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Analyses of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and precursors in fly ash samples collected at different points in post-combustion zone of Japanese machida incinerator

K. P. NAIKWADI and F. W. KARASEK*
Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)
and
H. HATANO[a]
Department of Chemistry, Kyoto University, Kyoto 606 (Japan)

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ABSTRACT

Several samples collected at the post-combustion zone of the Machida incinerator in Japan were analyzed for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated phenols (PCPs) and polychlorinated benzenes (PCBEs). All samples show lower levels of PCDDs and PCDFs in comparison to the levels observed in other samples from various incinerators around the world. The Machida incinerator in Japan shows ten times lower levels of PCDDS/PCDFs than the Ontario incinerator in Canada. Analyses of fly ash samples collected at different points in the post-combustion zone shows higher levels of PCDDs/PCDFs at points near the stack, and decreasing towards the combustion zone. That trend indicates the formation of PCDs/PCDFs in the electrostatic precipitator by catalytic activity of fly ash in addition to their probable formation in the incinerator furnace. Variations in normal operating conditions have no or very little effect on the amount of PCDDs/PCDFs formed. Municipal solid waste in Japan has been separated into combustible and non-combustible materials. Only the combustible materials were incinerated in the Machida incinerator, which is a fluidized bed design with CaO injection into the bed.

INTRODUCTION

A considerable volume of information has been accumulated on polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the last two decades. The

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[a] Visiting Professor at University of Waterloo during this study.

chemistry and toxicology of these compounds has been summarized in several reviews and texts[1–10]. The main sources currently of these highly toxic chemicals are herbicides[11], abandoned dump sites of industrial wastes[12] and products of municipal and industrial waste combustion[13,14].

Several publications show that the formation of PCDDs/PCDFs occurs in all municipal incinerators around the world[15–19]. However, there are considerable differences in the levels of PCDDs/PCDFs detected in the fly ash samples from the various incinerators. The formation of PCDDs/PCDFs in municipal solid waste (MSW) incineration has been considered to be a universal phenomenon and all incinerators pose a threat to a clean environment. But this understanding should be reassessed because under certain conditions some incinerators show negligible amounts of PCDDs/PCDFs in the fly ash and fall within the guidelines of environmental agencies. There are several benefits resulting from incineration of municipal waste such as reduction of the need for land filling and the generation of electricity and heat. Since the design and operational conditions of incinerators vary, it is important to analyze the fly ash from different incinerators and determine the operational conditions and factors involved in the formation of PCDDs/PCDFs that can eventually result in safe operation of incinerator with minimum environmental risks from PCDDs/PCDFs.

Work in our laboratories and others has established that the formation of PCDDs/PCDFs occurs by catalytic activity of fly ash[20–27]. Our laboratory has also been involved in analysis of fly ash samples from the different incinerators around the world for more than a decade[28–33]. The results revealed that the lower amounts of native PCDDs/PCDFs were detected in the fly ash sampes from the incinerator at Machida, Japan. Hence, we decided to explore in detail the effect of incinerator operation conditions and treatment of garbage prior to incineration on the formation of PCDDs/PCDFs as well as on the formation of such precursors as polychlorinated benzenes (PCBEs) and polychlorinated phenols (PCPs) in the Machida incinerator. Fly ash samples collected at different points in the post-combustion zone were analyzed to determine the levels of PCDDs/PCDFs at different points. The results from laboratory tests of catalytic activity of fly ash at different temperatures, and amounts of PCDDs/PCDFs detected in fly ash samples collected at different points and temperatures in the post-combustion zone can provide the information for postulation of possible mechanisms of formation PCDDs/PCDFs.

EXPERIMENTAL

Sample collection

Fifteen different fly ash samples were obtained from the Machida incinerator (Japan). Eight samples were collected at the post-combustion zone after electrostatic precipitation (point T in Fig. 1). Another two sets of samples (three each, B1, B2, B3 and C1, C2, C3) were collected at points X, Y and Z simultaneously.

Sample extraction

A 40–60-g portion of fly ash from each sample was separately soxhlet extracted using 350 ml of benzene for 48 h. The fly ash extract was then concentrated to 10 ml by rotary evaporation under aspirator vacuum and then transferred to a 25-ml pear

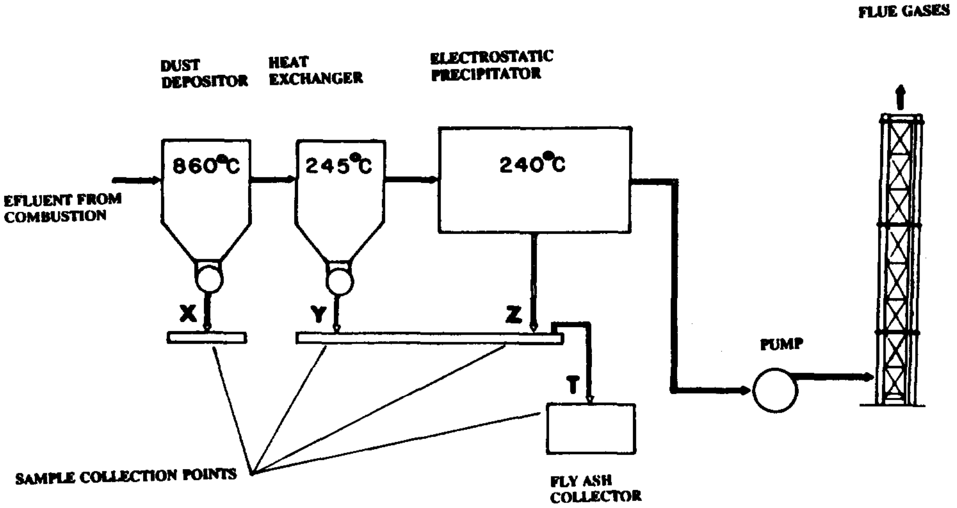

Fig. 1. Post-combustion zone of the Machida incinerator.

shaped flask and reduced to 1 ml by further rotary evaporation, then transferred to a 1-ml Reacti-vial. A final concentration of 150 μl was achieved by blowing a slow stream of high-purity nitrogen across the top of the vial. Exactly the same procedure was used for extraction and concentration of all fifteen samples.

Gas chromatographic (GC) and GC–mass spectrometric (MS) analysis

To estimate the concentration of organic compounds all samples were analyzed on a Hewlett-Packard HP-5880A gas chromatograph equipped with a flame ionization detector and a cool on-column injector. A 30 m × 0.32 mm I.D. DB-5 fused-silica capillary column (J & W Scientific, Rancho Cordova, CA, U.S.A.) was used.

The GC–MS system used was a Hewlett-Packard HP-5887A system equipped with dual [electron impact (EI) and chemical ionization (CI)] ion source and HP-1000 data system. Quantitation of PCBEs, PCPs, PCDDs and PCDFs and PCDFs was carried out using the GC–MS in the selected ion monitoring (SIM) mode. Qualitative identification of compounds in all samples was carried out using GC–MS in electron impact linear (EILIN) mode and probability base matching (PBM) library search of mass spectra for the peaks in total ion current trace (TIC) bases on 70 000 reference mass spectra. Total organic matter in each sample was estimated by using a standard mixture containing aliphatic hydrocarbons, aromatic hydrocarbons, chlorobenzenes, chlorophenols, PCDD and PCDF components. Average response factor area counts per nanogram was used to estimate the total organic matter.

GC conditions used were: injector temperature 50°C; initial temperature 80°C; program rate 4°C/min, to 160°C; then programmed to 300°C at 5°C/min, final time 10 min. The standard mixture used for quantitation of PCDDs, PCDFs, PCBEs and PCPs contains one isomer each of tetra-, penta-, hexa-, hepta- and octachlorodibenzodioxins and dibenzofurans as well as standard mixture of tetra- to hexachlorobenzenes and tetra- to pentachlorophenols. Three isotope ions (M, M + 2, M + 4 or M + 6) were monitored for tetra- to octachlorodibenzo-*p*-dioxins and dibenzofurans, tri- to hexachlorobenzenes and tri- to pentachlorophenols using GC–EISIM-MS.

Identification of compounds was confirmed using the following criteria: (1) The mass chromatograhic peaks must fall within a retention time "window" established for a specific class of isomers. (2) The mass chromatographic peaks produced by the component must exhibit the appropriate intensities for at least two major ions characteristic of the specific class being monitored. (3) The signal-to-noise ratio should be greater than 3.

Initially the retention windows were determined by using a mixture of PCDDs/PCDFs containing all possible isomers in tetra to octa congeners. For PCBEs and PCPs a single retention window was used where tri- to hexachlorobenzenes and tri- to pentachlorophenols were eluted.

RESULTS AND DISCUSSION

The amount of PCDDs, PCDFs, PCBEs and PCPs present in the eight fly ash samples from the Machida incinerator collected on eight different consecutive days exactly 24 h apart are shown in Table I. The results of the eight samples show that hexa- to octachlorodibenzodioxins and dibenzofurans are present in all samples. However, tetra- and pentachlorinated isomers are either not observed or are in the very low levels of 0.1 to 9 ng/g of fly ash in most of the samples. It should be noted that the levels of the relatively more toxic tetra and penta isomers as well as other PCDD and PCDF isomers in all these samples are extremely low as compared to the samples from other incinerators[20]. Even though the levels of PCDDs and PCDFs in all eight samples are low they are not uniform; sample 7 shows lowest amounts while sample 4 shows the highest levels. A general trend of an increase in the amount of PCDDs and PCDFs from tetra to octa isomers is observed. A comparison of the operating conditions (Table II) during sampling and the PCDDs and PCDFs detected at that time shows no correlation. From this observation it may be concluded that the amount of PCDDs and PCDFs formed depends on some other factors in the incinerators and small variation in normal operating conditions do not have significant effect on PCDDs/PCDFs formed.

The garbage treatment prior to incineration at Machida is different from other incinerators studied. Most of the solids, metallic materials and some plastics are separated from the combustible materials such as paper, wood and household refuse at the Machida incinerator. This may be significant with respect to dioxin formation. One of the mechanisms proposed for the formation of PCDDs and PCDFs is by reactions of molecular precursor species that are present during incineration, resulting in surface catalyzed synthesis of PCDDs/PCDFs on the fly ash via rearrangement, free radical condensation, dechlorination, dehydrogenation, trans-chlorination, isomerization and other similar molecular reactions[12]. From the reaction mechanisms established in organic chemistry, it can be presumed that all above said reactions can occur due to presence of different kinds of metal/metal oxides, inorganic halides and hydroxides formed in the incineration process. Inorganic halides and hydroxides can form in incineration process at high temperatures from traces of mineral acid, moisture and the

TABLE I

AMOUNTS OF PCDDs, PCDFs, PCBEs AND PCPs (ng/g FLY ASH) DETECTED IN MACHIDA FLY ASH SAMPLES

CDD = Chlorodibenzo-*p*-dioxin; CDF = chlorodibenzofuran; CBE = chlorobenzene; CP = chlorophenol.

Compound	*Sample numbers*							
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Dioxins								
Tetra-CDD	ND[a]	ND	0.4	2	ND	0.2	0.6	ND
Penta-CDD	4	ND	2	9	ND	0.7	1	1
Hexa-CDD	21	5	12	38	5	5	3	8
Hepta-CDD	49	13	26	77	18	14	5	29
Octa-CDD	89	19	41	171	37	36	11	56
Total	163	37	81	297	60	55.9	20.6	82
Furans								
Tetra-CDF	2	ND	2	9	0.6	0.5	0.7	1
Penta-CDF	11	5	7	37	4	2	2	5
Hexa-CDF	23	8	11	75	11	7	3	13
Hepta-CDF	62	15	36	177	35	18	12	32
Octa-CDF	87	13	41	181	32	23	9	33
Total	185	41	97	469	82.6	50.5	26.7	84
Chlorobenzenes								
Tri-CBE	4	2	5	28	3	3	2	4
Tetra-CBE	24	17	35	163	15	13	11	16
Penta-CBE	104	44	87	379	524	41	23	53
Hexa-CBE	124	25	71	284	49	40	17	47
Total	252	88	198	854	591	97	53	120
Chlorophenols								
Tri-CP	3	1	2	ND	ND	ND	ND	ND
Tetra-CP	10	4	3	38	1	0.6	0.6	0.3
Penta-CP	11	7	5	149	2	1	ND	0.3
Total	24	12	10	187	3	1,.6	0.6	0.6

[a] ND = Not detected.

small amounts of metals present in garbage.. These compounds could constitute catalysts on the surface of the fly ash produced to enhance the formation of PCDDs/PCDFs. Most of the metallic material is separated in the Machida incinerator prior to incineration, this fact could be one of the major reasons that Machida fly ash shows lower levels of PCDDs and PCDFs than other incinerators.

The amount of PCDDs, PCDFs and the precursors PCBEs and PCPs detected in the eight samples is shown in Table I. There is general trend in all samples where the amount of chlorinated isomers increases with increase in degree of chlorination. The amount of PCBEs detected in all samples is more than four times larger than that of PCPs. The total amount of PCDDs/PCDFs detected in a given sample is greater than the total amount of PCBEs (or sum of PCBEs and PCPs) present in that sample. From the total amount of PCDDs and PCDFs in a given sample as compared to that of total amount of PCBEs and PCPs, it seems that there is a definite correlation between high

TABLE II

INCINERATOR OPERATION CONDITIONS DURING SAMPLE COLLECTION AT MACHIDA

A and B are effluent trains.

Sample	*Garbage megatons/h*	*Dry air flow Nm^3/ton*	*Furnace temperature (°C)*	*Heat generated (kcal/kg)*
1	5.7	10138 (A) 12700 (B)	886	1670
2	5.7	11241 (A) 13136 (B)	835	1620
3	5.7	11265 (A) 13030 (B)	846	1730
4	4.4	13673 (A) 13405 (B)	883	2030
5	4.8	11182 (A) 13432 (B)	903	1920
6	4	13062 (A) 9393 (B)	926	2090
7	3.6	12895 (A) 10010 (B)	825	2260
8	4.2	10967 (A) 13467 (B)	920	2150

levels of PCBEs/PCPs and high levels of PCDDs and PCDFs. From laboratory experiments it is known that chlorophenols can be formed from chlorobenzenes which are precursors in the formation of PCDDs and PCDFs[6]. The reaction route in Fig. 2, shows the formation of PCDDs and PCDFs from PCBEs and PCPs.

The amount of chlorobenzenes formed and their conversions into chlorophenols and finally into PCDDs will depend on the temperature and the presence and amount of catalyst. If reaction I is slower than II, then there will be a lesser amount of PCPs than PCBEs. Since PCDDs and PCDFs are more stable than the chlorobenzenes and chlorophenols, reactions I and II proceed in a forward direction and result in an equal or higher amount of PCDDs and PCDFs formation to that of total PCBEs/PCPs. This is evident from the amount of PCBEs, PCPs, PCDDs and PCDFs observed in samples

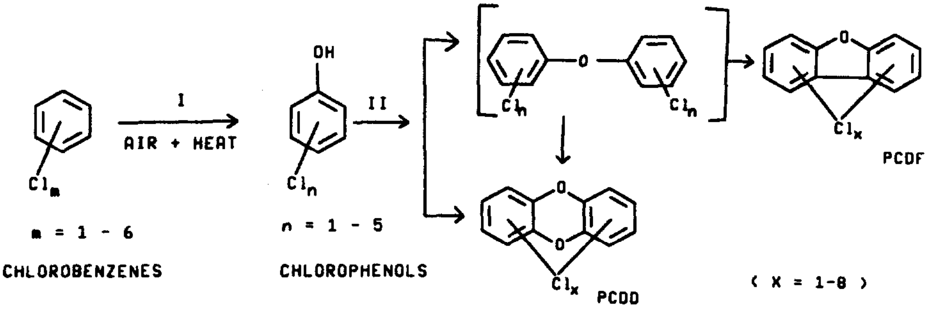

Fig. 2. Possible reaction scheme showing the formation of PCDDs and PCDFs from chlorobenzenes and chlorophenols.

1–8. Although this study is limited to only highly chlorinated benzenes, phenols dibenzodioxins and dibenzofurans, the results do give strong indication that support the surface catalytic mechanism and the formation of PCDDs and PCDFs during incineration of municipal garbage. This mechanism has been proved in laboratory experiments using fly ash and various precursors under various conditions. Attempts to correlate the amount of PCBEs, PCPs, PCDDs and PCDFs formed with that of incinerator operational conditions (Table II) such as amount of garbage, dry air flow, temperature profiles heat generated and dust absorbed during each sampling period were not conclusive.

Incineration processes are very complicated and analysis of fly ash collected at different points in the post-combustion effluent pathways has not been done. Present knowledge of the presence of PCDDs and PCDFs in fly ash is mainly based on the fly

TABLE III

AMOUNTS OF PCDDs, PCDFs, PCBEs AND PCPs (ng/g FLY ASH) DETECTED IN FLY ASH SAMPLES COLLECTED AT DIFFERENT POINTS IN POST-COMBUSTION ZONE OF MACHIDA INCINERATOR

CDD = Chlorodibenzo-*p*-dioxin; CDF = chlorodibenzofuran; CBE = chlorobenzene; CP = chlorophenol.

Compound	*Samples*					
	B1	*B2*	*B3*	*C1*	*C2*	*C3*
Dioxins						
Tetra-CDD	ND[a]	0.1	ND	ND	0.1	ND
Penta-CDD	ND	0.1	ND	ND	ND	ND
Hexa-CDD	ND	0.5	2	ND	0.6	1
Hepta-CDD	ND	0.5	7	ND	0.6	4
Octa-CDD	0.1	0.5	15	ND	0.7	10
Total	0.1	1.7	24	–	2	15
Furans						
Tetra-CDF	ND	0.2	0.3	ND	0.2	0.2
Penta-CDF	ND	0.5	3	ND	0.5	2
Hexa-CDF	ND	0.7	6	ND	0.9	6
Hepta-CDF	ND	0.8	14	ND	1	11
Octa-CDF	0.1	0.5	14	ND	0.6	10
Total	0.1	2.7	37.3	–	3.2	28.2
Chlorobenzenes						
Tri-CBE	2	15	2	1	14	1
Tetra-CBE	0.1	30	4	0.1	24	7
Penta-CBE	0.1	22	12	0.2	22	21
Hexa-CBE	0.1	5	9	0.1	5	13
Total	2.3	72	27	1,4	65	42
Chlorophenols						
Tri-CP	ND	2	2	ND	0.6	0.7
Tetra-CP	ND	1	2	ND	0.6	0.7
Penta-CP	0.1	4	9	0.1	2	3
Total	0.1	7	13	0.1	3.2	4.4

[a] ND = Not detected.

ash collected at the electrostatic precipitator. In our study fly ash was also collected at three different points in the post-combustion zone as shown in Fig. 1. The temperature at position X is higher (850°C) while it is decreased at points Y (245°C) and Z (240°C). The results of quantitation of two sets of samples (Set No. 1: B1, B2 and B3; and Set No. 2: C1, C2 and C3) collected at three different places (X, Y, Z, respectively) are shown in Table III.

For both sets of samples the total amount of PCBEs is in the order of B2 > B3 > B1 (set 1) and C2 > C3 > C1 (set 2). The amount of PCDDs and PCDFs found is in the order of B3 > B2 > B1 and C3 > C2 > C1. The smaller amount of PCBEs, PCDDs and PCDDs and PCDFs in the samples collected at point X could be related to the high temperature at this point. While the difference in amounts of PCBEs and PCDDs/PCDFs in samples collected at point X and Y is more than ten-fold, this difference decreased to less than two-fold in samples collected at point Z. These results can be explained based on the catalytic surface activity of fly ash particles. At point X the precursors concentrations (PCBEs and PCPs) are high, because they are not converted into PCDDs and PCDFs. At point Z, because of probably high catalytic activity due to optimum conditions these precursors are converted to PCDDs and PCDFs. The final result is an increase in PCDDs and PCDFs and a decrease in PCBEs in samples collected at point Z. The amount of PCBEs found in samples C3 and B3 as compared to total PCDDs and PCDFs in these samples are well in agreement with the results of samples 1–8 collected at the same point. This tends to indicate that the most toxic PCDDs and PCDFs congeners in addition to forming in the actual combustion

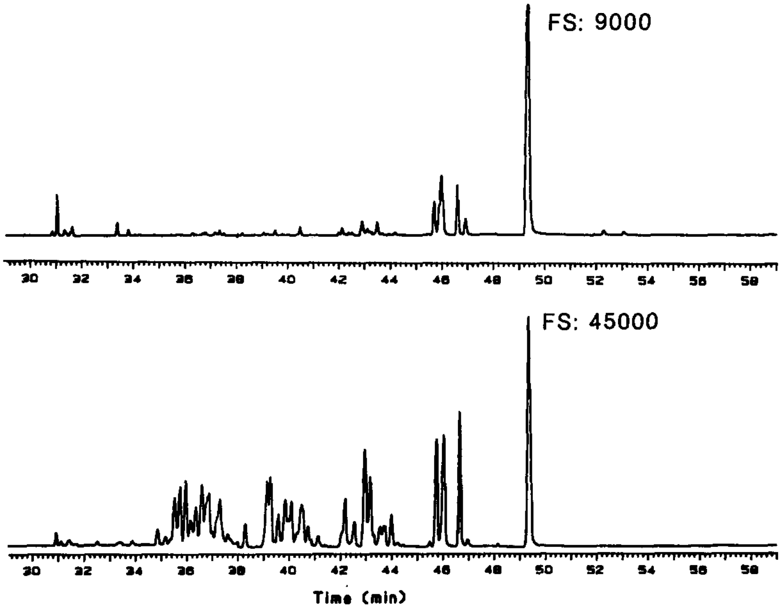

Fig. 3. Reconstructed added mass chromatograms obtained by analyses of (top) Machida sample No. 6 and (bottom) Ontario fly ash under identical GC–MS conditions. For GC conditions see experimental section. FS = full scale.

zones are also forming by surface catalytic activity on fine fly ash particles in the post-combustion zone and in the electrostatic precipitation region.

To determine the correlation of total organic matter (TOM) with that of the PCDDs and PCDFs formed all samples were analyzed using GC–EILIN-MS. The total organic matter in a given sample was estimated by using average response factor in area counts per nanogram for a standard mixture as described in the experimental section. The total organic matter estimated for the B and C series samples is in the order of B3 > B2 > B1 and C3 > C2 > C1 respectively. The lower levels of TOM observed in the order seen above can be correlated with a decrease in temperature. Comparison of the TIC traces of Machida and Ontario fly ash extracts is shown in Fig. 3, where only tetra- to octa-dibenzo-*p*-dioxins and dibenzofurans were monitored using GC–EISIM-MS. Both the TIC traces were drawn on the same scale, indicating high levels of dioxins detected in Ontario fly ash compared to Machida fly ash. In addition to that from the abundances of isomers in each congener group it can be seen that Machida fly ash does not show peaks for the relatively more toxic tetra- and pentadioxins and furans. The preponderance of the octadioxin in the Machida fly ash is apparent.

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