

Role of Inorganic Chlorine in the Formation of Polychlorinated Dibenzo-*p*-dioxins/Dibenzofurans from Residual Carbon on Incinerator Fly Ash

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NaCl was added to a solid waste incinerator fly ash to study its role in the formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF). Parameters that varied were as follows: chloride concentration, oxygen concentration, temperature, and time. None of these reaction conditions resulted in an increase in PCDD/F formation, compared to undoped ash. An essentially zero-order behavior was observed for NaCl. When added to aqueous extracted ash, from which the soluble inorganic chloride had been removed before the addition, formation rates increased, with an optimum for $[Cl^-] = 0.4 \text{ mmol/g}$ (1.5 wt %). These results suggested that NaCl acted only as a chlorinating reagent on fly ash when no other chlorine sources were available. Surprisingly, only PCDF was formed on the aqueous extracted ash after addition of NaCl. Apparently, the PCDD formation catalyst had been removed by the water.

Introduction

The formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/F) on fly ash surfaces, as observed in many waste incineration plants, requires the presence of chlorine in the feed. Both inorganic and organic forms of chlorine were identified as sources in PCDD/F formation under laboratory conditions. KCl was used in PCDD/F formation from carbon on silica, with copper as catalytic material (1). The role of the Cl^- was obvious in this case, since it was the only chlorine source present. HCl was the chlorinating agent for 1,2,3,4,7,8-H₆CDD on fly ash (2). This reaction was carried out in N₂, and therefore, chlorination had to occur via pathways other than the Deacon reaction, which requires O₂. Cl₂ was employed by Bruce et al. in the CuO-catalyzed formation of (mainly) PCDD from phenol (3). $[Cl_2]$ had a positive correlation with the amount of PCDD/F formed. Chlorophenols readily produced PCDD, and since C–Cl bonds previously existed in the reactant, these compounds could be viewed as both carbon and chlorine sources (4).

The de novo formation of PCDD/F from native carbon on fly ash occurred without use of additional chlorine sources (5). Therefore chlorine had to previously exist on the fly ash.

Preexisting C–Cl bonds in the carbon was one possible form of chlorine. A model mixture, consisting of Mg–Al–silicate, charcoal, KCl, and CuCl₂, contained up to 800 μg/g of C–Cl bonds after thermal treatment in air (6). Only 15% of these C–Cl bonds were found to be extractable, i.e., present in small organic compounds. The rest was incorporated in the macromolecular carbon. It was assumed that inorganic chloride transferred to carbon, while Cu²⁺ ions enhanced this process. After formation of these C–Cl bonds, oxidative degradation released a range of organohalogen compounds, including PCDD/F.

A study by Rigo et al. reviewed the relationship between the chlorine content of waste and PCDD/F formation in commercial-scale systems (7). No such relationship was found. Similar conclusions were drawn by Wilson et al. with regard to incineration of industrial, chlorine-containing, waste (8). Such findings illustrate the complexity of modeling PCDD/F formation, since a relationship between [chlorine] and PCDD/F formation on a laboratory scale was found by some authors (1, 3).

Solid-phase chloride appeared to play an important role in the formation of C–Cl bonds, and of subsequent PCDD/F. Therefore, we carried out a series of experiments with NaCl, the most common form of inorganic chlorine in household waste. When added to fly ash, Cl^- could control PCDD/F formation rates if the chlorination of carbon is slow compared to other reactions (oxidative breakdown). In our experiments, [NaCl], [O₂], temperature, and time were varied. In a number of experiments, the water-soluble chloride in the ash was removed through aqueous extraction, and NaCl added subsequently, to study formation at low $[Cl^-]$.

Experimental Section

Fly ash from a municipal waste incinerator in the United States was sieved to a particle size of <210 μm to increase homogeneity. It was then extracted with toluene for 48–72 h or heated in N₂ for 60 min at 300 °C, followed by 48 h of toluene extraction, to remove adsorbed organics (including native PCDD/F). This left residual carbon as the only reactant. Reaction mixtures consisted of 0.25–0.50 g of fly ash, 0–0.17 g of NaCl, and 0.36–0.75 g of glass beads; the total sample weight was 1 g. The ingredients were mixed physically. To prepare aqueous extracted ash, 4–6-g portions were mixed with 50 mL of deionized water and thoroughly shaken, filtered, and dried. The extract was titrated with AgNO₃ to determine the amount of Cl^- removed, typically 4–5 wt % (9). Reextraction of the ash did not produce any measurable Cl^- . Obviously, water-insoluble chloride could still be present on the ash. The same technique was used to determine the amount of NaCl added to fly ash in the reaction mixtures.

The mixture was placed in a Pyrex glass or quartz tube against a glass frit with a plug of glasswool at the upstream end of the bed. The tube was heated in a furnace for 60 min to the desired temperature under a stream of N₂. Once the mixture had reached the reaction temperature (251–548 °C), a mixture of 0–21% O₂ in N₂ was passed through the bed for 15–240 min at a rate of 92–96 or 175 mL/min. Any PCDD/F desorbing from the bed was collected in an ice-cooled trap filled with toluene.

After the experiment, the fly ash and cold trap fractions were combined, spiked with ¹³C₁₂-PCDD/F internal standard (one congener per T₄CDD-OCDD homologue and T₄CDF–H₇CDF homologue, 10–20 ng/spike) and Soxhlet-extracted in toluene for 24 h. The volume of the extract was then reduced in a rotary evaporator to a few milliliters. The extract

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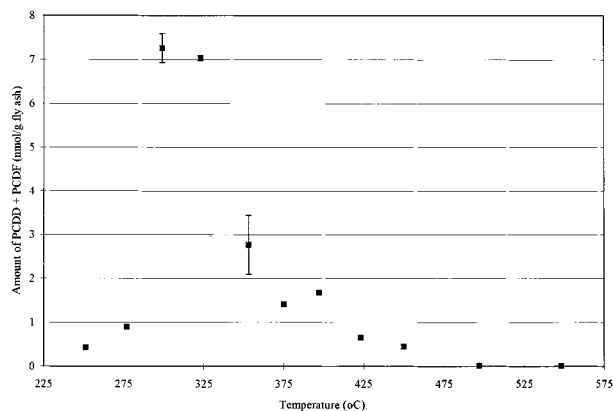


FIGURE 1. Formation of PCDD/F on fly ash as function of temperature. Conditions: mixture of 0.50 g of fly ash and 0.50 g of glass beads; reactant, residual carbon; 60 min; $T = 251\text{--}548\text{ }^{\circ}\text{C}$; flow, $95 \pm 4\text{ mL/min}$ of 10% O_2 in N_2 ($299\text{ }^{\circ}\text{C}$, $n = 4$. $353\text{ }^{\circ}\text{C}$, $n = 3$. Other T s: $n = 1$. Average values \pm standard deviation are shown for replicates.)

was further purified by column chromatography (acidified/alkaline silica followed by alumina). Finally, it was dissolved in 10 μL of tetradecane. Analysis was carried out on a combined gas chromatograph/mass selective detector, measuring M^+ , $\text{M}+2$, and $\text{M}+4$ for T_4CDD – H_7CDD and T_4CDF – H_7CDF and $\text{M}+2$, $\text{M}+4$, and $\text{M}+6$ for OCDD/F.

Blanks of the fly ash before experiments, NaCl, and glass beads contained negligible amounts of PCDD/F.

Results and Discussion

As a first part of our study, we investigated the dependence of PCDD/F formation on the temperature (reaction time = 60 min). The fly ash used contained carbon as the only organic material and had not been water-extracted. The results are shown in Figure 1. The optimum temperature found was around $300\text{--}325\text{ }^{\circ}\text{C}$, a range very typical for de novo formation (10). Experiments at 299 and $353\text{ }^{\circ}\text{C}$ were repeated to check reproducibility. The data at $353\text{ }^{\circ}\text{C}$ showed more scatter than at $299\text{ }^{\circ}\text{C}$, but the optimum formation around $300\text{--}325\text{ }^{\circ}\text{C}$ was very pronounced. Scatter in the data with fly ash without additives was most likely due to the inhomogeneous nature of this material. As the temperature increased, formation dropped quickly, approaching zero at $548\text{ }^{\circ}\text{C}$. A rise in temperature favored the formation of PCDF: the $[\text{PCDD}]:[\text{PCDF}]$ ratio dropped from ca. 0.8 at $299\text{ }^{\circ}\text{C}$ to almost 0 at $T > 423\text{ }^{\circ}\text{C}$. For PCDF, there was also a small decrease in the average degree of chlorination (which could vary between 4 and 8, on the basis of the analysis of all tetra-octa congeners), from 5.7 at $251\text{ }^{\circ}\text{C}$ to 5.2 at $450\text{ }^{\circ}\text{C}$.

The next step in our study involved addition of NaCl to the fly ash. We chose $299\text{ }^{\circ}\text{C}$ as the reaction temperature, since formation of PCDD/F at this temperature was the highest. Results are presented in Figure 2. A range of $[\text{Cl}^-]$ between 0 and 6 mmol/g fly ash (0–21 wt %) was studied, with rates of formation independent of $[\text{Cl}^-]$. In fact, the trend suggested a decrease in PCDD/F formation with increasing amounts of NaCl. Replicate experiments at $[\text{Cl}^-] = 1.1\text{ mmol/g}$ (4 wt %) showed some scatter, perhaps introduced by the NaCl, another variable in addition to the inhomogeneity of the fly ash. However, the duplicate runs at $[\text{Cl}^-] = 2.7\text{ mmol/g}$ (9.5 wt %) showed little scatter (Figure 2). The amount of fly ash/ Cl^- was kept constant while varying $[\text{Cl}^-]$, leading to a mixture of 50% fly ash/ Cl^- and 50% glass beads (triangles in Figure 2). Experiments at higher Cl^- concentrations contained therefore less fly ash. For comparison, runs were carried out with a mixture of 25% fly ash/75% glass beads to study the influence of a reduced amount of fly ash without Cl^- added (black dot in Figure 2). Diluting

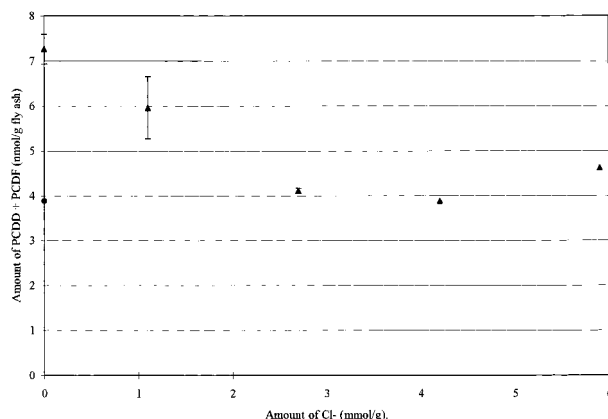


FIGURE 2. Influence of the NaCl concentration on PCDD/F formation at $299\text{ }^{\circ}\text{C}$. Conditions: 25%/75%, 0.25 g fly ash and 0.75 g glass beads (\bullet); 50%/50%, 0.50 g of (fly ash and 0–2.9 mmol Cl^- as NaCl) and 0.50 g glass beads (\blacktriangle); reactant, residual carbon; 60 min; $T = 299\text{ }^{\circ}\text{C}$; flow, $92 \pm 8\text{ mL/min}$ of 10% O_2 in N_2 . (25%/75%: $n = 2$. 0 mmol Cl^-/g , 50%/50%: $n = 4$. 1.1 mmol Cl^-/g , 50%/50%: $n = 3$. 2.7 mmol Cl^-/g , 50%/50%: $n = 2$. Other concentrations: $n = 1$. Average values \pm standard deviation are shown for replicates.)

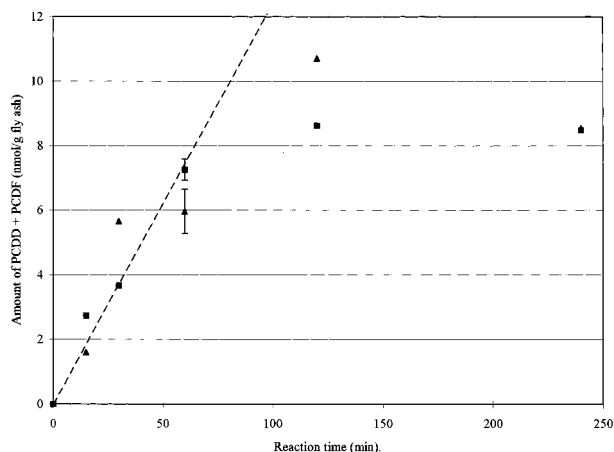


FIGURE 3. PCDD/F formation with and without NaCl as function of time at $299\text{ }^{\circ}\text{C}$. Conditions: 0.50 g fly ash, 0 (\blacksquare) or 0.55 (\blacktriangle) mmol Cl^- as NaCl, and 0.46–0.50 g glass beads; reactant, residual carbon; 15–240 min; $T = 299\text{ }^{\circ}\text{C}$; flow, $96 \pm 4\text{ mL/min}$ of 10% O_2 in N_2 . (60 min, no Cl^- : $n = 4$. 60 min, with Cl^- : $n = 3$. Other times: $n = 1$. Average values \pm standard deviation are shown for replicates.) Formation without NaCl was linear between 0 and 60 min (---); see text.

the fly ash in this manner reduced the formation. Addition of glass beads or NaCl appeared to have the same diluting effect, and Cl^- did not enhance formation rates of PCDD/F. NaCl did not affect the $[\text{PCDD}]:[\text{PCDF}]$ ratio or average degree of chlorination either. If more carbon were to be chlorinated by the Cl^- added, the latter could be expected to increase.

To further explore a possible role of NaCl in PCDD/F formation at $299\text{ }^{\circ}\text{C}$, both the reaction time and $[\text{O}_2]$ were varied. Since formation was highest with 1.1 mmol Cl^-/g (Figure 2), we chose this concentration for further study. Neither increased reaction times (Figure 3) nor variation of $[\text{O}_2]$ (Figure 4, reaction time = 60 min) activated NaCl toward producing more PCDD/F than on the undoped ash. Formation was linear between 0 and 60 min, and the experiments without NaCl (squares in Figure 3) could be fitted to a straight line with $r^2 = 0.97$ (including a point at $t = 0$ with no formation). At longer reaction times, the formation slowed and dechlorination/decomposition became important. Increased reaction times could favor Cl^- ion migration to active sites on the ash. Therefore, NaCl added might have a more

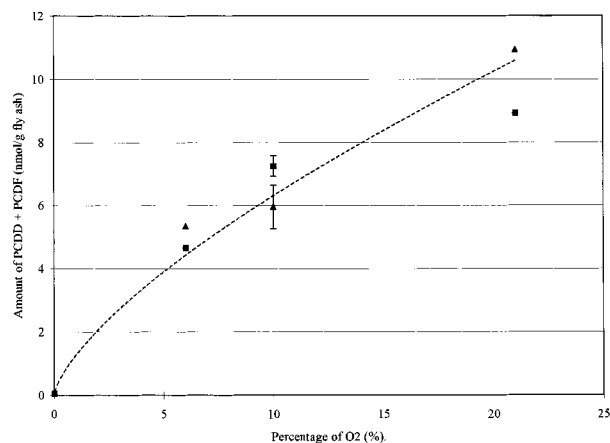


FIGURE 4. PCDD/F formation with and without NaCl as function of $[O_2]$ at 299 °C. Conditions: 0.50 g fly ash, 0 (■) or 0.55 (▲) mmol Cl^- as NaCl, and 0.46–0.50 g glass beads; reactant, residual carbon; 60 min; $T = 299$ °C; flow 93 ± 7 mL/min or 175 mL/min of 0–21% O_2 in N_2 . (10% O_2 , no Cl^- : $n = 4$. 10% O_2 , with Cl^- : $n = 3$. Other $[O_2]$: $n = 1$. Average values \pm standard deviation are shown for replicates.) Formation without NaCl was fitted to an exponential curve (---); see text.

pronounced effect at longer reaction times, but this was not observed. Varying $[O_2]$ between 6 and 21% increased formation of PCDD/F both with and without 1.1 mmol/g of Cl^- added to the ash. However, as shown in Figure 4, the Cl^- did not increase the amount of PCDD/F formed. For the experiments without NaCl, the results were fitted to an exponential curve with a reaction order of 0.7 in $[O_2]$. An order of 0.5 in $[O_2]$ for de novo formation was found by Altwicker et al. (11). Although the reaction time did not influence the [PCDD]:[PCDF] ratio, increasing $[O_2]$ yielded a higher ratio, both with and without Cl^- added. Similar results were found with de novo formation on another fly ash (12). At 6% O_2 , the ratio was ca. 0.5; it increased to ca. 1.1 at 21% O_2 . Varying time or $[O_2]$ did not influence the average degree of chlorination.

Because NaCl did not have any measurable effect on PCDD/F formation at 299 °C, the reaction temperature was varied for mixtures containing 1.1 mmol/g of Cl^- . Results are shown in Figure 5. It was clear that mixing fly ash with NaCl introduced considerable scatter in the data at various temperatures. For this reason, replicate experiments were carried out within the most relevant range of the de novo formation window (250–400 °C).

Despite the scatter, the overall trend did not support a significant influence of NaCl on rates of formation at any of the temperatures studied. With Cl^- added, the optimum temperature remained 300–325 °C. As was seen with the undoped fly ash, the [PCDD]:[PCDF] ratio decreased in the experiments with 1.1 mmol/g of Cl^- , as the temperature increased; from ca. 1.7 at 251 °C to ~ 0 at 497 °C. To corroborate the absence of any effect of added Cl^- on formation of PCDD/F, we varied $[Cl^-]$ at 353 °C. This temperature showed a (relative to the other temperatures) large margin of error in the runs with 1.1 mmol/g of Cl^- . The results are shown in Figure 6. As with the experiments at 299 °C, there was a decrease in PCDD/F formation when $[Cl^-] > 1.1$ mmol/g; the optimum was around 1 mmol Cl^- /g (ca. 4 wt %).

No reaction conditions could be found to activate NaCl. Our results suggested that PCDD/F formation is zero-order in $[Cl^-]$. However, the formation could be sensitive to $[Cl^-]$ at lower concentrations. The water-soluble fraction of inorganic chloride was 4–5% for our ash. Therefore, we had so far in effect only studied concentrations $> 5\%$, by adding NaCl to ash that already contained at least 4–5% of Cl^- .

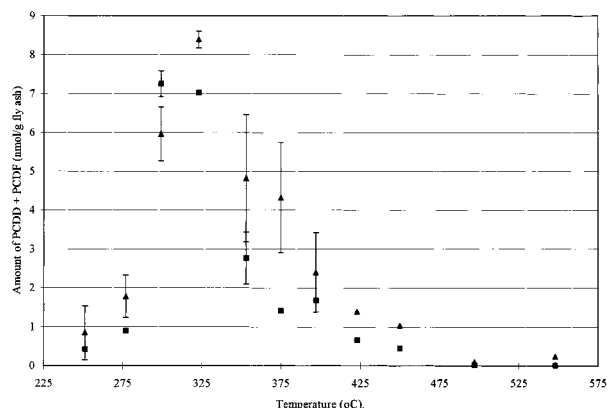


FIGURE 5. PCDD/F formation with and without NaCl as function of temperature. Conditions: 0.50 g fly ash, 0 (■) or 0.55 (▲) mmol Cl^- as NaCl, and 0.46–0.50 g glass beads; reactant, residual carbon; 60 min; $T = 251$ –548 °C; flow 96 ± 5 mL/min of 10% O_2 in N_2 . (251 °C, with Cl^- : $n = 3$. 277 °C, with Cl^- : $n = 2$. 299 °C, no Cl^- : $n = 4$. 299 °C, with Cl^- : $n = 3$. 323 °C, with Cl^- : $n = 2$. 353 °C, no Cl^- : $n = 3$. 353 °C, with Cl^- : $n = 7$. 375 °C, with Cl^- : $n = 2$. 397 °C, with Cl^- : $n = 2$. Other runs: $n = 1$. Average values \pm standard deviation are shown for replicates.)

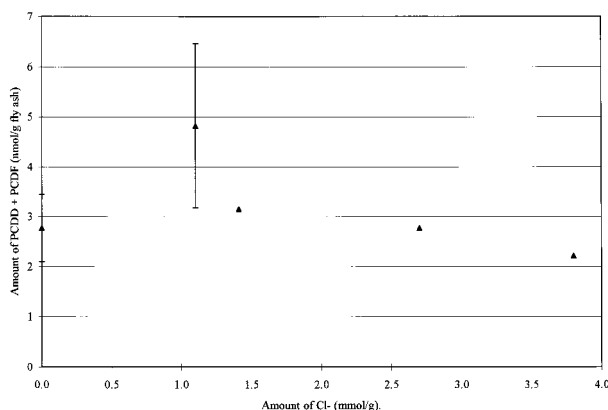


FIGURE 6. Influence of the NaCl concentration on PCDD/F formation at 353 °C. Conditions: 0.50 g fly ash, 0–1.9 mmol Cl^- as NaCl, and 0.36–0.50 g glass beads; reactant, residual carbon; 60 min; $T = 353$ °C; flow 96 ± 3 mL/min of 10% O_2 in N_2 . (0 mmol Cl^- /g: $n = 3$. 1.1 mmol Cl^- /g: $n = 7$. Other runs: $n = 1$. Average values \pm standard deviation are shown for replicates.)

Removal of the original, water-soluble, inorganic Cl^- from the ash enabled us to study the role of $[Cl^-]$ at concentrations $< 5\%$. This was achieved by aqueous extraction of the ash. Afterward, the ash was doped with various amounts of NaCl. Results are depicted in Figure 7. On the horizontal axis, the amount of Cl^- added (as NaCl) is shown.

The experiments were run at 299 and 353 °C. For added $[Cl^-] = 0$, formation was negligible. At higher concentrations, only PCDF formation was partially restored. The optimum $[Cl^-]$ was ca. 0.4 mmol/g (1.5 wt %), with formation at 353 °C more pronounced than at 299 °C. Since (presumably) other metal ions on the ash could be partially removed in an aqueous extraction, a direct comparison with runs with untreated ash was difficult. The ca. 0.9 nmol/g of PCDF formed at $[Cl^-] = 0.4$ mmol/g ($T = 353$ °C), was ca. 30% of the amount of PCDD/F found with the untreated ash at this temperature (Figure 2). This suggested that although NaCl could partially restore PCDF formation on aqueous extracted ash, part of the PCDF formation catalyst and the entire PCDD formation catalyst had been removed by the aqueous extraction. Hence, chlorine sources and/or transition metal mediated pathways could differ for PCDD and PCDF. Since the fly ash before aqueous extraction contained only 0.02%

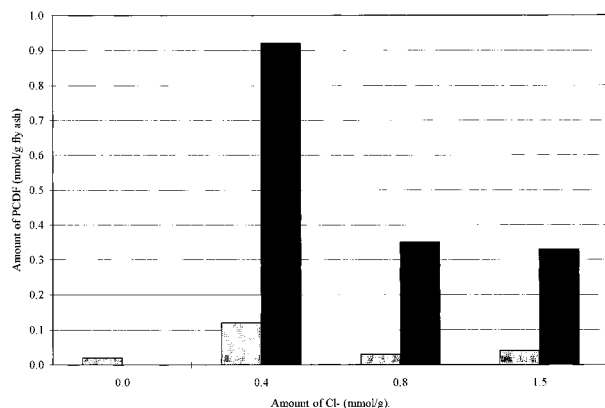


FIGURE 7. PCDF formation on aqueous extracted fly ash at 299 (gray) and 353 °C (black). Conditions: 0.50 g aqueous extracted fly ash, 0–0.75 mmol Cl⁻ as NaCl, and 0.45–0.50 g glass beads; reactant, residual carbon; 60 min; $T = 299$ or 353 °C; flow, 96 ± 2 mL/min of 10% O₂ in N₂. (All runs: $n = 1$.)

copper (based on extraction of ash with nitric acid, followed by atomic absorption measurements of the extract), this metal was probably unimportant as a catalyst and/or chloride source. Experiments in which 0.02% Cu²⁺ as CuCl₂ was added to aqueous extracted fly ash gave no PCDD/F formation (13). Instead, on the original ash iron (1.3%) could be the catalyst. Evidence of catalytic activity of iron(III) in de novo PCDD/F formation was supplied by Stieglitz et al. (14). The value of 1.3% could be higher if iron was present on the ash in a form that did not dissolve in nitric acid. Removal of (part of) the iron in the aqueous extraction could have reduced the formation potential of the ash after this extraction.

These results also explained why NaCl did not have an effect, when added to untreated ash. The optimum [Cl⁻] was around 0.4 mmol/g, which is lower than the amount of chloride naturally present on this ash. Addition of more Cl⁻ could not increase rates. Our results showed that adding NaCl to aqueous extracted ash was essential to restore at least some PCDF formation. Both before and after aqueous extraction ca. 100 µg of C–Cl bonds per gram of ash were present in the residual carbon (15). Apparently, these C–Cl bonds were not available for reactions, since only addition of inorganic chloride restored formation of PCDF.

The 0.4 mmol/g of Cl⁻ found as an optimum for PCDF formation, translating into ca. 1.5 wt %, appeared to be quite low. This was certainly true when compared to O₂, where no optimum was found and formation increased to at least [O₂] = 21%. From this study one would conclude that chlorine was unlikely to be the limiting reagent for de novo synthesis on a long (minute to hours) time scale. This would also

imply that the amount of NaCl in waste was only crucial if no other inorganic chlorides were present. However, as reported in the Introduction, Blaha found that at 6.6% Cl⁻ de novo formation was 3.5× higher than with 1.1% Cl⁻ (1). In a study of short-time scale, in-flight formation, Halonen et al. found no influence of [NaCl] on PCDD/F formation, with C_{10–13} aliphatic hydrocarbons as the fuel, in the range 0.25–1.0 wt % Cl⁻ (16). A value <0.25 wt % was not investigated. These findings illustrated that each combustion system could have its own optimum concentration (or threshold) of chlorine for PCDD/F formation, and generalizations across systems could not be made.

Acknowledgments

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