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PCDD/F and Other Micropollutants in MSWI Crude Gas and Ashes during Plant Start-Up and Shut-Down Processes

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Nonstationary combustion conditions at municipal solid waste incineration (MSWI) plants cause increased crude gas concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and other products of incomplete combustion (PIC). Such transient conditions occur, e.g., during and after start-up processes in MSWI plants. The start-up and shut-down processes of a MSWI plant were investigated in detail. PCDD/F and other PIC concentrations were determined in the crude gas, in the boiler ash, and in the ash from the electrostatic precipitator (ESP ash), with the outcome that only the start-up procedure significantly affected the concentrations of the organic pollutants in the flue gas and in the ESP ash. The shut-down procedure was evaluated as less problematic for the concentration of the organic pollutants. Moreover the concentration of the PCDD/F and other PIC in the boiler ash was determined as not influenced by shut-down and start-up processes. The homologue profiles and the congener patterns as well as the PCDF/PCDD ratio in the flue gas and in the ESP ash change during MSWI start-up. The changing patterns point at a transition from dominant de novo synthesis to precursor synthesis.

1 Introduction

During start-up and shut-down of municipal solid waste incineration (MSWI) plants, combustion conditions are impaired in comparison to normal operating conditions, even if high temperatures in the combustion chamber are ensured by back-up burners. PCDD/F concentrations in MSWI crude gas are also known to be elevated during and after transiently disturbed combustion conditions due to memory effects attributed to PCDD/F formation from carbonaceous deposits in the combustion chamber and/or in the boiler (*1*, *2*). These “high temperature” memory effects are not to be confused with effects of sorptive PCDD/F memory in the low-temperature part of the pollution control equipment as it was reported, e.g., for the memory effects in MSWI flue gas scrubbers (*3*, *4*).

Although longer periods of continuous operation are desired, most MSWI plants have to be shut down once per year for revision and many plants need additional shut-downs. Even a few start-up processes per year accompanied by high PCDD/F concentrations in the crude gas can significantly raise the annual PCDD/F emissions (*4*). Continuous 24 h/day, day after day measurement of the PCDD/F emissions (*5*) should include transient operation conditions, however this is not common in all countries. Hence, the emissions from starts and stops in many cases are not necessarily accounted for in the overall judgment of meeting the 0.1 ng/m^3 I-TEQ standard.

De Vries (*6*) reported high PCDD/F emissions during and after start-up of a Dutch MSWI plant. Compared to normal operation conditions, the levels in the gas phase as well as in the boiler ash were increased over a time period of at least 8 h (14 vs 0.07 ng/m^3 I-TEQ at normal operation). By optimizing the start-up procedure the PCDD/F emissions in the stack gas of this plant 4−6 h after start-up could be reduced to 0.24 ng/m^3 I-TEQ. Optimization of the start-up of another MSWI (*7*) lowered the PCDD/F concentration from 78 to 2.4 ng/m^3 I-TEQ during the heat-up phase with oil burners and from 52 to 12 ng/m^3 I-TEQ when waste feed started, in comparison to <1 ng/m^3 I-TEQ during normal operating conditions (*4*).

Hunsinger’s experiments at the “Tamara” MSWI pilot plant showed that PCDD/F formation during start-up could be decreased through optimization of the burner arrangement and the addition of sulfur to the fuel (*8*).

Optimization of the start-up process seems to be another task than optimization of the continuous operation of modern MSWI plants at good combustion conditions, where, e.g., ESP temperature seems to play a major role in PCDD/F formation (*9*).

We presently conduct a research program dealing with the development of an online “sensor” allowing detection of high PCDD/F-loaded filter dusts and ashes in order to selectively treat these materials, e.g., by reburning. To achieve this, it is essential to evaluate how operating conditions, especially during start-up and shut-down, influence the PCDD/F concentrations in the flue gas and in the solid residues. Therefore a closer appreciation of the PCDD/F formation mechanisms in the different matrices is indispensable.

2 Methods and Materials

Sampling was performed at a 10 t/h grate incinerator with a 4-pass tail-end boiler of a modern MSWI plant situated in Germany. The flue-gas cleaning system consists of an ESP, followed by two wet scrubbers operating at acidic and neutral pH. Further steps are SCR for NO$_x$ removal and polishing by active carbon injection/fabric filter. The plant’s back-up burners are operated with light fuel oil.

Several samples were taken at normal operating conditions within one month before the annual shut-down for

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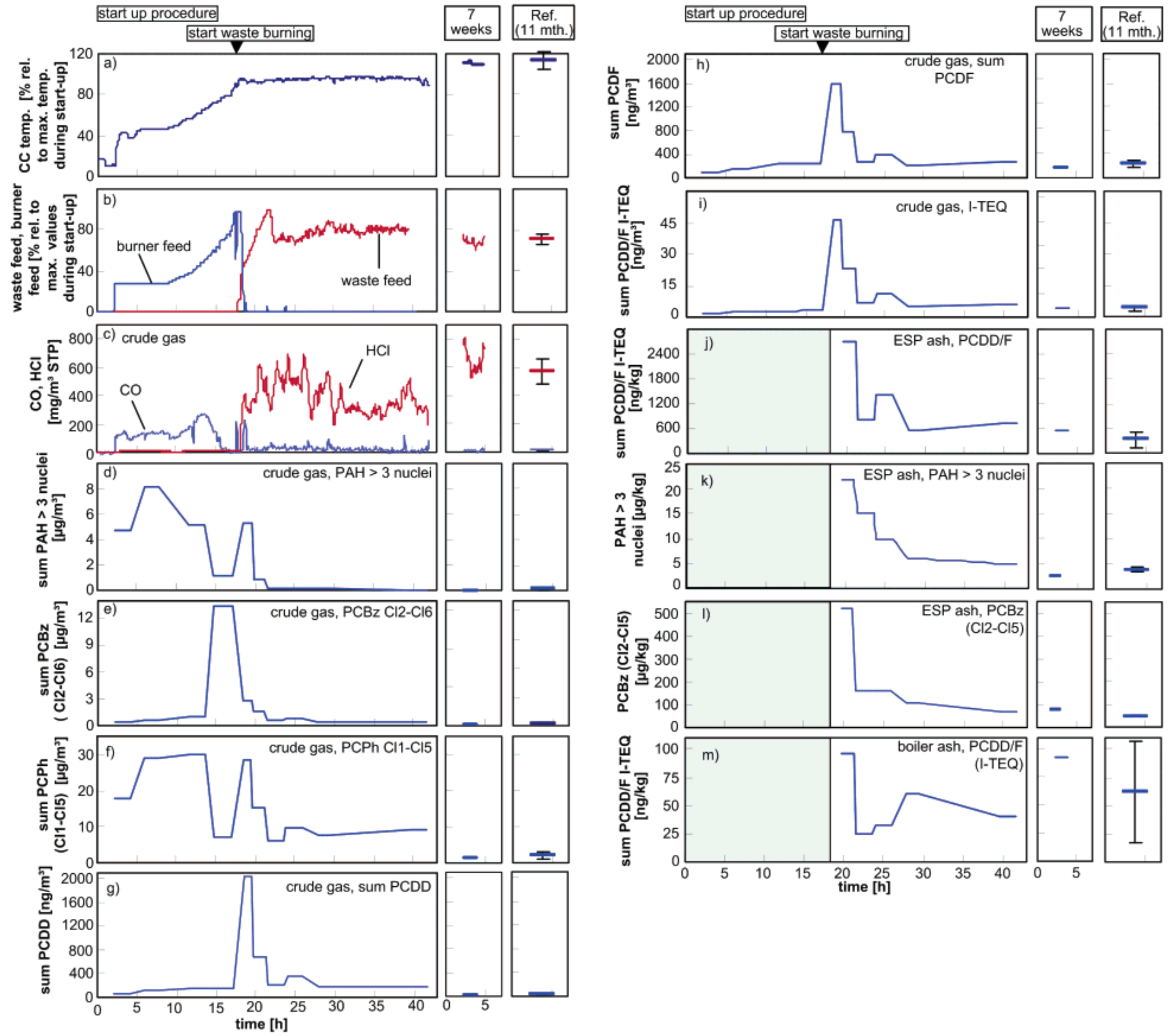

FIGURE 1. (a)−(k) Combustion chamber temperature (CC temp), CO and HCl crude gas concentrations, burner and waste feed, concentrations of PAH >3 nuclei, PCBz (Cl2−Cl6), PCPh (Cl1−Cl5), sum PCDD, sum PCDF, and PCDD/F (I-TEQ) in the crude gas, sum PCDD/F (I-TEQ), PAH >3 nuclei, and PCBz (Cl2−Cl6) in ESP ash, and sum PCDD/F (I-TEQ) in boiler ash, at start-up of the MSWI plant (PCDD/F and PIC concentrations as averages over the sampling periods, no ashes available during the heat-up period.

plant revision. Both the shut-down and the first day of the start-up procedure were followed by taking multiple successive samples. Further samples were taken 10 and 22 h after the start of the waste feed. Because deposits in the boiler build up slowly, a last sample was taken 7 weeks after start-up, when the boiler had reached the normal operation conditions again.

Crude gas was sampled downstream of the ESP between the external economizer and the wet scrubber at a flue gas temperature of approximately 180 °C. Sampling was not performed isokinetically due to the low dust concentration (typically less than 10 mg/m^3) and the very complex flow field at the sampling point. Sampling periods were adapted to the steps during start-up and shut-down, respectively. Apart from this, sampling was performed according to DIN EN 1948 (condensation + XAD2 adsorption method). Boiler ash and ESP ash samples were collected simultaneously to gas sampling. Sample treatment and analysis details are described in the Supporting Information which also contains a plant scheme showing the sampling locations.

All gas-phase concentrations were standardized to 273 K and 1013 h Pa dry gas.

3 Results and Discussion

3.1 Start-Up Procedure. After a plant revision, heating-up is a slow process, in order to avoid thermal stress for the refractory lining materials used in the combustion chamber. After warming up using steam, the incinerator was aerated and the back-up burners were fired at a low power. The combustion chamber temperature was then gradually raised by increasing the back-up burners feed rate. Waste was not fed until the minimum required combustion chamber temperature (850 °C) was reached. Figure 1 gives an overview over the changes during start-up.

3.1.1 PCDD/F and PIC in the Crude Gas during Start-Up. PCDD/F and PIC Concentrations. Whereas Figure 1 d−i show the changes in PIC and PCDD/F concentrations, a table stating the values measured is given in the Supporting Information. The horizontal parts of the concentration graphs illustrate the duration of the sampling periods.

During the heat-up period, the HCl concentration in the crude gas was lower (5−15 mg/m^3 STP) than at normal operation and also lower than during shut-down after burn out of residual waste on the grate. Once waste was fed, the HCl concentration rose to levels higher than 700 mg/m^3.

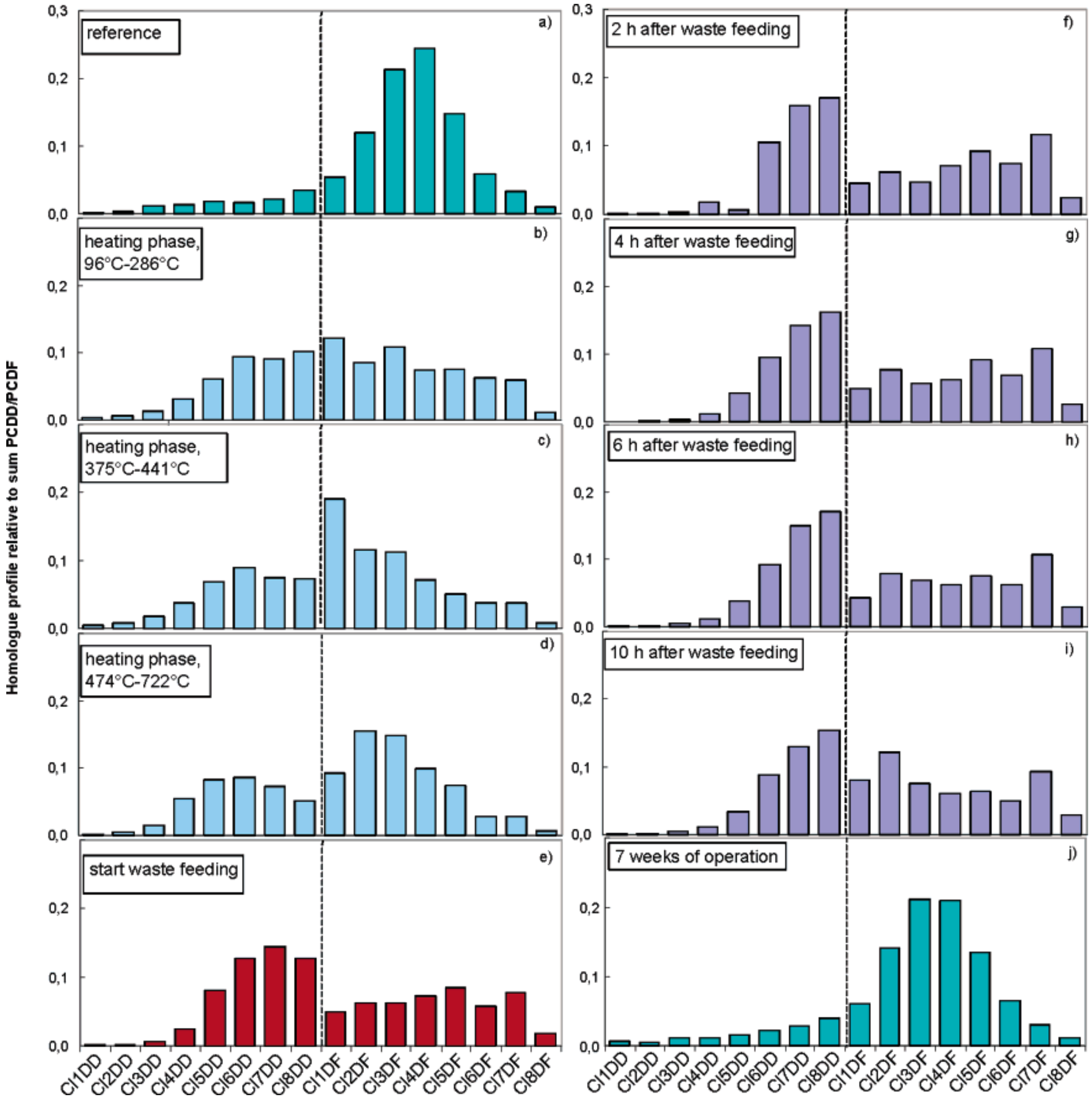

FIGURE 2. PCDD/F homologue profile in the crude gas during the start-up procedure.

As long as the combustion chamber had not reached a sufficiently high temperature, CO and PAH concentrations were high, indicating rather poor combustion conditions (cf. Figure 1 c and d). PCDD/F (I-TEQ) crude gas concentrations during the heat-up period were a little lower than those during normal operation with waste as the fuel. This result is contrary to observations made by Gass et al. (*4*), who determined maximum PCDD/F (I-TEQ) concentrations at the end of the heat-up phase. One reason for this difference may be the state of cleaning of the boiler section. The boiler investigated had been cleaned thoroughly by blasting and had very little residual deposits. Hence both chlorine content and catalytic activity were low.

However, the rather bad combustion conditions during heat-up with fuel oil, combined with residual deposits as a source of chlorine, were sufficient for the formation of halogenated PIC (cf. Figure 1 e and f). Remarkable was the difference in behavior of the PAH and PCPh concentrations on one hand and the concentrations of the PCBz on the other hand. Both PAH and PCPh concentrations were rather high during the heat-up phase, decreasing when the combustion chamber reached a high temperature. The PCBz concentration, in contrast, was low during almost the whole heat-up process, but went up at the end of the heat-up phase.

Immediately after waste was fed, PCDD/F concentrations in the crude gas increased by 1 order of magnitude compared to normal operating conditions (cf. Figure 1 g, h, i). At the same time, the PCBz concentration dropped and the PAH and PCPh concentrations reached a second maximum. PCDD/F concentrations in the flue gas clearly remained elevated during 12 h after switching to waste as the fuel. Even 22 h after the start of waste feed, the concentrations of PCBz and PCPh still were higher than those during normal operation.

Similar effects were observed in the ESP ash. PCDD/F, PAH, and PCBz concentrations in the ESP ash clearly were elevated after waste was fed compared to normal operation (Figure 1 j–l). Also in the boiler ash, PCDD/F concentrations seemed to be elevated after waste was fed (Figure 1 m). However, these values were within the normal variation range of the PCDD/F concentrations in the boiler ash.

PCDD/PCDF Homologue Profiles during Start-Up. During start-up, both the PCDD and the PCDF homologue profiles changed as well as the PCDF/PCDD ratio (cf. Figure 2 and Figure 2a in the Supporting Information). At normal operating conditions, PCDF were more prominent than PCDD (ratio PCDF/PCDD about 7). This observation is consistent with results from the analysis of PCDD/F profiles from large scale thermal processes in general, and MSWIs in particular, which supports the dominant role of the de novo synthesis as shown by Everaert et al. (*9*). The PCDF/PCDD ratio dropped to the range of 1–2 during the whole start-up process and stayed low even after waste was fed for at least 22 h. Seven weeks after start-up a high PCDF/PCDD ratio was reestablished, a period of time which is sufficient to build up a normal level of deposits in the boiler.

Changes in the homologue profiles resulted in changes in the degree of halogenation changed between the phase of heat-up and the phase when waste was burning. During the phase of heat-up, the degree of halogenation of PCDF (Cl1−Cl8) was lower than at normal operation, i.e., the homologue pattern was shifted towards the lower chlorinated homologues. After the start of waste feed, the degree of halogenation increased rapidly to the level that is observed at normal operating conditions. At the same time, the HCl concentration increased by a factor of 50. The total chlorine content of the flue gas is known to affect the homologue profile of the PCDD/F (*10*, *11*). Although the PCDD did not show the initial decrease in the degree of halogenation, the changes between heat-up phase and after the start of waste feeding were similar to the PCDF.

The change in the PCDF/PCDD ratio as well as the changes in the homologue profile also caused a change in the ratio $\sum$(PCDD + PCDF)/I-TEQ which is a measure for relative toxicity. During the heat-up phase, while the lower chlorinated species dominated the homologue profile, $\sum$(PCDD + PCDF)/I-TEQ was significantly higher than at normal operation, indicating lower relative toxicity. After waste feed, the values decreased, but still remained elevated compared to the values under normal operating conditions.

Figure 2 a−j shows in detail the change in the homologue profiles during the start-up process. Whereas at normal plant operation Cl3- and Cl4-dibenzofurans are the most prominent homologues, the dibenzodioxin formation was favored during heat-up with fuel oil. Two possible reasons are to be considered for this observation. The first one is the temperature distribution during start-up: during the heating phase, the flue gas duct is not in thermal equilibrium and large parts of the boiler are within a temperature range of 250−350 °C. Blumenstock reported favored formation of the PCDD below 450 °C and dominant PCDF formation at higher temperatures (*12*). The second reason is that during the heat-up phase, high amounts of chlorinated PIC were found, including rather high amounts of chlorophenols. PCDD formation is favored to proceed from precursor molecules such as chlorophenols (*1*, *13*−*17*).

The shift in chlorination degree during heat up was caused by a shift from high chlorinated PCDD (Cl7 and Cl8) toward tri- to hexachlorinated homologues. Accordingly, a shift from Cl3−Cl5-dibenzofurans toward Cl1−Cl3- DF was observed (cf. Figure 2 a−c). Increased formation of the lower chlorinated species during heat-up with the back up burners can be explained by the low availability of chlorine during the heat-up phase. Hence it is not surprising that when waste is fed, the homologue profile partially shifts back to the higher chlorinated homologues, because at that time a convenient chlorine source is present. Blumenstock observed a similar shift in the degree of halogenation during disturbed combustion conditions accompanied by a high ratio of PIC to HCl concentrations (*18*).

Although the PCDD/PCDF degree of halogenation was reestablished soon after waste was used as a fuel, the homologues profiles still were different from the profiles at normal operation. Both the distribution of the homologues groups remained changed and the formation of the PCDD remained elevated over an extended period of time which means a low PCDF/PCDD ratio.

A low PCDF/PCDD ratio indicates that the organic precursor condensation pathway, which produces predominately PCDD, is more important than the de novo pathway from solid carbon precursors (*9*, *19*). This result is consistent with the high amounts of PCPh determined when waste was fed. Wilken et al. made similar observations at a HWI (*20*). A possible reason for the elevated concentrations of chlorophenols during and after start-up is the fact that surface temperatures in the combustion chamber and in the boiler are lower than at normal operation conditions. At normal operation, surface temperatures are higher than the tube wall temperatures because of heat-insulating deposits. Building up a steady state of deposits, however, takes several weeks as can be deduced from the plant's records of temperatures inside of the boiler. As long as the wall temperatures are low, contact of the combustion gas may cause quenching of the combustion reactions, resulting in higher residual organic carbon load. Immediately after waste feeding, PCPh and PCDD/F are correlated to a higher degree than PCDD/F to PCBz. This suggests the importance of PCDD formation from precursors during elevated PCDD/F formation after start of waste feed. However, the catalytic activity of dust released from the waste burning seems to be crucial for PCDD/F formation: during warm up of the thoroughly cleaned boiler PCDD/F concentrations were low even as high PIC concentrations occurred.

To obtain more detailed information about possible formation pathways, congener patterns have been analyzed.

Tetrachlorodibenzodioxin and Tetrachlorodibenzofuran Patterns during Start-Up. According to Swerev's and Ballschmiter's pattern analyses of tetrachlorodioxins (Cl4DD) in MSWI crude gas and corresponding fly ash samples (*13*), the patterns mainly differ in 3 congeners. These are the 1,3,6,8-Cl4DD (D42), the 1,3,7,9-Cl4DD (D45), and the 1,3,7,8-Cl4DD (D44). Two types of patterns could be extracted either resembling the pattern yielded from the pyrolysis of 2,3-substituted chlorophenols or the pyrolysis of chlorophenols substituted in 2,6-position.

Some studies dealt with the explanation of the Cl4DD congener distribution from incineration processes as the product of interaction between formation and destruction processes under thermodynamic and kinetic aspects (*16*, *21*).

The start-up procedure and transiently disturbed combustion conditions show similarities: both cause memory effects and shifts in the homologues profiles (*1*, *6*, *8*, *18*). Therefore, we compared the congener patterns obtained during start-up when waste was fed to the patterns observed during a CO peak at another incinerator and to the patterns observed at normal (stable) operation conditions (Figure 3 a−c).

The Cl4DD isomer pattern of the sample when waste was fed was very similar to the pattern observed during disturbed combustion conditions (CO peak), although the samples were taken at different incinerators. Both patterns of samples from transient combustion conditions, however, contrasted with the pattern obtained at normal operating conditions. In both samples the 1,3,6,8-Cl4DD and the 1,3,7,9-Cl4DD dominated the isomer profile, whereas under normal operating condition the 1,3,7,8-Cl4DD (coeluting with 1,2,4,8- and 1,2,4,9-Cl4DD) dominated the profile. This result is consistent with thermodynamic calculations using computational molecular modeling methods. Basing on MOPAC calculations, Unsworth and Dorans showed 1,3,7,8-Cl4DD to be the most stable tetrachlorodioxin at 600 K (*22*) which was considered to match dioxin formation under the catalytic conditions of de novo synthesis.

Catalytic conversion of PIC has been shown to play a substantial role in PCDD/F formation in thermal processes. The fly ash catalyzed conversion of chlorophenols yielded 1,3,6,8- and 1,3,7,9-Cl4DD as the main tetrachlorodioxin congeners (*23*). Although both a copper catalyzed mechanism and the condensation of two 2,4,6-trichlorophenol molecules by radical reactions yield the same products, the authors favored the catalyzed mechanism.

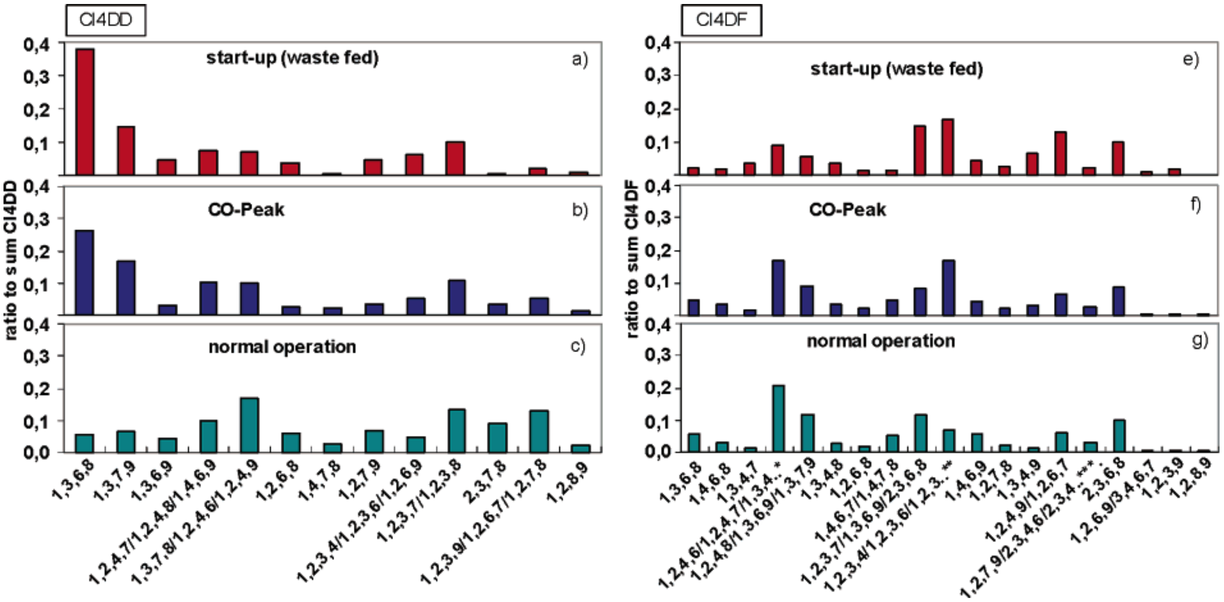

FIGURE 3. (a)−(f) Patterns of tetrachlorodibenzodioxins and tetrachlorodibenzofurans in the crude gas during start-up, at disturbed combustion conditions, and at normal operating conditions: *, includes 1,3,4,9/1,3,7,8; **, includes 1,2,3,8/1,6,7,8/2,4,6,7; *, includes 2,3,4,7/2,3,4,8/2,3,7,8.**

Changes in the dibenzofurans patterns are more complex and difficult to interpret, although there are differences between the pattern obtained during start of waste fed and CO peak on one hand, and the pattern at normal operation conditions on the other (cf. Figure 3 e−g). Further, a higher number of the PCDF isomers is coeluting than in the case of PCDD. For the full interpretation of the data and to obtain results which may give more information with respect to the reaction mechanisms which take place during PCDD/F formation in combustion processes, analysis of the isomer pattern of the other homologues groups will be necessary.

PCBz, PCPh, and PAH Profiles in the Crude Gas. During the start-up process not only were the concentrations of the other PICs observed (PCBz, PCPh, and PAH) different from normal operating conditions (cf. Figure 1) but also the PIC profiles (see Figures 3 and 4 in the Supporting Information).

At the start of the heat-up phase, the PCBz-profile showed much less Cl3- and more Cl6-Bz than the reference sample. With the increase of the combustion chamber temperature, the ratio of these two homologues groups was inversed. A shift again toward the Cl6-Bz then occurred at the start of waste feed. After the start of waste feed, the PCBz homologues profile gradually changed toward the profile observed under normal operating conditions.

The PCPh profiles during heat-up changed the opposite way: at low temperatures during heat-up the Cl1- and Cl2-Ph were increased whereas at the end of the heat-up process the relative amount of Cl4- and Cl5-Ph was higher. When waste was fed, the PCPh profile showed a significant change toward a profile containing more Cl1- and Cl2-Ph than under normal conditions. Like the PCBz profile, the PCPh profile then gradually approached the profile observed under normal operating conditions.

The rising amount of chlorine present might be an explanation for the shift toward a higher degree of halogenation of the PCBz at the start of waste feed. However, for the PCPh, this explanation does not hold. Both PIC groups have in common that at high total concentrations the low chlorinated homologues dominate the profile.

A marked difference between PCBz, PCPh, and the PCDD/F homologue profiles is the fact that the latter stayed changed for a longer period of time than the patterns of the PCBz and the PCPh profiles.

During the phase of heat-up, the PAH pattern was dominated by phenanthrene and was very different from the PAH patterns observed at normal operation conditions (see Figure 4 in the Supporting Information). After the start of waste feeding, the pattern switched and PAH with more than 3 nuclei dominated the pattern for several hours. The PAH with more than 3 nuclei (masses > 200 amu) are increased at the same time period in which elevated PCDD/F concentrations could be observed. These observations are consistent with observations during "memory-phases" after transient combustion conditions (*18*).

3.1.2 PCDD/F and PIC in Fly Ash and Boiler Ash. As mentioned before, one aim of our study was to evaluate the overall impact of shut-down and start-up conditions, thus including PCDD/F concentrations in the boiler ashes and filter dusts. In addition to PCDD/F concentrations in the ESP ash, we analyzed PCBz and PAH concentrations in the ESP ash.

During the start-up procedure, samples from ESP ash and boiler ash were taken simultaneously to the gas-phase samples. After waste was fed, PCDD/F concentrations in the fly ash (ESP ash) as well as in the crude gas (cf. Figure 1 and Table 2 in the Supporting Information) were increased by 1 order of magnitude and stayed elevated for at least 6 h. As boiler ash PCDD/F concentrations vary depending on the section of the boiler being rapped at the sampling interval, no significant changes could be detected during the start-up procedure.

Figure 4 shows the PCDD/F concentrations of the crude gas, the ESP ash, and the boiler ash as values relative to the average of 5 reference samples (horizontal line at level 1).

As mentioned before, no statistically significant changes could be detected during the start-up procedure in the boiler ash. All detected PCDD/F concentrations in the boiler ash are around the reference level.

Homologue Profiles of the PCDD/F in the ESP Ash. Because no ESP ash was collected during the heat-up phase, only the patterns of samples collected after start of waste feeding could be compared to the crude gas profiles. Figure 5 a−f represents the PCDD/F homologue profiles of the ESP ash samples taken simultaneously to the crude gas samples.

The PCDD profiles observed at the ESP ashes both of the reference samples and of the samples collected during start-

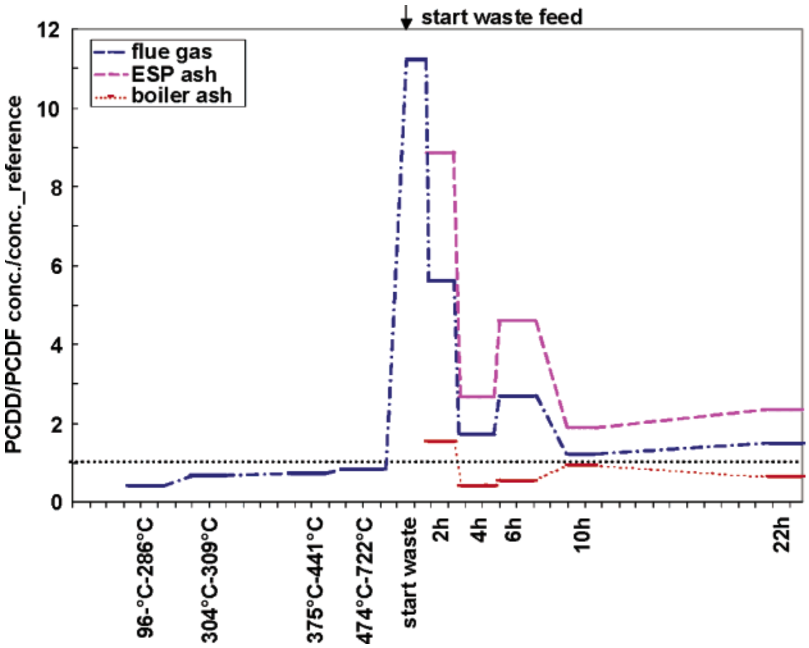

FIGURE 4. PCDD/F-concentrations in the crude gas, ESP ash, and boiler ash in relation to reference samples (no ash available before start of waste feed; PCDD/F concentration as the averages over the sampling periods).

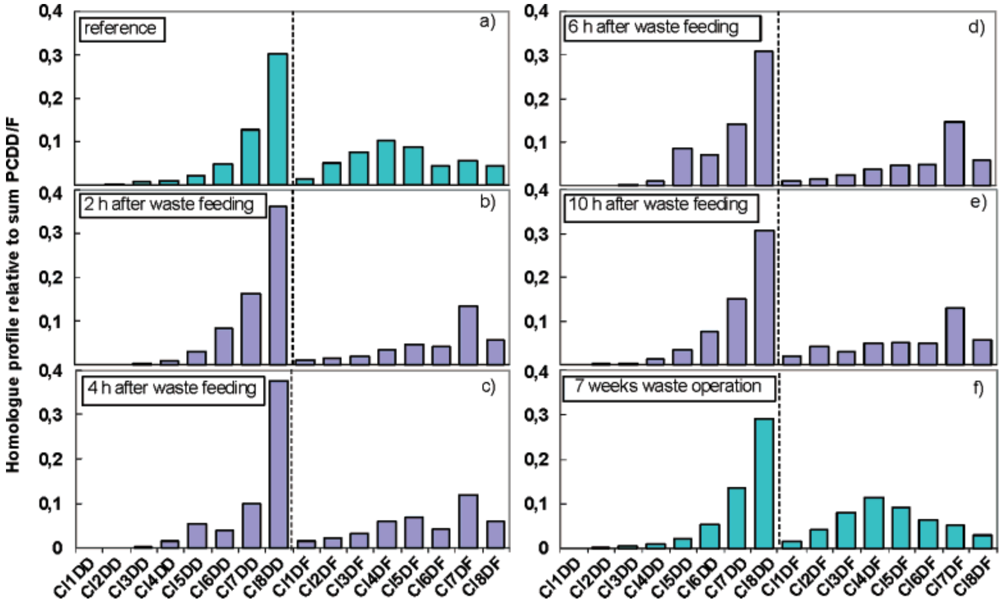

FIGURE 5. (a)—(f) PCDD/F homologue profiles in ESP ash during and after start-up.

up were dominated by Cl7- and Cl8-DD, which is in clear contrast to the crude gas samples. Only small changes in the ESP ash PCDD patterns could be observed during start-up, whereas the ESP ash PCDF profiles showed a shift toward Cl7- and Cl8-DF similar to the profiles of the crude gas samples.

The PCDF/PCDD ratio of the ESP ash decreased a little during the start-up process and stayed lowered for a period of at least 1 day. These changes corresponded to the changes observed in the crude gas. However, even at normal operation conditions, the ESP ash PCDF/PCDD ratio was much lower than the ratio observed in the gas phase.

The difference between the homologue profiles of crude gas and ESP ash samples clearly show the lack of equilibrium between gas and solid phase of the flue gas aerosol.

PIC Profiles in the ESP Ash. The profiles of the PCBz homologues and the PAH pattern are shown in Figure 5 of the Supporting Information. In contrast to the reference samples PCBz profile, the profile during start-up is dominated by highly chlorinated PCBz. This observation is consistent with the observations we made in the gas phase (cf. Figure 4 in the Supporting Information). Within 22 h after waste was fed, we observed a slow change in the PCBz profile back to the reference profile.

A similar behavior regarding the change in the PAH pattern after waste was fed was detected (see Figure 5 b in the Supporting Information).

It could be observed that the "memory effects" after plant start-up, as one transient combustion condition, affected not only the concentrations and profiles of PCDD/F and other PIC in the crude gas, but also the concentrations in the ESP ash. For the boiler ash, a similar effect could not detected. The start-up procedure did not affect the concentrations and patterns of the boiler ash. Between the homologue and the congener patterns from normal operating conditions and the start-up procedure, a clear change was recognized. This holds true both for the flue gas and for the ESP ash. Whereas under normal operating conditions, the 1,3,7,8-Cl4DD dominated the profile, the 1,3,6,8-Cl4DD and 1,3,7,9-Cl4DD dominate the isomer profile during transient combustion conditions (start-up procedure and CO-peak). This points possibly to a shift from the dominant de novo formation to the precursor formation pathway.

Thorough boiler cleaning, use of inert additives, and control of the ESP temperature have shown to be favorable to minimize PCDD/F formation during start-up. To evaluate in detail if there is a possible switch in PCDD/F formation mechanism between "normal operating" and transient combustion conditions, as the changed congener pattern in this study indicated, laboratory tests are necessary. At a full-scale incinerator, the operating parameters, such as composition of the fuel with varying concentration and catalytic activity, sorption and memory effects with varying temperature and residence time, could not be clearly defined and were uncertain. Considering this fact, it is very difficult to get confident mechanistic insight from such data. To clarify the question concerning the PCDD/F formation mechanism during transient combustion conditions, the uncertain and complex parameters from full-scale incinerators have to be reduced to easily and well-defined operating conditions in a laboratory-scale experiment, and the resulting patterns of the organic pollutants have to be analyzed.

3.2 Plant Shut-Down. The shut-down of a MSWI plant can be divided into two successive phases, i.e., a first phase (a) corresponding to the time interval between stopping the waste feed until the moment when the back-up burners are fired. The second phase (b) lasts from the start of back-up burner operation until the residual waste has been burned on the grate. Each phase lasted approximately one and a half hours. Samples were taken during the shut-down procedure in both phases. In addition to the PCDD/F-concentrations in the gas-phase, the concentrations of the PAHs with more than 3 nuclei, the PCBz (Cl2−Cl6), and the PCPh (Cl1−Cl5) were determined. Prior to the shut-down, reference samples had been taken on several days under normal operating conditions. The results are given in Table 3 of the Supporting Information. During the shut-down procedure, PCDD/F, PAH, and chlorobenzene concentrations in the crude gas were within the range observed during normal combustion conditions. The chlorophenol concentrations, however, were somewhat lower. The crude gas HCl concentration was between 500 and 800 mg/m^3 before the waste feed was stopped. The concentration went down to 200 mg/m^3 within phase (a) and then it dropped to 60−70 mg/m^3 during back-up burner operation. Throughout phase (b) the HCl concentration remained above 45 mg/m^3 probably due to releases from chloride-containing deposits. Obviously, the amount of chlorides deposited on the walls and on the heat exchanger tubes was sufficient to produce appreciable amounts of chlorinated compounds even if HCl concentrations in the gas had dropped to quite low values.

Similarly to the PCDD/F concentrations in the crude gas, the PCDD/F loads of the ESP ash and the boiler ash were not affected by the shut-down procedure in a significant way.

It should be mentioned that the elevated crude gas PCDD/F concentrations during start-up do not imply that stack gas emissions are exceeding the legal emission limit. The flue gas cleaning devices of modern MSWI plants are able to manage even high peaks in crude gas PCDD/F concentrations, and currently MSWI PCDD/F emissions are far below the 0.1 ng TEQ/m^3 standard, even when continuously monitored.

However, concerning the results of this study, it could be demonstrated that the start-up process constituted an important source of increased PCDD/F concentrations in the exhaust gases as well as in the filter dusts, like ESP ash. To keep the overall PCDD/F concentration from incineration processes as low as possible, the following recommendations could be given from the results of this study: (a) As primary measures, starts and stops at MSWIs in general should be minimized, and during start-up all flue gas cleaning equipment should be running. Back-up burner operation has to be optimized to have minimum PIC formation. Operation conditions, such as the ESP temperature, have to be accounted for minimizing the PCDD/F emissions from incineration processes. As secondary measures, the application of adsorption materials in the early stage of the start-up process are capable of minimizing the organic pollutants in the exhaust gases. Regarding the PCDD/F load in the ESP ash, we can gather from our examinations during the heat-up procedure that ESP ashes from start-up procedures should be selected for an extended period of time and treated, e.g., by re-burning.

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Supporting Information Available

Tables of analytical results, a scheme of the plant indicating sampling locations, and additional figures showing the changes in PCDD/F key ratios and PIC profiles from gas phase and ash samples. This material is available free of charge via the Internet at http://pubs.acs.org.

Abbreviations

CC temp.	combustion chamber temperature
ESP	electrostatic precipitator
HRGC−HRMS	high-resolution gas chromatography−high-resolution mass spectrometry
I-TEQ	"International" toxicity equivalents (NATO−CCMS)
MOPAC	molecular orbital calculations package
MSWI	municipal solid waste incineraort
NO_x	nitrogen oxides ($NO + NO_2$)
PAH	polycyclic aromatic hydrocarbons
PCBz	(poly-)chlorobenzenes
PCDD	polychlorinated dibenzo-*p*-dioxins
PCDF	polychlorinated dibenzofurans
PCDD/F	sum of PCDD and PCDF
PCPh	(poly-)chlorophenols
PIC	products of incomplete combustion
SIM	selected ion mode
STP	standard temperature and pressure

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