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Addink, R.; Cnubben, P.A.J.P.; Olie, K.

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FORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFLUORANS ON FLY ASH FROM PRECURSORS AND CARBON MODEL COMPOUNDS

R. ADDINK, P. A. J. P. CNUNBEN and K. OLE

Department of Environmental and Toxicological Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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Abstract—In this article the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) on waste incinerator fly ash is described. Model experiments were performed by heating organic-C-free fly ash with organic model compounds. Both chlorobenzenes and phenol form PCDD and PCDF via condensation reactions. Phenol is 10–540 times as reactive as the chlorobenzenes. A second (and separate) formation pathway is from oxidative breakdown of macromolecular carbon. This route was studied with hexane, toluene and three anthraquinone derivatives as carbon model compounds. Aliphatic, monocyclic aromatic and functionalized quinone parts of carbon may all contribute to PCDD and PCDF formation, but the latter pathway appears to be the most important. Functional groups play an important role in the potential of these various carbon parts to form PCDD and PCDF.

Key Words—Carbon model compounds, fly ash, functional groups, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, precursors.

1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are toxic compounds present in emissions from, among others, the paper industry[1], steel production[2] and waste incineration[3]. The structure and nomenclature of these compounds is given in Fig. 1. Formation in waste incineration facilities takes place in the post combustion zone at temperatures ranging from 200 to 600°C[4]. Residue particles (fly ash) are carried together with the off-gas into this low-temperature area of the incinerator, in which the gases are cooled down and passed through an air pollution control device before being emitted from the stack. Fly ash contains macromolecular carbon (called residual carbon)[5], various small organic compounds[6], chlorine atoms and metal ions[7], which are the basic ingredients for formation reactions. PCDD/PCDF formation proceeds through a heterogeneous catalyzed mechanism taking place on the fly ash surface[8].

In the literature two separate pathways have been postulated for fly ash catalyzed PCDD/PCDF formation: (i) small organic compounds (precursors) yield PCDD/PCDF and (ii) oxidative breakdown of residual carbon generates PCDD/PCDF. The precursors from mechanism (i) can be either already present on the fly ash surface or are adsorbed from the gas phase. An example of this category is condensation of chlorophenols to give almost exclusively PCDD[9]. Propene is another reactant in this category, which recently has been identified as being capable of formation of both PCDD and PCDF on fly ash[10]. Obviously a more complex set of reactions than with chlorophenols is involved, e.g. C-C bond formation, aromatization and chlorination.

Mechanism (ii) for PCDD/PCDF formation on fly ash is called "de novo synthesis" and involves macromolecular residual carbon structures. The percentage of residual carbon present on fly ash can be up to around 7%[5]. Oxidative breakdown of this carbon results in a great variety of compounds, including PCDD/PCDF, and chlorination precedes fragmentation of the residual carbon structure[11]. These reactions are catalyzed by Cu and Fe ions[12]. Some experiments suggest that the basic DD and DF structures already exist within the residual carbon and are released upon oxidative breakdown[13]. The chemical structure of the residual carbon naturally
present on fly ash is not known, but when removed from the fly ash and replaced by activated carbon, PCDD/PCDF formation readily occurs[14]. This suggests that the residual carbon on fly ash may have some properties in common with activated carbon. Soot contains almost equal amounts of carbon atoms in linear and in aromatic parts[15]. Carboxyl- and carboxyl-groups are present in other forms of carbon, like carbon black[16]. Residual carbon on fly ash may contain both aliphatic and aromatic fractions and also functional groups like CO, COOH and OH.

Whether these two formation routes are separate pathways in real incinerators depends on the degradation products formed from oxidative breakdown of residual carbon on fly ash. Oxidation of residual carbon generates, among others, chlorophenols [5]. If these compounds are formed at sufficiently high concentrations to give condensation reactions yielding PCDD, the route residual carbon→chlorophenol→PCDD exists. This seems indeed to be true for PCDD formation from activated carbon alone (i.e. without fly ash)[9]. Residual carbon could then yield PCDD/PCDF partially through direct release from the residual carbon structure and partially via intermediates. This would make the distinction of formation from precursors and from residual carbon artificial.

We carried out a series of experiments with nine different compounds to learn more about these two different pathways and the relation between them.

Chlorobenzenes and chlorophenols are both present in the flue gas of waste incineration plants[17] and structurally related to PCDD/PCDF, i.e. they are possibly good precursors. Previous research has shown that gas phase reactions of chlorinated benzenes in air yield PCDD/PCDF[18], but chlorobenzene[7] and 1,4-dichlorobenzene[13] did not give any PCDD/PCDF formation on fly ash. Because of this inconclusive evidence, chlorobenzene (containing one chlorine atom) and 1,2,4,5-tetrachlorobenzene and pentachlorobenzene (which need less chlorination to yield PCDD/PCDF) were tested for their ability to form PCDD/PCDF on fly ash. Phenol was chosen as a model compound for chlorophenols and studied under the same reaction conditions as the chlorobenzenes, to make a comparison of the reactivity of both compound classes possible. With this information we can also establish whether chlorobenzenes and chlorophenols are intermediates in de novo synthesis, i.e. to what extent mechanisms (i) and (ii) are related.

To model the second mechanism of de novo synthesis from residual carbon, we chose hexane as representing the aliphatic part of residual carbon and toluene to model the aromatic parts with an aliphatic (in this case methyl-) substituent. The influence of functional groups was studied through experiments with anthraquinone, 2-anthraquinone-carboxylic acid (hereafter: 2-aca) and 2,6-dihydroxy-anthraquinone (hereafter: 2,6-diOH). With the outcome of these experiments, we can determine what parts of the residual carbon structure are responsible for PCDD/PCDF formation and what is the role of the various functional groups (carbonyl, carboxyl and hydroxy).

Preliminary results of our investigation have been published elsewhere[19].

2. EXPERIMENTAL

2.1 Materials

The following materials were used: aluminum oxide 90 active, basic (activity stage 1, 70–230 mesh, Merck, Darmstadt, Germany); anthraquinone (97%, Aldrich Chemie, Steinheim, Germany); 2-anthraquinone–carboxylic acid (98%, Aldrich Chemie, Steinheim, Germany); carbon tetrachloride (distilled, Merck, Darmstadt, Germany); chlorobenzene (glass distilled grade, Aldrich Chemical, Milwaukee, Wisconsin, USA); copper(II)chloride (Janssen Chimica, Beerse, Belgium); dichloromethane (glass distilled grade, Rathburn, Walkerton, Scotland); 2,6-dihydroxy-anthraquinone (97%, Aldrich Chemie, Steinheim, Germany); fly ash from the Municipal Waste Incinerator, Zaanstad, The Netherlands; hexane (glass distilled grade, Rathburn, Walkerton, Scotland); hydrogen chloride (solution, 37%, Merck, Darmstadt, Germany); hydrogen chloride (gas, 4.0 grade, UCAR, Nieuw-Vennep, The Netherlands); methanol (glass distilled grade, Rathburn, Walkerton, Scotland); nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); nonane (98%, Aldrich Chemie, Steinheim, Germany); oxygen (4.5 grade, Hoekloos, Schiedam, The Netherlands); pentachlorobenzene (98%, Aldrich Chemie, Steinheim, Germany); phenol (p.a., Merck, Darmstadt, Germany); silica gel 60 (70–230 mesh, Merck, Darmstadt, Germany); silver nitrate (p.a., Merck, Darmstadt, Germany); sodium hydrogencarbonate (p.a., Merck, Darmstadt, Germany); sodium hydroxide (p.a., Baker Chemicals, Deventer, The Netherlands); sulphuric acid (95–97%, Merck, Darmstadt, Germany); 1,2,4,5-tetrachlorobenzene (98%, Aldrich Chemie, Steinheim, Germany); toluene (glass distilled grade, Rathburn, Walkerton, Scotland).

2.2 Experimental apparatus

Experiments are reported in Table 1, in which the following abbreviations are used: 2-aca is 2-anthraquinone–carboxylic acid, 2,6-diOH is 2,6-dihydroxy-anthraquinone.

2.2.1 Description of experiments 2a, 2b, 4, 7, 8 and 9. From the incinerator fly ash all organic material was removed by heating at 550°C for 90 minutes under a stream of air saturated with water. Reaction mixtures contained 88.9–99.8% fly ash, 1.9–2.0% CuCl₂ (not present in experiments 2b and 4) and 0.2–9.1% reactant. These ingredients were mixed by shaking. A little of the mixture (1.0–2.1g) was placed in a cylindrical sample basket and coupled with a glass inlet tube for introduction of a gas flow through the fly ash bed. A sample basket and inlet
tube were fit into a horizontal pyrex glass reactor and put into a furnace (Lenton CNC 1100 Split Tube Furnace with PID 808 temperature controller, Icestorshire, UK). A gas stream (N₂, O₂, HCl) was then introduced. The flow was controlled by Series 384 Side=Trak® mass flow controllers (Sierra Instruments, Monterey, CA, USA). The flow was checked before and after the experiment with a flow meter. The gases were mixed in a mixing chamber (V = 800 mL) containing ceramic pellets. Experiments lasted for 50–60 minutes, preceded by 10 minutes of heating in order for the sample basket, inlet tube and reactor to reach the setpoint temperature (348°C ± 7°C). During these 10 minutes the gas stream was already passing through the fly ash bed. Products evaporating from the fly ash surface were collected using a cold trap (60 ml toluene cooled with ice). After the experiment the fly ash bed was taken out of the furnace immediately and cooled to room temperature. The cold trap fractions were combined with the toluene used for Soxhlet extraction before the beginning of this extraction.

2.2.2 Experiment 3. A mixture of 98.0% fly ash and 2.0% CuCl₂ (2.0 g) was placed in a glass tube between two plugs of glasswool. A glass basket containing the reactant was placed at the beginning of the glass tube. The glass tube was heated to 10 minutes to the desired temperature. The rest of the experiment was carried out as described above.

2.2.3 Experiments 1, 5 and 6. Pure fly ash or a mixture of 98.0% fly ash/2.0% CuCl₂ (2.0–2.1 g) was placed in the cylindrical sample basket. The liquid reactants were vaporized into the gas stream by means of a motor-driven syringe (Braun Medical, Utrecht, The Netherlands) at a rate of 0.33–0.66 ml/h; the gas stream with the reactant passed the fly ash bed subsequently. In this technique a constant stream of reactant onto the fly ash. The rest of the experiment was carried out as described above.

2.3 Clean up

The fly ash samples were extracted with 50 ml of a 3% HCl solution and dried overnight. After adding 100 μl of a solution of 13C-labeled PCDF/F in nonane as internal standard, the sample was Soxhlet extracted with 400 ml toluene for 24 hours. The extract was concentrated to a few milliliters and brought onto a column, filled from top to bottom with 22% H₂SO₄ on silica, 44% H₂SO₄ on silica, silica and 33% NaOH on silica. The column was eluted with 50 ml hexane. The eluent was concentrated to a few milliliters. This extract was brought onto two consecutive columns filled with AgNO₃ on silica and Al₂O₃. The columns were eluted with 80 ml hexane, 20 ml 10% CCl₄ in hexane and 30 ml dichloromethane. The dichloromethane fraction was concentrated to a few milliliters and filtered on a HPLC filter. This extract was evaporated to dryness, and PCDD/F were then transferred into 50 μl methanol and injected into a HPLC for subsequent clean up. (Pump: Beckman, model 110A, liquid flow: 2.3 ml min⁻¹ of methanol; injection port: Altex 210 with 100 μl sample loop; detection: Beckman, 160 absorbance detector; wave length: 254 nm; pre column: Chrompack, 6 cm × 3.8 mm ID; column: Zorbax ODS, 30°C.) PCDD/F were separated in two fractions. Fraction 1 contained all PCDD/F congeners except OCDF; fraction 2 contained OCDF. The fractions were mixed with 2% NaHCO₃ in water and PCDD/F were isolated by shaking with 3 × 2 ml hexane. This extract was concentrated to a few μl and analyzed with GC-MSD.

2.4 Analysis

GC-MSD: Hewlett-Packard 5970 Mass Selective Detector coupled with Hewlett Packard 5890 GC; column: Supelco SP 2331 (60 m), for all PCDD/F except OCDF, J & W DB-5 (30 m) for OCDF; injection: cold on column injection (T = 110°C); T split = 250°C; inlet pressure: 12 psi He; temperature program SP-2331: initial T = 140°C (20 seconds), rate 30°C/min to T = 200°C (0 seconds), rate 3°C/min, final T = 250°C (44 minutes); temperature program DB-5: initial T = 140°C (0 seconds), rate 40°C/min, final T = 300°C (12 minutes). The T₄CDD, P₃CDD,
H₄CDD, H₆CDD and OCDD and T₄CDF, P₃CDF, H₄CDD, H₆CDF and OCDF congeners were determined by single ion monitoring measuring M⁺, M+2, M+4 and M+6 masses, detection limit 0.01 ng/g. Quantification: the following ¹³C-labeled congeners (Cambridge Isotope Laboratories, Woburn, MA, USA) were added for quantification, assuming equal response for all isomers within an isomer group (solution in nonane, concentrations 23–49 ng/ml): 2,3,7,8-T₄CDD; 2,3,7,8-T₄CDF; 1,2,3,7,8-P₃CDD; 1,2,3,7,8-P₃CDF; 1,2,3,4,7,8-H₆CDD; 1,2,3,4,7,8-H₆CDF; 1,2,3,4,6,7,8-H₇CDF; 1,2,3,4,6,7,8-H₇CDF; OCDD; OCDF.

Blanks were taken from all reactants, fly ash and CuCl₂ and analyzed for PCDD/PCDF. Concentrations were between 0.001 and 0.33 nanomole/g fly ash (Σ PCDD/PCDF). Carbon-free fly ash (treated at 550°C for 90 minutes) is no longer capable of PCDD/PCDF formation. This was determined by carrying out an experiment with 2.0 g of fly ash under the reaction conditions used. Results were 0.16 nanomole/g fly ash (Σ PCDD/PCDF).

3. RESULTS AND DISCUSSION

In Table 1 results of the compounds tested are reported. These include chlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and phenol as precursors. Hexane, toluene, anthraquinone, 2-anthraquinone-carboxylic acid (2-aca) and 2,6-dihydroxy-anthraquinone (2,6-diOH) were tested as carbon model compounds. In Fig. 2 the structure of the three anthraquinones is given.

3.1 \([\text{PCDD}]:[\text{PCDF}]\) ratios with precursors

Use of the \([\text{PCDD}]:[\text{PCDF}]\) ratios will provide information about the reaction mechanisms involved in the formation of these compounds.

Chlorobenzene (experiment 1) and 1,2,4,5-tetrachlorobenzene (Experiments 2a and 2b) form both PCDD and PCDF, as does phenol. Ratios of \([\text{PCDD}]:[\text{PCDF}]\) vary between 0.5 and 5.2 for the two chlorobenzenes, with a phenol value of around 1.1 being found. Experiment 3 with pentachlorobenzene yielded no more PCDD/PCDF than found in blanks.

As reported in the introduction, other authors found no PCDD/PCDF formation from chlorobenzenes on fly ash[7,13]. We used HCl as a chlorinating agent, which provides a chlorine source in addition to the chloride naturally present in fly ash. HCl was not used by these other authors. This might explain the opposite results found.

Formation of PCDD from chlorobenzenes can be explained by assuming oxidation to chlorophenols, followed by a condensation reaction as depicted in Fig 3. 1,3,6,8-T₄CDD is formed in Fig 3 through direct condensation of 2,4,6-trichlorophenol and 2,4,6-trichlorophenate. Formation of 1,3,7,9-T₄CDD through the Smiles rearrangement[20] is also shown. PCDF formation from chlorobenzenes proceeds through the reaction given in Fig. 4. In the second step of this condensation reaction, H₂ or Cl₂ may be eliminated too, depending on the chlorination pattern of the intermediate chlorodiphenylether[21]. Both mechanisms may be similar to the Ullmann condensation in which Cu(I) catalyzes the condensation of halogenated benzenes and phenolates to yield diphenylethers[22]. In that case the condensation reaction in Fig. 4 would be between a chlorobenzene and chlorophenate.

Chlorophenols can be formed from phenol by chlorination. PCDD formation from phenol (Experiment 4) can then be explained by the condensation reaction in Fig. 3. However, other authors found little or no PCDF formation from phenol[23]. The reaction phenol±chlorobenzenes has been observed on fly ash[7], which can form PCDF subsequently via the reaction in Fig. 4.

3.2 \([\text{PCDD}]:[\text{PCDF}]\) ratios with carbon model compounds

With hexane a \([\text{PCDD}]:[\text{PCDF}]\) ratio of 0.18–0.42 is found. Formation of both compounds from hexane requires a complicated reaction sequence, probably involving (oxy)chlorination, ring closure and aromatization. Aromatization of hexane is possible on Zn[24]. Our results show that a simple aliphatic molecule, which even lacks a double bond, can be converted to PCDD/PCDF.

Experiment 6 with toluene gives a \([\text{PCDD}]:[\text{PCDF}]\) ratio of 0.07–0.43. PCDD/PCDF formation from toluene on fly ash has been established before by De Leer et al., but was not quantified[25]. Isomer distributions found with toluene (see Section 3.7) suggest chlorophenols as intermediates in PCDD formation from toluene. However, the \([\text{PCDD}]:[\text{PCDF}]\) ratio measured with toluene is lower than that found with phenol, i.e. the route via chlorophenols is probably not predominant.

Of the three anthraquinone derivatives, the parent structure itself is not active in PCDD/PCDF forma-
Fig. 3. Formation route of PCDD from 2,4,6-trichlorophenols.

Fig. 4. Formation route of PCDF from chlorobenzenes and chlorophenols.

tion (Experiment 7): yields were not higher than found in anthraquinone itself. Experiment 8 shows that 2-aca forms PCDD and PCDF in a ratio equal to phenol (around 1.1) but 2,6-diOH (Experiment 9) has a ratio of at least 20. OCDD formation from this compound could not be quantified, hence the minimum value given here.

2,6-diOH has two OH-groups and condensation of two molecules leads to a DD structure in the middle of the condensation product, which could subsequently be released, explaining the strong tendency to form PCDD. Dissociation of 2,6-diOH could lead to two molecules of phenol and two molecules of CO. Phenol produces equal amounts of PCDD and PCDF, implying that this reaction is not predominant.

3.3 Conversion factors with precursors

In the last column of Table 1 conversion factors are reported for the nine reactants studied. The conversion was calculated by \((\sum_{i}c_{i}CDD-OCDD + \sum_{i}c_{i}CDF-OCDF/n \text{ mole of reactant}) \times 100\%\). Cure
importance of the OH-group, probably through carbon on fly ash is around 1:4: 1.4:1. For chlorobenzenes 10^-3% as a conversion factor and for carbon alone as reported by Luijk et al.[9]. However, the [PCDD] ratios found with 2-aca and 2,6-diOH are both >1, whereas the ratio in our experiments with carbon is approximately 0.3. If the quinone structures are indeed the most important source of PCDD/PCDF formation from carbon, a ratio >1 (as found with 2-aca and 2,6-diOH) would be expected. Additional research will be needed to clarify this issue.

3.5 Degree of chlorination

For all compounds tested the average degree of chlorination of the PCDD and PCDF formed was calculated (Table 2). Values for chlorobenzene are lower than for 1,2,4,5-tetrachlorobenzene. The degree of chlorination of both PCDD and PCDF is higher with phenol as reactant than with chlorobenzene, but the values found with phenol do not differ from 1,2,4,5-tetrachlorobenzene. Hence, the amount of chlorine in the starting compound does not influence the degree of chlorination of the resulting PCDD/PCDF, i.e. the availability of chlorine is not a limiting factor.

The same observation can be made for the carbon
Formed from chlorination of phenol on fly ash.

Important in incinerator flue gas and are likely chlorination being 2+8+3&7-+1-+4+6+9.

2,3,4,6-tetrachlorophenol. 1,2,3,4,6,8-H,CDD is formed from 2,4,6-tetrachlorophenol and pentachlorophenol. In a similar way 1,2,4,7,9; 2,6-diOH (iii) PCDF isomer distributions (not shown) suggest that with chlorobenzene and 1,2,4,5-tetrachlorobenzene, some congeners are formed out of each other by chlorination. These congeners are identical for both chlorobenzene, i.e. the chlorination pattern of 1,2,4,5-tetrachlorobenzene is not retained in the PCDFs formed. PCDF congeners formed from phenol have a tendency for 2,3,4,7, and 2,4,6,8-substitution (not shown).

3.6 Isomer distributions with precursors

The isomer distributions found in our experiments can be used to describe some mechanisms operative on fly ash. These distributions are obtained by setting e.g. $\sum T,CDD=100\%$, followed by calculating the individual contribution of each isomer within the homologue.

With chlorobenzene and phenol, high percentages (between 5 and 85%) of 2,3,7,8-T,CDD, 1,2,3,7,8-P,CDD, 1,2,3,4,7,8-H,CDD and 1,2,3,4,6,7,9-H,CDD are formed. This can be explained by assuming DD as an intermediate. Chlorination of DD follows an electrophilic mechanism, the order of substitution (not shown).

Part of the PCDD isomer distribution of phenol may be explained by condensation of chlorophenols as depicted in Fig. 3 too. Formation of 1,3,6,8- and 1,3,7,9-T,CDD is possible from coupling of 2,4,6-trichlorophenol. In a similar way 1,2,4,7,9; 1,2,4,6,8; 1,2,3,6,8 and 1,2,3,7,9-P,CDD can be formed by condensation of 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol. 1,2,3,4,6,8-H,CDD is formed from 2,4,6-tetrachlorophenol and pentachlorophenol. These three chlorophenols are the most important in incinerator flue gas and are likely to be formed from chlorination of phenol on fly ash.

Table 3 shows results of PCDD isomer distributions within homologues. The isomers that can be formed from these three chlorophenols are shown. Note that some isomers cannot be separated and only the sum is given. For the two T,CDD and four P,CDD isomers listed, the percentages formed with phenol are higher than with carbon. As described above, chlorophenols are not intermediates in PCDD formation from carbon on fly ash. Within the H,CDD isomer distributions showed a great variance and no conclusions can be drawn.

Calculated by setting $\Sigma T,CDD-OCDD$ or $\Sigma T,CDF-OCDF$ to 100% for each experiment, calculating the percentage of each DD or DF homologue, multiplying this percentage by the number of chlorine atoms of that homologue, adding these numbers for the five homologues and finally dividing by 100. (i): No PCDD/PCDF formed, (ii): 2-aca: 2-anthraquinone-carboxylic acid, (iii): 2,6-diOH: 2,6-dihydroxy-anthraquinone, (iv): Not calculated because the amount of OCDD could not be quantified.
Table 3. PCDD isomer distributions of phenol, hexane, toluene, 2-anthraquinone-carboxylic acid and carbon

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Phenol</th>
<th>Hexane</th>
<th>Toluene</th>
<th>2-aca (i)</th>
<th>Carbon</th>
</tr>
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<tbody>
<tr>
<td>1,3,6,8</td>
<td>33 ± 5%</td>
<td>24 ± 2%</td>
<td>75 ± 1%</td>
<td>54%</td>
<td>3%</td>
</tr>
<tr>
<td>1,3,7,9</td>
<td>15 ± 2%</td>
<td>16 ± 2%</td>
<td>25 ± 1%</td>
<td>35 ± 1%</td>
<td>3%</td>
</tr>
<tr>
<td>1,2,4,7,9</td>
<td>22 ± 5%</td>
<td>29 ± 5%</td>
<td>49 ± 7%</td>
<td>32%</td>
<td>9%</td>
</tr>
<tr>
<td>1,2,4,6,8 (ii)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,6,8</td>
<td>26 ± 2%</td>
<td>22 ± 2%</td>
<td>37 ± 5%</td>
<td>32 ± 1%</td>
<td>6%</td>
</tr>
<tr>
<td>1,2,3,7,9</td>
<td>12%</td>
<td>18%</td>
<td>14 ± 1%</td>
<td>20 ± 1%</td>
<td>9%</td>
</tr>
<tr>
<td>1,2,4,6,7,9,9</td>
<td>47 ± 1%</td>
<td>39 ± 6%</td>
<td>48 ± 18%</td>
<td>45%</td>
<td>9%</td>
</tr>
<tr>
<td>1,2,4,6,8,9,9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,6,8 (ii)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Obtained by setting, e.g., $\sigma_T, CDD = 100\%$, followed by calculating the percentage of each isomer within the group. (i): 2-aca: 2-anthraquinone-carboxylic acid. (ii): Peaks not separated during GC/MSD analysis; the sum is given.

4. CONCLUSIONS

Both chlorobenzenes and chlorophenols yield PCDD and PCDF on incinerator fly ash and contribute to formation of these toxic compounds during the process of waste incineration. The formation mechanism of both PCDD and PCDF involves condensation reactions of chlorobenzenes and chlorophenols.

Experiments with carbon model compounds suggest that aliphatic, monocyclic aromatic and functionalized quinone structures in carbon can form PCDD/PCDF. However, the reactivity of the quinones is so high that they could be responsible for almost all PCDD and PCDF formed from carbon, even if their relative concentration within the carbon structure is < 1%. However, certainty about this question can only be obtained with knowledge of the quinone concentration in the carbon residue in incinerator fly ash, which is lacking at the moment. OH- and COOH-groups are important in increasing the potential for PCDD/PCDF formation. These groups might provide better adsorption of the reactant to the fly ash surface. Furthermore, the presence of OH-groups gives the possibility of condensation reactions, which is absent with the COOH-group. Other effects—e.g. the activating and o/p directing properties of the OH-group in electrophilic aromatic substitution—might play a role too. Such a substitution might lead to side-reactions, eventually perhaps also generating PCDD and PCDF.

With the conversion factors measured, calculations show that neither chlorobenzenes nor chlorophenols is an important intermediate in PCDD/PCDF formation from carbon, i.e. mechanisms (i) and (ii) are separate pathways indeed. Their relative importance determines whether PCDD/PCDF formed in the post combustion zone stems from precursors or from de novo synthesis. Our experiments lasted for 50–60 minutes and simulate only PCDD/PCDF formation on collected fly ash particles (e.g. in an electrostatic precipitator used to remove fly ash particles from the flue gas stream). Uncollected fly ash will have a short (seconds) residence time in the post combustion zone before being
emitted from the stack. De novo synthesis has a long time scale (minutes to hours) and will make a negligible contribution to uncollected fly ash. The ratio between PCDD/PCDF originating from precursors and from carbon will therefore be different for these two categories of fly ash particles.

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