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Analysis of polybrominated diphenyl ether and tetrabromobisphenol A in plastic samples in Mongolia

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Abstract: This study was conducted to determine brominated flame retardants (BFRs) in electronic products in view compliance with the Restriction of Hazardous Substances (RoHS) and initiated by activities for implementation of the Stockholm Convention. Brominated flame retardants (BFRs) are synthetic additives mainly used in electrical and electronic appliances and in construction materials. Total 16 plastic casing samples were tested for threshold levels of polybrominated ethers. According the XFR results, the concentration of cadmium, lead, mercury and chromium were found below than Maximum Concentration Value (MCV) of RoHS, while the concentration of total bromine was exceeded the standard limitations in the samples. Only 1 out of the 16 plastic samples contains DecaBDEs while Tetrabromobisphenol (TBBP-A) is the major brominated flame retardants. However by the presence of one sample the average concentration of DecaBDE was above the RoHS limit of 1000 ppm as found in studies in other countries.

Keywords: persistent organic pollutants, brominated flame retardant, XFR, GC-ECD polybrominated diphenyl ethers, tetrabromobisphenol,

INTRODUCTION

The Stockholm Convention is a global treaty to protect human health and the environment from Persistent Organic Pollutants (POPs). In 1995, the Governing Council of the United Nations Environment Programme (UNEP) called for global action to be taken on POPs, which it defined as "chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment". Following this, the Intergovernmental Forum on Chemical Safety (IFCS) and the International Programme on Chemical Safety (IPCS) prepared an assessment of the 12 worst offenders, known as the dirty dozen. Stockholm Convention signed in 2001 and effective from May 2004, that aims to eliminate or restrict the production and use of POPs [1]. In May 2009, the Conference of the Parties amended the Stockholm Convention on POP to add certain brominated flame retardants. Like all POPs, these chemicals possess toxic properties, resist degradation and bio-accumulate. They are transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems. These chemicals have been widely used in many industrial sectors for the manufacture of a variety of products and articles, including consumer articles. Polybrominated diphenyl ethers (PBDEs) are a group of industrial chemicals which have been widely used as additive flame retardants such as electronics, furniture, upholstery and other products for improving fire resistance as additive flame retardants since 1970s [2]. Brominated flame retardants (BFRs) are synthetic additives mainly used in electrical and electronic appliances and in construction materials [3]. The group of substances are characterized by consisting of two benzene rings with 1-10 bromine atoms attached (Fig. 1). PBDEs are manufactured in three commercial mixtures: c-penta-BDE, c-octa-BDE and c-deca-BDE. While the production of c-octa-BDE has stopped around 2004 the c-deca-BDE products are widely added to electronic appliances such as television and computer. Over the past few decades much attention has been given to PBDEs in the environment because of their ubiquitous presence, bioaccumulation and potential effects on wildlife and humans. Although

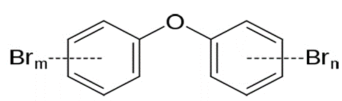

Fig. 1. Structure of polybrominated diphenyl ethers

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production stopped in the EU, United States and the Pacific Region in 2004, but there is no information that indicates its production in developing countries [4].

TBBP-A (Fig 2.) is the BFR used in the highest volume. It is not listed or suggested for the Stockholm Convention and not listed in the RoHS directive. TBBP-A is introduced in to polymer applications in either a reactive or an additive form. When TBBPA is used as an additive component, it does not become part of the polymer structure. When TBBPA is used as reactive flame retardant, the phenolic hydroxyl group react covalently and the TBBPA is corporate into the polymer matrix. TBBPA is most commonly used as a reactive flame retardant in epoxy resins for printed wiring boards (PWB). TBBPA is also used as the starting material for the production of TBBPA-derived flame retardants.

Global consumption of the most demanded BFRs, 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 [5, 6]. In recent years some screening on PBDE and other flame retardants have been performed in different regions in the world (A, B [7-10], C)

Up to now no monitoring of BFRs have been performed in Mongolia. Therefore in this study a preliminary screening have been done on BFRs in polymers in electronics (TV and computers) in Mongolia.

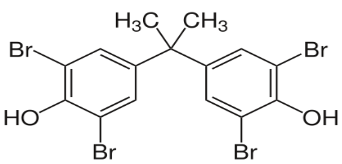

Fig. 2. Structure of tetrabromobiphenol A

EXPERIMENTAL

This study was designed as a two-tiered testing strategy that systematically identified key BFRs through a combination of non-destructive tests and confirmed through destructive chemical analysis. The two tiers consisted of: (1) initial screening for total bromine and some other substances using a hand-held XRF device, (2) chemical extraction of products and destructive quantitative analysis for PBDEs, TBBPA. Samples of plastics from cathode ray tube (CRTs) plastic casing of TVs and computers – electronic category known contain c-OctaBDE were sampled. In total 25 from TV CRT sets and 23 computer CRTs were taken from Ulaanbaatar, (Mongolia). The samples were specifically selected from waste storages and using places. The labels on the TVs and computer monitor plastic housings were examined for information on the manufacturer, brand, model, year and origin of production.

XRF analysis: From the economic point of view, XRF analysis as a screening method has already been provided to have great performance and effectiveness for sample analysis, supporting regulations such as RoHS and waste electrical and electronic equipment (WEEE). XRF has become the main measuring method used for RoHS due to its speed, accuracy and non-destructive analysis capability. In this analysis, lead (Pb), mercury (Hg), cadmium (Cd), total chromium (Cr), bromine (Br) was detected by X-ray fluorescence spectroscopy. In this study an Elvax ProSpector (Kiev, Ukraine) was used. The Elvax Prospector operates under control of the HP iPAQ PDA with 4-inches high resolution touch-screen display, providing high flexibility and usability of the system. In total 48 used computers and televisions were screened and all components of each individual item underwent an initial 30 second handheld XRF screening. The screening results in RoHS plastic samples were compared with MCV while is shown in Table 1.

Table 1. Maximum concentration value of RoHS

Substances	MCV, ppm
Lead (Pb)	1000
Mercury (Hg)	1000
Cadmium (Cd)	100
Chromium (Cr^{+6})	1000
PBBs (Polybrominated biphenyls)	1000
PBDEs (Polybrominated diphenyl ethers)	1000

PBDE and BFR analysis: Small pieces were cut of each 16 selected samples. These were subjected to PBDE analysis (UNIDO, Environmental Management Branch Stockholm Convention Unit Vienna International Center, Austria). Materials were extracted by dissolution/presipition in suitable solvents (THF/heptane). The extract was concentrated by rotary evaporation and filled into a volumetric flask (50 ml). Owing to the vapor pressures and polarity of PBDEs, GC is the most widely used technique to analyze the various congeners, by using electron capture detection (ECD), electron ionization-mass spectrometry (EI-MS), or electron capture negative ionization-mass spectrometry (ECNI-MS) as detector. The GC-ECD gives greater precision, accuracy, and limit of detection (LOD) values [11].

Aliquots of these extracts were analyzed by GC-ECD (Thermo) and quantified against external certified standards of PBDE. ECD is an appropriate detector for brominated aromatic compounds. The advantage of the detector is the robustness, the relative low costs and the ease of use.

RESULTS AND DISCUSSION

Table 2 shows the XRF results of selected 16 samples from all 48 measurements. The concentration in four categories, cadmium, lead, mercury and chromium showed lower contents than maximum allowable limit of RoHS. The total bromine contents were also computer did not find bromine by XRF screening.

In addition PBDE and TBBPA contents were analyzed by international standard for determination of regulated substances in electronics (IEC 62321) [3]. Tetrabromodiphenyl ethers - BDE - 47, pentabromo-diphenyl ethers BDE 99,100, hexabromodiphenyl ethers BDE153, 154, heptabromodiphenyl ethers BDE 183, octabromodiphenyl ethers BDE 196, 197, 203, nonabromodiphenyl ethers BDE 207, decabromo-diphenyl ethers 209 congeners and tetrabromo bisphenol A, tribromophenoxy ethane were analyzed by CG with ECD. Results were shown following 4 tables (Table 3 - 6).

Table 2. Contents of screening analysis by XRF spectrometry

Model of CRT computers and CRT television	Concentration of substances, ppm				
	Br	Cr	Cd	Hg	Pb
Samsung -1	72782±246	185±68	170±16	0±55	0±40
Samsung-2	75404±259	0±419	165±16	0±61	184±7
Samsung-3	71561±247	188±69	135±14	0±55	71±10
Samsung-4	87638±315	235±89	133±16	0±72	0±46
Samsung-5	87181±244	0±382	153±13	0±54	206±16
Samsung-6	66145±366	0±366	120±14	1441±59	0±7
LG-1	61506±214	0±318	178±5	1615±56	0±33
LG-2	66417±279	0±425	100±14	0±60	0±42
Packard Bell-1	92996±331	0±501	186±19	1575±70	0±49
Packard Bell-2	90411±317	456±123	178±18	0±70	190±19
Compaq-1	63462±248	0±398	0±82	0±55	0±42
Compaq-2	66273±249	0±395	116±14	0±59	183±17
Daewoo	62031±229	0±352	159±15	1372±55	0±34
Toshiba	120532±444	0±617	224±25	2741±109	0±62
Dell	100126±348	409±122	257±23	1450±68	0±58
Marco	21±1	0±53	51±	0±5	0±3

*limit of detection

Table 3. Analysis of PBDE and TBBPA in bromine positive plastic samples from WEEE

Congener	LOD*	Samples			
		Samsung - 1	Samsung - 2	Samsung - 3	Samsung - 4
		Results	Results	Results	Results
BDE 47	10	< LOD	< LOD	< LOD	< LOD
BDE 99	15	< LOD	< LOD	< LOD	< LOD
BDE 100	10	< LOD	< LOD	< LOD	< LOD
BDE 153	10	co-elute	co-elute	co-elute	co-elute
BDE 154	20	< LOD	< LOD	< LOD	< LOD
BDE 183	20	166	168	147	130
BDE 196	30	54	36	47	42
BDE 197	30	217	175	176	207
BDE 203	30	< LOD	< LOD	< LOD	< LOD
BDE 207	30	< LOD	< LOD	< LOD	< LOD
BDE 209	30	< LOD	< LOD	< LOD	< LOD
TBBP A	150	76694	71544	71188	76318
TBPE	20	37	< LOD	< LOD	37

*limit of detection

analyzed. Although total bromine (120532 ppm) exceeded the standard limit of RoHS, however, it is undeterminable whether total bromine exceeds the permitted concentration of RoHS or not, because BFR affiliated with TBBPA, brom epoxy and halogen free are mainly used for housing cover of display product.

Highest amount of total bromine were in Dell CRT computer is 100126 ppm and Toshiba CRT-TV is 120532 ppm respectively. In case of Marco CRT

All of the 4 tables were shown 15 out of 16 samples contained TBBPA as flame retardants. TBBPA is not

Table 4. (Continued) Analysis of PBDE and TBBPA in bromine positive plastic samples from WEEE

Congener	LOD*	Samples			
		Samsung -5	Samsung -6	LG-1	LG-2
		Results	Results	Results	Results
BDE 47	10	< LOD	< LOD	< LOD	< LOD
BDE 99	15	< LOD	< LOD	< LOD	< LOD
BDE 100	10	< LOD	< LOD	< LOD	< LOD
BDE 153	10	co-elute	co-elute	co-elute	co-elute
BDE 154	20	< LOD	< LOD	< LOD	< LOD
BDE 183	20	138	154	164	191
BDE 196	30	86	< LOD	< LOD	< LOD
BDE 197	30	201	179	376	425
BDE 203	30	< LOD	< LOD	< LOD	< LOD
BDE 207	30	< LOD	37	< LOD	< LOD
BDE 209	30	< LOD	< LOD	< LOD	< LOD
TBBP A	150	68771	77505	89589	925121
TBPE	20	< LOD	< LOD	< LOD	< LOD

*limit of detection

Table 5. (Continued) Analysis of PBDE and TBBPA in bromine positive plastic samples from WEEE

Congener	LOD*	Samples			
		Samsung -1	Samsung -2	Samsung -3	Samsung -4
		Results	Results	Results	Results
BDE 47	10	< LOD	< LOD	< LOD	< LOD
BDE 99	15	< LOD	< LOD	< LOD	< LOD
BDE 100	10	< LOD	< LOD	< LOD	< LOD
BDE 153	10	co-elute	co-elute	co-elute	co-elute
BDE 154	20	< LOD	< LOD	< LOD	< LOD
BDE 183	20	166	168	147	130
BDE 196	30	54	36	47	42
BDE 197	30	217	175	176	207
BDE 203	30	< LOD	< LOD	< LOD	< LOD
BDE 207	30	< LOD	< LOD	< LOD	< LOD
BDE 209	30	< LOD	< LOD	< LOD	< LOD
TBBP A	150	76694	71544	71188	76318
TBPE	20	37	< LOD	< LOD	37

*limit of detection

Table 6. (Continued) Analysis of PBDE and TBBPA in bromine positive plastic samples from WEEE

Congener	LOD*	Samples			
		Daewoo	Toshiba	Dell	Marco
		Results	Results	Results	Results
BDE 47	10	< LOD	< LOD	< LOD	< LOD
BDE 99	15	< LOD	< LOD	< LOD	< LOD
BDE 100	10	< LOD	< LOD	< LOD	< LOD
BDE 153	10	co-elute	co-elute	co-elute	co-elute
BDE 154	20	< LOD	< LOD	< LOD	< LOD
BDE 183	20	221	177	216	< LOD
BDE 196	30	< LOD	< LOD	54	< LOD
BDE 197	30	262	214	49	81
BDE 203	30	< LOD	< LOD	113	< LOD
BDE207	30	< LOD	< LOD	9228	< LOD
BDE 209	30	< LOD	< LOD	74244	< LOD
TBBP A	150	89705	90772	76345	< LOD
TBPE	20	< LOD	< LOD	< LOD	< LOD

*limit of detection

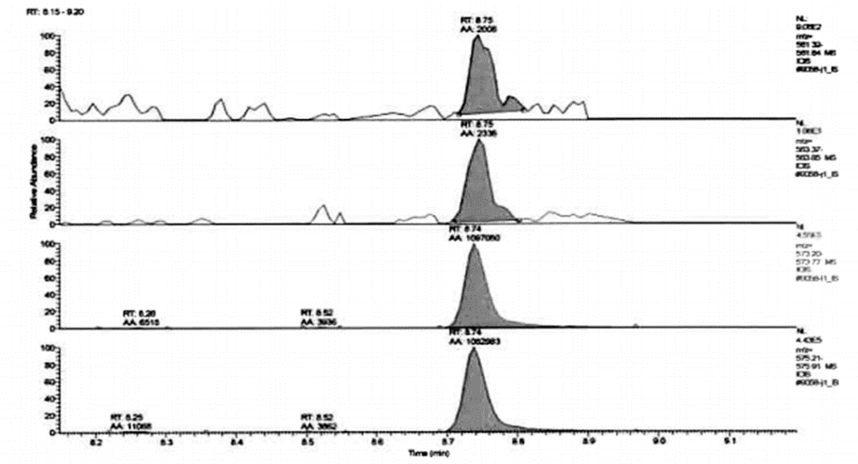

Fig. 3. HeptaBDE homologue traced monitored by GC-HRMS analysis

regulated by RoHS or Stockholm Convention. One of the 16 samples contained DecaBDE as flame retardants. The Dell (74244 ppm) is non-compliant to RoHS regulation (1000 ppm). This sample actually has sufficient DecaBDE to contaminate more than 70 other samples with DecaBDE (Table 6, BDE 209). So this sample gives a first indication that our average WEEE plastic is probably above RoHS directive for DecaBDE. Currently DecaBDE is not listed under Stockholm Convention and has currently no consequences in respect to POPs. However DecaBDEs is currently assessed in the [7] POP Reviewing Committee and has been found to meet the POPs criteria (UNEP 2013 a,b) [12, 13].

Almost all samples contained PBDE 183 which is listeed as POP in the Stockholm Convention (Table 3, 4, 5 and 6), at levels between 70 and 220 ppm.

This is below the RoHS limit of 1000 ppm. There is currently no specific limit for POP-PBDE from Stockholm Convention.

However in the EU POP regulation there is a limit for heptaBDE homologue of 10 ppm for tetraBDE, pentaBDE, hexaBDE and heptaBDE homologues. However it contains the exemption for recycling or for electronic equipment of 1000 ppm and therefore would be below this level.

CONCLUSIONS

According the XFR results, the concentration of cadmium, lead, mercury and chromium were found below than MCV of RoHS, while the concentration of total bromine was exceeded the standard limitations in the samples. 15 of 16 samples are in compliance with European RoSH directive; only 1 sample (DELL) contains c-DecaBDe as major BFR. However, some other issues are of special concern:

1. BDE 153 is completely co-eluted by TBBPA and cannot be analyzed with this method. However, BDE 153 is accompanied by BDEs153, 100, 99 and 47 in technical PentaBDE or with BDEs 154, 183, 197, 196, etc. in technical OctaBDE. As BDE 154 is below LOD in all samples.
2. HeptaBDE congener BDE 183 is detected in 15 of 16 samples with levels ranging from 73 to 221 ppm. ECD results have been checked with HRMS as displayed in Fig. 1. The upper to trace indicate native BDE 183, the lover two ^{13}C labeled BDE 183. MS data show positive detects of native BDE 183 confirm the ECD levels.
3. Sample (DELL) contains two major BFR: TBBP A and DecaBDE. Most other contains TBBPA as the major BFR with lower levels of BDE 183 as indicator for technical OctaBDE. Furthermore, TBPE has been detected at rather low levels (~37 ppm) in two samples. Such mixtures of BFR are not applied in virgin BFR plastics. Therefore, the presented clearly reveal recycling activities which have coextruded PBDE containing plastics with virgin plastic and TBBPA as new BFR additive.

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RESERENCES

1. Stockholm Convention (2001) http://chm.pops.int/default.aspx
2. Stockholm Convention Secretariat (2012) Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants
3. Morf L., Tremp J., Gloor R., Huber Y., Stengele M., Zennegg Markus. (2005) *Environ. Sci. Technol.* **39**, 8691-8699

4. Weber R. (2012) *Establishing inventories of POP-PBDEs listed under the Stockholm Convention.* Presentation Stockholm Convention Workshop, Ulaanbaatar December 2013
5. International electrotechnical commission (2008) International standard IEC 62321, Electrotechnical products.
6. Waeger *et al* 2010
7. Sindiku O., Babayemi J., Osibanjo O., Schlummer M., Schluep M., Watson A., Weber R. (2014) Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated falme retardants and heavy metals in E-waste polymers in Nigeria. *Env. Sci Pollute Res., DOI:10.1007/s11356-014-3266-0*
8. Babayemi J., Sindiku O., Osibanjo O., Weber R. (2014) Substance flow analysis of polybrominated diphenyl ethers in plastic from EEE/WEEE in Nigeria in the frame of Stockholm Convention as a basis for policy advice. *Env. Sci Pollute Res. DOI:10.1007/s11356-014-3266-0*
9. Wager P., Schluep M., Muller E. (2010) RoHS substances in mixed plasticts from waste electrical and electronic equipment. *Empa: St Gallen*
10. Gallen C., Banks A., Brandsma S., Baduel C., Thai P., Eaglesham G., Heffernan A., Leonards P., Bainton P., Mueller J.F. (2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products *Sci. Total Environ.,* 491-492, 255-265
11. Kim Y.J., Kang D.H., Kim M.G., Qureshi T.I. (2013) *Int. J. Environ. Res.,* **7**(4): 903-908
12. UNEP (2013a) Proposal a list decabromodiphenyl ether (commercial mixture, c-decaBDE) in Annexes A, B and/ or C to the Stockholm Convention on Persistent Organic Pollutants. 6 June 2013
13. UNEP (2013b) Report of the Persistent Organic Pollutants Review Committee on the work of its ninth meeting. UNEP/POPS/ POPRC.9/13