Autoshredder and electronic waste as sources of PBDE exposures in California

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Introduction

Levels of polybrominated diphenyl ethers (PBDEs) have been rising in the environment as a result of their increasingly widespread use, their persistence in the environment and their tendency to bioaccumulate in the food web[1]. High levels of PBDEs have been documented in California residents[2,3] and wildlife[3].

In an effort to identify and evaluate major waste streams containing PBDEs, various consumer electronic devices were examined. In addition, a systematic sampling of autoshredder waste was undertaken. Autoshredder waste is the material left after automobiles and appliances (refrigerators, ovens, etc.) are crushed and shredded to recover ferrous and non-ferrous metals. An estimated 300,000 tons of such wastes are generated annually in California[4]. Autoshredder waste streams are known to often exceed regulatory criteria for metals and PCBs. When below those regulatory thresholds, autoshredder wastes are used for daily cover in landfills. No regulation of PBDEs is currently in place.

Consumer electronics also pose a mounting waste handling problem. Heavy metals contained in the circuitry and liquid crystal displays (LCD) of such products may leach out into groundwater after disposal into landfills. Consumer electronics may also contain PBDEs and other brominated flame retardants in their plastic components. In response to these concerns, a study was undertaken to determine the total and extractable concentrations of regulated elements, as well as PBDEs in electronic waste for comparison with hazardous waste criteria. Based partly on this study, California designed a recycling program to divert discarded electronics from landfills[5]

Materials and Methods

Autoshredder waste: Samples were collected from several facilities throughout California. Samples were air dried and sieved through 2 mm sieve and analysed for metals, PCBs and PBDEs.

e-waste: Several electronic product types (computers, cell phones, printers, etc.) were identified, and four devices of each type (various brands and models), were analysed for regulated elements and PBDEs. Devices were dismantled individually, and components classified into millable parts [plastic casings; LCD panels; Cold Cathode Fluorescence Lamps (CCFLs); printed circuit boards (PCBoards) without capacitors or batteries], and non-millable parts (metal frames, wires, batteries). Only millable components were analysed for this study, while the weights of all components (both millable and non-millable were recorded). All components were ground to pass a2mm sieve. Procedural blanks consisting of plastic beads were processed through the grinder in between samples to eliminate carry over. Representative sub-samples were digested using EPA Method 3050 and analysed by ICP-AES (EPA Method 6010). CCFLs were frozen in liquid nitrogen before crushing in a plastic bag (to avoid volatilization and loss of mercury), and analysed by cold vapor atomic absorption. For all analytes, results measured in components were extrapolated to the entire device based on relative weights and with the assumption that non-processed components did not significantly contribute any regulated elements. Triplicate analyses showed satisfactory homogenization of samples, with an average relative standard deviation of 10%.

PBDE analysis: To measure PBDEs, both e-waste and autoshredder samples were extracted in a microwave oven (MARSX-CEM#XM 3086-10 min.;110*C; 200psi; 600w) with dichloromethane:acetone (1:1), concentrated by Kuderna-Danish; cleaned up through silica and alumina columns; solvent exchanged to o-xylene and analysed by dual column (DB5 and 1701) gas chromatography with electron capture detection.

Results and Discussion

Procedural blanks demonstrated the absence of cross contamination during grinding. All electronic devices tested exceeded at least one hazardous waste criterion, mainly lead and copper. Table 1 shows the types of products examined and the elements for which regulatory criteria were exceeded. Average concentrations of ΣPBDEs are also shown.

Figure 1 shows the ΣPBDE content (sum of all individual congeners measured) in the ewaste devices tested. It is noteworthy that different devices have quite different ΣPBDE content (from low ppb to percent levels), probably reflecting different manufacturing practices and year of manufacture. The pattern of individual PBDE congeners varies across products as shown in Figure 2 (computers), Figure 3 (microwaves) and Figure 4 (VCRs). High ppm to percent levels of PBDEs (mostly PBDE 209 but also PBDE 47 and PBDE 99) were measured in autoshredder waste.

PBDEs will be phased out by 2008. At that time, materials containing more than 0.1% of the Penta- and Octa-formulations of PBDEs will be banned, requiring appropriate waste handling. Regulations for handling these types of wastes are being considered.

Acknowledgment/Disclaimer

We thank Charles Corcoran, Chau Nguyentat and Peter Wood of the California Department of Toxic Substances Control for support and guidance. The ideas and opinions expressed herein are those of the authors and do not necessarily reflect the official position of the California Department of Toxic Substances Control.

References

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3 J She, MX Petreas, J Winkler, P Visita, M McKinney, D Kopec. Chemosphere 46:697-707, 2002

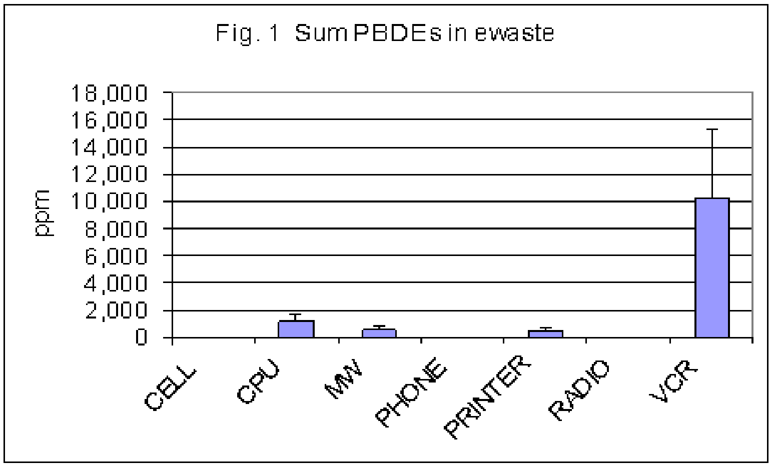
4 California's Automobile Shredder Waste Initiative

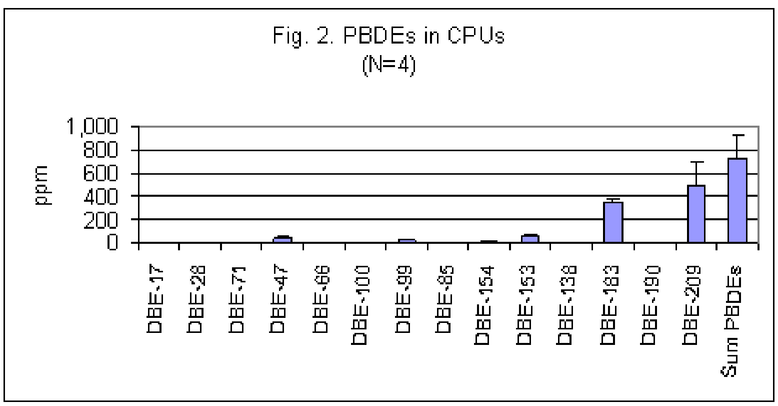
http://www.dtsc.ca.gov/HazardousWaste/HWMP_REP_ASW_draft.pdf

5 SB20 and SB 50 (Sher), The**Electronic** Waste Recycling Act of 2003, http://www.dtsc.ca.gov/HazardousWaste/CRTs/SB20.html

Table 1. Elements exceeding hazardous waste criteria and average PBDE concentrations (ppm) in various products analysed

PRODUCT TYPE	Elements exceeding Regulatory Criteria	ΣPBDEs (ppm)
Microwave Ovens	Pb	480
VCR	Sb, Cu, Pb	10,200
CPU	Sb, Cu, Pb	740
Printer	Cu, Pb, Sb	450
Cell	Sb, Cu, Pb, Cr, Ni	15
Telephone	Cu, Pb, Ni	10
Radio	Cu, Pb, Sb	10





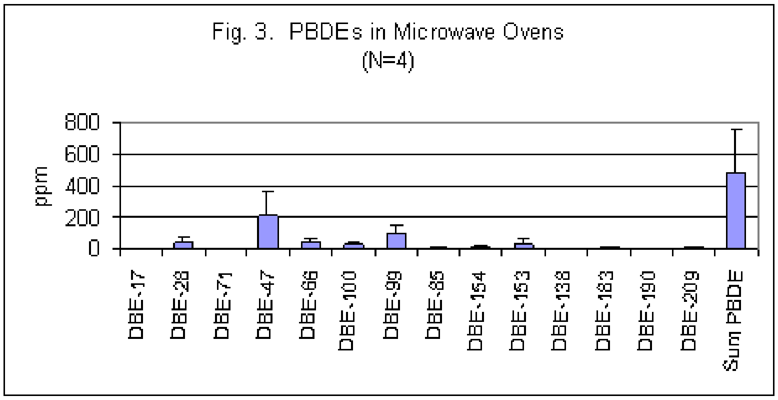


Fig. 3. PBDEs in Microwave Ovens
(N=4)
ppm
800
600
400
200
0
DBE-17
DBE-28
DBE-71
DBE-47
DBE-66
DBE-100
DBE-99
DBE-85
DBE-154
DBE-153
DBE-138
DBE-183
DBE-190
DBE-209
Sum PBDE

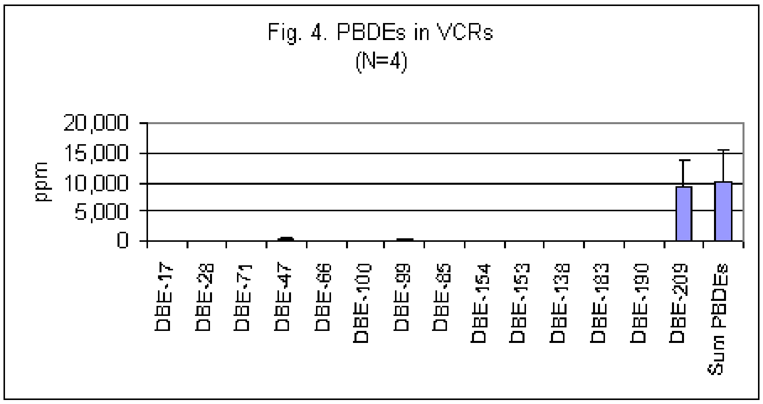


Fig. 4. PBDEs in VCRs
(N=4)
ppm
20,000
15,000
10,000
5,000
0
DBE-17
DBE-28
DBE-71
DBE-47
DBE-66
DBE-100
DBE-99
DBE-85
DBE-154
DBE-153
DBE-138
DBE-183
DBE-190
DBE-209
Sum PBDEs