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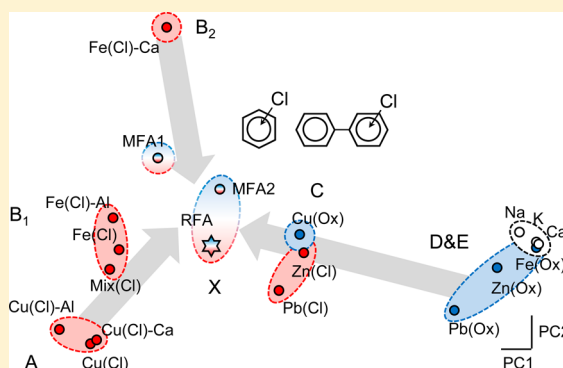
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Coexistence of Cu, Fe, Pb, and Zn Oxides and Chlorides as a Determinant of Chlorinated Aromatics Generation in Municipal Solid Waste Incinerator Fly Ash

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ABSTRACT: We investigated chemical determinants of the generation of chlorinated aromatic compounds (aromatic-Cl)s, such as polychlorinated biphenyls (PCBs) and chlorobenzenes (CBzs), in fly ash from municipal solid waste incineration. The influences of the following on aromatic-Cl)s formation in model fly ash (MFA) were systematically examined quantitatively and statistically: (i) inorganic chlorides (KCl, NaCl, CaCl₂), (ii) base materials (SiO₂, Al₂O₃, CaCO₃), (iii) metal oxides (CuO, Fe₂O₃, PbO, ZnO), (iv) metal chlorides (CuCl₂, FeCl₃, PbCl₂, ZnCl₂), and (v) “coexisting multi-models.” On the basis of aromatic-Cl)s concentrations, the $\sum \text{CBzs} / \sum \text{PCBs}$ ratio, and the similarity between distribution patterns, MFAs were categorized into six groups. The results and analysis indicated that the formation of aromatic-Cl)s depended strongly on the “coexistence condition”, namely multimodels composed of not only metal chlorides, but also of metal oxides. The precise replication of metal chloride to oxide ratios, such as the precise ratios of Cu-, Fe-, Pb-, and Zn-chlorides and oxides, may be an essential factor in changing the thermochemical formation patterns of aromatic-Cl)s. Although CuCl₂ acted as a promoter of aromatic-Cl)s generation, statistical analyses implied that FeCl₃ also largely influenced the generation of aromatic-Cl)s under mixture conditions. Various additional components of fly ash were also comprehensively analyzed.



INTRODUCTION

Anthropogenic thermal processes may unintentionally emit toxic chlorinated aromatic compounds (aromatic-Cl)s such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and benzenes (CBzs) into the environment. Since the late 1970s, municipal solid waste incineration (MSWI) has been a well-known anthropogenic source of PCDD/Fs.^{1,2} In particular, PCDD/Fs concentrate in the fly ash collected on the filter or inside the wall in the postcombustion zone.^{3,4} Unburned carbon, chlorine, oxygen gas, and trace metal compounds are key elements in generating aromatic-Cl)s.^{2,4–7}

Various researchers have studied promotion effects to generate aromatic-Cl)s by copper (Cu)^{8–15} and iron (Fe).^{16–20} Zinc (Zn) and lead (Pb) have been found in MSWI fly ash as major heavy metals^{21–24} and are related to the formation of aromatic-Cl)s.^{24–35} Specifically, Cu compounds have been studied as strong catalytic promoters (oxychlorination catalyst¹³) or sources of direct chlorination¹⁴ in the formation of PCDD/Fs,^{8–10,12,30} total/volatile organic chlorine,¹¹ PCBs,^{15,30} and CBzs^{15,30} in MSWI fly ash. In addition, Fe compounds also have been studied as catalytic surface promoters^{16,19} or oxychlorination catalysts²⁰ in the formation of PCDD/Fs,^{17,18,30} PCBs,³⁰ and CBzs^{19,30} in MSWI fly ash. Previously, we reported that trace Cu, Fe, Pb, and Zn chlorides and oxides in the solid phase influenced the formation of PCDDs, PCDFs, PCBs, and CBzs

in the postcombustion zone of MSWI by the “single” addition of metal compounds into a model sample.³⁰ However, a single addition experiment cannot replicate real MSWI fly ash, which is composed of multiple (or “multi”) metal compounds. Multivariate analysis techniques have aided in filling the gaps between single and multisystems, and Oberg et al.^{36–38} conducted a sequence of fly ash experiments using various additive conditions of multimetal chlorides or oxides. However, to date, there has been no study of metal chloride and oxide ratios, or their chemical forms, using a multiaddition model for real MSWI fly ash.

Synchrotron X-ray spectroscopic studies have revealed the ratios of metal chemical forms in various real MSWI fly ashes.^{13,24,34,35,39–42} If we perform synchrotron X-ray spectroscopic analyses of various metals (e.g., Cu, Fe, Pb, and Zn) in real MSWI fly ash, we obtain useful information to prepare a multimodel sample with replicated ratios of metal chlorides and oxides. By comparing the concentrations and distribution patterns of aromatic-Cl)s in real MSWI fly ash with the multimodel, we can better understand the contribution and role

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Table 1. Sample Component and Concentration, Σ CBzs to Σ PCBs Ratio, and Similarity of Distribution Patterns of the Residual Model Compared with RFA after Heating at 300 °C

sample name		component	concentration (ng/g)		Σ CB _{Zs} / Σ PCBs	distribution pattern			group name
			Σ CBzs	Σ PCBs		CBzs	PCBs	CBzs&PCBs	
No Metal									
K ^a	AC (3%), SiO ₂ (rest), KCl (10%Cl)	20	18	1.1		H			D&E
Na	AC (3%), SiO ₂ (rest), NaCl (10%Cl)	14	19	0.75		H			D&E
Ca	AC (3%), SiO ₂ (rest), CaCl ₂ (10%Cl)	17	25	0.68		H			D&E
Metal Chloride									
Cu(Cl) ^a	AC (3%), SiO ₂ (rest), KCl (10%Cl), CuCl ₂ (0.2%Cu)	15000	1200	13	H		M		A
Cu(Cl)-Al	AC (3%), Al ₂ O ₃ (rest), KCl (10%Cl), CuCl ₂ (0.2%Cu)	14000	940	15	H		M		A
Cu(Cl)-Ca	AC (3%), CaCO ₃ (rest), KCl (10%Cl), CuCl ₂ (0.2%Cu)	7800	350	23	H		M		A
Fe(Cl) ^a	AC (3%), SiO ₂ (rest), KCl (10%Cl), FeCl ₃ (0.5%Fe)	12000	210	57	H		M		B ₁
Fe(Cl)-Al	AC (3%), Al ₂ O ₃ (rest), KCl (10%Cl), FeCl ₃ (0.5%Fe)	2600	50	53	H		M		B ₁
Fe(Cl)-Ca	AC (3%), CaCO ₃ (rest), KCl (10%Cl), FeCl ₃ (0.5%Fe)	320	11	29	M	H	M		B ₂
Pb(Cl) ^b	AC (3%), SiO ₂ (rest), KCl (10%Cl), PbCl ₂ (1.0%Pb)	320	37	8.7	H	M	H		C
Zn(Cl) ^c	AC (3%), SiO ₂ (rest), KCl (10%Cl), ZnCl ₂ (2.0%Zn)	370	14	26	H	H	H		C
Metal Oxide									
Cu(Ox)	AC (3%), SiO ₂ (rest), KCl (10%Cl), CuO (0.2%Cu)	380	23	16	H	H	H		C
Fe(Ox)	AC (3%), SiO ₂ (rest), KCl (10%Cl), Fe ₂ O ₃ (0.5%Fe)	13	11	1.2		H			D&E
Pb(Ox) ^d	AC (3%), SiO ₂ (rest), KCl (10%Cl), PbO (0.2%Pb)	80	20	4.1		M			D&E
Zn(Ox)	AC (3%), SiO ₂ (rest), KCl (10%Cl), ZnO (2.0%Zn)	12	11	1.0		H			D&E
Coexistence									
Mix(Cl)	AC (3%), SiO ₂ (rest), KCl (10%Cl), CuCl ₂ (0.2%Cu), FeCl ₃ (0.5%Fe), PbCl ₂ (1.0%Pb), ZnCl ₂ (2.0%Zn)	9100	230	40	H		M		B ₁
MFA1	AC (3%), SiO ₂ +Al ₂ O ₃ +CaCO ₃ matrix (1:1:1, rest), KCl (3.3%Cl), NaCl (3.3%Cl), CaCl ₂ (3.3%Cl), CuCl ₂ (0.1%Cu), CuO (0.1%Cu), FeCl ₃ (0.25%Fe), Fe ₂ O ₃ (0.25%Fe), PbCl ₂ (0.5%Pb), PbO (0.5%Pb), ZnCl ₂ (1.0%Zn), ZnO (1.0%Zn)	260	11	23	M		M		X
MFA2	AC (3%), SiO ₂ +Al ₂ O ₃ +CaCO ₃ matrix (1:1:1, rest), KCl (3.3%Cl), NaCl (3.3%Cl), CaCl ₂ (3.3%Cl), CuCl ₂ (0.08%Cu), CuO (0.12%Cu), FeCl ₃ (0.1%Fe), Fe ₂ O ₃ (0.4%Fe), PbCl ₂ (0.9%Pb), PbO (0.1%Pb), ZnCl ₂ (0.5%Zn), ZnO (1.5%Zn)	140	7.4	19	H	H	H		X
Real Fly Ash									
RFA ^e	TOC (1.5%), Cl (14%), O (32%), Si (15%), Al (6.7%), Ca (9.5%), K (6.6%), Na (6.0%), Cu (0.26%), Fe (0.47%), Pb (0.75%), Zn (1.4%), Other elements (5.82%; S, Br, Mg, Sb, Ti, P, Sn, Ni, Cr, Mn, Sr, Cd, Ag, etc.)	120	10	12	-	-	-		X

^aUsing our previous concentration data in refs 45. ^bUsing our previous concentration data in ref 35. ^cUsing our previous concentration data in ref 34.

^dUsing our previous concentration data in ref 30. ^eChemical components in the RFA were referred from our previous studies.¹³ Bold values are ¹/₂ to 2 times the RFA value. H, high similarity. M, medium similarity. Blank, low similarity. -, not analyzed because of hierarchical clustering in the RFA.

of metal compounds under similar mixtures in real MSWI fly ash.

In the present study, we quantified aromatic-Cl_s such as PCBs and CBzs after heating to 300 °C, maximizing the concentrations of aromatic-Cl_s⁴³ under systematic experimental single, multi-, and real conditions. Some PCBs are contained in fly ash as dioxin-like PCBs. CBzs are known as precursors of dioxins and have representative single-benzene-ring structure. We previously found positive correlation between PCBs and CBzs using various model fly ashes.³⁰ In addition, we selected CBzs and PCBs for this study to use our previous results performed under the same experimental design.^{30,34,35,40} Ratios of Fe and Zn chlorides and oxides in real MSWI fly ash (hereafter RFA) were analyzed using the X-ray absorption near-edge structure (XANES) technique; previous studies have reported the XANES of the Cu K-edge and Pb L_{III}-edge of RFA.^{13,35} In addition to examining a multisystem of Cu, Fe, Pb, and Zn chlorides and oxides, we evaluated the effect of major

inorganic chlorides (KCl, NaCl, and CaCl₂)^{44,45} and base materials (silica, alumina, and calcium carbonate).^{18,46,47} Principal component analysis and hierarchical cluster analysis extracted characteristic components and allowed a similarity assessment of the distribution pattern and convergence in the RFA, using replicates of single and multiadditions.

MATERIALS AND METHODS

Sample Preparation. Representative RFA was collected using a bag filter (a type of dust collector) in the post-combustion zone of a continuous stoker-type MSWI in Japan, without the injection of lime or activated carbon. Weight concentrations of Cu, Fe, Pb, and Zn in the RFA were 0.26, 0.47, 0.75, and 1.4%, respectively, as measured previously.¹³ Total organic carbon (1.5%), chlorine (14%), oxygen (32%), and other base inorganic elements (Si, Al, Ca, K, and Na \geq 6.0%) were also major components of the RFA. The detailed RFA composition is shown in Table 1.

According to these chemical components of the RFA, we prepared various single and multimodel samples as shown in Table 1. Typical model samples, which were made by grinding in a mortar for approximately 10 min, contained a carbon source, a major chlorine source, base material, and metal compound(s). We used activated carbon (Shirasagi palm shell, 20–48 mesh (number of holes/inch); Takeda Pharmaceutical Co., Ltd., Osaka) as carbon source. Any organic compounds were removed by heating at 500 °C for 60 min under a stream of 100% nitrogen gas (100 mL/min).⁴⁸ Major chemical forms of chlorine in MSWI fly ash were reported to be potassium, sodium, and calcium chlorides,^{44,45} and therefore, KCl (purity 99.5%, special grade), NaCl (99.5%, special grade), and CaCl₂·2H₂O (99.0–103.0%, special grade) were used as major chlorine sources. On the basis of previous reports of the elements in RFA,^{4,13} we selected silica (SiO₂, special grade), alumina (Al₂O₃), and calcium carbonate (CaCO₃, 99.5%, special grade) as base materials.^{18,46,47} The following metal chlorides and oxides were used: CuCl₂ (98.0%), FeCl₃ (97.0%), PbCl₂ (99.0%, special grade), ZnCl₂ (98.0%, special grade), CuO (98.0%, special grade), Fe₂O₃ (95.0%), PbO (99.0%, special grade), and ZnO (99.0%, special grade). All of the reagents were purchased from Nacalai Tesque, Japan.

Fe K-Edge and Zn K-Edge XANES. Chemical forms of Fe and Zn in the RFA were analyzed by the XANES using beamline BL01B1 at the SPring-8 synchrotron radiation facility in Hyogo, Japan.⁴⁹ The RFA was ground in a mortar and pressed into a disk according to the methods of our previous studies.^{13,14,20,34} We placed the disk on a sample platform. The XANES spectra were detected in fluorescence mode using a 19-element Ge solid-state detector with a Si (111) two-crystal monochromator. The energy was calibrated at 8980.3 eV of Cu (foil) pre-edge.⁴¹ To analyze the representative existence ratio of Fe and Zn oxide and chloride, disks of reference standard materials were prepared. The Fe standards used were FeCl₃, FeCl₂, Fe₂O₃, Fe₃O₄, and FeO. In the case of Zn standards, including ZnCl₂ and ZnO, we used ZnCO₃, ZnS, and ZnFe₂O₄ in order to improve the goodness of fit and avoid overestimating the chloride ratio. We used the software REX2000 ver. 2.5.5 (Rigaku, Japan) for the analysis of the XANES spectrum. By using experimental and reference XANES spectra, we calculated the ratio of metal compounds using the linear combination fit (LCF) method.^{13–15,24,41} The residual value from LCF followed the formula $R = \sum (\text{XANES}_{\text{measd}} - \text{XANES}_{\text{calcd}})^2 / \sum (\text{XANES}_{\text{measd}})^2$. Considering the number of standard spectra, we decided optimal *R* value and fitting result. The ratio of Cu and Pb oxides and chlorides was previously analyzed using the LCF of the Cu K-edge and Pb L_{III}-edge XANES of the same RFA.^{13,35}

Heating Experiment and GC/MS Measurements of PCBs and CBzs. We placed 5 g of MFA sample into a quartz boat contained within a quartz tube (120 × 4 cm internal diameter), which was then placed in a preheated electronic furnace at 300 °C for 30 min under a flow of 10% O₂/90% N₂ delivered at 50 mL/min in order to simulate the post-combustion zone of a MSWI. After heating, the concentrations of aromatic-Cl_s in the residue were analyzed. We also analyzed aromatic-Cl_s in the gas phase using a toluene trap in an impinger at the outlet of the quartz tube. We found selective concentrations of aromatic-Cl_s in the residue after heating at 300 °C, which was consistent with our previous study conducted under the same experimental conditions.³⁰ In this study, we focused mainly on aromatic-Cl_s formation in the

residual phase. Sample pretreatment for the determination of aromatic-Cl_s was conducted according to Japanese Industrial Standards (JIS) K 0311 and 0312. We analyzed PCBs (Cl₂–Cl₈) and CBzs (Cl₂–Cl₆) using gas chromatography/mass spectrometry (GC/MS; QP2010, Shimadzu; and HP-6890/HP-5973, Hewlett-Packard; respectively). For each heating experiment, reproducible analyses of PCBs and CBzs were duplicated (*n* = 2). Duplicated results showed good reproducibility of congener profile. Median variabilities of CBzs and PCBs among all congeners were under 20%, respectively. So, this methodology ensured reproducibility and relative small variability. A previous report has described the detailed protocol of these methods.³⁰

Statistical Analysis. To characterize and categorize the distribution pattern of PCBs and CBzs, to predict and extract key metal compounds, and to fill the gap between single and multisystems, distribution patterns and quantitative data sets were statistically analyzed using principal component analysis (PCA) and hierarchical cluster analysis (HCA) by the Ward method using the add-in software Mulcel.⁵⁰ Ward method allows for the square sum of data in a cluster to be minimized. The detailed statistical procedures of PCA and HCA have been described previously.³⁰

■ RESULTS AND DISCUSSION

Chemical Forms of Cu, Fe, Pb, and Zn in the RFA. Our previous report describes the analysis of the chemical forms of copper in the RFA.¹³ From the LCF of the Cu K-edge XANES, 75% CuCl₂·3Cu(OH)₂, 14% CuCl, and 11% Cu(OH)₂ existed in the RFA. Therefore, the chloride to oxide ratio equaled 2:3. According to the chemical formula of the LCF result, CuCl₂ was applied as copper chloride, and we made the cupric oxide ratio match the ratio of Cu(OH)₂. We previously confirmed that the formation and concentration of aromatic-Cl_s by CuO does not differ from that by Cu(OH)₂.¹⁵

We previously found simple and good LCF results for the Pb L_{III}-edge XANES.³⁵ The linear combination of oxide and chloride spectra for lead fit the RFA spectrum sufficiently. The PbCl₂ to PbO ratio was 9:1. The chemical forms of Pb in MSWI fly ash have been reported to be chloride, oxide, and sulfide.^{21,22,41} Our previous study also revealed that PbCl₂ was more abundant than PbO;⁴¹ therefore, the chloride to oxide ratio of Pb in the RFA might reflect the general character of MSWI fly ash.

In the present study, we measured the additional XANES spectra of iron and zinc in the RFA as shown in Figure 1. Good LCF of the Fe K-edge XANES spectrum showed 76% Fe₂O₃, 10% FeCl₃, 10% FeCl₂, and 4% FeO in the RFA. In general, a major part of iron existed as crystalline hematite (Fe₂O₃), magnetite (Fe₃O₄), or wüstite (FeO) in MSWI fly ash.²¹ Using an X-ray absorption technique, noncrystalline iron chlorides (FeCl₂ and FeCl₃) could be detected.²⁰ Because the LCF of the Fe K-edge XANES was conducted properly, we devised an iron chloride to iron oxide ratio of 1:4. FeCl₃ was used as the representative iron chloride because the concentration of aromatic-Cl_s did not depend on valence of iron chloride.^{18,30} Fe₂O₃ was selected as the iron oxide because it represented the dominant iron form in the RFA (see Figure 1).

In terms of ZnCl₂ and ZnO, the Zn K-edge spectrum of the RFA was not a good fit (residual *R* value = 0.066). We therefore added standard spectra of ZnCO₃, ZnS, and ZnFe₂O₄ and reanalyzed. The linear combination of 24% ZnCl₂ + 21% ZnCO₃ + 42% ZnS + 13% ZnFe₂O₄ resulted in the best fit

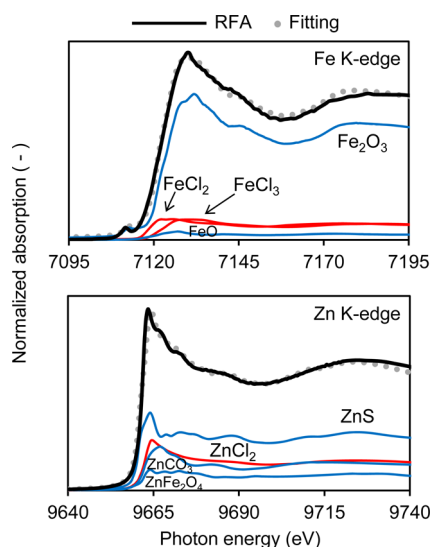


Figure 1. Fe K-edge and Zn K-edge XANES spectra of the RFA. R -values were 0.022 (Fe) and 0.033 (Zn). Chloride:oxide and other forms = 1:4 (iron) and 1:3 (zinc), respectively.

($R = 0.033$) as shown in Figure 1. Previous research indicated that zinc in MSWI fly ash existed mainly as chloride, oxide (e.g., ZnO , ZnCO_3), and sulfide (ZnS), with inert compounds (ZnAl_2O_4 , Zn_2SiO_4 , and ZnFe_2O_4) occupying only a minor portion of zinc compounds.^{22,40,41,51} Our analytical results were consistent with the previous studies. For instance ZnCl_2 had a stronger potential to generate aromatic-Cl_s than did ZnO .³⁰ To avoid overestimations of the ratio of ZnCl_2 to ZnO , the ratio was calculated as [(sum ratios of chlorides): (sum ratios of oxides and other forms)]. Therefore, the ZnCl_2 to ZnO ratio = (ratio of ZnCl_2): (sum ratios of $\text{ZnCO}_3 + \text{ZnS} + \text{ZnFe}_2\text{O}_4$) = 1: 3. From the results of these LCF analyses, we

determined the ratios of Cu, Fe, Pb, and Zn oxides and chlorides in the replicated multimodel sample abbreviated as MFA2 in Table 1.

Amount and Distribution of Aromatic-Cl from the RFA. Concentrations of ΣCBzs and ΣPCBs in the RFA were shown as 120 and 10 ng/g-ash, respectively (Table 1). The normalized congener distribution pattern of CBzs exhibited maximum P5-benzene and low D2-/T3-benzenes as shown in Figure 2 (left). Levels of PCBs indicated a peak of Cl_4 -biphenyls (Figure 2, right). The distribution patterns of CBzs and PCBs in the RFA matched those derived from general MSWI fly ashes.³⁰ The $\Sigma\text{CBzs}/\Sigma\text{PCBs}$ ratio (= 12) was also the same level as that found in general MSWI fly ash.³⁰ The $\Sigma\text{CBzs}/\Sigma\text{PCBs}$ ratio showed selectivity of these two aromatic-Cl_s formation. By comparing the $\Sigma\text{CBzs}/\Sigma\text{PCBs}$ ratios of model fly ashes with the RFA, we could assess and discuss the selectivity. Therefore, we considered the RFA to have representative properties of MSWI fly ash in terms of the generation of aromatic-Cl_s. To refer the chemical composition of the RFA, we prepared single and multimodel samples and assessed five factors, i.e., (i) inorganic chlorides, (ii) base materials, (iii) metal oxides, (iv) metal chlorides, and (v) coexistent multi models. The concentrations of ΣCBzs and ΣPCBs , and the ΣCBzs to ΣPCBs ratio were compared with these values of the RFA, and the normalized distribution pattern of homologues (D2-H6 benzenes and D2-O8 biphenyls) were statistically analyzed to examine the similarities between each factor and the RFA.

Inorganic Chloride (KCl, NaCl, and CaCl_2). Concentrations of ΣCBzs and ΣPCBs by the single addition of inorganic chlorides (MFA-K, -Na, -Ca) were the same level (14–20 and 18–25 ng/g, respectively) as shown in Table 1. Although inorganic chlorides dominated the major chemical form of chlorine in general MSWI fly ash in Japan,^{44,45} inorganic chlorides in the solid phase had a weak direct influence on the

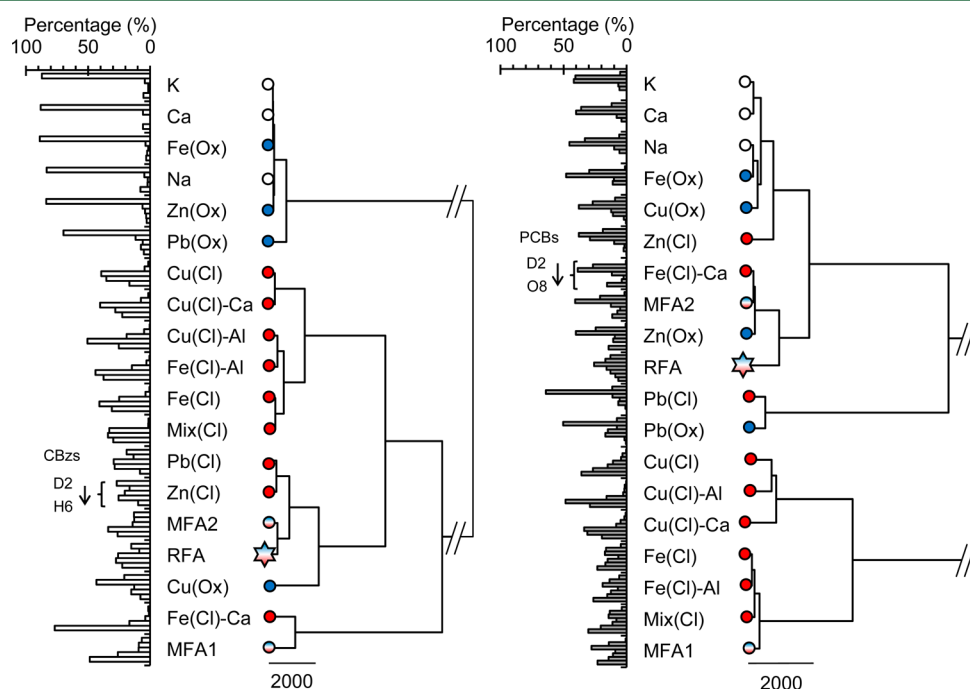


Figure 2. Hierarchical cluster analyses by normalized distribution patterns of CBzs (left) and by normalized distribution patterns of PCBs (right). Blue, red, and white circles indicate metal oxide, metal chloride, and no metal, respectively, in MFA. Blue plus red in one circle means coexistence of metal chloride and metal oxide.

formation of aromatic-Cl_s. The results for MFA-K, -Na, and -Ca were consistent with other studies;^{45,52,53} and the $\sum\text{CBzs}/\sum\text{PCBs}$ ratios were 1.1 (MFA-K), 0.75 (-Na), and 0.68 (-Ca), respectively. The ratio of this group indicated that it had the lowest level. The normalized distribution pattern was similar among all three inorganic chlorides. The acute peak of D2-benzenes and double peaks of T3-/T4-biphenyls displayed the characteristic pattern (Figure 2), which was similar to our previous reports.^{30,45} Therefore, KCl, NaCl, and CaCl₂ were involved in the same groups of CBzs, PCBs, and CBzs&PCBs by HCA (Figures 2 and 3). Since the concentration level and

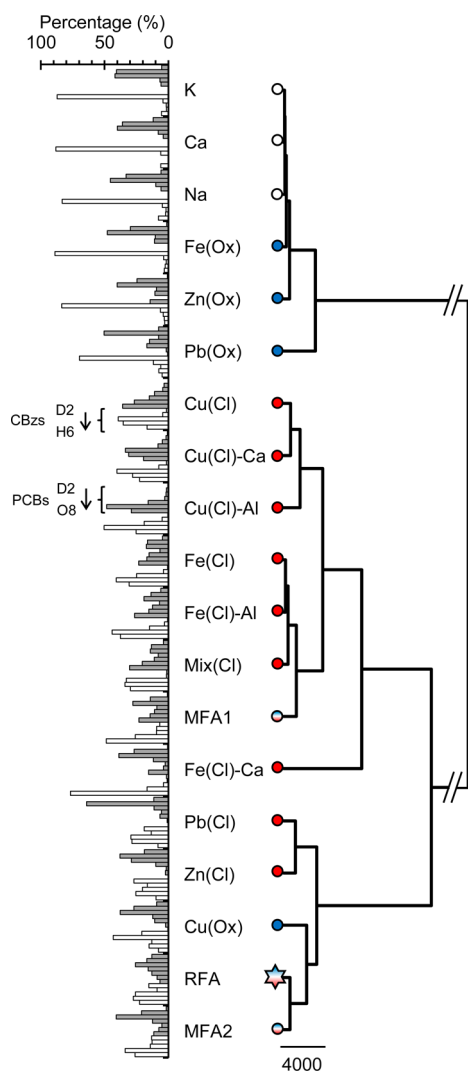


Figure 3. Hierarchical cluster analysis by normalized distribution pattern of all homologues of CBzs and PCBs (CBzs&PCBs). Colors in circles are described in the caption of Figure 2.

normalized distribution pattern were almost unchanged by the type of inorganic chloride, we selected KCl as a representative inorganic chloride in the case of the addition model of a single metal compound as explained in Table 1.

Base Material (SiO₂, Al₂O₃, and CaCO₃). We assessed three base materials using the addition of cupric or ferric chloride. In the case of MFA with cupric chloride, $\sum\text{CBzs}$, $\sum\text{PCBs}$, and the $\sum\text{CBzs}$ to $\sum\text{PCBs}$ ratio were quantified depending on additional silica (SiO₂), alumina (Al₂O₃), and calcium carbonate (CaCO₃), which are abbreviated as MFA-Cu(Cl),

-Cu(Cl)-Al, and -Cu(Cl)-Ca, respectively, in Table 1 in the following order: silica ($\sum\text{CBzs}$ = 15 000, $\sum\text{PCBs}$ = 1200 ng/g) > alumina (14 000, 940 ng/g) > calcium carbonate (7800, 350 ng/g); and silica ($\sum\text{CBzs}:\sum\text{PCBs}$ = 13) < alumina (15) < calcium carbonate (23). Silica showed a high chlorinating effect compared with other base materials. Schoonenboom et al.⁴⁶ reported a dechlorination of O8CDD/F on an alumina support with copper chloride as a catalyst. Our comparison between the distribution pattern of alumina with that of silica indicates that a similar dechlorination of O8-biphenyls (i.e., main path of O8- → H7-biphenyls) may occur (Figure 2, right). The relative inhibitory effect of CaCO₃ and lower chlorinated distribution pattern of CaCO₃ compared with that of silica were consistent with a similar study using MFA.⁴⁷ However, from the viewpoint of the distribution patterns in all samples, MFA-Cu(Cl), -Cu(Cl)-Al, and -Cu(Cl)-Ca were all contained in the same cluster as shown in Figures 2 and 3. In general, there was only a small variation in the distribution patterns of base materials and the CuCl₂ system in the same cluster.

We found significant differences in the concentrations of aromatic-Cl_s among base materials in coexistence with ferric chloride: SiO₂ ($\sum\text{CBzs}$ = 12 000, $\sum\text{PCBs}$ = 210 ng/g) > Al₂O₃ (2600, 50 ng/g) > CaCO₃ (320, 11 ng/g), as shown in Table 1 as MFA-Fe(Cl), -Fe(Cl)-Al, and -Fe(Cl)-Ca, respectively. Although this order was the same as the case of base materials with CuCl₂, the $\sum\text{CBzs}$ to $\sum\text{PCBs}$ ratio showed the opposite tendency: SiO₂ ($\sum\text{CBzs}:\sum\text{PCBs}$ = 57) > Al₂O₃ (53) > CaCO₃ (27). Ryan and Altwick¹⁸ reported $\sum\text{PCDD/Fs}$ formation as a strong function of base materials such as silica, alumina, and calcium oxide added with iron(II) chloride in model experiments. Our related results with CBzs and PCBs also showed the remarkable function of base materials. Focusing on a normalized distribution pattern of CBzs and PCBs, MFA-Fe(Cl) and -Fe(Cl)-Al barely differed. However, MFA-Fe(Cl)-Ca had a specific pattern of dominant H6-benzenes and T4-biphenyls peaks, and occupied a different branch in the cluster (Figures 2 and 3).

Metal Oxides and Chlorides. In previous research, we examined the influence of metal oxides and chlorides in silica and KCl mixtures on aromatic-Cl_s formation under differing amounts of Fe, Pb, and Zn.³⁰ Here we compare the results of our present study with our previous findings. Concentrations of $\sum\text{CBzs}$ and $\sum\text{PCBs}$ from metal oxide were clearly weaker than those from chlorides of the same metals as shown in Table 1. Compared with the RFA and MFA-K (no metal addition), the total concentration of summed CBzs and PCBs ($\sum\text{CBzs}$ and $\sum\text{PCBs}$) by function of metal oxides and chlorides (Table 1) followed the order MFA-Cu(Cl) ($\sum\text{CBzs}$ + $\sum\text{PCBs}$ = 15 000 + 1200 ng/g) > MFA-Fe(Cl) (12 000 + 210 ng/g) > MFA-Cu(Ox) (380 + 23 ng/g) > MFA-Zn(Cl) (370 + 14 ng/g) > MFA-Pb(Cl) (320 + 37 ng/g) > MFA-Pb(Ox) (80 + 20 ng/g) > MFA-K (20 + 18 ng/g) > MFA-Fe(Ox) (13 + 11 ng/g) ≈ MFA-Zn(Ox) (12 + 11 ng/g). This trend was different from our previous findings except for Fe₂O₃.³⁰ The 0.5% Fe, 1.0% Pb, and 2.0% Zn were 2.5, 5.0, and 10 times higher than the 0.2% Fe, 0.2% Pb, and 0.2% Zn used in our previous study. In this study, the $\sum\text{CBzs}$ values produced by ZnCl₂ and PbCl₂ were higher; however, we found the same order of $\sum\text{CBzs}$ by FeCl₃. The $\sum\text{CBzs}$ values from Fe₂O₃ and ZnO were lower by approximately 1/92 and 1/5, respectively, compared with the 0.2% metal case. However, the $\sum\text{PCBs}$ for FeCl₃, ZnCl₂, PbCl₂, Fe₂O₃, and ZnO did not differ with additional metal concentrations.

We found lower chlorinated distribution patterns with MFA-Zn(Ox), -Pb(Ox), and -Fe(Ox), higher chlorinated patterns with MFA-Cu(Cl), a mountain-like shape between the higher and lower patterns of MFA-Pb(Cl), -Zn(Cl), and -Cu(Ox), and specific distributions pattern with MFA-Fe(Cl). These four groups of metal oxides and chlorides almost matched our previous statistical groupings.³⁰ Thus, in relation to factors iii (metal oxides) and iv (metal chlorides), the high concentration and high chlorination by CuCl₂, and the semihigh concentration and the specific homologue pattern by FeCl₃ both had a positive catalytic potential to generate aromatic-Cl_s.^{7,11–14,18,20,30} The low concentration and low chlorination produced by Fe₂O₃, PbO, and ZnO might indicate their roles as inhibitors in the amount of metal of this study.^{30,32,33,54} The medium concentrations and mountain-like shape distribution patterns produced by CuO, PbCl₂, and ZnCl₂ balanced and may catalyze the formation of aromatic-Cl_s in solid phase.^{5,7,30,34,35} The individual characters of metal oxides and chlorides were then assessed under the multimodel systems described below.

Coexistent Condition [Mix(Cl), MFA1, and MFA2]. To reveal the real behaviors of factors in complex RFA, we attempted to replicate the formation of aromatic-Cl_s using models of multiple mixtures. Three multimodels were prepared: Mix(Cl), MFA1, and MFA2. Mix(Cl) was composed of a mixture of Cu, Fe, Pb, and Zn chlorides with AC + SiO₂ + KCl, in order to understand the behavior of the positive factor iv under this mixing condition. As shown in Table 1, the concentrations of \sum CBzs and \sum PCBs produced by Mix(Cl) of 9100 and 230 ng/g, respectively, were approximately $\frac{1}{3}$ and $\frac{1}{6}$ of the summations of each metal chloride (MFA-Cu(Cl) + Fe(Cl) + Pb(Cl) + Zn(Cl)), i.e., $15\,000 + 12\,000 + 320 + 370 \approx 27\,700$ ng/g in \sum CBzs; and $1200 + 210 + 37 + 14 \approx 1460$ ng/g in \sum PCBs. Because the thermo-chemical and thermo-physical behaviors of each metal chloride might change by mixing, no synergetic effect was occurred.^{34,35} Although the average values of \sum CBzs to \sum PCBs ratios derived from the four metal chlorides (= 26) showed the near value as the RFA (= 12), the \sum CBzs to \sum PCBs ratio of Mix(Cl) (= 40) indicated a higher value (Table 1). The distribution pattern of Mix(Cl) was similar to that of the RFA compared with single addition models. However, the mixing of four major trace metal chlorides produced higher concentrations of \sum CBzs, \sum PCBs, and \sum CBzs/ \sum PCBs than in the RFA. Therefore, we studied more inhibitory or coexistent factors in replicating inorganic chlorides (factor i), base materials (factor ii), and metal oxides (factor iii) of the RFA.

We represented MFA1 in Table 1 as a “half and half” weight ratio of metal chloride and metal oxide, under an equivalence mixture of three inorganic chlorides (KCl, NaCl, and CaCl₂) and three base materials (SiO₂, Al₂O₃, and CaCO₃). The values of \sum CBzs and \sum PCBs from a MFA1 of 260 and 11 ng/g were less than those from Mix(Cl) because additive metal oxides and base materials are thought to play main roles as inhibitors. The \sum CBzs to \sum PCBs ratio (= 23) of MFA1 had a value close to that of the RFA.

According to XANES analyses of the RFA, we prepared MFA2 replicating metal chloride to metal oxide ratios. This multimodel showed slightly lower levels of \sum CBzs (140 ng/g), \sum PCBs (7.4 ng/g), and \sum CBzs/ \sum PCBs (= 19) than MFA1, due to increased Fe₂O₃ and ZnO ratios in comparison with MFA1. These \sum CBzs and \sum PCBs concentrations, and \sum CBzs/ \sum PCBs ratio in MFA2 were almost same as those in the RFA. Compared with MFA1, normalized distribution patterns of CBzs and PCBs

were more similar to those of the RFA. We concluded that formation path of aromatic-Cl_s was strongly dependent on complex mixture conditions, such as multimodels (MFA1 and MFA2) composed of not only metal chlorides, but also of Cu, Fe, Pb, Zn oxides, a mixture of base materials (SiO₂:Al₂O₃:CaCO₃ = 1:1:1), and three major inorganic chlorides (KCl, NaCl, CaCl₂). In addition, these results suggest that relatively precise replication of metal chloride to oxide ratios (i.e., MFA2) may be essential in changing the thermochemical formation patterns of aromatic-Cl_s. Although replication of other chemical forms of metals such as sulfides and inert compounds should be further studied, we concluded that formation of aromatic-Cl_s was strongly dependent on a “coexistence” condition such as multimodels composed of not only metal chlorides, but also of metal oxides.

Total Assessment. Here, we discuss the causative factors in the generation of aromatic-Cl_s in MSWI fly ash using the entire data set shown in Table 1. The similarity of distribution pattern with that of our previous study³⁰ is described in the footnote of Table 1. The groups were named A, B (B₁ and B₂), C, D&E, and X, according to our previous grouping.³⁰ PCA of the total distribution patterns of CBzs and PCBs (CBzs&PCBs) was also used for the total assessment (Figure 4). Principal components

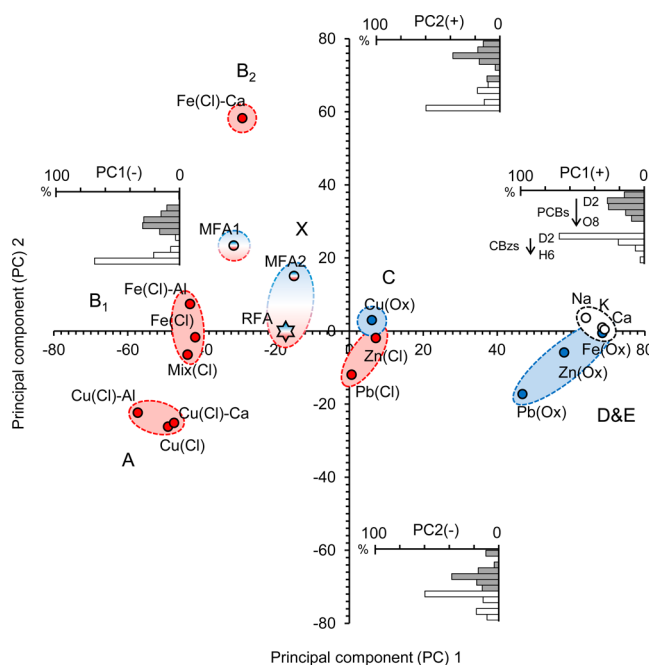


Figure 4. Principal component analysis (PCA) using a normalized distribution pattern of all homologues of CBzs and PCBs (CBzs&PCBs).

1 and 2 (PC1 and PC2) explained 70% and 12% (total of 82%) of the original data set, respectively. PC1 was interpreted as an indicator of lower CBzs (peak at D2-benzenes) and lower PCBs (peak at D3/D4-biphenyls), whereas PC2 was interpreted as an indicator of higher CBzs (peak at H6-benzenes) and medium PCBs (peak at D4-biphenyls).

We visually recognized the similarities in the RFA as the distance between groups and the RFA in PCA plot. Groups D&E with no metals (MFA-K, -Na, -Ca) and metal oxides (MFA-Fe(Ox), -Zn(Ox), -Pb(Ox)) were the farthest distance from the RFA. Groups D&E showed a high similarity in the distribution pattern of PCBs. However, these groups had a low

similarity in the distribution pattern of CBzs and CBzs&PCBs. Concentrations of \sum PCBs in MFA-Na, -Ca, and -Pb(Ox) were similar to those of the RFA (Table 1). Although inorganic chlorides are main chlorine sources in the solid phase, these chlorides made low contributions to the generation of aromatic-Cl_s. In addition, metal oxides other than CuO did not play a significant role as catalysts in aromatic-Cl_s formation.

Metal chlorides and CuO were located in a position near the RFA. These locations were separated by four groups A, B₁, B₂, and C in the PCA plot as shown in Figure 4. Group C of MFA-Pb(Cl), -Zn(Cl), and -Cu(Ox) had a center position in the PCA plot, which reflected medium distributions of CBzs and PCBs. High similarity in the distribution patterns of CBzs, PCBs, and CBzs&PCBs were found by HCA except for medium similarity of MFA-Pb(Cl) in that of PCBs (Table 1). Therefore, this group C might relatively contribute to aromatic-Cl_s generation in the real complex solid phase. Group A (MFA-Cu(Cl), -Cu(Cl)-Al, and -Cu(Cl)-Ca) was located in a similar position near RFA in the PCA plot. Similarities in the distribution patterns of CBzs, PCBs, and CBzs&PCBs were found in high, low, medium, respectively, of group A (Table 1). This suggested that CuCl₂ influenced the specific distribution pattern of aromatic-Cl_s regardless of the difference in base materials. Both MFA-Fe(Cl) and -Fe(Cl)-Al belonged in same group, B₁, as Mix(Cl). Therefore, the formation pattern of aromatic-Cl_s in Mix(Cl) may be mostly derived from FeCl₃. Similarity in the distribution patterns of CBzs, PCBs, and CBzs&PCBs was the same as group A. However, MFA-Fe(Cl)-Ca (group B₂) had a different isolated position in the PCA plot, which was derived from a higher chlorination of benzene (peak at H6-benzene). Although the distribution pattern of PCBs showed high similarity, those of CBzs and CBzs&PCBs showed medium similarities (Table 1). The generation of aromatic-Cl_s from the FeCl₃-addition model was affected by the base material.

MFA1 and MFA2 were closer to the RFA and belonged in group X. Compared with the high-similarity group C, group X showed a relatively low, but similar, order of concentrations of \sum CBzs and \sum PCBs to RFA. The \sum CBzs/ \sum PCBs ratio of group X was almost the same as that of RFA (Table 1). However, similarities of distribution patterns were different between MFA1 and MFA2. MFA2 showed higher similarities than MFA1. Based on concentrations of \sum CBzs and \sum PCBs, the \sum CBzs to \sum PCBs ratio, and the similarity of the distribution patterns of CBzs and PCBs, MFA2 was most similar in the formation path of aromatic-Cl_s in the RFA. Compared with MFA1, fractions of CuO, Fe₂O₃, PbCl₂, and ZnO in MFA2 increased 0.02%, 0.15%, 0.4%, and 0.5%, respectively. So, MFA2 shifted to positive in PC1 and negative in PC2 near RFA in the PCA plot (Figure 4). Therefore, ratios of metal chlorides and oxides were also a key factor to generate aromatic-Cl_s in the MSWI fly ash.

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Notes

The authors declare no competing financial interest.

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