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Distribution of Mono to Octa-chlorinated PCDD/Fs in Fly Ash from a Municipal Solid-Waste Incinerator

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We have estimated the concentration and distribution of the mono to octa-chlorinated congeners of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) in fly ashes at various sampling points in a large-scale municipal solid waste incinerator at Umeå, Sweden, as they cooled from 700 to 170 °C. Differences between the ashes were observed, the PCDD homologue profile was found to vary with temperature. The total amount of PCDD and PCDF increased as the temperature decreased in the postcombustion zone. The increase was due to both adsorption to the fly ash and formation of PCDD and PCDF. Mono- to trichlorinated PCDD predominated at high temperatures, whereas hepta- and octachlorinated PCDD predominated at temperatures below 400 °C. PCDF predominated over PCDD in the whole temperature range. However, the changes in homologue profile for PCDF were minor. The isomer distribution within the homologue groups was not changed as the temperature decreased in the postcombustion zone.

Introduction

Previous studies of emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) from full-scale municipal solid waste (MSW) incinerators have concluded that emissions to air are small, and that most of the tetra- to octa-chlorinated PCDD/F species are concentrated in the solid residues, such as fly ash and flue gas cleaning products (1–3). These residues must then be remediated or deposited in landfill sites. It has also been shown that the concentrations of tetra- to octa-chlorinated PCDD/F compounds in both flue gases and fly ash increase at the lower temperatures of the postcombustion zone (2, 4–8), and that fly ash can act as a catalyst for the formation of these species (9, 10).

There are four hypotheses regarding the mechanisms of formation of PCDD/F: (i) pyrosynthesis, (ii) de novo synthesis, (iii) formation from precursors, and (iv) chlorination/dechlorination. The second and third mechanisms are generally considered the most likely, and pyrosynthesis the least. Similarities between the distribution patterns and concentrations of the PCDD/F species formed have been cited in support of both the de novo (ii) and the precursor (iii) theories.

Although de novo synthesis has been defined as formation of PCDD/F from residual carbon, chlorine, and oxygen (10, 11), it is more accurately described as a series of

decomposition reactions in the carbon matrix. Iino et al. (11) have shown that PCDF congeners can be formed from polycyclic aromatic hydrocarbon species (PAHs), and have suggested that chlorination and oxygenation of preformed aromatic fragments may be one of the pathways in de novo PCDF synthesis.

Although the formation of PCDD from macromolecular carbon has been shown to proceed partly via chlorophenol intermediates, pathways to PCDF species do not generally appear to involve chlorophenol or chlorobenzene precursors, but rather biphenyls (12). These observations imply that the de novo and precursor pathways may be closely related (12, 13), and the traditional distinction between the two is becoming blurred (14, 15).

A chlorination mechanism for PCDD formation has been shown to predominate over de novo synthesis at the relatively low temperatures of the postcombustion zone of MSW incinerators (7), where both chlorination and dechlorination are known to occur (16). Wikström et al. have also demonstrated that different reactions involving dibenzo-*p*-dioxins and dibenzofurans can also make substantial contributions to the formation of PCDD/F species (16, 17).

The distribution of positional isomers for each PCDD/F homologue has been shown to be independent of combustion conditions such as temperature and gas velocity (17–21). However, both the overall conversion of dibenzo-*p*-dioxins and dibenzofurans (DD/DFs) and the degree of chlorination do vary significantly with temperature and gas velocity (19). Chlorination of lightly chlorinated congeners (17) and dechlorination of highly chlorinated congeners (22) have also been proposed as mechanisms that might influence PCDD/F isomer distributions.

To the best of our knowledge, there has been no previous analysis of the lightly chlorinated (mono to trichlorinated) congeners of PCDD/F in fly ash from a full-scale MSW incinerator, or of PCDD/F in fly ash from such a plant sampled at temperatures exceeding 500 °C. The objective of this study was to map the concentrations and distribution of mono to octa-chlorinated PCDD/F isomers in fly ashes collected from three various points in a full-scale MSW incinerator as they cooled from 700 to 170 °C.

Experimental Section

The fly ash used in this study was from the Däva combined heat and power plant, Umeå Energi, Umeå, Sweden, collected at three points (Figure 1). The plant has an incinerator with an effect of 65 MW and a capacity of 20 tonnes h⁻¹. NH₃ is added to decrease NO_x levels and active carbon and Ca(OH)₂ are added before the fabric filter. During the day, the ashes were collected the combustion conditions were the following; O₂ in the economizer varied between 6 and 8%, an average of CO ~20 mg/Nm³ (dry gas, 11% O₂), an average of HCl ~600 mg/Nm³ (dry gas, 11% O₂), H₂O varied between 16 and 17% before the textile filter. The temperature in the combustion chamber was ~1100 °C.

The ashes are individual samples and were collected during the same day but not simultaneously, and approximately 1 kg of ash was collected from the bottom of the superheater, a hopper in the heat exchanger and from the fabric filter. Ash A-700 was obtained from a point where the temperature of the flue gases exceeded 700 °C, ash B-350 from a cooler zone (300–400 °C), and ash C-170 from a textile filter with a working temperature of approximately 170 °C. The temperatures referred to are the temperature in the flue gas, which is measured continuously. However, the tem-

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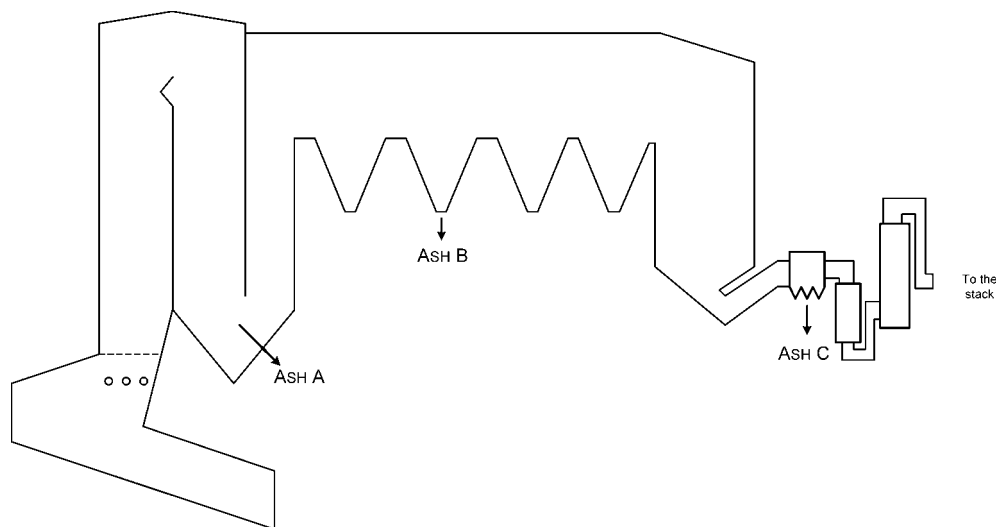


FIGURE 1. Schematic diagram showing ash collection locations.

TABLE 1. Characteristics of Ashes A, B, and C

	Ash A (>700 °C)	Ash B (400–300 °C)	Ash C (~170 °C)
DS ^a	99.8	99.5	98.8
C ^b	1.2	4.4	6.7
Cl ^b	0.93	2.1	4.3
SiO ₂ ^b	39.4	33.6	21.1
CaO ^b	19	22.1	28.2
Fe ₂ O ₃ ^b	5.56	4.74	2.88
S ^c	26500	21300	28100
Zn ^c	9940	1170	21300
Pb ^c	1170	1180	2540
As ^c	93.6	121	247
Cd ^c	25.4	43.6	142
Hg ^c	0.022	0.188	5
Cu ^c	1160	792	917

^a %; DS = dry substance. ^b % DS. ^c mg/kg DS.

perature from where ash A-700 and B-350 is taken is estimated because there are no measurements available from the exact sampling location. The fuel used was municipal solid waste and it consisted in rough terms of paper (newspaper, cardboards, wrapping papers, writing papers, paper sacks and soft papers) 18.1%, diapers 7.9%, plastic (soft, hard and wrapping) 8.1%, laminate (milk packages, butter packages and metal laminates) 4.1%, textile (textile, rubber and leather) 2.1%, glass 2.2%, kitchen sweepings 49.2%, remaining combustible 3.5%, metal 2.6%, remaining incombustible 1.5%, and hazardous waste 0.4%. The data are specified wet weight percentage.

Ashes were analyzed both for inorganic components and PCDD/F congeners. The inorganic analyses were performed by Analytica AB, Luleå, Sweden, and Bränslelaboratoriet Umeå AB, Umeå, Sweden, and the characteristics of the ashes are presented in Table 1. The major differences between the ashes were the content of C, Cl, Zn, and Hg. The high concentrations of Zn and Hg in ash C-170 is due to condensation of volatile metals and shows that the filter is successful in removing these metals from the flue gas. The PCDD/F analysis was performed at the Department of Chemistry, Umeå University. For the PCDD/F analysis two extraction methods were used: pressurized liquid extraction (PLE) using an ASE 200 system (Dionex, Sunnyvale, CA) equipped with 10 mL stainless steel cells according to EPA standard method 3545A), and Soxhlet extraction. The Soxhlet extraction was performed on two of the samples and the third sample was extracted with PLE. Prior to extraction the ash was homogenized.

The procedure for the PLE extractions was as follows: each cell was filled with approximately 4 g of ash and topped up with Na₂SO₄ before being sealed. The cell was then heated to a preset temperature of 150 °C for 7 min while a solvent mixture of glacial acetic acid in toluene (5% v/v) was pumped through it. After three of these extraction cycles, the extract obtained was concentrated, ¹³C-labeled internal standard was added, and it was divided into three portions (50:25:25). The internal standard consisted of the following ¹³C-labeled isomers: 2-MoCDD, 2,3-DiCDD, 2,3,7-TriCDD, 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2-MoCDF, 2,8-DiCDF, 2,4,8-TriCDF, 2,3,7,8-TeCDF, 1,2,3,7,8- and 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-, 1,2,3,6,7,8-, 1,2,3,7,8,9- and 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8- and 1,2,3,4,7,8,9-HpCDF, and OCDF.

In the Soxhlet extraction procedure, samples weighing approximately 3 g were thoroughly mixed with toluene-washed sand (20 g). After the addition of acetic acid (15 mL) and ¹³C-labeled internal standard, Soxhlet extraction with toluene (400 mL) was carried out for a total of 48 h, and the extract obtained was concentrated and divided into three portions (50:25:25). No differences were revealed between the extraction methods. Thus, mean values were calculated from both the extraction methods.

Analysis of PCDD/F follows EU standard methods 1948: 1–3 with small differences in the exact identity of the labeled standards used and the use of AX21-carbon. Samples were cleaned-up for the PCDD/F analyses by transferring 50% of each extract into a multilayer silica column, then eluting with *n*-hexane (30 mL) onto a super alumina column. This was eluted, in turn, with dichloromethane/*n*-hexane (60 mL, 1:1 v/v). The eluate was concentrated, purified further using a column containing a prewashed mixture of AX21-carbon and Celite (7.9:92.1 w:w), and then eluted sequentially with 40 mL of *n*-hexane (fraction 1) followed by cyclohexane: dichloromethane (1:1 v/v, fraction 2) and toluene (fraction 3). A ¹³C-labeled recovery standard (1,2,3,4-TeCDD, 1,2,3,4,6-PeCDF, 1,2,3,4,6,9-HxCDF, and 1,2,3,4,6,8,9-HpCDF) was added to fraction 3, (containing the PCDD/F), and this fraction was concentrated to a volume of 40 µL in tetradecane. The concentrations of the PCDD/F congeners were determined by gas chromatography-high resolution mass spectrometry (GC-HRMS), using an Autospec system (Fisons Instruments). For a more detailed description, see Liljelind et al. (23). The internal standards have been complemented with the ¹³C-labeled congeners 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF. The recoveries for the lightly chlorinated

TABLE 2. Concentrations of Mono up to Octa-chlorinated PCDD/Fs (pmol/g ash) in Ashes A, B, and C

	Ash A	Ash B	Ash C
total amount PCDD/F	31	205	641
PCDD	5.1	50	110
PCDF	26	155	531
Σ MoCDD	1.2	1.2	2.2
Σ MoCDF	2.3	10	42
Σ DiCDD	1.3	2.7	5.1
Σ DiCDF	4.1	20	90
Σ TriCDD	1.0	3.9	11
Σ TriCDF	9.6	65	205
Σ TeCDD	0.51	2.9	8.2
Σ TeCDF	4.8	20	87
Σ PeCDD	0.35	3.7	9.7
Σ PeCDF	2.7	15	53
Σ HxCDD	0.25	4.2	9.9
Σ HxCDF	2.0	12	32
Σ HpCDD	0.25	8.9	21
Σ HpCDF	0.44	7.0	14
OCDD	0.24	23	43
OCDF	0.31	5.9	8.4

PCDD/F were between 55 and 86% and for the highly chlorinated 60 to 98%.

Results

The concentrations of the PCDD/Fs in these ashes are presented in Table 2 and Figure 2. There were substantial differences in the distributions of PCDD/F homologues between the ashes. The distribution of the isomers within the homologue groups did not vary with temperature. The concentrations of mono to octa-chlorinated PCDD/Fs and the "toxic equivalents" (WHO-TEQ) were lowest (31 pmol/g and 0.1 ng WHO-TEQ/g, respectively) in the ash collected at the highest temperature (>700 °C). As the temperature fell in the postcombustion zone to 300–400 °C (see Table 2), the total concentration of PCDD/F congeners and the WHO-TEQ value increased to 205 pmol/g and 0.6 ng WHO-TEQ/g, respectively, whereas the corresponding values for the filter ash were 641 pmol/g and 1.8 ng WHO-TEQ/g, respectively.

PCDF congeners were present in higher concentrations than PCDD species in all ash samples, comprising 83, 75, and 83% of the total PCDD/F components of ashes A-700, B-350, and C-170, respectively (Table 2). The major PCDD isomers were the mono-, di and trichlorinated species in the high temperature ash, A-700, but their relative proportions fell and the proportions of the highly chlorinated species rose as the temperature declined and, consequently, HpCDD and OCDD species were the most abundant in the low temperature ash, C (Table 2).

In the ash from the highest temperature sampling zone, mono-, di-, and trichlorinated isomers was the predominant PCDD species (57%; Figure 2). At the lower temperatures of the postcombustion zone, two changes were observed: the relative proportions of PCDD species increased, and the component profile changed radically, with HpCDD and OCDD species becoming the major species, accounting for ca. 60% of the total PCDD content (Figure 2) in ash B-350 and C-170. The concentrations of mono-, di-, and trichlorinated PCDD congeners also increased (Table 2), but they collectively constituted about 15% of the total PCDD species at medium to low temperatures (Figure 2). The total concentration of PCDD increased 22-fold as the temperature decreased from >700 to 170 °C.

The most abundant PCDFs were the TriCDF species, followed by the tetra- to hexa-chlorinated PCDFs, and the hepta- and octa-chlorinated PCDFs were least abundant, in

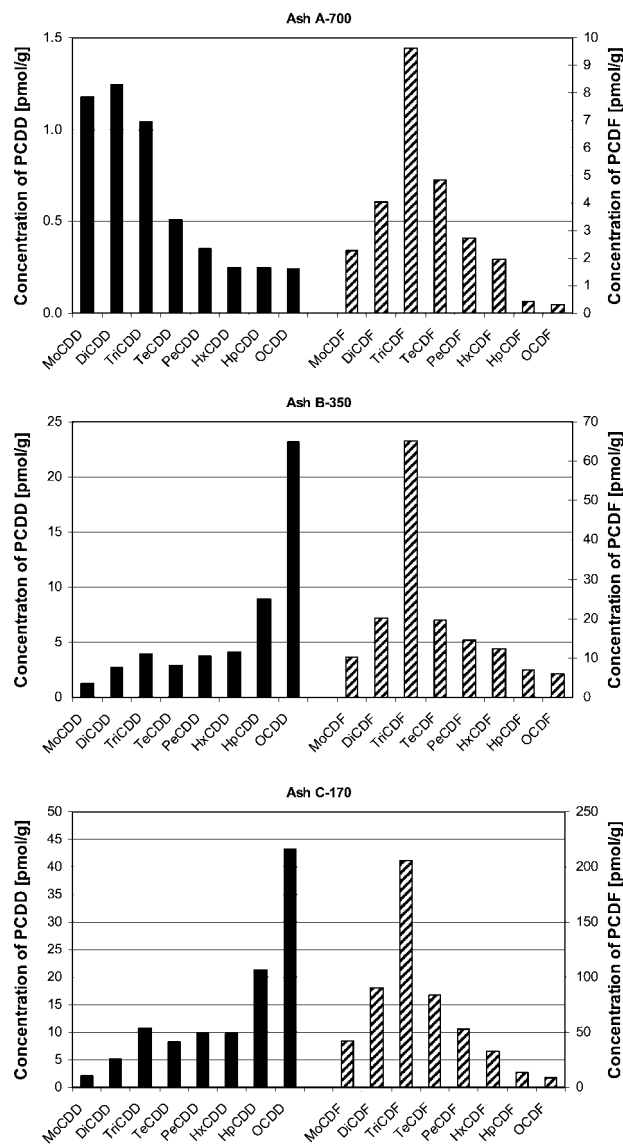


FIGURE 2. Homologue distribution patterns of mono up to octa-chlorinated PCDD and PCDF in ashes (a) A-700, (b) B-350, and (c) C-170.

all three ashes (Figure 2). The congener pattern for PCDF was practically unchanged when the temperature decreased in the postcombustion zone. However, there were indications of that the contribution of each congener group changed somewhat (Figure 2). The largest change was seen for HpCDF and OCDF, their proportions increased slightly. In addition, the total concentration of PCDF species increased 20-fold as the temperature decreased from over 700 to 170 °C.

The increases in the concentrations of the mono and dichlorinated PCDFs were greater than those of the mono- and dichlorinated PCDDs, the trichlorinated PCDD and PCDF isomers showed similar increases in concentration, whereas levels of the dioxins increased more than those of the furans among the more highly chlorinated tetra- to octa-chlorinated species.

The isomer patterns of specific homologues did not vary much with temperature generally (although differences may not have been evident due to the relatively small sample sizes). However, particular isomers seemed to be favored for some homologues. For the results presented below, all concentrations of the isomers can be seen in the Supporting Information.

Table 3 shows the dominant isomers for each PCDD and PCDF homologue, and their percentage contributions to the

TABLE 3. Major Isomers within Each Homologue Fraction (%) for Ashes A-700, B-350, and C-170

congener	isomer	Ash A-700	Ash B-350	Ash C-170
MoCDF	3-	39	42	38
MoCDD	2-	82	85	85
DiCDF	27- > 36-, 28- > 37- > 24- > 17- > 18- > 23-	72	75	75
DiCDD	27-, 23-, 28- > 13-	84	64	74
TriCDF	137- > 236- > 138- > 234-, 238- > 127- > 124-, 167-	50	48	52
TriCDD	237-, 146- > 138- > 137-	74	65	62
TeCDF	1378-, 1379- > 1268-, 1478-, 1467- > 1247- > 1236-, 1238-, 2468- > 1237-, 1369-	47	42	45
TeCDD	1378- > 1237-, 1238- > 1368- > 1247-, 1248-, 1369- > 1469-, 1278- > 1239- > 2378- > 1379-	70	80	79
PeCDF	12368-, 13479- > 12378- > 23479- > 12478- > 12479-, 13467- > 12347-, 23469- > 13468-	51	54	58
PeCDD	12468-, 12479- > 12368- > 12378- > 12379-	52	63	64
HxCDF	134678-, 124678- > 123467-, 123478- > 234678- > 123678-	70	75	75
HxCDD	123678- > 123679-, 123689-	43	41	37
HpCDF	1234678-	68	80	79
HpCDD	1234679-	61	54	54

total concentration of the respective homologues. For mono to octa-chlorinated PCDD, the distribution was as follows: the 2,3-, 2,7-, and 2,8-DiCDD isomers that coeluted predominated among the DiCDD species, and 2,3,7- and 1,4,6-TriCDD, also coeluting, were predominant among the trichlorinated dioxin isomers. Seven tetra-chlorinated dioxin isomers were present in particularly high concentrations and among the PeCDD species, five isomers accounted for more than half of the total concentration. Coelution of the various HxCDDs made the isomer patterns more difficult to distinguish than for PeCDDs, although 1,2,3,4,6,8-, 1,2,3,6,7,9-, and 1,2,3,6,8,9- isomers appeared to predominate. The two HpCDD isomers were present in roughly similar concentrations.

Among the monochlorinated furans, 3-MoCDF was present in the highest concentration and eight isomers predominated the DiCDF. Five isomers of the trichlorinated furans were favored. Although it was more difficult to pinpoint all of the predominant isomers of the tetra-chlorinated furans (due both to the large number of isomers and to complications caused by their coelution), 1,3,7,8- and 1,3,7,9-TeCDF appeared to be present at the highest concentration. On the other hand, among the penta-chlorinated species, certain isomers were clearly favored. The pattern for HxCDF (as for the HxCDD variants) was more difficult to distinguish than for the PeCDF species due to coelution of isomers.

Discussion

Our results, in accordance with previous findings (2, 4–8, 24), clearly show that the total concentrations of PCDD/F species increase in fly ash as the temperature in the postcombustion zone decreases to 170 °C, the working temperature of the fabric filter, (see Table 2). The increase in concentration is most likely a combination of adsorption to the ash and formation on the particles. Ash B-350 and C-170 had longer contact time with the flue gas compared with ash A-700, and therefore had more time to adsorb PCDD and PCDF. In addition, formation of PCDD and PCDF is favored in the temperature interval 250–450 °C.

Moreover, PCDF species predominate over PCDD species in a temperature-independent fashion and this could be an indication of that phenol condensation is an important formation mechanism (25). In the present study, we have analyzed the lightly chlorinated (mono- to trichlorinated) congeners of PCDD and PCDF, which have not been reported before and made the additional observation that mono-, di-, and trichlorinated PCDF isomers were present in higher concentrations than the hexa-, hepta- and octa-chlorinated isomers in the whole temperature interval. For the PCDD,

mono-, di-, and trichlorinated congeners were the most abundant PCDD isomers at high temperatures. Because of the high temperature, chlorination is not a probable formation pathway because very low concentrations of Cl₂ is present and therefore possible formation pathways could be phenol condensation and/or dechlorination of more highly chlorinated PCDD since dechlorination and destruction of PCDD/F is favored over formation at high temperatures. At lower temperatures (400– 300 °C) of the postcombustion zone, a shift in the homologue pattern for PCDD was observed and the contributions of tetra- up to octa-chlorinated PCDDs to the total concentration increased, which may be explained by adsorption of gas phase PCDDs onto the fly ash. Littaru (26) found that the heavier congeners in the tetra- to octa-range tended to accumulate on the ash. Moreover, the affinity of PCDD and PCDF congeners for fly ash varies across the whole mono to octa-chlorinated PCDD/F range, and the ratio of gas phase to particle bound PCDD and PCDFs is strongly affected by the temperature, vapor pressure, particle density and size distribution, and other particle properties. PCDD and PCDFs are classified as semivolatile compounds, with vapor pressures for most congeners of between 1×10^{-2} to 1×10^{-6} Pa at ambient temperatures. However, the vapor pressure is highly temperature-dependent, and can exceed 1×10^{-2} Pa at high temperatures, which increases the likelihood of PCDD and PCDF species being present in the gas phase rather than adsorbed on particles. In the temperature range of 250 to 125 °C, the vapor pressure decreases by a factor of approximately 1000, enabling both adsorption of PCDD and PCDF species onto ash and particle-mediated formation and/or chlorination/dechlorination. However, at temperatures slightly above 400 °C, the Deacon process for converting HCl to Cl₂ exhibits a rate maximum (27). This implies that chlorination could be one formation pathway in this temperature interval. This might partly explain the increase in Hp-OCDD/F contents of the ash at the lower temperatures of the postcombustion zone. The same shift but from the tetra- to the octa-chlorinated PCDD was observed by Düwel et al. (28). However, the shift occurred at a lower temperature than observed here.

The homologue profile was not as temperature-dependent for PCDF as the PCDD congeners (Figure 2), which points to different mechanisms of formation for these species. The increase in the concentration of the sum of all PCDD species was greater than the corresponding increase of all PCDF species at the lower temperatures of the postcombustion zone. We also observed that concentrations of mono-, di-, and trichlorinated dibenzofurans increased more than the

corresponding mono-, di-, and trichlorinated dibenzo-*p*-dioxins in this zone. Tetra-chlorinated PCDF and PCDD concentrations increased by approximately equivalent proportions, while for higher chlorinated species the dibenzo-*p*-dioxins increased more than the corresponding dibenzofurans. This also indicates that there are different formation mechanisms for PCDDs and PCDFs. The increase of PCDF:PCDD ratio between ash B-350 and ash C-170 from 3.1 to 4.8 could be assigned to a chlorination of the dibenzofurans molecule.

Combustion conditions, such as the temperature in the combustion zone and gas velocity, have substantial effects on the amounts of PCDD and PCDFs formed, and their degree of chlorination (7), but not the distribution of isomers within homologous series of PCDD/Fs (17–21). Thus, the distribution patterns of the isomers vary much less with combustion conditions than the distribution of the homologues themselves (29). However, the distribution of isomers within the homologue groups has been found to be dependent on many factors in the postcombustion zone, including (inter alia) the temperature (30), interaction time between gas and particles (31), available precursors (29), and presence of metals like CuCl₂ (32).

From the isomer pattern for each homologue group, it was indicated that several formation mechanisms contribute to the final distribution of PCDD and PCDF. Judging by the isomer patterns found in flue gases, chlorination seems to be an important pathway in the formation of PCDFs (33), whereas condensation of polychlorinated phenols seems to be the major route for formation of PCDDs. Various studies on the formation of PCDD/F from chlorophenols have shown that ashes with various characteristics may catalyze the dechlorination of polychlorinated phenols (PCPs) and/or PCDD/Fs, giving rise to PCDD/F isomer patterns different to those expected from a given mixture of PCPs (34). It is also known that dechlorination can occur at low temperatures (9), so this mechanism also probably contributed to the congener pattern of PCDD/Fs in our ash samples from the postcombustion zone.

Acknowledgments

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Supporting Information Available

A table with the concentration of all congeners (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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