PBDEs IN CALIFORNIA WASTE STREAMS

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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 physical/chemical properties that increase 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]. No regulation of PBDEs is currently in effect, but in 2006 the penta-BDE and octa-BDE commercial formulations will be phased out of use in new consumer products sold in California.

We identified, sampled and analyzed waste streams known to contain PBDEs, such as e-waste; autoshredder waste and biosolids (wastewater treatment plant sludges) and used information on volumes of these waste streams in an effort to identify and evaluate their relative contributions.

Materials and Methods

e-waste: A 2001 study estimated the volumes of discarded consumer electronics in California at 240,000 metric tons (MT)[4]. 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[5]. Devices were dismantled individually, and components classified into millable parts (plastic casings; LCD panels; Cold Cathode Fluorescence Lamps; printed circuit boards 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 a 2mm sieve. Procedural blanks consisting of plastic beads were processed through the grinder in between samples to eliminate carry over. 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 PBDEs

Autoshredder waste: Autoshredder waste is the material left after automobiles and major appliances (refrigerators, ovens, etc.) are crushed and shredded to recover ferrous and non-ferrous metals. An estimated 300,000 MT of such wastes are generated annually in California[6]. Autoshredder waste streams are known to often exceed regulatory requirements for metals and PCBs. When below those regulatory thresholds, these wastes are applied as alternative daily cover (ADC) in solid waste landfills. Samples were collected from all seven California autoshredder facilities in 2004. Samples were air dried and sieved through 2 mm sieve and analyzed for regulated metals, PCBs and PBDEs.

Effluents and Sludges: Sludge is known to contain PBDEs[7,8]. Approximately 750,000 dry MT of sludge were generated in California in 2005. Of those, about 250,000 dry MT are used for ADC[8]. Effluent and sludge samples were collected in 2005 from three major wastewater treatment plants that discharge into the San Francisco Bay. Effluent and sludge samples (1 L) were collected from each plant, once during the wet season (March 2005) and once during the dry season (August 2005).

PBDE analysis

Representative samples of e-waste and autoshredder waste were extracted in a microwave oven (MARSX-CEM#XM 3086-10 min.;110^{o}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. Triplicate analyses showed satisfactory homogenization of samples, with an average relative standard deviation of 10%.

Sludge and effluent samples were extracted and analysed for 48 PBDE congeners by HRGC-HRMS (in-house SOP based on USEPA Method 1614) by the East Bay Municipal Utility District's Analytical Laboratory.

Results and Discussion

e-waste: All electronic devices tested exceeded at least one hazardous waste criterion, mainly lead and copper. Concentrations of ΣPBDEs ranged from low ppm to percent levels (Figure 1). Concentrations varied by type of consumer electronic product. The congener profile was dominated by BDE-209 in all products.

Autoshredder waste: High ppm levels of PBDEs were measured in autoshredder waste. The congener profile was dominated by BDE-209 (Figure 2). PBDE levels were moderately correlated with PCB levels in the waste, probably reflecting waste handling practices of the various facilities.

Effluents: Table 1 shows the ΣPBDE concentrations (ng/L) in effluent samples from four plants of various capacities. ΣPBDE concentrations peaked as high as 74 ng/L during the wet season (March) when effluent discharge is generally higher. BDE-209 comprised up to 28% of the ΣPBDE mass in effluents. The average load to the San Francisco Bay was 3.7 kg/yr.

Sludges: Table 2 shows the ΣPBDE concentrations (ng/g dry wt) in sludge samples. These levels are within the levels reported for US sludge[9]. ΣPBDE concentrations peaked as high as 6,900 ng/g dry wt during the wet season (March). BDE-209 comprised up to 38% of the ΣPBDE mass in sludges. The average concentration (3,000 ng/g) was multiplied by the total weight of sludge generated (750,000 dry MT) to estimate the total PBDE contained in California sludge.

The relative contributions of the identified waste streams are shown in Fig 3. By far, e-wastes dominate the waste streams examined and waste management approaches should focus on these. Assuming that California uses 10% of the PBDE volume reported for North America (33,100 MT), it is clear that not all PBDEs can be accounted for. Either these estimates need revision or other waste streams remain unidentified. Household solid wastes should also be investigated.

Disclaimer

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.

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Figure 1. Total PBDE concentrations (ppm) in discarded consumer electronics (e-waste)

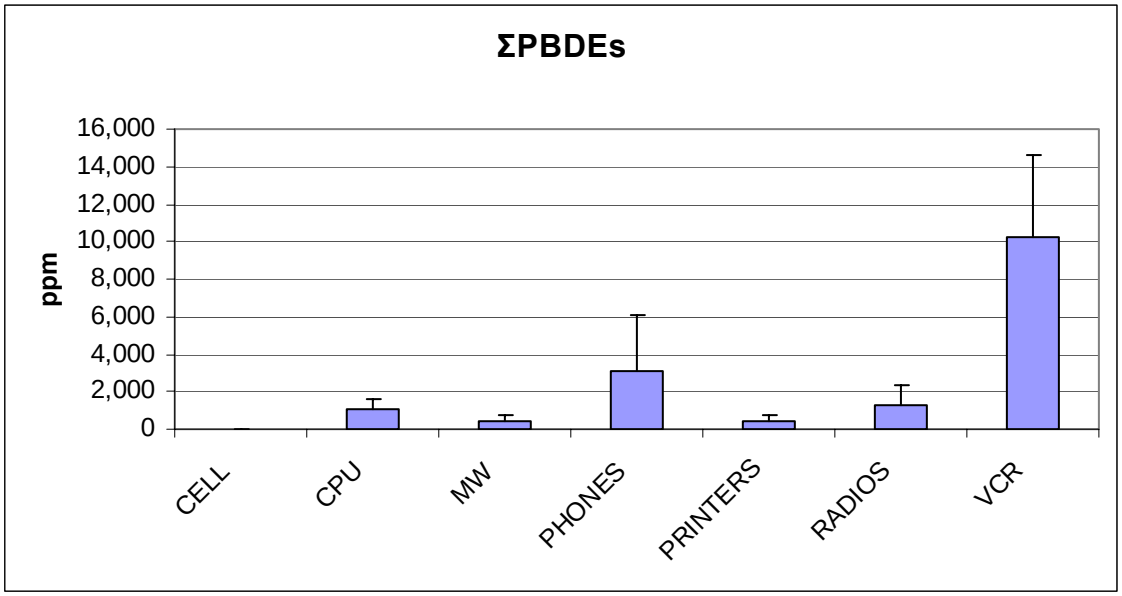

Figure 2 PBDE congener profile in autoshredder waste

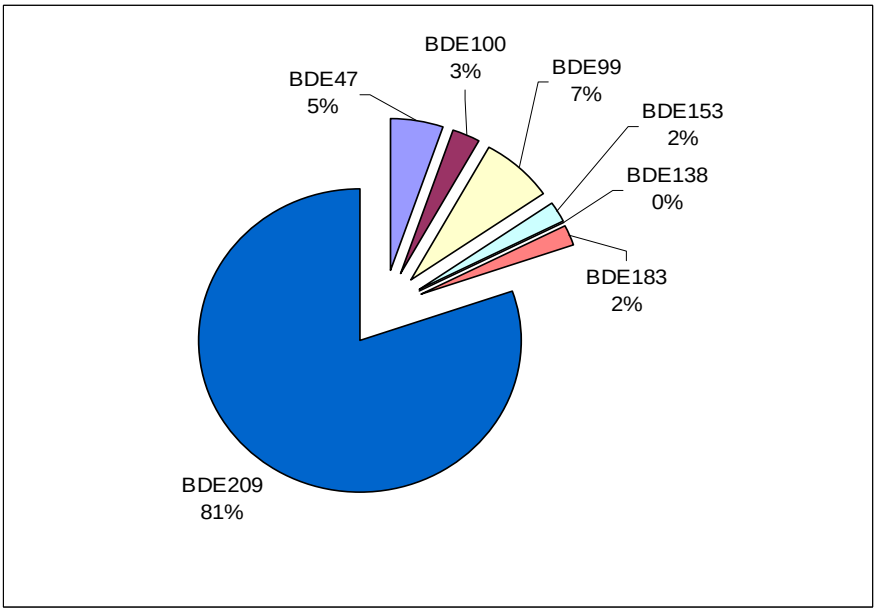

Table 1. PBDEs (ng/L) in Wastewater Treatment Plant Effluents

	Capacity	PBDE Concentrations in Effluent (ng/L)				Annual Load to SF Bay (kg/yr)	
	MG/yr	Mar-05	Aug-05	Mean	%Deca-BDE	Total PBDEs	Deca-BDE
Plant 1	29,200	72.2	59.5	66	15	7.3	1.1
Plant 2	16,826	73.5	51.7	63	14	4	0.6
Plant 3	43,800	16.7	11.9	14	28	2.4	0.7
Plant 4	6,935			29	6	0.9	0.1
Average				43	16	3.7	0.6

Plant 4 data from North (2004)

Table 2. PBDEs (ng/g dry wt) in Wastewater Treatment Plant Sludges

	Capacity	PBDE Concentrations in Sludge (ng/g dry wt)			
	MG/yr	Mar-05	Aug-05	Mean	%Deca-BDE
Plant 1	29,200	6,939	2,816	4,878	32
Plant 2	16,800	1,273	1,814	1,544	38
Plant 3	43,800	1,013	1,871	1,442	31
Plant 4	7,000			3,955	30
Average				2,955	33

Plant 4 data from North (2004)

Figure 3