

The influence of level and chlorine source on the formation of PCDD and PCDF during MSW combustion.

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Introduction

The influence of PVC (polyvinylchloride) content on the formation of chlorinated organic micro-pollutants, such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), during municipal solid waste (MSW) combustion has been discussed during the last several years. Different studies on the importance of the total amount of chlorine in the fuel on formation of PCDD/Fs have been performed, but the conclusions were contradictory. The influence of different combustion parameters, such as bed temperature, O₂-concentration, variation in HCl, H₂O concentration, temperature and residence time of the flue gas in the post-combustion zone, on PCDD/F formation was investigated by Fångmark *et al.* (1). In here study the amount of HCl in the flue gas was weakly correlated to formation and other parameters, such as the residence time in the post-combustion zone, were more important. Other laboratory reactor experiments combusting a waste with eight times higher PVC loading than a normal MSW found only a slight increase of chlorophenol in the flue gas (2). Wikström *et al.* has studied seven artificial MSW fuels with a chlorine variation between 0.12 and 1.7 wt %. They were combusted in a 5 kW laboratory fluidized bed reactor and the results showed no correlation between the chlorine source (organic or inorganic chlorine) and chlorine loading (less than 0.84 wt %) with the formation of PCDD/Fs and chlorobenzenes (3). A distinct increase in the formation of PCDD/F and chlorobenzenes was noticed when a fuel with approximately three times higher amount (1.7 wt % Cl) of PVC than a normal waste was combusted (3).

This project has studied how the amount of inorganic chlorine (present as sodium chloride, NaCl) and organic chlorine, bound in both pure PVC plastic and in PVC products, influenced the emission of PCDD/Fs during MSW combustion. Two frequently used PVC products, floor and cable, were chosen for closer study to investigate if the different additives in the products have any influence on the emissions. The chlorine content in the PVC products was about 25-wt %.

Material and Methods

Eight fuels with different chlorine content and chlorine sources were prepared by adding different amount of chlorine to an artificial MSW fuel mixture. The artificial MSW fuel is

entirely described in reference (4). Table 1 lists the chlorine levels, the four different chlorine sources, the heat capacity and the dry weight of the fuels.

Table 1 Chlorine level and the heat capacity of the fuel pellets. *% of DW

Element	Unit	1	2	3	4	5	6	7	8
DW	%	95.7	95.4	95.5	95.4	95.3	95.6	95.9	95.8
Heating value	MJ/kg	18.9	18.8	18.9	18.7	18.6	18.9	18.9	18.8
Cl _{organic Pure PVC}	%*	-	-	0.25	-	0.16	0.13	-	-
Cl _{organic PVC Floor}		0.10	-	-	-	0.08	-	0.35	-
Cl _{organic PVC Cable}		-	0.17	-	-	-	0.07	-	0.27
Cl _{inorganic (NaCl)}	%*	0.18	0.18	0.15	0.70	0.42	0.50	0.65	0.83
Cl _{total}	%*	0.28	0.35	0.40	0.62	0.66	0.70	1.0	1.1

The experiments were performed in a 5 kW laboratory scale fluidized bed reactor; a more detailed description of the reactor is given in reference (5). A total of 13 experiments were done. To minimize the effect of experimental systematic effects, the experiments were performed in random order. After 2 h of MSW combustion, two flue gas samples of organic compounds (denoted as sample A and B) were taken with a flue gas residence time in the post-combustion zone of 2.2 s. Each sample was taken isokinetically in the gas flow with the cooled probe technique for a duration of 50 min (6,7).

Table 3 The dividing of all samples into the three groups and their time-average CO concentration and CO-peak frequency during the sampling time.

Bad combustion			Normal combustion			Good combustion		
Sample	Peaks> 2000 ppm	CO	Sample	Peaks> 2000 ppm	CO	Sample	Peaks> 2000 ppm	CO
5 A	22	515	6 B	4	68	3 A	0	20
5 B	23	535	4 A	5	268	3 B	0	20
4 B	10	268	6 A	7	157	4 A ²	0	10
8 A	8	143	7 A	8	146	4 B ²	0	10
5 A	23	334	7 B	3	88	1 B ²	0	10
1 A	43	727	8 B	4	63	7 A ²	0	20
1 B	19	441	6 A	1	40	7 B ²	0	12
6 B	11	334	5 B	5	234			
			1 A ²	4	67			
			2 A	0	40			

Peaks>2000 ppm: Total number of CO-peaks over 2000 ppm during the complete sampling.

²: These samples were taken during repeated combustion experiments with these fuels.

Results

The intention was to perform all experiments during good and controlled combustion conditions to minimize the potential effect of experimental differences other than the chlorine content in the fuel. Unfortunately some disturbances in the feeding system influenced the combustion conditions, resulting in variations in the quality of combustion conditions. To

evaluate the data without the influence of different combustion conditions, the samples are divided into three groups: bad, normal, and very good combustion conditions (Table 3).

The data from the samples taken during normal combustion conditions were statistically evaluated with principal component analyses, PCA. The result and the two first components are given in Figure 1a and 1b. Variables close to each other in the loading plot (Figure 1a) indicate that they are closely correlated with each other while variables placed at the center of the loading plot are non-important variables for the model. Component 1 describes most of the important information relating to differences between the samples ($R^2=0.52$), which mainly is the difference in PCDD/F emission levels. The second component ($R^2=0.28$) describes the variation in the homologue isomeric pattern and O_2 and CO_2 between the different samples. The result of the PCA shows that the *Total Cl* in the pellets is correlated to formation of the higher chlorinated PCDD/F isomers. A study performed by Vehlow *et. al.* (8) in the TAMARA reactor showed a similar correlation between the higher chlorinated PCDD and the chlorine load.

No clear distinction between the source of the two PVC products, cable (fuels 8, 6 and 2) and floor (fuels 1, 5 and 7) can be found in the score plot (Figure 1b). This indicates that there is no particular difference in the formation of PCDD/Fs between the two PVC product sources.

The results from the PCA evaluation of the sample data taken during good combustion conditions show a high, positive correlation between the *Total Cl* level in the fuel, HCl, and Hepta-Octa chlorinated PCDD/F in the flue gas. A high, positive correlation between the amount of particles and the CO concentration in the flue gas with the amount of PCDD/F formed is found within the samples taken during bad combustion conditions. Even a negative correlation between the *Total Cl* and PCDD/F is noticed in these data, *i.e.* higher chlorine content in the fuels generates lower amounts of PCDD/F.

A single tailed ANOVA analyses of the 2,3,7,8-substituted isomers in the samples from the different chlorine sources showed no significant differences between the chlorine sources and the isomeric pattern formed during the combustion process ($F_{crit.}=2.27$, $F_{cal.}=0.0086$). This could indicate that the same formation reactions have taken place, independent of the chlorine source. Further investigation of how the two chlorine sources influence the formation of PCDD/F during low combustion efficiency conditions should be performed to enable a more complete answer on how the Cl-C chemical bonds influence formation mechanisms.

Conclusions

- Variation in combustion conditions due to problems with the fuel feeding system in some of these experiments influenced the emissions of PCDD/Fs more than the chlorine content of the MSW.
- Positive correlations between the Hepta-Octa chlorinated PCDD/F and the *Total Cl* content in the MSW were noticed in the samples taken during good and normal combustion conditions.
- The ANOVA analysis showed that there was no significant difference in the formation of PCDD/Fs between the two PVC products, virgin PVC and NaCl in this study.

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References

1. Fängmark I., van Bavel B., Marklund S., Strömberg B., Berge N. and Rappe C.; *Environ. Sci. Technol* **1993**, Vol 27, 1602-1610.
2. Kanters M.J. Van Nispen R., Louw R. and Mulder P., *Environ. Sci. Technol.*, **1996**, Vol 30, 2121-2126.
3. Wikström E., Lofvenius G., Rappe C., Marklund S., *Environ. Sci. Technol.*, **1996**, Vol 30, 1637-1644.
4. Wikström E. and Marklund S.; *Waste Manage Res* **1998**, vol 16.
5. Wikström E., Andersson P. and Marklund S.; *Rev. Sci. Instrum.* **1998**, vol 69, 1850-1859.
6. European standard, **1996**, EN 1948:1-3
7. Marklund S., Söderström G., Ljung K., Rappe C., Kraft M., Hagenmaier H.; *Waste Manage Res* **1992**, vol 10, 21-36.

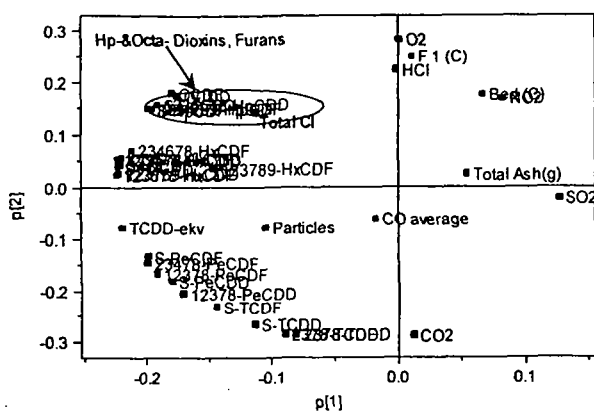


Figure 1a The loading plot from the PCA evaluation of the data combusted during normal combustion conditions. The complete model consists of 4 significant components with and total $R^2=0.92$ and a total $Q^2=0.61$.

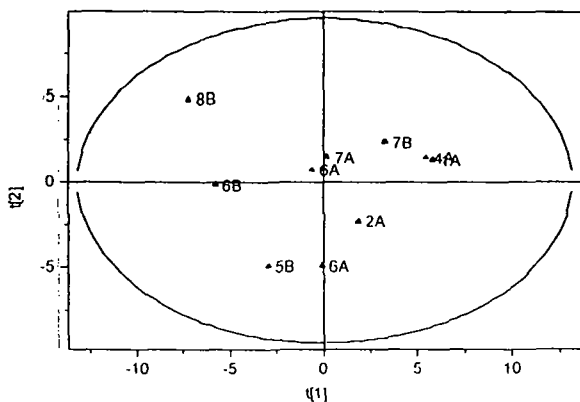


Figure 1b The score plot of the 10 samples taken during normal combustion conditions.