

PCDD/F-MEMORY FORMATION AFTER DISTURBED COMBUSTION CONDITIONS: NEW RESULTS FOR HAZARDOUS AND MUNICIPAL WASTE INCINERATION PLANTS

R.Zimmermann^{1,2,3*}, K.Neuer-Etscheid^{1,2,3}, H.Nordsieck², M.Sklorz², M.Blumenstock¹, K.-W.Schramm¹, A.Kettrup^{1,4}

¹SF Forschungszentrum Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Ingolstädter Landstraße. 1, D-86764 Neuherberg, Germany

²Universität Augsburg, Institut für Festkörperchemie, Professur für Analytische Chemie, Universitätsstraße 1, D-86159 Augsburg, Germany

³BIfA-Bayerisches Institut für Umweltforschung und -technik, Abteilung Umwelt und Prozeßchemie, Am Mittleren Moos 46, D-86167 Augsburg, Germany

⁴Lehrstuhl für Ökologische Chemie und Umweltanalytik, Technische Universität München, D-85748 Freising, Germany

*corresponding author, ralf.zimmermann@gsf.de

Introduction

Recent investigations at model incinerators (1), incineration pilot-plants (wood combustion, grate (2, 3)) and municipal waste incineration plants (grate (2) and fluidized bed (4)) pointed out that short disturbances of the combustion conditions can cause significant memory formation of PIC-compounds like PAH and PCDD/F for at least several hours. The reason for this memory emission is located in the high temperature region of the plants (> 400 °C) and is most likely associated with surface deposits which are formed during unstable combustion conditions. The memory emission is due to the degradation products of the carbonaceous layers (3). The high temperature formation of PCDD/F may be described as a high-temperature de-novo synthesis. In this paper new results on memory emissions of large plants are given. This includes results from a hazardous waste incineration plant (rotary kiln) as well as new results on municipal waste incineration.

Experimental

The samples were taken isokinetically with XAD-2 resin as adsorbent. Sampling positions were located in the stack gas (20 MW hazardous waste incinerator, HWI) and in the flue gas (22 MW municipal waste incinerator, MWI). PCDD/F measurements were performed by HRGC/HRMS. For a detailed description of the sampling, clean-up and analyzing procedure see references (5, 6). Low volatile compounds like chlorinated benzenes were adsorbed on *Carbotrap* adsorbent and measured by thermal desorption-GC/MS (5).

Results and Discussion

The recent results from municipal waste incinerators (MWI) and pilot plants depict that memory formation of PCDD/F occur after disturbed combustion conditions at grate or fluidized bed incinerators. In this work we focus on hazardous waste incineration in rotary kilns. Due to the in-stationary waste feeding (barrel uptake), the combustion conditions in hazardous waste incineration (HWI) plants are particularly unstable. In order to avoid increased emissions, HWI-plants usually are

FORMATION AND SOURCES

equipped with a separated post combustion chamber. Disturbed combustion condition at the HWI were induced by uptake of some barrels of highly calorific liquid waste into the rotary kiln without adapting the primary air. Such conditions can occur from time-to-time when wrongly declared waste barrels are burned. Measurements (stack gas, 70 °C) were performed prior to the uptake of the barrels with highly calorific liquid waste (normal conditions), during the phase of uptake (disturbed combustion) as well as during the first (memory 1) and second hour (memory 2) after the end of the disturbance. In Fig. 1 the results for this sequence is given for the PCDF homologues as well as for the homologues of the chlorinated benzenes.

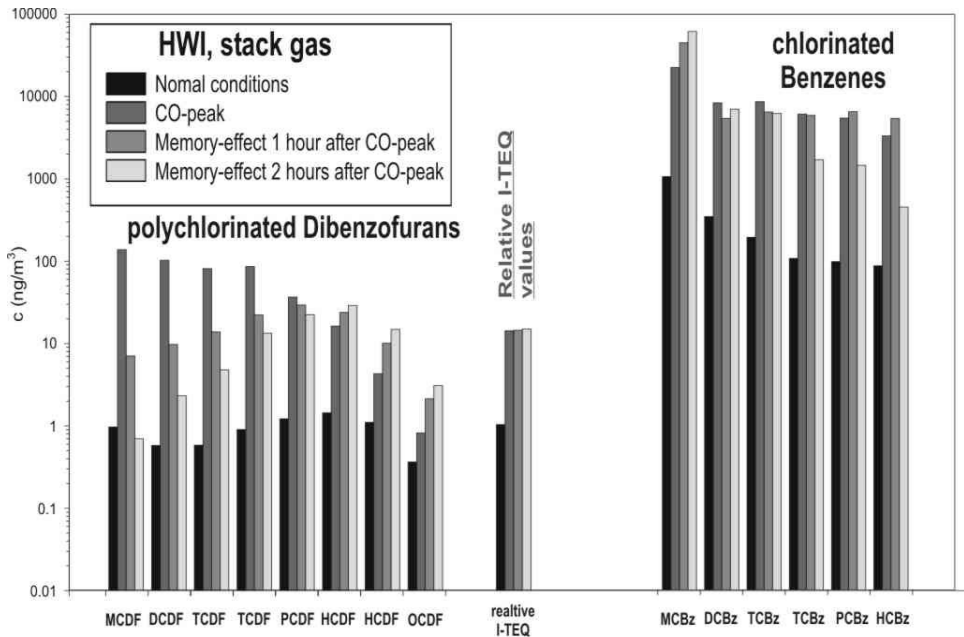


Figure 1. Homologue profiles of PCDF and PCBZ in the stack gas of a 20 MW HWI plant before, during and after a phase with disturbed combustion conditions

During the disturbed combustion conditions a dramatic increase (~ factor 200 – 90) of the concentrations of low chlorinated PCDF (mono- to tetrachlorodibenzofurans) can be observed. The penta- to octachlorodibenzofurans are also considerably increased (~ factor 30 – 2), but not as dramatic as the low chlorinated ones. The memory phases 1 and 2 are characterized by a rapid decrease of the concentration of the low chlorinated homologues while the emission concentration of penta- and hexachlorodibenzofuran homologues is relatively stable. For the hepta- and octachlorodibenzofurans a further increase is observed. The I-TEQ value is increased by an order of magnitude during the phase of disturbed combustion conditions and stays at this increased level during the subsequent memory phases 1 and 2. The dynamic of the homologue pattern compares well to the ones observed at a municipal waste incinerator ((2) and Fig. 2). Furthermore the results are in a line with the observations obtained at a pilot plant incinerator (grate with post combustion chamber): The high temperature of a post combustion chamber alone is not sufficient to avoid memory effects if sub-stoichiometric combustion condition occur.

FORMATION AND SOURCES

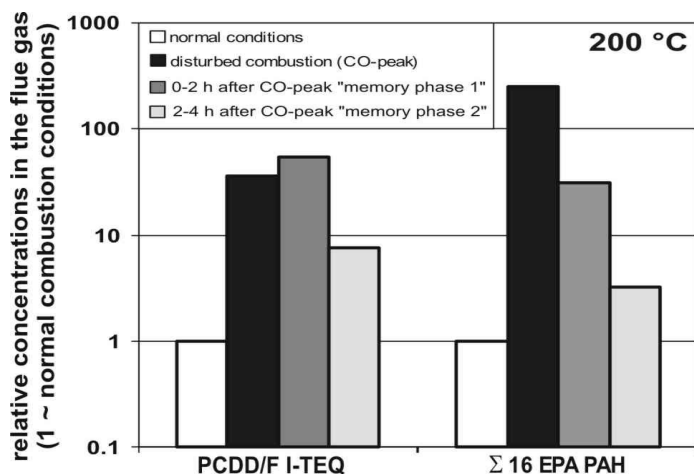


Figure 2. Memory formation of PCDD/F and PAH in the flue gas (prior to any flue gas cleaning measures) after a heavy disturbance of the combustion conditions at the MWI-plant.

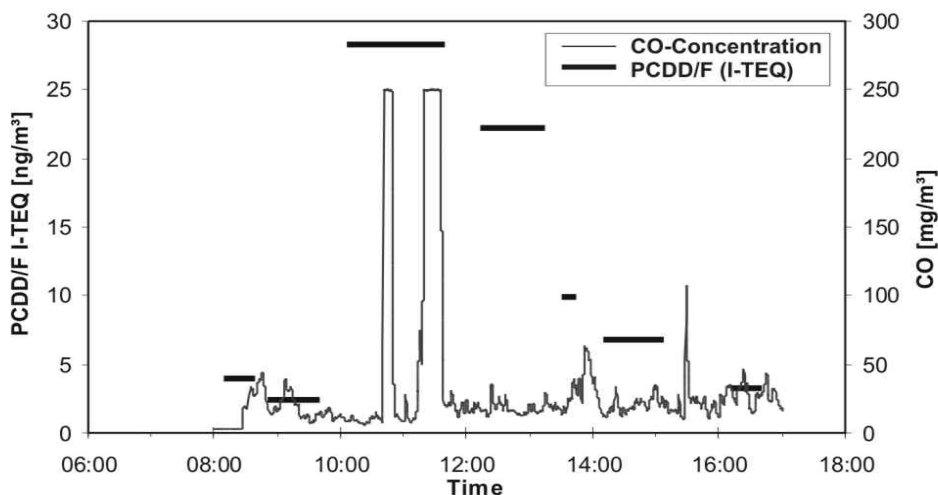


Figure 3. Time course of PCDD/F I-TEQ values and the CO-concentration in the the flue gas (prior to any flue gas cleaning measures) during and after 2 medium intense CO-peaks (estimated peak maximum ~ 300 mg/m³).

Interestingly the relative course of the low chlorinated benzene homologues (mono- to trichlorobenzene) is corresponding relatively well to the course of the I-TEQ, while the higher chlorinated benzenes show a less good similarity to the I-TEQ course. The here presented case represents a heavy disturbance of the combustion conditions, similar as in the case of the MWI-plant ((2). In Fig. 2 the course of the I-TEQ value in the flue gas (prior to the emission reduction devices) of

FORMATION AND SOURCES

the MWI-plant is depicted after a heavy disturbance. For the first memory phase even an increase of the I-TEQ value was observed. In order to get a more realistic impression on the course of the PCDD/F I-TEQ-value after less drastic disturbances an additional experiment was performed at the MWI-plant. Here a series of two medium strong CO-peaks (about 300 mg/m³, non-calibrated value) was generated by reduction of the primary air. In Fig. 3 the time course of PCDD/F I-TEQ values (black bars) and the CO-concentration (thin line) in the flue gas is shown before, during and after the two medium intense CO-peaks. Significantly increased PCDD/F I-TEQ values in the flue gas (memory PCDD/F-formation) are observed for a time span of more than 4 hours.

Conclusion

Memory formation of PCDD/F after disturbed or unstable conditions have been observed up to now at 4 different waste incineration plants (pilot plant/grate (2); MWI plant, grate (3); MWI-plant, fluidized bed (4) and HWI plant, rotary kiln, this work). This suggest that the memory PCDD/F formation effect is a general one and should be considered if dioxin reduction technologies are designed for new WI plants. The parallel occurrence of increased PAH and PCDD/F concentrations during memory formation phases may allow to develop a laser-based (REMPI) sensor for detecting and monitoring of memory events (7).

Acknowledgement

Funding of the research by the Deutsche Bundesstiftung Umwelt (projects AZ 04778 and AZ 12447) and the Bavarian State Ministry for Regional Development and Environmental Affairs (Project E 106) is gratefully acknowledged.

References

1. Lee, C. W.; Kilgroe, J. D.; Raghunathan, K. *Environmental Engineering Science* 1998, 15, 71-84.
2. Zimmermann, R.; Blumenstock, M.; Schramm, K.-W.; Kettrup, A. *Organohalogen Compounds* 2000, 46, 78-81.
3. Zimmermann, R.; Blumenstock, M.; Heger, H. J.; Schramm, K.-W.; Kettrup, A. *Environmental Science and Technology* 2001, 35, 1019-1030.
4. Weber, R.; Sakurai, T.; Ueno, S.; Nishino, J. *Organohalogen Compounds* 2001, 50, 438-442.
5. Blumenstock, M.; Zimmermann, R.; Schramm, K.-W.; Kettrup, A. *Chemosphere* 2001, 42, 507-518.
6. Schramm, K.-W.; Merck, M.; Henkelmann, B.; Kettrup, A. *Chemosphere* 1995, 30, 2249-2257.
7. Streibel, T.; Blumenstock, M.; Mühlberger, F.; Hauler, T.; Zimmermann R. *Organo-halogen Compounds* 2002 (this issue)