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GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC ANALYSIS OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND ORGANIC COMPOUNDS IN HIGH-TEMPERATURE FLY ASH FROM MUNICIPAL WASTE INCINERATION

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SUMMARY

Fly ash from a high-temperature rotary kiln municipal waste incinerator is generally considered to be free of organic compounds. Samples were analyzed for residual organic compounds by gas chromatography–mass spectrometry. Mass spectral identification revealed the presence of polychlorinated dibenzo-*p*-dioxins (PCDDs), but no detectable tetra-isomers or penta-isomers. Polychlorinated dibenzofurans (PCDDs) as well as chlorinated benzenes, chlorinated cyclohexanes, and chlorinated biphenyls were found. A qualitative correlation was found between the levels of PCDDs and PCDFs with these other chlorinated species, which may indicate them to be precursors in the formation of PCDDs and PCDFs even at high-temperature conditions. A discussion of physical parameters which may affect the formation of PCDDs and PCDFs during incineration is also presented.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two classes of compounds which have been recognized as being highly toxic. They have been found in precipitated fly ash from municipal incinerators worldwide[1-4]. It also appears that PCDDs are associated at higher concentrations with smaller diameter particles which escape electrostatic precipitation and are released into the environment[5,6].

Recent studies have shown that fly ash particles may play a catalytic role in the chlorination of organic species and adsorption of PCDDs[7,8]. PCDDs have also been observed to be formed by the exposure of coal to HCl and Cl_2 at 600°C[9]. The results demonstrated that octachlorodibenzo-*p*-dioxin (OCDD) and heptachlorodibenzo-*p*-dioxin (H_7CDD) were formed in greater amounts than either hexachlorodibenzo-*p*-dioxin (H_6CDD) or tetrachlorodibenzo-*p*-dioxin (TCDD). This is consistent with theoretical considerations of the heats of formation of PCDDs[10]. It was deduced that OCDD has the lowest heat of formation while TCDD isomers had the highest. It is

therefore expected that OCDD would be preferentially formed over any of the other PCDD congeners.

Fly ash particles from a high-temperature rotary kiln incinerator are generally considered to have little residual organic compounds[11]. In this study, such samples were analyzed by high-resolution gas chromatography–mass spectrometry (GC–MS) and shown to contain PCDDs and PCDFs. It is found that OCDD is in higher concentrations than the other congeners, and no tetra-isomers were detected. A parallel relationship was not found for the PCDFs. Detailed examination of the mass spectral data also shows the presence of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

EXPERIMENTAL

Sample collection

Fly ash was collected from a rotary kiln municipal incinerator in West Germany equipped with an after burner and an electrostatic precipitator. Three samples were taken in a three-month time period at an average after-burner furnace temperature of $1040 \pm 25°C$. Containers were cleaned with a sequence of sulphuric acid, chromate and distilled water. Storage of the fly ash was at room temperature and in the dark. After extraction the samples were placed in a freezer at *ca.* $-15°C$.

Sample extraction and concentration

The fly ash was extracted by placing it in a 300-ml round-bottomed flask with 200 ml of distilled-in-glass-grade benzene (Caledon Laboratories, Georgetown, Canada). The three weights for each sample were 50.2, 34.2, and 46.6 g. These mixtures were placed in an ultrasonic bath for 1 h. Thereafter, the benzene was filtered using a specially designed filtering apparatus[12]. An additional 100 ml of benzene was added to the fly ash and ultrasonicated for one half hour. The benzene was filtered and this procedure was repeated. Finally, the fly ash was given two washes with 25 ml of benzene. The solution was then concentrated by rotary evaporation under aspirator vacuum to *ca.* 10 ml. This was transferred with rinsings to a 25-ml pear shaped flask. The final extract was brought to less than 100 μl by further rotary evaporation under aspirator vacuum. This was placed in a 1.0-ml reacti-vial with PTFE-lined screw cap with rinsings and brought to a final volume of 100 μl by blowing a gentle stream of high-purity nitrogen across the top of the vial. Evaporation to dryness was avoided to minimize losses of the more volatile components[13,14].

Chromatographic analysis

A Hewlett-Packard 5880A gas chromatograph with a flame ionization detector and an on-column injection port was used. It was equipped with a 30 m × 0.25 mm I.D. fused-silica DB-5 cross-linked column for analysis. Carrier gas flow-rate was 1.5 ml/min and the injection port temperature was 275°C. The temperature was from an initial temperature of 80°C to a final temperature of 250°C at 4°C/min.

A Hewlett-Packard 5992 GC–MS–calculator system was utilized which was equipped with an on-column injection port, 50 m × 0.35 mm I.D. fused-silica SE-54 cross-linked capillary column, *x–y* plotter and floppy disk system. The effluent from the GC column was admitted into the mass spectrometer by a glass capillary restrictor.

Mass spectra were obtained by scanning from 500 to 50 a.m.u. at 330 a.m.u./sec. Spectra were taken from the top of the GC peak and stored on a floppy disk. Spectra taken prior to the peak were used in later background subtraction. The GC oven temperature program was the same as that for the 5880 GC. The software used was called DUAL-MODE, which allowed storage of total ion abundances and mass chromatograms in addition to mass spectra.

Selected PCDD and PCDF congeners were analyzed by using selected ion monitoring (SIM). The ions monitored for TCDD were 319.9 and 321.9 and for TCDF, 305.9 and 307.9. The ions selected for pentachlorodibenzo-p-dioxin (P_5CDD) through OCDD were 355.9, 389.8, 425.8, and 459.7, while for penta- through OCDF they were 339.9, 373.8, 409.8, 443.7. Six ions were monitored during each SIM analysis with a dwell time of 166 msec per ion. GC oven conditions were from an initial temperature of 80°C to 180°C at 10°C/min. The rate was then changed to 4°C/min to a final temperature of 270°C for 20 min.

SIM areas were used for quantification. PCDD congeners were quantified using a standard mixture of 1,2,3,4-TCDD, 1,2,3,4,7,8-H_6CDD, 1,2,3,4,6,7,8-H_7CDD and OCDD. P_5CDD was quantified by using a response factor intermediate to the TCDD and H_6CDD standards. PCDF was quantified by using a solution of TCDF (99% pure, manifacturer isomer unidentified) and OCDF. The intermediate PCDF congeners were quantified by using a linear interpolation of response factors between those of the two standards.

Before operating in either scanning or SIM mode, the mass spectrometer was tuned daily by the manufacturer supplied program AUTOTUNE using a perfluoro-tributylamine calibration standard.

RESULTS AND DISCUSSION

A list of compounds identified by GC–MS from the fly ash samples is given in Table I. A total of 82 individual compounds have been found and the retention times are given. These data show that the retention behaviour of the chromatographic column was very reproducible, since the retention times of the chlorobenzenes and biphenyl are the same for the three samples. This indicates that the compounds identified are probably unique for the sample set. Many organic compounds such as hydrocarbons, alkyl phthalates, alkyl benzenes, alkyl cyclohexanes, alkyl phenols and PAHs occur. These have been found in most fly ash analyzed from other municipal incinerators[1,15]. However, all three samples do contain chlorobenzenes, chlorocyclo-hexanes, chlorobiphenyl, and biphenyl, which may be precursors to PCDDs and PCDFs[16]. More uncommon compounds such as chlorotriazines and chlorothio-phenes have also been observed.

Fig. 1 represents the total ion current (TIC) from GC–MS analysis of the three samples. The numbered peaks correspond to the peak numbers identifying the compounds in Table I. Some interesting differences can be seen since the samples were taken at *ca.* 1-month intervals. The TIC for each sample was plotted to the same full scale so that the relative differences in concentration could be seen; all other parameters for analysis were constant including the injection volume. The estimated total organic content (TOC) for these samples was determined by using GC peak areas and an average organic compound response factor of ten area counts per nanogram based

TABLE I

COMPARISON OF MASS SPECTRAL PEAKS FROM HIGH RESOLUTION GC–MS ANALYSIS
OF EXTRACTS FROM A HIGH-TEMPERATURE MUNICIPAL INCINERATOR

No.	Compound	Ret. time	Samples peak no.		
			1	2	3
1	Benzaldehyde	4.4	1	1	–
2	Phenyl propyl ether	4.6	–	2	–
3	Cyclohexane	4.6	2	7	–
4	Hydrocarbon	4.7	–	3	–
5	Alkylbenzene	4.8	3	–	–
6	Alkylbenzene	4.9	4	–	–
7	Phenyl propyl ether	5.2	–	4	–
8	Alkylbenzene	5.3	–	5	–
9	Alkylbenzene	5.4	–	6	–
10	Alkylcyclohexane	5.4	5	–	–
11	Alkylcyclohexane	5.7	6	–	–
12	4-Methyldecane	5.8	–	–	1
13	Hydrocarbon	5.9	–	–	2
14	Methylcyclohexane	5.9	–	8	–
15	Hydrocarbon	6.0	–	–	3
16	Alkylbenzene	6.1	–	–	4
17	Phenol	6.1	7	9	–
18	Alkylcycloheptane	6.4	–	–	5
19	Alkylpropenoic acid	6.4	8	10	–
20	Alkylbenzene	6.4	–	–	6
21	Ethylhexanol	6.5	–	11	–
22	Hydrocarbon	6.6	9	–	7
23	Isobutylphenol	6.8	10	12	–
24	Alkylcyclohexane	7.0	–	–	8
25	Pentylphenol	7.1	11	–	–
26	Unknown	7.2	–	13	–
27	Alkylbenzene	7.2	–	–	9
28	Alkylbenzene	7.8	–	–	10
29	Pentylphenol	8.0	12	14	–
30	Naphthalene	8.6	–	15	11
31	Hydrocarbon	8.8	13	16	12
32	Hydrocarbon	9.1	–	17	13
33	Trichlorobenzene	9.4	14	–	–
34	Alkylcyclohexane	9.7	–	18	–
35	Tetrachlorothiophene	10.8	15	–	–
36	Hydrocarbon	10.8	–	–	14
37	Hydrocarbon	11.5	–	19	15
38	Dichlorocyclohexane	12.1	16	20	–
39	Biphenyl	14.1	17	21	16
40	Hydrocarbon	14.5	–	22	17
41	Dichlorocyclohexane	14.9	18	23	–
42	Dichlorocyclohexane	15.4	–	24	–
43	Hydrocarbon	16.4	–	25	–
44	Acenaphthalene	17.3	–	–	18
45	Dichlorocyclohexane	17.4	–	26	–

TABLE I *(continued)*

No.	Compound	Ret. time	Sample peak no.		
			1	2	3
46	Hydrocarbon	17.6	—	27	19
47	Pentachlorobenzene	18.3	19	28	20
48	Hydrocarbon	20.5	—	29	21
49	Methyltrichloromethyltriazine	21.4	20	—	—
50	Hydrocarbon	21.8	—	30	—
51	Hydrocarbon	23.3	—	31	22
52	Hydrocarbon	23.4	—	32	—
53	Hexachlorobenzene	23.8	21	33	23
54	Phenanthrene	25.8	—	—	24
55	Hydrocarbon	26.0	—	34	—
56	Hydrocarbon	26.2	—	.35	25
57	Dihydrolicorine	26.4	22	—	—
58	Methyltetrahydrothiophene	26.7	—	36	—
59	Pentachlorobiphenyl	26.9	23	—	—
60	Hydrocarbon	28.7	—	37	27
61	Alkylphenol	30.3	24	—	—
62	Dibutylphthalate	30.4	—	38	28
63	Hydrocarbon	31.1	—	39	—
64	Pentachlorobiphenyl	31.8	25	—	—
65	Sulphur (S_8)	32.0	—	40	—
66	Pyrene	32.9	—	—	29
67	Hydrocarbon	33.4	—	41	—
68	Fluoranthene	34.1	—	—	30
69	Hydrocarbon	34.5	—	42	—
70	Thiochloromethyltriazine	34.6	26	—	—
71	Hydrocarbon	35.4	—	43	—
72	Hydrocarbon	35.8	—	44	31
73	Hydrocarbon	36.5	—	45	—
74	Thiochloromethyltriazine	37.6	27	—	—
75	Hydrocarbon	38.0	—	46	32
76	Butylbenzylphthalate	39.2	28	—	33
77	Hydrocarbon	39.9	—	47	—
78	Triphenylene	41.7	—	—	34
79	Hydrocarbon	42.0	29	48	—
80	Dioctylphthalate	43.1	30	49	35
81	Hexadecane	43.8	—	50	—
82	Hydrocarbon	43.9	—	51	—

on previous work. In this manner the TOC were estimated as: sample 1, 1184 ng/g; sample 2, 1126 ng/g; sample 3, 400 ng/g. These amounts compare with 6000–9000 ng/g found on fly ash from other waste incinerators operating at lower temperatures.

It is observed that sample 1 contains higher amounts of biphenyl, chlorobenzenes, and chlorobiphenyl than either sample 2 or 3. In samples 2 and 3, the major constituents are hydrocarbons, alkyl benzenes, and alkyl phthalates. The chlorinated species are minor constituents and may reflect some differences in the waste feedstock. It also shows that relatively high amounts of other toxic chlorinated species can be generated by waste incineration at high temperatures.

The calculated concentrations of PCDD and PCDF congeners as determined

by SIM are shown in Table II. It is seen that none of the samples contained detectable TCDD and P$_5$CDD at the instrumental detection limit of 0.1 ng/μl. Criteria used for the positive identification of TCDD and TCDF were: correct retention time, correct chlorine isotope ratio and a signal which was greater than 2.5 times the noise level.
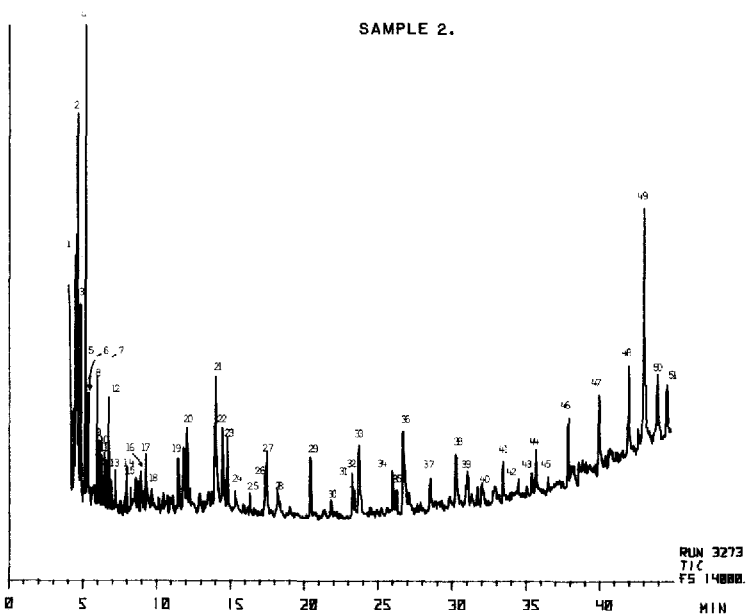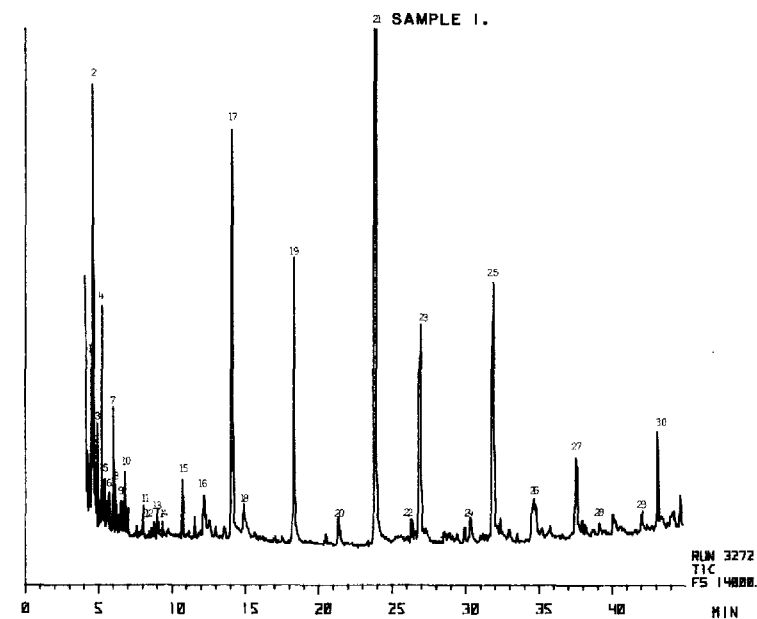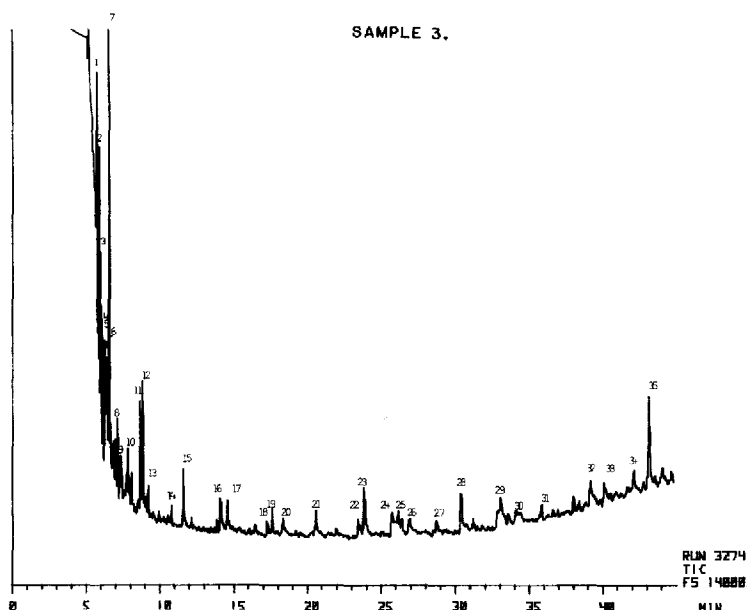

Fig. 1.

Fig. 1. Comparison of the total ion currents from the fly ash extracts from a high-temperature incinerator. Numbered peaks correspond to the compounds identified in Table I.

The reproducibility of this method of extraction and analysis has been recently determined to be 19 %[17]. Sample 1 contained more PCDDs than either of the other two samples. This is also true for the PCDFs. It is perhaps not surprising to find such levels of PCDFs and PCDDs in sample 1 because of the abundance of chlorobenzenes and chlorobiphenyls. A similar comparison can be made for samples 2 and 3. In these samples there are lower concentrations of PCDDs and PCDFs corresponding to

TABLE II

CALCULATED CONCENTRATIONS (ng/g) OF PCDDs and PCDFs IN HIGH-TEMPERATURE FLY ASH EXTRACTS

Compound	Sample		
	1	2	3
TCDD	N.D.*	N.D.	N.D.
P_5CDD	N.D.	N.D.	N.D.
H_6CDD	0.3	0.4	0.2
H_7CDD	2.5	0.6	0.6
OCDD	20	8.3	7.2
TCDF	28	1	0.8
P_5CDF	8	0.3	0.3
H_6CDF	8	0.4	0.6
H_7CDF	10	0.6	0.8
OCDF	14	0.3	0.4

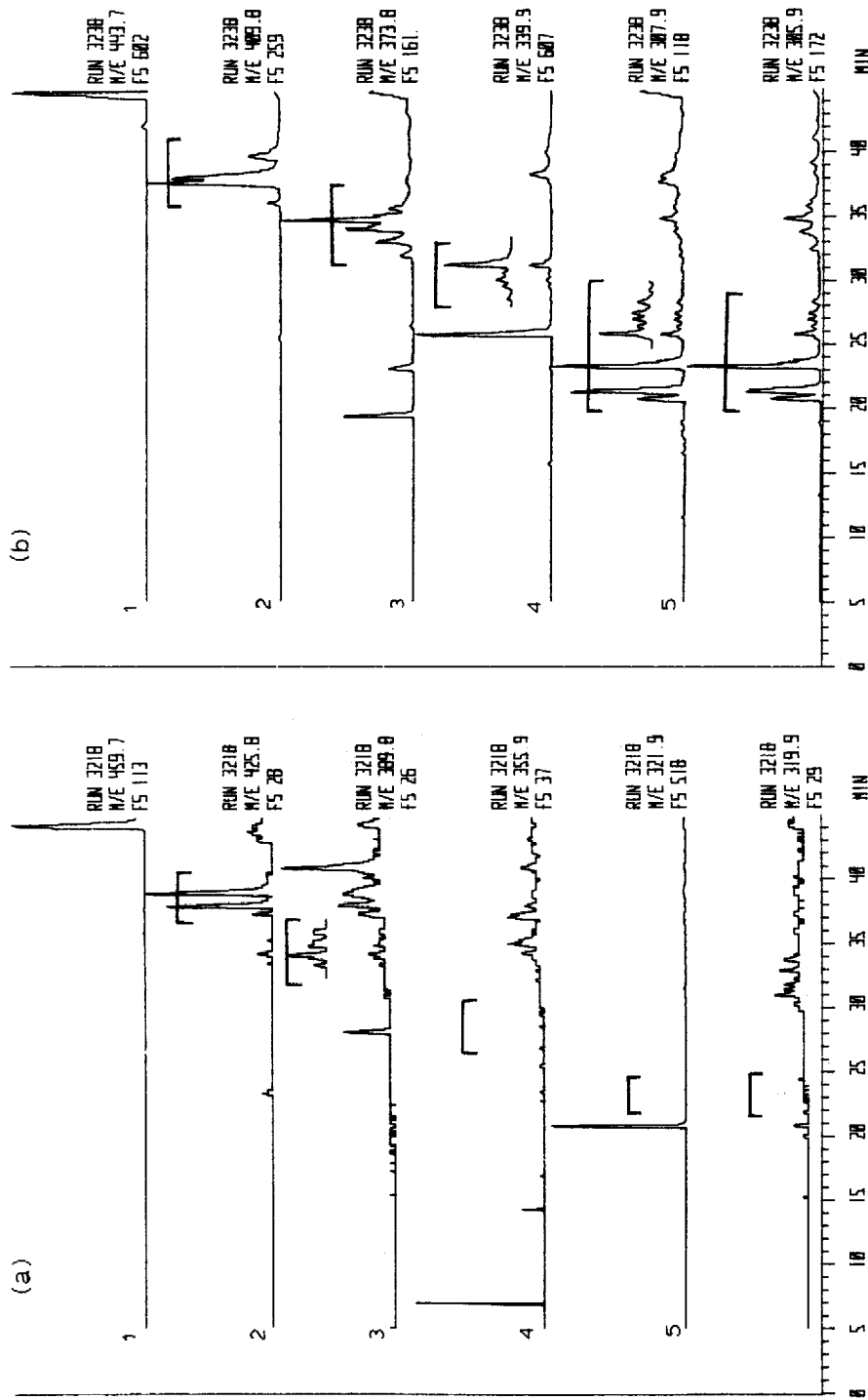* Instrumental detection limit was 0.1 ng/μl.

Fig. 2. SIM data obtained for sample 1 for PCDD (a) and PCDF (b) analysis. Inserts show the isomers on an expanded scale and brackets indicate the elution retention times for the congeners. (a): 1 = Octachlorodibenzo-*p*-dioxin; 2 = heptachlorodibenzo-*p*-dioxin; 3 = hexachlorodibenzo-*p*-dioxin; 4 = pentachlorodibenzo-*p*-dioxin; 5 = tetrachlorodibenzo-*p*-dioxin. (b): 1 = Octachlorodibenzo-*p*-dioxin; 2 = heptachlorodibenzofuran; 3 = heptachlorodibenzofuran; 4 = pentachlorodibenzofuran; 5 = tetrachlorodibenzofuran.

lower abundances of chlorobenzenes and chlorobiphenyls found in these samples. Fig. 2 shows the SIM data obtained for sample 1 for PCDD and PCDF analysis. The inserts show the isomers in an expanded scale for clarity.

The pattern of PCDD congeners is OCDD > H_7CDD > H_6CDD > (P_5CDD, TCDD). This is the same trend as observed by the laboratory chlorination of coal under HCl or Cl_2[9] and as predicted by the heats of formation[10]. No such trend is observed for PCDFs.

It can be surmised that the surface of the fly ash particle may play a role in the formation of PCDDs and PCDFs. PCDDs have been found to be more concentrated on smaller diameter particles, and to have the same pattern of congener abundance[5]. The influencing factor may be that these smaller particles have a greater surface area than larger particles.

Other physical parameters which may influence the final PCDD content of fly ash may be precursor concentration, temperature and oxygen flux. As seen in this study, the abundance of chlorobenzenes and chlorobiphenyls is associated with the PCDD and PCDF content. This has also been observed previously[1,18]. Temperature and oxygen flux no doubt affect the formation of PCDDs and PCDFs. Recent work has shown that PCDD concentrations in fly ash can be empirically modeled on these two parameters.

It is therefore evident that the formation of PCDDs and PCDFs during incineration involves complex interactions. This implies that the elimination of PCDDs and PCDFs during incineration cannot be fully attained by simple high-temperature furnaces. Further research must be conducted to study these interactions in a more quantitative manner.

ACKNOWLEDGEMENT

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