Bull. Environ. Contam. Toxicol. (2004) 73:479–486

DOI: 10.1007/s00128-004-0454-5

Bulletin of Environmental Contamination and Toxicology

Effect of Metal Nitrates on the Formation of PCDD/Fs During Newspaper Combustion

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Received: 17 March 2004/Accepted: 16 July 2004

Incineration is widely used in the treatment of the municipal solid waste. Incineration of wastes is expected to further increase in the future due to its two significant advantages over other methods of waste disposal: mass/volume reduction and energy recovery. However, the major disadvantage of incineration process is the emissions of toxic air pollutants, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and so on (Eiceman *et al.*, 1981). These toxic organic compounds could be released from the combustion of waste materials (You *et al.*, 1994; Wirts *et al.*, 1998; Piao *et al.*, 1999).

One of the main pathways has been proposed so far to explain the formation of PCDD/Fs during incineration: pyrosynthesis, that is, high temperature processes (Tuppurainen *et al.*, 1998). For example, dioxins are formed from natural woods and waste woods by combustion (Schatowitz *et al.*, 1994; Luthe *et al.*, 1998). They are also formed from sodium chloride (NaCl)-impregnated woods (Luthe *et al.*, 1998) and a mixture of wood and plastic wastes (Sinkkonen *et al.*, 1995) during combustion. There have been many studies on the formation of dioxins under various conditions (Wikstrom and Marklund, 2000; Iino *et al.*, 2000; Ishibashi *et al.*, 2000).

The source of chloride has been one of the major concerns in studies of dioxin formation in furnaces. It is found that both organic and inorganic chlorides can be a precursor of dioxins by combustion of waste materials. Municipal and industrial wastes generally contain chlorinated compounds such as NaCl, KCl and polyvinyl chloride (PVC) that can react as a chlorine source in incinerators (Stieglitz *et al.*, 1989; Halonen *et al.*, 1995; McNeill *et al.*, 1998). Although there are still many unknown formation mechanisms of dioxins in the high temperature processes, PVC is considered one of the compounds most responsible for the formation of PCDD/Fs in waste incinerators. Under high temperature combustion, HCl and hydrocarbons released from PVC can produce chlorinated species, which are thought as precursor of PCDD/Fs (Christmann *et al.*, 1989; Theisen *et al.*, 1989).Furthermore, the addition of HCl usually yields higher amounts of PCDD/Fs (Wirts *et al.*, 1998). In addition, metals in fly ash can affect the

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formation of PCDD/Fs and PAHs (Olie *et al.*, 1998; Wey *et al.*, 1998). However, systematic studies on the effect of some metals upon these products from waste materials combustion have been scarcely investigated.

In the present study, we mainly investigated the catalytic effect of some metal nitrates upon the composition and amount, as well as toxicity equivalency quantity (TEQ) of PCDD/Fs in the emissions from combustion of newspaper with NaCl at difference furnace temperatures. By using the nitrates, the characteristics of metal effect on the dioxin formation could be studied without influences of counter ions of metals, such as chlorides and sulfates. In addition, PCDD/Fs in the emissions from combustion of newspaper containing only NaCl at different temperatures were examined for comparison. Samples collected were analyzed for PCDD/Fs by gas chromatography/mass spectrometry (GC/MS) in order to investigate the characterization of PCDD/Fs formation during the combustion of newspaper.

MATERIALS AND METHODS

Newspapers (top circulation in Japan) purchased from a local store were soaked in a 3% (w/v) NaCl solution or the NaCl mixed with 1% (w/v) metal nitrate solutions for 1 h. The metal nitrates used were Al, Co, Cu, Fe, Ni and Zn. The newspapers were dried in an electric oven at 120 °C prior to use in the experiment. The amounts of NaCl and the nitrates adsorbed onto newspapers (20 g) were 2.4–2.8 and 2.2–2.5 g, respectively. Isotope-labeled dioxins for internal standards were obtained from Wellington Laboratories, Inc. The concentration of PCDD/Fs was determined by spiking ^{13}C-labeled compounds containing 2,3,7,8-PCDD/Fs homologues and 1,2,3,4-TCDD. All organic solvents for dioxin analysis were purchased from Wako Pure Chemicals Co., Inc. (Tokyo, Japan). All reagents used were of analytical grade and were used without further purification.

The schematic diagram of a tube-type furnace and detailed combustion procedure was previously reported (Katsumata *et al.*, 2003). The combustion samples were two types, *i.e.*, 20 g of NaCl-impregnated newspaper and 20 g of NaCl + metal nitrates-impregnated newspaper. All samples were combusted at 2 h, and then exhaust gas samples were collected for 6 h at room temperature. Dust in the exhaust gas was collected on silica wool. PCDD/Fs in the exhaust gas were adsorbed onto XAD-2 resin. After the furnace was cooled to the room temperature, silica wool and XAD-2 resin were extracted for 24 h with toluene. The quartz tube and connection lines were washed with 100 mL toluene. The extracts and washes were then combined. The combined samples were concentrated, and were cleaned with multilayer silica gel and alumina column chromatography. The volume of sample solutions was adjusted to exactly 50 μL under nitrogen flow.

The PCDD/Fs analysis was performed using a Hewlett-Packard (HP) model 6890 GC

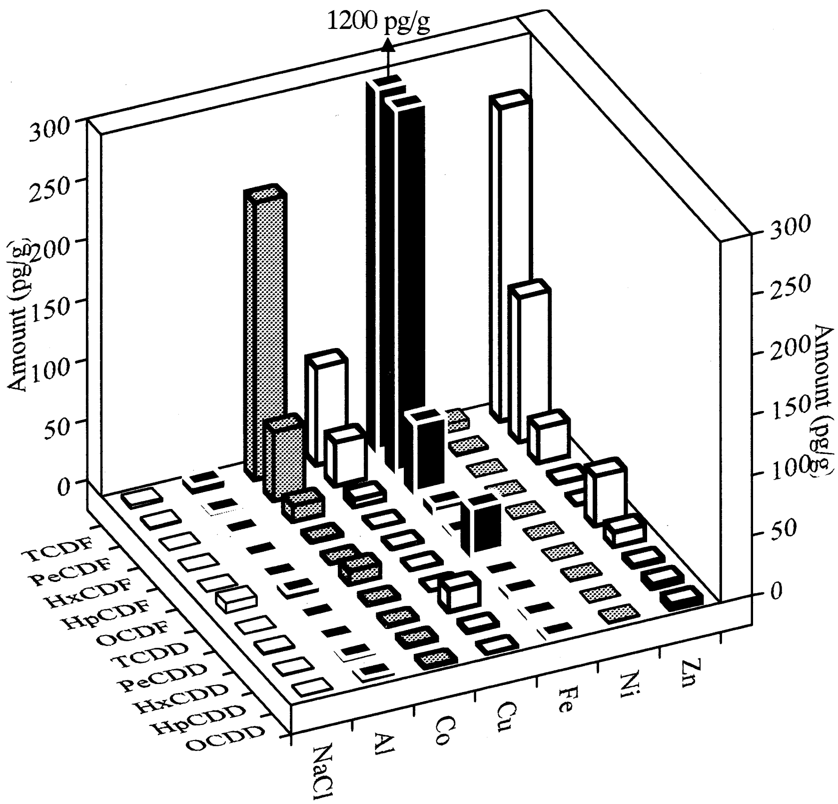

Figure 1. Amount of PCDD/Fs formed from newspaper combustion at 500 °C.

interfaced with a JMS-700D double focus MS (JEOL, Japan). The GC was equipped a CP-Sil 88 capillary column (60 m x 0.25 mm i.d.) for Cl_{4-6} dioxins or a CP-Sil 8 capillary column (30 m x 0.25 mm i.d.) for $Cl_{7,8}$ dioxins. The program of oven temperatures was same as the previous report (Katsumata *et al.*, 2003). These experiments were conducted in triplicates and the results showed at the mean values. The relative standard deviations were 8–15% and the detection limit was previously reported (Katsumata *et al.*, 2003).

RESULTS AND DISCUSSION

The combustion of newspaper was carried out at 500 °C in the absence and presence of metal nitrates. These results are shown in Fig. 1. There were no significant differences in PCDF composition among the combustion samples. The amount of PCDFs formed in the samples according to the number of chlorides was $Cl_4 > Cl_5 > Cl_6 > Cl_7 > Cl_8$, except in the case of nickel nitrate. On the other hand, PCDD composition was considerably different by the kind of co-existing metal nitrates. For example, HxCDD was predominantly formed in the presence of copper or nickel nitrates. In another cases,

Table 1. Amount and TEQ of PCDD/Fs from newspaper combustion at 500 °C.

	Amount (pg/g)	TEQ (pg/g)
NaCl	14	0.13
$NaCl+Al(NO_3)_3$	25	2.8
$NaCl+Co(NO_3)_2$	320	5.7
$NaCl+Cu(NO_3)_2$	140	2.4
$NaCl+Fe(NO_3)_3$	1,600	27
$NaCl+Ni(NO_3)_2$	13	0.33
$NaCl+Zn(NO_3)_2$	470	11

TCDD was higher concentration than that of PCDD isomers. Formation of all PCDFs was significantly higher than that of all PCDDs in all samples. PCDFs composed 57 –97 % of the total dioxin formed in the exhaust gases. For instance, all PCDFs was 35-fold all PCDDs in the presence of iron nitrate. The ratio of all PCDF to all PCDD ranged from 1.3 (aluminum nitrate) to 35 (iron nitrate). These results were in accordance with the results obtained from municipal solid waste combustion (Wikstrom and Marklund, 2000), and newspaper and wood combustion (Yasuhara *et al.*, 2001; Katsumata *et al.*, 2003).

Table 1 summarizes total amount of PCDD/Fs obtained from newspaper combustion in the presence of metal nitrates. When newspaper containing only NaCl was combusted, the total amount of PCDD/Fs was 14 pg g^{-1} and the TEQ value was 0.13 pg g^{-1}. It can be seen from Fig. 1 and Table 1 that cobalt, copper, iron and zinc nitrates catalyzed the formation of PCDD/Fs from newspaper combustion. Especially, iron nitrate showed most catalytic effect for the formation of PCDD/Fs, *i.e.*, total amount of PCDD/Fs from combustion of newspaper with NaCl and iron nitrate increased greater than 100-fold compared with newspaper containing NaCl. Previously, it has been reported that the addition of copper chloride and oxide enhanced PCDD/Fs from PVC combustion (Wang *et al.*, 2002; Shibata, *et al.*, 2003). These facts were consistent with the results of the present study. On the other hand, in the case of nickel nitrate total amount of PCDD/Fs was 13 pg g^{-1} and the TEQ value was 0.33 pg g^{-1}. These values were almost the same as those of newspaper combustion with NaCl. Therefore, nickel nitrate does not seem to work for the formation of PCDD/Fs as a catalyst. Although the total amount of PCDD/Fs in the presence of copper nitrate was 6 times than that of aluminum nitrate, TEQ value of Al was higher than that of Cu. This fact shows that the addition of aluminum nitrate effectively enhanced for the formation of 2,3,7,8-PCDD/Fs homologues.

Effect of combustion temperature on the formation of PCDD/Fs was examined at 300, 500 and 700 °C. The tested metal nitrates were Co, Fe and Zn. Total amount of PCDD/Fs is shown in Table 2. In all samples, total amounts of PCDD/Fs were quite low with 2.0 – 6.0 pg g^{-1} as compared with treating at higher combustion temperature when

Table 2. Amount and TEQ of PCDD/Fs from newspaper combustion.

	Temperature (°C)	Amount (pg/g)	TEQ (pg/g)
NaCl	300	2.0	0.092
	500	14	0.13
	700	20	0.41
$NaCl+Co(NO_3)_2$	300	6.0	1.3
	500	320	5.7
	700	30	0.36
$NaCl+Fe(NO_3)_3$	300	4.6	0.41
	500	1,600	27
	700	18,000	430
$NaCl+Zn(NO_3)_2$	300	2.2	0.21
	500	470	11
	700	33	0.26

newspaper was combusted at 300 °C. The low concentration of PCDD/Fs would be because newspaper was carbonized without burning. In addition, the following things would be also considered as reasons of these results. One is that HCl formed from NaCl during combustion was low concentration as mentioned later. Another is that catalytic effect of metals for the formation of PCDD/Fs did not fully work at 300 °C. As seen in Table 2, the formation of PCDD/Fs increased with increasing combustion temperature in the presence of NaCl or NaCl and iron nitrate. When newspaper was combusted at 700 °C in the presence of iron nitrate, as compared with treating at 300 °C, total amount of PCDD/Fs formed was 18,000 pg g^{-1} corresponding to about 4,000 times. Furthermore, TEQ value also increased at 700 °C and was 430 pg g^{-1}. Wang *et al.* (2002) reported that the formation of PCDD/Fs from PVC increased with increasing addition of $CuCl_2$ and combustion temperature. Chlorine source is necessary for the formation of PCDD/Fs. As described later, HCl is one of important inorganic chlorine sources for the production of PCDD/Fs. When HCl was injected into gasoil combustion gases, including methane, propane and ethylene, production of PCDD/Fs was observed (de Fre, 1986). It is hypothesized that HCl is formed at first from NaCl or PVC by high temperature and that PCDD/Fs are produced subsequently (Takasuga *et al.*, 1995). Recently, it was reported that the conversion ratios of HCl from NaCl were 50 % at 300 °C and >80 % over 700 °C quantitatively (Takasuga *et al.*, 2000). These results are good agreement with the results obtained from this study. However, the highest concentration of PCDD/Fs was obtained at 500 °C combustion of newspaper in the presence of cobalt and zinc nitrates. These phenomena were not completely understood. It is presumably that Co and Zn have catalytic effect for the dechlorination and destruction of PCCD/Fs and/or for the formation of other organic compounds. Actually, it was reported that copper compounds showed a considerable dechlorination/hydrogenation reaction for OCDD and OCDF (Weber *et al.*, 2002).

As described above, the results of this study show that cobalt, iron and zinc nitrates catalyzed the formation of PCDD/Fs from combustion of newspaper containing NaCl. The catalytic effect of metal nitrates on the formation of PCDD/Fs is discussed by making iron nitrate into a typical model. Iron nitrate ($Fe(NO_3)_3$) was converted to iron oxide (Fe_2O_3) by heating, followed by the formation of iron chloride ($FeCl_3$) by the reaction with HCl from NaCl pyrolysis. Iron chloride was used to convert a part of HCl to Cl_2 and decomposed itself to supply chlorine source for the PCDD/Fs formation at high temperature. The chemical reaction for the formation of PCDD/Fs can be regarded as follows:

$$\text{Newspaper} \xrightarrow{\Delta} \text{organic compounds (aromatic ring structures)} \quad (1)$$

$$NaCl + H^+ \xrightarrow{\Delta} HCl + Na^+ \quad (2)$$

Reaction 2 was reported by Buser (1987). HCl released from Reaction 2 is converted to Cl_2, and Cl_2 reacts with aromatic compounds released from Reaction 1 followed by the formation of chlorinated compounds.

$$2HCl(g) + 1/2O_2 \xrightarrow{\Delta} Cl_2(g) + H_2O(g) \quad (3)$$

$$\text{Aromatic compounds(g)} + Cl_2(g) \xrightarrow{\Delta} \text{Chlorinated compounds} \quad (4)$$

Reaction 3 can be catalyzed by iron oxide from iron nitrate, which can be seen in Reaction 5 (Hagenmaier *et al.*, 1987; Grifin, 1987; Steiglitz *et al.*, 1989).

$$\begin{aligned} &Fe_2O_3 + 6HCl \xrightarrow{\Delta} 2FeCl_3 + H_2O \\ &2FeCl_3 \xrightarrow{\Delta} 2FeCl_2 + Cl_2 \qquad (5) \\ &2FeCl_2 + 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 4HCl + H_2 \end{aligned}$$

These reactions could be occurred the chlorination of aromatic compounds such as benzene, phenols and biphenyl, and enhance the PCDD/Fs formation. In addition, PCDD/Fs could form from chlorination of dibenzo-*p*-dioxins and dibenzofurans.

In conclusion, all metal nitrates examined, except nickel nitrate, showed a catalytic effect for the formation of PCDD/Fs from combustion of newspaper. Especially, iron nitrate effectively catalyzed. These results suggested that metal compounds are possibly the one of main factors to the PCCD/Fs formation from waste materials combustion in incinerator.

Acknowledgments. This work was performed at Satellite Venture Business Laboratory (SVBL), Mie University.

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