

## **Presence of polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB), chlorinated benzenes (PCBz) and polycyclic aromatic hydrocarbons (PAH) under various combustion conditions in a post combustion chamber**

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### **Introduction**

The flue gases of combustion processes, e.g. from waste incineration plants, contains a variety of products of incomplete combustion, such as chlorinated aromatics and polycyclic aromatic hydrocarbons (PAH) (1). Investigations on the formation mechanisms of chloroaromatics in large scale incinerators pointed out, that there are two temperature ranges of formation of polychlorinated dibenzo-*p*-dioxins or -furans (PCDD/F). Within the low temperature range at about 300 °C, the majority of the PCDD/F are formed by heterogeneously catalyzed reactions on fly ash particles (2). The second range of formation at high temperatures with a maximum at about 700 °C is far less investigated and is considered to be responsible for PCDD/F formation in presence of precursor-compounds (3). The study presented focuses on the formation of PCDD/F, polychlorinated biphenyls (PCB) and polychlorinated benzenes (PCBz) as well as on PAH in the temperature regime of the high temperature PCDD/F formation range at a pilot incinerator. Also the temperature regime at the post combustion chamber, the residence time, the mixing of the flue gases and carbonmonoxide as an important combustion parameter were measured to elucidate the formation pathways of the different classes of compounds.

### **Analytical Methods and Materials**

A waste incineration pilot plant was subject of investigation. The plant uses a gasification step on a stoker system with subsequent post combustion of the gasification gases in a spatially separated afterburner chamber. After the post combustion step, the flue gases pass a heat exchanger, dust-precipitator and an activated coke filter, respectively the incinerator has a capacity of approximately 100 kg waste per hour with a thermal power of 0.5 MW.

Different but stationary combustion conditions were. The flue gases were sampled at the outlet of the post combustion chamber. The incinerator was fed with wood chips partially contaminated with organic substances. Wood combustion is known to be an important source of PAH and is also considered to be responsible for a not negligible part of the emission of PCDD/F (4).

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In order to reduce the temperature in the post combustion chamber and to decrease the temperature gradient, nitrogen was added at the top of the post combustion chamber during four of the nine experiments in amounts of 70 m<sup>3</sup>/h up to 100 m<sup>3</sup>/h.

Sampling was performed close to the outlet of the post combustion chamber using a isokinetically sampling system from *Ströhlein*®, Germany with a cooled probe. The flue gas exhibited temperatures between 670 °C and 940 °C. An impinger system filled with ethoxyethanol as keeper was used for trapping the semi-volatile compounds (PCDD/F, PAH and PCB). The sampling rate was 1 Nm<sup>3</sup>/h and the sampling time was about 1 h. An internal <sup>13</sup>C<sub>12</sub> standard cocktail for the PCDD/F and PCB was added to the Ethoxyethanol before it was stirred for 24 h with a mixture of water/toluol (9/1, v/v). The cleaning is described elsewhere (5).

The volatile PCBz were sampled simultaneously via a small bypass sampling stream from the *Ströhlein*® sampling train. A cartridge (I.D.=6 mm) containing 2 g activated charcoal with internal <sup>13</sup>C<sub>6</sub> standard (one isomer for each degree of chlorination) followed by a second „back-up“ cartridge indicating breakthroughs of analyts filled with 1.5 g charcoal. Sampling rates were about 80 l/h and the temperature was hold at 70 °C to avoid condensation in the tubes. The chlorinated benzenes were eluated with 2 ml of H<sub>2</sub>S according to NIOSH guideline N<sup>o</sup> 1501 (1984). A cleanup for the PCBz was not necessary. PCDD/F were measured at HRGC/HRMS (HP 5890 series II/MAT 95) and PCB/PCBz at HRGC/LRMS (HP 5890 series II/SSQ 7000). Recoveries for PCDD/F, PCB and PCBz were between 60% up to 100%, no breakthroughs for the PCBz were observed. PAH were analyzed a HPLC (HP 1100) coupled to a UV detection system without any pre-cleaning. Quantification was performed via external calibration. All flue gas concentrations were calculated to normal conditions: dry air, 273K, 1013hPa and 11%O<sub>2</sub> (≡Nm<sup>3</sup>).

## Results and Discussion

For this preliminary analysis, the information about the analyzed compounds in the flue gas has been reduced either to the sum of all isomers/homologues (for PAH, PCB, PCBz) or to the I-TEQ values (PCDD/F). Further on, the residence time of the flue gas, the temperature regime in the post combustion chamber (e.g. temperature at the top of the chamber and at the probe), the CO-concentration as well as the nitrogen amount added is considered.

A statistical analysis (principal component analysis, PCA) of the results has been performed in order to figure out correlations between combustion parameters and formation of the investigated compounds (6). The first two principal components describe 57 % (PC1) and 20% (PC2) of the variance of the data set (total 77%).

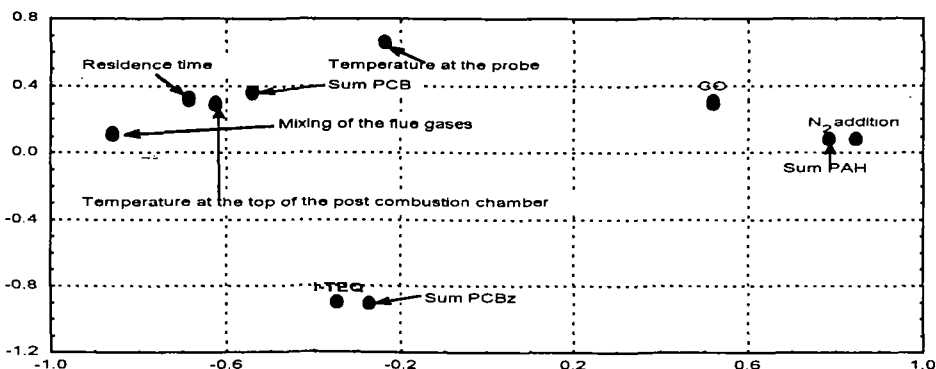


Figure 1: PCA for the whole set of experiments (*N<sub>2</sub> added* denote the nitrogen added at the top at the post combustion chamber, see methods and materials)

Considering the first principal component PC1, there are two groups of points in the PCA: The first group is due to the I-TEQ, the sum of all chlorinated benzenes (sum PCBz). Further on, the sum of all chlorinated biphenyls belongs to this group, but separated according to PC2. The second group is due to the PAH content, the CO-concentration in the flue gas and N<sub>2</sub>-addition. As mentioned above, the second principal component PC2 separates the sum of all chlorinated biphenyls from the I-TEQ values and the sum of all chlorinated benzenes (sum PCBz) the temperature regime in the post combustion chamber, the residence time and the mixing of the flue gases.

It is obvious, that the CO-concentration is a good indicator for the sum of the PAH. This result is not true for individual PAH species on a highly time resolved time scale, as recently has been shown by on-line REMPI-TOFMS PAH-measurements at the plant (7). That the nitrogen addition correlates with increased CO- and PAH-emissions may be caused by a decreased temperature gradient in the post combustion zone (i.e. less good burning out). The formation of chlorinated biphenyls (sum PCB) was heavily influenced by the temperature regime in the post combustion zone, the residence time and the mixing of the flue gases in contrast to the other chlorinated aromatics. The results of the PCA are in good accordance with results from laboratory scale incinerator experiments by Fångmark et al. (8).

However, in the present study the formation of PCB seems to be different from the other chlorinated aromatics, which may be a hint on different formation mechanisms of PCDD/F and PCB. But the good accordance of PCDD/F and PCB on the PC 1 may be caused by the precursor character from PCB for the PCDF (i.e. formation of PCDF from PCB via an oxidation followed by an internal ring closure, 9). Nevertheless it has to be taken into account, that the high sampling temperature (the analyts are quenched very rapidly in the cooled probe) may be responsible for this effect. The latter mentioned reaction pathway may achieve importance during the first formation range at 300 °C. Investigations at a hazardous waste incinerator from Kaune et al. (10), for example, pointed out that some PCB may be good indicators for I-TEQ values.

During the observation of a malfunction in the post combustion chamber, combustion partially was extinguished for a time span of some minutes. Directly after the sampling time (1h) of this event a further experiment was started in order to study the recovery of the emission levels. The incident caused a far-reaching variation in the compound profiles. Figures 2 and 3 show the PCDD/F and PAH before, during and after the post combustion malfunction.

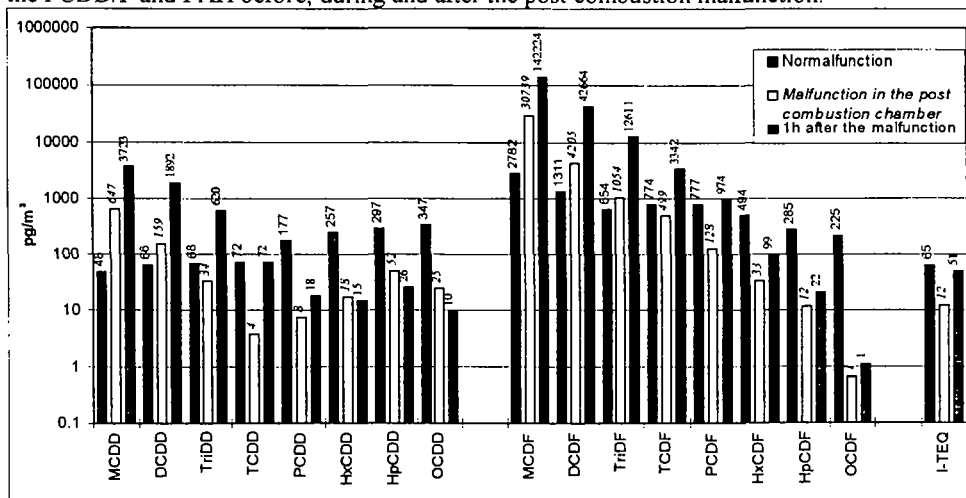


Figure 2: Homologue profiles of the PCDD/F concentration in the raw gas before, during and after a post combustion chamber malfunction.

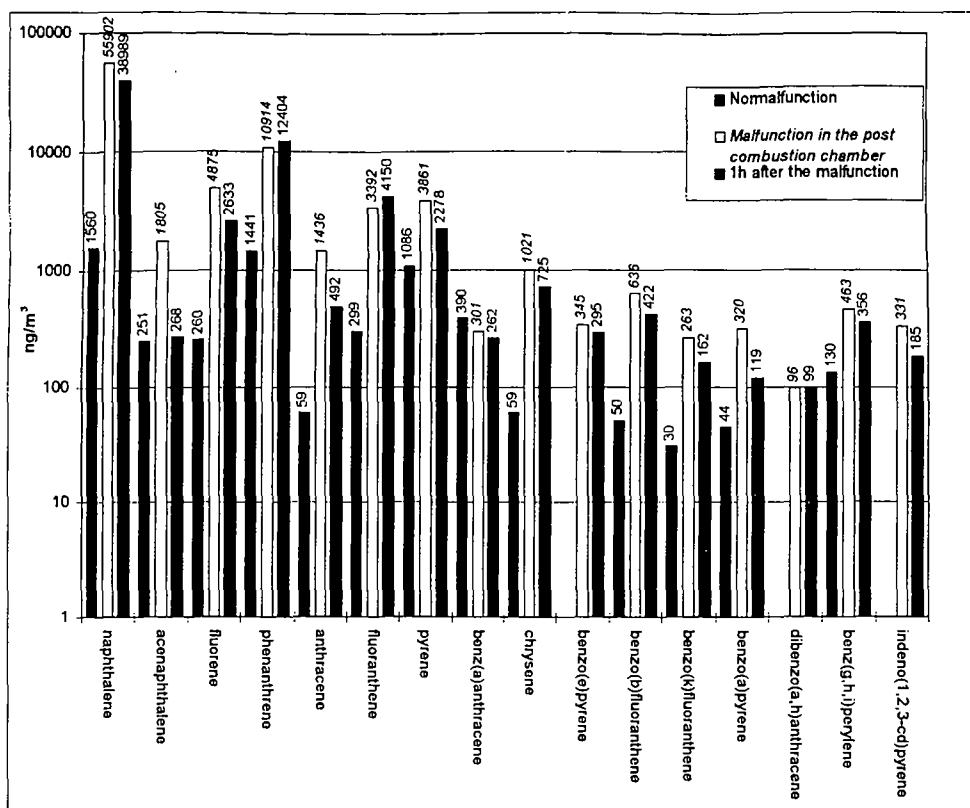


Figure 3: PAH profiles variation in the raw gas before, during and after a post combustion chamber malfunction.

The observed PCDD/F profiles under normal combustion conditions are in good accordance with the literature as shown by the relation between PCDD and PCDF is  $<1$  (11). However during and after the malfunction, dramatic deviation from this pattern are observed. The malfunction of the combustion chamber led to the smallest I-TEQ-value in the whole data set. The lower chlorinated (mono- to tri) PCDD/F congeners (which does not contribute to the I-TEQ value) are considerably increased while the higher chlorinated congeners are depleted. One hour after the malfunction, the lower chlorinated PCDD/F are at even higher levels than during the malfunction. The higher chlorinated congeners are also increased with respect to the malfunction. It should be remarked, that for flue gases from different combustion processes often exhibit qualitatively similar homologue PCDD/F profiles are reported if the higher chlorinated congeners are considered solely. Differences in the patterns were observed for the lower chlorinated (mono- to trichloro) PCDD/F (12).

Thus, it seems to be advisable to consider the mono- to octachlorinated dioxins and furans if the formation mechanism should be elucidated. An additional consequence of the observed differences in behavior of low and high chlorinated PCDD/F congeners is, that the low chlorinated PCDD/F can not be used as indicators for estimation of I-TEQ value.

Particularly interesting is the observed „memory“ effect of the plant. Although temperatures are very high in the combustion chamber (700 °C and higher), the malfunction influences the flue gas concentrations for at least several hours. Thus we assume, that the observed memory effects most likely are caused by surface based effects.

A possible scenario may be, that during the malfunction the surfaces of the reactor were coated with a layer of soot. The freshly formed carbon-soot surface is highly catalytically active and

thus may be responsible for the shift in the PCDD/F homologue patterns. One of the degradation products of the soot layer could be PAH, causing the memory observed for the PAH-emission. Soot formation in flames and further PAH generation is also reported by Hunag J. and Senkan S. M. (13).

### Conclusions

1. PAH formation in a post combustion chamber is correlated with the CO concentration in the flue gas. The concentration of I-TEQ in the flue gas is roughly related to the concentration of chlorinated benzenes. Therefore, we assume a different formation pathway for PAH and PCDD/F in the post combustion process.
2. Low chlorinated PCDD/F should not be considered as indicator parameters for I-TEQ emission estimation.
3. Observed memory effects are most likely caused by surface effects.

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### References

1. Wienecke J., Kruse H., Huckfeldt U., Eickhoff W. and Wassermann O.; *Chemosphere*, **1995**, 30, 907.
2. Hagenmaier H., Brunner H., Haag R. and Kraft M.; *VDI-Berichte 634*, **1987**, 557.
3. Ghorishi Behrooz S. and Altwicker E. R.; *Hazardous Waste and Hazardous Materials*, **13**, **1996**, 11
4. Schatowitz B., Brandt G., Gatner F., Schlumpf E., Bühler R., Husler P. and Nussbaumer T.; *Chemosphere*, **1994**, 29, 2005.
5. Schramm K. W., Merk M., Henkelmann B., Kettrup A.; *Chemosphere*, **1995**, 30, 2249
6. Harmann H.; *Modern Factor Analysis*, **1970**, Chicago. London, The University of Chicago Press, 2nd edition.
7. Heger H. J., Zimmermann R., Dorfner R., Griebel H., Beckmann M., Kettrup A., Boesl U.; *Analytical Chemistry*, **1998**, in preperation.
8. Fängmark I., Bavel v.B., Marklund S., Strömberg B., Berge N. and Rappe C.; *Environmental Science and Technology*, **1993**, 27, 1602.
9. Choudry G. and Hutzinger O.; *Current Topics in Environmental and Toxicological Chemistry*; Gordon and Breach Science publishers, New York, **1983**.
10. Kaune A., Lenoir D., Nikolai U. and Kettrup A., *Chemosphere*, **1994**, 29, 2083.
11. Marklund S., Fängmark I. and Rappe C.; *Chemosphere*, **1992**, 25, 139.
12. Bacher R., Swerev M. and Ballschmitter K. H.; *Environmental Science and Technology*, **1992**, 26, 1649.
13. Huang J. and Senkan S. M.; *Twenty-sixth symposium (International) on combustion/The Combustion Institute*, **1996**, 2335.