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Screening of halogenated aromatic compounds in some raw material lots for an aluminium recycling plant

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Abstract

Four samples of scrap raw materials for an aluminium recycling plant were screened for the occurrence of persistent halogenated aromatic compounds. The samples contained waste from handling of electric and electronic plastics, filter dust from electronic crusher, cyclone dust from electronic crusher and light fluff from car shredder. In our screening analyses, brominated flame retardants were observed in all samples. Polybrominated diphenyl ethers (PBDE) were identified in all samples in amounts of 245–67450 ng/g. The major PBDE congeners found were decabromo- and pentabromodiphenyl ethers. 1,1-bis(2,4,6-tribromophenoxy)ethane, hexabromobenzene, ethyl-pentabromobenzene, tetrabromobisphenol-A, pentabromotoluene and dimethyl tetrabromobenzene were observed in all scrap samples. The concentrations of PCBs, PCNs (polychlorinated naphthalenes) and nona- to undecachlorinated terphenyls in some of these scrap samples were remarkably high.

Keywords: Aluminium; Ethers; Terphenyls

1. Introduction

Halogenated organic compounds are potentially harmful contaminants in the environment as they are persistent and bioaccumulative. Earlier, main concern has been focused to chlorinated compounds, but recently, brominated compounds have received increased attention. Very scarce data on the potential ecotoxicological effects of anthropogenic organic brominated compounds are available. Numerous organobromine compounds are produced naturally—more than 1600 individual substances were known in 1999 (Gribble, 2000). Some of these are identical to man-made organobromine compounds.

Brominated organic compounds are widely used as flame retardants. Flame retardants are added to different materials such as synthetic textiles, carpets, coatings, adhesives, paints, plastics and electronic components. Often 10–20% by weight is added to products. Most common brominated flame retardants (BFRs) are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD), decabromodiphenyl ether (DeBDE), octabromodiphenyl ether (OBDE) and pentabromodiphenyl ether (PeBDE). Their annual sales in 1999 were total 204,325 metric tons (BSEF, 2000). In recent years, trace concentrations of BFRs, especially PBDEs, have been found to increase alarmingly in environmental biota and human tissues (Bergman, 2000).

First studies on BFRs in biosphere took place on PBBs after Firemaster accident in Michigan in 1973 (Anderson, 1989) and on PBDEs (Andersson and Blomkvist, 1981). Especially lower brominated BDEs gained interest as their levels in human mother's milk were found to increase exponentially during last decennia (Meironyte et al., 1999). BFRs were also found to form an occupational hazard in electronic recycling plants and other similar working environments (Sjödin et al., 2001).

The biomagnification rates of tri-, tetra- and penta-BDEs in aquatic ecosystem have been measured to be even higher than the rates for all PCBs (Burreau et al., 1999; Manchester-Neesvig et al., 2001). Fate and possible impact of BFRs in environment has been recently reviewed (de Wit, 2002).

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Some polybrominated dibenzofurans (PBDFs) and polybrominated dibenzo-*p*-dioxins (PBDDs) are formed during pyrolysis and thermal decomposition of BFRs (Buser, 1986; Thoma et al., 1986; Dumler et al., 1989a,b; Hutzinger et al., 1989; Striebich et al., 1991; Luijk et al., 1991; Lorenz and Bahadir, 1993). There exist 5020 theoretically possible halogenated (bromine/chlorine) dioxins and furans and more than 400 of these are 2,3,7,8-substituted (Buser, 1987). For example, formation of TeXDD (X = Cl, Br) and TeXDF (X = Cl, Br) was observed in experimental combustion of municipal solid waste (MSW) that contained some DeBDE, tetrabromobisphenol or hexabromocyclodecane (Söderström and Marklund, 2000). Very scarce data on eventual emissions to the environment or environmental concentrations of (PBDFs) or (PBDDs) could be found.

Polychlorinated aromatic substances emitted from the smelters producing recycled aluminium from metal scrap have been of concern as persistent bioaccumulative toxic substances. The PBTs previously measured in emissions of the smelters are polychlorinated benzenes (PCBz), naphthalenes (PCN), phenols (PCP), biphenyls (PCB), dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) (Aittola et al., 1993, 1996). Also, formation of sulfur analogues of PCDFs, polychlorinated dibenzothiophenes (PCDT), has been observed (Sinkkonen et al., 1994). Recently, concentrations of PBDEs have been measured and a great number of other brominated organic aromatic substances have been identified in ash samples from an aluminium smelter plant (Sinkkonen et al., 2003).

In this work, samples of scrap raw materials for an aluminium recycling plant were screened for the occurrence of persistent halogenated aromatic compounds. The samples contained waste from handling of electric and electronic plastics, filter dust from electronic crusher, cyclone dust from electronic crusher and light fluff from car shredder. Originally, it was obvious that the material contains BFRs, but more information on their structures and amounts were needed to resolve the fate of the material, whether it could be used further as raw material in recycling processes or if special waste treatment procedures were needed.

2. Materials and methods

The raw material (scrap) samples were from the aluminium smelter (ALS) in the metal reclamation plant of Kuusakoski ldt in Heinola, South Finland. Shredded mixed metal scrap (from old cars, electronic scrap, etc.) is processed in heavy media plant where aluminium is floated from heavier metals (Cu, brass, Zn, Pb, Stainless steel, etc.) with ferrosilicon water suspension. Aluminium fraction is cleaned from non-metals (mainly from plastics) with eddy current separator. Cleaned floated aluminium is dried in rotary drier (about 150–200 °C). Dry-floated aluminium is melted in rotary salt furnace and induction furnaces. Further details are presented in our recent paper that reports on the occurrence of polyhalogenated aromatic substances in oven ash from recycled aluminium production (Sinkkonen et al., 2003). For this study, four samples (R1–R4) of the scrap material delivered to the plant were selected for preliminary estimation of its appropriateness to be used as raw material in the production of recycled aluminium. Sample R1 is electronic plastics; waste from handling of electric and electronic scrap. Sample R4 is light fraction of auto shredder residue (ASR). Samples R3 and R4 are filter and cyclone dust from electric and electronic scrap crushers. Due to nonhomogeneity of the samples, the concentrations obtained do not necessarily represent the overall concentrations in the whole samples.

Several aliquots of the samples were taken and analysed. All samples were solvated separately in hexane (Rathburn), dichloromethane (Mallinckrodt) and toluene (Rathburn) or Soxhlet extracted with toluene for 48 h. Internal standards added for identification and quantification of the known substances were 2,4,6-trichlorobiphenyl (PCB30), $^{2}H_5$-labelled 2,3,4,5,6-pentachlorodiphenyl ether (DE116-d5, from Dr. Ehrenstorfer), and $^{13}C_{12}$-labelled tetra- to octachloro 2,3,7,8-substituted PCDDs and PCDFs (Wellington Laboratories). After extraction, all samples were shaken with concentrated sulfuric acid and fractionated by Florisil (Florisil®PR, Fluka, 60–100 mesh) and carbon (SK-4 Carbon 80/100, Alltech) column chromatography. The first fraction from the Florisil (1 g) column was eluted with 15 ml of hexane (F1) and the second fraction with 15 ml of dichloromethane (F2). Fractions F1 and F2 were further fractionated by carbon (50 mg) column chromatography. In case of the fraction F1 elution was first done with 10 ml of hexane (F1C1) and then reversed elution with 12 ml of toluene (F1C2). In the case of fraction, F2 elution was first done with 10 ml of dichloromethane/hexane 1:1 (v/v) (F2C1) and then reversed elution with 12 ml of toluene (F2C2).

PCBs were determined by GC/ECD using a Nordion Micromat HRGC 412 gas chromatograph equipped with two 25-m quartz capillary columns (NB-1701 and NB-54, 0.25 mm, 0.25 μm). The temperature of the detectors was 320 °C and the temperature of the injector was 250 °C. Helium 1 ml/min was used as carrier gas and argon/methane 95:5 (v/v) as make up gas for the detectors. Temperature program was 150 °C–5 °C/min–250 °C (20 min). The GC/MS analyses were done with a Fisons AutoSpec mass spectrometer connected to HP 5890 Series II gas chromatograph, equipped with a 25 m long, 0.2 mm inner diameter fused silica column, coated with 0.11 μm layer of HP-5 stationary phase. The mass spectrometer was operated in the electron ionisation (EI) mode with an ionisation potential of 70 eV. Helium was used as carrier gas. In the quantitative determinations selected ion monitoring (SIM) mode was used. Further analyses of PBDEs (especially hepta- to decabromodiphenyl ethers) were done using a short, 10 m long HP-5 column (Sellström et al., 1998), and the ionisation potential was decreased to 30 eV.

For structure screening of chlorine, bromine or mixed chlorine-bromine substances in the different fractions low resolution mass spectrometry with full scan mode (GC/LRMS) was used. The temperature program 100 °C (1 min)–20 °C/min–180 °C–5 °C/min–300 °C (20 min) was applied. Most abundant new compounds were detected as peaks in total ion current chromatogram (TIC) and their mass spectra recorded. Fragmentation patterns of mass spectra were analysed with aid of literature and by isotope cluster simulation (ICLU; Viktorovskii et al., 1999; Sinkkonen et al., 2001).

3. Results

A large number of brominated organic substances were observed. All samples R1-R4 contained polybrominated aromatic compounds known as flame retardants. The concentrations were quite high. The most abundant polybrominated aromatics identified were 1,1-bis(2,4,6-tribromophenoxy)ethane, tetrabromobisphenol-A and tri- to decabromodiphenyl ethers. Hexabromo- and pentabromobenzene were the most abundant bromobenzenes and ethylpentabromobenzene and dimethyl tetrabromobenzene the most abundant alkylbromobenzenes. Nonhomogeneity of the samples and lack of labelled model compounds made any exact quantitation impossible. Some estimation of the relative concentrations in individual samples was done by comparing the EI ion intensities of the molecular ions and main fragment ions in the total mass spectra or in the reconstructed ion chromatograms.

PBDEs were recognised by their EI mass spectra. All PBDEs have a very strong M$^+$ ion and major, often base peak fragment ions M$^+$–Br$_2$ (M$^+$-158) with the typical clusters due to bromine isotopes. PBDEs were found in all samples in amounts of 245–67450 ng/g. The concentrations of PBDEs were calculated from the SIM chromatograms by the normal way using the internal standard and a mixture of non-labelled PBDEs (from Dr. Jiwei Hu). The major PBDE congeners observed were pentabromodiphenyl ethers and decabromodiphenyl ether. Additionally, sample R1 contained large amounts of tetra-, hexa- and nonabromodiphenyl ethers. The semiquantitative concentrations of PBDEs are shown in Table 1.

Table 1
Concentrations of PBDEs s in the scrap raw material samples (ng/g)

	R1	R2	R3	R4
TeBDE	300	30	70	50
PeBDE	1500	1500	550	150
HxBDE	650	100	100	20
HpBDE	150	10	30	5
OctaBDE	250	20	30	5
NonaBDE	4600	10	30	5
DecaBDE	60,000	70	250	10
Σ PBDEs	67,450	1740	1060	245

Table 2
PCB concentrations (ng/g) in the scrap raw material samples

	R1	R2	R3	R4
PCB 28	480–14,450	0	0	0–620
PCB 52	350–5120	110–660	0–510	280–1650
PCB 101	550–6110	130–1690	1000–2020	70–770
PCB 138	670–5930	20–1910	840–1640	50–1660
PCB 153	430–3730	90–1350	550–1050	30–1000
PCB 180	299–5580	260–450	210–420	20–280
PCB 105	410–4840	0–1030	400–710	30–850
PCB 118	730–8470	0–2220	870–1580	60–730
PCB 128	160–12,440	185–330	170–440	10–440
PCB 156	90–6670	90–140	90–230	10–220
PCB 209	0–1860	0	0	0
Σ PCBs	4169–75,200	885–9780	4130–8600	560–8220

PBDD/Fs were preliminary screened from the TIC chromatograms by reconstructed ion chromatograms using the values of the molecular ions. All EI mass spectra of PBDDs and PBDFs show a relatively intense M$^+$ ion cluster. In EI/selected ion monitoring (SIM) MS at least three members of this cluster should be monitored (Donnelly et al., 1987, 1989). Direct SIM mode is more sensitive, but only a limited number of ions per injection can be analysed. No PBDFs or PBDDs were observed in these scrap samples.

All samples contained quite high concentrations of PCBs and PCNs. Polychlorinated terphenyls (nona-, deca- and undecachloro-) in high concentrations were observed in some sample fractions. These were observed as large peaks in the TIC chromatograms hiding other peaks of eventually more interesting compounds. No SIM mode analyses were made for PCNs and polychlorinated terphenyls. Concentrations of PCBs in the scrap samples are shown in Table 2.

4. Discussion and conclusions

The present screening analyses show the need for further studies on BFRs in scrap materials to be processed in recycling plants. As well evaluation of the possible ecotoxicological or human risks caused by different BFRs and their transformation products is needed. BFRs and their different transformation products in emissions from metal reclamation processes can be a major source of novel halogenated PBTs to the environment. Different brominated aromatic compounds have been found in ash samples (Sinkkonen et al., 2003) from aluminium recycling plant. Because bromine or any bromine compounds, contrary to chlorine, are not added into the process during the recycling process, the compounds in ash and emission samples are believed to originate from BFRs in the scrap raw materials. Transformation and decomposition of these original compounds probably occur during the reclamation process.

The origin of the high concentrations of PCBs and PCNs in the scrap samples is not known. The scrap material is very heterogeneous being collected from several different places and containing materials and equipment prepared in different countries. High concentrations of PBDEs, especially the very high concentration of DeBDE in sample R1, are supposed to be due to abundant BFR use in plastic and electronic materials.

The amount of waste and scrap (old cars, computers, other electronics, plastics, etc.) produced yearly is a great problem globally. For environmental and economical reasons, there is a need for recycling of many kinds of materials. However, there exists the risk that in the handling and recycling of materials by different methods, there occur some releases of harmful compounds to the environment and appropriate monitoring is needed.

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