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Formation of PCDDs, PCDFs, and Coplanar PCBs from Plastic Containing Curtains during Combustion in an Incinerator

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Accidental fires in modern buildings generate large amounts of dioxin pollutants, as well as other bioaccumulative organochlorines, because of the many household products and building materials that contain polyvinyl chloride (Ahling et al., 1978). The distribution pattern of dioxins found in ambient air from domestic house fire accidents, with various household products containing polyvinyl chloride, was consistent with that of dioxins collected from experimentally combusted polyvinyl chloride (Theisen et al., 1989). We have reported on the formation of dioxins, PCDDs, PCDFs, and coplanar PCBs from the combustion of various organic chloride materials, such as polyvinyl chloride (Katami et al., 2002; 2004a; 2004b; Yasuhara et al., 2001; 2002; 2003; 2005a; 2005b; 2005c; 2006).

Although building-standard laws require interior housing materials, such as wallpapers and curtains, to be more flame resistant, more than 90% of the flame-resistant ingredients in use contain polyvinyl chloride. Furthermore, other building materials that are composed of 0.5% (w/w) plastic products may contain hard polyvinyl chloride (41.9%), soft polyvinyl chloride (33.7%), and other various plastics (24.4%). Therefore, to assess the role of polyvinyl chloride in the formation of dioxins from accidental house fires, we experimentally combusted curtains treated with polyvinyl chloride or phosphorous compounds, and we analyzed the sample and exhaust gases.

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Materials and Methods

Isotope-labeled PCDDs, PCDFs, and coplanar PCBs (non-ortho-PCBs and monoortho-PCBs) for internal standards (10 ng/mL n-nonane) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The solution for the sampling-spike recovery test was prepared by adding 0.0005 ng/μL each of $^{13}C_{12}$-1,2,3,4-T_4CDD; 1,2,3,4,7,8-H_6CDF; and 1,2,3,4,6,7,8-H_7CDF solution to a 1 mL n-nonane solution. The solution for the clean-up-spike recovery test was prepared by adding 0.005 ng/μL each of $^{13}C_{12}$-2,7-D_2CDD; 2,3,7-T_3CDD; 2,3,7,8-T_4CDD; 1,2,3,7,8-P_5CDD; 1,2,3,6,7,8-H_6CDD; 1,2,3,4,6,7,8-H_7CDD; 1,2,3,4,6,7,8,9-O_8CDD; $^{13}C_{12}$-2,3,7,8-T_4CDF; 1,2,3,7,8-P_5CDF; 1,2,3,4,7,8-H_6CDF; 1,2,3,4,7,8,9- H_7CDF; 1,2,3,4,6,7,8,9-O_8CDF; $^{13}C_{12}$-3,3′,4,4′-T_4CB; 3,4,4′,5-T_4CB; 3,3′,4,4′,5- P_5CB; 2′,3,4,4′,5-P_5CB; 3,3′,4,4′,5,5′-H_6CB; 2,3′,4,4′,5,5′-H_6CB; and 2,3,3′,4,4′,5,5′-H_7CB to a 100 μL n-nonane solution. For the solution of the internal standards, a 2 μL n-nonane solution containing 0.25 ng/μL each of $^{13}C_{12}$-1,3,6,8-T_4CDD; 1,2,3,7,8,9-H_6CDD; and 2,2′,3,4,4′,5,5′-H_7CB was prepared. n-Nonane was bought from Kanto Chemical Co., Inc. (Tokyo, Japan). Two different commercial curtains, which passed the flame-resistance test conducted by the Enforcement Regulation of Fire Protection Law, were obtained from Sangetsu Co., Ltd. (Nagoya, Japan). Commercial curtain (Sample I) consisted of 100% acrylic fiber treated with polyvinyl chloride (chlorine content 21%, w/w) and commercial curtain (Sample II) consisted of 100% polyester fiber treated with a phosphorous compound (chlorine content less than 0.01%, w/w). Samples I and II were combusted in an incinerator previously used (Yasuhara et al., 2001). The incinerator was equipped with two subsidiary combustion burners (Kato Burner Co., Ltd., Gifu, Japan)—one at the upper part of the combustion chamber (550 mm from grate) and the other near the grate (150 mm from grate)— with a heat supply of 30,000 kcal/h. Propane gas (97.6%), containing < 0.0005% of Cl and 0.0008% of sulfur, was used for fuel. The firebricks structuring the inside walls of the combustion chamber and the fire clay forming the grate were changed after each experiment in order to avoid any contamination from the previous experiment. The two subsidiary burners were turned on 1 h prior to combustion of the samples in order to maintain a constant temperature, and the burners remained on because of the samples' fire resistant-potential. Air for combustion was supplied from pipes located at the four corners of the combustion chamber. Optimum combustion was obtained by adjusting an air valve attached to the pipes. The combustion chamber and flame temperatures were measured at the center of the combustion chamber and at the grate by a LK-1200 thermo-couple conductor interfaced to a CT-1310 digital thermometer (Custom Co., Ltd., Tokyo, Japan). Samples I and II were cut into 20 cm squares and were placed in the incinerator with a 30 sec interval between placements. Sample I (1.648 g) was combusted in 1 h and 40 min. Sample II (1.139 g) was combusted in 1 h and 25 min. Exhaust gases were collected using a previously reported method (Katami et al., 2002; Yasuhara et al., 2003). Gas samples were collected at the sampling port located between the combustion chamber and the cyclone. Sample preparation was conducted using a previously reported method (Yasuhara et al., 2002). The chloride content in the combustion samples was measured by a TOX-100 Total Organic Halogen Analyzer (Dia Instruments Co., Ltd., Chigasaki, Japan). Continuous measurement of carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2) in combustion samples was performed by a Horiba PG-230 Gas Analyzer (Horiba, Ltd., Kyoto, Japan). Hydrogen chloride (HCl) concentration in exhaust gas was measured by a Yokogawa IC-7000S Ion Chromatograph (Yokogawa Analytical Systems, Inc., Tokyo, Japan). Analysis of dioxins (PCDDs, PCDFs, and coplanar PCBs) was performed by a previously reported method (Yasuhara et al., 2002), using a Hewlett-Packard (HP) model 5890 gas chromatograph (GC) interfaced to Micromass double focus MS (Auto Spec ULTIMA, England).

Table 1 Conditions and contents of incinerator and concentrations of CO_2, CO, Cl, and HCl in the exhaust gases from combustion of acryl fiber (Sample I) and polyester fiber (Sample II) curtains

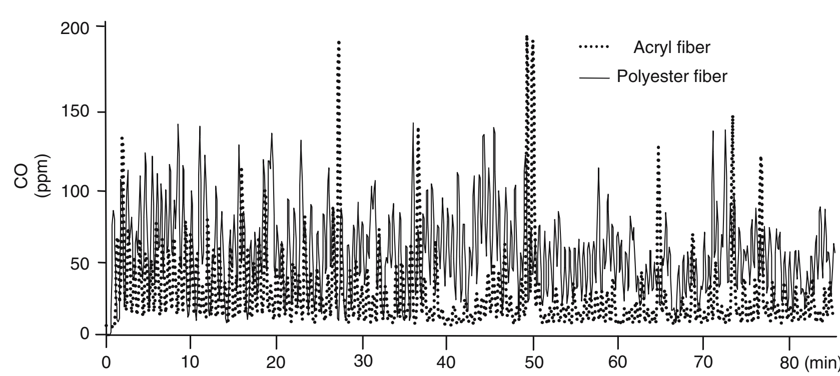
Combustion sample	Sample I	Sample II
Cl content (wt%)	21	< 0.01
Combustion amount (kg/h)	0.99	0.80
Average grate temp. (°C)	999	960
Average chamber temp. (°C)	860	813
Ave. exhaust gas temp. (°C)	611	580
Ave. amt. of dry exhaust gas (m3N /h)	245	240
Average oxygen conc. (%)	12.5	13.0
Average CO_2 conc. (%)	5.9	5.7
Average CO conc. (ppm)[a]	21	63
Water content (%)	10.7	11.1
Average HCl conc. (mg/m3N)[a]	1100	10

[a] Relative to 12% oxygen

Results and Discussion

The recovery efficiencies of standard dioxins from Samples I and II with sampling-spike were 78.2 and 74.2% for $^{13}C_{12}$-1,2,3,4-T_4CDD; 83.1 and 71.1% for $^{13}C_{12}$-1,2,3,4,7,8-H_6CD; and 112.9 and 74.7% for $^{13}C_{12}$-1,2,3,4,7,8,9-H_7CDF, respectively. The recovery efficiencies of standard dioxins from Samples I and II with clean-up-spike were75.4% and 92.1% for $^{13}C_{12}$-2,3,7,8-T_4CDD; 85.8% and 108.6% for $^{13}C_{12}$-1,2,3,7,8-P_5CDD; 88.5% and 116.9%

Fig. 1 CO content in the exhaust gases during combustion of curtain samples



for $^{13}C_{12}$-1,2,3,6.7,8- H_6CDD; 80.2% and 74.5% for $^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD; 69.1% and 65.3% for $^{13}C_{12}$-1,2,3,4,6,7,8,9 -O_8CDD; 74.6% and 87.4% for $^{13}C_{12}$-2,3,7,8-T_4CDF; 72.6% and 95.3% for $^{13}C_{12}$-1,2,3,7,8-P_5CDF; 84.8% and 111.7% for $^{13}C_{12}$-1,2,3,4,7,8- H_6CDF; 72.5% and 67.6% for $^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF; 68.6% and 66.4% for $^{13}C_{12}$-1,2,3,4,6,7,8,9-O_8CDF; 74.6% and 65.7% for $^{13}C_{12}$-3,3′,4,4′-T_4CB; 86.1% and 69.0% for $^{13}C_{12}$-3,4,4′,5-T_4CB; 65.1% and 58.5% for $^{13}C_{12}$-3,3′,4,4′,5-P_5CB; 107.5% and 97.5% for $^{13}C_{12}$-2′,3,4,4′,5-P_5CB; 57.7% and 55.5% for $^{13}C_{12}$- 3,3′,4,4′,5,5′-H_6CB; 96.4% and 85.6% for $^{13}C_{12}$-2,3′,4,4′,5,5′-H_6CB; 89.2% and 64.0% for $^{13}C_{12}$-2,3,3′,4,4′,5,5′-H_7CB in the present study. The recoveries of both the sampling spikes and the clean-up spikes for PCDDs and PCDFs were satisfactory values of over 60%. Table 1 shows combustion conditions of the incinerator and concentrations of inorganic gases in the exhaust gases from curtain samples.

As Figure 1 illustrates, the CO content in the exhaust gases fluctuated within 200 ppm during the combustion of acryl fiber and polyester fiber curtains. The temperature inside the incinerator was steadily maintained throughout the combustion (near 1000°C), suggesting that the combustion occurred efficiently. Table 2 shows the results of PCDD, PCDF, and coplanar-PCB analysis in the exhaust gases from curtain samples combusted in an incinerator.

Total numbers of congeners analyzed were 75 for PCDD, 134 for PCDF, and 12 for non-ortho and mono-ortho coplanar PCB. PCDFs comprised 74.3% and 78.6% of the total dioxins formed in the exhaust gases from Sample I (acryl fiber curtain) and Sample II (polyester fiber curtain), respectively. Among the PCDDs formed, P_5CDD formed in the greatest amount an acryl fiber curtain (Sample I: 0.258 ng/g sample, 1.02 ng/m^3 exhaust gas) from and H_6CDD from a polyester fiber (Sample II: 0.082 ng/g sample, 0.275 ng/m^3 exhaust gas). Among the PCDFs formed, T_3CDF formed in the greatest amount from Sample I (1.07 ng/g sample, 4.30 ng/m^3 exhaust gas) and M_1CDF from Sample II (1.95 ng/g sample, 6.52 ng/m3 exhaust gas). Mono-ortho coplanar PCB formed more than non-ortho coplanar PCB.

Generally, the higher the number of chlorine, the less PCDD or PCDF was produced both from Samples I and II. A chlorine content ratio of acryl fiber/polyester fiber curtains was over 2,100 (Table 1). On the other hand, a dioxin formation ratio of acryl fiber/polyester fiber curtains obtained was 3.0 from PCDDs, 1.9 from PCDFs, 1.3 from coplanar PCBs, and 2.0 from total dioxins. The significant low ratio of dioxin formation compared with that of the chlorine content may be because of the inhibitory effect of high temperature combustion toward the dioxin formation. The results indicate that the formation of dioxins from materials with high chlorine content upon combustion can be reduced by a high temperature treatment. Table 3 shows toxicity equivalency quantity (TEQ) of dioxins found in exhaust gases from combustion of acryl fiber (Sample I) and polyester fiber (Sample II) curtains. The TEQ was calculated using a previously reported method (Van den Berg et al., 1998). TEQ values of samples were also calculated in ng/m^3 in order to compare the results to the published data. The total TEQ values of exhaust gas from Samples I and II were 0.268 and 0.051 ng-TEQ/m^3,

Table 2 Amounts of dioxins found in exhaust gases from combustion of acryl fiber (Sample I) and polyester fiber (Sample II) curtains

Dioxin	Number of congeners	Amount of dioxins			
		Sample I		Sample II	
		ng/g	ng/m^3	ng/g	ng/m^3
PCDDs					
M_1CDDs	2	0.042	0.169	0.009	0.030
D_2CDDs	10 0	.075	0.301	0.060	0.099
T_3CDDs	14	0.152	0.608	0.041	0.134
T_4CDDs	22	0.426	1.71	0.111	0.366
P_5CDDs	14	0.258	1.02	0.074	0.240
H_6CDD	10	0.254	1.02	0.082	0.275
H_7CDDs	2	0.133	0.535	0.073	0.244
O_8CDD	1	0.061	0.245	0.049	0.162
Total	1.40	5.63	0.469	1.55	
PCDFs					
M_1CDFs	4	1.04	4.16	1.95	6.52
D_2CDFs	16	0.566	2.28	0.096	0.323
T_3CDFs	27	1.07	4.30	0.207	0.690
T_4CDFs	38	0.855	3.44	0.164	0.549
P_5CDFs	28	0.655	2.64	0.174	0.574
H_6CDFs	16	0.460	1.85	0.085	0.278
H_7CDFs	4	0.279	1.12	0.062	0.210
O_8CDF	1	0.150	0.604	0.024	0.080
Total	5.07	20.4	2.76	9.22	
Non-ortho Co-PCBs					
T_4CBs	2	0.105	0.420	0.062	0.208
P_5CB	1	0.025	0.100	0.010	0.033
H_6CB	1	0.008	0.031	0.003	0.009
Total	0.138	0.551	0.075	0.250	
Mono-ortho Co-PCB					
P_5CBs	4	0.178	0.717	0.164	0.546
H_6CBs	3	0.031	0.127	0.024	0.080
H_7CB	1	0.007	0.026	0.007	0.022
Total	0.216	0.870	0.195	0.648	
Total Co-PCBs	0.353	1.42	0.270	0.898	
Total PCDDs + PCDFs + Co-PCBs	6.81	27.4	3.50	11.7	

Table 3 Toxicity equivalency quantity (TEQ) of dioxins found in exhaust gases from combustion of acryl fiber (Sample I) and polyester fiber (Sample II)

		Sample I		Sample II	
Dioxin	No. of congener	ng-TEQ/g	Ng-TEQ/m^3	ng-TEQ/g	ng-TEQ/m^3
PCDDs					
T_4CDD	1	0.003	0.013	0.001	0.002
P_5CDD	1	0.012	0.050	0.002	0.007
H_6CDDs	3	0.003	0.013	0 0.003	
H_7CDD	1	0.001	0.003	0	0.001
O_8CDD	1	0	0	0	0
Total	0.019	0.079	0.003	0.013	
PCDFs					
T_4CDF	1	0.003	0.010	0.004	0.013
P_5CDFs	2	0.026	0.106	0.007	0.022
H_6CDFs	4	0.014	0.055	0.003	0.010
H_7CDF	1	0.001	0.008	00.001	
O_8CDF	1	0	0	0	0
Total	0.044	0.179	0.011	0.035	
Total PCDDs + PCDFs	0.063	0.258	0.014	0.048	
Co-planar PCBs					
T_4CBs	2	0	0	0	0
3,3′4,4′,5-P_5CBs	5	0.003	0.010	0.001	0.003
3,3′,4,4′,5,5′-H_6CBs	4	0	0	0	0
2,3,3′,4,4′,5,5′-H_7CB	1	0	0	0	0
Total	0.003	0.010	0.001	0.003	
Grand total	0.052	0.066	0.015	0.051	

respectively. It is obvious that Sample I, which has a much higher chlorine level, has a much higher value of TEQ than Sample II. The amount of the most potent carcinogen, 2,3,7,8-T_4CDD (factor 1) was 0.013 and 0.002 ng-TEQ/m^3 in Samples I and II, respectively. The amount of another factor 1 PCDD, 1,2,3,7,8-P_5CDD, was 0.050 and 0.007 ng-TEQ/m^3 in Samples I and II, respectively. The levels of these potent carcinogenic PCDDs must play a significant role in the TEQ values of exhaust gases.

The formation pattern of dioxin congeners from an acryl fiber curtain (Sample I) was similar to that from a mixture of polyethylene and polyvinyl chloride (Katami et al., 2002). There is some correspondence between dioxin formation and chlorine content of combustion samples. Many building materials, including curtains, contain plastics with chlorides, such as polyvinyl chloride. Therefore, it is expected that dioxin is formed in fire accidents in buildings, including common domestic houses. Furthermore, laboratory combustion tests, conducted by Theisen et al. (1989), demonstrated 20–1,200 ppb levels of total PCDDs/PCDFs in samples obtained from real fire accidents. Therefore, it is confirmed that curtains treated with chlorine containing materials, as a method of fireproofing, produces dioxins upon combustion and therefore warrants further investigations on the possible influences of additives to building materials and the formation of dioxin during accidental fires. Table 3 shows toxicity equivalency quantity of PCDD, PCDF, and coplanar PCB found in curtain samples.

The results of the present study indicate that dioxins are formed from curtains containing plastics, such as PVC, upon incineration. The accidental fires of domestic house fires or fires in public buildings may also be sources of dioxin pollution in waste water. Furthermore, it should be noted that firefighters and bystanders at these fires may be exposed to dioxins from burning plastic-containing household products.

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