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Influence of combustion conditions on the PCDD/F-, PCB-, PCBz- and PAH-concentrations in the post-combustion chamber of a waste incineration pilot plant

M. Blumenstock [a], R. Zimmermann [a,b,*], K.-W. Schramm [b], A. Kettrup [a,b]

[a] *Lehrstuhl für Ökologische Chemie und Umweltanalytik, Technische Universität München, D-85354 Freising, Germany*
[b] *GSF-Forschungszentrum für Umwelt und Gesundheit, Institut für Ökologische Chemie, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany*

Abstract

Experiments at a pilot scale waste incinerator (0.5 MW thermal power) showed that the conditions in the post-combustion chamber (650–900°C) are strongly influencing the formation of chlorinated and non-chlorinated aromatics. Non-optimal combustion conditions resulted in increased concentrations of mono- to trichlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) and polycyclic aromatic hydrocarbons (PAH), while chlorinated benzenes (PCBz), polychlorinated biphenyls (PCB) and the higher chlorinated PCDD/F are only weakly affected or even decrease. The changes in concentration of the compounds investigated over a time span of hours gave hints on 'memory effects' in this combustion zone. For mono- and dichlorinated benzenes, a high correlation ($r^2 = 0.80$) with the international toxicity equivalent (I-TEQ) value of PCDD/F was observed. As recently has been demonstrated, this correlation can be utilized for an indirect on-line measurement of the I-TEQ by a novel laser mass spectrometric technique (REMPI–TOFMS). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Waste incineration; Post combustion chamber; Flue gas; PCDD/F; I-TEQ; PCB; PCBz; PAH; Principle component analysis (PCA); Memory effects; Surrogate compounds; REMPI–TOFMS

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1. Introduction

The flue gases of combustion processes, e.g., from waste incineration plants, contain an array of products of incomplete combustion (PIC), such as chlorinated aromatics and polycyclic aromatic hydrocarbons (Wienecke et al., 1995). Investigations on the formation mechanisms of chloroaromatics in large scale incinerators have demonstrated that there are two temperature ranges for the formation of PCDD/F. Within the low temperature range of about 300°C, PCDD/F are formed by heterogeneously catalyzed reactions on fly ash from precursor compounds (Hagenmaier et al., 1987). The second formation window at high temperatures with a maximum at about 700°C is far less investigated and is considered to be responsible for PCDD/F formation via the so-called de novo synthesis from carbon-like structures (Ghorishi Behrooz and Altwicker, 1996). In this work the influence of combustion parameters on the formation of PCDD/F, PCB and PCBz, as well as on PAH and other non-chlorinated aromatics (BETX and methylated naphthalenes) at high temperatures in the post-combustion chamber are investigated. This study is motivated by recent concepts for an indirect on-line monitoring of surrogate compounds in e.g. flue gases of incineration processes by means of laser mass spectrometry (*R*esonance-*E*nhanced *M*ulti-*P*hoton *I*onization–*T*ime-*O*f-*F*light *M*ass *S*pectrometry, REMPI–

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[*] Corresponding author.
E-mail address: Blumenstock@GSF.de (R. Zimmermann).

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TOFMS) (Heger et al., 1999). In order to figure out suited on-line measurable indicators for both, the occurrence of toxic compounds like PAH or PCDD and the identification of specific combustion conditions, a chemometrical data analysis has been performed.

2. Methods and materials

A waste incineration pilot plant was the subject of our 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 (Beckmann et al., 1997). Different stationary combustion conditions were investigated. The flue gases were sampled at the outlet of the post-combustion chamber. The incinerator was fed with waste wood chips which were 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 significant percentage of the PCDD/F emissions (Schatowitz et al., 1994).

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 70–100 m^3/h.

Isokinetic sampling was performed close to the outlet of the post-combustion chamber using a 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 was used for trapping the semi-volatile compounds (PCDD/F, PAH and PCB). The sampling rate was 1 N m^3/h and the sampling time was about 1 h. An internal $^{13}C_{12}$ standard cocktail for the PCDD/F (for Cl_{1-3}DD/F only three standards were available: 2,7 DCDD, 2,3,7 TriCDD and 2,8 DCDF) and PCB (from Cl_2CB to Cl_{10}CB) with at least one labeled congener for each degree of chlorination was added to the ethoxyethanol before it was stirred for 24 h with a mixture of water/tolune (9/1, v/v). The clean-up procedure is described elsewhere (Schramm et al., 1995). In order to achieve higher recoveries of the low chlorinated PCDD/F and biphenyls, the elution of the acidified silica column was performed with 2 vol% of dichloromethane in the hexane fraction. Quantification for Cl_1DD was performed by the labeled Cl_2DD congener and for the Cl_{1-2}DF with the labeled Cl_3DF congener.

The more volatile PCBz were sampled simultaneously from a small bypass sampling stream of the Ströhlein® sampling train. Glass cartridges (I.D. = 6 mm) containing 2 g activated charcoal with $^{13}C_6$ internal standard (one isomer for each degree of chlorination) were used for trapping. A second 'back-up' cartridge filled with 1.5 g charcoal was used for indication of analyte breakthrough. Sampling rates were about 80 l/h and the temperature was held at 70°C to avoid condensation of water in the tubes. The chlorinated benzenes were eluted with 2 ml of CS_2 according to NIOSH guideline No. 1501 (1984). A cleanup for the PCBz was not necessary. These cartridges were also spiked with $^{13}C_6$ benzene, $^2H_8$ toluene, $^2H_{10}$ ethylbenzene and $^{13}C_6$ naphthalene for internal calibration of the analysis for BETX, naphthalene and methylated naphthalene.

For each sample the glass inlet of the probe was changed and all the other glass instruments were cleaned. All samples of the experiment set were worked up in parallel in the laboratory, so that the risk of contamination was minimized.

PCDD/F were measured using HRGC/HRMS (HP 5890 series II/MAT 95) and PCB/PCBz/BETX/naphthalenes using HRGC/LRMS (HP 5890 series II/SSQ 7000 or Varian 3400/its 40 tracker). Recoveries for PCDD/F, PCB and PCBz were from 60% to 100%. No breakthrough for the PCBz and BETX were observed. PAH were analyzed with an 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, 273 K, 1013 h Pa and 11 vol% O_2 (≡N m^3).

A statistical analysis (principal component analysis (PCA)) of the results has been performed in order to determine whether relationship exist between combustion parameters and formation of the investigated compounds (Morrison, 1988).

3. Results and discussion

First the dataset was treated with PCA to clarify the information about the influence of different combustion parameters on the formation of PIC. For the statistical treatment, the analytical data for all considered groups of compounds was reduced to the sum of homologues. The residence time of the flue gas, the temperature gradient in the post-combustion chamber, the CO concentration as well as the nitrogen amount added were the combustion parameters considered in the PCA.

The first two principal components describe 57% (PC1) and 20% of (PC2) of the variance of the data set (total 77%).

Although, it is difficult to pick up 'real' information from the loading axis of a PCA, the plot provides hints and trends for grouping of variables in the data set. Considering the first principal component PC1, the variables form two groups in the PCA: The first group is due to the I-TEQ, the sum of all chlorinated benzenes and the temperature gradient from top to the bottom of the post-combustion chamber, depicted in the left part of Fig. 1. Also, the oxygen excess seems to be correlated with the formation of PCBz and PCDD/F. Further on, the sum of all chlorinated biphenyls (sum PCB) and the residence time in the post-combustion chamber system belong to this group, but are separated according to PC2. The second group is given by the PAH/BETX content, the CO concentration in the flue gas and N_2 addition. As mentioned above, the second principal component PC2 separates the sum of all chlorinated biphenyls and the residence time in the post-combustion chamber from the I-TEQ values, the sum of all chlorinated benzenes, the temperature gradient in the post-combustion chamber and the oxygen content.

It is obvious that the CO concentration is a good indicator for the sum of the PAH. However, this is not valid for individual PAH species and not on a highly resolved time scale, as recently has been shown by on-line PAH measurement in waste incineration flue gas with a REMPI–TOFMS instrument (Zimmermann et al., 1997; Zimmermann et al., 1998; Heger et al., 1999). The correlation between nitrogen addition and increased CO and PAH emissions may be caused by a decreased temperature gradient in the post-combustion zone (i.e., decreased combustion efficiency) or by inhomogeneous mixing effects. The results of the PCA are in good agreement with results from laboratory scale incinerator experiments by Fängmark et al. (1993).

The score plot (Fig. 2) clearly pointed out that the operation conditions of the plant (e.g., temperature, nitrogen addition or the change from combustion to gasification in cases 4, 6 and 7) significantly influences PIC emissions. Nitrogen addition on the one hand causes a fast quenching of the flue gases and therefore reduces the amount of formed chlorinated aromatics; on the other hand, the handling of the post-combustion processes became much more difficult and the BETX and PAH concentrations increased dramatically. It should be emphasized that the dynamics of the formation of aromatic compounds are complex and cannot be described by a single parameter like the CO content.

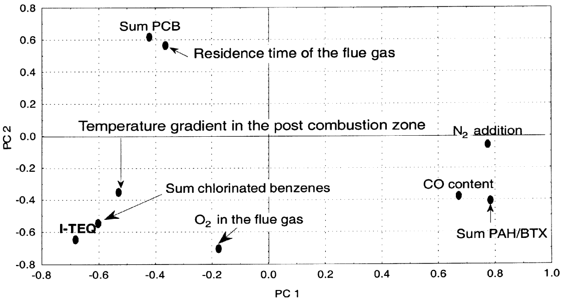

Fig. 1. PCA for the whole set of experiments (N_2 *addition* means the nitrogen added at the top at the post combustion chamber). Note that the axis of the principle components are scaled according their percentage of the total explained variance respectively their eigenvalues.

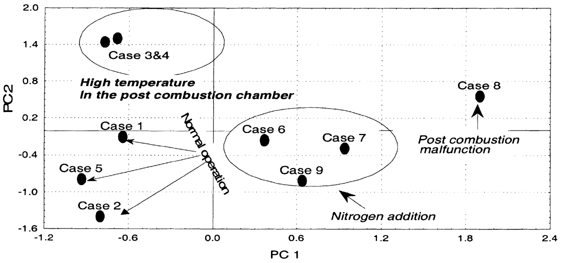

Fig. 2. Score plot form to the PCA loading plot (Fig. 1).

In this study, the formation of PCB seems to be different from the other chlorinated aromatics, which may be a hint of different formation mechanisms of PCDD/F and PCB (i.e., separated according to PC2 in Fig. 1). The close proximity of PCDD/F and PCB with respect to the PC1 may be caused by the precursor character of the PCB for the PCDF (i.e., formation of PCDF from PCB via an oxidation followed by an internal ring closure) (Choudry and Hutzinger, 1983). Investigations at a hazardous waste incinerator from Kaune et al. (1994), for example, pointed out that some PCBs are good indicators for I-TEQ values. In Fig. 3, the PCB homologues ($Cl_{2-8}CB$) showed more or less stable profiles for all nine experiments with different combustion conditions. By comparison, the lower chlorinated PCDD/F ($Cl_{1-2}DD/F$) and also the PAH showed completely different behavior (Figs. 4 and 5).

An additional result of the study arose from the observation of a malfunction in the post-combustion chamber. During this incident the post-combustion processes were heavily disturbed for a time span of some minutes. Directly after the sampling time (1 h) a further experiment was started in order to study the recovery of the emission levels. The incident caused a lasting effect on the compound profiles. Figs. 3 and 4 show the PCDD/F and PAH before during and after the post-combustion malfunction.

The observed PCDD/F profiles under normal combustion conditions are in good agreement with the literature. For example, the ratio of PCDD to PCDF is <1 (Marklund et al., 1992). However, during and after the malfunction, dramatic deviations from the 'standard' profiles are observed. The malfunction of the combustion chamber led to the lowest I-TEQ value in the whole data set. The lower chlorinated (mono- to tri) PCDD/F congeners, which do not contribute to the I-TEQ value, are considerably increased while the higher chlorinated

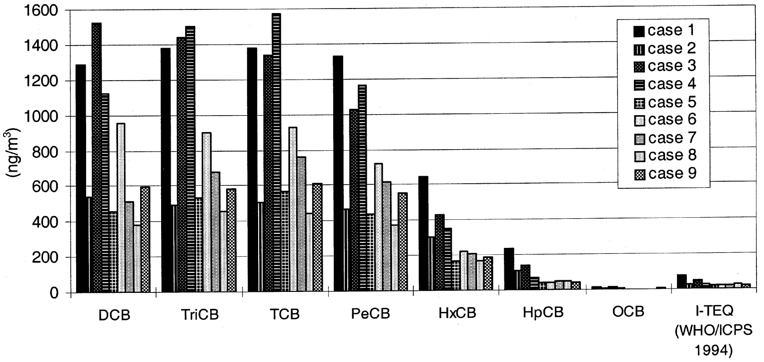

Fig. 3. Homologue profiles of the PCB concentration in the flue gas for all the nine experiments (*linear* scale of the *y*-axis).

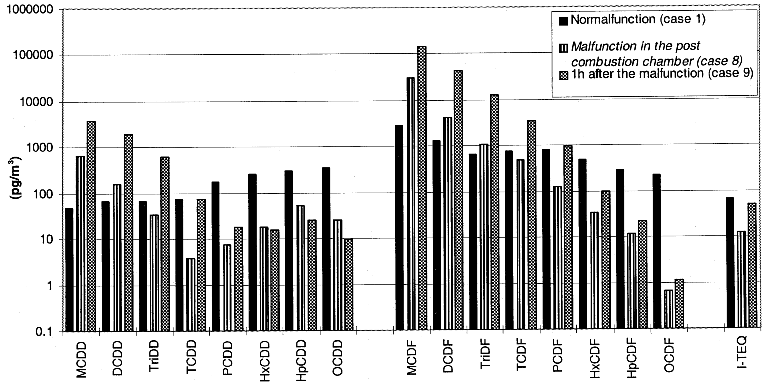

Fig. 4. Homologue profiles of the PCDD/F concentration in the flue gas before, during and after a post-combustion chamber malfunction (*logarithmic* scale of the *y*-axis).

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 also increased in comparison with the results obtained during malfunction. Here it should be remarked that flue gases from different combustion processes often exhibit qualitatively similar homologue PCDD/F profiles if only the higher chlorinated congeners are considered. Differences in the profiles were observed for the lower chlorinated (mono- to trichloro) PCDD/F as shown in Fig. 4 and in the literature for soot deposits (Bacher et al., 1992). In contrast to the concentration increase of the Cl_{1-2}DD/DF, the PCB homologues (Fig. 3, Cl_1CB not analyzed) did not show a similar effect.

Unchlorinated dibenzo-*p*-dioxin and dibenzofuran was quantified (Table 1) in order to rule out simple chlorination reactions for the increased concentrations of Cl_{1-3}DD/DF. During the malfunction the concentrations of all investigated compounds increased significantly. Even the unchlorinated dibenzo-*p*-dioxin and dibenzo furan were present in the microgram range.

However, like the PAH all these compounds reached their normal level 1 h after the malfunction, while the PCDF concentrations were still rising. For that we assume that simple chlorination reactions in the gas phase are not sufficient to explain the long term concentration increase for the Cl_{1-3}DD/DF, perhaps surface (obtained during malfunction of the combustion chamber) driven processes might be the main source for these compounds. Kaiser et al. (1998) reported that in the heat recovery zone of combustion facilities between 700°C and 300°C the concentrations of PAH decreases due to their decomposition or adsorption on soot/fly ash particle. Based on this observation, we assume that the concentrations of the PAH will decrease as they move forward to the stack.

Particularly interesting is the observed ‘memory’ effect of different PIC compounds in 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. The residence time of the combustion gases is very short in comparison to the observed memory time scale. Thus,

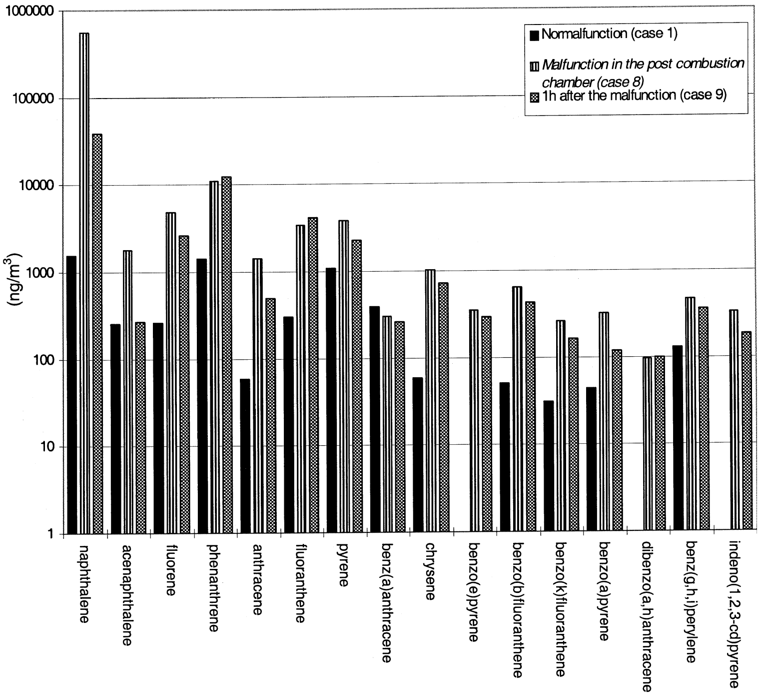

Fig. 5. PAH profile variation in the raw gas before, during and after a post-combustion chamber malfunction (*logarithmic* scale of the *y*-axis).

Table 1
Concentrations of non-chlorinated aromatics in the raw flue gas prior to any flue gas cleaning devices (remark: biphenyl, dibenzo-*p*-dioxin, dibenzofuran were determined from the charcoal tubes and quantified against $^{13}C_6$ naphthalene)

Compound (μg/m^3)	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	Case 9
Benzene	7.24	4.18	5.29	8.52	7.23	9.75	7.68	13799.83	9.35
Toluene	7.66	9.73	9.12	16.96	13.40	17.85	18.60	3322.47	14.33
Ethylbenzene	1.47	1.31	1.49	3.10	4.04	2.17	1.76	1185.73	2.38
m/*p*-xylene	5.47	5.26	6.74	16.26	21.70	8.04	7.34	1123.23	9.17
o-xylene	1.74	2.20	2.24	5.78	5.73	2.83	1.87	418.30	2.66
Naphthalene	1.56	0.74	0.75	2.94	3.07	1.90	2.95	550.90	38.99
Biphenyl	1.01	1.44	1.79	2.15	1.42	2.01	1.83	452.99	3.57
Methylnaphthalene (sum)	0.37	n.d.	1.16	3.08	0.90.	n.d.	1.09	1471.91	4.37
Dimethylnaphthalene (sum)	2.14	n.d.	2.64	1.74	1.53	2.24	n.d.	241.78	n.d.
Dibenzofuran	0.39	0.36	1.48	2.32	0.72	1.00	2.43	96.17	2.55
Dibenzo-*p*-dioxin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21.78	n.d.

we conclude that the observed memory effects most likely are caused by surface based effects via de novo synthesis especially for PCDF. Furthermore we can exclude memory effects from the sampling system, because we changed the glass inlet of the probe and the glass instrument before each experiment.

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. It might be suggested that the shift is a dechlorination reaction of the higher chlorinated homologues, but this will require high concentrations of these homologues, which were not observed at all. The degradation products of the soot layer could be PAH, causing the memory observed for the PAH emission (Haung and Senkan, 1996).

One goal of the study is the identification of surrogate compounds for I-TEQ that are measurable with REMPI–TOFMS. Due to molecular–physical reasons, lower chlorinated compounds are more easily measured by the REMPI–TOFMS method (Zimmermann et al., 1996). Therefore, lower chlorinated PCDD/F and PCBz are the two classes of substances that in principle should be taken into account for an indirect on-line monitoring of I-TEQ by REMPI–TOFMS. However, summarizing results above, it is not recommended to use the lower chlorinated PCDD/F homologues as single indicators for the I-TEQ emission. Gullett and Wikström (1998) described also that $Cl_{1-3}DD/DF$ homologues were no good surrogates for the prediction of the I-TEQ, though by using selected congeners as I-TEQ surrogate in a multivariate regression analysis, an enhanced accuracy of prediction can be achieved. However, for the elucidation of the formation pathways of PCDD/F, it seems to be advisable to consider the mono- to octachlorinated dioxins and furans.

Finally, it should be not underemphasized that lower chlorinated benzenes show a high correlation to the I-TEQ. This is shown in Fig. 6, where a regression plot of the sum of the concentrations of 1,2 dichlorobenzene and monochlorobenzene versus the I-TEQ is presented. The correlation between PCBz and PCDD/F firstly was described by Olie et al. (1982). Öberg and Bergström (1985) suggested the use of hexachlorinated benzene as surrogate for PCDD/F monitoring. More recently, Kaune et al. (1998) investigated, whether several higher chlorinated compounds, including pentachlorobenzene, are suitable as I-TEQ indicators. Wikström et al. (1996) found a relation between the 17 toxic PCDD/F congeners and chlorinated benzenes ($Cl_{3-6}CBz$) during combustion of wastes with different chlorine content. Our recent studies revealed a close correlation of I-TEQ and monochlorobenzene in the flue gases of a hazardous waste incinerator ($r^2 = 0.82$) (Blumenstock et al., 1999). Using this correlation, we recently were able to perform the first indirect on-line measurement of the I-TEQ at a full scale industrial plant by REMPI–TOFMS (Zimmermann et al., 1999).

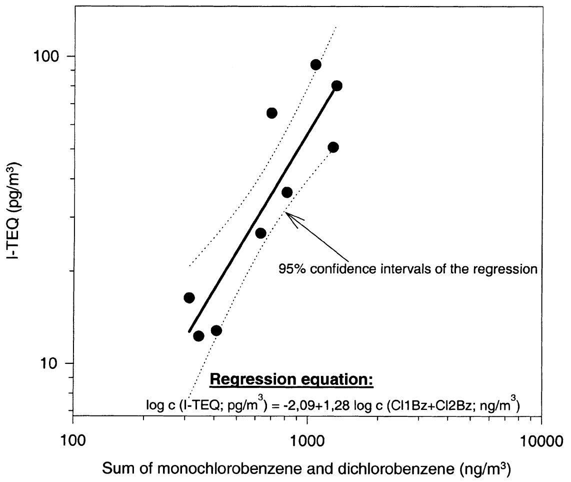

Fig. 6. Sum of monochlorobenzene and 1,2-dichlorobenzene as surrogate for the I-TEQ value.

4. Conclusions

PAH formation in a post-combustion chamber is correlated with the CO concentration obtained from nitrogen addition in the flue gas. The concentration of PCDD/F in the flue gas is influenced by the temperature gradient in the post-combustion chamber and is correlated to the concentration of chlorinated benzenes. Therefore, we assume different formation pathways for PAH, PCDF, PCB/PCBz and PCDD in the post-combustion processes.

The observed close relationship between lower chlorinated benzenes and the I-TEQ value supports the suggested (Zimmermann et al., 1994) and currently firstly realized (Zimmermann et al., 1999) approach of indirect I-TEQ monitoring in the flue gas of waste incinerators by REMPI–TOFMS.

A malfunction at the post-combustion chamber caused drastic changes in the emission patterns of PAH and PCDD/F. Particularly interesting is the 'long term' character of the change in the emission pattern, induced by a 'short term' malfunction in the post-combustion device ('memory effect'). We presume that a deposition layer, possibly soot, generated during the malfunction on the post-combustion chambers inner wall could be responsible for the observed effects.

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