PERGAMON

Chemosphere 43 (2001) 227–234

CHEMOSPHERE

The influence of level and chlorine source on the formation of mono- to octa-chlorinated dibenzo-*p*-dioxins, dibenzofurans and coplanar polychlorinated biphenyls during combustion of an artificial municipal waste

E. Wikström *, S. Marklund

Department of Chemistry, Environmental Chemistry Umeå University, SE-901 87 Umeå, Sweden

Received 27 September 1999; accepted 5 April 2000

Abstract

The formation of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and the three coplanar polychlorinated biphenyls (pPCBs) was studied during labscale fludized bed combustion of eight artificial municipal solid waste (MSW) fuel mixtures. The level of chlorine as well as the chlorine source varies within the different fuel mixtures. Four different chlorine sources were studied, viz, an inorgnaic (NaCl) and three organic sources, pure PVC plastic and two products (floor and cable) and the total chlorine level varies between 0.28% and 1.1%. The experiments were performed in a 5 kW laboratory scale fluidized bed reactor. A correlation between the total chlorine in the fuel and the formation of the hepta- and octa-chlorinated PCDD/F homologues was found. However, the most important variable for changes in the PCDDs/Fs and pPCBs formation was disturbance in the combustion condition and not the variation in chlorine content of the fuel. Furthermore, no differences in formation between the chlorine sources could be seen. © 2001 Published by Elsevier Science Ltd.

Keywords: PVC; NaCl; PCDD/F; PCB; Labscale fluidized bed reactor; MSW

1. Introduction

The influence of the polyvinylchloride (PVC) content on the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during municipal solid waste (MSW) combustion has been discussed during the last several years. Studies on the importance of the total amount of chlorine in the fuel for the formation of chlorinated organic pollutants have been performed, but with contradictory conclusions. Fängmark et al. (1993) investigated how variations within different combustion parameters, such as bed temperature, O_2-, HCl-, H_2O-concentrations, temperature and residence time of the flue gas in the post-combustion zone effected the PCDD/F formation. The study showed a weak correlation between the amount of HCl in the flue gas and the formation of PCDDs/Fs; other parameters, such as the residence time in the post-combustion zone, were more important. The amount of HCl added to the reactor in that study corresponded to combustion of a waste containing approximately 2.2% of PVC. Further, combustion experiments was performed by Kanters et al. (1996) in a smaller laboratory scale reactor (1 g fuel/experiment). The reactor was fed

---

* Corresponding author. Tel.: +1-919-541-5548; fax: +1-919-541-0554. Present address: U.S. EPA (MD-65), National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA.

E-mail address: wikstrom.evalena@epa.gov (E. Wikström).

PII: S 0 0 4 5 - 6 5 3 5 (0 0) 0 0 1 5 5 - 7

with an artificial MSW fuel that contained eight times higher PVC loads than normal. Only a slight increase of the chlorophenol concentration in the flue gas could be discerned in this experiment. The same laboratory reactor was fed with an chlorine-free artificial MSW, and additional HCl was added to the wet carrier air. Already at such low level as 0.1 g HCl/(norm) m^3 added, the chlorophenol level in the flue gas was doubled. Further increasing in the HCl level (up to 2 g HCl/(norm) m^3) did not cause any significantly higher chlorophenol formation. As a comparison, the average HCl level during MSW combustion in full scale plants varies between 0.35 and 0.90 g/(norm) m^3, i.e., a level lower than 2 g HCl/(norm) m^3 which indicates that higher chlorine loads in the MSW do not results in increased outputs of chlorophenols. The only experiment with a low level of chlorophenols was the one without HCl added to the flue gas.

The aim of this study was to investigate how the amount of inorganic chlorine (introduced as NaCl) and organic chlorine, bound in PVC plastic, influenced the emission of PCDD/Fs and coplanar polychlorinated biphenyls (pPCBs) during MSW combustion. One pure virgin PVC material and two frequently used PVC products; floor (product name Norvinyl) and cable (product name Alcatel) were chosen to study the behavior of different additives in PVC products and what influence these had on the emissions of chlorinated organic pollutants.

2. Materials and methods

Eight fuels with different chlorine content and chlorine sources were prepared by adding different amounts of chlorine to an artificial MSW fuel mixture. The chlorine content of pure PVC plastic is about 56 wt% and due to the amount of added additives in the PVC floor and PVC cable the chlorine content is lower in these product (25 wt%). The artificial MSW is a mixture of eight material fractions, paper, plastic, laminate, textile, glass, kitchen and garden sweepings, remaining combustible and remaining incombustible (metals). The fractions are then well mixed and pelletized into fuel pellets. The properties, composition and elementary content of the artificial MSW are further described in Wikström and Marklund (1998a). Table 1 lists the total chlorine levels, the chlorine origin from the four different sources, the heat capacity and the dry weight of the fuels.

In total, 13 experiments were performed in the 5 kW laboratory scale fluidized bed reactor (Fig. 1); a detailed description of the reactor is given in Wikström et al. (1998b). The reactor was carefully cleaned between each experiment and the sand bed was replaced with 450 ml unused, washed sifted sand (250–125 μm), to minimize the memory effects. The reactor is equipped with electrical pre-heating systems; three at the freeboard and four at the convector section, to prevent unwanted temperature variations and to achieve stable temperature conditions faster. To minimize the effect of cold walls and reactions with sooty wall surface, the reactor was pre-heated with propane for about 3 h before the pellets fuel feeding was started. Table 2 lists the settings of the airflows, the effect of the fuel feeder and electrical pre-heating systems, pre-heated secondary air was used in this study. The listed measured temperatures in the reactor and convector section are shown as average temperatures ± the standard deviation among the 13 experiments.

The inorganic gases CO_2, CO and O_2 were continuously measured at the end of Section 3 in the convector. One IR-instrument, Siemens Ultramat 22 P for CO_2 and CO (0–1000 ppm) and one, ECOM SG-PLUS instrument that uses electrochemical cells to determine the amount of O_2, CO (100–10,000 ppm) in the flue gases were used.

When the temperature conditions in the reactor were stable, the MSW fuel feeding was started. After one hour of MSW combustion a particulate matter sample was taken at the end of convector part five. The sampling period was 60 min, which corresponds to a flue gas sample of 1.6 m^3. Parallel with this sample another two samples were taken at convector part four to determine the HCl level in the flue gas. The samples were collected in an H_2CO_3/HCO_3 buffer; the volume of the flue gas in

Table 1
Chlorine level and heat capacity of the fuel pellets

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
Total Cl	%*	0.28	0.35	0.40	0.62	0.66	0.70	1.0	1.1

* % of dry weight.

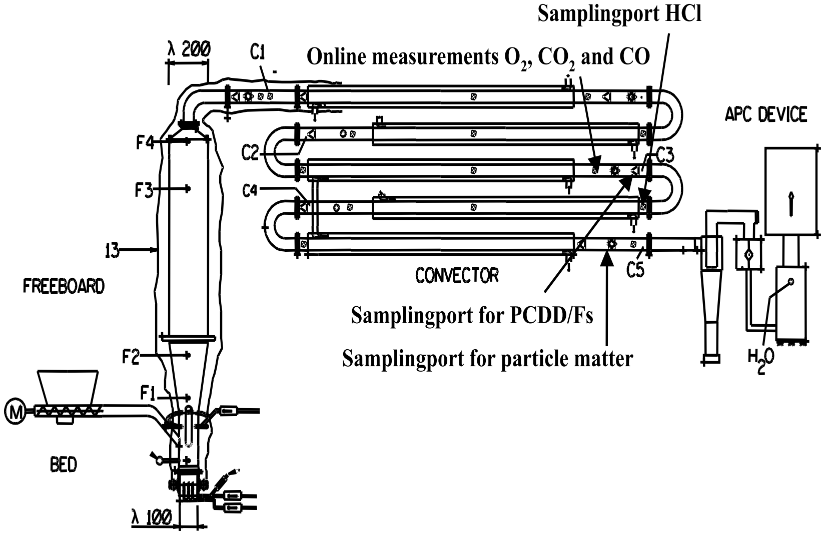

Fig. 1. Drawing of the 5-kW laboratory scale fluidized bed reactor. The sampling ports used in this study are marked with arrows.

each sample was about 50 dm^3. The chlorine ion concentration was then determined by ion chromatography according to method SS-EN ISO 10304-1, and the HCl level in the flue gas was calculated. Directly after the particle sampling, two consecutive samples (denoted as sample A and B) for determination of the PCDD/Fs were started, i.e., in total 26 flue gas samples were taken (13×2). Due to one unsuccessful sampling the real number of samples were 25 instead of 26. The samples were taken after convector part three and were performed according to European standard EN 1948:1 with the isokinetically cooled probe technique. The gas volume was noramlized (norm) to 1 atm dry gas at 0°C and 10% CO_2 (Marklund et al., 1992; European standard 1997). The residence time of the flue gas was 4.6 s in the freeboard and further 2.2 s in the convector section (port 1–3). The sampling time for each sample was 50 min, which corresponds to a sample volume of 0.75 m^3. The samples were analyzed for mono- to octa-PCDD/Fs and the three coplanar PCBs #77, #126 and #169. The extraction and clean-up procedure was performed according to standard methods (Marklund, 1990; van Bavel et al., 1992). The sampling train was spiked with ^{13}C labeled compounds before the sampling was started, this enables correction of the levels for losses during the sampling and clean-up procedure. The PCDD/Fs and the pPCBs were analyzed with a sector magnetic HRGC/HRMS (VG 70 S, with a Supelco 2330 column).

Table 2
The parameter settings during the experiments and achieved temperatures in the reactor and convector section. The location of the thermocouple can be seen in Fig. 1

Parameter	Setting	
Fuel and airflows		
Fuel	940 g/h (4.9 kW)	
Primary air	80 l/min	Pre-heating temperature: 25°C
Secondary air	70 l/min	Pre-heating temperature: 150°C
Temperature settings		Measured temperature
Bed section	700°C	Bed: 860 ± 32
Middle section	600°C	F1: 910 ± 30 F2: 840 ± 21
Top section	800°C	F3:750 ± 52 F4: 760 ± 64
Convector 1	400°C	C1: 630 ± 12
Convector 2	350°C	C2: 419 ± 5
Convector 3	300°C	C3: 351 ± 6
Convector 4	250°C	C4: 292 ± 7 C5: 281 ± 7

2.1. Principal component analysis

Principal component analysis (PCA) was used to evaluate similarities and dissimilarities within the resulting data. An exhaustive description of the method used in PCA can be found in Jolliffe (1986) and Jackson (1991). The primary intention of PCA is to obtain an overview of the dominant "pattern" in a data set. The data set is divided into *objects* (here; each PCDD/F flue gas sample period) and measured *variables* (here; e.g., concentrations of different PCDD/F homologues and CO levels during the sampling period). The *variables* is used to characterize the *objects*, e.g. the unique PCDD/F homologue level in the flue gas for each sampling period. The results of the PCA are visualized by two figures, a so-called score plot and a loading plot. Samples with similar PCDD/F emissions and pattern will be located close to each other in the score plot, while those which have divergent emission pattern will be located further apart. The loading plot shows how the measured variables relate to each other. Variables close to each other in the loading plot correlate, and variables diagonally across from each other have a negative correlation. The most important variables for the PCA model are located far from the origin and the insignificant variables are positioned close to the origin in the loading plot. Since the variables characterize the objects, it is possible to establish which variables (here: a specific homologue concentration) that are responsible for the separation of the samples in the score plot by examining the loading plot. Prior to the PCA, the data was scaled to unit variance and mean-centered. Cross-validation was used to calculate the number of principal components (PC) to be included to provide a significant valid model. The total fraction of the systematic variation in the data explained by the model is expressed as an R^2 value and the prediction ability of the model is expressed as a Q^2 value. The validity of a model is decided by the R^2 and Q^2 value (<1.0).

3. Results and discussion

Table 3 lists the measured levels of PCDDs, PCDFs, pPCBs, O_2, CO_2, CO, HCl, particulate matter and number of CO-peaks in the flue gas during each sampling. The O_2-, CO_2- and CO-levels are all calculated as average values during the PCDD/F sampling period ($\sim$50 min). The O_2 level in the 13 experiments varies between 10.3% and 13.3% while the corresponding variation in CO_2 emission is between 8.0% and 11.0% of CO_2. One of the largest differences between the experiments is the variation in CO emission (9–727 ppm). The higher CO emissions was caused by uncontrolled disturbances of the fuel feeding system of the reactor. A PCA evaluation (not shown) of the complete data set showed that the efficiency of the combustion conditions is a parameter that influences the formation of PCDDs/Fs and pPCBs more than the total chlorine content in the fuel (validity of the model: $R^2 = 0.86$, $Q^2 = 0.51$). A positive correlation between PCDDs/Fs, pPCBs formation and CO concentration was noticed. A conclusion that can be seen in Table 3 as well. Even, a negative correlation between the Total Cl and formation of PCDDs/Fs and pPCBs was found within the complete data set.

To evaluate the data with minimal influence from different combustion conditions, the samples were divided into three groups: taken during bad, fair and good combustion conditions (Table 3). The samples were divided according to their emissions of CO during the sampling period and number of CO-peaks over 2000 ppm. The data from the samples taken during fair and good combustion conditions were further evaluated together as one group. The average PCDD and PCDF profile of the 17 samples taken during good and fair combustion are shown in Fig. 2. The average profile agrees with an average PCDD/F profile found in full-scale MSW combustors, which shows that the formation conditions (e.g., catalytical reactions, temperatures) are similar in the labscale and full-scale systems.

A plot of the total chlorine load in the fuels versus the emissions of I-TEQs during good and fair combustion conditions are shown in Fig. 3. A larger variation within the same chlorine level is discerned than between the different chlorine levels, consequently no correlation between the chlorine content and the emissions appears to exist with in the data set ($R^2 = 0.07$).

Further evaluation of the data was done with PCA. This model consists of 17 observations (all samples taken at fair and good combustion conditions) and 25 variables: mono- to octa-PCDD/F homologues, the three pPCBs the O_2, CO_2, CO, HCl, particulate matter and Total Cl in the fuel. The two first components of the model are shown in Figs. 4 and 5. Component 1 describes most of the important information relating to differences between the samples ($R^2 = 0.50$), which is mainly the difference in PCDD/F and pPCB emission levels. The second component ($R^2 = 0.28$) mainly describes the variation in the homologue pattern between the different samples. The loading plot (Fig. 4) show as well a distinct correlation between the formation of the chlorinated homologues of the PCDDs/Fs and pPCBs. For example, the PeCDD, PeCDF and PeCB (#126) are placed close to each other in the loading plot, the same can be seen for the tetra- and hexa-chlorinated homologues (Fig. 4). This similarity indicates that they are formed through a similar formation mechanism. A correlation between the Total Cl in the pellets and formation of the higher chlorinated PCDD/F; namely the hepta- and octa-chlorinated congeners can be noticed as well in the loadingplot. A separate PCA evaluation (not shown) of the ten samples taken during good combustion conditions showed as well a significant positive correlation between the Total Cl level in the fuel, HCl, hepta- and octa-chlorinated PCDDs/Fs in the flue gas (Validity of the model: $R^2 = 0.91$, $Q^2 = 0.60$). A study performed by Vehlow et al. (1996) in the TAMARA reactor found a similar correlation between the higher chlorinated PCDDs and the chlorine load in the fuel.

Our study shows that the amount of chlorine in the waste is not the limiting parameter for formation of chlorinated compounds. The amount of chlorine is presented in percentage levels in the waste, which is

Table 3
The levels of PCDD/Fs, pPCBs (as (norm) m^3), O_2, CO_2, CO, HCl and particulate matter in the flue gas in all experiments

	Good combustion										Fair combustion						
	3A	3B	4A[a]	4B[a]	1A[a]	1B[a]	7A[a]	7B[a]	6A[a]	2A	6A	6B	4A	7A	7B	8B	5B[a]
1–8 CDF (ng/m^3)	177	170	57	47	103	134	73	90	648	501	593	1194	116	471	219	960	911
1–8 CDD (ng/m^3)	18	17	12	9	13	19	16	18	62	53	68	126	16	66	41	170	101
I-TEQ (ng/m^3)	4.4	4.0	1.3	1.0	2.2	3.5	1.6	2.0	16.0	11.6	13.8	25.8	2.9	11.4	5.4	22.4	21.1
PCB #77 (ng/m^3)	0.8	0.6	0.2	0.1	0.3	0.3	0.2	0.2	4.1	3.7	2.0	5.5	0.5	1.2	0.6	1.9	NA
PCB #126 (ng/m^3)	0.5	0.4	0.2	0.1	0.3	0.2	0.2	0.2	3.0	2.6	4.1	10.5	0.5	1.8	0.9	3.7	NA
PCB #169 (ng/m^3)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.7	0.6	1.8	3.7	0.2	0.8	0.4	1.1	NA
O_2 %	11.1	10.8	12.3	12.1	12.3	12.8	12.9	13.3	10.7	11.9	12.1	12.0	11.7	11.9	12.1	12.8	10.3
CO_2 %	10.3	10.5	8.5	8.8	8.7	8.1	8.5	8.0	10.3	NA	8.7	8.9	9.4	8.9	8.6	8.3	10.5
CO (ppm)	20	20	9	10	67	10	20	12	40	40	157	68	121	146	88	63	234
Number of CO-peaks[b]	0	0	0	0	4	0	0	0	1	0	7	4	5	8	3	4	5
HCl (mg/Nm^3)	150	520	250	750	960	580	370	720	160	NA	230	350	320	470	600	1050	220
PM (mg/Nm^3)[c]	650	650	2300	2300	700	700	1100	1100	1200	830	620	620	560	650	650	1200	870

	Bad combustion							
	5A	5B	4B	8A	6B[a]	5A[a]	1A	1B
1–8 CDF (ng/m^3)	1730	1360	1090	2600	425	547	4700	25 000
1–8 CDD (ng/m^3)	555	139	157	445	49	52	628	3900
I-TEQ (ng/m^3)	39.0	29.0	27.4	87.8	12.0	16.0	106	670
PCB #77 (ng/m^3)	3.6	1.3	2.8	7.8	2.2	2.1	12.3	40.5
PCB #126 (ng/m^3)	13.2	6.2	6.2	36.7	2.6	3.3	35.1	433.9
PCB #169 (ng/m^3)	5.8	3.1	2.8	10.3	0.8	0.9	13.1	15.0
O_2 %	11.2	10.8	11.2	12.6	9.5	10.9	10.7	10.9
CO_2 %	9.6	10.1	9.9	8.5	11.0	10.6	10.9	9.6
CO (ppm)	515	535	268	143	334	334	727	441
Number of CO-peaks[b]	22	23	10	8	11	23	43	19
HCl (mg/Nm^3)	240	730	420	1100	260	290	NA	NA
PM (mg/Nm^3)	680	680	560	1200	1200	870	1000	1000

[a] These samples were taken during a second (repeated) combustion experimental run.

[b] Number of CO-peaks: Total number of CO-peaks over 2000 ppm during the sampling period of chlorinated organic compounds.

[c] PM: Particulate matter.

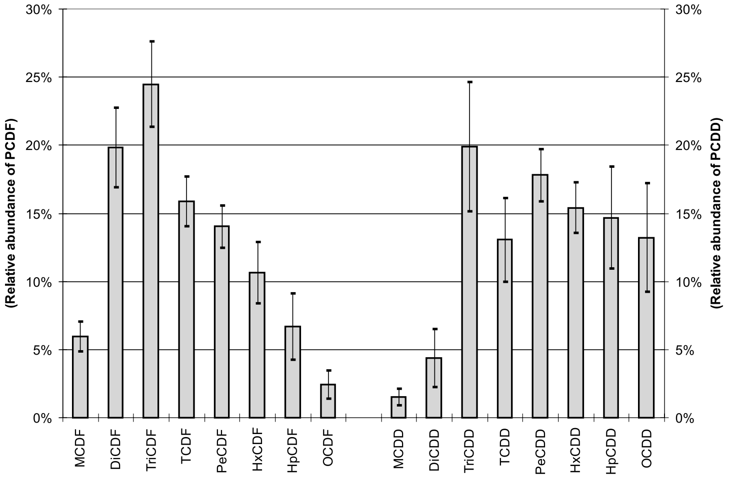

Fig. 2. The relative abundance ± the 95% confidence interval of PCDD and PCDF in the samples taken during good and fair combustion conditions.

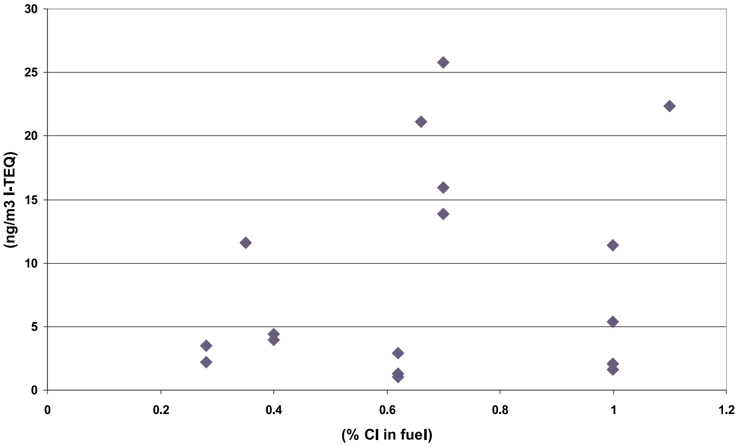

Fig. 3. The total Cl level of the fuel and the I-TEQ level in the 17 samples taken during good and fair combustion condition.

magnitudes higher than the amount of chlorine needed for formation of chlorinated compounds, such as PCDDs/Fs. If the chlorine level is less than 1% or more is not significant for the formation, since the chlorine is present in excess amount already at very low (< 0.1) percentage level. In a previous investigation, the formation of PCDD/Fs and chlorobenzenes was studied during combustion of seven artificial MSW fuels with a chlorine content varying between 0.12 and 1.7 wt% (Wikström et al. 1996). The results showed no correlation between the chlorine source (organic or inorganic chlorine), chlorine loading (if less than 0.84 wt%) and the formation of PCDD/Fs and chlorobenzenes. However, a distinct increase in the formation of PCDD/F and chlorobenzenes was noticed when a fuel with 1.7 wt% of chlorine was combusted. A correlation that cannot be seen in this data set. The major differences between these two studies are the complicity of the waste mixture, which probably effects the catalytic activity of the fuel. The recently used fuel origin from a much more complex mixture than the previous one. The lower catalytic activity of the fuel could be the reason why the high chlorine level showed significant higher emissions with this fuel and not with the more complex fuel.

Furthermore a single-tailed ANOVA analysis of the 2,3,7,8-substituted congeners in the samples from the four different chlorine sources was done to evaluate if the isomer pattern of these isomers changed between the

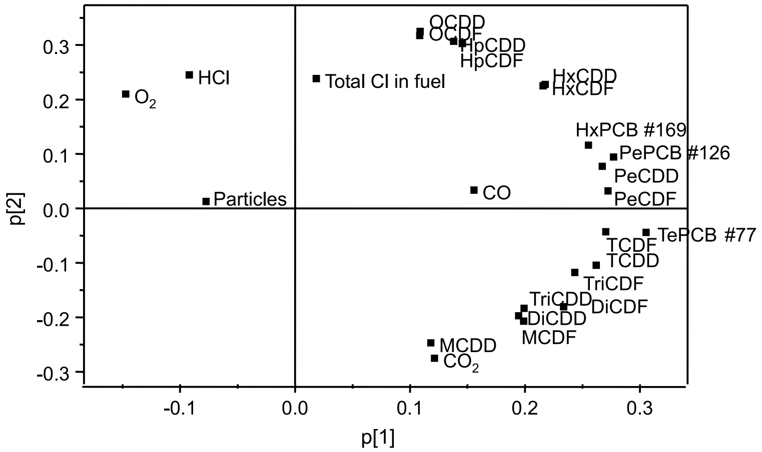

Fig. 4. The loading plot from the PCA evaluation of the data combusted during fair and good combustion conditions. The complete model consists of four significant components with a total $R^2 = 0.88$ and a total $Q^2 = 0.57$.

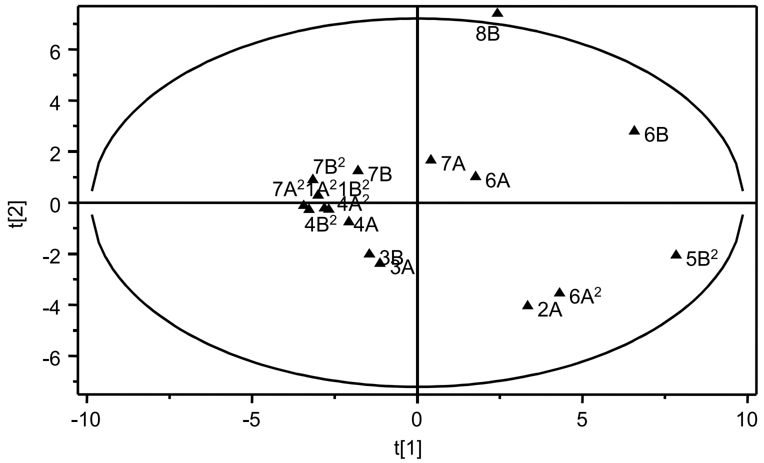

Fig. 5. The score plot of the 17 samples taken during fair and good combustion conditions.

sources. The calculation showed no significant differences between the chlorine sources and the congener pattern formed during the combustion process ($F_{\text{crit.}} = 2.27$, $F_{\text{cal.}} = 0.0086$). The same congener pattern and the correlation between the Cl-homologues in Fig. 4 indicates that the chlorinated organic compounds are formed through the same mechanism independently of the chlorine sources. One explanation could be that they are formed in two steps, one where the organic skeletons (e.g., the dibenzofuran) are formed and a consecutive secondary chlorination reaction as shown by Wikström and Marklund (2000).

Further research is needed on how the two chlorine sources, inorganic and organic, influence – and contribute to – the formation of chlorinated organic pollutants during combustion under less efficient conditions in order to obtain better insights in formation pathways and mechanisms.

4. Conclusions

- Variation in combustion conditions is a parameter that influenced the emissions of PCDDs/Fs and pPCBs more than the chlorine content of the artificial MSW fuel (0.28–1.1% Cl).
- Positive correlations between the hepta- and octa-chlorinated PCDDs/Fs and the Total Cl content in the MSW were noticed in the samples taken during good and fair combustion conditions.
- The ANOVA analysis showed that there was no significant difference in the formation of PCDD/Fs be-

tween the two PVC products, pure PVC and NaCl in this study.

Acknowledgements

The study was supported by TFR (Swedish Research Council for Engineering Sciences, *Teknikvetenskapliga Forskningsrådet in Swedish*) and Norsk Hydro AB. Special thanks to Per Liljelind, Gunilla Söderström, Lisa Börjeson, Gunilla Löfvenius and Maria Hjelt for all their help with experimental and laboratory work.

References

European Standard, 1997. Stationary source emissions-determination of the mass concentration of PCDDs/PCDFs. EN, 1948, pp. 1–3.

Fängmark, I.E., van Bavel, B., Marklund, S., Strömberg, B., Berge, N., Rappe, C., 1993. Influence of combustion parameters on the formation of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, benzenes and biphenyls and polyaromatic hydrocarbons in a pilot incinerator. Environ. Sci. Technol. 27, 1602–1610.

Jackson, J.E., 1991. A user guide to principal components. Wiley, ISBN-0-471-62267-2.

Jolliffe, I.T., 1986. Principal component analysis. Springer, ISBN-0-387-96269-7.

Kanters, M.J., VanNispen, R., Louw, R., Mulder, P., 1996. Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste. Environ. Sci. Technol. 30, 2121–2126.

Marklund, S., 1990. Dioxin emissions and environmental imissions, Environmental Chemistry, Umeå University, Sweden.

Marklund, S., Söderström, G., Ljung, K., Rappe, C., Kraft, M., Hagenmaier, H.-P., 1992. Parallel sampling using various sampling techniques at a Swedish municipal solid waste incinerator. Waste Manage. Res. 10, 21–36.

van Bavel, B., Fängmark, I.E., Marklund, S., Söderström, G., Ljung K., Rappe, C., 1992. Quantitative analysis of organic trace compounds by isotope dilution: Formation of the non-ortho PCBs 77, 126, 169 during incineration. Organohalogen Compound vol. 8, pp. 225–228.

Vehlow, J., Rittmeyer, C., Prang-Stotz, G., Vogg, H., Mark, F.E., Kayen, H., Freiesleben, W., Lescuyer, J.-L., 1996. Co-combustion of waste plastics and municipal solid waste in the Karlsruhe test incinerator TAMARA, Solid Waste Manage. Thermal Treat. Waste-to-Energy Technology, pp. 405–414.

Wikström, E., Marklund, S., 1998a. Combustion of an artificial municipal solid waste in a laboratory fluidised bed reactor. Waste Manage. Res. 16, 342–350.

Wikström, E., Marklund, S., 2000. Secondary formation of chlorinated dipenzo-*p*-diokins, dibenzofurans, biphenyls, benzenes and phenols during MSW combustion. Environ. Sci. Technol. 34, 604–609.

Wikström, E., Andersson, P., Marklund, S., 1998b. Design of a laboratory scale fluidized bed reactor. Rev. Sci. Instr. 69, 1850–1859.

Wikström, E., Löfvenius, G., Rappe, C., Marklund, S., 1996. 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. 30, 1637–1644.