EVALUATION OF THE FORMATION OF CHLORINATED DIOXINS FROM THE INCINERATION OF VARIOUS TYPES OF PLASTIC

Terada A[1], Fujimori T[1,2], Takaoka M[1]

[1]Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto, Japan, 615-8540, terada.ayano.52n@st.kyoto-u.ac.jp, 2Faculty of Advanced Science and Technology, Ryukoku University, Shiga, Japan, 520-2194.

Introduction

Plastics are widely produced and used worldwide1. In Japan, more than 10 million tons of plastics are produced every year and about 8.5 million tons of plastic are disposed of[2]; some of this is utilized for energy recovery or disposed of by incineration. Chlorinated dioxins are produced during waste incineration[3,4], with studies of the relationship between plastic incineration and dioxin production largely focusing on chlorinated plastics (mainly polyvinyl chloride [PVC][5,6]). Although some studies of the incineration of chlorine-free plastics in the presence of hydrochloric acid have been conducted[7,8], few have focused on structural differences in chlorine-free plastics. However, inorganic chlorine, such as sodium chloride (NaCl), is also present in many waste streams subjected to incineration[9], and it is likely that dioxins are generated due to the influence of inorganic chlorine sources in actual waste, even when chlorine-free plastics are burned.

In this study, plastic incineration tests simulating waste incineration were conducted. We analyzed polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) in the sample residue (bottom ash), particulates from the inside wall and glass wool (fly ash), and the exhaust gas to investigate the effects of NaCl and plastic structure on dioxin generation.

Materials and methods

Materials: We investigated six types of plastic in this study: polypropylene (PP; Sigma-Aldrich), polystyrene (PS; Polyscience, Inc.), polyethylene (PE; Scientific Polymer Products, Inc.), polyethylene terephthalate (PET; Sigma Aldrich, containing 30% glass fiber), PVC (Nacalai Tesuque, Inc.), and polyvinylidene chloride (PVDC; Saran wrap®; Asahi Kasei Corporation). The plastics were freeze-ground by liquid nitrogen using a freezing mill (Sample Prep 6770) and passed through a 250-µm mesh sieve.

Samples: The incineration samples consisted of plastic powder, NaCl (1.0 wt% as Cl; Nacalai Tesuque, Inc.) and copper powder (0.003wt%; FUJIFILM Wako Pure Chemical Corporation), with a total weight of 1.0 g. The weight ratio of chlorine was determined based on previous studies[10]. Copper chloride is a catalyst that enhances the formation of aromatic organic halogen compounds[11]. In multiple solid waste streams, copper is typically present in its metallic form, which is chlorinated under incineration[12,13]. We therefore added metallic copper to the sample to ensure a copper content typical of municipal solid waste (MSW)[14]. The PVC and PVDC samples comprised plastic and copper powder, with chlorine contents of 56.8% for PVC and 64.3% for PVDC[15].

Incineration test: Using a high-temperature tube furnace (KRB-24HH; Isuzu Seisakusho Co., Ltd.), we heated a 1.0 g sample for 60 min (**Figure 1**). The temperature was set to 850°C and the measuring gas was pure air (Sumitomo Seika Chemicals Company, Ltd.) at a flow rate of 200 mL/min. The incineration conditions were set to represent the sample load of a typical waste incineration plant (5–10 kg/g/m^3), and the residence time was 13.2 s. After the incineration, the residue on the quartz boat (bottom ash), the particulates from the inside wall and glass wool (fly ash), and the exhaust gas collected by the toluene trap (gas) were collected. We analyzed the concentrations of PCDD/Fs and DL-PCBs in each matrix.

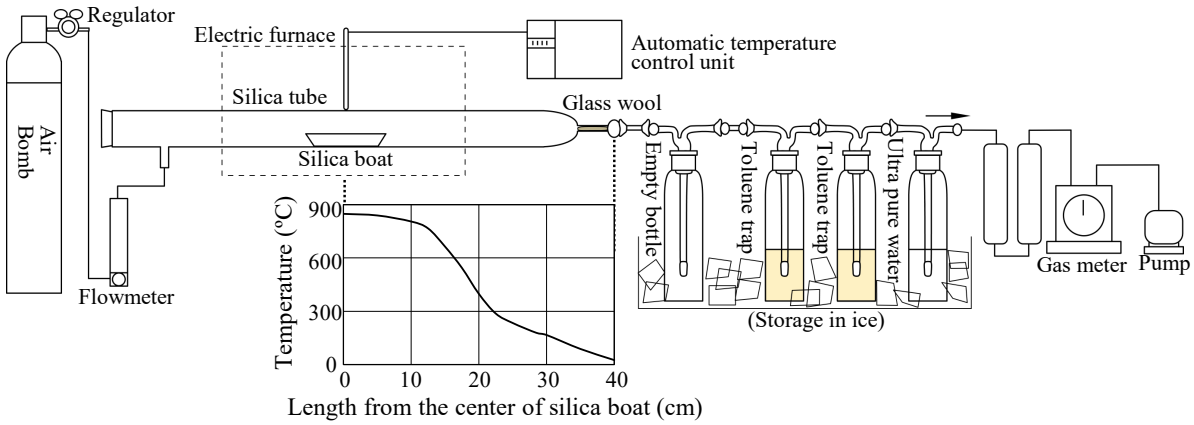

Figure 1: Structure of the tube furnace.

Results and discussion

We found that PCDD/Fs and DL-PCBs were generated when chlorine-free plastic was incinerated at 850ºC with NaCl (**Table 1**, **Figure 2a**). The total amount of chlorinated dioxins (total amount of PCDD/Fs and DL-PCBs) generated per unit weight of plastic was 150 ng/g-plastic for PP, 37 ng/g-plastic for PS, 96 ng/g-plastic for PE, 940 ng/g-plastic for PET, 5,100 ng/g-plastic for PVC, and 9,100 ng/g-plastic for PVDC. The order of magnitude was PVDC > PVC > PET > PE > PP > PS. Chlorine-containing plastics (PVC, PVDC) exhibited higher total PCDD/F and DL-PCB generation. Even for chlorine-free plastics, there was a difference of about 25 times between PET (highest generation) and PS (lowest generation). There was a tendency for PCDFs to dominate the generated chlorinated dioxins (i.e., PCDDs, PCDFs, and DL-PCBs): PCDFs accounted for more than 70% of the chlorinated dioxins generated by all six types of plastics.

Table 1: Concentration of chlorinated dioxins from incineration tests (ng/g-plastic).

	PP				PS				PE			
Compounds	Bottom ash	Fly ash	Gas	Total	Bottom ash	Fly ash	Gas	Total	Bottom ash	Fly ash	Gas	Total
TeCDDs	0.49	4.7	N.D.	5.2	0.18	0.47	N.D.	0.64	0.1	3.1	N.D.	3.2
PeCDDs	0.79	1.6	N.D.	2.4	0.51	N.D.	N.D.	0.51	N.D.	1.5	N.D.	1.5
HxCDDs	1.4	0.35	0.0047	1.8	1.4	N.D.	0.0028	1.4	N.D.	0.73	N.D.	0.73
HpCDDs	1	0.13	0.011	1.2	1.6	0.045	0.0077	1.7	0.15	0.26	0.0096	0.42
OCDD	0.35	0.12	0.0081	0.48	0.75	0.081	0.01	0.84	N.D.	0.081	0.012	0.094
Total PCDDs	4.1	6.9	0.024	11	4.5	0.59	0.02	5.1	0.24	5.7	0.022	6
TeCDFs	0.053	96	N.D.	96	N.D.	24	N.D.	24	0.0061	51	N.D.	51
PeCDFs	0.12	31	N.D.	31	0.022	2.2	N.D.	2.3	N.D.	24	N.D.	24
HxCDFs	0.14	4.1	0.013	4.2	0.13	0.14	N.D.	0.27	N.D.	6.9	N.D.	6.9
HpCDFs	0.11	0.33	0.01	0.44	0.12	0.028	0.0037	0.16	0.018	1.2	0.0061	1.2
OCDF	0.043	0.073	0.0065	0.12	N.D.	0.053	0.0059	0.059	N.D.	0.13	0.0077	0.14
Total PCDFs	0.47	130	0.031	130	0.28	26	0.0096	27	0.024	83	0.014	83
PCDDs+PCDFs	4.5	140	0.053	140	4.7	28	0.031	33	0.26	89	0.035	90
nonortho PCBs	0.035	3.7	2.4	6.1	0.035	2	2.4	4.5	0.022	2	4.3	6.3
mono-ortho PCBs	0.043	1.2	0.01	1.3	0.043	0.33	0.02	0.39	0.051	0.77	0.014	0.84
Total DL-PCBs	0.077	4.9	2.4	7.4	0.077	2.4	2.4	5	0.073	2.6	4.3	7
Total Dioxins	**4.7**	**140**	**2.4**	**150**	**4.9**	**28**	**2.4**	**37**	**0.35**	**92**	**4.3**	**96**

	PET				PVC				PVDC			
Compounds	Bottom ash	Fly ash	Gas	Total	Bottom ash	Fly ash	Gas	Total	Bottom ash	Fly ash	Gas	Total
TeCDDs	0.12	8.4	N.D.	8.5	0.06	26	0.0032	26	N.D.	11	N.D.	11
PeCDDs	0.15	17	N.D.	17	0.1	62	N.D.	62	0.011	13	N.D.	13
HxCDDs	0.38	28	0.0046	29	0.19	120	0.011	120	0.13	25	0.0021	25
HpCDDs	0.52	35	0.014	35	0.14	190	0.018	190	0.17	52	0.0034	53
OCDD	0.23	24	0.029	25	0.04	190	0.018	190	0.091	140	0.0068	140
Total PCDDs	1.4	110	0.046	110	0.52	600	0.05	600	0.39	230	0.012	230
TeCDFs	N.D.	190	N.D.	190	N.D.	680	0.078	680	0.03	4600	0.089	4600
PeCDFs	N.D.	210	N.D.	210	N.D.	680	0.026	680	N.D.	1400	0.046	1400
HxCDFs	N.D.	190	N.D.	190	N.D.	1000	0.024	1000	N.D.	520	0.011	520
HpCDFs	0.064	120	0.012	120	0.018	1300	0.024	1300	0.032	360	0.0059	360
OCDF	N.D.	35	0.016	35	N.D.	740	0.024	740	N.D.	430	0.0089	430
Total PCDFs	0.064	760	0.028	760	0.018	4400	0.17	4400	0.062	7300	0.16	7300
PCDDs+PCDFs	1.5	870	0.076	870	0.54	5000	0.22	5000	0.46	7500	0.17	7500
nonortho PCBs	0.041	41	9	50	0.02	60	5.6	66	0.039	390	1.6	390
mono-ortho PCBs	0.15	22	0.035	22	0.05	68	0.03	68	0.064	1200	0.013	1200
Total DL-PCBs	0.19	61	9	70	0.07	130	5.6	130	0.1	1600	1.7	1600
Total Dioxins	**1.7**	**930**	**9**	**940**	**0.6**	**5100**	**5.8**	**5100**	**0.55**	**9100**	**1.8**	**9100**

Among the three matrices (bottom ash, fly ash, and gas), the largest concentrations of chlorinated dioxins were measured in fly ash. This was the case for both PCDDs and DL-PCBs, although large amounts of PCDDs were also detected in bottom ash by PP and PS incineration, and DL-PCBs were also detected in gas by PP, PS, and PE incineration. Almost all the DL-PCBs detected in gas were non-ortho PCBs, while those detected in bottom ash and fly ash were both non-ortho and mono-ortho PCBs.

The concentration of chlorinated dioxins per unit weight of chlorine is shown in **Figure 2b**. For chlorine-free plastics, the concentration was calculated by converting the value per weight of chlorine contained in NaCl. For PVC and PVDC, the concentration was calculated by converting the value per weight of chlorine in the polymer structure of the plastic. The concentration per unit weight of chlorine was 15,000 ng/g-Cl for PP, 3,500

ng/g-Cl for PS, 9,400 ng/g-Cl for PE, 92,000 ng/g-Cl for PET, 9,200 ng/g-Cl for PVC, and 14,000 ng/g-Cl for PVDC. The concentrations were highest for PET incineration, and there were no differences among the other five plastics, with PET having about 6–26 times higher generation per weight of chlorine. It was therefore concluded that there was no large difference in generation of chlorinated dioxin between chloride in NaCl and polymers.

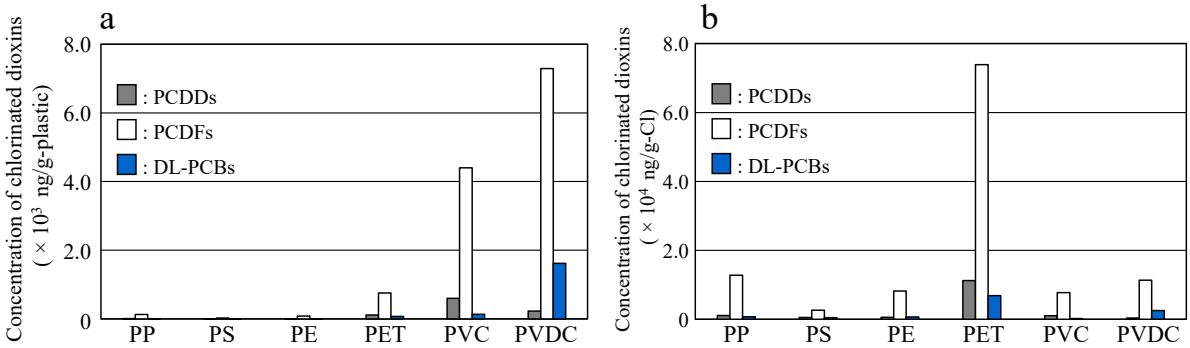

Figure 2: 3: Concentration of chlorinated dioxins from plastic incineration.
a. Concentration per unit weight of plastic(ng/g-plastic)
b. Concentration per unit weight of chlorine(ng/g-Cl).

The toxicity equivalent quantity (TEQ) values for chlorinated dioxins from plastic incineration are shown in **Table 2**. The total TEQ was 2.7 ng-TEQ/g-plastic for PP, 0.54 ng-TEQ/g-plastic for PS, 1.8 ng-TEQ/g-plastic for PE, 17 ng-TEQ/g-plastic for PET, 70 ng-TEQ/g-plastic for PVC, and 39 ng-TEQ/g-plastic for PVDC. The order of magnitude was PVC > PVDC > PET > PP > PE > PS, which differed from that for the total amount of chlorinated dioxins. Among the PCDDs, 2,3,7,8-TeCDD contributed most to the toxicity in PP, PS, and PE, while 1,2,3,7,8-PeCDD contributed most to the toxicity in PET, PVC, and PVDC. Among the PCDFs, 2,3,7,8-TeCDF (PP, PS, PE, PVDC), 2,3,4,7,8-PeCDF (PP, PE, PET, PVC, PVDC), and 1,2,3,6,7,8-HxCDF (PVC, PVDC) made the largest contribution to the overall toxicity. For DL-PCBs, most of the toxicity was derived from 3,3',4,4',5-PeCB (#126).

Table 2: Toxicity equivalent quantity in chlorinated dioxins (ng-TEQ/g-plastic)

PP				PS				PE			
Gas	Bottom ash	Fly ash	Total	Gas	Bottom ash	Fly ash	Total	Gas	Bottom ash	Fly ash	Total
0.00085	0.033	2.6	2.7	0.00033	0.031	0.51	0.54	0.00055	0.00098	1.8	1.8
PET				**PVC**				**PVDC**			
Gas	Bottom ash	Fly ash	Total	Gas	Bottom ash	Fly ash	Total	Gas	Bottom ash	Fly ash	Total
0.0011	0.0032	17	17	0.0026	0.00084	70	70	0.00023	0.0012	39	39

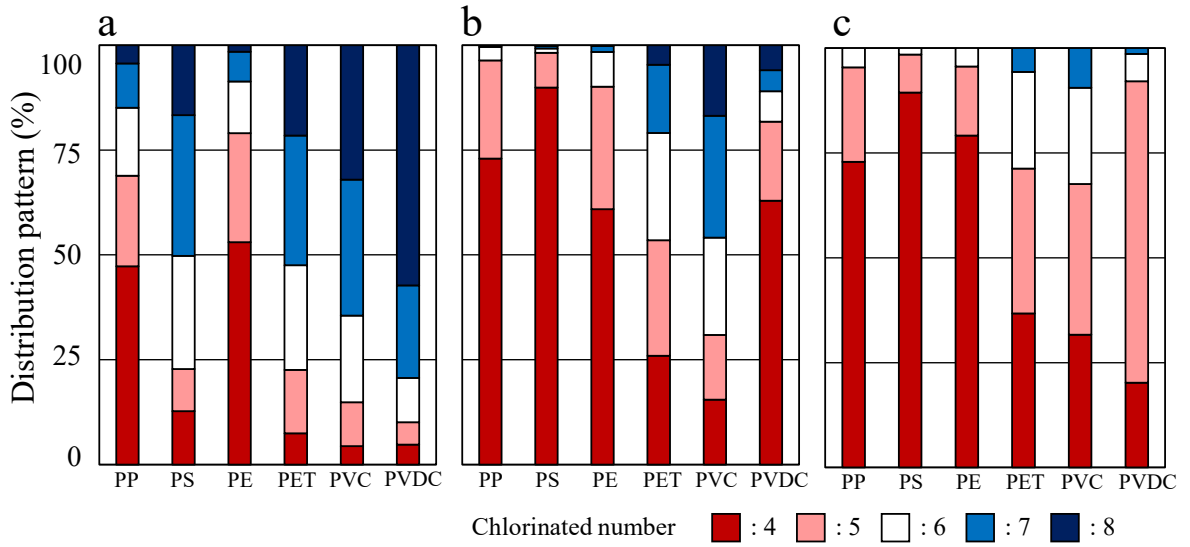

Figure 3: Distribution pattern of chlorinated dioxins (a. PCDDs, b. PCDFs, c. DL-PCBs)

The distribution patterns of the homologues are shown in **Figure 3**. The PCDDs tended to produce the most highly chlorinated homologues, and PET, PVC, and PVDC were more likely to produce highly chlorinated homologues than PP, PS, and PE. The distribution pattern differed between PCDDs and PCDFs, especially in the case of PVDC incineration, where most of the PCDDs were 7- and 8-chlorinated homologues, whereas most of

the PCDFs were 4-chlorinated homologues. According to a previous study[16], a feasible pathway for the generation of PCDFs is the dichlorination of 8-clorinated compounds, but this does not apply to PCDDs. The homologue distribution of PVDC may have differed significantly in terms of PCDD/Fs due to this difference in the dechlorination process.

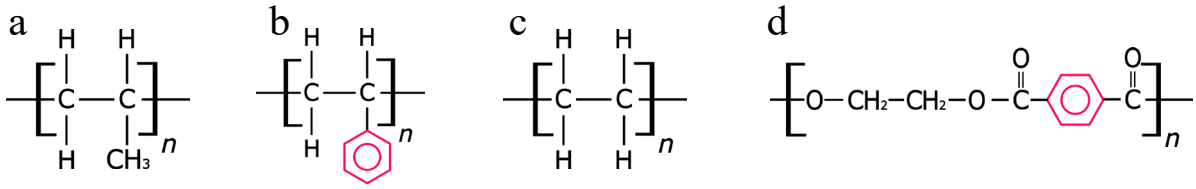

Figure 4: The polymer structure of four chlorine-free plastics. a. PP, b. PS, c. PE, d. PET.

The highest concentration of chlorinated dioxins among the four chlorine-free plastics was generated from PET. The structure of the plastic polymers is illustrated in **Figure 4**, which shows that PET contains benzene rings in the polymer. Although PS also contains benzene rings in the polymer, it generated the lowest concentration of chlorinated dioxins, likely due to differences in the positioning of the benzene rings in the polymers. In PET, the benzene rings are positioned within the main chain, whereas PS contains benzene rings in the side chains. A previous study of the incineration of plastic polymers with PVC[17] revealed that the similarity between PS and PE was high, while that between PS and PET it was low. The dioxin formation mechanism was therefore thought to differ between PS and PET, which suggests that differences in the position of the functional groups also affected the formation mechanism.

Conclusion

This study confirmed that chlorinated dioxins can be produced via the incineration of chlorine-free plastics with inorganic chlorine. Although the concentration of chlorinated dioxins from chlorine-containing plastic was much higher, more than 50% of the discarded plastics in Japan are PE and PP[2]. The effects of incinerating chlorine-free plastic cannot therefore be ignored. The quantity of chlorinated dioxins produced per unit weight of chlorine was similar among plastics, with the exception of PET. Among the three matrices (fly ash, bottom ash, and gas), the concentration of chlorinated dioxins was highest in fly ash, especially for PCDFs.

Among the chlorine-free plastics, PET produced the largest quantity of chlorinated dioxins and tended to produce highly chlorinated products. In contrast, the amount generated by PS, which like PET also contains a benzene ring in its structure, was small, and low-chlorinated products tended to be more easily generated. Therefore, it is necessary to conduct experiments on other plastics with a structure containing benzene rings in the main chain, such as polycarbonate.

Acknowledgements

This study was supported by Grant-in-Aid for Young Scientists (A) (Project No. 17H04718) and Grant-in-Aid for Scientific Research (B) (Project No. 20H04353). The analysis of chlorinated dioxins was carried out by the Kansai Environmental Management Technology Center.

References

1. Geyer R., Jambeck J. R., Law K. L. (2017) *Science Advances*. 3(7): e1700782.
2. Plastic Waste Management Institute, (2020) http://www.pwmi.or.jp/pdf/panf2.pdf. 18 June 2021.
3. Olie K., Vermeulen P. L., Hutzinger O. (1977) *Chemosphere*. 8: 455-459.
4. Brzuzy P. L., and Hites R. A. (1996) *Environmental Science & Technology*.30(6): 1797-1804.
5. McNeill I. C., *et al*. (1997). *Polymer Degradation and Stability.* 62: 145-155.
6. Kim K., Hong K., Ko Y., Kim M. (2004) *Journal of the Air & Waste Management Association*. 54: 555-562.
7. Ohta M., *et al*. (2004) *Chemosphere*. 54: 1521-1531.
8. Takasuga T., *et al*. (2007) *Archives of Environmental Contamination and Toxicology.* 53: 8-21.
9. Kanters M. J., Van Nispen R., Louw R., Mulder P. (1996) *Environmental Science & Technology*.30: 2121-2126.
10. Wikström E., *et al.* (1996) *Environmental Science & Technology.* 30: 1637-1644.
11. Fujimori T., Takaoka M., Takeda N. (2009) *Environmental Science & Technology.* 43: 8053-8059.
12. Zhang H., He P., Shao L. (2008) *Science of the Total Environment.* 402: 257-267.
13. De Micco G., Bohé A. E., Pasquevich D. M. (2007) *Journal of Alloys and Compounds*. 437: 351-359.
14. Fujimori T., Toda A., Mukai K., Takaoka M. (2020) *Journal of Hazardous Materials.* 382: 121030.
15. Ishibashi N. (2002) Ritsumeikan University. Doctoral thesis.
16. Iino F., Imagawa T., Gullett B. K. (2000). *Environmental Science & Technology.* 34: 3143-3147.
17. Katami T., Yasuhara A., Okuda T. Shibamoto T. (2002) *Environmental Science & Technology.* 36:1320-1324.