Environ Sci Pollut Res (2015) 22:14489–14501
DOI 10.1007/s11356-014-3266-0

12TH IHPA FORUM AND SELECTED STUDIES ON POPS

Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria

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Received: 2 December 2013 / Accepted: 26 June 2014 / Published online: 27 July 2014

Abstract Polybrominated diphenyl ethers (PBDEs) were the first brominated persistent organic pollutants (POPs) listed in the Stockholm Convention. Parties to the convention are currently establishing inventories for developing action plans for the environmentally sound management of PBDE-containing materials. The major use of commercial octabromodiphenyl ether (c-OctaBDE) has been in casings from cathode ray tube (CRT) TVs and computer monitors. Large quantities of used e-waste and electronic equipment have been exported to developing countries with Nigeria being a major importer in Africa. The casings from 382 TVs and computers imported from major world regions to Nigeria were sampled in backyards and waste dumps. The samples were screened with X-ray flourescence (XRF) for bromine and analysed by gas chromatography/ electron capture detection (GC/ECD) for brominated flame retardants (BFRs). A high proportion of the CRT casings (61 %) contained more than 10,000 ppm bromine from BFRs. Decabromodiphenyl ether (DecaBDE) was the major flame retardant used in TV sets and tetrabromobisphenol A (TBBPA) for computer CRTs.

The screening suggests that average PBDE levels (of c-OctaBDE+DecaBDE) in Nigerian-stockpiled CRT casings were 1.1 % for TV and 0.13 % for PC CRTs. These are above the Restriction of Hazardous Substances (RoHS) limit and should be separated for RoHS compliant recycling. The Nigerian e-waste inventory of 237,000 t of CRT plastic would therefore contain approx. 594 t c-OctaBDE and 1,880 t of DecaBDE. In Nigeria, as for most developing countries, there is currently no adequate e-waste management, plastic separation or destruction capacity. The data highlight the urgent need to develop environmentally sound management for this large material flow.

Keywords PBDE · BFRs · WEEE · Inventory · Plastic recycling · RoHS

Responsible editor: Roland Kallenborn

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-3266-0) contains supplementary material, which is available to authorized users.

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Introduction

Brominated flame retardants (BFRs) are used mainly to reduce flammability of polymer materials such as polyurethane foams, polystyrene, other plastics or synthetic fibres used in plastic, furniture, vehicles, textiles and also in the plastics and printed circuit boards of electronic equipment (Alaee et al. 2003; Sakai et al. 2001; Alcock et al. 2003). Many different brominated flame retardants are on the market (OECD 1995; Lassen et al. 1999; Shaw et al. 2010; Guerra et al. 2011). Use has increased in recent years (Arcadis 2011), and the BFRs used in the greatest quantities are tetrabromobisphenol A (TBBPA) derivatives, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) (De Wit 2002; Lassen et al. 1999). Phosphorous and chlorinated flame retardants (CFRs) are also increasingly used (Arcadis 2011; Bergman et al. 2012).

Many BFRs and CFRs are highly persistent and contaminate the environment as a result of discharges from production plants, from the use of consumer products and from the end of life material flows (Allen et al. 2008; Imm et al. 2009; Shaw et al. 2010; Wong et al. 2007). BFRs are omnipresent in the environment and as a result of bioaccumulation are found in biota and human tissues (Hale et al. 2006; Fernandez et al. 2007; Shaw et al. 2010). A wide range of toxic effects have been demonstrated (Hale et al. 2006; Shaw et al. 2010) including activation of several endocrine effects (Hamers et al. 2006; Legler 2008). BFRs are therefore increasingly of concern for global health considering the relevance of endocrine disrupting chemicals (Shaw et al. 2010; WHO and UNEP 2013).

As a consequence, commercial pentabromodiphenyl ether (c-PentaBDE) and certain congeners of commercial octabromodiphenyl ether (c-OctaBDE) and hexabromobiphenyl (HBB) have recently been added to Annex A of the Stockholm Convention (05/2009) (Stockholm Convention 2009a, b) and are thus officially recognised as persistent organic pollutants (POPs). More recently, Norway has proposed decabromodiphenyl ether (DecaBDE) for listing in the Stockholm Convention (UNEP 2013a). As part of this process, the POPs Review Committee concluded in 2013 that DecaBDE meet the POPs criteria of Annex D of the Convention (UNEP 2013a, b).

The listing of POP-PBDEs prohibits their production, use, import and export with some defined exemptions. Furthermore, article 6 of the convention requires that wastes containing POPs have to be managed in a manner protective of human health and the environment (Stockholm Convention 2001). The new listing therefore requires parties of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of the PBDEs listed under the Stockholm Convention (POP-PBDEs) from stockpiles and wastes. The listing of PBDEs includes, uniquely for the convention, specific exemptions allowing for recycling and the use in articles of recycled materials. This possibility of including POPs in recycled products may lead to exposure in the recycling stage (and future recycling cycles) and in use of recycled products generating new health and environmental risks (Stockholm Convention 2010a, b). The convention therefore provides guidance to the 179 parties to appropriately manage the PBDE-containing polymers by a technical paper (Stockholm Convention 2010a, b), by recommendations for risk reduction (Stockholm Convention 2011) and by publishing a "Guidances on Best Available Techniques and Best Environmental Practice for the Recycling and Disposal of Articles containing POP-PBDE" (Stockholm Convention 2012a).

After a POP is listed, countries which have ratified the convention are obliged to develop an action plan to manage the POP-containing materials in an environmentally sound manner. As basis for this, inventories for the POPs are developed. Guidance on the development of an inventory of POP-PBDEs has been published to support this task (Stockholm Convention 2012b) and is now in use.

Plastic in waste electrical and electronic equipment (WEEE or e-waste) is considered to contain the largest share of POP-PBDEs in the waste stream (Petreas and Oros 2009; Schlummer et al. 2007; Wäger et al. 2010, 2012; Stockholm Convention 2012b). Therefore, careful management of WEEE plastic will be an important task for the effective implementation of the Stockholm Convention.

For many years, the majority of e-waste, including the plastic fraction, was exported to China from the USA and Europe (BAN/SVTC 2002; Wong et al. 2007; Labunska et al. 2014). African countries such as Nigeria have also received large volumes of used EEE and e-waste as well (BAN and Basel Action 2005; Basel Convention 2011; Nnorom and Osibanjo 2007, 2008). Furthermore, developing countries are now generating increasing amounts of their own e-waste (Basel Convention 2011; UNEP and United Nation Environment Programme 2009). Because the primitive recycling of e-waste has resulted in large contaminated sites in China and other developing countries, the management of e-waste has become a priority action in the Basel Convention and under Strategic Approach to International Chemicals Management (SAICM).

The challenge is now how to practically control PBDE in articles/products and in the recycling flows. This is a particular problem for developing/transition countries without state of the art recycling plants and with little or no monitoring or measurement capacity for the hazardous contaminants in e-waste. These countries also lack appropriate destruction facilities (Weber et al. 2013) which leads to open burning or dumping of hazardous wastes often causing widespread environmental pollution (Sepulveda et al. 2010; Weber et al. 2011; Wong et al. 2007).

Detailed assessment of the average content of PBDE in WEEE plastic has only been undertaken for European recycling facilities (Wäger et al. 2010, 2012). The average concentrations from this European study were also used as the POP-PBDE impact factor for WEEE plastic in the Stockholm Convention Inventory Guidance (Stockholm Convention 2012b).

The objectives of this study were to assess the presence of the POP-PBDE and other BFRs, to develop an inventory for Nigeria of POP-PBDEs in plastic of cathode ray tubes (CRTs) from TV sets and computer monitors and to develop impact factors for CRT plastic in EEE/WEEE from different world regions. A screening for other substances included in the Restriction of Hazardous Substance (RoHS) regulations was also performed. Initial results were presented at the Dioxin Conferences in 2011 and 2012 (Sindiku et al. 2011, 2012).

While it is known that c-PentaBDE and c-OctaBDE production stopped in 2004 (Stockholm Convention 2012b), the specific detail of annual usage in different regions of the world is largely unknown. We therefore also wanted to establish a preliminary data set of CRTs from different regions screened and analysed with the details of the production region, year of production and manufacturer (supporting information). The data were also compared with a data set of 100 CRT monitor casings screened for BFRs from Germany.

Materials and methods

Sampling

A total of 382 plastic samples from 158 TV CRT casings and 224 computer CRT casings imported from different regions were taken from eight locations in Ogun State and Lagos State in southwest Nigeria (Table 1). Sampling was carried out between January and March 2011. The samples were specifically selected from waste storage sites, electronic workshops, roadsides, dumpsites and dismantling sites (Figure S1) thus covering the locations where a large portion of WEEE in Nigeria is stored or dumped. The labels on the TVs and computer monitor casings were examined for information on the manufacturer, brand, model, serial number, year and origin of production. As cut-off date, samples from 2006 was chosen on the basis that c-OctaBDE was last been produced in 2004 (Stockholm Convention 2012b) and was then possibly used for one or two more years as flame retardant from stocks. The information was immediately recorded, and about 250-cm^2 samples were cut from each CRT using simple tools (Figure S2). A hole was made in the samples, and a metal tag (Figure S3) was attached with the aid of a safety pin (Figure S4). These were transferred to the workshop where 40 mm×40 mm squares were cut (Figure S5) and packaged in labelled envelopes (Figure S6).

One hundred TV casings from a German recycling plant sampled 2009 were analysed for comparison. The manufacturer was recorded for each item, but the year of manufacture has not been recorded. As the lifetime of television sets in Germany is approximately 15 years (Rotter and Chancerel 2011), most or all of these samples would have been produced before 2005.

Table 1 Number of CRT samples collected in Nigeria from the main regions of production

Region	Computer	Televisions	Total
Europe	50	100	150
Asia	100	58	158
America	74	0	74
Total	224	158	382

Chemicals

All solvents and reagents were of analytical grade. Analytical n-hexane, tetrahydrofuran (THF) and toluene were purchased from Merck (Darmstadt, Germany). All technical standards of c-OctaBDE, commercial decabromodiphenyl ether (c-DecaBDE), TBBPA and 1,2-bis-tribromophenoxyethane (TBPE) were purchased from Wellington Laboratories (Guelph, ON, Canada). Details including CAS numbers are given in supporting information (Table SI 5).

Polytetrafluoroethylene (PTFE) syringe filters (0.45 μm) were purchased from Carl Roth GmbH (Karlsruhe, Germany).

Semi-quantitative analysis by energy dispersive X-ray fluorescence (ED-XRF)

The 382 plastic samples were screened for bromine, chlorine and phosphorous, and heavy metal content including lead, mercury and cadmium were determined using XRF in the laboratory. The samples were subjected here to energy dispersive X-ray fluorescence analysis (X-lab 2000, Spectro, Kleve, Germany) in order to quantify bromine as first indication of the possible presence of organobromine compounds or brominated polymeric materials used as flame retardants. The system was equipped with a palladium X-ray tube. Squared samples were fixed on a sample plate of the analytical instrument and subjected to a screening method for solid samples applying vacuum. This method applies three targets (molybdenum 40 kV, corundum 50 kV and HOPG 15 kV) and an automatic matrix correction basing on the Compton peak.

Extraction method

The 231 samples which tested positively for bromine were further analysed. Historically, Soxhlet extraction with methanol/isopropanol as solvents (Riess and van Edlik 1998) or supercritical fluid extraction with different solvents (Altwaiq et al. 2003), pressurized liquid extraction with iso-octane (Schlummer et al. 2005), microwave-assisted extraction with methanol/isopropanol (Vilaplana et al. 2008, 2009) and ultrasonication with isopropanol (Pöhlein et al. 2005) have proved to be useful as fast extraction methods to screen for BFRs in plastic fractions from WEEE. For a quantitative extraction, the dissolution and precipitation method has given the highest yields. Therefore, extraction was undertaken by the dissolution and precipitation method (Schlummer et al. 2005); 0.5 g of the samples were dissolved in 9 g of tetrahydrofuran and precipitated with 40 g of n-hexane in aluminium foil-coated 100-ml glass vials. The supernatant was separated from the precipitated polymer, and an aliquot was passed through a 0.45-μm PTFE syringe filter (Schlummer et al. 2005). Filtered extracts of samples which exhibited high bromine levels in XRF screening were diluted 100-fold with toluene prior to analysis.

Instrumental analysis

The instrumental analysis was carried out using a gas chromatograph (Trace GC Ultra, Thermo, Dreieich, Germany) coupled with electron capture detection (ECD, ^{63}Ni, 370 MBq). The GC was equipped with a ZB-5 HT inferno (15 m×0.25 mm×0.1 μm, Phenomenex, Aschaffenburg, Germany) as stationary phase. Temperatures of GC split/splitless injector and detector were set at 295 and 320 °C, respectively, and the oven temperature was programmed as follows: 140 °C (1 min), 20 K/min (280 °C), 4 K/min (300 °C), 20 K/min (325 °C).

Selected samples were analysed by high-resolution mass spectrometry (HRMS, MAT 95, ThermoFinnigan, Bremen, Germany) for confirmation of the BFR mixtures. The HRMS was coupled to a HP 5890 GC (HP, Waldbronn, Germany) applying the GC column and GC programme described above. HRMS measurements were undertaken in multiple ion detection (MID) mode with electron impact ionisation (70 eV, ion source temperature 300 °C). Details of the monitored masses of target and qualifier ions as well as their time windows are included in the supporting information (Table SI 6).

BFRs were identified by comparison of retention times with external technical standards of c-OctaBDE, c-DecaBDE, TBBPA and TBPE. The same standards were used for quantitative assessment.

Selected samples were also analysed for Polybrominated dibenzo-p-dioxin/polybrominated dibenzofurans (PBDD/PBDF), and these results are published in another paper (Sindiku et al. 2013, 2014).

Quality control/quality assurance

To minimise background contamination, all potential sources of instrumental and procedural contamination were eliminated. ED-XRF is recognised as an analytical approach with a precision of ±20 % if applied in screening mode which is considered to be sufficient for the assessment of whether a plastic part contains high (>1 % or 10,000 ppm), medium (0.1 to 1 % or 1,000–10,000 ppm), low (0.01 to 0.1 % or 100 to 1,000 ppm) or almost no bromine (<0.01 or <100 ppm). The limit of detection (LOD) of the method for bromine is about 5 ppm.

For quality control, two polymeric-certified reference materials (polyethylene, EC 681, IRMM, Geel, Belgium, and polyvinyl chloride, PLPVC-3, Breitlaender, Wesel, Germany) were analysed on each day of the analytical screening procedure. Standard concentrations covered a range from 10 to 1,000 μg/g of bromine, cadmium, lead, chromium and mercury.

BFR analysis was performed according to IEC-62328-2008. GC-ECD was calibrated before each use in order to check the ECD for linearity and sensitivity. LOQs of BFR was calculated from the lowest calibration level and accounted for 10 to 25 μg/g polymer. Blank injections were used to check for cross-contamination from sample to sample. The GC-HRMS system was calibrated and checked with standard mixtures of commercial BFR before each use.

The identification of the most relevant BFRs present in the sample was considered complete when the calculated bromine level accounted for at least 50 % of the concentration from measurements by X-ray fluorescence.

Results and discussion

Results of sampling activities

A total of 382 CRT samples were collected—224 from computers and 158 from TV sets—and year and origin noted. The distribution of samples by region of origin (production or assembly) is shown in Table 1. For computer monitors, the highest proportion were produced in Asia (100), followed by America (74) and Europe (50). Most of the TV samples were produced in Europe (100), followed by Asia (58). None came from America, and this reflects the stockpiled CRTs in Nigeria as TVs were not imported from the USA while PC were imported from each of these three importing regions.

The spread of the time of production was from 1987 until 2006 for computers and from 1981 to 2004 for TVs. This period is considered the most relevant for the use of POP-PBDEs as their production is thought to have been stopped in 2004 (Stockholm Convention 2012b). These CRT casings are abundant in Nigeria, as in other African countries, in backyards and waste dumps (see pictures in supporting information of some sampling locations) and are therefore relevant for the inventories of PBDEs and their management.

The data were also compared with a data set, listed in the supporting information, of 100 TV CRT casings from a German recycling plant from a 2009 sampling campaign.

XRF screening

X-ray fluorescence (XRF) instruments have previously been successfully used as a non-destructively method to determine the presence of bromine or heavy metals in computers (Brigden and Santillo 2006), plastics from e-waste (Schlummer et al. 2007; Wäger et al. 2012) and for screening brominated compounds in consumer products (Li et al. 2006; Allen et al. 2008). XRF was therefore used to measure levels of heavy metals and to screen all 382 CRT casings for bromine as a surrogate for the presence of BFRs and chlorine as an indicator of polyvinyl chloride (PVC) and/or chlorinated flame retardants. Phosphorous was also measured to indicate the presence of phosphorous-based flame retardants.

Screening results for bromine, chlorine and phosphorous in the CRT casings

A total of 32.9 % of the sampled TVs and 66.1 % of computers contained bromine at a concentration above 1 % considered to be flame retarded with BFRs (Fig. 1; details in Supporting Information Tables SI 1-SI 4). In addition, 7.6 % of the computer casings and 15.8 % of the TVs casings contained measurable bromine levels between 0.01 to 1 %. Such low concentrations of bromine/BFRs in these samples are not sufficient to function as flame retardant and were probably not specifically added for this purpose in these CRT casings. These casings probably contained partly recycled WEEE plastic containing some residual BFRs.

A high percentage of the CRT casings therefore contained BFRs (see Fig. 1; Table 2; details in Supporting Information Tables SI 1-SI 4). A total of 75 % of the CRT casings from

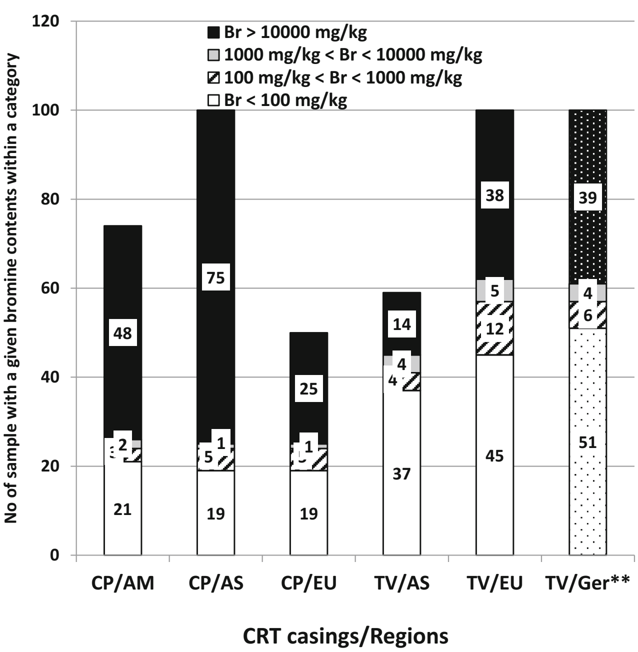

Fig. 1 Distribution of bromine content within a category in casings of CRT TVs (TV) and computer monitors (CP) from different world regions (*AM* America, *AS* Asia and *EU* Europe) sampled in Nigeria. **Compared to TV CRT casings sampled at a German e-waste recycling facility (TV/GER sampled in 2009)

computer monitors from Asia (*n*=100) were flame retarded with BFR (bromine content 1 to 9.9 %) compared with 65 % of samples (1 to 10.2 %) from the USA (Table SI 1). Of the computers produced/assembled in Europe (*n*=50), 50 % where flame retarded with BFRs (1 to 9.4 %).

By contrast, just 38 % of the television CRT casing from Europe[1] (*n*=100) and 24.1 % of those from Asia (*n*=58) were flame retarded with BFRs (1 to 10.5 % of bromine).

The distribution of BFRs in the 100 TV CRT casings sampled 2009 at a German recycling plant was very similar compared to the TV CRT casings sampled in Nigeria from EU (Fig. 1; Table SI 2 and 3). This indicates that the CRT casing with European origin sampled in Nigeria (selecting samples from 1980s to 2006) is similar to the German/European distribution for TV CRT casings processed in waste management in 2009.

These data show that television CRT casings were less often flame retarded with BFRs than computer monitors (approx. 30 vs 70 %) and that computer monitors manufactured in Europe contain a lower percentage of BFRs than those from the USA and Asia. This is probably due to different flammability standards (Shaw et al. 2010).

Between 0.1 and 20.6 %, chlorine was found in 132 of the screened 224 computer casings (Table SI 1) and in 22 of the 100 plastic casing screened from TVs from Europe at between 0.1 and 9.8 % (Table 2; details in Tables SI 1 and 2). Some of these samples were probably treated with chlorine-based organic flame retardants (CFRs) while the samples containing <3 % chlorine were most probably impacted by the recycling of plastic containing PVC.

Organic phosphorous-based flame retardants (PFRs) tend to be used in blends of acrylonitrile butadiene styrene (ABS) and polystyrene (PS) such as polycarbonate/acrylonitrile butadiene styrene (PC/ABS) and polyphenylene oxide/polystyrene (PPO/PS). Seventy of the screened 224 computer casings from the three regions contained between 0.1 and 2.0 % phosphorous indicating that about 30 % of these samples contained organic phosphorous compounds (Table SI 1 and 2). Only 23 of the screened 158 television casings from the three regions contained phosphorous at a level between 0.1 and 1.0 % indicating that about 15 % of these samples contained organic phosphorous compounds. These concentrations of PFRs are too low for fire proofing CRT casings. However, organic phosphorous-based stabilizers such as Irganox and Irgafos products are commonly used in polymers including styrenics and are usually applied at levels below 1 %. Further assessment is needed, but it appears that PFRs were probably not responsible for most of cases where

[1] As mentioned above, TV sets from the USA are not imported as second-hand electronics since the systems used in USA and Nigeria are not compatible.

Table 2 Concentration ranges (mg/kg) of selected elements determined by XRF in the Nigerian and the German sampling study

Material type/region	Number screened	Average (range) concentration (ppm)						
		Bromine (Br)	Chlorine (Cl)	Phosphorous (P)	Lead (Pb)	Mercury (Hg)	Cadmium (Cd)	Antimony (Sb)
CP/America	74	45,639 (<5–101,600)	5,246 (<50–16,670)	3,816 (<250–20,440)	119 (<5–327)	11.21(<15–57)	23.13 (<5–169)	5,594 (<5–12,570)
CP/Asia	100	50,647 (<5–99,410)	8,882 (<50–24,430)	2,245 (<250–17,440)	162 (<5–2,871)	8.76 (<15–50)	25.42 (<5–122)	7,000 (<5–41,670)
CP/Europe	50	32,632 (<5–93,950)	11,890 (<50–22,280)	4,241 (<250–14,840)	100 (<5–584)	11.52 (<15–51)	15.15 (<5–48)	4,386 (<5 –10,570)
TV/Asia	58	18,249 (<5–106,400)	1,859 (<50–19,040)	814 (<250–8,700)	103 (<5–1,951)	11.99 (<15–73)	7.11 (<5–79)	1,841 (<5–10,660)
TV/Europe	100	27,645 (<5–104,900)	7,908 (<50–20,640)	710 (<250–10,090)	201 (<5–3,000)	8.53 (<15–99)	18.81 (<5–400)	3,202 (<5–11160)
German sampling campaign								
TV/Europe	100	24,509 (<5–111,900)	14,857 (<50–203,400)	284 (<250–11,400)	147 (<5–1,914)	<15	49 (<5–344)	15,921 (<5–93,950)

phosphorous was detected indicating that until 2004 PFRs were not frequently used in CRT casings.

Screening results of heavy metals in CRT plastics (Table 2; Table SI 1–3)

From the screened plastic of computer and TV casings from the three regions, the mercury content was found by XRF to be between <15 and 99.1 ppm which is below the 1,000-ppm limit set by the RoHS directive for homogeneous materials (2002/95/EC). This is consistent with the findings in e-waste from small household appliances from residual household waste stream of the city of Dresden/Germany where half of the samples tested contained Hg, but none exceeded the RoHS limit (Dimitrakakis et al. 2009).

The cadmium content of all the screened plastics of computer and television casings was <400 ppm (supporting information) with only seven samples, all predating the RoHS directive coming into force in 2006, exceeding the 100 ppm RoHS limit (Table SI 1 and 2).

From television CRT casings, four samples, produced between 1986 and 1994, out of the 158 screened plastic casing exceeded the RoHS limit for lead of 1,000 ppm (Table SI 2). Just one computer CRT casing from China (produced 2002) exceeded 1,000 ppm (2,870 ppm); the remainder contained <580 ppm with more than 80 % samples below 100 ppm (Table SI 1).

The mean antimony levels were 4,605 ppm and the median 5,088 ppm. These levels are high compared with other heavy metals because antimony trioxide (Sb_2O_3) is often used as a synergist in combination with BFRs to increase flame retardancy (WHO 1997).[2] Antimony has been identified as a critical resource in industrialized countries and a strategic/specialty metal with the main production in China (UNEP 2011). The current management of flame-retarded plastic represents a substantial and non-sustainable loss of this valuable element.

Comparison with other studies

The results for bromine, antimony, chlorine and some RoHS relevant heavy metals in our screening are compared with literature data for WEEE plastics in Table 3. The average bromine and heavy metal levels were in reasonable agreement with average concentration or concentration ranges in other studies (Table 3). In two studies, considerable higher levels of lead above 1,000 ppm were detected (Morf et al. 2007; Fink et al. 2000). The most probable reason is that plastic taken from shredders can partly contain fine parts of metals that are attached to the plastic fraction while in our case, the plastic

[2] Antimony and its compounds do not have a flame retarding effect on their own, but they act synergistically with bromine.

Table 3 Comparison between current levels of bromine and heavy metals and PBDE in WEEE plastic compared to literature data (concentrations in mg/kg)

Element	RoHS limit	This study	Wäger et al. 2012	Dimitrakakis et al. 2009	Morf et al. 2007	Vehlow and Mark 1997	Fink et al. 2000
Pb*	1,000	147*	12–7,800	34	1,900	100–200	500–1,000
Cd	100	19	0.01–159	38	160	30–240	200–2,000
Hg	100	10	0.01–8.08	5.3	0.31	–	–
Cl	–	2,200	–	–	8,600	1,900–11,000	–
Br		100–106,000*	64–55,000	5,300	–	4,300–41,000	150–250,000
PBDE	1,000	4,740	Up to 7,800***				
Sb	–	4,600	–	2,000	3,500	2,000–13,000	1,000–80,000

*In particular, polyvinyl chloride (PVC) for cables and wires is known to contain lead compounds added as a stabilizer (European Stabiliser Producers Association 2012) which was not included in the current study focusing on CRT casings

**The average bromine concentration of the current study was 36,000 ppm

***Concentration depended on the WEEE category. Levels of c-OctaBDE above RoHS limit where only detected in WEEE plastic fraction of CRTs from computers (Wäger et al. 2010)

were removed manually and therefore separated from any metals.

Monitoring and analysis of BFRs in the bromine positive samples

All samples which tested positive for bromine were analysed for a range of BFRs (TBPE, TBBPA, c-OctaBDE, c-DecaBDE) using GC-ECD (Table SI 4). Selected samples were also analysed by GC/MS.

Samples containing POP-PBDEs and c-DecaBDE

Five samples out of the 158 television samples analysed contained c-OctaBDE and related POP-PBDEs with concentrations ranging from 0.1 to 29.00 % (see Table 1; Table SI 4). All five samples where produced before 1990, and four of these TV sets were manufactured in Europe and meant that the average concentration for all 159 TV samples was 0.27 % c-OctaBDE which considerably exceeds the maximum permissible RoHS limit of 0.1 % (European Commission 2003). Furthermore, a further 24 samples (15 %) contained c-DecaBDE with concentrations ranging from 0.086 to 23.7 % (average 5.7 %). This corresponds to an average concentration for the 159 TV CRT casings of 0.86 % which exceeds the RoHS limit by a factor of more than 8.

The consequence of these high average levels of POP-PBDEs is that the polymers from the CRT casings from TVs in Nigerian e-waste can, according to RoHS regulation, only be recycled into electronic uses after removing the bromine-containing CRT casings or by removing the BFRs by dissolution techniques such as the CreaSolv process (Schlummer et al. 2006; Freegard et al. 2006).

Three out of the 224 computer CRT samples contained c-OctaBDE with concentration ranging from 0.87 to 5.09 % (see Table 1; Table SI 4), but only one 2003 sample from the USA contained >1 % c-OctaBDE (5.09 %). The remaining two samples contained slightly <1 % indicating that the contamination was likely to be the result of recycling of polymers containing c-OctaBDE rather than the intentional addition as a flame retardant. The c-OctaBDE concentration averaged over all 224 computer CRTs was 0.05 %—below the RoHS limit of 0.1 %. There is, however, uncertainty about the level which will be established for low POPs limit for POP-PBDE by the Basel Convention working group and in national legislation, and the recommendation of the Conference of Parties is to separate POP-PBDE-containing polymers rather than to recycle them.

Fifteen percent (24 out of 159) of the TVs samples contained c-DecaBDE with an average concentration of 5.7 % (range 0.07 to 23 %) which corresponds to an average overall concentration of 0.86 % for the total TV samples (see Table 4). This is more than eight times the 0.1 % RoHS limit.

Table 4 TV and PC CRTs where c-OctaBDE/POP-PBDEs have been detected

Sample type	Conc. of c-OctaBDE (%)	Country (production)	Brand	Year of manufacture
TV CRT	29.00	UK	ITT Consumer Color TV	1986
TV CRT	6.41	Germany	Saba Color TV	1986
TV CRT	0.10	China	Anitech Color TV	1989
TV CRT	0.66	Germany	Saba Color TV	1983
TV CRT	5.93	Germany	Saba Color TV	1988
PC CRT	5.09	USA	Compaq	2003
PC CRT	0.95	USA	IBM	2005
PC CRT	0.87	China	Compaq	2003

Ten of the 224 computer samples contained c-DecaBDE with an average concentration of 1.28 % (range 0.26 to 5.4 %). This corresponds to an overall average concentration of 0.08 % for all 224 PC CRTs and is close to the RoHS limit value.

It needs to be highlighted that according to Wäger et al. (2010)), also WEEE categories other than 3 and 4 contain DecaBDE.

Samples containing other flame retardants

The flame retardants TBBPA and TBPE were major BFR replacements of c-OctaBDE for ABS. TBBPA is one of the most widely used BFRs in the electronics industry (Sjödin et al. 2003) and is currently used in HIPS and ABS/PC blends as a replacement for DecaBDE. TBBPA and TBPE are less bioaccumulative and exhibit lower PBDD/F formation potentials than PBDEs (Ebert and Bahadir 2003).

TBBPA was found in 101 of the 224 computer samples with an average concentration of 7.34 % (range 0.11 to 16.5 %). The overall average concentration for all 224 samples was 3.31 %. By contrast, only eight TV samples contained TBBPA with an average concentration of 6.9 % (range 0.03 to 16.7 %). The overall average concentration for total TV polymers was 0.35 %.

TBPE was found in 17 of the 224 computer samples with an average concentration of 6.63 % (range 0.25 to 39 %) and 0.5 % over all 224 samples. Only nine TV samples contained TBPE. The average concentration was 10.5 % (range 0.16 to 36.5 %) and an overall average concentration for TV polymers of 0.59 %.

We did not detect other BFRs in these CRTs produced between 1980s and 2006 such as e.g. decabromdiphenylethane used as alternative for DecaBDE. This is probably because of the increased use of alternative BFRs only after about 2004. However, 45 XRF samples (14 televisions and 31 computers) which screened positive for bromine did not show a response in the ECD. This indicates the presence of oligomeric BFRs or BFRs chemically bound to the polymers such as TBBPA derivatives.

Comparison of BFRs levels in WEEE plastic with other studies

Previous studies have also measured BFRs (mainly PBDEs, PBB, TBBPA and TBPE) in WEEE polymers (Schlummer et al. 2007; Huang et al. 2010; Wäger et al. 2010, 2012) (Table 3).

The most detailed study on the derivation of PBDE impact factors for WEEE plastic was conducted by the Swiss EMPA and monitored different WEEE plastic fractions from several European WEEE recyclers (Wäger et al. 2010; Table 3). For a meaningful comparison, the different e-waste/WEEE categories need to be assessed separately (Wäger et al. 2010, 2012). In the Waeger study, only the WEEE categories 3 (ICT equipment) and 4 (consumer equipment) contained measurable levels of c-OctaBDE and only CRT casing fraction contained c-OctaBDE close or above the RoHS limit of 0.1 %. This study was the first to show that by far, the largest proportion of POP-PBDEs was present in CRT casings and the finding was subsequently incorporated into the Stockholm Convention inventory guidance (Stockholm Convention 2012b) and has triggered the current monitoring study of the POP-PBDEs levels in CRT casings of TVs and computers in Nigeria. The factors for c-OctaBDE levels for computer CRTs in the Swiss study were 0.25 % and for TV CRTs were 0.087 %. The c-OctaBDE levels in this Nigerian study were of similar orders of magnitude albeit with higher values for TV CRTs (0.27 %) and somewhat lower values for computer CRTs (0.05 %) in our study. The higher levels in our TV samples might be due to TVs in Nigeria being older (several from the 1980s containing c-OctaBDE) than those in the European study. The lower values might be explained by the fact that only a few computers produced in 1980s are present in Nigerian WEEE (4 out of the 224 computer samples) but were largely produced after 1995 (Table SI 1) and that the first generation of computers from the 1980 up to 1994 have not been/are not exported to Africa but end up mainly in the European recycling stream.

PBDEs were detected in about 20 % of all the plastic casings of TVs and computers analysed in our study. This is somewhat lower than in the study of Schlummer et al. (2007) who detected PBDEs in about 40 % of all BFR-containing CRT casings from German households.

Riess et al. (2000) reported low percentages (3 % of samples) of TBBPA and TBPE use in CRT casings. Wäger et al. (2012) detected TBBPA in mixed WEEE plastic mostly at levels between 0.1 to 1 % with highest levels in plastics from CRT monitors of PC with average levels of 3.7 % (Wäger et al. 2012). This is consistent with our study in detecting high level in TV CRT casings but lower concentration in computer casings.

Inventory of total BFRs in Nigerian CRT plastic

An essential component of the action plan for the management of POPs in a country is an inventory of the respective wastes and stocks. To address this challenge for WEEE, Nigeria has recently conducted a EEE/WEEE inventory as part of the implementation of the Basel Convention (Ogungbuyi et al. 2012). Data on total volumes of CRTs in Nigeria has been established as part of this inventory of EEE/WEEE and totals 791,300 t including 237,000-t plastic (216,000 t from TV casings and 21,000 t from computer CRT casings). From these figures and the average concentration of c-OctaBDE derived from the current study, we estimated that there are 594 t of c-

Table 5 Estimated total c-OctaBDE, DecaBDE and TBBPA (tonnes) in Nigerian CRT casings

Calculation base	Category	c-OctaBDE	hexaBDE	heptaBDE	c-DecaBDE*	TBBPA*
Impact factors SC inventory guidance (2012)	TV	188	21	81		
	PC	54	6	23		
	Total	242	27	104		
Measured impact factors from this study	TV	583	64	251	1,860	755
	PC	11	1	5	20	695
	Total	594	65	256	1,880	1,450

*TBBPA and c-DecaBDE are not listed in the Stockholm Convention. However DecaBDE is currently assessed by the POPs Reviewing Committee for possible listing (UNEP 2013)

OctaBDE in CRT plastic in Nigeria (Table 5). From the homologue distribution for c-OctaBDE (Stockholm Convention 2012b), it can be calculated that this c-OctaBDE contains approx. 65 t of hexaBDE and 256 t of heptaBDE listed as POPs in the Stockholm Convention. The majority is present in the plastic of TV CRT casing (Table 5). Use of the lower impact factors from the SC inventory approach (Stockholm Convention 2012b) would give a total of 242 t c-OctaBDE containing 27 t hexaBDE and 104 t heptaBDE (Table 5). The explanation for the significant difference between these results is that the factors for the SC inventory guidance were derived from monitoring in European WEEE recycling facilities processing more recent TV CRTs compared to the TV stocks in Nigeria assessed in this study. Our samples contained several TVs from the 1980s with c-OctaBDEs (Table SI 2). The factors derived in this study from measurements of Nigerian TV CRT stocks are probably more appropriate for the EEE/WEEE stockpiles in the African region where still, these older TV CRTs are stockpiled.

Using the same approach, the total amount of c-DecaBDE (1,880 t) and TBBPA (1,450 t) were estimated as current stock in Nigerian CRT casings (Table 5). While for c-OctaBDE, the CRT casings are considered to contain the largest proportion of overall use (Stockholm Convention 2012b), this is unlikely to be the case for c-DecaBDE and TBBPA which were used more widely also in other WEEE categories. Therefore, the total volume of c-DecaBDE and TBBPA in Nigerian (W)EEE and other stocks is likely to be considerably higher than the current estimate only considering CRTs.

Implication of PBDE and BFR levels for recycling

TV and computer monitors provide two of the most plentiful sources of plastics from e-waste since the plastic content in these two product groups varies between 10 and 40 % with an average concentration of 30 % (Stockholm Convention 2012b). The major plastic part of a monitor is the rear part of the casings, which is easily separated for recycling. These plastic parts are normally removed by hand and give a clean polymer fraction consisting mainly of ABS and HIPS for recycling.

Currently, Nigeria is in the process of setting up plastic recycling facilities with a large national program for managing the enormous material flow of plastics. The material and substance flow of POP-PBDEs and the challenges and pollution threats are described in another paper (Babayemi et al. 2014). As part of this recycling approach, it has to be ensured that plastics containing hazardous chemicals are phased out and, vitally, do not enter sensitive product applications as listed by the Stockholm Convention PBDE BAT/BEP guidance (see Table 6; Stockholm Convention 2012b).

Waste plastic intended to be recycled and subsequently used for electronic equipment have to comply with the RoHS directive (European RoHS, China RoHS and others) which means that PBDEs (including c-OctaBDE and DecaBDE) must not exceed a 0.1 % threshold.

The average concentration in our TV casings was far above the RoHS limit, and therefore, bromine-containing polymers need to be separated before further recycling could be RoHS compliant. The computer CRT casings we tested were close to the RoHS limit and might possibly be recycled without further separation of bromine-containing plastic. The Stockholm

Table 6 Some sensitive plastic uses where POP-PBDEs and other hazardous substances should not be present in plastic used for recycling (Stockholm Convention 2012a)

- Toys and other plastic goods with exposure risk to babies and children
- Food packaging;
- Food containers;
- Silos, storages and piping for food and animal feed;
- Kitchen equipment;
- Refrigerator interior; freezer interior*
- Water tanks and water pipes, in particular tanks used for drinking water pipes;
- Plastic parts with direct contact such as furniture, handles of tools and doors.

*The recycling of polymers from WEEE polymers containing no critical chemicals is encouraged following cradle to cradle principle, e.g. polymers from refrigerators/fridges to refrigerators/fridges

Convention recommends, however, the separation of POP-PBDE containing plastic before recycling (Stockholm Convention 2012b) as noted above. This recommendation is to avoid dilution of the pollutants with broader exposure even in more sensitive uses (Table 6) and a higher probability to bioconcentrate. Not separating the bromine-containing fraction additionally has the drawback of monitoring in the further production to assure RoHS compliance.

The Stockholm Convention listing of PBDE contains an exemption for recycling as described above. The requirement is that the recycled products should be treated in an environmentally sound manner and are not exported. This would mean a labelling and control of products produced from such recycling which is a challenge considering the absence of labelling schemes for most of the cheap plastic products. The presence of PBDEs and other BFRs in plastic toys or plastic household products including food-contact articles (Chen et al. 2009, 2010; Samsonek and Puype 2013) demonstrate that the recycling of WEEE and other BFR-containing plastic is badly controlled for these sensitive uses. These sensitive uses are not covered by the RoHS directive which only restricts the use of PBDE for electrical and electronic equipment, and this probably results in the diversion of contaminated recyclate to other, even more sensitive, uses (Table 6).

Solutions to protect recycling flows include the separation of the PBDE/BFR-containing plastic by methods including 'sink and float' technology or the separation of the PBDEs/BFRs from the plastic by dissolution technology. Separation techniques and their limitations are described in the Stockholm Convention BAT/BEP guidance (Stockholm Convention 2012b).

As c-OctaBDE has mainly been found in samples from the 1980s, it is possible that a large proportion of POP-PBDE might be separated by manual techniques given appropriate training and experience as suggested by the Stockholm Convention BAT/BEP guidance and a related Swedish report (Retegan et al. (2010); Stockholm Convention 2012b). However, as c-DecaBDE-containing plastics are still being produced, they cannot be separated in this simple manner and would require a separation of all BFR-containing plastic. Full separation would have the co-benefit of removing from the recycling stream the large quantities of PBDD/PBDF present in Nigerian WEEE plastic (Sindiku et al. 2013). Such sorting can be performed by sink and float approaches or by handheld XRF or automated X-ray transmission (XRT) screening aiming to separate all BFR containing plastic.

For the further recycling of BFR-containing plastic, extractive approaches such as the CreaSolv® process have been proposed but have not yet been used commercially although the feasibility and economy of this process has been demonstrated in three studies (Schlummer et al. 2006, 2012; Freegard et al. 2006).

Conclusion

The study demonstrates that a high proportion of CRT casings from TVs and computers (formerly) imported from Europe, Asia and America to Nigeria contain BFRs. POP-PBDEs appear to be present largely in TV CRT casings from the 1980s while DecaBDE, which is still being used, is present in all the CRT casings and other EEE/WEEE produced over the last 30 years. These flame-retarded plastics have been stockpiled for many years in Nigeria and other developing countries which lack appropriate management and treatment technologies. The legacy of contamination is continuing with the continued production and use of DecaBDE which has now been recognised as meeting the POP criteria of Annex D (UNEP 2013b). Furthermore, as DecaBDE is known to debrominate to the currently listed POP-PBDEs, the continuing use will add to the POPs inventories in countries already struggling to manage their POPs stockpiles (Weber et al. 2013).

The efforts of the 179 parties to the convention to inventory and sustainably manage PBDE-containing wastes could also generate data to give in a more holistic picture of past PBDE use and the presence of PBDEs, including DecaBDE, in plastics and other materials. The use of XRF screening in combination with laboratory analysis could be used for similar studies in other countries—possibly coordinated by Stockholm/Basel Convention Centres. Such coordination activities could usefully be extended to other hazardous substances present in recycling flows of WEEE and other wastes in order to safeguard recycled materials from contamination—an essential and urgent priority to move towards a more circular economy.

In Nigeria, as in most developing countries, appropriate management of plastic casing and other e-waste is lacking, and there are few technologies for separation. This needs to be addressed as part of the development of plastic recycling in Nigeria considering the large quantities of POP-PBDEs and other brominated aromatic chemicals included in wastes and their potential associated exposure risk in/from recycling. Wastes should be specifically sorted, classified and labelled to ensure that the plastic fraction containing PBDEs and hazardous chemicals are not recycled into sensitive uses (Table 6). It is preferable that they are not recycled but thermally recovered with the potential recovery of energy and bromine (Stockholm Convention 2012b). Such thermal/recovery or destruction, however, needs appropriate technologies rarely found in developing countries. The challenges of recycling and the associated exposure risk from these POPs stockpiles in developing countries highlight the need for a more integrated and environmentally sound management of these material flows. The producers of the electronics, producers of flame-retarded plastic and producers of the flame retardants should establish a framework for appropriately managing these resources/wastes and for applying extended producer responsibility as required by the recently established legislative frameworks in Nigeria and some other African countries.

Acknowledgments Funding from the Norwegian government to the Stockholm Convention Secretariat for the financing of this project is appreciated.

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