Changes in PCDD/PCDF formation Processes During Instationary Phases of Combustor Operation

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Introduction

Elevated PCDD/PCDF formation has been observed during and after transiently disturbed operating conditions both at municipal waste incineration (MWI) plants, hazardous waste incinerators and during combustion of wood[1,2,3,4]. In many of these cases memory effects could be observed. Equally, start-up processes have been recognized as an important source of PCDD/PCDF emission from modern MWI plants[5,6,7,8].

During and after transient phases of impaired combustion conditions significant changes in PCDD/PCDF homologues profiles have been detected and discussed[2]. Wikström et al. experimentally demonstrated Zimmermann's hypothesis of carbon black deposits in the boiler to be the cause of these memory effects[9].

Although changes between predominating PCDD/PCDF formation mechanisms have to be suggested, no approach analysing the PCDD/PCDF fingerprints has been published so far.

In this study transient phases of operation conditions at different incineration plants were investigated and the PCDD/PCDF fingerprints were analysed to get more detailed information about possible PCDD/PCDF formation mechanisms.

Methods and Materials

Sampling was performed at two grate incinerators of MWI plants located in Bavaria. At one plant (MWI I) transiently disturbed combustion conditions producing carbon monoxide peaks were provoked by throttling the air supply and / or by overcharging the grate. Crude gas samples were taken at the end of the boiler section. Sampling and analysis were performed according to DIN EN 1948 isokinetically (condensation + XAD2 adsorption method).

At the other plant (MWI II) crude gas samples were taken during and after a start-up process. The plant's back-up burners were operated with light fuel oil. Crude gas was sampled downstream of the ESP between the external economiser and the wet scrubber. With regard to the low dust concentration (typically less than 10 mg/m^3) and the complex flow field at the sampling point, we dispensed to isokinetic sampling. Apart from this, sampling and analysis were performed according to DIN EN 1948.

On both plants reference sample were taken before and after the test runs at adequate time distance. PCDD/PCDF concentrations were determined by HRGC-HRMS. Samples were measured with a BPX5 and a DB5-MS column. All results were standardised to 273 K and 1013 hPa. Non-2,3,7,8-substituted PCDD/PCDF congeners were assigned to the chromatographic peaks according to literature. They were quantified basing on the corresponding 2,3,7,8-substituted $^{13}C_{12}$ labelled internal standards[10,11,12,13,14].

Results and Discussion

Many reports deal with the PCDD/PCDF isomer distribution when discussing possible PCDD/PCDF formation pathways or sources[15,66,17,18,19,20,21]. Several of them give detailed information on the tetrachlorodibenzodioxin isomers (tetra-CDD)[15,16].

Results from laboratory experiments about isomer distribution of tetra-CDD, formed from chlorophenols by gas phase reactions or pyrolysis, are widely consistent. 1,3,6,8-tetraCDD and 1,3,7,9-tetraCDD are found to be formed from 2,4,6-trichlorophenol (and 2,3,4,6-tetrachlorophenol) and 1,3,7,8-tetraCDD from 2,3,4-trichlorophenol (and 2,3,4,5-tetrachlorophenol)[16,20]. Zoller et al. also found 1,2,6,9-, 1,2,6,7- und 1,2,8,9-tetraCDD to be formed at the pyrolysis of mixed 2,3,4- and 2,3,6-trichlorophenates[22]. Although 1,3,6,8-, 1,3,7,9 and 1,3,7,8-tetraCDD are the most abundant found among tetra-isomers in the municipal waste incineration effluents[15,16,21], it is misleading to assume PCDD formation in MWI solely by direct reactions from phenols. Laboratory experiments with catalyzed slow combustion of carbon[17,18,19] and fly ash mediated pyrolysis of pentachlorophenol yielded patterns similar to each other, leading to several pattern prediction models. These models, using a superposition of thermodynamic stability and reactivity[15], basing on the consideration of a dechlorination mechanism (termed the “IIG model”)[20] or simply calculating thermodynamic stability[24], result in tetra-CDD similar to each other and also similar to the patterns we observed under normal MWI operation conditions (i.e. at good burn-out). In all these patterns 1,3,6,8-, 1,3,7,9 and 1,3,7,8-tetraCDD are important peaks although accompanied by many other tetra-CDD isomers. Figure 1 (a-d) shows exemplarily tetra-PCDD isomer patterns from gas phase reaction of 2,4,6-trichlorophenol (a), fly ash mediated pyrolysis of pentachlorophenol (b), copper catalysed combustion of carbon (c) and an isomer pattern predicted from MOPAC/MNDO calculations (d).

The test runs under transient operation conditions yielded substantially elevated PCDD/PCDF concentrations in the flue gas. Both after the CO-peaks and after start-up significant memory effects were to be observed. During the test runs and during the memory phases the homologue profiles, the ratio PCDF/PCDD and the ratio of total PCDD/I-TEQ (“reduced toxicity”) were different from the values at normal operation conditions[23], suggesting changes in dioxin formation mechanisms.

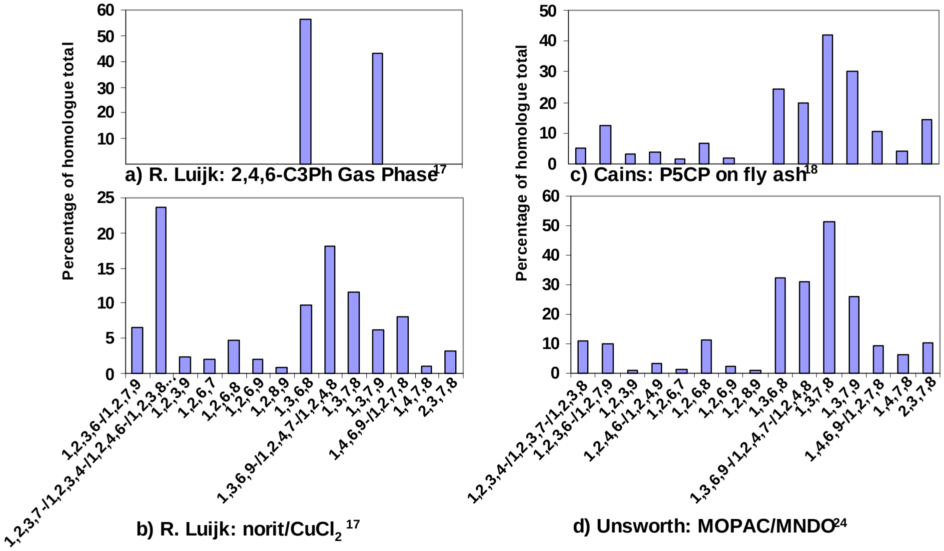

Figure 1a-c: Tetrachlorodibenzodioxin .isomer patterns from precursor experiments, from de-novo experiment and from the MOPAC/MNDO model

As different PCDD/PCDF homologue profiles do not necessarily imply different isomer patterns and changes in mechanism, we re-evaluated the chomatograms of the tetra-PCDF-ion trace of the samples analysed. Figure 2 (a-b) shows the tetra-PCDD isomer pattern from a CO experiment at incinerator I and figure 2 (c-d) shows the tetra-PCDD isomer pattern from the start-up process at incinerator II.

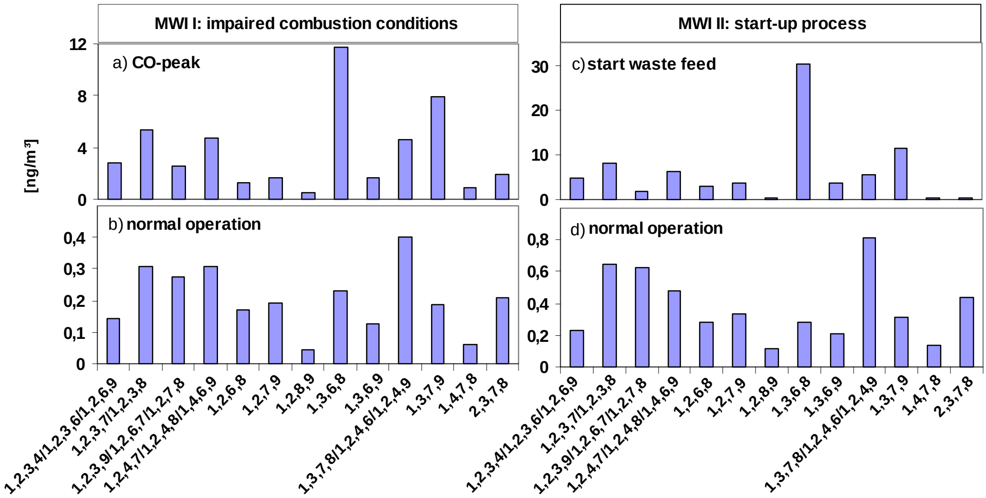

Figure 2a-e: Tetra-PCDD isomer distribution from a CO-experiment, from a start-up process and corresponding patterns at normal operation

Both at the CO-experiment and at the start-up process significant changes in the tetra-PCDD isomer pattern were to be observed. During the CO-peak as well as during the start-up process the 1,3,6,8-tetraCDD and the 1,3,7,9-tetraCDD rose by far more than the other congeners. The resulting pattern is similar to PCDD patterns observed from precursor experiments from the pyrolysis of 2,4,6 und 2,3,4,6 Cl-phenol, termed as "2,6 pattern" by Ballschmiter[15,16]. Under normal operating conditions at both incinerators the 1,3,7,8-tetraCDD (coeluting with 1,2,4,6- and 1,2,4,9-tetraCDD) was the most prominent congener. This pattern both resembles Ballschmiter's "2,3 pattern"[15,16] and the tetra-PCDD patterns yielded by "de-novo"-experiments and formation from pentachlorophenol by condensation and dechlorination.

Ballschmiter et al. reported 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol to dominate the group of trichloro- and tetra-chlorophenols, respectively, by a factor of ten and more[25] in MWI flue gas samples, which is in agreement with the chlorophenols congener distribution we observed.

Figure 3 a-h shows the PCDD/PCDF and PCPh concentrations during start-up process and during the CO-experiment. Each point of the curves represents the average over a sampling period of about two hours for each sample. Please note the x-axis is not representing the real time scale of the start-up process, which took approx. 36 h.

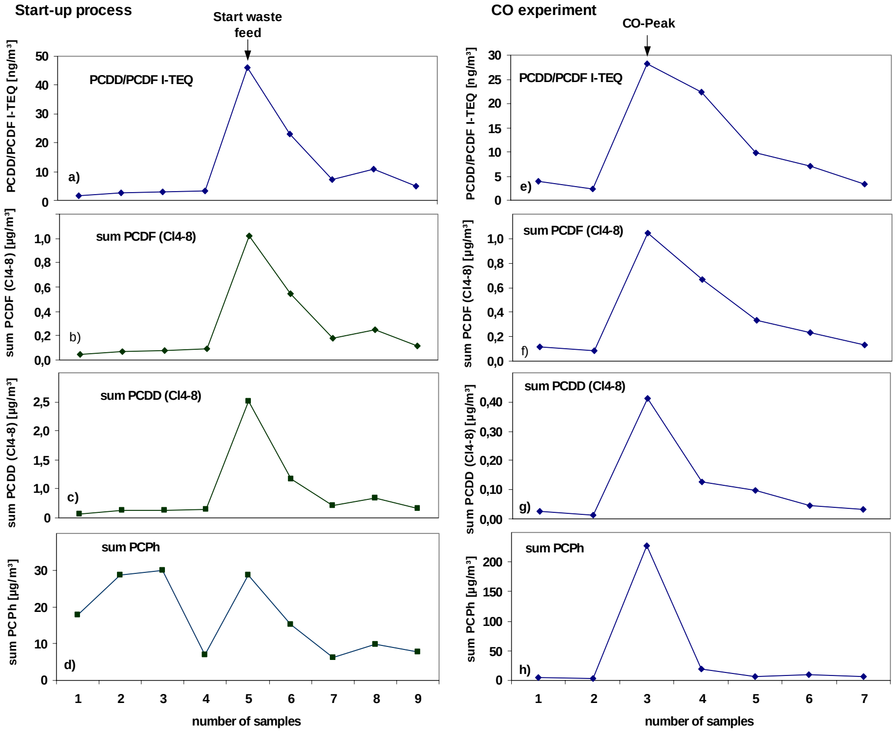

Figure 3a-h: Concentrations of PCDD/PCDF and PCPh during start-up procedure and CO experiment

The curves of the PCPh and sum of PCDD concentrations are in strong correlation to each other, excepted during the time before waste feeding at the start-up process. PCDF show a different course, clearly to be seen at the CO experiments results. During heat-up burner operation, many

other PICs such as fatty acids PAHs and chlorobenzenes were found at elevated levels until the combustion chamber was heated up.
Differences between the two processes of transient combustion conditions were observed in the persistence of the changed isomer distribution. Whereas the 1,3,6,8-tetraCDD and 1,3,7,9-tetraCDD dominated isomer pattern during the CO-peak, changed back to the normal pattern within hours, at the start-up process the pattern remained changed for at least one day after the start of waste feeding.

Re-evaluating chromatographic data from test runs performed by Blumenstock[1,2], we could observe the same shift in the tetra-PCDD isomer pattern during transient combustion conditions at different incinerators operated with different fuels. Obviously the shift in the pattern neither depends on the type of incinerator and nor on the fuel.

Comparing our results with literature data, we can describe the pattern observed as a typical “2,6 pattern” for the tetra-PCDD isomers during transient combustion conditions. PCDD formation via (catalysed?) chlorophenol condensation seems to be an important formation part during transiently impaired combustion conditions. Under normal operation conditions and during memory phases however, PCDD/PCDF formation seems to base on catalysed reactions from other organic compounds or from “black” carbon. Both reactions yield congener mixtures closer to the thermodynamically stable patterns which can be described by the models mentioned.

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