

## Effect of poly(vinyl chloride) and hydrogen chloride as a chlorine source on the formation of PCDDs and PCDFs in model waste incineration

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### Introduction

Municipal waste incinerators are an important source of emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs, together: PCDD/Fs). Some factors that affect PCDD/F formation in incineration processes are combustion conditions and waste composition such as chlorine and metal contents. Especially, chlorine is an essential ingredient in the PCDD/F formation. Chlorine contents in the waste have a significant influence on their homologue profiles as well as their amounts<sup>1</sup>. Many research groups have investigated the role of chlorine in their formation<sup>2-4</sup>. It was reported in combustion experiments of model wastes containing poly(vinyl chloride) (PVC) or sodium chloride (NaCl) that hydrogen chloride (HCl) concentration in flue gas is in proportion to Cl content in the waste<sup>5</sup>. This could mean that PCDD/Fs are formed through chlorination via HCl independent of a Cl source.

The aim of this study is to investigate the role of chlorine in the PCDD/F formation in municipal waste incineration. As a first step, combustion experiments were performed on model wastes containing PVC and containing no PVC with HCl gas supplied to the combustion chamber. HCl was used as a main Cl source of the PCDD/F formation in the latter experiment. A comparison of the amounts of PCDD/Fs formed, their homologue profiles and their congener distributions would elucidate the difference in the role as a Cl source in their formation between PVC in the waste and HCl injected to the combustion chamber.

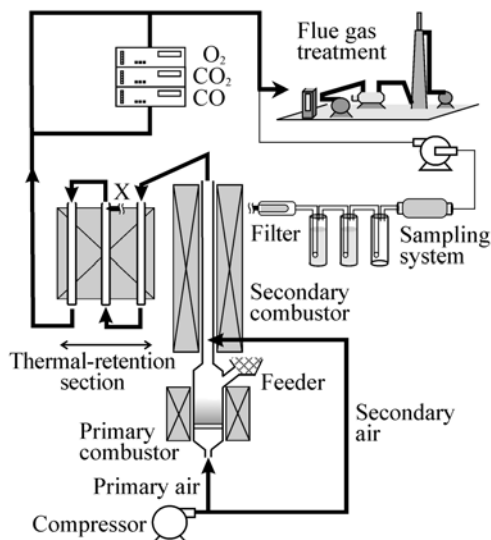
### Methods and Materials

**Experimental setup:** The main combustion section in the experimental setup consisted of primary and secondary combustors (Figure 1). The primary combustor was a laboratory-scale fluidized-bed reactor (60 mm diam., 300 mm tall). The fluidized material was 100–140 µm silica sand, and the static bed height was 100 mm. The secondary combustor was a freeboard section (30 mm diam., 1450 mm tall). All parts of the main combustion section coming in contact with flue gas were made of quartz. The postcombustion section connected the main combustion section with the thermal-retention section. The thermal-retention section consisted of 3 glass tubes (30 mm diam., 300 mm tall). Air was supplied to the primary and secondary combustors by a compressor. The excess air ratio was set to 1.3 in the primary combustor and 0.7 in the secondary combustor; in total, air was supplied at twice the stoichiometric ratio. The temperature was independently kept at 700 °C in the

primary combustor, 900 °C in the secondary combustor, and 350 °C in the thermal-retention section with electric heaters.

Fresh sand was used for the fluidized material in each experiment, because even trace amounts of residues such as chlorine and catalyst in the sand and on the inner surfaces of the reactor strongly affect the PCDD/F formation. After each experiment, the inner surfaces of the reactor in contact with flue gas were washed to prevent effects of experiment order. In case washing could not remove the contamination, the quartz parts were replaced with new material. Sampling for PCDD/F analysis was carried out for 4 h after the thermal-retention section (point X). Details for the sampling, analysis and identification of PCDD/Fs are described elsewhere<sup>6</sup>.

**Figure 1:** Schematic diagram of experimental setup.



**Model wastes:** Model wastes were used, so as to have a strictly defined waste composition. Three types of model wastes (designated A, B, and C) were used. The base ingredients of the model waste were 45% unbleached pulp powder, 40% flour, and 15% wood powder. In addition to the base ingredients, some additives were mixed as a chlorine source and a catalyst (Table 1). Polyethylene (PE) was mixed to examine the effects of the molecular structure of the additive on the PCDD/F formation in incineration. All ingredients were ground separately, mixed mechanically, and then pelletized into particles (1–3 mm diam.). Model wastes were supplied to the fluidized-bed reactor at 100 g/h. HCl gas (10% in nitrogen) was supplied for chlorine injection with the primary air to the bottom of the fluidized-bed reactor in the combustion experiments of wastes B and C so that the feed rate of chlorine was the same as that in the experiment of waste A containing PVC. The combustion experiment was performed once for each waste.

## Results and Discussion

**Table 1:** Model wastes.

Model waste	A	B	C
Additives	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ PVC	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ PE <sup>1)</sup>	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
Cl content [wt%]	1.24	0.17	0.20
Cu content [wt%]	0.09	0.09	0.10
Higher calorific value [kJ/g]	19.30	19.34	19.42

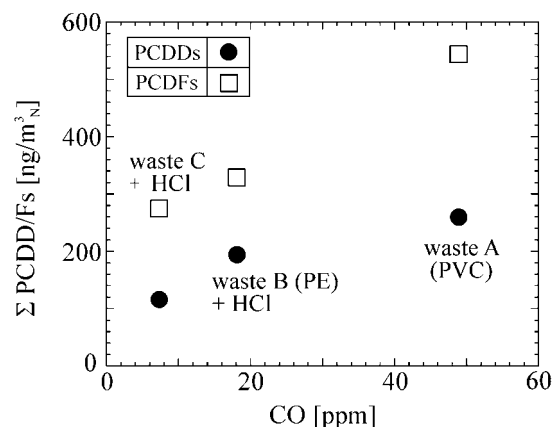
1) The carbon content of polyethylene (PE) mixed in model waste B is the same as that of PVC mixed in A.

**PCDD/F concentration:** The total concentrations of tetra- through octa-chlorinated dibenzo-*p*-dioxins (T4CDDs through O8CDD) and dibenzofurans (T4CDFs through O8CDF) were the highest in waste A (PVC) and the lowest in waste C (Figure 2). The average CO concentration in flue gas was positively correlated with the concentrations of PCDDs and PCDFs. The main reason of the highest PCDD/F concentration in waste A is probably that HCl concentration around the waste in combustion field was higher than in the case HCl gas was injected to the reactor because Cl came out of PVC in the waste A. This results in higher concentrations of CO, products of incomplete combustion (PICs), and HCl around the waste, which enhances the PCDD/F formation<sup>5</sup>. In waste B, PE in the waste causes incomplete combustion in a lack of oxygen locally, and then the CO and PCDD/F concentrations could increase. This influence contributes to enhancing the PCDD/F formation in the waste A (PVC), too. These results indicate that the molecular structures of PVC and PE affect combustion since the higher calorific values of the three wastes are almost the same (Table 1).

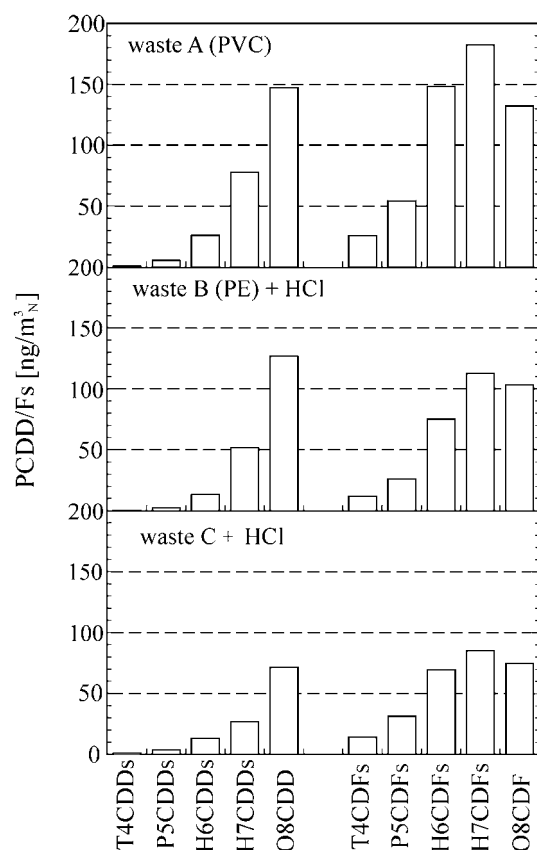
**Homologue profile and congener distribution:** Homologue profiles of PCDDs and PCDFs are almost similar in all the experiments (Figure 3). The more-chlorinated species are formed, which shows that copper catalyzes chlorination because tetra- to hexa-chlorinated species are the principal species formed in the absence of the catalyst<sup>7</sup>. The similar results were obtained in the series of the experiments on the model wastes with 0.45wt% Cl content.

It has been reported in the experiments on the temperature of the primary and secondary combustion zones that their homologue profiles, as well as the CO concentration in flue gas and the amounts of PCDD/Fs formed, significantly changed in the different combustion temperature though the same

**Figure 2:** CO concentration in flue gas and PCDD/F concentrations at sampling point X.



**Figure 3:** Homologue profiles of PCDDs and PCDFs in combustion experiments on model wastes A, B, and C.

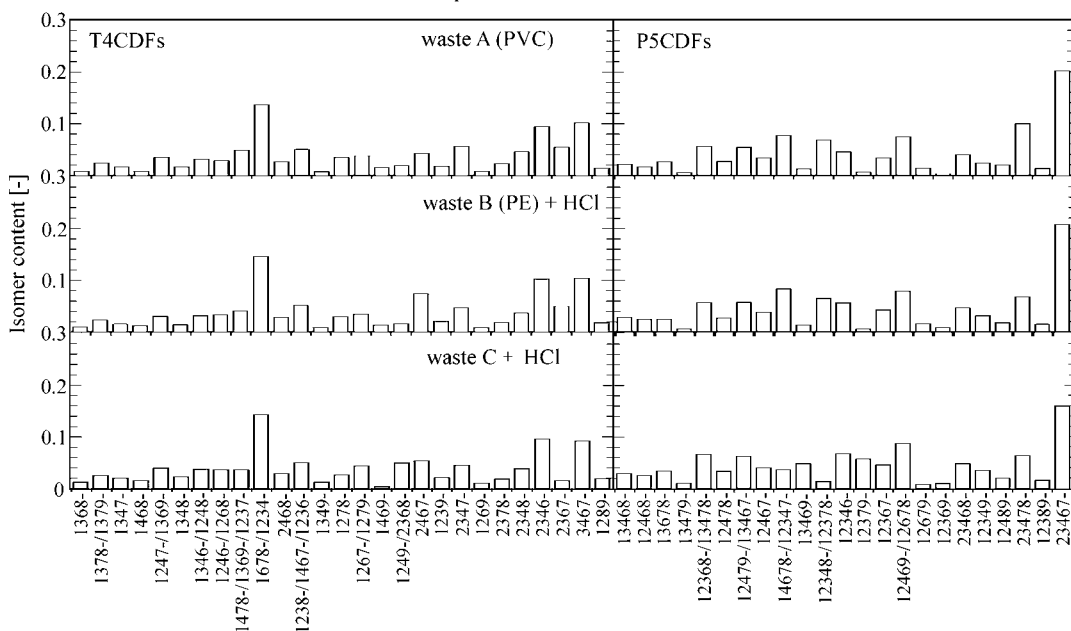


model waste was used in the same feed rate <sup>1</sup>. The temperature change exerts an influence on combustion reactions in the furnace. This probably affect not only the PCDD/F formation but also chlorination reactions, leading to the changes of their homologue profiles. On the other hand, in the present results, the CO concentration and the amounts of PCDD/Fs formed changed but their homologue profiles were almost similar in all the experiments (Figure 3). This shows that the CO and PCDD/F concentrations are not directly connected to the homologue profiles. The changes of combustion reactions that are caused by the molecular structures of PVC and PE in the waste enhance the formation of CO and PICs, which increases the amounts of PCDD/Fs formed. However, these hardly affect chlorination reactions in their formation. These results indicate that the role of injected HCl is the same as that of PVC in the waste as a Cl source in the PCDD/F formation.

The proportions of PCDD/F congeners to the sum of all in the homologue in these experiments show similarities to the fluidized-bed pattern <sup>8</sup>. These are characteristic substitution patterns that are observed in the combustion experiments in the presence of copper in the waste <sup>7</sup>. 2,3,4,6,7-P5CDF are selectively formed. 2,3,4,6-, 3,4,6,7-T4CDFs and 2,3,4,6,7,8-, 1,2,3,4,6,7-H6CDFs are also major congeners, which are deeply connected to the formation of 2,3,4,6,7-P5CDF. The congener distributions of T4CDFs and P5CDFs are shown in Figure 4 because these patterns show the effects of the waste composition on the PCDD/F formation distinctively.

The congener distributions are almost similar in all the experiments as well as the homologue profiles. This means that there is no difference in the main mechanisms of the PCDD/F formation between the experiments on combustion of the waste containing PVC and that containing no PVC with HCl injection. In the case of waste A, chlorine in PVC is almost converted to HCl once and reacts with PICs, leading to PCDD/Fs. These results also indicate that the molecular structures of PVC and PE in the waste have no direct influence on the PCDD/F formation mechanisms.

**Figure 4:** Congener distributions of T4CDFs and P5CDFs in combustion experiments on model wastes A, B, and C.



**References**

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