ASSESSING POP-PBDEs AND BFRs IN E-WASTE POLYMERS IN NIGERIA

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Introduction

Commercial pentabromodiphenyl ether (c-PentaBDE)[A] and certain congeners of commercial Octabromodiphenyl ethers[A] (c-OctaBDE) were added to Annex A of the Stockholm Convention (SC) (05/2009)[1,2]. Therefore these listed PBDEs (POP-PBDEs) are officially recognised as persistent organic pollutants (POPs) under the Stockholm Convention which prohibits production, use, import, and export with some defined exemptions. Furthermore Article 6 of the Convention requires that wastes containing POPs has to be managed in a manner protective of human health and the environment[3]. The new listing therefore requires parties of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of POP-PBDEs[A] from stockpiles and wastes. The listing of PBDEs, unlike the original Stockholm POPs, includes specific exemptions allowing for recycling and the use in articles of recycled materials containing these chemicals. This possibility to include POPs in recycled products lead to exposure in the recycling stage (and future recycling cycles) and in use of recycled products generating new health and environmental risks[4,5]. Recommendations have been developed from the POPs Reviewing Committee for the Stockholm Convention Conference of Parties based on a technical report[4] and have been adopted[5]. Guidelines have been developed on the inventory of POP-PBDE[6a] and for recycling and disposing POP-PBDE-containing articles and products to provide guidance to parties on how best to manage POP-PBDE containing materials[6b].

The challenge is now how to practically control PBDE in articles and the recycling flows. This is in particular a problem for developing/economy in transition countries where state of the art recycling plants with monitoring capacity do not exist and measurement capacity is not established. These countries lack appropriate destruction facilities which leads to open burning or dumping of such hazardous wastes causing environmental pollution.[7-12].

Plastic in certain electrical and electronic equipment and related waste (EEE/WEEE) is considered to contain the largest share of POP-PBDEs in the material/waste flow followed by polyurethane foam in car/transport, furniture, construction, mattresses or baby products[5,13]. While for many years the largest amount of used EEE and WEEE exported from the US and Europe was mainly shipped to China, African countries such as Nigeria or Ghana were receiving large volumes since some time as well.[7,9-11] In addition those countries are generating an increasing amount of their own e-waste.[9,14] While the main incentive for e-waste recycling is the recovery of precious and other metals, increasing oil prices mean that plastic is also increasingly recycled or recovered. Nigeria has already developed some plastic recycling activities and currently the government is planning to develop more than 20 plastic recycling facilities. In this instance it needs to be assured that hazardous chemicals including POPs, other persistent toxic substances including heavy metals are controlled and phased out where feasible and do not end up in sensitive recycled plastic products like children toys or household goods.

The objective of this study is a screening of POP-PBDE and other (brominated) flame retardants in plastic from TV sets and computer monitors (containing the main plastic share of electronics) present in Nigeria. In a first study phase 382 samples have been screened for their bromine content[15]. In this follow-up study the 213 bromine positive tested samples were analysed for POP-PBDE and other brominated flame retardants (BFR) content.

Materials and methods

Sampling: Samples of plastics from cathode ray tube plastic casings (CRTs) of TVs and computers – a electronic category known possibly contain c-OctaBDE were sampled. In total 158 from TV CRT sets and 224 computer CRTs were taken from eight locations in Ogun state and Lagos state in south west Nigeria. Sampling

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[A] The listing of POPs PBDEs include tetrabromodiphenyl ethers, pentabromodiphenyl ethers, hexabromodiphenyl ethers and heptabromodiphenyl ether. The OctaBDE, nonaBDE ethers and the decaBDE homologue are not listed as POPs. However the debromination of these highly brominated diphenyl ethers can lead to the formation and release of POP-PBDEs[4].

was carried out in January to March 2011. The samples were specifically selected from waste storages, electronics workshops, roadsides, dumpsites and dismantling sites. The labels on the TVs and computer monitor plastic housings were examined for information on the manufacturer, brand, model, serial number, year and origin of production.

Sample preparation and measurement: Small pieces were cut of each polymer samples (approx. 100 x 50 mm). These were subjected to X-ray fluorescence analysis (X-lab 2000, Spectro, Kleve, Germany) in order to quantify bromine, chlorine, cadmium and lead semi-quantitavely.

In aluminium foil coated 100 ml glass vials, 1 g of the samples were dissolved in 9 g of tetrahydrofuran and precipitated with 40g of n-hexane. The supernatant was separated from the precipitated polymer and an aliquot was passed through a 45 µm PTFE syringe filter. Filtered extracts were then diluted with the 100-fold amount of toluene and subjected to GC-ECD analysis (TraceGC, Thermo) equipped with a ZB-5 MS inferno (15m x 0.25 mm x0.1µm, Phenomenex). GC injector and detector temperatures accounted for 295˚C and 320˚C respectively and the oven temperature was programmed as follows: 140°C (1min), 20K/min (280°C), 4K/min (300°C), 20K/min (325˚C).

BFR were identified by comparison of retention times with external technical standards of c-OctaBDE, commercial Decabromodiphenyl ether (c-DecaBDE), Tetrabromobisphenol A (TBBPA) and 1,2- bis-tribromophenoyethane (TBPE). The same standards were used to quantify their amount.

***Quality control**:* The measured bromine content was calculated from the quantified amounts of specific BFR and compared to the bromine level measured by X-ray fluorescence.

a) the extraction process may not have been complete, b) the ECD detector was not completely stable over all 500 injections and c) the X-ray fluorescence analysis provides only semi-quantitative data, the identification of the most relevant BFR present in the sample were considered complete, when the calculated bromine level accounted for at least 50% of the measured concentration.

Results and discussion

1. Selection and XRF screening of samples

The ranges of the year of production were 1987-2006 for computers, and 1981-2004 for TVs. This time span is considered being the most relevant for the use of POP-PBDEs as their production is thought to have been stopped in about 2004[4]. The numbers of samples with the regions of origin (production or assembly) are shown in Table 1. A total of 382 CRT samples were collected - 224 from Computers and 158 from TV sets – and year and origin noted. For computer samples, the highest proportion was from Asia (100), followed by America (74), and then Europe (50). Most of the TV samples were obtained for Europe (100), followed by Asia (58), and none from America[B]. This broadly reflects presence of these e-wastes in Nigeria.

The samples had been screened with XRF and positive tested samples have been further analysed by GC-ECD and GC-MS for PBDEs and other brominated flame retardants. In this first sampling campaign of plastics entering and present in Nigeria, TV sets and computers were targeted. These two electronic groups contain the largest share of plastic in e-waste. Furthermore the recycling of the plastic of these e-products is of particular interest from an economic perspective.

Results from XRF screening

152 of the 224 screened computer CRT casings contained BFRs. 70 of the screened 224 computer casings from the three regions contained phosphor at a level between 0.1 to 2.0% indicating that about 31.3% of these samples were equipped with phosphor organic flame retardants (PFRs). Only 6.5% of computer monitor casings did not contain flame retardant systems based on BFRs or PFRs.

61out of the 159 TV CRT casings contained BFRs. Phosphor levels were low in almost all the TV samples showing that the TV casing from Asia and Europe have not been treated with phosphorus flame retardants.

2. Results from instrumental analysis

All samples that where tested positive to bromine were analysed for different type of brominated flame retardants using GC-ECD. Some bromine positive samples did not show a response in the ECD indicating a oligomeric BFR. Also, a group of samples that shows a similar ECD pattern which does not belong to the 4 indicated BFRs (TBPE, TBBPA, c-OctaBDE, c-DecaBDE) are been analysed with GC/MS.

[B] Second hand TVs are not imported from the US as the systems are not compatible.

Samples containing POP-PBDEs

5 samples out of the 159 Television samples analysed had c-OctaBDE and related POP-PBDEs with concentration ranging from 0.1% to 29.00% (see table 1). All c-OctaBDE containing TV samples where produced before 1990 and 80% of these TV sets were manufactured in Europe (please note that second hand TVs from the US are not sent to Nigeria[B]). These impacted samples resulted in an average concentration for all 159 TV samples of 0.69% c-OctaBDE and therefore above the maximum permissible level of 0.1% as stipulated by the RoHS Directive 2011/65/EU Annex II. Therefore these polymers can only be used for recycling into electronics after removing the bromine containing casings.

3 samples out of the 224 computer CRT sample screened for BFRs had c-OctaBDE with concentration ranging from 0.87% to 5.09% (see table 1) Only one sample (a Compaq produced 2003 in USA) from all screened computers contained c-OctaBDE added as a BFR at a level of 5%. The other two c-OctaBDE positive tested samples contained c-OctaBDE at around 1% indicating that the c-OctaBDE rather stem from recycling of c-OctaBDE containing polymers. The average concentration recalculated to total polymers of the 224 computer CRTs was 0.05%. While this average concentration is below the maximum permissible RoHS limit of 0.1% it is currently not known what low POPs limit will be suggested by Basel Convention. The recommendation from the Conference of Parties is to separate POP-PBDE containing polymers and not to recycle them.

Table 1: TV and PC CRTs where OctaBDE have been detected

SAMPLE Type	Conc. of c-OctaBDE (%)	Country (production)	Brand	Year of manufacture
TV CRT	29.00	U.K	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	U.S.A	Compaq	2003
PC CRT	0.95	U.S.A	IBM	2005
PC CRT	0.87	China	Compaq	2003

Samples containing other flame retardants

The major flame retardants in the screened TV CRTs were Decabromodiphenylether (DecaBDE), followed by TBPE, TBBPA also all at higher levels compared to c-OctaBDE.

24 samples out of the 159 TVs samples (15%) analysed for BFRs contained c-DecaBDE with concentrations ranging from 0.086% to 23.7% (average 5.7%) which corresponds to an average concentration of 0.86% for the polymers 159 CRT TV screened and therefore more than 8 times above the RoHS limit. 7 Television sample had TBBPA with concentration ranging from 0.85% to 16.9%, average concentration for total polymer of 0.90%.

The major (other) flame retardants detected in computers CRTs were TBBPA, followed by TBPE and c-DecaBDE present in higher concentration than c-OctaBDE. 10 samples out of the computer sample analysed for BFRs had c-DecaBDE with concentration ranging from 0.26% to 5.4% (average 1.28% which corresponds to an average concentration of 0.08% for the polymers from all 224 CRT PCs screened and therefore is around the RoHS limit value. 102 samples out of the computer sample analysed for BFRs had TBBPA with concentration ranging from 0.10% to 17.7% with average concentration of 5.0%.

3. Calculation of total brominated flame retardants in Nigerian CRTs

The data on total CRT volume in Nigeria has been established in the inventory of EEE/WEEE and amounts to 791325 tonnes containing 237000 tonnes plastic[16]. From the average concentration of c-OctaBDE (and POPs hexaBDE and heptaBDE therein) derived from this study we estimated the total amount of c-OctaBDEs in CRT plastic in Nigeria to 1327 tonnes (including 146 tonnes hexaBDE and 570 tonnes HeptaBDE) (Figure 2). The POP-PBDE inventory using the SC inventory approach[6a] (tier 2) resulted in an estimate of 284 tonnes c-OctaBDE (31 tonnes hexaBDE and 122 tonnes heptaBDE). Therefore amount of c-OctaBDE in TVs derived from this study was estimated 2.7 times higher compared to the factors suggested by the SC POP-PBDE inventory guidance[6a]. The probable reason is that the factors for the SC inventory guidance were derived from monitoring in European WEEE recycling facilities having probably more recent WEEE equipment processed compared to the WEEE stocks in Nigeria assessed in this study. The factors derived in this study reflecting the Nigerian CRT stock situation is probably more appropriate for the EEE/WEEE stockpiles in the African region.

It is highlighted that the average concentration and therefore inventory of DecaBDE (4968 tonnes) and TBBPA (1944 tonnes) was higher in the CRT plastic compared to c-OctaBDE (Figure 1). While for c-OctaBDE the CRT casings are considered to contain the largest share of overall use[6a], for c-DecaBDE and TBBPA also other uses are relevant. Therefore their total amount in other EEE/WEEE and other uses can also be regarded relevant.
A concept is needed for the management of c-OctaBDE and other BFR containing material flows in Nigeria.

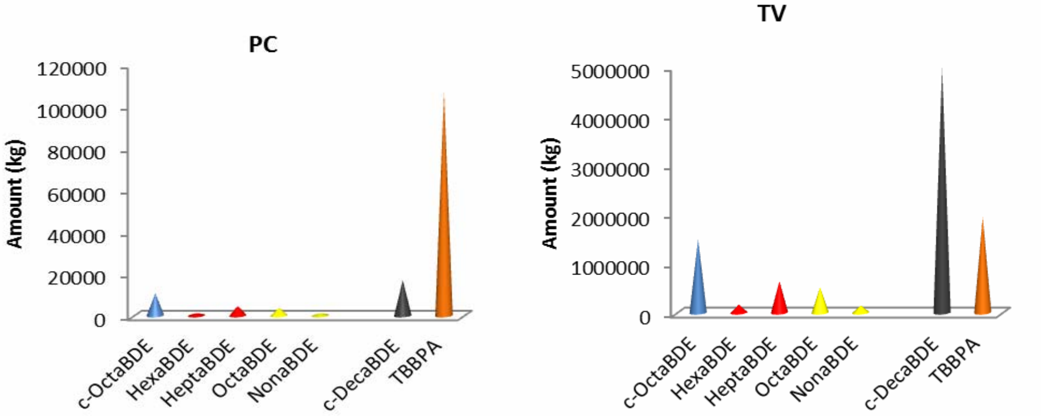

Figure 1: Total amount of PBDEs and TBBPA (kg) in polymer fraction of TV and Computer CRTs in Nigeria.

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