

Secondary formation of PCDDs, PCDFs, PCBs, PCBzs, PCPhs and PAHs during MSW combustion.

E. Wikström, Åsa Persson and S. Marklund

Institute of Environmental Chemistry Umeå University, S-901 87 Umeå, Sweden.

Introduction

Different organic micro-pollutants (OMP), such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPhs) and polyaromatic hydrocarbons (PAHs) may be formed during all kinds of high temperature processes. How the organic compounds are formed is not completely understood, since many very complex formation mechanisms are involved in the process. Many studies have shown that the most important formation of these OMPs takes place at the low temperature range between 450-250 °C, so-called "secondary formation." Fängmark *et al* (1) studied the influence of the temperature profile and residence time of secondary formation of PCDD/Fs, PCBzs and PCBs during combustion of MSW in a laboratory reactor. The highest levels were formed at a temperature of 340 °C and with a residence time of 2.9 s. The homologues of the OMPs that are formed in lower temperature range can be formed by oxychlorination of particulate carbon (*i.e.* *de novo* synthesis) or from smaller organic compounds, precursors, or chlorination or dechlorination reactions of OMPs formed during higher temperature reactions. Whether the formation of the different homologues is controlled by kinetic or thermodynamic mechanisms has not been completely investigated and remains unclear.

The aim of this study was to investigate how the concentration levels and homologue profiles of the OMPs changed during secondary formation in the convective region of a laboratory scale reactor during MSW combustion. Simultaneous flue gas sampling, before and after the convector, was undertaken during the experiments.

Material and Methods

The experiments were performed in a 5 kW laboratory scale fluidized bed reactor with an artificial MSW fuel. The reactor and the fuel are entirely described by Wikström *et al.* in reference 2 and 3. Eleven experiments were performed under different combustion conditions to evaluate the influence of different combustion parameters on the formation of OMPs. The experiments and the experimental design are described in reference 4. Samples were taken simultaneously at two different locations at the convector to investigate how the levels, patterns, and profiles of the OMPs changed during the low temperature, secondary reactions, *i.e.* the post-combustion reactions. The changes between the experiments due to the differences in combustion conditions will not be discussed in this abstract. During each experiment, one

sample was taken at the beginning of the convector at 650 °C, after a flue gas residence time of 4.5 seconds. The other sample was taken at the end of the convector after subsequent 4 seconds of residence time. The temperature at this sampling port was 215 °C. The sampling of OMPs was done isokinetically with the cooled probe technique and the gas volume was normalized to 1 atm dry gas at 0 °C (5,6). All flue gas samples were analyzed for mono-octa Cl PCDD, mono-octa Cl PCDF, tri-deca Cl PCBs, di-hexa Cl PCBzs, di-penta Cl PCPhs and 13 PAHs (Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Dibenso(a,h)anthracene, Indeno(1,2,3-cd)pyrene, Benso(a)pyrene, Benso(b)fluoranthene, Benso(k)fluoranthene, Chrysene, Benso(g,h,i)perylene and Benso(a)anthracene). Two PCBs homologues, Tri- and O-CB have to be excluded from the study due to analytical disruptions, which made the comparison of the samples uncertain. The extraction and clean-up procedure was performed according to standard methods (7,8). The PCDD, PCDF were analyzed with a HRGC/HRMS and the PCB, PCPh, PCBz and PAH were analyzed with HRGC/LRMS.

Results and Discussion

Changes in levels during the post formation reactions.

Secondary formation is very important for the formation of PCDFs and PCBzs. The total levels increase by about factors of 30 and 100 for the PCDFs and PCBzs, respectively. The secondary formation of the PCDDs and PCPhs are not as high as for the PCDFs, only a factor of 15. Findings that are consistent with the results of I. Fängmark *et. al.* who showed that the PCDFs and PCBzs increased more than the PCDDs during the secondary formation (1). The total amount of PAHs in the flue gas is not dependent on the secondary formation in the lower temperature range; most of the PAHs are formed in the combustor. This is a result that was expected and which is in accordance with results in other studies (9,10). It's difficult to define a general picture about how the levels of PCBs have changed due to secondary formation. The amount of tetra-deca PCBs in the flue gas has only increased by a factor of two, and the increasing rate is very different among the 11 samples. The total increasing rate of the penta-deca PCBs shows a different picture, with 15 times higher levels after the secondary formation reactions. One explanation of the differences could be that the tetra PCBs are chlorinated to higher chlorinated PCBs, and small concentrations of PCBs are formed via *de novo* reactions. This occurrence causes a lower increasing rate of the total tetra-deca PCBs than the penta-deca PCBs. A decrease in the levels of PCBs and PAH downstream of the boiler was also found in experiments performed in the TAMARA reactor (11). A thermal degradation of the PCBs and PAH downstream the boiler was suggested as an explanation.

The relative concentration levels for the chlorinated organic compounds between the two sampling points in our study shifts, with the main reason for the change being the high formation rate of the PCDFs and PCBzs. The relative order after the combustor at 650 °C is: PCPh>PCBz>PCB>PCDF>PCDD. The order shifts to PCBz>PCPh>PCDF>PCB>PCDD after the secondary formation.

Change in profiles during the post formation reaction

A PCA analysis of the data was done to statistically evaluate the changes of the profiles for the OMPs from the samples taken at the two temperatures and with different residence times. Figures 1a and b show the results from the analysis. The model has five significant components and a R² value of 0.84 and a Q² value of 0.54. The objects (2x11 samples) divide into two groups in the score plot (Figure 1b) one with the higher temperature samples and one group that

contains the samples taken at the end of the convector, the lower temperature samples. The changes within these two groups result from the changes due to different combustion conditions during the 11 experiments. These shifts and changes will be discussed later in a full paper. Component 1 in the loading plot shows the major changes between the OMPs content in the flue gas before and after the secondary formation. The samples before the convector section at 650 °C have a higher relative concentration of the MCDF, PeCDD, DiCPh, TeCB and DiCBz. This is the reason for the right-hand-side position of the "high" temperature samples in the score plot and the separation from the "low" temperature samples. Samples taken at the lower temperature have higher relative amounts of the TriCDF, HpCDD, TriCPh, HpCB, NCB, and the PeCBz.

The average relative homologue profiles in the two sampling ports are in agreement with the profiles found in the TAMARA reactor (11). Figure 2 shows the average relative homologue profile of all chlorinated OMPs and the most interesting PAHs. A shift among the PAH compounds is noticed during the post-combustion reaction. The relative concentration of the tri-cyclic PAHs, phenanthrene, and anthracene are higher. Some of the homologues such as MCDD, PeCPh, TeCBz, and HxCBz are present in very low relative amounts and/or the changes between the two sampling points are not significant.

Conclusions

Higher chlorinated homologues are formed in higher amounts after the secondary formation than in the higher temperature range. It is difficult to distinguish whether the thermostability of the homologues or chlorination reactions influence homologue formation during the reactions, but the clear predominance of the higher chlorinated homologues of all OMPs indicate that chlorination reactions occurred in the convector of the reactor.

All homologue classes of the PCDD, PCDF, PCBzs and PCPhs increased during the secondary formation. Therefore, the reactions appear to be *de novo* synthesis of these compounds combined with chlorination reactions. Thermal destruction appears to prevail for the PAHs and the PCBs, together with chlorination reactions for the PCBs.

Acknowledgment

TFR (Swedish Research Council for Engineering Sciences, Teknikvetenskapliga Forskningsrådet in Swedish) and Norsk Hydro AB supported the study.

References

1. Fängmark I., Strömberg B., Berge N. and Rappe C.; *Environ. Sci. Technol* 1994, Vol 28, 624-629.
2. Wikström E., Andersson P. and Marklund S.; *Rev. Sci. Instrum.* 1998, vol 69, 1850-1859.
3. Wikström E. and Marklund S.; *Waste Manage Res.* 1998, vol 16.
4. Wikström E. and Marklund S. *Organohalogen Compounds*, 1997, Vol 31, 532-537.
5. Marklund S., Söderström G., Ljung K., Rappe C., Kraft M., Hagenmaier H.; *Waste Manage Res* 1992, vol 10, 21-36.
6. European Standard, 1996, EN 1948:1-3
7. Marklund S. (*Thesis*), University of Umeå, Sweden 1990, ISBN 91-7174-496-7.
8. van Bavel B, Fängmark I, Marklund S, Söderström G, Ljung K., Rappe C.; *Organohalogen Compounds*, 1992, Vol 8, 225-228.
9. Fängmark I., van Bavel B, Marklund S., Strömberg B., Berge N. and Rappe C.; *Environ. Sci. Technol* 1993, Vol 27, 1602-1610.
10. Andersson P. and Marklund S.; *Chemosphere*, 1998, Vol 36, 1429-1443.
11. Wanke T. and Vehlow J.; *Organohalogen Compounds*, 1996, Vol 27, 403-408.

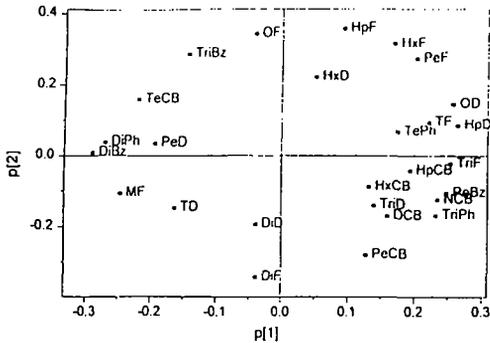


Figure 1a The loading plot from the PCA of the data. The R^2 value for component 1 is 0.33 and 0.24 for component 2. To simplify the text in the figure were the name of the normal abbreviations of the OMPs shorted down e.g. MCDF=MF, PeCDD=PeD, DiCBz=DiBz,

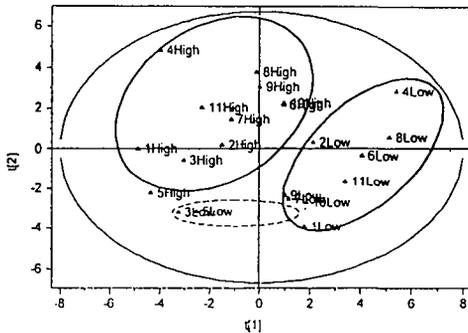


Figure 1b The score plot from PCA evaluation of the data. The samples have divided into two distinct classes. except for two samples taken at the low temperature. These two samples have a relative higher amount of MF, DiPh, DiCBz and TeCB than the other samples do, taken after the secondary formation.

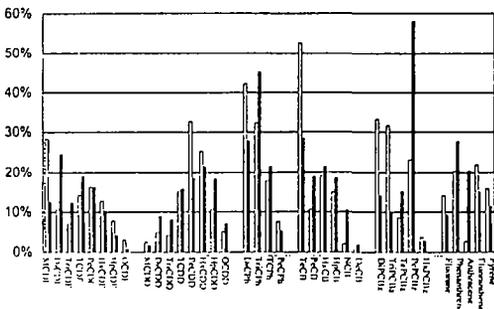


Figure 2 The average relative (e.g. the relative concentration of the homologue MCDF of all the PCDF homologues) concentration profile of all the studied OMPs. The light bars represent the samples taken at 650 °C and the dark bars the samples taken at the lower temperature.