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Formation of Dioxins from Incineration of Fallen Leaf

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Leaf burning leads to air pollution, which may cause certain health problems. During fall and winter, tremendous amounts of fallen leaves form across the world. In developed countries, such as the United States and Japan, homeowners continuously rake up fallen leaves in their yards. Treatment of these fallen leaves has begun to receive much attention by environmental scientists. The open burning of leaves in the homeowner's yards produces a number of toxic chemicals, including low-molecular-weight aldehydes and ketones, which cause irritation of the eyes, nose, throat, and lungs. Moreover, smoke from burning leaves contains carcinogenic polynuclear aromatic hydrocarbons (Friedman and Calabrese 1977) and dioxins (Yasuhara et al. 2001). London plane tree branches produced 174 pg/g PCDDs and 1990 pg/g PCDFs upon combustion at 403–525 °C (Yasuhara et al. 2001).

MATERIALS AND METHODS

In order to elucidate the details of dioxin formation in a combustion, fallen leaves of the cherry tree (*Prunus yedoensis* Matsum) and the Konara oak tree (*Quercus serrata* Thunb) were combusted in a small-scale incinerator under well-controlled conditions and the exhausted gases were subsequently analyzed for dioxins (PCDDs, PCDFs, and coplanar PCBs).

Isotope-labeled PCDDs, PCDFs, and coplanar PCBs (non-ortho-PCBs and mono-PCBs) for internal standards (10 ng/mL n-nonane) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Recovery tests of dioxins were conducted using a 1 mL n-nonane solution containing 0.0005 ng/μL each of standard isotope-labeled dioxins for the sampling-spike recovery test, and a 100 μL n-nonane solution containing 0.005 ng/μL each of standard isotope-labeled dioxin for the solution of the clean-up-spike recovery test. 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, $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD, and $^{13}C_{12}$-2,2',3,4,4',5,5'-H_7CB was prepared. n-Nonane was bought from Kanto Chemical Co., Inc. (Tokyo, Japan).

Fallen leaves were collected from the suburbs of Gifu, Japan. The leaves were allow to dry in the atmosphere for two months. Dried leaves of the cherry tree (average Cl content was 0.074%, w/w) and the Konara oak tree (average Cl content was 0.023%, w/w) were combusted in a small-scale incinerator used in a previous study (Katami et al. 2002). Cherry tree leaves (4020 g) were combusted at 722–770°C for 1 hr and 31 min. Konara oak tree leaves (3550 g) were combusted at 675–707°C for 1 hr and 29 min.

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The measurement of chloride content, carbon monoxide, carbon dioxide, hydrogen chloride, and oxygen in samples was performed by a method previously reported (Yasuhara et al. 2001). The exhaust gas samples were collected at the sampling port located between the combustion chamber and the cyclone using the apparatus previously reported (Katami et al. 2000). Dioxins were analyzed by a gas chromatography/mass spectrometry method previously reported (Yasuhara et al. 2001).

Combustion ash (10 g) and 100 mL of distilled water were mixed in an 300 mL Erlenmeyer flask for 6 h using a shaker. The solution was filtered with a 0.8 µm membrane filter followed by a 0.45 µm membrane filter. The solution obtained (leachate) was analyzed for chloride ions and for inorganic elements. Elementary analysis of the combustion ash was conducted using an EA1108 elementary analyzer (Fisons Instruments, Milano, Italy). Inorganic elements—Al (0.3); Ca (0.3); Cu (0.06); Fe (0.06); Mg (0.06); K (5); Na (1.0); B (0.3); and S (2)—in the combustion ash were analyzed by an inductively coupled plasma-atomic emission spectrometer (Nippon Jarrell-Ash Model 750 ICP-AES, (Tokyo, Japan) used under the following conditions: frequency, 27.12 MHz; radio frequency power, 1.1 kW; flow-rate of coolant gas (Ar), 20 L/min; carrier gas flow-rate, 0.5 L/min; observation height above coil, 18 mm; sample uptake rate, 1.2 mL/min; integration time, 5 s. Values in parentheses are detection limits (mg/L).

A Hewlett-Packard (HP) model 5890 gas chromatograph (GC) interfaced to Micromass double focus MS (Auto Spec ULTIMA, England) and equipped with a 60 m x 0.32 mm i.d. (d_f = 0.2 µm) SP-2331 bonded-phase fused-silica capillary column (Supelco, Bellefonte, PA) for Cl_{1-6}-PCDDs and Cl_{1-6}-PCDFs, a 30 m x 0.25 mm i.d. (d_f = 0.25 µm) DB-5 bonded-phase fused-silica capillary column (J &W Scientific, Folsom, CA) for $Cl_{7,8}$-PCDDs and $Cl_{7,8}$-PCDFs, or a 60 m x 0.32 mm i.d. (d_f = 0.25 µm) DB-5 bonded-phase fused-silica capillary column (J &W Scientific, Folsom, CA) for coplanar PCBs was used. Gas chromatographic oven temperatures were programmed from 130°C to 190°C at 20°C/min and then to 250°C at 2°C/min for the SP-2331 column, programmed from 130°C to 280°C at 10°C/min for the 30 m-DB-5 column, and programmed from 150°C (held for 1 min) to 185 °C at 20 °C/min and then programmed at 2°C to 245°C (held for 3 min), at 6°C to 290°C (held for 10 min) for a 60 m-DB-5 column. The linear velocity of the helium carrier gas was 30 cm/sec. The injector temperatures were 250°C for the SP 2331 column and 280°C for the DB-5 columns. MS ion source temperatures were 250°C for the SP-2331 column and 289°C for the DB-5 column. MS ionization voltage was 35 eV.

RESULTS AND DISCUSSION

The recovery efficiencies of standard PCDDs and PCDFs with sampling-spike were 83 ± 3.6% for $^{13}C_{12}$-1,2,3,4,-T_4CDD; 83 ± 4.2 for $^{13}C_{12}$-1,2,3,4,7,8-H_6CDD; and 97 ± 2.7% for $^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF. The recovery efficiencies of standard PCDDs, PCDFs, and coplanar PCBs with clean-up-spike were 79 ± 3.7% for $^{13}C_{12}$-2,7-D2CDD; 84 ± 3.6% for $^{13}C_{12}$-2,3,7,-T_3CDD; 89 ± 3.7% for $^{13}C_{12}$-2,3,7,8-T_4CDD; 82 ± 1.0% for $^{13}C_{12}$-1,2,3,7,8-P_5CDD; 90 ± 3.6% for $^{13}C_{12}$-1,2,3,6,7,8-H_6CDD; 84 ± 5.5% for $^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD; 88 ± 5.1% for $^{13}C_{12}$-1,2,3,4,6,7,8,9-O_8CDD; 81 ± 2.6% for $^{13}C_{12}$-2,3,7,8-T_4CDF; 82 ±3.7% for $^{13}C_{12}$-1,2,3,7,8-P_5CDF; 90 ± 2.8% for $^{13}C_{12}$-1,2,3,4,7,8-H_6CDF; 83 ± 5.8% for $^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF; 86 ± 5.2% for $^{13}C_{12}$-1,2,3,4,6,7,8,9-O_8CDF; 85 ± 1.2% for $^{13}C_{12}$-3,3’,4,4’-T_4CB; 83 ± 1.9% for $^{13}C_{12}$-3,,4,4’,5-T_4CB; 89 ± 5.1% for $^{13}C_{12}$-3,3’,4,4’,5-P_5CB; 81 ± 3.2% for $^{13}C_{12}$-2’,3,4,4’,5-P_5CB; 87 ± 4.6% for $^{13}C_{12}$-

3,3',4,4',5,5'-H_6CB; 85 ± 5.3% for $^{13}C_{12}$-2,3',4,4',5,5'-H_6CB; and 87 ± 1.8% for $^{13}C_{12}$-2,3,3',4,4',5,5'-H_7CB. The values are mean ± SD ($n = 5$). The recoveries of both the sampling spikes and the clean-up spikes were satisfactory values of over 79%.

Table 1 shows the concentrations of CO_2, CO, and Cl^- in the exhaust gases from the leaf samples along with the conditions in the incinerator.

Table 1. Conditions of incinerator and concentrations of CO_2, CO, and Cl^- in the exhaust gases.

	Combustion leaf samples	
Conditions and Concentrations	Cherry tree	Konara oak tree
Cl content (wt%)	0.074	0.023
Combustion amount (kg/h)	2.64	2.40
Grate temp. (°C): Range	757–636	670–591
Average	705	635
Chamber temp. (°C): Range	770–722	707–675
Average	746	692
Ave. exhaust gas temp. (°C)	480	513
Ave. amt. of dry exhaust gas (m^3N /h)	218	237
Average oxygen conc. (%)	15.4	16.0
Average CO_2 conc. (%)	4.2	5.5
Average CO conc. (ppm)[1]	240	270
Water content (%)	9.6	10.8
Average Cl^- conc. (mg/m^3N)[1]	15	15

[1] Relative to 12% oxygen.

Elementary analysis of the combustion ash resulted in 0% nitrogen, 7.5% carbon, and 0% hydrogen from the cherry tree leaves and 0% nitrogen, 7.3% carbon, and 0% hydrogen from the Konara oak tree leaves. Concentrations of inorganic elements in the leachate from the combustion ash were 9.5 mg/L Al; 4.2 mg/L B; 11 mg/L Ca; < 0.06 mg/L Cu; < 0.06 mg/L Fe; 4400 mg/L K; < 0.06 mg/L Mg; 300 mg/L Na; 270 mg/L Cl; and 180 mg/L S from cherry tree leaves and 0.4 mg/L Al; 1.2 mg/L B; 340 mg/L Ca; < 0.02 mg/L Cu; < 0.06 mg/L Fe; 1000 mg/L K; < 0.02 mg/L Mg; 23 mg/L Na; 74 mg/L Cl; and 130 mg/L S from Konara oak tree leaves. The most abundant inorganic element in both kinds of leaves was K. Combustion ash from the Konara oak tree leaves also contained a high level of Ca (340 mg/L). Concentrations of Ca, K, and Na indicate that the main chlorine sources were KCl or NaCl for the cherry tree leaves and $CaCl_2$ or KCl for the Konara oak tree leaves. Generally, formation of Cl_4–Cl_8-PCDDs and Cl_4–Cl_8-PCDFs was less in the samples where the chlorine source was $CaCl_2$: the Konara oak tree leaf samples, the total of Cl_4–Cl_8-PCDDs and Cl_4–Cl_8-PCDFs was 0.680 ng/g; in the cherry tree leaf samples where the chlorine source was NaCl, the total of Cl_4–Cl_8-PCDDs and Cl_4–Cl_8-PCDFs was 1.74 ng/g (Katami et al. 2002).

Table 2 shows the analytical results of dioxins in the exhausted gases collected

Table 2. Amounts of PCDDs, PCDFs, and coplanar PCBs found in the exhausted gases from combustion of leaf samples.

	Amounts of dioxins (ng/g)	
Chemical	Cherry tree leaf	Konara oak tree leaf
M_1CDDs	0.016	0.074
D_2CDDs	0	0.034
T_3CDDs	0.039	0.024
T_4CDDs	0.056	0.029
P_5CDDs	0.078	0.025
H_6CDDs	0.097	0.033
H_7CDDs	0.091	0.011
O_8CDDs	0.062	0.008
Total PCDDs	0.439	0.237
M_1CDFs	1.65	5.36
D_2CDFs	1.36	2.50
T_3CDFs	1.38	1.43
T_4CDFs	0.478	0.335
P_5CDFs	0.382	0.141
H_6CDFs	0.281	0.064
H_7CDFs	0.165	0.025
O_8CDFs	0.049	0.009
Total PCDFs	5.74	9.86
Co-PCBs	0.192	0.141
Grand total	6.37	10.2
TEQ (ng-TEQ/g)[1]	0.039	0.012

[1] Toxicity Equivalency Quantity

from a chamber port, along with the toxicity equivalency quantity (TEQ) of the samples (Van den Berg et al. 1998).

The Konara oak tree leaf sample produced more dioxins (total, 10.2 ng/g) than the cherry tree leaf sample (total 6.37 ng/g). Chlorine concentrations in the cherry tree leaf sample (0.074%) and in the Konara oak tree leaf sample (0.023%) did not correspond with the total dioxin formation. This may be due to the fact that the average grate-temperature for the cherry tree leaf sample was relatively high (705°C); consequently, the formation of Cl_1–Cl_3-PCDDs and Cl_1–Cl_3-PCDFs was not consistent.

PCDFs comprised 89% and 92% of the total dioxins in the cherry tree leaf sample and in the Konara oak tree leaf sample, respectively. M_1CDFs were the primary component. PCDDs comprised only 6.9% and 2.3% of the total dioxins in the cherry tree leaf sample and the Konara oak tree leaf sample, respectively. The most potent dioxins, T_4CDDs, comprised 11.8% and 12.2% of total PCDDs formed in the cherry tree leaf sample and the Konara oak tree leaf sample, respectively. The TEQ value of the cherry tree leaf samples (0.039 ng-TEQ/g) was higher than that of the Konara oak tree leaf samples (0.012 ng-TEQ/g). This may be due to the fact that T_4CDDs were present in higher quantities in the cherry tree leaf samples (0.052 ng/g) than in the Konara oak tree leaf samples (0.029 ng/g).

The present study indicates that fallen leaves produce 6–10 ng/g levels of dioxins upon combustion. The TEQ concentration values of the cherry tree leaf samples (0.48 ng-TEQ/m^3) and the Konara oak tree leaf samples (0.12 ng-TEQ/m^3) were slightly higher than the maximum allowable level (0.1 ng-TEQ/m^3) in the exhaust gases set by the government of Japan. Therefore, it is important to incinerate fallen leaves in well-controlled systems, in order to minimize the formation of dioxins. Furthermore, burning fallen leaves in a homeowner's yard is not recommended.

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