Behavior and control of brominated flame retardants and polyhalogenated compounds in a municipal bulky waste shredder system

Shin-ichi Sakai[1], Hidetaka Takigami[2], Shin Takahashi[3], Takumi Takasuga[4], Tsuyoshi Hirakawa[5] and Keijiro Tomoda[5]

1 Kyoto University, Environmental Preservation Center, Sakyo-ku, Kyoto, 606-8501, Japan
2 National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Japan
3 Ehime University, Matsuyama, Japan
4 Shimadzu Techno Research Corporation, Kyoto, Japan
5 Towa Kagaku, Hiroshima, Japan

Introduction

Shredder plants for the treatment of end-of-life vehicles and electronic and electrical equipment have been considered potential sources of polyhalogenated compounds (LUA 1997, UNEP 2006). However, the fate and behavior of polyhalogenated organic compounds during the processes of shredding wastes are not well known despite the fact that these processes have been conducted in a wide variety of applications for material recycling and waste volume reduction. In this study, the behavior of polychlorinated and polybrominated compounds, i.e., brominated flame retardants (BFRs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) in flue gas samples were investigated together with a dioxin-like activity measured by the DR-CALUX (Dioxin-Responsive Chemical-Activated LUciferase gene eXpression assay) in a full-scale shredder plant for the treatment of municipal bulky waste. We compared the results with with those of a previous pilot-scale plant study carried out on three different types of waste materials (Takigami et al. 2005). The controllability of the compounds during the currently adopted flue gas treatment was evaluated.

Materials and Methods

For the full-scale plant testing, municipal bulky waste consisting of waste household electrical appliances and waste furniture made of wood, plastics and metals was processed. Figure 1 shows a schematic flow diagram of the full-scale shredder plant. The shredder processes were a hammer shredder and a blade shredder, and wastes were treated at a rate of 20 t/h (hammer shredder) or 2 t/h (blade shredder) during field measurements. The bag filter (BF) and activated carbon (AC) filter were connected in order to treat the raw gas which collected surrounding the hammer shredder and blade shredder. The cooling tank, dehumidification tower, mist separator and AC filter were connected in order to treat and dehumidify the raw gas discharged from the hammer shredder, and steam was injected to prevent explosions.

The target compounds were extracted with toluene in a Soxhlet extractor (solids) and by

liquid-liquid extraction in a separation funnel (liquids). The combined extracts were cleaned up for the determination of PCDD/Fs (4-8 chlorinated), PCBs (dioxinlike PCBs and total PCBs), PBDD/Fs (4-8 brominated), PBDEs (polybrominated diphenyl ethers, 1-10 brominated), TBBPA (tetrabromobisphenol A) and hexabromocyclododecane (HBCD) by individual adsorption chromatography (multilayer silica column and activated carbon column). For analysis of these compounds, an HRGC/HRMS system was used. The presence of dioxin-like compounds was determined using the DR-CALUX assay. To obtain the assay fractions, column chromatography was conducted in a way similar to that used for chemical analysis (PCDD/Fs, PCBs, PBDD/Fs and PBDEs) without adding internal standards. The contribution of the detected PBDD/F and PBDE congeners was estimated based on their analytical concentrations and their CALUX-TEFs (Behnisch et al. 2003).

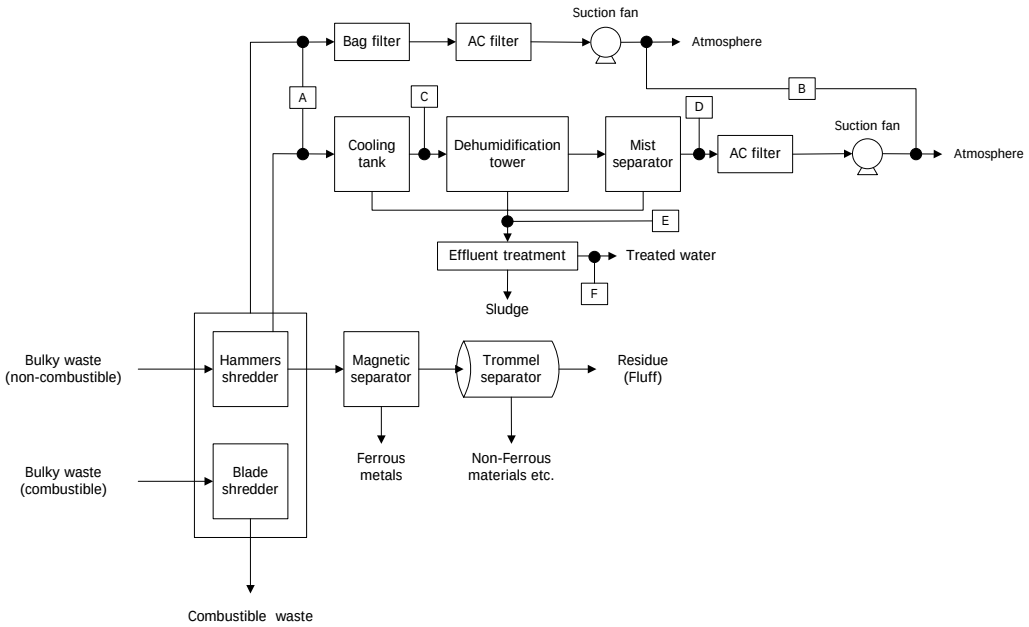

Fig.1 Full-scale plant diagram and sampling points. A, Shredding gas; B, emission gas; C, flue gas after cooling tank; D, flue gas after mist separator; E, effluent; F, treated water.

Results and Discussion

BFRs and chlorinated/brominated organic compounds detected in shredder gas and the gas purified from it are shown in Table 1. When the PBDE levels in full-scale bulky waste shredder gas were compared with those observed in the previous pilot-plant study of three kinds of material, they were found to be in the following order: wood and BFR plastic waste (21,000-160,000 ng/m^{3}N) >> municipal bulky waste in full-scale plant (88-120 ng/m^{3}N) > wood and plastic waste (3-19 ng/m^{3}N), wood waste (2.7-8 ng/m^{3}N). PBDE levels observed in the full-scale shredding of municipal bulky

waste were intermediate between the pilot shredding levels with and without BFRs, but much closer to the levels observed without BFRs. WHO-TEQ and PBDEs-TEQ also tended to levels intermediate between those observed with and without BFRs. The estimated CALUX-TEQ values obtained for the brominated compounds (168-920 pg/m^{3}N, 'PBDD/F'-TEQ and 'PBDE'-TEQ for the raw gas sample from wood and BFR waste in the pilot plant) corresponded approximately to the difference between the experimentally observed CALUX-TEQ (100-900 pg/m^{3}N) and WHO-TEQ (2.9-5.1 pg/m^{3}N). However, in the full-scale bulky waste shredding, CALUX-TEQs were obtained in the range 60-93 pg/m^{3}N, of which PBDE-derived TEQ was only 0.34-0.49 pg/m^{3}N. Characterization of unknown CALUX-TEQs is the subject of future research.

Table 1 Chlorinated/brominated organic compounds and TCDD-equivalent in shredding plants

		Full-scale Plant		Pilot-scale Plant					
		Bulky Waste		Wood Waste		Wood & Plastic Waste		Wood, Plastic & BFR Waste	
		Comminution	Comminution with steam injection	Comminution	Compression	Comminution	Compression	Comminution	Compression
Shredding gas	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	CALUX-TEQ	93	60	14	250	8.9	180	100	900
	WHO-TEQ	0.27	9.7	2.8	2.7	2.2	0.37	2.9	5.1
	PBDD/F-TEQ	-	-	-	-	-	-	76	270
	PBDEs-TEQ	0.49	0.34	0.0065	0.0092	0.011	0.059	92	650
	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	PCDDs	79	190	420	1500	280	390	350	1100
	PCDFs	54	270	160	290	170	92	220	640
	dl-PCBs	2000	63000	350	1400	120	760	250	1500
	S(PCDD/Fs+dl-PCBs)	2100	63000	930	3200	570	1200	820	3200
	PBDDs	ND	ND	ND	ND	ND	ND	170	3300
	PBDFs	130	940	ND	ND	ND	ND	70000	270000
	S(PBDD/Fs)	130	940	ND	ND	ND	ND	70000	270000
	Unit	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N
	PBDEs	88	120	2.7	8	3	19	21000	160000
	TBBPA	21	73	56	89	33	60	760	35000
	HBCD	26	24	-	-	-	-	-	-
Emission gas after shredding gas purification		Full-scale Plant		Pilot-scale Plant					
		Bulky Waste		Wood Waste		Wood & Plastic Waste		Wood, Plastic & BFR Waste	
		Comminution (Emission from gas purification)	Comminution with steam injection (Emission from gas purification)	Comminution (Emission from gas purification)	Compression (Emission from gas purification)	Comminution (Emission from gas purification)	Compression (Emission from gas purification)	Comminution (Emission from gas purification)	Compression (Emission from gas purification)
	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	CALUX-TEQ	ND(<0.5)	27	ND(<2.0)	ND(<2.0)	ND(<2.0)	ND(<2.0)	ND(<2.0)	ND(<2.0)
	WHO-TEQ	ND	1.2	0.00009	0.00009	0.00035	0.00049	0.00031	0.00033
	PBDD/F-TEQ	-	-	-	-	-	-	-	-
	PBDEs-TEQ	0.0018	0.0051	0.0015	0.00027	0.00036	0.00053	0.0024	0.0032
	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	PCDDs	ND	40	ND	0.4	ND	0.22	ND	0.9
	PCDFs	ND	4.2	ND	0.37	0.64	0.41	0.36	0.84
	dl-PCBs	ND	9300	1.2	8.7	4.1	4.9	3.5	3.8
	S(PCDD/Fs+dl-PCBs)	ND	9300	1.2	9.5	4.7	5.5	3.9	5.5
	PBDDs	ND	ND	ND	ND	ND	ND	ND	ND
	PBDFs	ND	100	ND	ND	ND	ND	ND	ND
	S(PBDD/Fs)	ND	100	ND	ND	ND	ND	ND	ND
	Unit	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N
	PBDEs	0.35	18	0.28	0.11	0.077	0.17	0.52	0.76
	TBBPA	0.2	7.5	<2	<2	<2	<2	<2	<2
	HBCD	<0.4	<0.6	-	-	-	-	-	-

Our observations of the behavior of chlorinated/brominated organic compounds during the processes of gas purification revealed that they have a high removal ratio in both full-scale and pilot-scale plants. The full-scale plant operating by comminution with steam injection yielded the following removal ratios during gas purification: PCDDs, 78.9%; PCDFs, 98.4%; dl-PCBs, 85.2%; PBDFs, 89.4%; and PBDEs, 85.0%. The activated carbon filter had a removal effect, as shown in Figure 3. The final emissions were low compared with the reported values for WHO-TEQ (0.0578-1.103 ng/m^{3}N) in shredder plants for the treatment of end-of-life vehicles and electronic and electrical equipment in the Flemish region (Francois et al. 2004). However, the final emissions from the comminution were a little higher than in the pilot-plant experiments, indicating that more careful management of active carbon filters is needed. In the comminution system with steam injection, there was a wastewater stream. Measured values in the effluent were 43 ng/L (13 pg-WHO-TEQ/L) of PCDDs/Fs+dl-PCB, 1.2 ng/L (2.4 pg-TEQ/L) of PBDDs/Fs and 180 ng/L of PBDEs, which are more than the limit of 10 pg-WHO-TEQ/L. Wastewater treatment involving biological processes, chelate adsorption, coagulation or carbon adsorption is essential to achieve removal ratios of 99.8-99.9%.

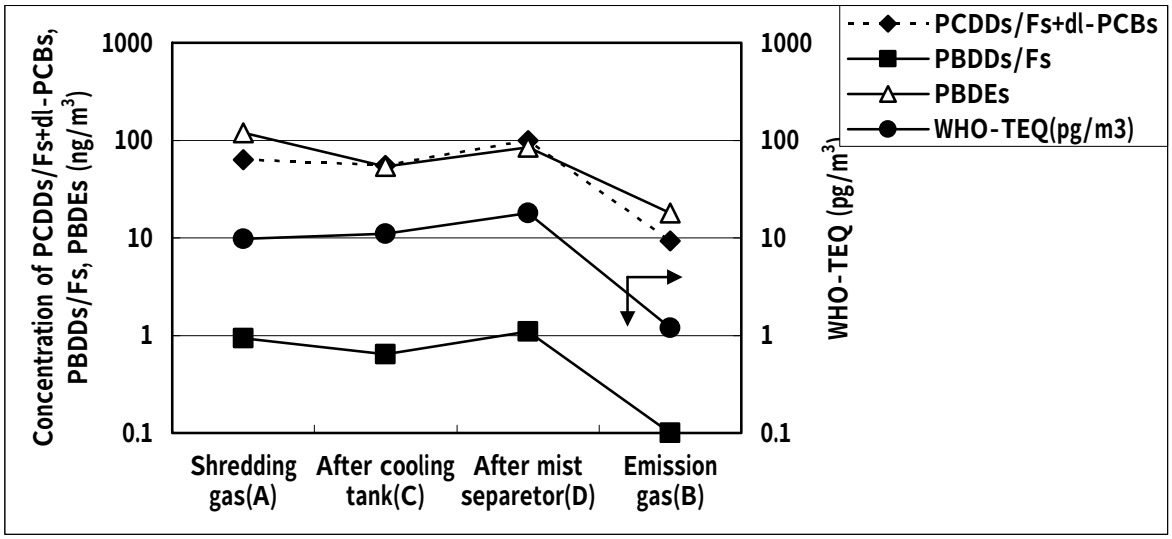

Fig. 2 Behavior of PCDDs/Fs+dl-PCBs, PBDDs/Fs, PBDEs and WHO-TEQ in a flue gas system

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UNEP/POPS/EGBATBEP.2/CRP.37 2006. Section VI.K, Part III Source category (k): Shredder plants for the treatment of end-of-life vehicles