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Role of Temperature and Hydrochloric Acid on the Formation of Chlorinated Hydrocarbons and Polycyclic Aromatic Hydrocarbons During Combustion of Paraffin Powder, Polymers, and Newspaper

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Abstract. Formation of chlorinated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) were determined using a laboratory-scale incinerator when combusting materials at different temperatures, different concentrations of hydrochloric acid (HCl), and when combusting various types of polymers/newspaper. Polychlorobenzenes (PCBz), polychlorophenols (PCPhs), polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and their toxic equivalency (TEQ) and PAHs were highlighted and reported. Our results imply maximum formation of chlorinated hydrocarbons at 400°C in the following order; PCBz≥PCPhs>>PCDFs>PCDDs>TEQ on a parts-per-billion level. Similarly, a maximum concentration of chlorinated hydrocarbons was noticed with an HCl concentration at 1000 ppm with the presence of paraffin powder in the following order; PAHs>PCBz≥PCPhs>>PCDFs>PCDDs>TEQ an a parts-per-billion level. PAHs were not measured at different temperatures. Elevated PAHs were noticed with different HCl concentrations and paraffin powder combustion (range: 27–32 µg/g). While, different polymers and newspaper combusted, nylon and acrylonitrile butadiene styrene (ABS) produced the maximum hydrogen cyanide (HCN) concentration, concentrations of PCDD/FS, dioxin-like polychlorinated biphenyls (DL-PCBs), and TEQ were in a decreasing order: polyvinylchloride (PVC)<newspaper<polyethyleneterephthalate (PET)< polyethylene (PE)< polypropylene (PP)< ABS = blank. Precursors of PCBs were in a decreasing order: PP<nylon<PE<newspaper<ABS<PVC<blank<PET. Precursors of PCDD/Fs were in a decreasing order: newspaper <PP=nylon<PE<ABS<PVC= blank<PET. BTX formation was in a decreasing order; PE<nylon<newspaper<ABS<PP. PAHs formation were elevated with parts-per-million levels in the decreasing order of PP<nylon<PE<newspaper<blank<ABS< PET<PVC.

Formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as a result of municipal solid waste incinerators (MSWI) was discovered in 1977 (Olie *et al.* 1977). Particularly, formation of PCDD/Fs in MSWI's and industrial solid waste incinerators (ISWIs) involved complex and heterogeneous chemistry (Huang and Buekens, 1995; Fiedler, 1998; Tuppurainen *et al.* 1998; lino *et al.* 1999a, b; 2000; 2001). European Union (EU) member countries have set limit values for PCDD/DF emissions for hazardous waste incinerator plants of 0.1ng I-TEQ/Nm^3. According to the latest inventory of PCDD/DF, emissions from MSWI's in Japan were 812 g-TEQ/y until 2001 (Suzuki *et al.* 2004). Consequently, insight into the formation of toxic contaminants is of the utmost important. The presence of PCDD/Fs in incinerator fly ash has led to laboratory-scale modeling in the formation process. Earlier reviews summarized the most important trends in formation chemistry (Addink and Olie 1995; Altwicker 1996; Fiedler 1998; Stieglitz 1998, Huang and Buekens 1999; Weber and Hagenmaier 1999). In our earlier study, we demonstrated the formation of dioxin during burning of newspaper, kerosine, paraffin powder, and plastics with dioxin-free fly ash (Takasuga *et al.* 2000). In general practice, hydrochloric acid (HC1) was formed from sodium chloride (NaCl) when heating NaCl, which contains waste along with clay (Yasuhara *et al.* 2001). Other studies demonstrated that copper chloride ($CuCl_2$) is a major source of PCDD/Fs (Wang *et al.* 2002; Ryu *et al.* 2003; Shibata *et al.* 2003). In addition, in order to understand the formation of dioxins from HC1 and $CuCl_2$, studies are needed not only on PCDD/Fs but also an other chlorinated hydrocarbons such as polychlorobenzenes (PCBz) and polychlorophenols (PCPhs) (Hagenmaier *et al.* 1987). Besides, burning experiments suggested that polycyclic aromatic hydrocarbons (PAHs) are the

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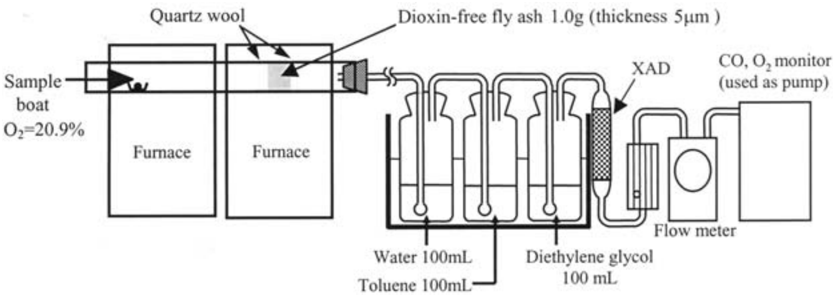

Fig. 1. The experimental apparatus employed for the first and second objective of this study

predominant chemicals evolved during these complex reactions (Takasuga *et al.* 2003).

Recent studies reported formation of PCDD/Fs during combustion of newspapers with the presence of NaCl and polyvinyl chloride (PVC) (Yasuhara *et al.* 2001). Yasuhara and the co-workers also reported the formation on PCDD/Fs coplanar PCBs during combustion of plastics, newspaper, and pulp (Yasuhara *et al.* 2002, 2005) in an incinerator with the presence of inorganic chlorides and various woods (Yasuhara *et al.* 2003). More experiments and theoretical studies to elucidate the details of orhanohalogen compound formation in combustion are urgently needed. Considering those facts, we developed a laboratory-scale incinerator in order to understand the formation of toxic contaminants with three different objectives: (1) temperature - dependent formation of PCDDs, PCDFs, PCDD/DF-TEQ, PCBz, and PCPhs during the burning of paraffin powder, dioxin-free fly ash, and at various degrees of temperature; (2) formation of PAHs PCDDs, PCDFs, PCDD/DF-TEQ, PCBz, and PCPhs at different HCl concentrations, the presence of paraffin powder and newspaper impregnated with dioxin-free fly ash; and (3) formation of PAHs, PCDDs, PCDFs, polychlorinated biphenyls (PCBs), TEQ, benzene, toluene, xylene (BTX), HCN, precursors of PCBs and PCDD/Fs, and carbon monoxide (CO) from polyethylene (PE), polyethyleneterephthalate (PET), nylon, newspaper, polypropylene (PP), acrylonitrile butadiene styrene (ABS), and polyvinylchloride (PVC) plastic particles with a modified incinerator that differs from first two objectives instrument. Based on the formation of PAHs, PCBz, PCPhs, PCDD/Fs, DL-PCBs, TEQ using I-TEF values were calculated and discussed.

Materials and Methods

Samples

Fly ash was obtained from the electrostatic precipitator of MSWI. The fly ash was subjected into thermial heat at 500°C for 2 h in the presence of a nitrogen stream that removed 99.99 % of PCDD/Fs, sieved to 5um thickness, which served as dioxin-free fly ash. This dioxin-free fly ash was used as a catalyst. However, it contained unburnt carbon in the range of 2.0–2.2%. HC1 applied to the combustion was purchased from Takachiho Chemical Ind., Ltd., Tokyo, Japan. The polymer sample materials employed were the commercially available films PE and PET (Futamura Chemical Ind., Co., Ltd., Nagoya, Japan), nylon (Mitsubishi Chemical Kohjin PAX Corp., Tokyo, Japan), PP (Daicel Chemical Ind., Ltd., Osaka, Japan), paraffin powder (Kyoto Chemical Company, Kyoto, Japan), ABS and PVC (local hardware shop). Prior to the experiment, PE, PET, nylon, newspaper, PP, ABS, and PVC were either cut into tiny pieces or powdered with a heavy grinder.

Experiment

For the first two objectives, the incinerator apparatus shown in Fig. 1. was employed as described elsewhere (Ohta *et al.* 2002, 2004). The apparatus consisted of a O_2=20.9%/N_2 balance meter that connected with the flow meter and quartz tube. The diameter of the quartz tube is 25 mm with a 1000-mm length that mainly travels inside the double furnace (600 mm) with a furnace temperature of 900°C and 300°C, respectively. The samples for the formation test were placed in the sample boat located in the quartz tube in furnace 1. Sampling unit for the PCDD/Fs, PCBz, PCPhs, and PAHs was classified as an ice-bath with three impinger and Amberlite® XAD. The impinger 1 contains 100 mL water. The impinger 2 and 3, respectively, contain 100 mL toluene and 100 mL diethylene glycol, respectively. The impinger was connected with Amberlite® XAD in which sampling was done along with the impinger. The Amberlite® XAD unit was finally connected with a flow meter with a pump and a CO, O_2 CO_2 monitoring meter. After the completion of each experiment the back end of the quartz tube, the impinger,was rinsed with H_2O, acetone, and toluene for consecutive analysis. For the first objective, paraffin powder (10 μg) was sprayed 100 times (total 1g) in a duration of 2 h. The HCl concentration was maintained as 100 ppm, which is a general incinerator concentration at solid burning conditions. The furnace temperature was adjusted to 100°C, 200°C, 300°C, 400°C, and 500°C in dioxin-free fly ash zone. Three blank tests were conducted prior to the real experiment with the aforesaid temperatures.

For the second objective, HCl concentrations were adjusted to 10, 50, 100, 500, and 1000 ppm in order to understand its impact on the formation of target compounds. The experiment was mainly conducted with paraffin powder with fly ash. Three blank tests were conducted prior to the sample experiment. The experiment was also conducted with dioxin-free paraffin powder and newspaper. Extraction and cleanup procedures and analysis were the same as JIS K 0311 methods with minor modifications (Takasuga *et al.* 2000).

For the third objective, an experimental apparatus was developed with a O_2=20.9%/N_2 balance meter that further connected with a flow meter and a quartz tube (Fig. 2). The diameter of the quartz tube is 25 mm with a 1000-mm length that mainly travels inside the double furnace (600 mm) with both furnace temperatures set to 900°C. The samples for the formation test were placed in the sample boat located in the quartz tube in furnace 1. For PCDD/Fs and PAHs analysis, sampling was done in three impingers and a two Amberlite® XAD's. The impinger 1 contains 100 mL toluene with 200 mL H_2O. The impinger 2 and 3, respectively, contain 150 mL toluene and 150 mL diethylene glycol. The last impinger was connected with Amberlite® XAD-1 and 2. For HCN, the ice-batch contains impingers filled with 30 mL of 0.1 mol/L NaOH solution. For BTX analysis, a 10-L Flek sampler bag was fixed to the incinerator. The impinger and

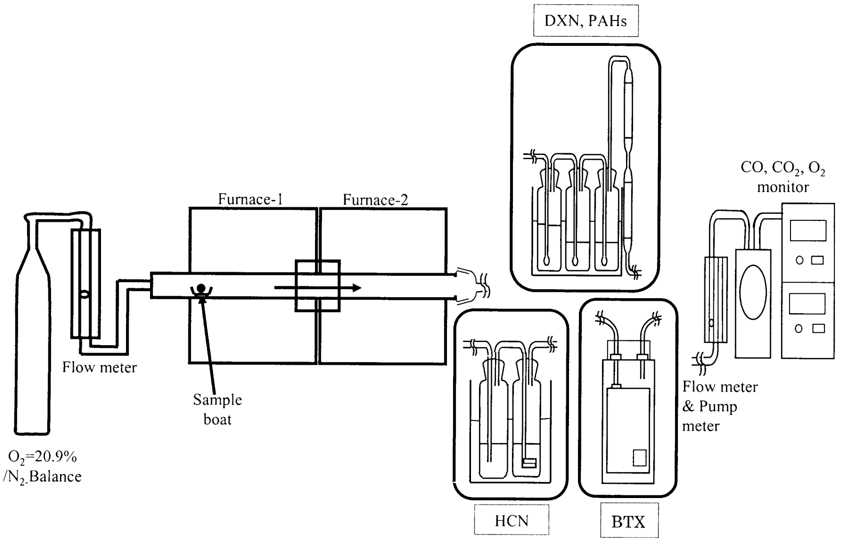

Fig. 2. The experimental apparatus employed for the third objective of this study

Amberlite® XADs were finally connected with a pump and a CO, O_2, CO_2 monitoring meter (Fig. 3). After the completion of each experiment, the back end of the quartz tube, the impinger, was rinsed with H_2O, acetone, and toluene. The sampling speed and gas flow were set to 2.0 L/min trapping time. For dioxin and PAHs analysis, a 1-g sample was used 100 cycles with 20-μg sample each time (until completion of CO, CO_2, and O_2, monitor cycles), whereas 200- and 100-μg samples were used for HCN and BTX analysis with 20 and 10 cycles, respectively, with non-chlorinated polymers. The interval between test repetitions was approximately 1.5 min. Residence time in the second stage furnace was calculated as approximately 3 s.

Combustion

First Objective. Seven experiments (Exp-A to G) were conducted for first objective (Table 1). For blank, in Exp-A paraffin was not included and in Exp-B paraffin was included, fly ash was not used, and the temperature was 300°C (Table 1). From Exp-C to Exp-G, paraffin powder and fly ash were included while temperatures were adjusted to 100°C, 200°C, 300°C, 400°C, and 500°C, respectively, for Exp-C, D, E, F, and G (Table 1).

Second Objective. Eight experiments (Exp-H to -O) were conducted for the second objective with paraffin powder as a catalyst excluding Exp-M. Nevertheless, HC1 concentrations were adjusted 10, 50, 100, 500, 1000, 100, 100, and 1000 ppm, respectively, for Exp-H, I, J, K, L, M, N, and O (Table 2). An additional five experiments (Exp-P to T) were conducted for the second objective with newspaper as a catalyst and the difference in HCl concentration was 10, 50, 100, 500, and 1000 ppm, respectively, for Exp-P, Q, R, S, and T (Table 3). Ten more experiments (Exp-U to AD) were conducted with the presence of fly ash and HC1 concentrations of 10, 50, 100, 500, and 1000 ppm for paraffin powder and newspaper samples separately and the formation of PAHs was monitored (Table 4).

Third Objective. Eight experiments were conducted with blank (without any sample), PE, PET, nylon, newspaper, PP, ABS, and PVC, respectively (Table 5). All solid samples (PE, PET, nylon, newspaper, PP, ABS, and PVC) were ground and filtered mechanically and then particles of 1–3 mm in diameter were selected and used for combustion.

Chemical Analysis

After combustion of each experiment, water, toluene, and diethylene glycol were mixed and liquid–liquid extraction was employed with toluene. Quartz wool and Amberlite® XAD-2 were soxhlet extracted for 16 h with 300 mL toluene. Liquid–liquid extracts were combined with soxhlet extract and the volume was reduced to 20 mL by a rotary evaporator. The cleanup of the PCBz and PCPhs was performed from 20- to 50-μL of the crude extract after adding ^{13} C_{12}-PCBz and $^{13}C_{12}$-PCPhs as an internal standard. In order to remove -OH group from PCPhs, the trimethylsilylation (TMS) procedure was employed. For PCDD/Fs, in 2 mL of crude extract $^{13}C_{12}$-labeled 2,3,7,8-chlorine substituted tetra-, penta, hexa-, hepta, and octa-PCDD/Fs were spiked and passed through a multilayer silicagel column (multilayer consists of silica, 10% $AgNO_3$/silica, silica, 22% H_2SO_4/silica, 44% H_2SO_4/ silica, silica, 2% KOH/silica, silica) using hexane as a mobile phase. The eluants were further separated using alumina column using hexane and 10% dichloromethane/hexane (V/V) as a mobile phase. The hexane was discarded while 10% dichloromethane/hexane was further subjected to HPLC, porous graphitized carbon column cleanup, and eluted with hexane. For DL-PCBs, PCDDS, and PCDFs, the eluants from alumina column were further separated with active carbon-silicagel impregnated column chromatography with 25% DCM in hexane as a pre-fraction, which elutes DL-PCBs and toluene as a post-fraction elute PCDD/Fs. For PAHs analysis, 16 species of $^{13}C_{12}$-PAH standards were spiked to crude extract in a GC-vial and analyzed directly. In case of any abnormal peaks in the sample, it was further subjected to silicagel column cleanup and eluted with 10% dichloromethane/hexane, evaporated, and purged under a gentle stream of nitrogen gas. All the samples were analyzed using high-resolution gas chromatography–high-Resolution mass spectrometry (HRGC-HRMS), while BTX was analyzed by low-resolution mass spectrometry (HRGC-LRMS). For analysis of HCN, the JISK0102 method was adopted. Particularly, a Flek-sampler bag gas chromatograpgy-flame ion detector (GC-FID) was used and then a scanning test was confirmed using GC-MS quadrapule.

Quantification and Identification

A Micromass Autospec Ultima high-resolution mass spectrometer with a Hewlett Packard (HP 6980) series gas chromatograph was used with DB-5 MS (60 m, 0.32 mm, 0.25 μm) capillary column for the separation of DL-PCBs and PCDD/Fs quantification and identification.

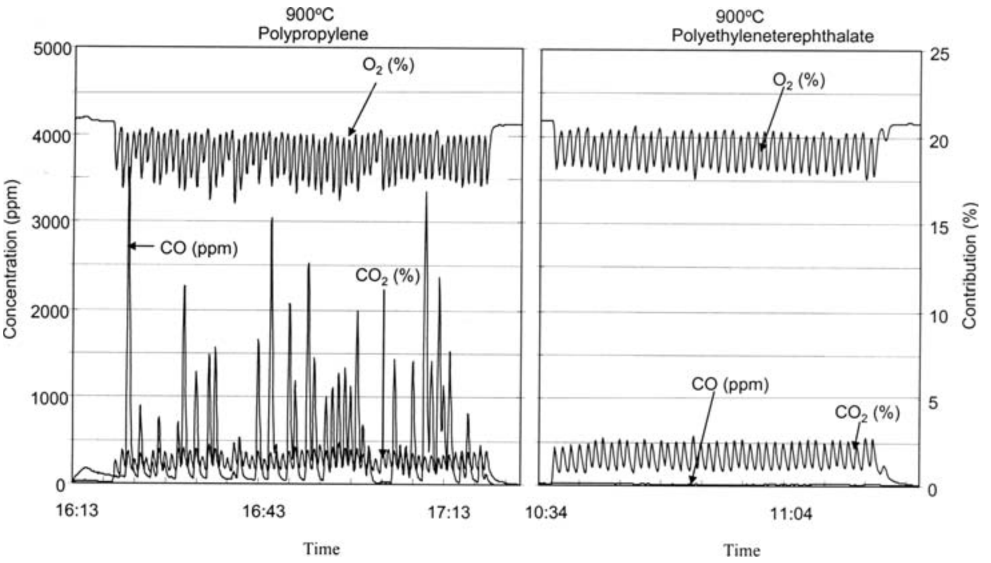

Fig. 3. Percentage evolution of CO_2 and O_2 and concentration (ppm) of CO in popypropylene and polyethyleneterephthalate-samples

The temperature conditions were as 150°C for 1min. (20°C/min) to 185°C (1 min) to 3°C/min to 245°C (10 min) to 6°C/min to 290°C (14 min) for HRGC/HRMS. The interface temperature was programmed at 5–10°C higher than the maximum value of each temperature program. The carrier gas was helium with a flow of 1 ml/min. and the electron impact ionization energy was 35–40e*V*. The MS was operated in selected ion monitoring for each congener group at a resolution >10,000 (10% valley). Two ions were monitored for each isomer and congener group. The recoveries of the ^{13}C-labeled DL-PCBs, PCDD/Fs, PCBz, PCPhs, and PAHs were greater than 75%. Toxic equivalency (TEQ) concentrations were calculated based on I-TEF value. The concentrations of BTX, HCN, precursors of PCBs and PCDD/Fs, and PAHs were expressed as ng/g dry sample basis while TEQ of PCDD/Fs and DL-PCBs represents pmol dry sample basis and CO was expressed on a parts-per-million (ppm) basis (Fig. 3).

Quality Assurance and Quality Control

Before each test run, the quartz tube with no sample was held at a target temperature for 30 min, then air was passed in for 30 min, which proceeding with nitrogen feed, and a blank test was performed at the target temperature without sample. In order to maintain the quality of the work, we used a disposable impinger for each sample experiment. The quartz tube, impinger-connecting tubes, Amberlite® XAD compartment, and both of the furnace units were washed with water, aceton, and toluene after combustion of each sample. In case the inner surface of any parts did not become clear enough, it was replaced with new parts. For every sample, complete combustion was confirmed with flow meter and CO, CO_2, and O_2 monitor meters. CO, CO_2, and O_2 monitor meters also functioned as a pump to release unwanted gas or fumes from the apparatus. The incinerator setup was carefully planned to suppress the influences of experimental conditions except the waste composition.

Results and Discussion

Impact of Temperature

Concentrations of PCBz, PCPhs, PCDDs, PCDFs, and toxic equivalency (TEQ) were minimum in the blank run (Exp-A to C). Particularly, paraffin powder did not show any impact on the formation of chlorinated hydrocarbons (Exp-B), while fly ash did (Exp-C). Among blank experiments, results in general reveal a less pronounced increase of hydrocarbons (except Dichlorobenzenes "DiCBzs"). The Presence of DiCBzs in blank experiments clearly shows the background concentrations and, therefore, DiCBzs in experimental samples <450 ng/g should be ignored. maximum chlorinated hydrocarbon concentration was noticed in Exp-F at 400°C (Table 1). Total concentrations of PCBz, PCPhs, PCDDs, and PCDFs on a nmol or pmol basis are shown in square brackets in Table 1. In general, the results indicate that the presence of paraffin powder, fly ash, and 100-ppm HC1 concentration, and a 400°C temperature favor a l00 1000-fold greater formation of chlorinated hydrocarbons. Formation of chlorine (on a percentage basis) was slightly higher in Exp-E (Table 1). Although an increased formation of chlorinated hydrocarbons was observed, chlorine percentage showed less pronounce (± 10 %). At 300°C temperature, PCBz, PCPhs, and PCDD/Fs showed maximum chlorine percentage. Comparison with our earlier study with the paraffin powder mixed with 0.5% NaCl and incinerated with various temperatures produced elevated PCBz and PCPhs at 1050°C (Fig. 4), while, combustion of PVC alone showed concentrations similar to paraffin powder mixed with 0.5% NaCl and incinerated at 600°C or 750°C (Fig. 4).

The homologue profiles of the PCBz, PCPh, PCDD, and PCDF were different between experiments (Table 1). At 300°C, T4CBz and T4CPh were higher, which corresponds to the conversion of T3CBz at 400°C and D2CBz or T3CBz and MlCPh or D2CPh at 500°C. Mono and or lower chlorinated homologues of CBz, CPh, PCDD, and PCDF were comparatively higher in lower temperature conditions and or more than 400°C. On the other hand, isomer profiles of CPhs were found to be similar at all temperatures (Fig. 5) in which 2,4-D2CPh formed maximum at all temperatures while 3,5-D2CPh were minimum (Fig. 6). Wikstrom and Marklund (2000) demonstrated that dominating CPh congeners were the 2,4,6-substituted congeners. Greater formation of 2, 4-D2CPh was probably due to the ortho-para activating properties of the

Table 1. Thermal formation of PCBz, PCPhs, PCDD/DFs, and TEQ (ng/g) with HCl, paraffin powder, and fly ash

	Experment						
	A	B	C	D	E	F	G
Sample	None	Paraffin	Paraffin	Paraffin	Paraffin	Paraffin	Paraffin
HCl concentration	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm
Fly ash	Absence	Absence	Presence	Presence	Presence	Presence	Presence
Temperature (°C)	300	300	100	200	300	400	500
Chlorobenzene (Cl%/MW)							
MlPCBz (0.316/113)	10	10	200	190	290	1200	9300
D2PCBz (0.483/147)	230[a]	450[a]	320[a]	210	4300	37,000	10,000
T3PCBz (0.587/182)	22	10	150	120	10,000	65,000	9000
T4PCBz (0.657/216)	10	20	13	50	15,000	41,000	4400
P5PCBz (0.705/251)	10	10	10	120	14,000	23,000	1600
H6PCBz (0.747/285)	59	130	41	310	6200	5800	380
PCBzs [nmol.]	310	600	730 [5]	1000 [5.5]	50,000 [230]	170,000 [920]	35,000 [230]
Cl%			48	58	65	60	50
Chlorophenols (C1%/MW)							
Ml PCPhs (0.276/129)	100	150	390	550	6700	25,000	15,000
D2PCPhs (0.436/163)	200	250	230	170	3500	26,000	6000
T3PCPhs (0.539/198)	100	100	230	260	11,000	45,000	1000
T4PCPhs (0.612/232)	130	100	190	110	16,000	46,000	70
P5CPCPhs (0.666/267)	120	100	33	11	5500	5800	50
PCPhs [nmol.]	450	400	1100 [6.5]	1100 [7.1]	43,000 [220]	150,000 [800]	22,000 [160]
Cl%			44	40	53	50	33
PCDDs (C1%/MW)							
TeCDDs (0.441/322)	0.01	0.01	0.20	0.20	100	540	75
PeCDDs (0.498/357)	0.01	0.01	0.08	0.40	240	760	42
HxCDDs (0.545/391)	0.01	0.02	0.10	1.6	470	610	19
HpCDDs (0.584/426)	0.01	0.02	0.08	3.2	600	260	6.6
OCDD (0.617/460)	0.01	0.02	0.11	6.1	640	62	1.1
PCDDs [pmol]	0.05	0.07	0.57 [0.002]	11 [0.027]	2100 [5]	2200 [6.1]	140 [0.42]
Cl%			52	59	57	51	48
PCDFs (C1%/MW)							
TeCDFs (0.464/306)	0.02	0.03	4.9	3.1	1400	7300	1000
PeCDFs (0.521/341)	0.02	0.03	0.68	1.9	1300	5400	600
HxCDFs (0.568/375)	0.01	0.02	0.17	2.2	1100	2700	250
HpCDFs (0.607/410)	0.01	0.01	0.15	3.3	850	970	66
OCDF (0.640/444)	0.01	0.01	0.88	5.1	420	170	6.0
PCDFs [pmol]	0.06	0.09	6.7 [0.02]	16 [0.04]	5100 [14]	17,000 [50]	1900 [5.9]
Cl%			50	59	57	51	50
Total PCDD/DFs	0.10	0.16	7.3	27	7200	19,000	2000
TEQ (pmol)			0.10	0.20	95	300	32

HCl, hydrochloric acid; [a]Background levels. PCBz, PCPhs, PCDDs, PCDFs, TEQ, and PAHs respectively, polychloro benzene, polychlorophenols, polychlorinated dibenzo-p-dioxins, dibenzofurans, toxic equivalency, and polycyclic aromatic hydrocarbon. The values were rounded.

OH- group in the phenol molecule generate CPhs, which substituted 2,4,6-positions (ortho-para position). Furthermore, before secondary formation at lower temperatures, the CPh pattern is dominated by the (2,4-, 2,5-) substitutions. These two isomers coelute in the analysis, but considering the prevalent ortho-para substitution, the 2,4-CPhs is much more probable than the 2,5-CPh.

Changes within the PCBz and PCPhs levels and profiles/ caused by were secondary reactions. The PCBz and especially P5CBz have the highest secondary formation of all studied chlorinated hydrocarbons. Whether increased PCBz levels originate from *de novo* synthesis or from chlorination of available benzenes is difficult to conclude due to lack of benzene and MICBz analyzes. Nevertheless, the CBz profile is shifted from a dominance of D2 and T3CBz profile to a clear dominance by P5CBz (Wikstrom and Marklund, 2000).

PCDD/Fs are also formed from natural woods and waste woods by combustion. They are also formed from sodium chloride (NaCl)-impregnated woods and a mixture of wood and plastic wastes upon combustion. It appears that both organic and inorganic chlorides can be a precursor of PCDD/Fs in incinerators. Ohta *et al.* (2002) reported PCDD/Fs can be formed by heating air alone, presumably from trace amounts of hydrocarbons and chlorine compounds contained in the air. Other studies demonstrate PCDD/Fs formation was temperature-dependent in the range of 300°C–500°C, with the maximum observed around 300°C (Shibata *et al.* 2003). The total formation at 300°C appeared high for PCDD/Fs in the experimental range, and decreased with increasing temperature (Stieglitz *et al.* 1989; Addink *et al.* 1991; Suzuki *et al.* 2004), thus, this temperature region is given special attention. Greater concentrations of chlorinated hydrocarbons at 400°C in this

Table 2. Formation of PCBz, PCPhs, PCDDs, PCDFs, PAHs, and TEQ with varied concentrations of HCl and with the presence of fly ash and parrafin powder as a catalyst

	Experiment							
	H	I	J	K	L	M	N	O
Sample	Paraffin	Paraffin	Paraffin	Paraffin	Paraffin	Nothing	Paraffin	Paraffin
HCl^a concentration	10 ppm	50 ppm	100 ppm	500 ppm	1000ppm	100ppm	100ppm	1000ppm
Fly ash	Presence	Presence	Presence	Presence	Presence	Absence	Absence	Absence
Chlorobenzene (C1%/MW)								
MlPCBz (0.316/113)	120	490	130	23	200	10	10	85
D2PCBz (0.483/147)	2600	16,000	8500	4400	8800	230^a	450^a	670^a
T3PCBz (0587/182)	1800	22,000	33,000	20,000	34,000	22	10	95
T4PCBz (0.657/216)	830	1400	20,000	25,000	33,000	10	20	21
P5PCBz (0.705/251)	250	4500	7300	17,000	20,000	10	10	10
H6PCBz (0.747/285)	170	920	1300	4800	4300	59	130	130
PCBzs [nmol]	5800	58000	70,000	71000	100,000	310	600	1000
Cl%	55	58	61	64	63			
Chlorophenols (Cl%/MW)								
MlPCPhs (0.276/129)	5100	15,000	37,000	2200	2600	100	150	600
D2PCPhs (0.436/163)	1300	14,000	47,000	6800	5500	200	250	1200
T3PCPhs (0.539/198)	330	11,000	30,000	24,000	28,000	100	100	520
T4PCPhs (0.612/232)	110	7100	26,000	27,000	31,000	130	100	570
PSCPCPhs (0.666/267)	150	1500	4200	9500	9800	120	100	270
PCPhs [nmol]	7000	49,000	144,000	70,000	77,000	450	400	3200
Cl%	33	44	45	57	57			
PCDDs (C1%/MW)								
TeCDDs (0.441/322)	6.0	250	290	290	250	0.01	0.01	0.39
PeCDDs (0.498/357)	2.5	210	310	630	980	0.01	0.01	0.10
HxCDDs (0.545/391)	0.86	150	240	830	1100	0.01	0.02	0.10
HpCDDs (0.584/426)	0.30	53	86	570	790	0.01	0.02	0.07
OCDD (0.617/460)	0.17	13	18	250	320	0.01	0.02	0.12
PCDDs [pmol]	10	680	940	2600	3400	0.05	0.07	0.77
Cl%	47	50	50	54	54			
PCDFs (C1%/MW)								
TeCDFs (0.464/306)	94	1800	2400	2900	2900	0.02	0.03	5.0
PeCDFs (0.521/341)	29	1000	1400	2500	2900	0.02	0.03	0.72
HxCDFs (0.568/375)	5.5	390	610	1500	1400	0.01	0.02	0.17
HpCDFs (0.607/410)	0.94	130	200	710	730	0.01	0.01	0.09
OCDF (0.640/444)	0.30	21	29	180	170	0.01	0.01	0.07
PCDFs [pmol]	130	3300	4600	7800	8100	0.06	0.09	6.0
Cl%	48	50	50	52	52			
Total PCDD/DFs	140	4000	5540	10,000	12,000	7.4	28	7200
TEQ (pmol)	1.8	62	99	170	170	0.12	0.20	95
PAHs^b	32	27	30	31	31	NA	NA	NA

HCl, hydrolchloric acid; ^{a}Background concentrations. ^{b}Indicates μg/g concentration levels. PAHs, polycyclic aromatic hydrocarbons; NA, not analyzed. The values were rounded.

study are probably due to the design of the incinerator or the presence of paraffin powder. HCl, and fly ash. Many studies have been reported on the generation and emission of PCDD/Fs in municipal incineration and other combustion of plastic resins, involving either homogeneous gas-phase reactions or post- furnace processes involving fly ash. It has been proven in previous experiments that the formation of PCDD/Fs depends on temperature, and in these tests the temperature was optimal for the formation of PCDD/Fs, at least after the gas cooler, where it was from 350°C to 444°C (Asikainen *et al.* 2002).

It is generally recognized that more PCDFs are formed than PCDDs in combustion process such as in municipal solid waste incinerators (Luijk *et al.* 1994; Addink and Olie, 1995; Weber *et al.* 1999), which is also confirmed in this study (Table 1). This tendency is thought to be caused by the rapid formation and slow decomposition of PCDFs, in addition to the relative difficulty of their decomposition by oxygen. PCDDs were less stable than confirmed by other measurements using fly ash and analysis in MSWI's, where more PCDFs were present than PCDDs (Addink and Altwicker, 1998). Other studies illustrate that PCDFs tend to form dominantly in the high temperature (e.g., combustion) zone and are successively trapped in the low temperature zone. Especially, T4CDF is the most dominant homologue contained in the wet zone and outlet gas. Another study also indicated a high level of PCBz formation leads to high levels of PCDFs formation (Ohta *et al.* 2004).

The ratio of PCDFs to PCDDs of the combustion gas is known to be generally high. The high ratio of PCDFs to PCDDs may be characteristic when combusting PVC. In the

Table 3. Formation of PCBz, PCPhs, PCDDs, PCDFs, PAHs and TEQ with varied concentrations of HCl with the presence of newspaper and fly ash as a catalyst

	Experiment				
	P	Q	R	S	T
Sample	Newspaper	Newspaper	Newspaper	Newspaper	Newspaper
HCl concentration	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
Fly ash	Presence	Presence	Presence	Presence	Presence
Chlorobenzene (C1%/MW)					
M1PCBz (0.316/113)	330	290	380	120	130
D2PCBz (0.483/147)	3600	7200	1900	4600	2600
T3PCBz (0.587/182)	2600	13,000	11,000	9800	4200
T4PCBz (0.657/216)	1300	9200	13,000	10,000	6500
H6PCBz (0.747/285)	470	4600	8100	8000	7500
PCBzs [nmol.]	8400 [50]	36,000 [190]	37,000 [180]	35,000 [170]	25,000 [120]
Cl%	55	60	64	63	65
Chlorophenols (C1%/MW)					
MIPCPhs (0.276/129)	16,000	5800	6500	9200	7400
D2PCPhs (0.436/163)	2200	4500	7400	10,000	9400
T3PCPhs (0.539/198)	550	10,000	18,000	18,000	35,000
T4PCPhs (0.612/232)	180	7500	10,000	11,000	7400
P5CPCPhs (0.666/267)	55	1700	2800	3500	4200
PCPhs [nmol.]	19,000 [140]	30,000 [160]	45,000 [240]	52,000 [280]	63,000 [340]
Cl%	31	50	51	50	51
PCDDs (C1%/MW)					
TeCDDs (0.441/322)	37	62	61	57	32
PeCDDs (0.498/357)	28	130	200	140	98
HxCDDs (0.545/391)	16	210	350	350	290
HpCDDs (0.584/426)	6.7	170	320	380	480
OCDD (0.617/460)	3.5	140	290	450	910
PCDDs [pmol.]	91 [0.26]	710 [1.8]	1200 [3]	1400 [3.3]	1800 [4.2]
Cl%	49	55	56	57	59
PCDFs (C1%/MW)					
TeCDFs (0.464/306)	95	730	1100	800	490
PeCDFs (0.521/341)	35	530	840	730	510
HxCDFs (0.568/375)	11	310	530	510	460
HpCDFs (0.607/410)	2.8	170	320	390	470
OCDF (0.640/444)	0.34	53	130	210	420
PCDFs [pmol.]	140 [0.45]	1800 [5.3]	2900 [8.5]	2600 [7.5]	2400 [6.4]
Cl%	49	52	52	53	56
Total PCDD/DFs	230	2500	4141	4100	4200
TEQ (pmol)	2.6	36	57	51	44
PAHs[a]	1.2	2.2	3.2	2.2	1.8

HCl, hydrochloric acid. [a]Indicates μg/g concentration level. The values were rounded.

current study, all PCDF homologues were greater (especially T4CDF over T4CDD) at all temperatures. Further more, T4CDF to O8CDF homologues were greater at 500°C compared to T4CDD to O8CDD. Overall, temperature plays a considerable role in the variation of homologue profiles. PCDF were generally 5–10-fold higher than PCDD (Mininni *et al.* 2004), which is in good agreement with the conclusions by Weber and Hagenmaier (1999) who found a l0-fold greater PCDF over PCDD in exhaust gas. The higher formation can be explained by the much higher level of PCDF present in flue gas, which corresponds to an easier formation during chlorination. Also, production of PCDF is supposed to proceed via formation of main predibenzofuran structures (hydroxyl biphenyls or hydroxylated dibenzo ethers), which lead to chlorination dibenzofurans (Hell *et al.* 1997; Scholz, 1997; Weber and Hagenmaier, 1997).

Impact of HC1 Concentration

Elevated concentrations of PCBz, PCDDs, PCDFs, and TEQ were noticed, Exp-L (Table 2) whereas PCPhs were greater in Exp-J. However, PAHs were homogeneous in all experiments. Three blank tests (Exp-M to Exp-O) with the absence of fly ash and presence and absence of paraffin powder at 100-ppm and 1000-ppm HC1 concentrations were also conducted. The results provided a very less pronounced formation of all the target compounds (except D2PCBz). Concentrations of PAHs were several hundred times greater than chlorinated hydrocarbon analogues. This may be due to the greater proportion of hydrocarbons in the gas stream of the test apparatus rather than chlorinated compounds (Johansson and Bavel, 2003).

Homologue profiles of PCBz, PCPhs, PCDD, and PCDF were different depending upon the HCl concentrations

Table 4. Concentrations of PAHs (ng/g sample) during burning of paraffin powder/newspaper with different HCl concentrations and fly ash as a catalyst

	Experiment									
	U	V	W	X	Y	Z	AA	AB	AC	AD
HCl concentration	10 ppm		50 ppm		100 ppm		500 ppm		1000 ppm	
Fly ash	Presence		Presence		Presence		Presence		Presence	
Sample	Paraffin	Newspaper	Paraffin	Newspaper	Paraffin	Newspaper	Paraffin	Newspaper	Paraffin	Newspaper
Naphthalene	9000	550	11,000	910	8400	960	8000	940	13,000	770
Acenaphthylene	6700	96	3600	390	6700	710	6200	380	3700	320
Phenanthrene	4500	190	3400	250	4100	480	4600	250	4200	210
Pyrene	2500	78	1900	160	2300	99	2600	150	2200	120
9H-Fluorene	1800	7	1700	100	1800	140	1700	100	1900	76
Fluoranthene	1600	130	1500	140	1500	280	2100	140	1700	110
Anthrathene	1400	15	1100	61	1500	130	1600	44	1400	36
Benzo[a]pyrene	1100	15	580	31	1100	67	1300	15	670	3
Benzo[a]anthrathene	700	8	540	36	620	61	690	33	640	26
Benzo[g,h,I]perylene	520	22	320	24	440	50	550	23	390	14
Indeno[l ,2,3-cd]pyrene	430	19	290	25	370	53	480	24	360	18
Benzo[b]fluoranthene	410	29	230	40	360	86	430	41	300	34
Crysene	350	21	240	38	320	75	350	38	320	32
Acenapthene	230	2.8	170	5.8	220	11	240	5.5	230	3.8
Benzo[k]fluoranthene	240	6	150	16	220	30	260	15	210	12
Dibenzo[a,h]anthrathene	37	0.96	21	3.5	30	6.4	36	3.3	29	2.8
Total PAHs	32,000	1200	27,000	2200	30,000	3200	31,000	2200	31,000	1800

Hcl, hydrochloric acid. The values were added.

(Table 2). D2- and T3CBz were greater at 10 and 50 ppm HC1 concentrations, while increasing HCl concentrations yield an increasing homologue profile that is similar to PCPhs but not to PCDD/Fs (Table 2). Isomer profiles of chlorinated hydrocarbons were found to be similar at all HCl concentrations (results not shown). For example, D2CPhs do not have influence on HC1 concentrations especially for the 2,3-, 2,4-, 2,5, 2,6-, 3,4-, and 3,5- isomers. These results indicated that *ortho* and *para*-orient reaction in chlorophenol ring might be a possible explanation. On the whole, paraffin powder increased greater formation of all target chemicals. In MSWI's, the combustion gases generally include HCl at concentrations of several hundred ppm or higher, originating from NaCl and other chlorides commonly found in waste materials. It is believed this may lead to the formation of PCDD/Fs during the incineration of materials having no chlorine (Lenoir *et al.* 1991).

HC1 Concentration & Newspaper Catalyst

Uniform concentrations of PCBz were noticed (Exp-Q to Exp-S) at all HCl concentrations except 10- and 1000-ppm (Table 3), whereas, PCPhs, PCDDs, PCDFs, TEQ, and PAHs were greater in Exp-R and Exp-S (Table 3). Again concentrations of PAHs were several hundred times greater than chlorinated hydrocarbon analogues. Wang *et al.* (2002) reported that PAH were more predominant compounds than PCDD/Fs. Homologue profiles of PCBz, PCPhs, PCDDs, and PCDFs were similar to the experiment conducted with paraffin powder. Concentrations of PCBz, PCPhs, PCDDs, PCDFs, TEQ, and PAHs were 2 to 10 orders greater when apply paraffin powder as catalyst rather than the newspaper. TEQ concentrations were several orders greater when combusting paraffin powder than newspaper (Fig. 7). Especially, TEQ steadily increased from 50 ppm to 500 ppm HCl concentrations. At maximum HCl concentrations during the combustion of newspaper and fly ash, TEQ slightly declined or were stationary. This was true in the case of paraffin powder combust with fly ash.

The results also suggest a fly ash catalyzed PCDD/Fs formation is a possible cause although there was a limit in dioxin formation when "active chlorine site" in dioxin-free fly ash was the only chlorine source. Furthermore, the presence of chlorinated hydrocarbons may lead to form chlorinated compounds. Therefore, fly ash is responsible for the formation of PAHs rather than the HCl source. Particularly the "active site control type reaction" in fly ash is a critical stage for the formation of chlorinated compounds. For example, in the heating chamber, the fly ash was greatly attracted by hydrocarbons when compared to HCl. The time of reaction by hydrocarbons might be comparatively longer than that of chlorinated compounds. Consequently, heavier chlorinated compounds had less chance to contract the "active reaction site" in fly ash. Basically, in the fly ash "active site," the Deacon type of reaction can be expected in which the continuous back reaction of both $CuCl_2$ and $FeCl_3$ play a chlorine source in experimental instrument. For instance, in case of absence of a chlorine source (HCl acid), the Deacon reaction will be restricted and, therefore, formation of chlorinated compounds can be expected to be limited. For example, a 10–50 ppm HCl concentration was not enough for the formation of chlorinated hydrocarbons.

Table 5. Concentrations (ng/g) of chlorinated hydrocarbons and PAHs during combustion of various polymers and newspaper

Sample	Blank	PE	PET	Nylon	Newspaper	PP	ABS	PVC
HC1								584,000,000
HCN	<3000		<3000	12,000,000		73,000	1,000,000	<3000
CO (ppm)	13	310	20	730	790	400	49	170
$\%CO_{2(V/V)}$	<0.2	1.4	1.5	0.90	0.80	1.1	1.0	0.40
$\%\ O_2\ (_{V/V})$	21	19	19	20	20	19	20	20
Total PCDFs	0.02	0.04	0.14	0.01	0.23	0.07	0.01	12
Total PCDDs	0.03	0.03	0.17	0.06	0.15	0.05	0.06	3.4
Total Coplanar PCBs	0.07	0.16	0.12	0.08	0.15	0.18	0.08	0.19
Total PCDD/DFs + PCBs	0.13	0.24	0.43	0.15	0.53	0.29	0.14	16
TEQ[a]	0.58	1.2	4.3	0.07	5.4	0.95	0.59	130
Biphenyl	300	120,000	170	130,000	50,000	370,000	650	450
Dibenzofuran	27	8400	17	13,000	39,000	14,000	360	28
Dibenzodioxin	<10	<10	<10	<10	<10	<10	<10	<10
Benzene	<3000	26,000,000	<3000	12,000,000	2,800,000	730,000	2,300,000	<3000
Toluene	<3000	33,000	<3000	200,000	170,000	38,000	75,000	60,000
Xylene	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000
Naphthalene	10,000	1,200,000	7600	2,200,000	780,000	2,600,000	6400	4300
Acenaphthylene	<10	1,300,000	<10	1,500,000	270,000	1,400,000	360	26
Acenaphthene	<10	6800	<10	11,000	3900	13,000	62	100
9H-Fluorene	590	130,000	260	170,000	44,000	220,000	580	1300
Phenanthrene	500	670,000	410	760,000	250,000	940,000	860	410
Anthrathene	360	140,000	260	190,000	49,000	240,000	280	280
Fluoranthene	60	490,000	61	560,000	180,000	520,000	360	51
Pyrene	130	380,000	120	500,000	160,000	620,000	200	94
Benzo[a] anthrathene	<10	85,000	<10	89,000	29,000	120,000	58	37
Crysene	<10	95,000	<10	100,000	38,000	130,000	68	20
Benzo[b] fluoranthene	50	140,000	37	150,000	48,000	180,000	100	40
Benzo [k] fluoranthene	<10	45,000	<10	42,000	14,000	58,000	22	<10
Benzo[a]pyrene	<10	140,000	<10	160,000	38,000	170,000	22	<10
Indeno[l ,2,3-cd]pyrene	<10	86,000	<10	110,000	28,000	140,000	18	<10
Benzo[g,h,i]perylene	<10	120,000	<10	140,000	33,000	130,000	11	<10
Dibenzo[a,h]anthrathene	<10	9300	<10	9000	3700	14,000	<10	<10
Total 16 PAHs	12,000	5,000,000	8700	6,700,000	2,000,000	7,500,000	9400	6700

PE, polyethylene; PET, polyethyleneterephthalate; PP, polypropylene, ABS, Acrylonitrile butadiene styrene; PVC, polyvinylchloride; TEQ, Toxic Equivalent Quantity. [a]pgTEQ/g basis. The values were rounded.

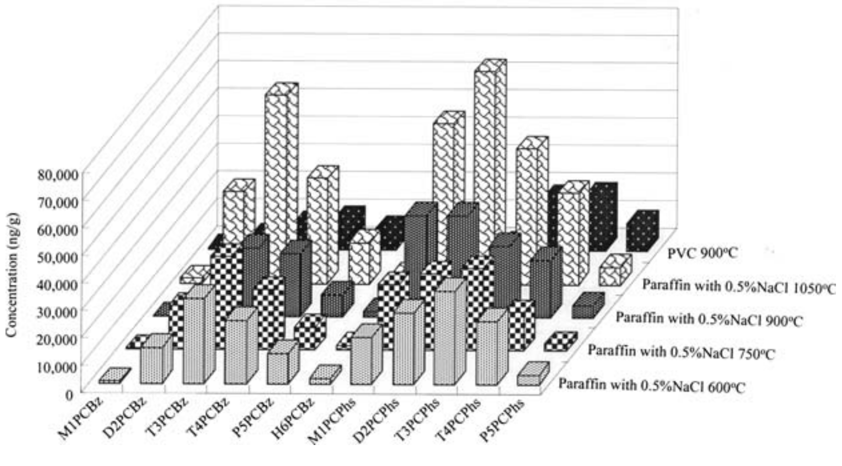

Fig. 4. Homologue distribution of PCBz and PCPhs in paraffin powder mixed with 0.5% NaCl and PVC at varied temperatures

Overall, the results of this study in general indicated that HCI and unburnt hydrocarbon with the dioxin-free fly ash formed PCBz, PCPhs, and PCDD and PCDFs. Especially, the formation of PCDD and PCDF even at 100°C and suggested the dioxin-free fly ash had catalytic reaction and, therefore, pronounced formation (Table 1). Based on our results, we can emphasize that the Deacon type of reaction explains the increased formation of most of chemicals, namely;

$$2R-H+2[CuCl_2\,\text{or}\,FeCl_3]+(O)\,d\,2R-Cl+2[CuCl\,\text{or}\,FeCl_2]+H_2O \qquad (1)$$

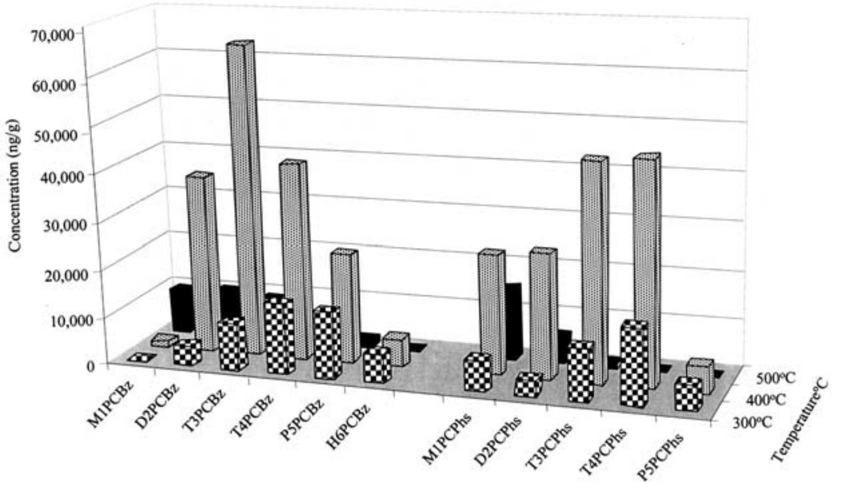

Fig. 5. Homologue distribution of PCBz and PCPhs in fly ash at varied temperatures

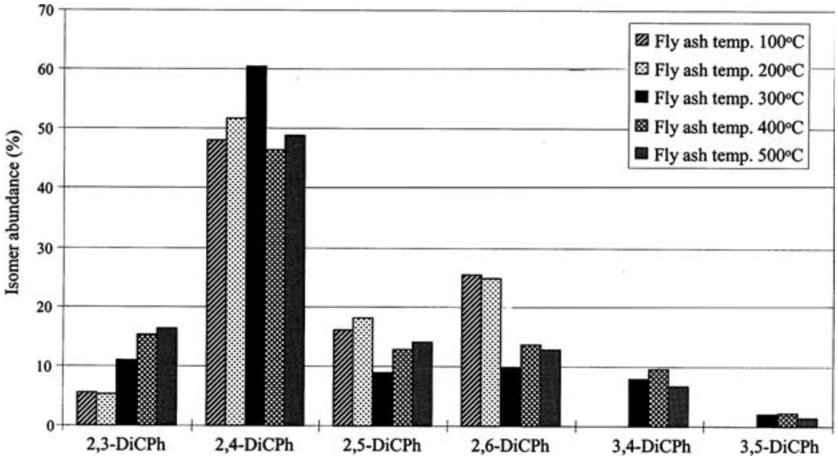

Fig. 6. Isomer abundance (%) of dichlorophenols in fly ash at varied temperatures

$$2[\mathrm{CuCl\ or\ FeCl_2}] + 2\mathrm{HCl} + (\mathrm{O})\ \mathrm{d}\ 2[\mathrm{CuCl_2\ or\ FeCl_3}] + \mathrm{H_2O} \quad (2)$$

Furthermore, the presence of metal chloride in the fly ash and hydrocarbons in the gas stream found major contributors for the increased chlorinated hydrocarbons. Chlorine gas is also reported to generate by Deacon reaction between oxygen and HCl acid. CuO is considered to be an oxygen source and also a catalyst (Born *et al.* 1993; Froese and Hutzinger 1996a,b). It has also been reported that the formation of PCDD/Fs in mixture samples of carbon and fly ash was repressed in a condition where there was no oxygen, such as nitrogen in atmosphere (Addink and Olie, 1995). Chlorine is necessary for the formation of PCDD/Fs. Municipal and industrial wastes generally contain chlorinated compounds such as NaCl, KCl, and PVC that can react as a chlorine source in the incinerators (Stieglitz *et al.* 1989, 1996; McNeil *et al.* 1998; Stieglitz 1998). PVC is considered one of the compounds most responsible for the formation of PCDD/Fs in waste incinerators. PVC has both superior mechanical and chemical properties and is used for various types of moldings. Disposal of PVC is being reduced by recycling; however, municipal and industrial wastes still contain a large quantity of PVC. PVC can be decomposed easily combustion, and acts as a chlorine source for the formation of PCDD/Fs (McNeil *et al.* 1998). Furthermore, fly ash in incinerator contains significant amounts of basic PCDD/DF precursors, PCBz and PCPhs, in particular, at concentrations one order of magnitude higher than those of PCDD and PCDF. These precursors are strongly bound to fly ash. At 250–400°C, they become important components of *de novo* synthetic reactions yielding PCDD, PCDF, and PCB on solid particles contained in flue gas. During PCDD and PCDF formation, the reactivity of PCPhs is much higher than that of PCBz (Bures *et al.* 2003). Very reactive phenols can also be transformed into PCDF and PCDD via their condensation reactions (Grabic *et al.* 2002), in contrast to PCBz dehalogenations (Bures *et al.* 2003).

Irrespective of temperature and HC1 concentration, homologue profiles of PCDD/Fs were dominated by low chlorinated analogues (Tables 1 and 2). Mininni *et al.* (2004) reported

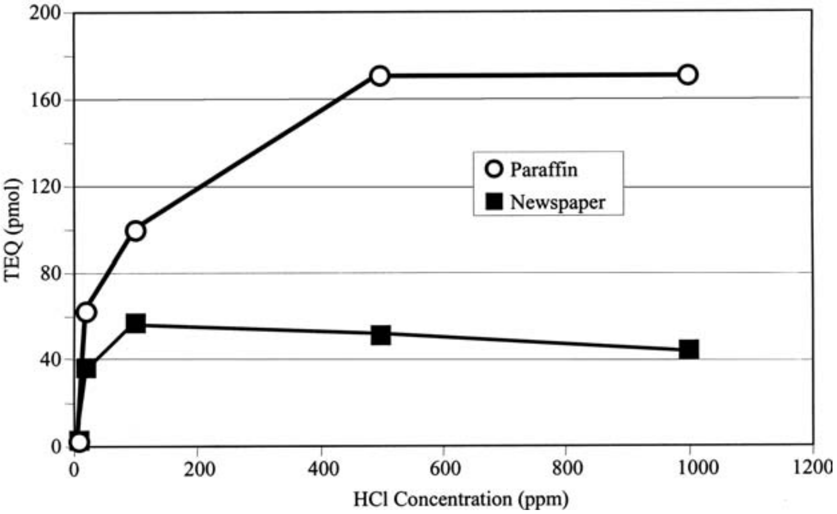

Fig. 7. Toxic equivalency estimation (PCDD/DF-TEQ) when burning paraffin powder and newspaper at varied HCl concentrations

similar results in pilot incineration tests of sewage sludge spiked with organic chlorine. As for as their discussions, homologue profile depends on after burning temperature. Experimental tests at different oxygen concentrations show that oxygen deficiency leads to the formation of PCDF, and especially P5CDF and T4CDF. On the contrary, when oxygen increases a higher formation of PCDD occurs. Corresponding to our study, Yasuhara *et al.* (2001) reported that the amount of dioxins formed in the samples according to the number of chlorides was P5CDD>T4CDD>H6CDD>H7CDD>O8CDD in PCDD isomers and T4CDF>P5CDF>H6CDF>H7CDF and O8CDF in PCDF isomers.

HCl Concentration: Catalysts and PAHs

Formation of PAHs was maximum irrespective of the experiments with different catalysts as well as HCl concentrations (Table 4). Particularly, monochlorinated derivatives of naphthalene, acenaphthalenes, and phenanthrene concentrations were predominated, while acenaphthene and dibenzo[a,h]anthrathene showed lower concentrations. Similar findings were also observed after combustion of PVC (Wang *et al.* 2003). Comparatively, paraffin powder produced 30 times greater concentrations of PAHs than newspaper (Table 4). Based on these results, it can be explained that chlorinated compound formation was greatly influenced by the catalytic reaction of fly ash. Furthermore, the presence of hydrocarbons may lead to form chlorinated compounds at a considerable level. Therefore, fly ash is responsible in the formation of PAHs when compared to the HCl source. Particularly, the ‘‘active site control type reaction’’ in fly ash is a critical stage for the formation of polycyclic aromatic compounds. The time of reaction by hydrocarbons might be comparatively longer than chlorinated compounds. Consequently, heavier chlorinated compounds had less chance to have contact with the ‘‘active reaction site’’ in fly ash.

Combustion of Polymers

The CO concentration is usually used as a practical parameter for indicating changes in combustion conditions in a furnace. Higher levels of copper in the waste are associated with decreased CO concentration in the flue gas, which means that copper promotes combustion. This suggests that the amount of other products of incomplete combustion (PICs) should also decrease with increasing copper. Figure 3 shows the range of CO concentrations and CO_2, O_2 consumption contributions (%) from polypropylene (PP) and polyethyleneterephthalate (PET). There is no difference in the O_2 and CO_2 contribution in both samples. However, the CO concentration was greatly enhanced in PP suggesting different combustion pathways exist between two polymers. It is known that water is generally involved in CO combustion, and it is therefore possible that water generated in the PP substrate combustion contributed to the lowering of the CO concentrations during the coated film combustion. The CO peak observed in PP suggests the occurrence of a two-step combustion reaction, with the first step comprising a dehydrochlorination reaction accompanied by CO and CO_2 generation and formation of the residue, and the second step comprising its gradual oxidation (Ohta *et al.* 2004). As is also evident from Figure 3, the O_2 consumption was higher during the PP combustion than during the PET combustion, in stoichiometrical correspondence with the presence of the PP substrate.

Blank analysis was performed prior to polymer/newspaper combustion experiments (Table 5). The results showed a formation of detectable limits of few target compounds. The concentrations of HC1, HCN, PCDFs, PCDDs, DL-PCBs, TEQ; BTX, precursors such as biphenyl, dibenzodioxins, dibenzofuran, and 16 polycyclic aromatic hydrocarbons (PAHs) are also shown in Table 5. The blank study was conducted without fly ash and, thus, the results were considered to be a theoretical formation of the thermo-chemical process. The HCN formation was explained to be nitrogen containing compounds such as ABS and nylon. The HCN concentration levels were reasonable. However, levels in PP likely to be formation from additive hindered amine anti-oxidant processes. The study of Mingjim Piao’s pyrolysis experiment (Piao *et al.* 1999) demonstrated that PAHs were formed at an incinerator temperature of 900°C due to the aliphatic hydrocarbons was converted as PAHs with benzene ring. The formation of PCBz has also been determined during combustion of PVC (Ahling *et al.* 1978). These results were compared with our study and the results imply that PE, PP, nylon, and newspaper formed elevated levels of BTX and PAHs. Particularly, benzene, naphthalene, acenaphthalene found to be μg/g levels, the Benzo[a]pyrene with μg/g levels. The lower levels were found for PET, ABS, and PVC with 1/4000-fold less levels. It is probable that the presence of oxygen in PET might impact the low formation of PAHs.

We also determined the precursors of PCBs, PCDD/Fs, in order to understand the formation mechanism of DL-PCBs and PCDD/Fs. It should be worth indicating that DL-PCBs and PCDFs were detected in all the samples while PCDDs were less than 10-ng/g. It is assumed that chlorinated dioxins might have formed during the reaction of the chlorophenol dimerization effect (Takasuga *et al.* 2002a,b). These results indicated that the formation mechanism of PCBs and PCDFs was different from PCDDs. The formation of PCB and PCDF could be explained as a pyrolysis effect and the formation of chlorine from the carbon skeleton might be a suitable explanation.

In terms of the TEQ and homologues of PCDD/Fs and DL-PCBs, in nylon, ABS levels were similar to blank levels and, therefore, nylon, ABS concentration considered to be negligible. The PE, PP, and PET levels were slightly higher but considered to be equal to the blank due to the background levels (e.g., incinerator contamination). The elevated levels of TEQ in PVC were considered to the influence of Cl contents which is 57% of parent compound and thus 1 to 100- million of chlorinated aromatics occur to form during this stage. Nevertheless, these values are several magnitudes less when compare to the parent Cl contents. Some reports indicated PCDD/Fs contributed more than 90% (on average 97.3%) to the total TEQ in the stack emission, suggesting a minor impact of DL-PCBs from combustion sources on the total environmental TEQ burden.

A group of compounds that are known to be present in bottom ash are chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs). Several Cl-PAHs are regarded as priority pollutants by the US Environmental Protection Agency (USEPA) and the European Environment Agency (EEA). They known to be persistent in soil, have low biodegradability, high lipophilicity, and some are carcinogenic to humans (IARC, 1987). Naphthalene and phenanthrene as the most abundant PAHs in all samples (Fangmark *et al.* 1993; Johansson and Bavel, 2003) in one of the UK study, most abundant individual PAH was benzo[g,h,i]perylene. PAHs are strongly bound to ash and are not released to the environment during deposition on a small-scale open air landfill.

Impact of HC1 concentration, paraffin powder, and fly ash as a catalyst on the formation of PAHs was prominent. Especially in all HCl concentrations, total concentrations of 16-PAHs were 26.7 to 31.5 μg/g sample (Table 2). However, instead of paraffin powder when newspaper was used as a catalyst, PAHs concentration declines in all 5 HC1 concentrations (1.2 to 3.2 μg/g sample) (Table 3). Consequently, paraffin powder and newspaper have been employed separately to see the formation difference (Table 4). Concentrations of PAHs were several magnitudes greater in paraffin powder (27 to 32 sample) than in newspaper (1.2 to 3.2 μg/g sample). Combustion of polymers yielded concentrations of PAHs several magnitude greater than combustion of HC1 and catalyst alone. Particularly, PP produced 7500 μg/g followed by nylon (6700 μg/g), PE (5000 μg/g), and news paper (2000 μg/g). PVC, PET, and ABS showed the PAHs concentration as less than blank levels (Table 5). In a previous study (Johansson and Bavel, 2003), the sum of 16 USEPA's PAHs was found to vary from 480 to 3590 μg/kg. The amounts of carcinogenic PAHs were between 89 and 438 μg/kg ash. The maximum levels of carcinogenic PAHs exceed the Swedish generic guidelines for sensitive land use.

Chlorinated poly cyclic aromatic hydrocarbons (Cl-PAHs) are released from combustion of polyvinylchloride (PVC) at different furnace temperatures. PAHs formation from the combustion of PVC polymer was greater at the furnace temperature of 900°C than at 600°C (Wang *et al.* 2002). The result shows that the species and the levels of Cl-PAHs increased with increasing furnace temperatures within the experimental range of 600–900°C. Furnace temperature, airflow, the burning time and the combustion duration have an effect on the levels of Cl-PAHs in the emissions from PVC combustion. During combustion under high temperature, HCl is first released from PVC, and then PAHs are produced in the cooler zone of the furnace by cyclisation reaction of gaseous hydrocarbon fragments formed by incomplete combustion. But the PVC burning with a flame, which can be observed, started approximately at 4s (900°C) and 45s (600°C) after the boat containing PVC plastics was positioned in the oven. Due to this delay of PVC burning with decreasing furnace temperature, most HCl may leave along with airflow, and a temperature-dependent equilibrium between HCl and Cl_2:$2HCl\ (g) + 1/2\ O_2 \rightarrow Cl_2\ (g) + H_2O\ (g)$ can shift to the reverse reaction, thus reducing the opportunity of PAHs exposure to Cl_2. Therefore, less Cl-PAHs formation was found at a lower furnace temperature of 600°C (Wang *et al.* 2003).

Interest has been focused on Cl-PAHs since some of them have also been shown to have stronger toxicity and mutagenic properties than their corresponding PAHs in test systems for biological activity. Lofroth *et al.* (1985) found that 7-chlorobenzo[a]anthracene and 6-chlorochrysene showed strong direct mutagenic effects. The latter compound has also been shown to have a high affinity to the tetrachlorodibenzo-p-dioxin (TCDD) receptor (Toftgard *et al.* 1985) and to be a potent aryl hydrocarbon hydroxylase (AHH) inducer (Franzen *et al.* 1988). Concentrations of benzo[a]anthrathene and 6-chlorochrysene were not influenced by any concentrations of HC1 (Table 4). When combustion various polymers, PE, nylon, newspaper and PP produced higher PAHs but toxic PAHs were less than other analogues (Table 5).

Our earlier study concluded (1) materials without chlorine but with the presence of fly ash as a catalyst produce PCDD/Fs, (2) inorganic and organic materials in the furnace were a major chlorine source of HCl to form PCDD/Fs, (3) the observations also proved that PCDD/Fs also formed with the presence of NaCl burning with dioxin-free fly ash apart from PVC, and (4) it is quite apparent that chlorinated chemicals such as PCBz, PCPhs, and PAHs are major chemicals that evolve during heating of dioxin-free fly ash catalytic reaction rather than PCDD/Fs and their toxic equivalency (TEQ) (Takasuga *et al.* 2000, 2002a,b, 2003).

In the current study, with our experimental conditions, 400°C with paraffin powder, 100 ppm HCl concentration, and fly ash formed a large amount of PCBz, PCPhs accompanied by a small amount of PCDFs and PCDDs. Furnace temperature and air supply and fly ash had an influence on the formation of these toxic organics. An HCl concentration of 1000 ppm produced significant amount of PAHs followed by PCBz, PCPhs but less PCDFs, PCDDs. Instead of paraffin, when newspaper was used as a catalyst, a 500-ppm HCl concentration yielded greater PAHs, PCBz, PCDFs, and PCDDs. On the other hand, different concentrations of HCl, paraffin powder, and newspaper as catalyst showed no variation in concentrations between PAHs. However, paraffin powder produced a greater amount of PAHs than the newspaper. Furnace temperature and air supply had a greater influence on the formation of target compounds. These results suggest that metal chlorides are possibly the main factors in the formation of PCDD/Fs from the incinerator, although speculative effects of other metal chlorides have not been investigated. Eventually, combustion of various polymers prevailed. PVC showed greater PCDD/Fs, DL-PCBs and TEQ. Nylon and PP showed greater precursors of PCBs, PCDD/Fs, and PAHs, while PE had greater benzene concentrations. The results of experiments with PP, PET, and PE, indicate that fly ash, temperature, and *de novo* synthesis of PCPhs play a primary role in the formation of PCDD/Fs during combustion of these non-chlorinated polymers.

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