoses - Cat. 3: Flat screen monitors
C	<ul style="list-style-type: none"> - Average concentrations of one or more RoHS substances are in the vicinity or above the corresponding RoHS MCVs 	<ul style="list-style-type: none"> - Cat. 2: Small household appliances w/o screens - Cat. 2: Small appliances for high temperature applications - Cat. 3: ICT equipment w/o CRT & flat screens - Cat. 3: Printers - Cat. 4: Consumer equipment w/o CRT & flat screens - Cat. 2,6,7: Small household appliances, tools, toys, leisure and sport equipment - Cat. 2,3,4,6,7: Small appliances w/o screens - Cat.3,4: ICT and consumer equipment w/o CRT & flat screens
D	<ul style="list-style-type: none"> - Average concentrations of one or more RoHS substances are well above the corresponding RoHS MCVs 	<ul style="list-style-type: none"> - Cat. 3: CRT monitors - Cat. 4: CRT TVs

Cat: WEEE Category

9 Implications

The results of the present study have different implications, which depend on the perspective taken. In the following, some possible implications each from a RoHS product - and a waste classification perspective are described.

a) Implications from a RoHS product perspective

Applying RoHS MCVs to evaluate the recovery potential of mixed plastics from the treatment of WEEE is strictly speaking only valid for the specific case where plastics recovered from WEEE is used in newly marketed EEE. For other intended uses, there would be no restriction for DecaBDE, in particular. Nevertheless, considering that international and European regulations are expected to become more restrictive with regard to BFRs (see sections 3.1.2, 3.1.3 and 3.1.6) in the near future, it appears to be reasonable to apply the RoHS MCV for a general evaluation of the recovery potential of mixed plastics as a first approximation.

Based on the classification in Table 8-1 and under consideration of fundamental waste management principles such as the dilution prohibition (see e.g. (EC 2008)), we propose the following guidelines for a recovery of plastics out of mixed plastics from WEEE treatment as a starting point for further discussions with the relevant stakeholders:

- The fate of mixed plastics fractions allocated to groups B, C and D has to be traced from the moment they are generated up to the point where the plastics are either reintegrated into new products or properly disposed of.
- Plastic recyclers who accept mixed plastics fractions allocated to groups B, C and D have to demonstrate that their process allows to separate plastic types with elevated RoHS Substance concentrations from plastic types with low or no RoHS Substance concentrations.
- For mixed plastic fractions falling into group B, plastic recyclers have to demonstrate that
 - i. the classification of a fraction of specific origin into group B is adequate (e.g. by periodical measurements) and
 - ii. the recovered plastics comply with the RoHS Directive and
 - iii. the remaining fraction containing elevated RoHS Substance concentrations is properly disposed of;
- For mixed plastic fractions allocated to groups C and D, additional measures are to be taken to guarantee that they are not diluted with plastics from other origin with lower or no RoHS Substance concentrations.
- Should these conditions not be fulfilled, mixed plastic fractions from categories B to D are to be properly disposed of.

b) Implications from a waste classification perspective

Within Europe, the question, if a mixed plastic fraction from WEEE treatment is to be classified as a hazardous waste or not, is answered differently. The results of a classification of the mixed plastic fractions investi-

gated in this study according to the Commission Decision 2000/532EC and to the Swiss practice are shown below. The classifications are to be considered tentative and might have to be revised by the responsible authorities.

Application of European Union waste legislation

Considering the Commission Decision 2000/532/EC ((EC 2000), for each of the mixed plastics fractions investigated in the sampling campaign the majority of samples would not have had to be classified as hazardous waste. Table 9-1 lists those mixed plastics fractions, where a classification as hazardous waste would have been required for single samples.

Table 9-1: Mixed plastic fractions considered in the sampling campaign, where a classification as hazardous waste according to the Commission Decision 2000/532/EC ((EC 2000)) would have been required

Mixed plastics fraction from	Substance exceeding the limit value
Small appliances w/o CRT- and flat screens (M1)	- lead (one sample of seven)
Small household appliances, tools, toys, leisure and sports equipment (M2)	- lead (one sample of two)
CRT monitors (P31)	- OctaBDE (one sample of five)
<i>Mixed plastics from cooling and freezing appliances (all plastics except foams) (P12)</i>	- <i>chromium (one sample of six)</i>
<i>Mixed plastics from printers (P33)</i>	- <i>chromium (one sample of three)</i>

in italics: worst case consideration assuming that the total chromium concentrations measured in the sampling campaign correspond to hexavalent chromium

Swiss practice

According to the Swiss practice (FOEN 2010b); (Hauser 2010); see also 3.1.4), for mixed plastics from small household appliances, CRT monitors and CRT TVs, the majority of the samples investigated in the sampling campaign would have had to be classified as hazardous waste. The mixed plastics fractions, for which a hazardous waste classification would have been required for at least one sample are listed in Table 9-2.

Table 9-2: Mixed plastic fractions considered in the sampling campaign, where a classification as hazardous waste according to the Swiss practice would have been required

Mixed plastics fraction from	Substance exceeding the limit value
Small appliances w/o CRTs & flat screens (M1)	- DecaBDE (one sample of seven)
Small household appliances, tools, toys, leisure and sports equipment (M2)	- Cadmium (one sample of three)
ICT and consumer equipment w/o CRTs and flat screens (M3)	- OctaBDE (one sample of three) - DecaBDE (one sample of three)
Large household appliances w/o cooling and freezing appliances (C1)	- DecaBDE (one sample of six)
Small household appliances (C2)	- Cadmium (two samples of three)
CRT monitors (P31)	- OctaBDE (one sample of five) - DecaBDE (five samples of five)
CRT TVs (P41)	- OctaBDE (two samples of seven)) - DecaBDE (six samples of seven))

10 Outlook

In the present study, several questions could not or only partly be answered because they were either not investigated or depend on future developments. These questions, some of which are listed below, will have to be addressed in future studies or be answered by coming changes in legal framework.

- Which substances contribute to the unspecified bromine content in plastics from WEEE, and what will be the outcome of their risk assessment according to REACH? The present study indicates that total bromine concentrations in mixed plastics are at least partly due to an application of brominated flame retardants which were not specifically measured in this study (PentaBDE, OctaBDE, DecaBDE, DecaBB, HBCD, TBBPA).
- What are the impacts of a shift to phosphorus based flame retardants with regard to i.a. recyclability and environmental impacts? The present study indicates that phosphorus based flame retardants are applied, in particular, in WEEE category 3 and 4 appliances.
- How far is the unintentional production of PBDDs and PBDFs an issue for the different WEEE plastics treatment steps?
- How will the concentrations of REACH- and RoHS-regulated substances in WEEE plastics develop in the coming years?
- How far will future developments on the international level (e.g. the Stockholm Convention) and European level (e.g. the REACH regulations and the RoHS Directive) affect the conclusions of this study?

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Annexes

Annex 1: Sampling manual

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1. Introduction

1.1 The WEEE Forum plastics study

Plastics from waste electrical and electronic equipment (WEEE) contain a multitude of diverse additives such as colorants, flame retardants, fillers and stabilisers. These additives may include dangerous substances (for instance brominated flame retardants, heavy metals and others) which might restrict the possibilities for an environmentally sound recovery of plastics. In particular, plastics recycling might lead to direct emission into the environment (e.g. polybrominated dibenzodioxins and dibenzofurans), or result in an increased dissipation of harmful substances.

In a study commissioned by the WEEE Forum, a detailed sampling campaign with subsequent chemical analysis of plastics with high recovery potential is performed, the focus being laid on hazardous substances according to the RoHS Directive. In particular, the study aims at identifying plastics that can be recovered without significant unwanted negative ecological consequences, and technical requirements which must be met by the WEEE dismantlers to allow for an environmentally sound plastics recovery in the recycling plants.

1.2 Scope of sampling campaign

The study comprises plastics from WEEE that occurs with recycler of WEEE Forum members in different European countries. Thus, the sampling campaign includes mechanical and manual WEEE recyclers all over Europe, who generate mixed plastics fractions out of WEEE. For this study, if possible only recyclers with processes, where temperatures of 200 °C are not exceeded, should be considered.

2. Sampling procedure

2.1 Step-by-step procedure – Overview

Step	Task	Remarks	Reference
1	Define input categories / product types	<ul style="list-style-type: none"> Is defined prior to the sampling campaign by the responsible WEEE forum member in coordination with the WEEE forum 	Chapter 2.2 Table 1
2	Collect input material quantity	<ul style="list-style-type: none"> Approx 20 tonnes for mixed WEEE categories and WEEE categories Appropriate (realistic) quantity for single product types (to be confirmed with Empa – Esther Müller) 	Chapter 2.3
3	Choose the fraction to be sampled	<ul style="list-style-type: none"> One fraction only, most relevant 	Chapter 2.4
4	Define sampling location	<ul style="list-style-type: none"> If possible directly from the output flow Otherwise from a container 	Chapter 2.5
5	Take the samples	Consider guidance on <ul style="list-style-type: none"> required number and size of samples and sampling period and interval 	Chapter 2.6 Chapter 2.7
6	Prepare the samples	Consider guidance on <ul style="list-style-type: none"> mixed sample preparation and sample reduction 	Chapter 2.8
7	Package the samples	<ul style="list-style-type: none"> Use stable package material and label the samples 	Chapter 2.9
8	Document the sampling procedure	<ul style="list-style-type: none"> Keep records of all required information according to the standard protocol during the entire sampling procedure Photo documentation 	Chapter 2.10 Standard protocol

2.2 Input categories and product types

The following categories and product types shall be analysed:

Table 1: Analysed Mixed WEEE categories, WEEE categories and single product types.

Mixed WEEE categories	Cat. 2,3,4,6,7	Small appliances w/o screens (CRTs, flat screens)
	Cat. 2,6,7	Small household appliances, tools, toys, leisure and sport equipment
	Cat. 3,4	ICT and consumer equipment w/o screens (CRTs, flat screens)
WEEE categories	Cat. 1	Large household appliances
	Cat. 2	Small household appliances
	Cat. 3	ICT equipment w/o screens (CRTs, flat screens)
	Cat. 4	Consumer equipment w/o screens (CRTs, flat screens)
Single product types	Cat. 1	Cooling and freezing appliances (only inside lining)
	Cat. 2	- Coffee machines - Vacuum cleaners - Small appliances for high temperature applications
	Cat. 3	- CRT Monitors - Flat screen monitors - Printer
	Cat. 4	- Copying machines - CRT TV's - VCR and DVD players - Gaming consoles

The processed mixed WEEE category, WEEE-category, or single product type has to be described in detail in the sampling protocol.

2.3 Input quantity

The starting point for a representative sampling procedure is a quantity of approx. 20 tonnes input material into the recycling process for all mixed WEEE categories and WEEE categories, which should correspond to about 3-7 tonnes of plastics. These 20 tonnes of material preferably should be processed in a single batch episode.

The input quantity for the sampling of single product types ideally corresponds to 3 – 7 tonnes of plastics as well. However in most cases this will not be possible. Hence the samples should be drawn from as much input material as can be achieved with an appropriate effort and within an acceptable time frame. Please confirm suggested sampling quantities with Esther Müller (Phone: +41 71 274 7844; Mail: esther.mueller@empa.ch) and clarify further steps.

To avoid any cross-contaminations, in case of a mechanical processing, the facility/equipment should be cleaned prior to the sampling episode.

The exact input quantity has to be quoted in the sampling protocol.

2.4 Fraction to be sampled

The output of a WEEE recycling process often contains various plastic containing fractions, depending on the characteristics of the recycling process. Only one of these fractions needs to be sampled. It is suggested to sample the fraction which has the highest chance to be directed into a plastics recycling process; this can be done according to criteria such as plastics share/amount or fraction quality (e.g. plastic grain size, share of impurities).

The criteria applied shall be documented in the sample protocol.

If the considered output fraction contains impurities such as metals or glass, and the facility makes use of technologies to separate plastics from the impurities, please apply these technologies to obtain plastic samples with as little impurities as possible.

If a product type is processed manually (e.g. manual dismantling of plastic housings of TV or computer monitors), the dismantled plastics of all the input material shall be collected and then shredded down to a grain size of 20 – 50 mm. The samples are taken from the shredded plastic fraction.

The sampled fraction has to be described in detail in the sampling protocol.

2.5 Sampling location

2.5.1 Sampling from a falling stream

When sampling is performed from a falling stream (e.g. at the outlet of a continuous mechanical treatment process), the sample is taken directly from the output flow of the plastic fraction over the whole cross section of the flow profile.

The following 3 special cases can be distinguished:

- If the width and the depth of the stream are small, put a sampling container into the stream using a single one directional action. It is recommended to place the sampling container at 90° to the falling output flow. Hold the sampling container in place for the period specified to gather the specified volume of material.
- If the width of stream is large and depth is small, insert the container at one end of the stream and, at a uniform rate designed to collect the required amount of material, move the container through the width of the stream to the opposite end
- If width and depth of stream are large, follow the method as described above but repeat procedure at 90° to the first direction of sampling.

The applied procedure has to be described in the sampling protocol.

2.5.2 Sampling from a container

If it is not possible, to take samples directly from the output flow, the samples can be taken from the corresponding collecting container with a shovel or a sampling container. Sample the material that has fallen into the container at each individual sampling time (sampling interval, see chapter 2.7.2) taking into account the required sample size (sample size, see chapter 2.6.2).

The applied procedure has to be described in the sampling protocol.

2.6 Required number and size of sample

2.6.1 Number of samples

The resulting 3 – 7 tonnes of plastics are sampled with eight single samples. Four randomly chosen single samples each are mixed to a mixed sample. The resulting two mixed samples are, if necessary (see Table 2), reduced to the size of laboratory samples (for the preparation and reduction of the mixed sample see chapter 2.8).

2.6.2 Size of samples

The sample size depends on the grain size of the sampled fraction and is defined according to table 2.

Table 2: Minimum volume of single, mixed and laboratory sample (according to LAGA, 2001)

Max. grain size [mm]	Min. volume of single sample [litre]	Min. amount of single sample [kg]	Min. volume of mixed sample [litre]	Min. amount of mixed sample [kg]	Amount of Lab.- sample [kg]
> 2 bis < 20	1	0.5	4	2	2
> 20 bis < 50	2	1	8	4	2
> 50 bis < 120	5	2.5	20	10	5

The sizes of the single-, mixed and the laboratory samples are to be documented in the sampling protocol.

2.7 Sampling period and interval

2.7.1 Sampling period

The 20 tonnes of input material should be processed as a batch. The sampling period corresponds to the processing time of 20 tonnes of input material. This period varies depending on the recycling process (facility size, processing speed etc.).

2.7.2 Sampling interval

To define the sampling interval, the required processing time of the input material is divided by 8. The first sample is taken after the first eighth of the sampling period.

The sampling time has to be documented in the sampling protocol.

2.8 Methods for mixed sample preparation and reduction

2.8.1 Mixed sample preparation

Identify an area sheltered from the effects of wind and rain, preferably flat and large enough to allow ease of access around the whole sample when spread on the surface.

Place a clean protective floor covering, preferably an unused plastic sheeting, on the ground to protect the sample from contamination by the floor surface. All tools used for mixed sample preparation should have been cleaned in order to reduce the risk of cross-contamination.

Mix four of the single samples to a mixed sample by using the conical heap method. i.e. form a conical heap by depositing shovel by shovel on the peak of the new cone in such a way that the sample runs down all sides of the cone and is evenly distributed so that different particle sizes become well mixed. The size of the shovel should be of such size that this action could be repeated on at least 20 occasions in order to transfer the full amount of material.

Repeat the forming of a conical heap three times, to guarantee that the material is thoroughly mixed.

The mixed sample size has to be documented in the sampling protocol.

2.8.2 Mixed sample reduction

In case the two mixed samples have a size each bigger than the required laboratory sample size (see table 2), they have to be reduced, which is done by coning and quartering. Otherwise, the laboratory sample corresponds to the mixed sample.

After having applied the conical heap method (see above) flatten the last (third) cone by inserting the shovel repeatedly and horizontally onto the peak of the cone to form a flat heap, which has a uniform thickness and diameter.

Quarter the flat heap along the two diagonals intersecting at right angles using a shovel inserted vertically into the material. Discard one pair of opposite quarters and shovel the remainder into a stockpile. If necessary, repeat the process of mixing and quartering until the volume of remaining sub-sample is equal to the desired size.

The laboratory sample size has to be documented in the sampling protocol.

2.9 Packaging and sending of mixed sample

The plastic samples should be packaged into stable and clean plastic bags or sealable boxes. Every bag/box should be clearly labelled. The label must contain the name of the recycler (**can be made anonymous if recycler name mustn't be displayed**), name of fraction, name of laboratory sample and date of laboratory sample preparation.

Table 3: Example of label of laboratory sample.

Recycler:	(e.g. Company X Recycling)
Name of Fraction:	(e.g. Fine-grained plastic fraction)
Name of laboratory sample:	(e.g. FG-L1)
Date of laboratory sample preparation:	(e.g. 26.11.2009)

The samples shall be sent to the following address:

EMPA
Technology and Society Lab
Esther Müller
Lerchenfeldstrasse 5
CH-9014 St. Gallen
Switzerland

2.10 Record of sampling procedure

The sampling procedure has to be recorded in detail in the sampling protocol.

If the proposed sampling procedure cannot be followed in some of the required actions, please contact Esther Müller ((Phone: +41 71 274 7844; Mail: esther.mueller@empa.ch) to clarify further steps.

All deviations of the proposed sampling method have to be recorded in detail in the sampling protocol.

2.11 Photographical documentation

In addition, the sampling should be accompanied by a photographical documentation. Pictures are required of:

- the input material , from which the samples were taken from;
- the resulting output fractions, including the plastics fraction from which the samples are taken from;
- the sampling location;
- the execution of the sampling;

- the mixed sample preparation;
- the reduction to the laboratory fraction size (if necessary)
- the packaging and storage of the mixed samples.

3. References

LAGA PN 98: Richtlinie für das Vorgehen bei physikalischen, chemischen und biologischen Untersuchung im Zusammenhang mit der Verwertung / Beseitigung von Abfällen. Mitteilung der Länderarbeitsgemeinschaft Abfall (LAGA) 32, December 2001.

DIN EN 14899: Characterization of waste – Sampling of waste materials – Framework for the preparation and application of a sampling plan. 2005. Appendant Technical Reports CEN/TR 15310 – 1 to CEN/TR 15310 – 5, 2006.

Annex 2: Sampling protocol

Sampling Protocol

1. Information on WEEE recycling facility and processes

General	
Contact person responsible for sampling	
Name of company/facility, address and contact person	(this information is not compulsory, if the recycler name mustn't be displayed please make it anonymous by indicating: system name, country, Recycler A-B-C)

Input	
WEEE categories processed (indicate all WEEE categories processed in the facility)	
Other non-WEEE plastic fractions processed in the facility	
Total annual throughput of all (mixed) WEEE-categories and single product types addressed in the sampling campaign)	

Recycling processes	
Describe the main recycling steps (sorting, shredding ...) under special consideration of the plastic flows and possible losses, material changes (temperature!) or cross contaminations (e.g. lead from solder); declare the processing temperatures in particular.	
Describe the additional sampling preparation steps (if any, e.g. shredding, separation of plastics from impurities) under special consideration of the plastic flows and possible losses, material changes (temperature!) or cross contaminations (e.g. lead from solder); declare the processing temperatures in particular.	

Output	
Describe the plastic containing output fractions (fraction type, average composition including impurities, e.g. glass or metal)	
Briefly describe the present, subsequent treatment steps for the plastic containing output fractions leaving the recycling facility (country, type of process, type of disposal or recovery, if any). .	

2. Information on sampling procedure

Description of categories, products and fractions:
<p>Please describe which categories/products you are taking samples of and which plastics fractions you have in your output flows, Characterize the fraction you sample in detail (grain size, content etc.). Include pictures of the sampled fraction.</p>
<p>Indicate, if the processed mixed or WEEE category belongs to the regular recycling process or if the mixed or WEEE category is only processed due to the plastic sampling project.</p>
<p>If you sample just one single product type: indicate if you remove certain plastic fractions (e.g. plastic drawers of refrigerators) before processing the product</p>
<p>If you sample just one single product type: Estimate the quantity of the product as a percentage of its corresponding WEEE-category.</p>

Description of the sampling procedure:
Describe where and how the single samples were taken from the output flow. Include pictures of the sampling location and the execution of the sampling
Describe the sample size and the sampling period and interval.
Describe the mixed sample generation and reduction.
Description of sample storage:
Describe where and how the samples are stored. Include pictures of the storage location and the stored samples itself.
Deviations from proposed sampling procedure:
Please indicate any deviations. Deviations have to be discussed previous to the sampling with Esther Müller (Phone: +41 71 274 7844; Mail: esther Mueller@empa.ch)

3. Record of sampling procedure

Category/Product: (Small appliances without screens)					
Fraction Name: (Fine-grained plastic fraction)					
Sampling Location: (Output of Shredder)					
Input quantity: (20 tonnes)					
Single Sample Number	Single Sample Name	Date	Time	Weight kg	Remarks/Deviations
1	(FG1)	(25.11.2009)	(07.35)	(0.9)	
2	(FG2)	(25.11.2009)	(09.15)	(1.1)	
3	
4					
5					
6					
7					
8					

Mixed Sample						
	Mixed Sample Name	Date	Time	Weight kg	Mixed out of samples	Remarks/Deviations
	(FG-M1)	(26.11.2009)	(09.10)	(4.1)	(FG1, FG3, FG6, FG7)	
	(FG-M2)	(26.11.2009)	(09.30)	(3.9)	(FG2, FG4, FG5, FG8)	
Laboratory Sample (fill out only if it is necessary to reduce the mixed sample)						
	Lab. Sample Name	Date	Time	Weight kg	Reduced out of mixed sample	Remarks/Deviations
	(FG-L1)	(26.11.2009)	(09.20)	(2.0)	(FG-M1)	
	(FG-L2)	(26.11.2009)	(09.40)	(2.0)	(FG-M2)	

Important note: Each sample should have a unique, clearly identifiable and relatable name!

Blank record of sampling procedure

Category/Product:					
Fraction Name:					
Sampling Location:					
Input quantity:					
Single Sample Number	Single Sample Name	Date	Time	Weight kg	Remarks/Deviations
1					
2					
3					
4					
5					
6					
7					
8					

Mixed Sample						
	Mixed Sample Name	Date	Time	Weight kg	Mixed out of sample	Remarks/Deviations
Laboratory Sample (fill out only if it is necessary to reduce the mixed sample)						
	Lab. Sample Name	Date	Time	Weight kg	Mixed out of mixed sample	Remarks/Deviations

Important note: Each sample should have a unique, clearly identifiable and relatable name!

Annex 3: Results of the chemical analyses

Anonymized results of heavy metals analyses (grey rows: repeated samples not considered in sections 6.1 and 6.2; brown numbers in italics: detection limit, effective concentrations are below this value)

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Heavy metals (quantitative)				Heavy metals (semiquantitative)					
					lead	cadmium	chromium	mercury	antimony	lead	cadmium	chromium	copper	mercury
			[t]	[kg]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]
C1	C1a	no	500	2.1	93.4	6.22	68	0.24	29	120	5	110	510	<i>0.5</i>
C1	C1b	no	217	5.6	302	15.2	670	0.52	260	330	8.6	860	>9200	<i>1.2</i>
C1	C1c	no	25	3.7	379	8.88	549	0.51	300	520	5.7	770	>15000	<i>1.2</i>
C1	C1d	no	37.5	4.5	816	2.35		0.09	170	970	0.5	140	>22000	<i>1.3</i>
C1	C1e	no	37.5	5.4	189	1.93		0.34	70	200	0.7	150	>60000	<i>1.1</i>
C1	C1f	no	37	4.7	735	4.41		0.08	280	770	2.1	450	>59000	<i>1.9</i>
C2	C2a	no	19	1.5	336	48.9		2.01	>3700	350	29	75	>3700	<i>1.8</i>
C2	C2b	no	20	2.1	572	159		0.11	66	650	54	240	1100	<i>0.7</i>
C2	C2c	no	n.a.	1.5	1480	124		8.08	71	>1900	46	560	>13000	<i>1.1</i>
C3	C3a	no	20	2.3	4140	12.5	444	3.73	>2000	>2700	6	430	>16000	<i>3.1</i>
C3	C3b	no	n.a.	2	458	9.42		0.11	>1000	510	3	330	>26000	<i>2</i>
C3	C3c	no	20	2.5	3270	21.1	756	0.73	>2600	>2600	12	740	>15000	<i>3.6</i>
C4	C4a	no	2.5	1.5	1330	11.2		0.23	>550	>1800	5.6	73	>7600	<i>1.4</i>
C4	C4b	no	2.5	1.5	1390	12.7		0.18	>560	1500	5.7	68	>7300	<i>1.3</i>
M1	M1a	no	60	2	172	16.2	50.8	0.92	34	230	7.9	150	1000	<i>0.5</i>
M1	M1b	no	n.a.	2	1230	62		0.66	>760	>1800	28	440	>33000	<i>2.6</i>
M1	M1c	no	n.a.	1.5	2860	13.1		0.28	>1700	>1700	5	110	>28000	<i>2.1</i>

Category	Sample code	Plastics manually dismantled	Heavy metals (quantitative)					Heavy metals (semiquantitative)						
			Input quantity	Sample amount	lead	cadmium	chromium	mercury	antimony	lead	cadmium	chromium	copper	mercury
			[t]	[kg]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]
M1	M1d	no	10.5	2.9	3380	30		2.9	>1100	>4800	17	300	>21000	2.7
M1	M1e	no	40	5.4	7800	30.6		0.45	>610	>6300	12	490	>67000	3.3
M1	M1f	no	20	2.6	1040	14.6	417	5.21	>900	920	7.4	780	>9500	1.6
M1	M1g	no	20	1.5	1800	17.6	110	1.25	>670	>3500	9.5	140	>24000	2
M1	M1h	no	n.a.	1.9	1350	102		2.18	>690	>1800	41	390	>38000	2.2
M1	M1 washed	no	20	1.5	1390	31		0.33	>610	>2300	16	65	>17000	1.5
M2	M2a	no	20	2.1	1020	68.4	491	0.74	330	1200	30	790	>3100	1.1
M2	M2b	no	18.3	1.5	5260	35.8	1290	1.53	38	>2900	13	1900	>10000	2.1
M2	M2c	no	20	1.9	736	138	817	0.61	>430	850	64	1500	>5700	1
M2	M2 washed	no	18.3	1.5	161	22.7		0.37	29	220	9.3	260	>4300	0.5
M3	M3a	no	10.8	2.7	98.8	10.5		0.36	400	140	4.5	210	>3900	0.9
M3	M3b	no	10.8	1.5	131	13.9		0.33	>940	160	7.5	130	740	1.2
M3	M3c	no	13.9	1.5	2470	11.5		0.45	>2000	>2900	4.2	340	>11000	2.1
P11	P11a	no	n.a.	2.7	435	28.3		0.2	26	610	13	30	>8500	0.7
P11	P11b	no	15.6	2.1	744	37.2	212	0.38	46	760	22	200	>15000	0.9
P11	P11c	no	n.a.	1.5	61.9	3.4	158	0.14	8.2	55	1.8	250	150	0.4
P11	P11d	no	24	3.5	482	29.9	239	0.01	30	680	19	220	>14000	0.9
P11	P11e	no	130	1.6	1720	47.8	20.3	0.1	44	>1900	30	63	1000	0.8
P12	P12a	no	n.a.	2.7	414	12.3		0.33	37	530	7.2	3.8	>3100	0.6

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Heavy metals (quantitative)			Heavy metals (semiquantitative)						
					lead	cadmium	chromium	mercury	antimony	lead	cadmium	chromium	copper	mercury
			[t]	[kg]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]	[mg/kg DM]
P12	P12b	no	n.a.	1.5	286	10.3	982	0.01	34	330	6.5	1200	>27000	0.9
P12	P12c	no	n.a.	2.2	310	27.9		0.04	110	360	15	120	>43000	1.2
P12	P12d	no	4.5	2.4	231	10.3		0.02	17	330	3.8	3.8	>5500	0.5
P12	P12e	no	23	3.1	1310	18.9	43	0.12	79	>1700	13	19	>28000	1.2
P12	P12f	no	20	1.5	182	21.3		0.07	16	320	11	3.5	>5200	0.5
P12	P12 washed	no	130	1.5	1340	44		0.15	34	1400	27	67	>1900	0.8
P22	P22a	no	0.57	1.8	268	11.6	54.7	0.41	110	390	6.4	160	>2700	0.7
P22	P22ba	no	0.57	1.8	422	35.1	77.3	0.2	80	610	29	170	>3500	0.7
P23	P23a	no	0.62	1.5	161	105	1460	0.16	>430	220	75	1800	>6100	1.2
P24	P24a	no	1.4	2.4	726	5.5		1.26	140	960	5	160	>2000	0.8
P24	P24ba	no	1.4	2.6	651	19.5		0.76	>510	540	11	500	>21000	1.4
P31	P31a	yes	2.4	1.5	238	7.29		0.06	>5400	550	7.5	140	1200	2.4
P31	P31b	yes	n.a.	1.5	40.3	28		0.22	>11000	160	14	78	1300	3.5
P31	P31c	yes	23	2.5	83.1	18.8		0.08	>13000	160	6.2	100	740	3.6
P31	P31d	yes	n.a.	1.5	44.8	6.22		0.01	>13000	170	1.8	68	190	3.7
P31	P31e	yes	20	4.2	16.4	5.21	4.2	0.52	>4200	79	6.4	74	220	2.3
P31_P41	P31_P41a	yes	40	5.3	262	8.5	26.8	0.12	>1500	300	7.1	130	>4700	1.2
P31_P41	P31_P41b	yes	21	5.1	155	9.88	261	0.15	>6600	320	12	360	1400	3.4
P32	P32a	yes	1.45	1.5	19.6	1.85		0.11	>930	33	1.9	63	420	0.5

Category	Sample code	Plastics manually dismantled	Heavy metals (quantitative)				Heavy metals (semiquantitative)								
			Input quantity [t]	Sample amount [kg]	lead [mg/kg DM]	cadmium [mg/kg DM]	chromium [mg/kg DM]	mercury [mg/kg DM]	antimony [mg/kg DM]	lead [mg/kg DM]	cadmium [mg/kg DM]	chromium [mg/kg DM]	copper [mg/kg DM]	mercury [mg/kg DM]	
P32	P32b	yes	0.62	9.9	72.7	0.01			0.04	>980	100	0.6	71	>1700	1.3
P32	P32c	yes	0.54	3.5	152	0.47			0.04	>600	210	0.3	180	>1700	1.1
P33	P33a	no	7	1.8	1810	4.63	1230		0.2	>2100	1100	0.8	1400	>16000	2.9
P33	P33b	no?	n.a.	2.6	474	1.04			0.63	>630	590	0.3	220	>9500	1.3
P33	P33c	yes	9	1.5	12.9	0.14	9.5		0.02	>940	28	0.3	20	34	0.9
P41	P41a	yes	3.6	1.5	269	3.5			0.19	>1500	430	1.1	70	130	1.2
P41	P41b	yes	n.a.	1.5	12.3	78			0.05	>1400	47	97	20	120	1
P41	P41c	yes	21	1.5	66.9	21.6			0.14	>2200	130	8.3	50	690	1.2
P41	P41d	yes	n.a.	1.5	12.4	6.15			0.07	290	22	1.8	590	25	0.5
P41	P41e	yes	n.a.	1.5	28.5	35.3			0.12	>1900	61	13	50	340	1.9
P41	P41f	yes	15	6	96.3	3.72	11		0.08	>2100	180	4	86	15	1.2
P41	P41g	yes	15	3.6	103	1.44	14.4		0.1	130	170	1	65	270	0.4

Anonymized results of halogens/sulphur - and BFR analyses (grey rows: repeated samples not considered in sections 6.1 and 6.2; brown numbers in italics: detection limit, effective concentrations are below this value)

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Elements (semiquantitative)				Flame retardants (quantitative)					bromine (calculated)
					bromine	chlorine	phosphorus	TBBPA	DE-71 (PentaBDE)	HBCD	DE-79 (OctaBDE)	BDE 209 (DecaBDE)	DeBB	
			[t]	[kg]	[mg/kg DM]	[mg/kg DM]	[% v. DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[mg/kg DM]
C1	C1a	no	500	2.1	210	>2700	<i>0.011</i>	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	<i>0.1</i>	<i>0.02</i>	<i>336</i>
C1	C1b	no	217	5.6	>1300	>5800	<i>0.0012</i>	0.05	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	0.8	<i>0.02</i>	<i>934</i>
C1	C1c	no	37.5	3.7	>2100	>9100	<i>0.0015</i>	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	1.6	<i>0.02</i>	<i>1581</i>
C1	C1d	no	37.5	4.5	>1500	>35000	<i>0.0019</i>	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	<i>0.1</i>	<i>0.02</i>	<i>336</i>
C1	C1e	no	37	5.4	>420	>6600	0.13	0.06	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	<i>0.1</i>	<i>0.02</i>	<i>359</i>
C1	C1f	no	19	4.7	>970	>6700	0.11	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	0.3	<i>0.02</i>	<i>502</i>
C2	C2a	no	20	1.5	>20000	>3100	<i>0.011</i>	4.4	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	0.1	<i>0.02</i>	<i>2920</i>
C2	C2b	no	37.5	2.1	>600	>6300	<i>0.011</i>	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	<i>0.1</i>	<i>0.02</i>	<i>336</i>
C2	C2c	no	n.a.	1.5	>510	>4000	<i>0.011</i>	0.44	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	<i>0.1</i>	<i>0.02</i>	<i>583</i>
C3	C3a	no	20	2.3	>15000	>3000	0.06	6.39	<i>0.05</i>	<i>0.2</i>	0.4	0.9	<i>0.02</i>	<i>5034</i>
C3	C3b	no	n.a.	2	>11000	>4400	0.51	0.94	<i>0.05</i>	<i>0.2</i>	<i>0.05</i>	0.1	<i>0.02</i>	<i>878</i>
C3	C3c	no	20	2.5	>15000	>3600	<i>0.011</i>	5.57	<i>0.05</i>	<i>0.2</i>	0.1	2	<i>0.02</i>	<i>5227</i>
C4	C4a	no	2.5	1.5	>6000	>5600	<i>0.011</i>	0.71	0.13	<i>0.2</i>	0.15	0.9	<i>0.02</i>	<i>1542</i>
C4	C4b	no	2.5	1.5	>5000	>6900	<i>0.011</i>	1.13	0.1	<i>0.2</i>	0.15	0.7	<i>0.02</i>	<i>1602</i>
M1	M1a	no	60	2	330	>1700	<i>0.011</i>	<i>0.02</i>	<i>0.05</i>	<i>0.2</i>	0.05	<i>0.1</i>	<i>0.02</i>	<i>336</i>
M1	M1b	no	n.a.	2	>6300	>10000	<i>0.0012</i>	2.55	<i>0.05</i>	<i>0.2</i>	0.15	0.7	0.09	<i>2462</i>
M1	M1c	no	n.a.	1.5	>9200	>3800	0.23	0.02	0.14	<i>0.2</i>	1	1.2	<i>0.02</i>	<i>2062</i>

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Elements (semiquantitative)				Flame retardants (quantitative)					
					bromine	chlorine	phosporus	TBBPA	DE-71 (PentaBDE)	HBCD	DE-79 (OctaBDE)	BDE 209 (DecaBDE)	DeBB	bromine (calculated)
					[mg/kg DM]	[mg/kg DM]	[% v. DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[mg/kg DM]
M1	M1d	no	10.5	2.9	>7000	>3700	0.24	3.7	0.05	0.2	0.05	0.2	0.02	2590
M1	M1e	no	40	5.4	>6800	>12000	0.0015	0.53	0.05	0.2	0.2	0.6	0.02	1170
M1	M1f	no	20	2.6	>7600	>11000	0.31	1.28	0.05	0.2	0.05	0.3	0.02	1245
M1	M1g	no	20	1.5	>4400	>8100	0.011	1.4	0.05	0.2	0.32	0.9	0.02	2027
M1	M1h	no	n.a.	1.9	>5900	>7700	0.011	1.18	0.05	0.2	0.38	0.8	0.02	1862
M1	M1 washed	no	20	1.5	>3800	>15000	0.011	1.91	0.05	0.2	0.71	0.1	0.02	1972
M2	M2a	no	20	2.1	>2100	>6600	0.011	0.92	0.05	0.2	0.3	0.6	0.02	1479
M2	M2b	no	18.3	1.5	160	>2100	0.011	0.07	0.05	0.2	0.05	0.1	0.02	365
M2	M2c	no	20	1.9	>2200	>9900	0.011	1.12	0.05	0.2	0.05	0.4	0.04	1250
M2	M2 washed	no	18.3	1.5	210	440	0.22	0.06	0.05	0.2	0.05	0.1	0.02	359
M3	M3a	no	10.8	2.7	>5700	>1000	0.011	0.66	0.05	0.2	0.19	0.5	0.02	1156
M3	M3b	no	10.8	1.5	>8900	>3500	0.011	3.57	0.05	0.2	1.56	0.5	0.02	3955
M3	M3c	no	13.9	1.5	>15000	>9600	0.39	3.78	0.07	0.2	0.38	1.4	0.05	3932
P11	P11a	no	n.a.	2.7	180	>28000	0.011	0.02	0.05	0.2	0.05	0.1	0.02	336
P11	P11b	no	15.6	2.1	320	>22000	0.0013	0.02	0.05	0.2	0.05	0.2	0.02	419
P11	P11c	no	n.a.	1.5	64	230	0.011	0.03	0.05	0.2	0.05	0.1	0.02	341
P11	P11d	no	24	3.5	190	>16000	0.0013	0.02	0.05	0.2	0.05	0.1	0.02	336
P11	P11e	no	130	1.6	250	>52000	0.0019	0.02	0.05	0.2	0.05	0.1	0.02	336
P12	P12a	no	n.a.	2.7	250	>23000	0.011	0.02	0.05	0.2	0.05	0.1	0.02	336

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Elements (semiquantitative)				Flame retardants (quantitative)					
					bromine	chlorine	phosporus	TBBPA	DE-71 (PentaBDE)	HBCD	DE-79 (OctaBDE)	BDE 209 (DecaBDE)	DeBB	bromine (calculated)
					[mg/kg DM]	[mg/kg DM]	[% v. DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[mg/kg DM]
P12	P12b	no	n.a.	1.5	160	>19000	0.0014	0.02	0.05	0.2	0.05	0.1	0.02	336
P12	P12c	no	n.a.	2.2	>580	>27000	0.0019	0.02	0.05	0.2	0.05	0.5	0.02	668
P12	P12d	no	4.5	2.4	110	>16000	0.0012	0.03	0.05	0.2	0.05	0.1	0.02	341
P12	P12e	no	23	3.1	>520	>51000	0.0023	0.02	0.05	0.2	0.05	0.4	0.02	585
P12	P12f	no	20	1.5	88	>17000	0.011	0.02	0.05	0.2	0.05	0.1	0.02	336
P12	P12 washed	no	130	1.5	230	>50000	0.0019	0.02	0.05	0.2	0.05	0.1	0.02	336
P22	P22a	no	0.57	1.8	>1100	>7700	0.011	0.03	0.05	0.2	0.05	0.7	0.02	839
P22	P22ba	no	0.57	1.8	>430	>12000	0.011	0.03	0.05	0.2	0.05	0.2	0.02	424
P23	P23a	no	0.62	1.5	>1800	>14000	0.0015	1.04	0.05	0.2	0.17	0.5	0.02	1364
P24	P24a	no	1.4	2.4	>1100	>29000	0.0013	0.02	0.05	0.2	0.05	0.1	0.06	368
P24	P24ba	no	1.4	2.6	>4400	>9800	0.011	0.11	0.05	0.2	0.05	0.8	0.03	978
P31	P31a	yes	2.4	1.5	>26000	>6900	1.2	13.1	0.05	0.2	0.51	1.5	0.02	9578
P31	P31b	yes	n.a.	1.5	>55000	>2600	0.5	37.3	0.05	0.2	0.14	4.4	0.1	26036
P31	P31c	yes	23	2.5	>55000	>8100	0.44	63	0.05	0.2	0.66	1.3	0.15	39077
P31	P31d	yes	n.a.	1.5	>54000	>12000	0.22	54.6	0.05	0.2	10.6	7.8	0.1	47328
P31	P31e	yes	20	4.2	>26000	>13000	1.3	20.4	0.05	0.2	0.79	1	0.11	13764
P31_P41	P31_P41a	yes	40	5.3	>9000	>6800	0.011	1.3	0.05	1	1.09	3.4	0.14	5349
P31_P41	P31_P41b	yes	21	5.1	>38000	>10000	1.1	40.5	0.05	1	1.02	1.5	0.02	26747
P32	P32a	yes	1.45	1.5	>4000	220	0.22	1.16	0.05	0.2	0.1	0.1	0.02	1048

Category	Sample code	Plastics manually dismantled	Input quantity	Sample amount	Elements (semiquantitative)				Flame retardants (quantitative)					bromine (calculated)
					bromine	chlorine	phosphorus	TBBPA	DE-71 (PentaBDE)	HBCD	DE-79 (OctaBDE)	BDE 209 (DecaBDE)	DeBB	
			[t]	[kg]	[mg/kg DM]	[mg/kg DM]	[% v. DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[g/kg DM]	[mg/kg DM]
P32	P32b	yes	0.62	9.9	>10000	>1700	3.3	1.73	0.05	0.2	0.05	0.1	0.02	1344
P32	P32c	yes	0.54	3.5	>6900	480	3.5	0.45	0.05	0.2	0.05	0.1	0.02	589
P33	P33a	no	7	1.8	>17000	>2800	0.36	4.12	0.05	0.2	0.09	0.4	0.02	3035
P33	P33b	no?	n.a.	2.6	>6900	>1700	0.011	0.06	0.05	0.2	0.05	0.1	0.02	359
P33	P33c	yes	9	1.5	>8900	>1500	0.011	0.02	0.05	0.2	0.05	0.1	0.02	336
P41	P41a	yes	3.6	1.5	>10000	>5000	0.011	0.38	0.05	0.2	1.03	5	0.04	5405
P41	P41b	yes	n.a.	1.5	>12000	>2500	0.011	0.52	0.05	0.2	0.05	3.5	0.02	3453
P41	P41c	yes	21	1.5	>17000	>5400	0.011	0.77	0.05	1	0.67	7.8	0.53	8672
P41	P41d	yes	n.a.	1.5	>3200	30	0.87	0.02	0.05	0.2	0.05	2.9	0.02	2660
P41	P41e	yes	n.a.	1.5	>9300	>12000	0.011	0.87	0.05	0.2	3.54	3.6	0.07	6540
P41	P41f	yes	15	6	>14000	>4000	0.011	4.65	0.05	2	0.66	7.3	0.22	11037
P41	P41g	yes	15	3.6	>1500	790	0.27	0.11	0.05	0.2	0.1	0.8	0.02	1009