FORMATION OF PCDD/Fs DURING CO-COMBUSTION OF NON-CHLORINATED PLASTICS WITH PVC AND NaCl

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The role of polyvinyl chloride (PVC) and sodium chloride (NaCl) salts as organic and inorganic sources of chlorine in the formation of PCDD/Fs was investigated in a simple lab-scale incinerator simulating a batch-type combustor operating at around 500°C. Non-chlorinated polymers were incinerated separately with PVC and NaCl. As compared to NaCl, PVC yielded 45, 43, and 16 times more total PCDD/Fs with PS, PE, and PP, respectively. Maximum TEQ of 27 ng per gram of plastic was detected in the combination of PE and PVC, while with NaCl the same non-chlorinated polymer produced only 1 ng-TEQ/g. A TEQ value of 13 ng/g was detected in PVC sample incinerated individually.

Key Words : polychlorinated dibenzo-p-dioxins, furans, plastics, PVC, NaCl, batch-type combustors

1. INTRODUCTION

Large amount of polyvinyl chloride (PVC), solvents, paints, refrigerants, and many other chlorine containing materials are common components of modern waste. PVC and its precursors, vinyl chloride monomers and ethylene dichloride are the largest consumers of chlorine in the world[1]. Considering the easy access made by numerous PVC products into our household, it can be expected that a large part of them eventually end up in municipal solid waste (MSW) streams. Apart from PVC, polyethylene (PE), polypropylene (PP), polystyrene (PS), and many other polymers are extensively used in households and, thus found in considerable amounts in residential solid wastes. In many countries, such wastes disposal practices consist of incineration in well-regulated MSW incinerators or disposal in landfill sites. Many communities, however, still practice unregulated backyard burning using barrels or small-sized household combustors for the disposal of their residential solid wastes. Likewise, many poorly regulated batch-type combustors are still in operation throughout the world for incinerating bulky and other household wastes. Hence, there is a probability that large parts of the above-mentioned plastics are incinerated in such batch-type combustors with poor and unregulated burning conditions.

Combustion of PVC along with other plastics is suspected to generate thousands of products of incomplete combustion (PIC) predominantly comprised of naphthalene, chlorinated benzene, and phenols[2]. The last two compounds are suspected precursors for the formation of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs or simply dioxins). A number of chlorinated hydrocarbons are known or suspected carcinogens[3] and others such as dioxins are suspected to be a class of chemicals capable of interfering with human hormonal systems and popularly known as endocrine disrupters[4].

Although PVC is only a small percentage in MSW, it is a significant source of chlorine in the waste stream. Totsch and Gaensslen[5] calculated that the contribution made by PVC to the total chlorine load of MSW is almost 45%. While the Cl atoms in PVC make it one of the major suspects of PCDD/Fs emission from the MSW incineration, there is a clear lack of data supporting a direct link. In 1984, tests were carried out on the formation of PCDD/Fs from a French incineration plant using waste to which PVC and chlorophenols were added. Even a 300% increase in the PVC load did not alter the PCDD/Fs content of the ash[5]. An analysis of more than 1900 PCDD/Fs test results from 169 facilities conducted by Rigo et al.[6]- to investigate the effect that waste feed chlorine content (especially components like PVC, mixed plastics and salt) has on PCDD/Fs concentrations in the gaseous products

of combustion at waste incineration facilities - did not find any direct link between fuel chlorine content and PCDD/Fs concentrations in flue gas. Similarly, the investigation conducted by Guilani et al.[7] on MSW with varied PVC content did not find any notable increase in PCDD/Fs emission in flue gas. Wikstrom et al.[8], however, observed an increased formation rate of PCDD/Fs when the chlorine content increased to a threshold value of 1%. Observations reported by Wirts et al.[9] revealed that co-combustion of PVC with other polymers did not yield much concentrations of PCDD/Fs. However, there was a considerable increase in the emission from the same polymers, when they were combusted together with hydrogen chloride. Kanters et al.[2] did not observe any significant increase in the emission of chlorophenol when the PVC load was increased 8-fold in the simulated MSW sample combusted in a lab-scale apparatus.

Nevertheless, many studies contradicting those observations are available. Theisen et al.[10] analyzed residue samples obtained from a real fire accident in a PVC storage facility. Almost 1200 ng/g of total PCDD/Fs were detected. A combustion experiment involving unburned PVC material from the same accident yielded a total PCDD/Fs concentration of 21,000 ng/g. Experiments conducted by Yasuhara and Morita[11] on the thermal decomposition of 1-1.5 g of vinyldene chloride polymer (used as wrapping film) at 500 °C produced significant concentration of 3 and 4-chlorodibenzofuran isomers. Recent studies conducted in Japan are more revealing. An investigation carried out by Tatsuichi et al.[12] found a significant emission from both bottom ash and flue gas when PVC was incinerated in a small-sized combustor. As compared to 0.017, and 0.0019 ng-TEQ of PCDD/Fs (including coplanar PCBs) in flue gas from the combustion of one gram of paper and wood, respectively, an equivalent amount of PVC combustion produced 140 ng-TEQ of PCDD/Fs. Further, the PCDD/Fs and coplanar PCBs concentration in the flue gas increased from 0.28 to 5.6 ng-TEQ per gram of sample, when 2% PVC was added to a sample containing 49% paper, 49% leaf, and 2% PE.

Likewise, Ikeguchi and Tanaka[13] reported to measure considerable concentrations of HCl gas and PCDD/Fs in the flue gas during a simulated open burning experiment of electric cable coatings, plastics used for agricultural use, and wood waste (possibly contaminated with chemicals) obtained from construction sites. The chlorine content of plastics for agricultural use was around 47% and that of cable coatings was around 20%. The plastics were found to emit 3500 mg of HCl and 104 ng-TEQ of PCDD/Fs per m^3 of flue gas. The plastics

were followed by electric cables with respective values of 1400 mg and 37.4 ng-TEQ. Wood waste produced 52 mg of HCl and 10.6 ng-TEQ of PCDD/Fs in the flue gas. In the same experiments, insignificant PCDD/Fs concentrations were detected in samples obtained from the combustion of leaves and tree branches. This research clearly demonstrated a correlation between emitted HCl gas and PCDD/Fs found in both flue gas and residues.

Teraoka et al.[14] found a 60 times increase in PCDD/Fs (including coplanar PCBs) emission in flue gas when 1.5% of chlorinated plastics was added to a sample consisting of 87.5% paper, 3.7% textiles, and 7.3% non-chlorinated plastics. An addition of 5% electric cables increased the PCDD/Fs output to 571 ng-TEQ from 67 ng-TEQ per m^3 of flue gas, and around 34 times increase in PCDD/Fs concentrations in bottom ash was observed.

Apart from PVC, sodium chloride salt is another significant source of chlorine in MSW. NaCl as an inorganic source of chlorine is mainly derived from kitchen garbage. The chlorine content of pure NaCl is around 60.65% and that of pure PVC is 56.77%. Since the percentage of both kinds of chlorine is about the same, i.e. 50%, in overall composition of dry MSW[2], it is also equally important to assess the differences and similarities of dioxin emission from these two chlorine sources. The combination of various plastics and NaCl can be found in different food packages. Wikstrom et al.[8] did not find any distinction in the formation rate of chlorinated micropollutants between the two different chlorine sources, while Lenoir et al.[15] did find a distinction in PCDD/Fs formation when incinerated at high temperatures.

Therefore, the disagreement surrounding the correlation between PCDD/Fs emission and the amount of PVC, as well as the roles of different chlorine sources in PCDD/Fs emission still exist. In addition, all the researches available so far mainly focused on well-regulated MSW incinerators operating at high temperatures. The behavior of different chlorine sources on the formation of PCDD/Fs in unregulated backyard burning conditions or in poorly regulated batch-type combustors, where temperature does not reach a level sufficiently enough to combust all samples, has not been investigated properly. The low combustion temperature and various other poor combustion conditions associated with small-scale batch-type combustors or backyard burnings make them a potential source of increased PCDD/Fs emission.

Lemieux et al.[16] demonstrated that backyard burning emits more PCDD/Fs on a mass of refuse
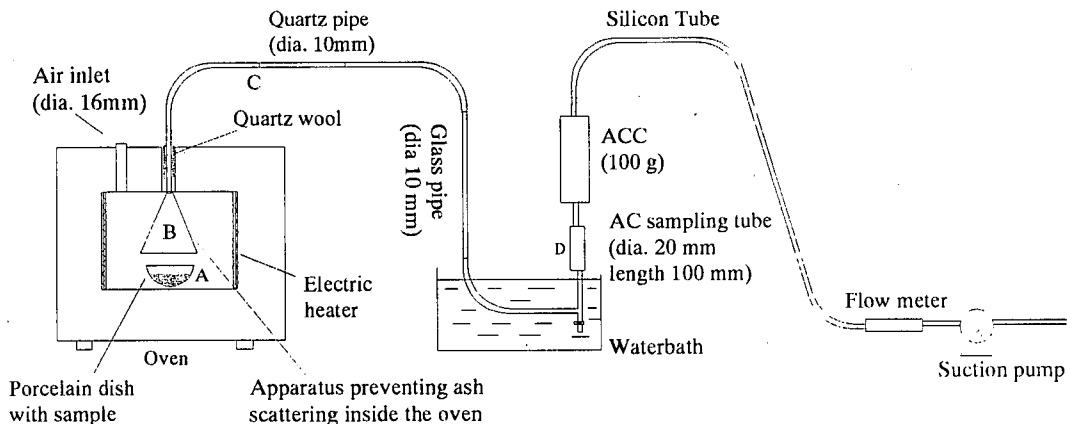
Fig. 1 Schematic diagram of lab-scale incinerator (not in scale)

burned basis than various types of MSW incinerators.

In the light of the above-mentioned problems, this research aims to evaluate the relative PCDD/Fs emission potential of PVC and NaCl as organic and inorganic sources of chlorine, respectively during combustion with other polymers at higher compositions and lower combustion temperature than generally applied by other researchers. In this study, a set of co-combustion experiments of different polymers separately with PVC and NaCl is conducted and the concentrations of PCDD/Fs in the total sample (soot + gas + residues) were measured using the following methodology.

2. METHODOLOGY

(1) Lab-scale incineration experiments: Sample preparation and combustion

In this study, the experiments were carried out in a simple lab-scale incinerator to avoid the interference of uncontrolled combustion conditions and memory effects often found in full-scale incineration experiments. A schematic diagram of the combustion apparatus is shown in **Fig. 1**.

The reactor consisted of an oven equipped with an electric heater with internal dimensions of $260 \times 150 \times 110$ mm. The premixed samples were placed in a small porcelain vessel inside the oven. A conical shaped quartz apparatus (B) was installed above the porcelain dish (A) to prevent scattering of fly ash all over the oven. Emitted flue gas was conveyed from the oven with 10-mm ⌀ quartz and glass combined pipe (C). The flue gas was cooled down in a water bath before it passed through the air pollution control device. A tube (10 cm × ⌀ 2 cm) plugged at both ends with previously decontaminated cotton, and filled with a

Table 1 Co-combustion samples

| Run | Combination | | | | Total sample wt. (g) |
	Sample combination	weight (g)	Others	wt. (g)	
I	AC Blank	10	-	-	10.00
II	NaCl + PP	0.5+0.5	Fe_2O_3	0.05	1.05
III	NaCl + PS	0.5+0.5	Fe_2O_3	0.05	1.05
IV	NaCl + PE	0.5+0.5	Fe_2O_3	0.05	1.05
V	PVC + PP	0.5+0.5	Fe_2O_3	0.05	1.05
VI	PVC + PS	0.5+0.5	Fe_2O_3	0.05	1.05
VII	PVC + PE	0.5+0.5	Fe_2O_3	0.05	1.05
VIII	PVC	0.5	Fe_2O_3	0.05	0.55

combination of granular (⌀ 4.5mm) and powdered activated carbon (D), was installed immediately after the water bath to capture fly ash and soot contained in the flue gas escaping from the oven. The effluent gas was treated with activated carbon column (ACC) and discharged into the atmosphere. Since this is a comparative study aimed at determining relative concentrations of PCDD/Fs from different chlorine sources in various samples, the portion of PCDD/Fs that possibly could not be captured by the activated carbon sampling tube (D) was neglected. Additionally, the use of activated carbon (D) made it possible to obtain only solid sample and thus liquid phase separation of PCDD/Fs from samples could be avoided. A suction pump was used to maintain a constant airflow rate of 10 L/min for 30 min to ensure a complete combustion of samples.

Seven samples were incinerated with randomized combustion sequence to avoid systematic errors. The size and combination of samples are presented in **Table 1**. Powder PVC (Wako Pure Chemical Industries), NaCl, and pellets of PE, PP, and PS were obtained from the dealers. Selection of non-chlorinated polymers was based on their relative abundance in MSW. Separate combustion experiments of individual non-chlorinated polymers

Table 2 Instrumental conditions of extraction in ASE

Cycles	2- 3
Heat	9 min.
Static	15 min.
Flush %	60 vol
Purge	120 sec.
Pressure	2000 psi
Temperature	180 °C
Solvent	Toluene 100%

were not conducted in this study. A blank sample comprised of only AC was extracted for PCDD/Fs to determine the background concentration.

There is a clear lack of agreement among the researchers on the range of temperature 'most favorable' for dioxin formation. Donghoon et al.[17] cited that a temperature range of 250-450°C in the off-gas treatment system such as EPs, was adequate for the PCDD/Fs formations, while other researchers suggest a temperature as high as 600°C[9),18)]. In a field survey of poorly regulated existing batch-type small-scale waste incinerators extensively used for bulky and other household wastes combustion in Yamaguchi Prefecture, Japan, we found that the combustion temperatures inside the furnace remains in the range of 300-500°C during the entire active combustion period. Lemieux et al.[16] conducted four runs of open burning simulation in a hut and reported that the temperatures were in 250-700°C range for a significant portion of the run time and maximum mean temperature achieved was 592°C. Therefore, in this study the combustion temperature was selected as 500°C.

Different kinds of metals are present in real residential solid wastes and they are believed to catalyze the PCDD/Fs formation[19]. Cu^{2+} is believed to be a strong catalyst, whereas Fe^{3+} is considered another possible catalyst[20]. The amount of iron found in MSW is much greater than that of copper. Hence, in these experiments around 0.05g of Fe_2O_3 was added to all samples as a catalyst.

After 30 minutes of active combustion, the heater was switched off and the oven was allowed to cool down for almost four hours or until the temperature inside the furnace declined to around 50°C. During the cooling period the air pump was kept running. After that, the porcelain vessel (A), conical quartz apparatus (B), the portion of outlet pipe up to the activated carbon sampling tube (C) and activated carbon (D) were removed from the combustor and extracted as explained in the next section.

Between the experiments, the reactor and the quartz tubes were subjected to high temperature blank combustion at 850-900°C for 2-3 hours to minimize the memory effect. Attempts were made
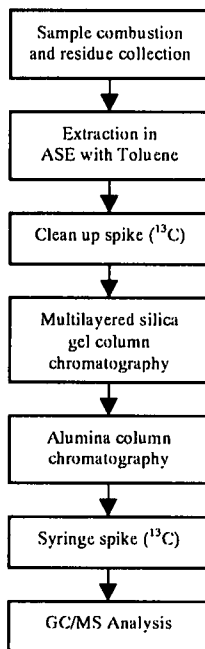

Fig. 2 Flow chart of PCDD/Fs laboratory analysis

to keep the combustion parameters, such as temperature, flow rates, etc. as well as the sample sizes identical within the different experiments. The only variation between the experiments was the form of chlorine.

(2) Sample extraction and purification

The portion of the outlet pipe up to the activated carbon tube (C), porcelain dish (A), and the apparatus installed to prevent the ash flying (B) were properly cleaned with high graded acetone. The pipes were filled with acetone and left overnight. After 12 hours, they were wiped with pieces of paper attached to a thin Teflon pipe. The liquid containing acetone and fly ash wiped from the pipes was collected in a beaker and left to evaporate overnight at room temperature. The solid sample thus obtained from the cleaning of glassware was combined with the activated carbon from the sampling tube and extracted with toluene using the accelerated solvent extraction (ASE 200 DIONEX). The instrumental conditions of extraction are given in **Table 2**.

Sample pretreatment and clean up were performed according to the simplified flow chart of PCDD/Fs analysis depicted in **Fig. 2**. The analytical procedure is a modified version of the 'Standard Method of Dioxins Measurement and Analysis of Samples from Waste Treatment' prepared by the Ministry of Health and Welfare, Japan in 1997 excluding the HCl pretreatment procedure. In actual standard method, the sample is recommended to be pretreated
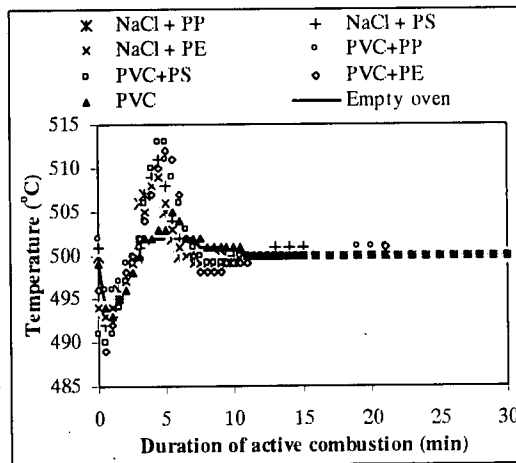
Table 3 Instrumental conditions of GC/MS

GC	Hewlett Packard HP6890
MS	JEOL GCmate MS-BU20
Capillary columns	
For T_4 to H_6	SP-2331:ϕ 0.25mm × 60m, 0.20μm (film)
For H_7 and O_8	HP-5: 30m×ϕ 0.25mm, 0.25μm (film)
Temp. program	
SP-2331	150°C (2min)- (20°C/min)- 200°C - (2°C/min)- 260 °C (35.5min)
HP-5	150°C (2min)- (20°C/min)- 200°C - (5°C/min)- 270 °C (11.5min)
Injector temp.	260°C(SP-2311), 270°C(HP-5)
Ion chamber temp.	260°C
Ionization current	300μA
Ionization voltage	37eV
Ion accelerating voltage	2.5kV
Carrier Gas	He
Injection	Split/Splitless
Ionization mode	EI
Ion monitoring	SIM
Resolution	3000

Table 4 Minimum limit of PCDD/Fs determination

Homologues	quantitative limit (ng/g)
TCDDs	0.005
PeCDDs	0.01
HxCDDs	0.03
HpCDDs	0.03
OCDD	0.04
TCDFs	0.003
PeCDFs	0.007
HxCDFs	0.04
HpCDFs	0.007
OCDF	0.02

Fig. 3 Temperature profiles in the reactor during co-combustion experiments

with HCl. After the acid pretreatment the liquid phase undergoes different steps of separation during which large amount of various solvents is used. Since the purpose of this study is to compare relative concentrations of PCDD/Fs in specified samples, the modification can be considered as justifiable taking into account the time and amount of solvents saved. As shown in **Fig.2**, after the combustion experiment, AC from sampling tube and residues obtained from cleaning pipes and other apparatus were combined and extracted in ASE with toluene. The volume of the extract was then reduced in a rotary evaporator to a few millimeters dissolved in decane. After repeated addition of hexane and condensation, the sample was finally mixed with hexane to obtain a volume of 5 mL for further cleaning up after spiking it with 50μL $^{13}C_{12}$-PCDD/Fs internal standard or clean up spike.

The clean up consisted of two steps: combined silica and aluminium oxide columns. The purpose of clean up is to selectively adsorb non-dioxins extract prior to PCDD/Fs determination. The multilayered silica gel column consisted of layers of silica impregnated with H_2SO_4, KOH and $AgNO_3$ using 0.9 g of silica as a spacer in between the layers. The alumina column consisted of a layer of previously activated in high temperature aluminium oxide between two layers of sodium sulfate.

(3) Sample analysis
The sample extracts were condensed to a volume of 50 μL in dichloromethane by passing through N_2 gas. After spiking the final extract with 10 μL of recovery standard solution or syringe spike, tetra through octa PCDD/Fs concentrations were determined using the gas chromatography and mass spectrometry (GC/MS). Coplanar PCBs in the samples were not measured in this study. Instrumental conditions of GC/MS are shown in **Table 3**. Minimum limit of PCDD/Fs determination in GC/MS expressed in terms of ng per gram of incinerated plastics is presented in **Table 4**.

3. RESULT AND DISCUSSION

(1) General
The oven and the air pump were kept running at respective set values of 500°C and 10 L/min, for one hour before every experiment to achieve a steady burning condition prior to actual sample combustion. The temperature profiles obtained from the combustion of each sample are depicted in **Fig.3**. Most of the samples yielded almost similar temperature fluctuation patterns. Since the oven door had to be opened to insert the sample inside the

furnace, the temperature profile shows an initial decline in all cases. Thereafter, it increased steadily until the self-ignition of sample occurred. In all samples, temperature fluctuation continued for almost 10 minutes and then it remained constant for the entire period of active combustion. The temperature profile of the empty oven did not show any abnormal fluctuations, indicating that the rise in temperature during sample combustion was solely caused by self-ignition.

As compared to the samples with NaCl, incineration of samples with PVC resulted in the formation of more products of incomplete combustion (PIC) as evident from the intensity and duration of soot-containing smoke observed during the combustion. The soot thus produced stuck to quartz and glass pipe walls (C) carrying flue gas, and clogged the AC sampling tube (D), causing a slight decline in the air flow rate, which was, however, immediately adjusted to the initial value of 10 L/min.

In all samples with PVC, production of bottom ash was almost negligible. The residue in the porcelain dish (A) was predominantly comprised of Fe_2O_3. It was expected given the sample size of only one-gram. However, in samples with NaCl, the resulting temperature was apparently not enough to volatilize all NaCl and a part of NaCl remained unburned in the porcelain dish. Although the dark residue attached on the apparatus installed to prevent fly ash scattering (B) greatly varied from one sample to another, a definitive trend could not be observed. Moisture generated during the combustion of samples with PVC, however, was observed to be higher than that with NaCl. The combustion of PVC sample without addition of any other polymer did not result in any residues and the generation of soot-containing smoke was noticeably less. The maximum temperature achieved during the combustion of the sample was also lower than that of other samples. It might be due to lower calorific value of PVC as compared to PP, PS and PE, and the absence of additional fuel available in other samples.

As stated earlier a blank sample of activated carbon was analyzed for PCDD/Fs to determine a possible contamination. No PCDD/Fs were detected in the extracted blank sample. Thus, possibility of any contamination of activated carbon used for further experiments is excluded.

(2) Total concentrations of PCDD/Fs and TEQ values of samples

Total PCDD/Fs and toxicity equivalent (TEQ) values of all samples are presented in **Fig. 4**. The values depicted in the figure correspond to the total amount of plastic in each sample.
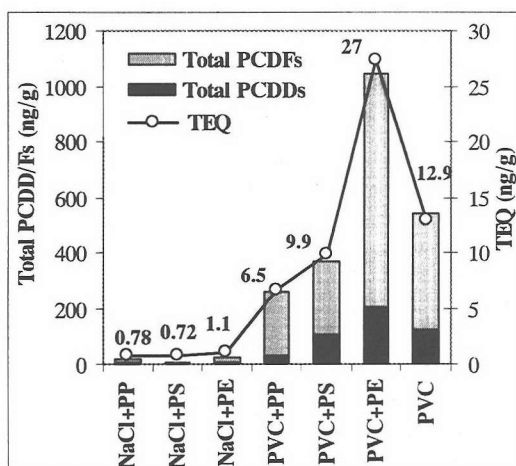

Fig. 4 Total PCDD/Fs and TEQ values of samples

All not detected values of 2,3,7,8 substituted congeners are set to zero to calculate the TEQ values. As evident from the figure, compared to NaCl, PVC yielded much higher concentrations of PCDD/Fs and TEQ values with all three polymers. The highest detected TEQ of 27 ng/g was measured in the sample with PVC and PE, and the minimum TEQ of 0.72 was detected in the sample with NaCl and PS. As compared to NaCl, PVC produced 43 times more total PCDD/Fs and 25 times more TEQ when combusted with PE. Lenoir et al.[15] also reported to obtain much higher concentration of PCDD/Fs in flue gas when PE was combusted with PVC than with NaCl at higher temperatures.

Similarly, with PS total PCDD/Fs production was 45 times higher and TEQ was 14 times higher, and with PP they were 16 and 8 times, respectively. A TEQ of 13 ng/g was detected in individual PVC sample combusted only with Fe_2O_3. The highest concentration of 2,3,7,8-TCDD (3.3 ng/g) was also detected in the last sample. However, the individual PVC sample should be compared cautiously with other PVC + plastic samples because as evident from **Fig.3** the temperature profile in this sample was slightly different from other samples.

From **Fig. 4,** it can be deduced that the addition of PE to PVC enhanced the formation of PCDD/Fs, whereas the addition of PP and PS to equal amount of PVC had an opposite effect. These speculations of enhancement or suppression of PCDD/Fs yields by the addition of individual polymers cannot be validated with limited data presented in this study. Further research is needed to understand precise roles of individual polymers. Nonetheless, **Fig. 4** distinctly indicates a much greater role of PVC in the formation of PCDD/Fs comparing with NaCl at combustion conditions applied in this study. The PCDD/Fs emission from samples with NaCl

detected in this study is in agreement with the observations made by Katami et al.[21].

Since NaCl has much higher melting point (800 °C) than that of PVC or other plastics, the set temperature of 500°C was not enough to completely volatilize NaCl as evident from the unburned NaCl remained in the porcelain dish. Hence, it can be speculated that the combustion condition was more favorable for smooth incineration and subsequent volatilization of samples with PVC. Consequently, the formation of PCDD/Fs was much less in samples with NaCl as compared to those with PVC. The emission of PCDD/Fs from NaCl at high temperatures, however, is not investigated in this research. Our aim was to investigate the emission potential of different chlorine sources in conditions generally found in poorly regulated small-scale batch-type incinerators or completely unregulated backyard burnings, where temperature remains low. However, it is important to mention that even with higher combustion temperature and longer incineration time Katami et al.[21] detected very low PCDD/Fs when PE and PS were combusted together with NaCl. Similar observations were reported by Lenoir et al.[15], who detected 0.75 μg PCDD/Fs per m^3 of flue gas obtained from the combustion of PE and NaCl as compared to 8 μg/m^3 of PCDD/Fs obtained when NaCl was replaced by equal amount of PVC.

(3) PCDD/Fs congener profiles of samples with PVC and NaCl

The co-combustion of PVC with all three polymers, PE, PP, and PS, yielded considerably higher concentrations of PCDFs than PCDDs, which is consistent with the results obtained in other similar laboratory scale experiments[16],[20]. The PCDF/PCDD ratios of 2.5, 4.1, and 6.6 were obtained for PVC samples with PS, PE, and PP, respectively, and that of individual PVC sample was 3.3. Homologue profiles of PCDD/Fs resulted from the combustion of PVC with other plastics are shown in **Fig. 5.** The weight distribution of PCDD homologues in all samples increased with increasing degree of chlorination except for octa-groups:

OCDD<TCDDs<PeCDDs<HxCDDs<HpCDDs

In case of PCDFs, generally the following trend was observed:

OCDF<HpCDFs< TCDFs<PeCDFs <HxCDFs

The combination of PVC and PS, however, showed a slightly different pattern of PCDFs with rather high concentration of penta and tetra groups. The combustion of the PVC-only sample produced a completely different congener profile as illustrated in **Fig. 6.**
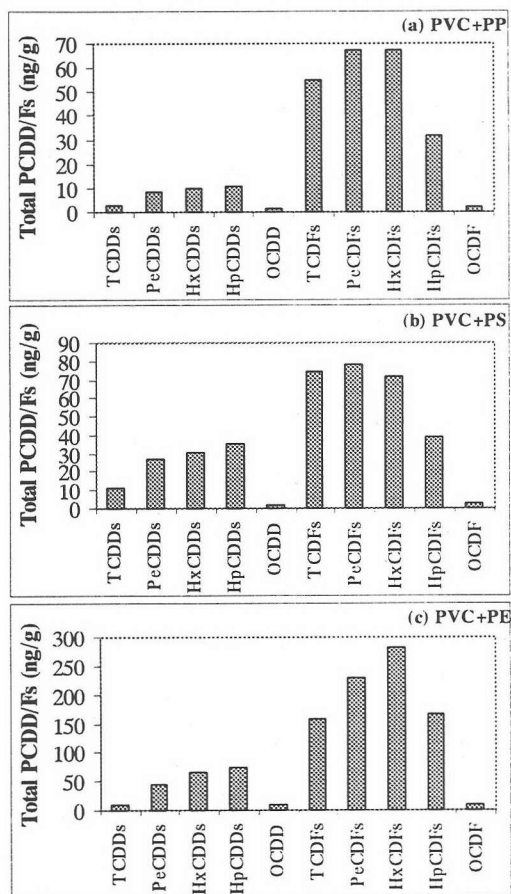
Fig. 5 Homologues of PCDD/Fs obtained from co-combustion of PVC with (a) PP, (b) PS, and (c) PE.
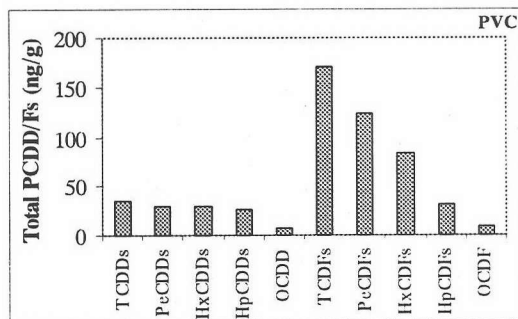
Fig. 6 Homologues of PCDD/Fs obtained from combustion of individual PVC sample

The weight distribution of both PCDDs and PCDFs homologues decreased with increasing degree of chlorination in this sample:

OCDF<HpCDFs<HxCDFs<PeCDFs <TCDFs

A possible explanation for this shift might again be linked to the temperature profile, which was different from other PVC + plastics samples.

Table 5 Concentrations of 2,3,7,8 substituted congeners and TEQ distribution by groups (ng/g)

Congener	WHO-TEF (1998)[22]	NaCl+PP	NaCl + PS	NaCl+PE	PVC+PP	PVC+PS	PVC+PE	PVC
2378-TCDD	1	0.20	0.00	0.00	0.10	0.23	0.21	3.29
12378-PeCDD	1	0.35	0.39	0.29	0.84	2.79	4.86	1.18
123478-HxCDD	0.1	0.00	0.00	0.42	1.13	2.77	6.48	1.41
123678-HxCDD	0.1	0.00	0.41	0.46	1.07	2.64	7.18	2.26
123789-HxCDD	0.1	0.00	0.57	0.68	0.93	3.16	5.15	2.32
1234678-HpCDD	0.01	1.19	1.12	1.05	3.72	12.51	28.06	9.91
OCDD	0.0001	0.87	0.24	0.49	1.32	2.25	8.74	6.63
Total 2,3,7,8 substituted PCDDs		**2.6**	**2.7**	**3.4**	**9.1**	**26.3**	**60.7**	**27.0**
2378-TCDF	0.1	0.13	0.09	0.07	1.28	1.30	3.54	4.32
12378-PeCDF	0.05	0.00	0.19	0.56	6.62	8.83	22.75	13.61
23478-PeCDF	0.5	0.00	0.17	0.54	4.26	4.79	14.50	6.75
123478-HxCDF	0.1	0.66	0.00	1.38	11.60	14.25	50.51	14.29
123678-HxCDF	0.1	0.00	0.36	0.97	8.10	7.67	31.65	7.98
123789-HxCDF	0.1	0.86	0.35	0.00	1.16	0.94	4.35	1.74
234678-HxCDF	0.1	0.52	0.40	0.70	3.75	3.89	17.17	6.30
1234678-HpCDF	0.01	0.44	0.46	2.75	16.40	19.66	84.17	15.72
1234789-HpCDF	0.01	0.09	0.12	0.76	4.12	5.67	26.16	3.45
OCDF	0.0001	0.66	0.02	0.19	1.82	2.49	10.21	8.94
Total 2,3,7,8 substituted PCDFs		**3.3**	**2.2**	**7.9**	**59.1**	**69.5**	**265.0**	**83.1**
Total 2,3,7,8 substituted PCDD/Fs		**6.0**	**4.9**	**11.3**	**68.2**	**95.8**	**325.7**	**110.1**
TEQ by group	7 PCDDs	0.56	0.50	0.46	1.29	4.00	7.24	5.17
	10 PCDFs	0.22	0.22	0.65	5.25	5.90	20.22	7.71
	Total TEQ	**0.78**	**0.72**	**1.11**	**6.55**	**9.90**	**27.45**	**12.88**

NaCl produced the dioxin to furan ratios of 3.11 and 1.29 with PE and PP, respectively. The only sample producing a PCDF/PCDD ratio of less than one was the sample with NaCl and PS. PCDD/Fs congener profiles of samples with NaCl are depicted in **Fig.** 7. Samples with NaCl also produced analogous congener patterns as in case of PVC and other plastics but with much lesser amount of total PCDD/Fs. No hexa isomers were detected in the NaCl sample with PP, and with PE and PS no tetra isomers were detected.

The TEQ distribution by groups and concentrations of 17 2,3,7,8-substituted congeners are presented in **Table 5**. The average percentage contributions made by 7 PCDDs and 10 PCDFs to the total TEQ values in samples with PVC and other polymers were 29 and 71%, respectively, and that of individual PVC sample was 40 and 60%, respectively. On the other hand, the composition of toxic congeners in samples with NaCl was found to be quite different. The average contributions of dioxins and furans in those samples were 61 and 39%, respectively.

The predominant toxic congeners in PVC+ other polymer samples were 23478-PeCDF, 12378-PeCDD, 123478-HxCDF and 123678-HxCDF with respective percentage contributions of 28,20,17, and 11% to the total TEQ values, respectively. Other congeners contributed the rest. In case of the individual PVC sample, the contribution of 2378-TeCDD and 23478-PeCDF were identical with 26% each. In samples with NaCl, the contribution made by 12378-PeCDD was much higher than other
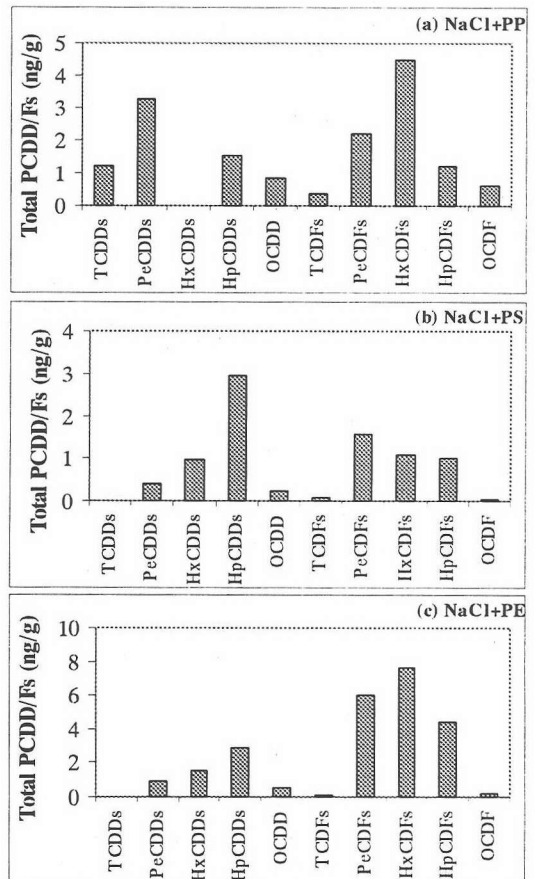

Fig. 7 Homologue of PCDD/Fs obtained from co-combustion of NaCl with (a) PP (b) PS, and (c) PE.

congeners with an average value of 42%.

The confirmation of catalytic role of Fe_2O_3 in the formation PCDD/Fs was beyond the scope of this study and, hence, combustion of samples without Fe_2O_3 for the analysis of PCDD/Fs was not carried out. However, during the trial burn it was observed that addition of Fe_2O_3 markedly reduced the generation of soot and helped increase the temperature within the oven.

4. CONCLUSION

Based on the above discussion, various conclusions and observations can be made.

Non-chlorinated polymers were found to emit much higher amounts of PCDD/Fs when incinerated in a batch together with PVC than with NaCl at a temperature around 500°C. The highest TEQ value of 27 ng/g was detected in the PVC + PE sample, while with the same non-chlorinated polymer NaCl produced only 1 ng-TEQ per gram of incinerated plastic. As compared to NaCl, PVC produced 45, 43, and 16 times more total PCDD/Fs with PS, PE, and PP, respectively. PVC combusted individually without the addition of any other polymer also produced a significant concentration of PCDD/Fs and yielded different homologues and temperature profiles from other samples.

This research contradicts the conclusion made by various researchers that the form and source of chlorine do not influence the formation of PCDD/Fs. From the results presented, we can speculate that the organic source of chlorine is more available for the formation of PCDD/Fs during the combustion conditions applied in this study. Further studies are needed to explain the phenomenon more precisely.

Some researchers suggest that in a well-controlled combustion process, incineration of PVC does not influence the PCDD/Fs emission[8]. Nonetheless, the combustion process in household combustors and small-scale batch-type incineration plants, widely used for bulky and other residential solid waste and wastes from construction sites, cannot be well controlled or they are poorly controlled. This research illustrated an important role of PVC in the formation of PCDD/Fs. Therefore, elimination of PVC and other organic sources of chlorine from such waste streams will probably be helpful in reducing the emission of PCDD/Fs significantly.

However, due to lower combustion temperature in our experiments, a part of NaCl remained unburned, which might have influenced the volatilization of NaCl and consequently the overall formation of PCDD/Fs in samples incinerated together with NaCl. At higher combustion temperature, more PCDD/Fs emission is expected from NaCl. This aspect, is not investigated further in this research because our aim was to examine the emission potential of different chlorine sources in conditions generally found in poorly regulated small-scale batch-type incinerators operating at lower to medium temperature range.

Further studies on catalytic effect of Fe_2O_3 and on the effect of variation in the level of organic source of chlorine in the formation of PCDD/Fs would lead to additional information. Experiments on the emission of PCDD/Fs from combustion of various PVC consumer products will provide this investigation with more practically useful information.

REFERENCES

1) Engineering Materials Handbook, Engineered Plastics, Vol. 2, ASM International, 1988.

2) Kanters, M.J., Van Nispen, R., Louw, R. and Mulder, P.: Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste, *Environ. Sci. Technol.*, Vol. 30, pp.2121-2126, 1996.

3) Ahlert, R.C. and Brown, F.C.: Chlorine and chlorine chemistry, *Environmental Progress*, Vol.17, No.2, pp.161-167, 1998.

4) Colborn, T., Dumanoski, D. and Myers, J.P.: *Our Stolen Future*, Plume/Penguin, USA, 1996.

5) Totsch, W. and Gaensslen, H.: *Polyvinylchloride: Environmental aspects of a common plastic*, Elsevier Applied Science, NY, USA, p.84, 1992.

6) Rigo, H.G., Chandler, A.J. and Lanier, W.S.: Relationship between chlorine in waste streams and dioxin emissions from combustors, *American Society of Mechanical Engineers*, December 1995.

7) Guilani, M., Cernuschi, S. and Ghezzi, U.: The emission of dioxins and related compounds from the incineration of municipal solid wastes with high contents of organic chlorine (PVC), *Chemosphere*, Vol.19, Nos.1-6, pp.407-411, 1989.

8) Wikstrom, E., Lofvenius, G., Rappe, C. and Marklund, S.: Influence of level and form of chlorine on the formation of chlorinated dioxins, dibenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor, *Environ. Sci. Technol.*, Vol.30, pp. 1637-1644, 1996.

9) Wirts, M., Lorenz, W. and Bahadir, M.: Does co-combustion of PVC and other plastics lead to enhanced formation of PCDD/F, *Chemosphere*, Vol.37, No.8, pp.1489-1500, 1998.

10) Theisen, J., Funcke, W., Balfanz, E. and Konig, J.: Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials, *Chemosphere*, Vol.19, Nos.1-6, pp.423-428, 1989.

11) Yasuhara, A. and Morita, M.: formation of chlorodibenzofurans by thermal decomposition of vinyldine chloride polymer, *Chemosphere*, Vol.18, Nos.9/10, pp.1737-1740, 1989.

12) Tatsuichi, S., Soufuku, M., Komeiji, T. and Iwasaki, Y.: Study on formation factor of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls emitted from domestic incinerator – The relationship between polyvinyl chloride (PVC) ratios in waste and dioxin concentrations,

J. Jpn. Soc. Atmos. Environ., Vol.36, No.1, pp.13-21, 2001 (in Japanese).

13) Ikeguchi, T. and Tanaka, M.: Measurement of dioxin emission from simulated open burning experiments, in *Proceedings of 20th Meeting of Municipal Waste Management Committee*, Japan, pp.406-408, February 1999 (in Japanese).

14) Teraoka, T., Murata, H., Nakao, T., Aozasa, O., Ohta, S. and Miyata, H.: The actual situation of dioxin analogues pollution from unregulated light waste incinerator, *9th Symposium on Environmental Chemistry: Program and Abstracts*, pp.20-23, Sapporo, Hokkaido, Japan, June 20-22, 2000 (in Japanese).

15) Lenoir, D., Kaune, A., Hutzinger, O., Mutzenich, G. and Horch, K.: Influence of operating parameters and fuel type on PCDD/PCDF emissions from fluidized bed incinerator, *Chemosphere*, Vol.23, pp.1491-1500, 1991.

16) Lemieux, P.M., Lutes, C.C., Abbott, J.A. and Aldous, K.M.: Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels, *Environ. Sci. Technol.*, Vol.34, pp.377-384, 2000.

17) Donghoon, S., Sangmin C., Jeong-Eun O. and Chang, Y.S.: Evaluation of PCDD/F emission in municipal solid waste incinerators, *Environ. Sci. Technol.*, Vol.33, pp.2657-2666, 1999.

18) Karasek, F.W. and Dickson, L.C.: Model studies of polychlorinated dibenzo-p-dioxin formation during municipal refuse incineration, *Science*, Vol.237, 14 August 1987.

19) Addink, R. and Olie, K.: Mechanism of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems, *Environ. Sci. Technol.*, Vol.29, No.6, pp.1425-1435, 1995.

20) Huang, H. and Buekens, A.: On the mechanism of dioxin formation in combustion processes, *Chemosphere*, Vol.31, No.9, pp. 4099-4117, 1995.

21) Katami, T., Yasuda, Y., Okuda, T. and Yamamoto, S.: Survey of dioxins (PCDD/Fs) in exhaust gas from small-sized incinerators. Part III: formation of dioxins from incineration of plastics containing no chlorine in the presence of sodium chloride, *9th Symposium on Environmental Chemistry: Program and Abstracts*, pp.230-231, Sapporo, Hokkaido, Japan, June 20-22, 2000 (in Japanese).

22) WHO - World Health Organization: WHO experts re-evaluate health risks of dioxins, Press release WHO/45, 3 June 1998.

非塩素系プラスチックとPVCおよびNaClとの混合燃焼における PCDD/Fsの生成

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ポリ塩化ジベンゾーパラージオキシン（PCDDs）およびポリ塩化ジベンゾフラン（PCDFs）の生成に対するポリ塩化ビニル（PVC）および塩化ナトリウム（NaCl）の有機および無機塩素源としての寄与について，500℃で運転されるバッチ式焼却炉を想定した実験室スケールの簡易燃焼炉を用いて検討した．PVCおよびNaClと3種類の非塩素系プラスチックとを組み合わせて燃焼させた結果，PS，PE，PPとPVCとの組み合わせでは，NaClの場合よりもそれぞれ45，43，16倍のPCDD/Fsを生成した．PEの場合，PVCとの組み合わせではプラスチック1g当たり27ng-TEQの発生量であったが，NaClとの組み合わせでは1ng-TEQ/gであった．また，PVCだけを燃焼させた場合は13ng-TEQ/gであった．