CONCENTRATION DISTRIBUTIONS OF PCBS, CHLOROBENZENES AND METALS BY PARTICLE SIZE OF FLY ASH

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Introduction

Formation of chlorinated aromatic compounds from municipal solid waste incineration (MSWI) is known to occur on the surface of fly ash[1]. Some kinds of metals act as catalysts and have an important role for the formation[2]. To reduce the emission of chlorinated aromatic compounds from MSWI, it is necessary to find the substance inhibiting the formation or destructing them. In this research, to obtain the information more about the relation between chlorinated aromatic compounds and metals, the concentration distributions of PCBs, chlorobenzenes (CBzs) and metals by particle size of MSWI fly ash were investigated.

Materials and Methods

Fly ashes A to H were sampled from electrostatic precipitators (ESP) in eight continuous stoker type municipal solid waste incinerators. Fly ashes A, F and H were sampled from the same ESP. Each fly ash was classified into 4 fractions (over 500μm, 106-500μm,44-106μm and under 44μm) by particle size using a sieving machine.

Before soxhlet extraction, 10 g of a fraction was treated with 200mmol-H^+ HCl for 2 hours. Then, it was filtered under suction over a glass fiber filter and washed 3 times with distilled water. Soxhlet extraction was performed for all samples overnight (approx. 24hr) with 200 ml toluene. Extracts were cleaned up by chromatography on multi-layer silica columns and then were concentrated by a rotary evaporator and nitrogen blowing. All extracts were analyzed using HRGC/LRMS (HP6890/HP5973). A fused silica column (HP-5MS: 60m, 0.25mm i.d., 0.25μm film thickness) was used. D2CBzs to H6CBzs and D2CBs to O8CBs were determined. PCBs isomers were identified by the retention time and the peak pattern for congeners of a reference[3]. ^{13}C-H6CBz and ^{13}C-PCBs (#28, #52, #101, #118, #138) were used as internal standards.

Na, Mg, Al, K, Ca, Ti, Mn, Fe, Cu, Zn, Cd, Sb and Pb were measured using ICP-AES (ICPS-8000: Shimadzu) after 100mg of a fraction was digested with the mixture of 5ml of HNO_3, 2ml of HCl and 3ml of HF using a microwave oven (MDS-2000: CEM corp.). Ni, Cr, Cl, Br and S were measured using X-ray fluorescence analysis (XRF-1700: Shimadzu). Se, Hg and As were measured by instrumental neutron activation adsorption in Kyoto University research reactor. Unburned carbon content was measured by total organic carbon meter (TOC-5000: Shimadzu) after acid treatment.

Results and Discussions

The weight percents, CBzs, PCBs, Co-PCBs and unburned carbon content in each fraction of fly ash by particle size are shown in Table 1. The fraction of over 500μm was mainly consisted of black flakes that were generated by burning paper.

Table 1 The weight percents, CBzs, PCBs, Co-PCBs and unburned carbon content in each fraction of fly ash

	Particle size	Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E	Fly ash F	Fly ash G	Fly ash H
Weight	>500 μm	1.1	12.5	3.2	2.2	5.4	1.2	7.7	3.4
(%)	106-500 μm	40.4	52.4	43.4	32	37.1	30.2	46.9	42.7
	44-106 μm	49.8	25	48.8	39.3	37.9	58	34.7	46.2
	<44 μm	8.7	10.1	4.6	26.5	19.6	10.6	10.7	7.7
	Total	100	100	100	100	100	100	100	100
CBzs	>500 μm	4300	300	1500	3500	1400	10000	1300	1600
(ng/g)	106-500 μm	550	78	510	610	280	900	430	450
	44-106 μm	600	130	380	660	780	830	570	720
	<44 μm	850	240	180	870	650	780	720	1900
	Total	640	130	460	760	600	960	580	730
PCBs	>500 μm	76	18	25	27	28	390	56	190
(ng/g)	106-500 μm	20	9.5	19	19	24	48	27	130
	44-106 μm	26	16	17	31	29	48	40	150
	<44 μm	44	30	18	35	33	29	46	180
	Total	25	14	18	28	28	50	36	150
Co-PCBs	>500 μm	35	4.2	20	32	14	1200	12	150
(pg-TEQ/g	106-500 μm	6.1	6.4	22	30	39	120	14	93
	44-106 μm	27	19	24	71	62	130	37	110
	<44 μm	40	24	10	76	48	65	39	110
	Total	20	11	22	58	48	130	25	100
Unburned	>500 μm	26	6.2	27	38	50	31	45	18
carbon	106-500 μm	1.5	0.91	4.2	4.5	4.6	1.1	2.2	1.4
content	44-106 μm	0.0	0.89	1.7	2.2	2.6	0.45	1.8	2.3
(%)	<44 μm	0.59	0.94	0.86	1.2	2.0	0.29	2.6	5.9
	Total	0.94	1.6	3.6	3.4	5.8	1.0	5.4	2.8

Chlorobenzenes

Total concentration of CBzs in fly ash ranged from 130 to 960ng/g. The concentrations in both fractions of over 500μm and under 44μm were higher than those in other fractions except fly ash C and F. The homologue pattern of CBzs by particle size in fly ash A was shown in Fig.1. The concentrations of higher chlorinated benzenes were higher than those in other homologues. This pattern was commonly observed in all fractions and all fly ash. The amount of CBzs by particle size was calculated by multiplying the concentration of CBzs and weight of the fraction by particle size. The fraction contained the largest amount of CBzs was 44-106μm. Although the weight of fly ash was very small and ranged from 1.1 to 12.5% in the fraction of over 500μm, the ratio of amount in that fraction to total amount increased by 7.5 to 27.8%.

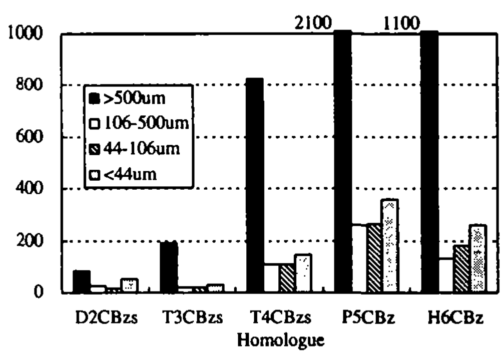

Fig.1 The homologue pattern of CBzs in each fraction of fly ash

PCBs

Total concentrations of PCBs and Co-PCBs ranged from 14 to 150ng/g and 11 to 130 pg-TEQ/g, respectively. The concentrations in both fractions of over 500μm and under 44μm tended to be higher than those in other fractions, but the concentration pattern of PCBs by particle size was more vague than that of CBzs. The homologue pattern of PCBs by particle size in fly ash A was shown in Fig.2. The concentrations of H7CBs and O8CBs were lower than those in other homologues. Although there was no difference by the kinds of fly ash about this pattern, the change of pattern was observed by the particle size. The concentration of lower chlorinated biphenyls in the fraction of over 500μm was higher than that in other fractions. Therefore, the TEQ concentration of Co-PCBs was slightly different from the concentration of PCBs by particle size. The fraction contained the largest amount of PCBs was 44-106μm. Although the ratio of amount in the fraction of over 500μm to total amount increased in comparison to the weight percent of fly ash in that fraction, the increasing rate became small.

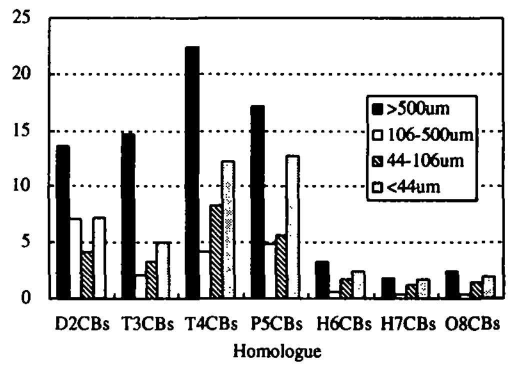

Fig.2 The homologue pattern of PCBs in each fraction of fly ash

The Relationship between CBzs, PCBs, Co-PCBs, Unburned Carbon and Elements

Correlation coefficients between CBzs, PCBs, Co-PCBs unburned carbon and elements were shown in Table 2. In all fractions mutual relationship between CBzs and Co-PCBs was sufficiently estimated. This may indicate that PCB #126, which is most toxic isomer, is formed from CBzs on the surface of fly ash. In the fraction of over 500μm, there was no relation between chlorinated aromatics compounds and elements. In the fractions of 106-500μm and 44-106μm, heavy metals such as Fe, Cu, Zn, Sb and Pb had positive and close relation to CBzs or PCBs. This may be evidence that their metals promote the formation of CBzs or PCBs. On the other hand, Ti had negative relation to CBzs and PCBs so that Ti or Ti compounds was considered to act on the destruction of CBzs and PCBs or the inhibition of their formation. Before this research, unburned carbon content was estimated to have close relation to CBzs and PCBs which were incomplete combustion products, but the correlation coefficients between unburned carbon content and them was great in only a fraction of under 44μm. In future, it is necessary to integrated further information about fly ash such as species of heavy metal or unburned carbon in order to inhibit the formation of chlorinated aromatic compounds on the surface of fly ash.

References

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2. Olie K., Addink R. and Schoonenboom M. (1997) J. Air & Waste Manage. Assoc. **40**, 101-105
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Table2 Correlation coefficients between CBzs, PCBs, Co-PCBs, unburned carbon and elements

	No. of data	CBzs	PCBs	Co-PCBs	No. of data	CBzs	PCBs	Co-PCBs
	>500 μm				106-500 μm			
CBzs (ng/g)	8	1.00			8	1.00		
PCBs (ng/g)	8	0.83	1.00		8	0.19	1.00	
Co-PCBs (pg-TEQ/g)	8	0.91	0.94	1.00	8	0.61	0.70	1.00
Unburned carbon (%)	8	0.12	-0.09	0.00	8	-0.03	-0.33	-0.26
Na (mg/kg)	8	-0.04	0.23	-0.10	8	0.08	0.87	0.60
Mg (mg/kg)	8	-0.02	0.29	0.04	8	0.00	0.47	0.15
Al (mg/kg)	8	0.25	0.11	0.12	8	-0.42	-0.46	-0.62
K (mg/kg)	8	0.03	0.22	-0.08	8	0.19	0.78	0.57
Ca (mg/kg)	8	0.16	0.25	0.21	8	0.13	-0.49	0.09
Ti (mg/kg)	8	-0.01	-0.08	-0.02	8	-0.36	-0.57	-0.66
Mn (mg/kg)	8	-0.15	0.20	-0.11	8	0.03	0.51	0.25
Fe (mg/kg)	8	0.09	0.43	0.17	8	0.14	0.39	0.55
Ni (mg/kg)	8	-0.27	-0.05	-0.21	8	0.00	-0.07	-0.02
Cu (mg/kg)	8	0.22	0.53	0.22	8	0.37	0.81	0.65
Zn (mg/kg)	8	0.27	0.47	0.20	8	0.65	0.64	0.84
Cd (mg/kg)	8	0.15	0.23	0.00	8	0.44	0.50	0.64
Sb (mg/kg)	8	0.10	0.45	0.14	8	0.69	0.37	0.69
Pb (mg/kg)	8	0.16	0.46	0.15	8	0.59	0.79	0.86
Cr (mg/kg)	2	-	-	-	7	-0.65	0.03	-0.12
Se (mg/kg)	2	-	-	-	7	0.03	0.79	0.74
Br (mg/kg)	2	-	-	-	7	0.28	0.90	0.83
Hg (mg/kg)	2	-	-	-	5	0.15	0.37	0.27
As (mg/kg)	2	-	-	-	5	0.41	0.66	0.50
Cl (mg/kg)	8	-0.23	0.17	-0.17	8	0.03	0.79	0.34
S (mg/kg)	8	0.27	0.32	0.09	8	0.05	0.98	0.56
	44-106 μm				<44 μm			
CBzs (ng/g)	8	1.00			8	1.00		
PCBs (ng/g)	8	0.42	1.00		8	0.90	1.00	
Co-PCBs (pg-TEQ/g)	8	0.77	0.64	1.00	8	0.93	0.77	1.00
Unburned carbon (%)	8	0.22	0.34	0.15	8	0.80	0.93	0.67
Na (mg/kg)	8	0.53	0.80	0.50	8	0.72	0.71	0.60
Mg (mg/kg)	8	0.44	0.67	0.40	8	0.59	0.48	0.51
Al (mg/kg)	8	-0.01	-0.09	-0.14	8	0.32	0.13	0.30
K (mg/kg)	8	0.53	0.67	0.42	8	0.65	0.58	0.51
Ca (mg/kg)	8	0.14	-0.54	0.03	8	-0.54	-0.64	-0.35
Ti (mg/kg)	8	-0.57	-0.45	-0.50	8	-0.16	-0.25	-0.12
Mn (mg/kg)	8	0.08	0.40	0.29	8	0.31	0.27	0.25
Fe (mg/kg)	8	0.66	0.56	0.68	8	0.63	0.49	0.56
Ni (mg/kg)	8	0.54	0.24	0.17	8	-0.14	-0.09	-0.08
Cu (mg/kg)	8	0.56	0.66	0.50	8	0.66	0.50	0.53
Zn (mg/kg)	8	0.59	0.55	0.68	8	0.42	0.27	0.38
Cd (mg/kg)	8	0.23	0.08	0.29	8	-0.09	-0.16	0.01
Sb (mg/kg)	8	0.60	0.44	0.56	8	0.37	0.28	0.31
Pb (mg/kg)	8	0.74	0.61	0.72	8	0.50	0.29	0.47
Cr (mg/kg)	7	-0.63	0.00	-0.20	7	-0.17	-0.08	-0.07
Se (mg/kg)	6	-0.07	0.25	-0.13	7	0.11	0.13	0.05
Br (mg/kg)	7	0.58	0.78	0.61	7	0.67	0.75	0.54
Hg (mg/kg)	5	0.13	0.73	0.76	5	0.98	0.98	0.86
As (mg/kg)	5	0.67	0.64	0.41	4	0.40	0.14	0.23
Cl (mg/kg)	8	-0.45	0.38	-0.27	8	-0.17	0.13	-0.22
S (mg/kg)	8	0.67	0.43	0.58	8	0.47	0.24	0.40