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Brominated Flame Retardants in Waste Electrical and Electronic Equipment: Substance Flows in a Recycling Plant

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Brominated flame retardants (BFRs) are synthetic additives mainly used in electrical and electronic appliances and in construction materials. The properties of some BFRs are typical for persistent organic pollutants, and certain BFRs, in particular some polybrominated diphenyl ether (PBDE) congeners and hexabromocyclododecane (HBCD), are suspected to cause adverse health effects. Global consumption of the most demanded BFRs, i.e., penta-, octa-, and decaBDE, tetrabromobisphenol A (TBBPA), and HBCD, has doubled in the 1990s. Only limited and rather uncertain data are available regarding the occurrence of BFRs in consumer goods and waste fractions as well as regarding emissions during use and disposal. The knowledge of anthropogenic substance flows and stocks is essential for early recognition of environmental impacts and effective chemicals management. In this paper, actual levels of penta-, octa-, and decaBDE, TBBPA, and HBCD in waste electrical and electronic equipment (WEEE) as a major carrier of BFRs are presented. These BFRs have been determined in products of a modern Swiss recycling plant applying gas chromatography/electron capture detection and gas chromatography/mass spectrometry analysis. A substance flow analysis (SFA) technique has been used to characterize the flows of target substances in the recycling process from the bulk WEEE input into the output products. Average concentrations in small size WEEE, representing the relevant electric and electronic appliances in WEEE, sampled in 2003 amounted to 34 mg/kg for pentaBDE, 530 mg/kg for octaBDE, 510 mg/kg for decaBDE, 1420 mg/kg for TBBPA (as an additive), 17 mg/kg for HBCD, 5500 mg/kg for bromine, and 1700 mg/kg for antimony. In comparison to data that have been calculated by SFA for Switzerland from literature for the 1990s, these measured concentrations in small size WEEE were 7 times higher for pentaBDE, unexpectedly about 50% lower for decaBDE, and agreed fairly well for TBBPA (as an additive) and octaBDE. Roughly 60% of the total bromine input determined by SFA based on X-ray fluorescence analysis of the output materials of the recycling plant cannot be assigned to the selected BFRs. This is an indication for the presence of other brominated substances as substitutes for PBDEs in electrical and electronic equipment. The presence of BFRs, in particular PBDEs in the low grams per kilogram concentration range, in the fine dust fraction recovered in the off-gas purification system of the recycling plant reveals a high potential for BFR emissions from WEEE management and point out the importance for environmentally sound recycling and disposal technologies for BFR-containing residues.

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Introduction

Flame retardants (FRs) are used to protect potentially flammable organic materials by increasing the resistance to ignition and delaying the spread of fire. FRs have routinely been applied for several decades for a wide spectrum of appliances such as furniture, textiles, building material and insulation, motor vehicle equipment, and electrical and electronic equipment (E&E equipment) (*1*−*3*). Brominated flame retardants (BFRs) are the largest market group of organic FRs and accounted for about 310 000 metric tons or 25% of the total FR consumption in 2001 (*4*, *5*).

Trends of BFR Production and Consumption. The production of BFRs has increased rapidly during the last two decades and has doubled between 1990 and 2000 (*5*). Annual growth of the BFR market is estimated to increase by 4−8% (*1*, *4*). About 40% of all bromine consumed worldwide is currently used for BFR production. BFR formulations are applied annually to over 2.5 million tons of polymers, which are used mainly in E&E equipment, furniture, upholstery, building materials, and transportation (*1*, *4*) in concentrations up to 30 wt % (*6*). There are more than 75 different BFRs commercially available (*7*). The five major marketed BFRs are tetrabromobisphenol A (TBBPA) with the largest production volume, followed by three technical mixtures of polybrominated diphenyl ethers (PBDEs), which are known as decabromodiphenyl ether (decaBDE), octabromodiphenyl ether (octaBDE), and pentabromodiphenyl ether (pentaBDE), and hexabromocyclododecane (HBCD) (*2*, *7*−*10*). The worldwide market demand in 2001 in metric tons was reported to be 119 700 for TBBPA, 56 100 for decaBDE, 16 700 for HBCD, 7500 for pentaBDE, and 3790 for octaBDE, respectively (*11*). In 2000, these five BFRs accounted for about two-thirds of world demand for BFRs (*5*). The market demand and applications of BFRs are different in America, Asia, and Europe and depend on national legislation and downstream user preferences (*12*). E&E equipment is one of the most important fields of application for selected BFRs in consumer and commercial products (*5*).

Concern about Environmental Fate and Human Exposure. PBDEs and HBCD are ubiquitous environmental contaminants and were detected in ambient and indoor air, sewage sludge, sediments, and a wide spectrum of aquatic and terrestrial wildlife (*6*, *13*, *14*). Certain PBDE congeners were found even in environmental compartments (*15*) and

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biota (*15*, *16*) in remote areas far from locations where they are produced and/or used. There is a growing concern about persistence, bioaccumulation, and possible adverse health effects of certain BDE congeners, in particular BDE-47, and HBCD (*7*, *17*). Several studies have reported rising concentrations of some BFRs in past decades, both in the environment and in humans (*7*, *18*−*23*). However, investigations of PBDEs in milk of primiparous women over the time period 1996−2001 in Sweden indicate a trend for decreasing PBDE body burdens after 1998 (*24*), and the results of PBDE analyses in a pasture, archived between 1930 and 2004 in the U. K., show a similar indication of a recent decline for all congeners except BDE-28 (*20*). This may be due to restrictions on the use of these substances in Scandinavia and the European Union. The release of PBDEs from consumer products treated with these compounds and the resulting contamination of food, indoor air, dust, and clothes leads to exposure of the general human population (*12*, *25*). Ingestion of house dust, dietary ingestion of animal and dairy products, and inhalation of indoor air are considered to be the most relevant exposure routes for all life stages other than the infant (*26*, *27*). Indoor air in an electronics goods recycling plant in Sweden was found to be contaminated with higher concentrations of PBDEs and TBBPA compared to other workplace environments (*28*). Julander and co-workers (*29*) reported on the investigation of FRs in different dust fractions in an electronics recycling facility. BDE congeners 209 and 183 were dominant in the inhalable dust fraction, and BDE-209 was measured in this fraction at a concentration 10 times higher than that in total dust. Elevated blood serum levels of BDE congeners 153, 183, and/or 209 have been detected also among computer technicians and electronics dismantlers (*30*), indicating bioavailability of the more highly brominated PBDEs and higher exposure to PBDEs at these workplaces. Furthermore, there is a scientific controversy about the transformation of BFRs, in particular PBB and PBDEs, into polybrominated and mixed polybrominated−polychlorinated dibenzo-*p*-dioxins and/or dibenzofurans (PBDD/Fs, PXDD/Fs, respectively) under certain conditions. Some authors reported that PBDD/Fs and PXDD/Fs can be formed either when processing PBDE-treated plastics at an elevated temperature or when incineration occurs under incomplete or uncontrolled conditions (*12*, *31*, *32*), resulting in emission of these highly toxic substances and exposure of humans and the environment (*12*). However, Hamm et al. (*33*) concluded from their experiment that neither debromination of decaBDE nor formation of PBDD/Fs occurred.

Substance Flow Analysis. In a national substance flow analysis (SFA) carried out for Switzerland and covering the whole life cycle of penta-, octa-, and decaBDE as well as TBBPA, major sources and final sinks have been identified (*34*). The results of this SFA provide information about key processes and major material flow pathways. The data can be used for risk assessment of the selected BFRs and are instrumental in improving strategies to reduce the exposure to and emissions of these substances to the environment. The study further identified the substance flows from consumption to solid waste management processes to be relevant for the PBDEs and TBBPA and concluded that waste electric and electronic equipment (WEEE) accounts for the largest flow of the investigated BFRs compared to other waste fractions, such as, for example, automotive shredder residues and construction waste. According to the literature, roughly 75% of all imported octaBDE was disposed through WEEE in the late 1990s. For TBBPA, the percentage is 66%, for decaBDE it is 44%, and for pentaBDE it was estimated to be 2%. For HBCD, no data is available up to now.

Scope of the Presented Work. Our study aimed to determine the actual concentration levels and substance flows for penta-, octa-, and decaBDE, TBBPA, and HBCD in WEEE to be treated in a state-of-the-art WEEE treatment plant in Switzerland for the following reasons: (a) E&E equipment has become one of the most important applications for BFRs, in particular octa- and decaBDE and TBBPA, (b) the turnover of WEEE in waste management facilities has grown rapidly over the last two decades, and (c) the data about actual concentrations of BFRs in WEEE as well as the BFR flows in waste fractions to be recycled or disposed of are scarce. The continuously growing amounts of WEEE to be disposed of raises questions about the behavior and fate of BFRs and toxic heavy metals and aims for emission control and health protection measures in recycling plants. As E&E equipment is an important FR application sector, WEEE could be used to monitor changes in the composition of flame retardants used in this field, in particular after the ban of certain PBDEs, e.g., octaBDE, in Europe. The results of this study will serve as a database for updating risk assessments (e.g., exposure estimation for workers and consumers and determination of sources and routes of emission) for the selected BFRs and for developing adequate waste management strategies and processes.

Restrictions for PBDEs in the European Union. As a consequence of the results of risk assessments for penta-, octa-, and decaBDE (*35*−*37*) and other research activities in this field, the European Union (EU) has banned the use of polybrominated biphenyl (PBB) and penta- and octaBDE in new E&E equipment by July 1, 2006 (*38*). Penta- and octaBDE have been banned for use in all applications in the EU since August 15, 2004 (*39*), and plastics containing BFRs must be separated from WEEE prior to recovery and recycling by December 2006 (*40*). For decaBDE, the May 2004 conclusion of the risk assessment report found "no identified risks" to either human health or the environment from the use of decaBDE (*37*). But further restrictions on the use of decaBDE are presently under consideration in the EU because the substance is of concern as a possible persistent, bioaccumulative and toxic(PBT) substance. The Swedish Chemicals Inspectorate recently concluded that, based on the precautionary principle and due to the current uncertainties, it is appropriate to prevent the further release of decaBDE into the environment and recommended to the Swedish Government to draw up and announce a national ban on decaBDE (*41*).

Experimental Section

The substance flow analysis that is presented in this paper was carried out in a modern state-of-the-art WEEE recycling plant in Switzerland with a WEEE throughput of 30 000 metric tons per year (Figure 1). The entire recycling process includes about 40 different processes. The plant does not produce sewage water. Off-gas loaded with dust is filtered by an efficient bag-filter system.

The WEEE fractions considered in this study are characterized as small electrical and electronic equipment waste (sWEEE). It includes small household appliances (e.g., toasters and vacuum cleaners), office and communication appliances (e.g., personal computers and monitors, printers, phones, and fax and photocopy machines), entertainment electronics (e.g., television (TV) sets, videos, camcorders, radios, HiFis, and portable compact disk (CD players), and small size E&E equipment (e.g., plugs and mobile phones). The contribution of these fractions accounts for approximately 90% of pentaBDE, octaBDE, decaBDE, and TBBPA in WEEE (*11*). The gross sample size of the prepared sWEEE mixture processed during the experiment was 230 metric tons, representing approximately 0.6% of the annual Swiss sWEEE.

To establish the SFA, mass flows of the sWEEE input and output fractions as well as substance concentrations in the relevant output fractions have been determined during a 3 day operating period (for 8 h each day) according to a

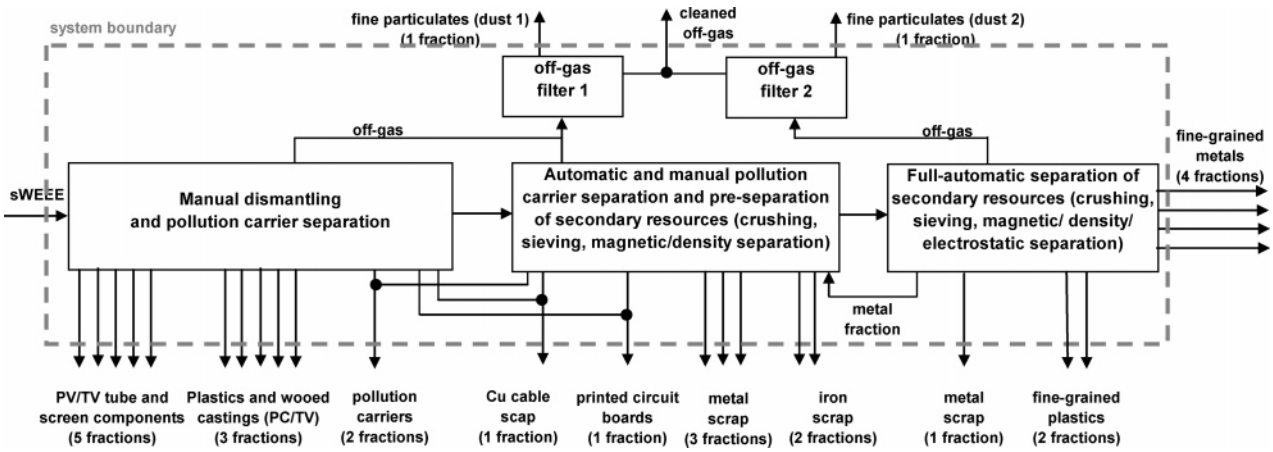

FIGURE 1. Scheme of the WEEE treatment plant IMMARK, Regensdorf, Switzerland, including system boundary and investigated output fractions.

TABLE 1. Sampling Plan

			sampling/preparation/analysis				
fractions		mass flow determination	number of composite samples taken during the experiment	number of grab samples in a composite sample	weight of individual grab sample (kg)	pre-preparation on site (crushing <15 mm)	number of composite samples prepared and analyzed in the laboratory
input	sWEEE	yes	ns[a]				
output	pollution carriers (2 fractions)	yes	ns				
	batteries	yes	ns				
	capacitors	yes	4	16	0.5	yes	na[b]
	fine particulates (2 fractions)						
	dust 1	yes	4	16	0.5	no	2
	dust 2	yes	4	16	0.5	no	2
	Cu cable scrap (1 fraction)	yes	4	20	1	yes	2
	printed circuit boards (1 fraction)	yes	6	20	1	yes	3
	PC/TV tube and screen components (5 fractions)	yes	ns				
	plastics and wooden castings PC/TV (3 fractions)						
	wooden TV housings	yes	2	20	1	yes	2
	plastic TV/PC housings	yes	6	20	1	yes	4
	TV housing rear covers	yes	2	20	1	yes	2
	fine-grained plastics (2 fractions)						
	fraction 1 (2−10 mm)	yes	6	20	1	no	4
	fraction 2 (<2 mm)	yes	6	20	1	no	4
	fine-grained metals (4 fractions)						
	fraction 1 (5−10 mm)	yes	6	20	0.5	no	3
	fraction 2 (<2 mm)	yes	6	20	0.5	no	2
	fraction 3	yes	6	20	0.5	no	na
	fraction 4	yes	6	20	0.5	no	na
	metal scrap (4 fractions)	yes	ns				
	iron scrap (2 fractions)	yes	ns				
	cleaned off-gas	no	ns				

[a] Not sampled. [b] Not analyzed.

sampling plan (Table 1). Regarding the selected BFRs, only 11 output fractions are relevant. The content of the selected BFRs in the other output fractions can be neglected in a first attempt (<0.1% of BFR flow in sWEEE input). Although the remaining 15 output fractions are important for mass flows of other substances investigated in the same experiment (e.g., heavy metals), we do not treat these in this paper. According to our estimations (Supporting Information), the off-gas release of the target substances is less than 0.002% of the input flow in the sWEEE and therefore negligible compared to substance flows in the analyzed output fractions.

Mass flows of the sWEEE input and all relevant output fractions of the recycling plant have been measured by a calibrated balance or a weight bridge. BFR target compounds in the relevant output fractions were extracted with toluene in an ultrasonic bath and analyzed by either gas chromatography/electron capture detection (GC/ECD) for PBDEs and HBCD or gas chromatography/mass spectrometry (GC/MS) with electron impact (EI) ionization for TBBPA and for verification of the GC/ECD analytical work. DecaBDE (BDE-209), TBBPA, HBCD, and the technical mixtures penta- and octaBDE in the samples have been identified by comparing the chromatographic retention time and mass spectra with standard solutions of reference samples. Quantification of PBDEs and HBCD was performed with the internal standard method by the peak area of the ECD signal. Decachlorobiphenyl (PCB-209) has been used as an internal standard. 2,2′,4,4′-TetraBDE (BDE-47) and 2,2′,4,4′,5-pentaBDE (BDE-99) were used to quantify pentaBDE. 2,2′,3,4,4′,5′,6-HeptaBDE (BDE-183) and another abundant congener with unknown structure (probably 2,2′,3,3′,4,4′,6,6′-octaBDE/BDE-197) were used for quantification of octaBDE in the analyzed samples. TBBPA was quantified using GC/MS with EI based on m/z 529/531/527/544. Calibration curves of target compounds

TABLE 2. Average Concentrations of Selected BFRs, Bromine and Antimony in sWEEE in Switzerland (A) Experimentally Determined in the Present Study and (B) Estimated in a Literature-Based National Substance Flow Analysis for Switzerland (*34*)

	(A) experimentally determined concentrations at IMMARK WEEE recycling plant, 2003			(B) SFA based estimate for the end of the 1990s
		uncertainty level (95% confidence interval $\approx 2\sigma$)		
substance	mean value (mg/kg)	(mg/kg)	(%)	mean value (mg/kg)
pentaBDE[a]	34	±4	±10	5
octaBDE[b]	530	±30	±6	390
decaBDE[c]	510	±35	±7	1200
TBBPA	1420	±90	±6	1800
HBCD	17	±4	±21	na[d]
Br	5500	±300	±5	na
Sb	1700	±200	±12	na

[a] Calculated as the technical mixture Bromkal 70-5 DE. [b] Calculated as the technical mixture Great Lakes Chemicals DE-79. [c] Calculated as BDE-209. [d] Not analyzed.

were obtained from seven standard solutions in the concentration range between 0.2 and 10 μg/mL. The calibration with technical pentaBDE and octaBDE was based on the congeners mentioned earlier. Antimony and bromine were determined by energy-dispersive X-ray fluorescence analyses using a pellet technique with a matrix modifier. For more detailed information about sample preparation and analysis, see the Supporting Information. The sWEEE input was not analyzed due to very high heterogeneity.

The substance flows of the output fractions were calculated by multiplying their mass flows by the respective concentrations of the substances. Substance flows and concentrations in the sWEEE input into the recycling plant were calculated by performing mass balances, assuming that input mass equals the sum of the mass among the output fractions for each substance. To fulfill this assumption, the entire sWEEE input has to be processed into output fractions and no accumulation is occurring in the process during the experiment. Also unanalyzed output fractions (e.g., iron scrap) may be a potential problem. But due to the high separating performance of the plant, only negligible amounts of plastics are found in these fractions. The general law of propagation of error by Gauss was applied to calculate uncertainties.

Details about the recycling plant, the investigated WEEE fractions, the experimental setup, the sampling, sample preparation on site and in the laboratory, and details regarding the analytical methods and quality assurance are provided in the Supporting Information.

Results and Discussion

Concentrations and Flows in the sWEEE. Calculated average concentrations of PBDEs (penta- and octaBDE, quantified as technical mixtures Bromkal 70-5 DE and Great Lakes Chemicals DE-79, respectively, and decaBDE, quantified as BDE-209), TBBPA, and HBCD as well as bromine and antimony in the sWEEE input are given in Table 2. The sWEEE input concentrations are calculated from the analyzed concentrations of the target substances in all relevant output materials and mass flows, based on mass balance assumptions. These concentrations represent the load of BFRs in a representative sample of sWEEE that was disposed of in Switzerland in 2003. The range of uncertainty quoted corresponds approximately to the 95% confidence interval ($\sim 2\sigma$) for the gross sample in this experiment. The highest concentrations are detected for TBBPA. Octa- and decaBDE concentrations (calculated as technical mixtures) are roughly 3 times lower than those of TBBPA. The concentrations of pentaBDE and HBCD are more than 1 or 2 orders of magnitude lower than the detected TBBPA levels.

Up to now, no representative experimental data for BFR concentrations in sWEEE are available for Switzerland. However, Kuhn and co-workers have published a market survey on the occurrence of selected BFRs in new marketed E&E equipment in Switzerland in 1999−2002 (*42*). From 366 products, 486 plastic objects that were related to E&E equipment (311 objects), transportation (62 objects), construction materials (102 objects), and bulk plastics (11 objects) were analyzed. Only 37 of 486 (7.6%) plastic objects contained detectable amounts of one or several target BFRs, i.e., decabromobiphenyl (in 2 samples), octaBDE (4 samples), decaBDE (in 15 samples), TBBPA (in 11 samples), and HBCD (in 8 samples), whereas bromine in the grams per kilogram concentration range was found in 105 (21.6%) plastic samples, supposing that other brominated flame retardants may be present. PentaBDE was not detected at all. The ratio Br/Sb was within the range of 2.0−3.0. It is somewhat surprising that the results for BFR concentrations in sWEEE presented here disagree with the findings of this market survey that was carried out 2−3 years earlier in the same country. This is specially the case for pentaBDE but for the other BFRs as well. However, we have to consider by discussing these results that sampling surveys normally are not suitable to deliver representative results, and therefore a reliable interpretation is impossible. To our knowledge very few measurements of BFRs in comparable sWEEE have been published for other countries up to now. Substance concentrations in a fraction of small electrical equipment were determined in a German study in 1996 (*43*). The average concentration of the sum of PBDEs was found to be 340 mg/kg. This is 3 times lower than the sum of penta-, octa-, and decaBDE in sWEEE determined in the present study. Since the total bromine content was 3400 mg/kg compared to 5500 mg/kg in this study and the content of the flame retardant synergist antimony was 900 mg/kg compared to 1700 mg/kg in our work, it may be concluded that PBDE levels have increased over the past decade. But because of a rather different composition of the WEEE input (a higher content of small household E&E equipment) investigated and the fact that the investigated amount of waste in the study in Lower Saxony was only 11 tons compared to 230 tons in the current study, the comparability to this study is rather limited. Nevertheless, the results of both investigations point out that BFR levels are relevant to be considered in the development of waste management systems and strategic product management decisions regarding the potential of these substances to cause health risks for workers in waste treatment processes, impair the quality of recycled materials, and/or pollute environmental compartments. A research group in Japan modeled time-series substance flow analysis for PBDEs and TBBPA in waste TV sets. They predicted for a business-as-usual scenario (no substitution) and assuming bromine contents from the late 1990s that the amount of bromine from BFRs in waste plastic covers of TV sets will increase until at least 2020 by almost a factor of 4 compared to the year 2000 (*44*). The experimental results of our present study confirmed approximately the average concentrations of BFRs—with the exception of pentaBDE—in sWEEE estimated in the substance flow analysis study for Switzerland (*34*). Table 2 provides a comparison of the results of these two studies. The present investigation has shown that the concentration of pentaBDE was 7 times higher and octaBDE was roughly 40% more concentrated in sWEEE than concentrations estimated from the literature-based SFA. However, the measurements have shown 55% lower values for decaBDE and 20% lower contents for TBBPA. Taking the content of reactive TBBPA in printed

circuit boards into account, the detected TBBPA concentration in this work would be 40% higher than the value estimated in the literature-based SFA (*34*). This finding is in agreement with the increasing global use of TBBPA (*1*). The uncertainty of the literature-based SFA results is high (more than ±100%), due to limited data and a rather high uncertainty for the estimated lifetime of consumer goods. Taking this uncertainty into account, the actual experimental results can be regarded as plausible with the exception of pentaBDE. The following hypotheses can supply possible explanations for the relatively high concentration of pentaBDE in sWEEE: (a) literature-based data do underestimate the use of pentaBDE in E&E appliances for the past decades, (b) pentaBDE is still occurring as a contaminant in more highly brominated technical PBDEs, (c) the sWEEE input during the experiment included more older pentaBDE-containing E&E products, indicating longer product lifetimes than estimated, or (d) despite of the large gross sample of 230 tons an unintentional fraction with a high pentaBDE content was treated unknowingly during the experiment (e.g., polyurethane foam). Prevedouros et al. (*45*) estimated production, consumption, and atmospheric emissions of pentaBDE in Europe between 1970 and 2000. According to their study, the flow of pentaBDE in disposed E&E equipment is estimated for Europe in the range of 17−60 metric tons per year within the time period 2000−2005. Through the use of the relationship of the numbers of inhabitants between Europe and Switzerland only, the corresponding flow of pentaBDE in Switzerland is estimated to be in the range of 0.6−2.3 metric tons per year. On the basis of the experimental results of this study, the pentaBDE flow in disposed sWEEE in Switzerland is estimated to be 4.1 metric tons per year. This shows likewise a much higher flow by roughly a factor of 2−6 derived from our actual measurements in sWEEE compared to literature data provided by Prevedouros and co-workers (*45*).

In addition to selected BFRs, the total bromine content of the sWEEE was analyzed, too. This allows determination of the proportion of the total bromine that can be assigned to PBDEs, TBBPA, and HBCD. The total bromine flow during the experiment was 1260 kg. The sum of the bromine flows assigned to the investigated BFR substances was calculated by multiplying the substance flows of the BFRs by the corresponding bromine contents (71% for pentaBDE, 79% for octaBDE, 83% for decaBDE, 59% for additive TBBPA, and 75% for HBCD). The bromine flow attributed to PBDEs, TBBPA, and HBCD accounts in total for about 400 kg. TBBPA is used either as an additive (i.e., quasi-dissolved in the polymer matrix) or reactive (i.e., covalently bound to the polymer) flame retardant. It has to be noted that only the TBBPA portion that is present as an additive FR could be detected by the applied analytical technique. Considering the fact that TBBPA is used only in the reactive form in printed circuit boards, it is justifiable to assign the bromine content in printed circuit boards to reactive TBBPA. By estimation of the content of reactive TBBPA in printed circuit boards by 5.3% (w/w), an additional bromine flow of 120 kg is calculated. Nevertheless, it remains a difference of about 740 kg bromine to the total Br input flow, accordingly roughly 60% of the total bromine detected, which could not be assigned to the measured target BFRs. Figure 2 shows the allocation of bromine to the analyzed BFR target compounds in sWEEE according to the concentrations determined in the experiment. It can be concluded that besides these five best known BFRs other brominated substances are applied for E&E equipment, either additionally or as substitutes to replace the investigated BFRs. The British Environment Agency listed in 2003 about 80 flame retardants requiring further investigation because of high tonnage, aquatic hazard, potential PBT/vPvB properties, or other possible risks (*46*). Among

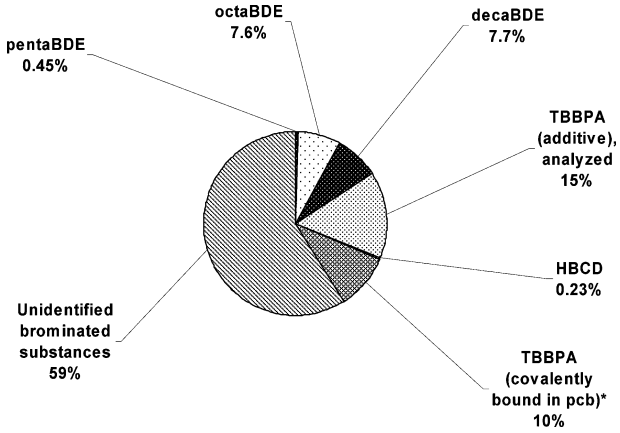

FIGURE 2. Bromine share of the investigated BFRs related to the total bromine input flow during the experiment in the WEEE recycling plant, 2003. Figures for penta- and octaBDE refer to the bromine content of the technical mixtures (Bromkal 70-5 DE and Great Lakes Chemicals DE-79, respectively) for decaBDE, TBBPA, and HBCD to the bromine content of the individual substances. For TBBPA, the estimated amount of bromine covalently bound in printed circuit boards (pcb's) estimated according to literature data is given.

these substances, brominated compounds (e.g., TBBPA derivatives, brominated phthalates, phenols, aryls, alkanes, alkyl esters, and phosphates) are most numerously represented. Measurements in dust fractions collected in indoor air of a recycling plant (*29*) refer likewise to the use of other BFRs, such as 1,2-bis(2,4,6-tribromophenoxy)ethane and decabromodiphenyl ethane. For these substances and other substitution candidates, little information is available in the literature about production and uses, emissions, environmental fate, exposure, and possible health risks. Therefore attention should be given also to BFRs that are considered for substitution of existing high-production-volume BFRs.

BFR Concentrations in the Plastic Fraction of sWEEE. By application of substance flow analysis, it is possible to calculate the BFR concentrations in the plastic parts of the entire sWEEE input during the experiment only. The following average concentration values result for the plastic fraction only: pentaBDE 125 mg/kg, octaBDE 2 g/kg, decaBDE 1.8 g/kg, TBBPA 5.6 g/kg, and HBCD 60 mg/kg. These data may be considered as representative for the load of the selected BFRs in sWEEE that have been disposed of in 2003 in Switzerland. The data may serve to control the impact of measures in the phaseout and/or risk reduction for these BFRs, such as the ban of penta- and octaBDE in new E&E equipment in the EU in 2004 (*39*), the obligation to separate BFR plastics from E&E equipment prior to recovery and recycling, becoming effective in EU member states in December 2006 (*40*), or voluntary industry commitments to substitute selected BFRs for certain appliances with other brominated or bromine-free FRs (*46*).

BFR Concentrations in Typical sWEEE Fractions. Mean concentrations of penta-, octa-, and decaBDE, TBBPA, and HBCD and for Br and Sb, which are related to the application of FRs, are given for selected output fractions of the investigated WEEE treatment plant in Table 3. The highest PBDE values in these fractions are found for decaBDE in TV housing rear covers (13 g/kg). The average concentration of decaBDE in personal computer/television (PC/TV) housings amounts to only one-third of this value. The highest concentrations of octaBDE were found in plastic PC/TV housings and TV housing rear covers, both amounting to 7.5 g/kg. The pentaBDE concentration was 50 mg/kg, both in plastic PC/TV housings as well as in TV housings rear covers. These results demonstrate—as already mentioned above—that literature-based data (*34*) about the contents of penta-

TABLE 3. Mean Concentration of Selected BFRs, Bromine, and Antimony in Separately Analyzed Components of Representative sWEEE from the Swiss Market[a]

	Cu cable scrap	printed circuit boards	TV housings (wood)	TV/PC housings (plastic)	TV housing rear covers
pentaBDE[b]	25 ± 10	17 ± 7	10 ± 4	50 ± 3	50 ± 20
octaBDE[c]	100 ± 150	10 ± 1	10 ± 4	7500 ± 600	7700 ± 3600
decaBDE[d]	170 ± 110	27 ± 9	20 ± 30	4800 ± 400	13000 ± 9000
TBBPA	5.0 ± 2.0	43 ± 18	80 ± 40	23000 ± 2000	7300 ± 3000
HBCD	25 ± 10	10 ± 1	10 ± 4	50 ± 3	1400 ± 1300
Br	na[e]	32000 ± 5000	160 ± 80	44000 ± 2000	26000 ± 18000
Sb	na	2100 ± 100	57 ± 1	16000 ± 5000	na
Br/Sb ratio	nd[f]	15	2.8	2.8	nd

[a] Uncertainty is expressed as an approximate of the 95% confidence interval (~2σ). All concentration values are given in mg/kg. [b] Calculated as the technical mixture Bromkal 70-5 DE. [c] Calculated as the technical mixture Great Lakes Chemicals 79DE. [d] Calculated as BDE-209. [e] Not analyzed. [f] Not defined.

and decaBDE in WEEE could not be confirmed. Plastic components in E&E equipment to be disposed of in recent years show higher concentrations of pentaBDE than were expected based on the available literature. OctaBDE concentrations amounted to about 75% of the average values expected in PC/TV housings and TV housing rear covers for older (10.5 g/kg) and newer (9.4 g/kg) appliances according to Morf and co-workers (*34*). DecaBDE levels in TV housing rear covers are situated in the middle of the range of estimated values for old (15 g/kg) and newer (10 g/kg) appliances. In PC/TV housings, decaBDE values amount to only one-third of the values for older and half of the values for newer equipment (production dates from the past century change). Normally, decaBDE concentrations in high-impact polystyrene (HIPS) used in TV casings amounted to 10−12%. The results of our investigation point out, even more than estimates presented in ref *34*, that the TV castings that were produced with the decaBDE flame retardant exhibit a rather low proportion of all TV castings on the European market in the last 10 years. A trend for decreasing decaBDE in TV and PC monitors in Europe due to the introduction of eco-labels (e.g., according to the Swedish TCO'95 and '99 standards BFRs are not allowed) starting more than 10 years ago is probably responsible for this fact (*34*). Concentrations of additive TBBPA are 23 g/kg for PC/TV housings and 7.3 g/kg for TV housing rear covers. These values are much lower than estimates of 57 g/kg as they have been reported for plastics in older and newer monitor housings (*34*). But the estimates in ref *34* also include an undefined amount of reactive TBBPA. The highest concentrations of HBCD have been detected in TV housing rear covers (1.4 g/kg). BFR concentrations in wooden TV housings were by factors lower, but not negligible, compared to those of the plastic housing parts. BFRs in wooden TV housings could originate from secondary contamination of the wood material from BFR-containing plastic particles or dust in the crushing process of the treatment plant.

Table 3 includes also results for total bromine and antimony contents. These results can be used to verify the plausibility of the analyses for additive BFRs due to the fact that antimony trioxide is used as a synergistic coadditive in combination with BFRs, facilitating the reduction in total flame retardant levels needed to achieve a desired level of flame retardancy (*2*). Analytical data for wooden TV housings and plastic TV/PC housings both show Br/Sb ratios in a typical range from 2:1 to 4:1, as reported in the literature for BFR applications (*10*). For printed circuit boards, the ratio is far out of the usual range due to the high content of reactive TBBPA without a need for antimony as a synergist.

Fate of BFRs in the Recycling Process

Determination of Substance Transfer Coefficients of the WEEE Treatment Process. An objective of this substance flow analysis was to determine transfer coefficients. These partitioning coefficients characterize the distribution of the selected target substances from the sWEEE input into the different output streams of the recycling plant. However, to be able to keep the given financial frame of this project, it was not possible (a) to sample and analyze output streams, which were expected to be negligible for characterizing relevant flows of the target substances, e.g., diffuse off-gas flows or bulk iron scrap fractions, and (b) to analyze the substance flows in processes outside of the system boundary of the core WEEE treatment process in the plant (Figure 1), i.e., further purification steps for fine-granulated metal fractions to reduce impurities and contaminants. Despite these limitations, the transfer coefficients given in Figure 3 can serve as valuable information to assess the substances' behaviors in a state-of-the-art WEEE recycling plant when treating similar sWEEE fractions. This information is also valuable to estimate potential environmental and human health risks associated with different reuse and disposal options for the diverse output fractions.

Distribution of Br and BFRs into Output Fractions. Bromine as well as the investigated BFRs are transferred to 80% and more into the output "plastics and wooden castings (PC/TV)" fractions and "fine-grained plastic" fractions 1−2. The transfer into the "fine-grained plastic" fractions 1−2 is for pentaBDE nearly 100%, for the other BFRs at least 60%, and for bromine 75%, respectively. Of the bromine that is transferred into the "printed circuit board" fraction, 10% is most possibly related to reactive TBBPA. No octa- and decaBDE as well as no additive TBBPA and only 1% of pentaBDE and HBCD are transferred into the "printed circuit boards" fraction. Roughly 8−10% of the bromine and pentaBDE in the sWEEE input end up in the "fine particulates" fraction. For the other BFRs, the transfer into this fraction is approximately 3%. In the case of a recycling process that is not equipped with an efficient air pollution control device as the modern plant in this study, a significant flow of dust-borne BFRs may be transferred into the environment. Portions between 3.6% and 17% of the mass flow of the investigated BFRs and about 8% of the total bromine flow are transferred into the "fine-grained metal" fractions 1−4. Due to the operation of further purification steps for fine-granulated metal fractions outside the defined system boundary mentioned above, it is possible to lower the transfer of plastic-borne impurities into these metal fractions significantly. But the efficiency of this process was not determined in this study.

Implications for Exposure Assessment and Pollution Prevention. Risk assessment as well as risk reduction strategies for pollutants should rely on actual and accurate data. Reliable data about the production rates, application, stocks in the anthroposphere, mass flows into environmental compartments during use and disposal, and final sinks are

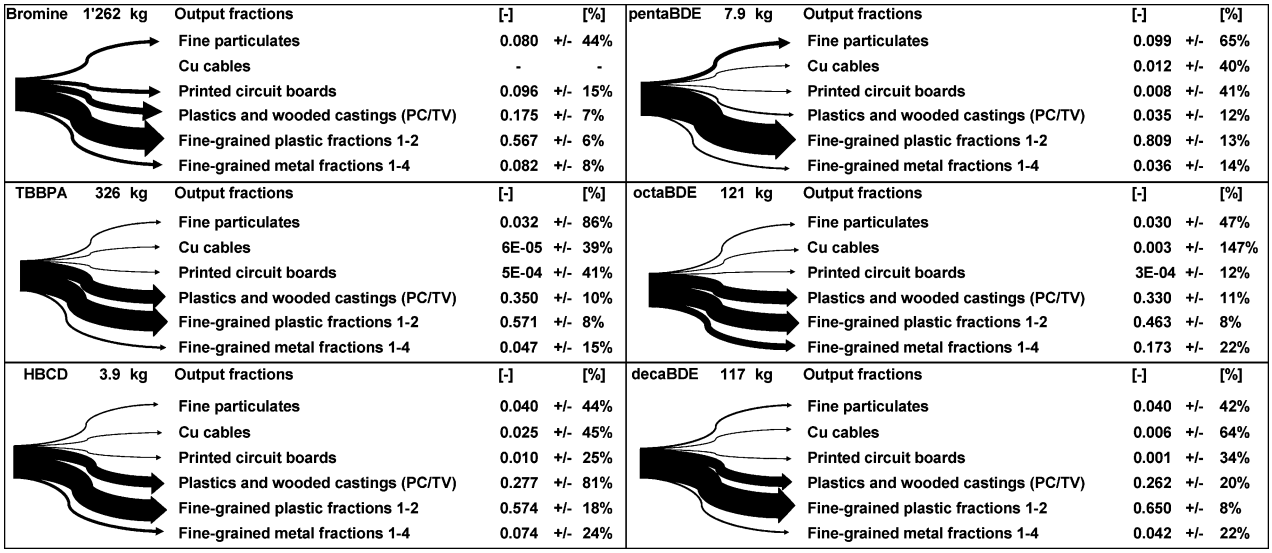

FIGURE 3. Input mass flows (kg) and mass transfer coefficients of selected BFRs and bromine from the sWEEE input into output streams of the investigated WEEE treatment plant. The relative range of uncertainty quoted corresponds approximately to the 95% confidence interval.

needed. In a global market, as it applies in particular to the E&E appliances sector, it is difficult to trace the flow of BFRs contained in finished and semifinished products between product use and disposal. With respect to BFRs, Prevedouros and co-workers point out the importance of pentaBDE emissions during product use and after their lifetime (*47*). The stocks of BFR-containing products need to be analyzed and quantified. This will enable (a) the stock to be actively managed, (b) the emissions to be estimated, (c) future waste flows to be forecasted, and (d) flows into landfills and diffuse emissions from these to be controlled and minimized, permitting suitable landfill rehabilitation programs to be established. The results of the present study serve as a first baseline to fulfill these important objectives by providing actual values for the BFR concentrations in sWEEE to be disposed of and the associated substance flows into the output fractions generated in a modern recycling plant. Although this study did not focus on the fate of the output fractions, the results serve as a base for evaluating different reuse and disposal scenarios. For the investigated plant, metals in iron and metal scrap and printed circuit boards are recovered in ferrous and non-ferrous metal processes with state-of-the-art air pollution control systems (reuse). Plastic fractions are treated in state-of-the-art municipal waste incineration plants. Pollution carriers (e.g., PCB capacitors, batteries and accumulators, Hg relays, and switches) are either treated in high-temperature incineration plants designed for the thermal treatment of hazardous waste, which fulfill the emission limit value for PCDDs/PCDFs and related compounds of 0.1 ng TEQ/m^3 (PCB-containing capacitors), or in a special recycling plant for the recovery of metals from batteries, accumulators, and Hg-containing materials.

Further monitoring of the flows in sWEEE disposal periodically is planned using the methodology established for this work. In addition to the well-known "classic" BFRs, alternatives (substitutes) should be monitored as well to assess the mass flows, behavior in waste treatment processes, exposure of man and environment, and possible hazards/risks arising from the use of these substances.

Although the data about exposure to BFRs and exposure routes at workplaces is rather limited today, the available results indicate clearly a significant uptake of more highly brominated PBDEs in workers and a potential for in vivo formation of lower PBDEs in these persons (*30*). The available studies show considerable variation for BFRs in indoor air and dust fractions between workplaces and processes (*28*, *29*) as well as for BFR concentrations in the blood of exposed workers in various occupational environments (*30*). Therefore, we suggest further experimental investigations to characterize occupational exposure to BFRs, possible adverse health effects for exposed humans, and the emission of these substances into the environment under different operating conditions of WEEE treatment facilities with emphasis on BFR concentrations in fine-grained dust and absorption rates of particle-borne BFRs by inhalation.

In the present work, neither the emission of PBDD/Fs and PXDD/Fs to the environment (atmosphere) nor their possible formation in the WEEE treatment processes were investigated. However, in view of the concentrations of brominated organic compounds, in particular PBDEs, and metals, e.g., copper (which under certain conditions can catalytically enhance the formation of halogenated dibenzodioxins/dibenzofurans in parts of the plant, e.g., where elevated temperatures prevail (*32*, *48*)) in sWEEE, a more detailed investigation of the presence of PBDD/Fs and PXDD/Fs in selected output products, fine-grained dust, indoor air, and (filtered) off-gas would be desirable.

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Supporting Information Available

Additional information about the experimental setup, sampling, sample preparation, analysis of the target substances, and results of quality assurance. This material is available free of charge via the Internet at http://pubs.acs.org.

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