Supporting Information (SI)

Influence of Cu, Fe, Pb and Zn Chlorides and Oxides on Formation of Chlorinated Aromatic Compounds in MSWI Fly Ash

Takashi Fujimori^{1}, Masaki Takaoka¹, Nobuo Takeda²*

1. Department of Urban and Environmental Engineering, Graduate School of Engineering, Kyoto
University, Katsura, Nisikyo-ku, 615-8540, Kyoto, Japan

2. Eco-Technology Research Center, Ritsumeikan University, Noji Higashi 1, 1-1 Kusatsu, 525-8577,
Shiga, Japan

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Materials and Method

Real and Model Fly Ashes

Five real fly ashes were collected from the inlets or outlets of electrostatic precipitators and bag filters, involving no lime injection, at four stoker-type MSWIs in Japan.

Model fly ash was prepared from activated carbon (Shirasagi palm shell, 20-48 mesh; Takeda Pharmaceutical Co., Ltd., Osaka). Any organic compounds were removed by heating at 500°C for 60 min under a stream of 100 % nitrogen gas (100 mL/min). The product is referred to as “AC” in this paper. The model fly ash was admixed with different metal species by grinding in a mortar for about 10 min in the proportions: AC (3.0 wt%), potassium chloride (KCl; 10 wt% Cl), metal compound (0.2 wt% metal), and silicon dioxide (SiO₂; remainder). The percentages of carbon, metal, and chlorine in each model fly ash mixture were determined by the procedure used in real fly ash, as described in our earlier study (14). We ensured that the same amount of each metal (Cu, Fe, Pb and Zn) was present in each of our model fly ashes, to allow a direct comparison of their relative influences. The metal percentage used, 0.2 wt%, is that of mean value of Cu in four kinds of real fly ashes. A blank model fly ash (Blank) without any metal compound was prepared from a mixture of AC, KCl, and SiO₂. The metal species used were CuCl₂·2H₂O (97% pure); Cu₂(OH)₃Cl in the mineral form atacamite (high purity; Nichika Corp., Kyoto); CuO (97.5%); FeCl₃·6H₂O (99%); FeCl₂·4H₂O (>99%); Fe₂O₃ (95%); PbCl₂ (99%); PbO (99%); ZnCl₂ (98%); and ZnO (99%). All of these metallic compounds, except Cu₂(OH)₃Cl, were purchased from Nacalai Tesque Inc., Kyoto, Japan. Molar percentages of Cu, Fe, Pb and Zn in each model fly ash were 0.06, 0.07, 0.02 and 0.06 mol%, respectively.

Detection of Chlorinated Organic Compounds in Real and Model Fly Ashes

In our earlier study, the concentrations of PCDDs and PCDFs in real fly ash were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (17). In the current work, PCBs and CBzs were analyzed by HRGC/low-resolution MS (HP-6890/HP-5973). Sample

pretreatment for the determination of chlorinated aromatic compounds was according to Japanese Industrial Standards (JIS) K 0311 and 0312.

The experimental heating procedure is shown in Fig. S1. We placed 5 g of model fly ash into a quartz boat contained within a quartz tube (120 cm × 4 cm internal diameter), which was then placed in a preheated electronic furnace at 300°C for 30 min under a flow of 10% oxygen/90% nitrogen delivered at 50 mL/min, to simulate the post-combustion zone of a MSWI. After heating, the concentrations of chlorinated aromatic compounds in the model fly ash residue and in the gas phase collected in an impinger containing 100 ml of toluene were analyzed separately. For each heating experiment, reproducible analyses of the PCBs and CBzs were duplicated ($n = 2$). Concentrations of PCBs and CBzs as shown in Table S1 and S2 are mean values, respectively. The concentrations of PCDDs and PCDFs in a model fly ash containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were measured three times ($n = 3$) to confirm reproducibility. The concentrations with standard deviations of chlorinated aromatic compounds from the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ model fly ash were (ng/g ash): PCDDs, $25,000 \pm 15,000$; PCDFs, $21,000 \pm 6,400$; PCBs, $1,400 \pm 150$; and CBzs, $31,000 \pm 3,200$. These concentrations of PCDFs, PCBs and CBzs are of the same order as those from a model fly ash of the similar composition reported by Stieglitz et al. (S1), confirming the correctness of our analytical procedures. Thereafter, concentrations of PCDDs and PCDFs in MSWI fly ashes and model fly ashes containing admixed metallic compounds, except $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, were measured only once ($n = 1$).

Principal Component Analysis

To combine the different information concerning the concentrations of chlorinated aromatic compounds, we analyzed our data by principal component analysis (PCA), using the procedures shown in Fig. S4. The data sets for each of the PCDDs, PCDFs, PCBs and CBzs were rescaled by the common logarithm and standardized procedure of equation (2) (mean = 0, variance = 1). The standardized data are referred to as $[\text{PCDDs}]_i$, $[\text{PCDFs}]_i$, $[\text{PCBs}]_i$ and $[\text{CBzs}]_i$, where i refers to the metallic compound. The correlation matrix R for each of these variates was calculated, and the eigenvalue and eigenvector of each matrix R were determined. The contribution ratio is defined as the ratio of an eigenvalue divided by the sum of eigenvalues. In this study, the contribution ratio was 95% for the first principal component Z_1 , implying that most rare data concerning each chlorinated aromatic compound can be explained by one component, Z_1 . Weighting coefficients of each variate were calculated from the eigenvectors. Using the weighting coefficients, the score of the first principal component Z_1 was calculated from the correlation matrix R as:

$$Z_1 = 0.50 \times [\text{PCDDs}]_i + 0.50 \times [\text{PCDDs}]_i + 0.50 \times [\text{PCBs}]_i + 0.50 \times [\text{CBzs}]_i,$$

$$\text{contribution ratio} = 95\%.$$

The Z_1 score is representative in combining information of rare data and expressing “total” amounts of chlorinated aromatic compounds via each weighting coefficient. The total amount of chlorinated aromatic compounds was ordered for each metallic compound (i) by the Z_1 score.

Hierarchical Cluster Analysis by Ward's Method

The hierarchical cluster analysis of Ward allows for the square sum of data in a cluster to be minimized (20) (see text reference).

In brief, a data set consisting of p maps, each of which has q grid points, can be represented by p points in a q -dimensional Euclidian space. Vector $\mathbf{x}_a$ and $\mathbf{x}_b$ are

$$\mathbf{x}_a = {}^t(x_{1a}, x_{2a}, \dots, x_{pa}), \mathbf{x}_b = {}^t(x_{1b}, x_{2b}, \dots, x_{pb}).$$

The measure of the similarity between a and b is the Euclidian root-mean-square distance d between $\mathbf{x}_a$ and $\mathbf{x}_b$

$$d_{ab} = \{\sum_i (x_{ia} - x_{ib})^2\}^{1/2}.$$

The distances can be greatly affected by differences in scale among the dimensions from which the distances are computed. Therefore, we standardized each dataset by equation (2).

Table S1. Concentrations (ng/g) of PCDDs, PCDFs, PCBs and CBzs in residues of heated model fly ashes at 300 °C for 30 min under 50 mL/min of 10% oxygen gas (balance of nitrogen gas) stream. $n(\text{Cl})$ is average number of chlorine.

	ng/g	CuCl ₂ ·2H ₂ O	Cu ₂ (OH) ₃ Cl	FeCl ₃ ·6H ₂ O	FeCl ₂ ·4H ₂ O	CuO	Fe ₂ O ₃	Blank	ZnCl ₂	PbCl ₂	ZnO	PbO
PCDDs	T4	29	68	83	68	37	4	1.8	6.3	3.8	0.11	0.045
	P5	63	230	250	98	21	1.5	1.4	1.7	1.2	0.0041	0.022
	H6	1200	2000	830	180	6.7	0.99	1.5	0.42	0.38	0.047	0.04
	H7	4700	3800	960	120	2.2	0.39	0.63	0.17	0.35	0.055	0.032
	O8	19000	13000	730	75	1	0.28	0.78	0.2	1.2	0.18	0.072
PCDFs	T4	140	440	63	19	9.7	0.15	0.17	0.54	0.39	0.079	0.034
	P5	880	750	230	52	7.9	0.068	0.12	0.29	0.32	0.042	0.017
	H6	2200	1700	610	150	6.9	0.051	0.13	0.22	0.35	0.047	0.026
	H7	5100	3500	1000	270	6.1	0.053	0.17	0.16	0.41	0.074	0.033
	O8	12000	7900	1500	420	4.8	0.072	0.3	0.15	0.79	0.15	0.055
PCBs	D2	5.4	8.1	9.2	3	2.1	2.1	2.3	1.2	1.6	1.1	1.5
	T3	42	38	38	13	6.3	10	12	11	8.3	5.9	9.8
	T4	420	390	140	41	8.8	6	3.5	2.7	16	2.4	1.5
	P5	210	78	24	6.9	2.9	1.2	1.3	2.4	7.7	0.78	2.9
	H6	190	130	33	7.2	2.5	1.4	0.78	0.38	5	0.77	3.3
	H7	260	190	24	6.9	0.52	0.66	0.52	0.33	0.58	0.35	0.33
	O8	300	190	19	6.2	0.13	0.32	0.2	0.13	0.29	0.04	0.13
CBzs	D2	1400	2300	3900	530	78	1000	410	120	70	44	56
	T3	4100	3200	1300	340	160	150	81	16	25	8.9	9.4
	T4	10000	7800	4500	1300	49	31	10	9	11	1.7	4.8
	P5	7500	5000	4500	1400	57	17	5.1	12	17	1.7	6
	H6	7900	5600	2600	1100	29	10	4.8	9.3	40	1.5	4
Sum	PCDDs	25000	19000	2900	540	68	7.2	6.1	8.8	6.9	0.40	0.21
	PCDFs	21000	14000	3400	910	35	0.39	0.89	1.4	2.3	0.39	0.17
	PCBs	1400	1000	290	84	23	22	21	18	40	11	20
	CBzs	31000	24000	17000	4700	370	1200	510	170	160	58	80
$n(\text{Cl})$	PCDDs	7.7	7.5	6.6	5.9	4.6	4.7	5.4	4.4	4.9	6.2	6.1
	PCDFs	7.3	7.1	7.0	7.0	5.5	5.4	6.1	5.2	6.2	6.2	6.1
	PCBs	5.5	5.3	4.4	4.3	3.8	3.5	3.3	3.4	4.1	3.5	3.7
	CBzs	4.3	4.1	3.7	4.2	3.2	2.2	2.2	2.4	3.2	2.3	2.5

Table S2. Concentrations (ng/g) of PCDDs, PCDFs, PCBs and CBzs in toluene trap in impinger (Ref. Figure S1) after heated model fly ashes at 300 °C for 30 min under 50 mL/min of 10% oxygen gas (balance of nitrogen gas) stream.

	ng/g	CuCl ₂ ·2H ₂ O	Cu ₂ (OH) ₃ Cl	FeCl ₃ ·6H ₂ O	FeCl ₂ ·4H ₂ O	CuO	Fe ₂ O ₃	Blank	ZnCl ₂	PbCl ₂	ZnO	PbO
PCDDs	T4	0.48	0.026	0.018	0.022	0.36	0.020	0.0096	0.0064	0.0022	0.0038	0.0026
	P5	0.32	0.015	0.012	0.017	0.21	0.012	0.0066	0.0044	0.0014	0.0034	0.0016
	H6	0.37	0.017	0.014	0.024	0.24	0.013	0.012	0.0064	0.0030	0.0072	0.0028
	H7	0.40	0.028	0.011	0.016	0.50	0.009	0.022	0.0060	0.0048	0.011	0.0032
	O8	3.0	0.20	0.050	0.030	10	0.040	0.17	0.040	0.030	0.14	0.016
PCDFs	T4	0.28	0.013	0.0046	0.0060	0.20	0.004	0.0050	0.0024	0.0022	0.16	0.0024
	P5	0.35	0.0074	0.0060	0.0070	0.16	0.005	0.0070	0.0026	0.0012	0.0024	0.0018
	H6	0.45	0.016	0.010	0.011	0.29	0.008	0.014	0.0048	0.0024	0.0044	0.0030
	H7	0.83	0.064	0.019	0.016	1.2	0.015	0.034	0.0098	0.0064	0.0090	0.0066
	O8	5.0	0.12	0.034	0.022	12	0.028	0.092	0.016	0.014	0.034	0.0080
PCBs	D2	1.1	1.0	0.58	0.25	0.025	0.45	0.13	0.080	1.0	0.066	0.11
	T3	0.59	0.21	0.63	0.19	0.023	0.39	1.4	0.22	1.2	0.38	0.57
	T4	0.77	0.35	0.63	0.14	0.058	0.52	3.9	0.67	2.0	0.24	0.95
	P5	0.2	0.37	0.63	0.10	0.029	0.10	2.2	0.25	0.70	0.42	0.34
	H6	0.28	0.37	0.051	0.069	0.98	0.073	2.1	0.31	0.98	0.24	0.31
	H7	0.45	0.40	0.081	nd	nd	nd	1.1	0.26	0.79	0.34	0.18
	O8	0.53	0.60	0.11	nd	nd	0.022	0.83	1.0	0.63	0.14	2.7
CBzs	D2	2800	1400	11000	540	100	140	36	18	15	18	28
	T3	850	440	440	43	20	32	2.8	2.8	1.8	2.7	4.0
	T4	650	260	120	16	1.2	7.3	0.58	0.89	1.3	0.90	0.90
	P5	300	130	10	7.2	0.53	3.2	3.5	1.3	1.3	2.2	1.6
	H6	84	70	1.5	8.8	0.30	1.5	13	0.48	1.1	1.2	2.7
Sum	PCDDs	4.6	0.29	0.11	0.11	11	0.094	0.22	0.063	0.041	0.17	0.026
	PCDFs	6.9	0.22	0.074	0.062	14	0.060	0.15	0.036	0.026	0.21	0.022
	PCBs	3.9	3.3	2.7	0.75	1.1	1.6	12	2.8	7.3	1.8	5.2
	CBzs	4700	2300	12000	620	120	180	56	24	21	25	37

nd: not detected

Table S3. Order of concentration and average number of chlorines [$n(\text{Cl})$] for PCDDs, PCDFs, PCBs and CBzs in each group.

Group	Metal Cmpd.	PCDDs ($\text{Cl}_4\text{-Cl}_8$)		PCDFs ($\text{Cl}_4\text{-Cl}_8$)		PCBs ($\text{Cl}_2\text{-Cl}_8$)		CBzs ($\text{Cl}_2\text{-Cl}_6$)	
		Conc. ng/g	$n(\text{Cl})$	Conc. ng/g	$n(\text{Cl})$	Conc. ng/g	$n(\text{Cl})$	Conc. ng/g	$n(\text{Cl})$
A	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	10^4	7.5–7.7	10^4	7.1–7.3	10^3	5.3–5.5	10^4	4.1–4.3
	$\text{Cu}_2(\text{OH})_3\text{Cl}$								
B	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$10^2\text{--}10^3$	5.9–6.6	$10^2\text{--}10^3$	7.0	$10^1\text{--}10^2$	4.3–4.4	$10^3\text{--}10^4$	3.7–4.2
	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$								
C	CuO	$10^0\text{--}10^1$	4.6–4.9	$10^0\text{--}10^1$	5.5–6.2	10^1	3.8–4.1	10^2	3.2
	PbCl_2								
D	Fe_2O_3	10^0	4.4–5.4	$10^{-1}\text{--}10^0$	5.2–6.1	10^1	3.3–3.5	$10^2\text{--}10^3$	2.2–2.4
	Blank								
	ZnCl_2								
E	ZnO	10^{-1}	6.1–6.2	10^{-1}	6.1–6.2	10^1	3.5–3.7	10^1	2.3–2.5
	PbO								

Table S4. Chlorinated aromatic compounds in real fly ash from general municipal solid waste incinerators. The data for PCDDs and PCDFs ($n = 39$) are from our previous study (17) and the literature (22-30). The data for PCBs and CBzs ($n = 5$) were determined in the present study.

n = 39 (fly ashes) from our previous study and 9 literatures								n = 5 (fly ashes) in this study							
		Mean		SE		Min-Max				Mean		SE		Min-Max	
		ng/g	%	ng/g	%	ng/g	%			ng/g	%	ng/g	%	ng/g	%
PCDDs	T4	23	6	7	0.5	0.1-200	1-11	PCBs	D2	4.8	14	2.3	1.3	1.3-15	12-19
	P5	62	13	17	1.1	0.9-450	3-31		T3	5.3	19	1.8	3.1	1.7-13	9.9-29
	H6	140	23	43	1.3	1.4-1100	9-37		T4	8.5	24	4.4	1.1	2.4-28	21-27
	H7	140	28	37	1.3	1.8-1000	12-47		P5	5.9	14	3.4	0.7	1.3-21	12-16
	O8	120	29	30	2.2	1.6-730	9-61		H6	5.1	12	3.1	1.1	1.2-19	8-15
									H7	4.5	9	3.0	1.4	0.9-18	6-14
		Mean		SE		Min-Max				Mean		SE		Min-Max	
n(Cl)		6.5		0.05		6.1-7.1				n(Cl)		4.2		0.14	
		Mean		SE		Min-Max				Mean		SE		Min-Max	
PCDFs	T4	68	26	10	1.9	5.9-250	5-45	CBzs	D2	45	12	15	4.9	19-110	1-29
	P5	99	28	19	1.1	5.1-500	12-39		T3	64	10	20	2.1	11-130	4-16
	H6	100	23	21	0.9	4.5-520	12-35		T4	180	23	82	2.6	32-530	16-31
	H7	74	15	17	1.2	1.4-290	4-35		P5	350	31	210	2.4	34-1300	25-38
	O8	46	7	15	1.2	0.3-400	1-29		H6	340	24	240	5.1	28-1400	13-41
		Mean		SE		Min-Max				Mean		SE		Min-Max	
n(Cl)		5.4		0.07		4.8-6.4				n(Cl)		4.2		0.23	
		Mean		SE		Min-Max				Mean		SE		Min-Max	
PCDD/PCDF ratio		1.1		0.18		0.2-4.4		PCBs/CBzs ratio		0.049		0.0098		0.017-0.081	
Region	Europe: Czech, Germany, Sweden, Switzerland														
	Asia: Japan, Taiwan														
	North America: United States of America														
Year	From 1987 to 2008														
Point	Inlet or outlet of Electrostatic precipitator														
	Bag, textile, or fabric filter														
	Cooler zone														
	Economizer														
Temperature	60 - 400 °C														

Point	Inlet or outlet of Electrostatic precipitator				
	Bag filter with or without sprayed activated carbon				
SE: standard error

Figure S1. Heating device.

Figure S2. PCDD/PCDF ratio of model fly ashes added various metallic compounds. PCDD/PCDF ratio of MSWI fly ash is 1.1 ± 0.18 (mean $\pm$ standard error).

Figure S3. PCBs/CBzs ratio of model fly ashes added various metallic compounds. PCBs/CBzs ratio of MSWI fly ash is 0.049 ± 0.0098 (mean $\pm$ standard error).

Figure S4. Procedure of principal component analysis (PCA). Score $Z_1 = 0.50 \times [\text{PCDDs}]_i + 0.50 \times [\text{PCDFs}]_i + 0.50 \times [\text{PCBs}]_i + 0.50 \times [\text{CBzs}]_i$ (contribution rate = 95%).

Supporting References

S1. Stieglitz, L.; Zwick, G.; Beck, J.; Bautz, H.; Roth, W. Carbonaceous particles in fly ash -a source for the de-novo-synthesis of organochlorocompounds. *Chemosphere* **1989**, *19*, 283-290.