

## 2. MECHANISMS OF FORMATION OF DIOXIN-LIKE COMPOUNDS DURING COMBUSTION OF ORGANIC MATERIALS

More than a decade of combustion research has contributed to a general understanding of the central molecular mechanisms that form CDDs/CDFs emitted from combustion sources. Current understanding of the conditions necessary to form CDDs/CDFs were primarily derived from studies of full-scale municipal waste combustors (MWCs), augmented with observations involving the experimental combustion of synthetic fuels and feeds within the laboratory. However, the formation mechanisms elucidated by these studies are generally relevant to most combustion systems in which organic material is burned with chlorine.

Intensive studies have examined MWCs from the perspective of identifying the specific formation mechanism(s) that occurs within the system. This knowledge may lead to methods that prevent the formation of CDDs/CDFs and their release into the environment. Although much has been learned from such studies, a method that completely prevents CDDs/CDFs from forming during the combustion of certain organic materials in the presence of a source of chlorine and oxygen is still unknown. The wide variability of organic materials incinerated and thermally processed by a wide range of combustion technologies that have variable temperatures, residence times, and oxygen requirements adds to this complex problem. However, central chemical events that participate in the formation of CDDs/CDFs can be identified by evaluating emission test results from MWCs in combination with laboratory experiments.

CDD/CDF emissions from combustion sources can potentially be explained by three principal mechanisms that should not be regarded as being mutually exclusive. In the first mechanism (referred to as “pass through”), CDDs/CDFs are present as contaminants in the combusted organic material; they pass through the furnace and are emitted unaltered. This mechanism is discussed in Section 2.1. In the second mechanism (referred to as “precursor”), CDDs/CDFs ultimately form from the thermal breakdown and molecular rearrangement of precursor ring compounds, which are defined as chlorinated aromatic hydrocarbons that have a structural resemblance to the CDD/CDF molecules. Ringed precursors that emanate from the combustion zone are a result of the incomplete oxidation of the constituents of the feed (i.e., products of incomplete combustion). The precursor mechanism is discussed in Section 2.2. The third mechanism (referred to as “*de novo* synthesis”) is similar to the precursor mechanism and is

1 described in Section 2.3. *De novo* synthesis describes a pathway of CDD/CDF formation from  
2 heterogeneous reactions on fly ash (particulate matter [PM]) involving carbon, oxygen, hydrogen,  
3 chlorine, and a transition metal catalyst. With these reactions, intermediate compounds that have  
4 an aromatic ring structure are formed.

5 Studies in this area suggest that aliphatic compounds, which arise as products of  
6 incomplete combustion, may play a critical role in initially forming simple ring molecules, which  
7 later evolve into complex aromatic precursors. CDDs/CDFs are then formed from the  
8 intermediate compounds. In both the second and the third mechanism, formation occurs outside  
9 the furnace, in the so-called post-combustion zone. Particulate-bound carbon is suggested as the  
10 primary reagent in the *de novo* synthesis pathway.

11 Section 2.4 presents an overview of studies that have investigated the role that chlorine  
12 plays in forming CDDs/CDFs. Although chlorine is an essential component for the formation of  
13 CDDs/CDFs in combustion systems, the empirical evidence indicates that for commercial-scale  
14 incinerators, chlorine levels in feed are not the dominant controlling factor for rates of CDD/CDF  
15 stack emissions. There are complexities related to the combustion process itself, and some types  
16 of air pollution control equipment tend to mask any direct association. Therefore, the chlorine  
17 content of fuel and feeds to a combustion source is not a good indicator of levels of CDDs/CDFs  
18 emitted from the stack of that source.

19 Section 2.5 discusses the generation and formation of coplanar PCBs. The presence of  
20 coplanar PCBs in stack emissions from combustors is an area in need of further research.  
21 Evidence to date suggests that PCB emissions are mostly attributable to PCB contamination in  
22 waste feeds and that emissions are related to the first mechanism described above. However,  
23 newly published research has also indicated that it is possible that PCBs form in much the same  
24 way as described in the second and third mechanisms identified in the formation of CDDs/CDFs  
25 within the post-combustion zone.

26 Section 2.7 provides a closing summary of the three principal formation mechanisms and  
27 the role of chlorine. From the discussions in this chapter, it should be evident that no clear  
28 distinction exists between the precursor and the *de novo* synthesis mechanisms of CDD/CDF  
29 formation. Both formation pathways depend on the evolution of precursors within combustion  
30 gases, the interaction of reactive fly ashes, a generally oxidative environment, the presence of a  
31 transition metal catalyst, the presence of gaseous chlorine, and a favorable range of temperature.

1 The temperature of the combustion gases (i.e., flue gases) is perhaps the single most important  
2 factor in forming dioxin-like compounds. Temperatures between 200 and 450 °C are most  
3 conducive to the formation of CDDs/CDFs, with maximum formation occurring at around  
4 350 °C. If the temperature falls outside this range, the amount of CDDs/CDFs formed is  
5 minimized.

## 6 7 **2.1. MECHANISM 1 (PASS THROUGH): CDD/CDF CONTAMINATION IN FUEL AS** 8 **A SOURCE OF COMBUSTION STACK EMISSIONS**

9 The first mechanism involved in stack emissions of CDDs/CDFs is the incomplete  
10 destruction of CDD/CDF contaminants present in the fuel or feeds delivered to the combustion  
11 chamber. Not all of these molecules are destroyed by the combustion system, thus allowing trace  
12 amounts to be emitted from the stack. Most work in this area has involved the study of  
13 incineration of municipal solid waste (MSW), where CDDs/CDFs were analytically measured in  
14 the raw refuse fed into the incinerator. CDDs/CDFs are ubiquitous in the environment (air,  
15 water, and soil) and in foods and paper; therefore, they clearly are present in municipal waste  
16 (Tosine et al., 1983; Ozvacic, 1985; Clement et al., 1988; Federal Register, 1991a; Abad et al.,  
17 2002).

18 Abad et al. (2002) have provided contemporary measurements of CDDs/CDFs in raw  
19 MSW. Twenty-two samples were collected and analyzed for CDDs/CDFs over a one year period  
20 from September 1998 through September 1999. The congeners that dominated the total mass of  
21 CDDs/CDFs were the OCDD and 1,2,3,4,7,8,9-HpCDD. Figure 2-1 displays the mean CDD and  
22 CDF congener distribution from this study. Abad et al. (2002) found that the I-TEQ  
23 concentration in the MSW was highly variable and ranged from 1.55 to 45.16 ng I-TEQ/kg  
24 MSW.

25 A number of studies have provided evidence that most of the CDDs/CDFs present in the  
26 MSW are destroyed during combustion (Abad et al., 2002; Clement et al., 1988; Commoner et  
27 al., 1984, 1985, 1987; Hay et al., 1986; Environment Canada, 1985). These studies have  
28 involved a mass balance of the input versus output of CDDs/CDFs at two operational MWCs.  
29 The mass of CDDs/CDFs outside the incinerator furnace was found to be much greater than the  
30 mass of CDDs/CDFs in the raw MSW fed into the incinerator, and the profiles of the  
31 distributions of CDD/CDF congeners were strikingly different. Primarily, the more highly

1 chlorinated congeners were detected as contaminants in the waste, whereas the total array of  
2 tetra- to octa-CDDs/CDFs could be detected in the stack gases. Moreover, the ratio of the total  
3 concentration of CDDs in the MSW in relation to the total CDF concentration was greater than 1,  
4 whereas in typical incinerator stack emissions, this ratio is less than 1 (meaning more  
5 dibenzofurans are emitted than dioxins). Such evidence gives the conclusion that CDDs/CDFs  
6 are being synthesized after the contaminated feed has been combusted (Abad et al., 2002).  
7 Moreover, it is expected that the conditions of thermal stress imposed by high temperatures  
8 reached in typical combustion would destroy and reduce the CDDs/CDFs present as  
9 contaminants in the waste feed to levels that are 0.0001 to 10% of the initial concentration,  
10 depending on the performance of the combustion source and the level of combustion efficiency.  
11 Stehl et al. (1973) demonstrated that the moderate temperature of 800 °C enhances the  
12 decomposition of CDDs at a rate of about 99.95% but lower temperatures result in a higher  
13 survival rate.

14 Theoretical modeling has shown that unimolecular destruction of CDDs/CDFs at 99.99%  
15 can occur at the following temperatures and retention times within the combustion zone: 977 °C  
16 with a retention time of 1 sec, 1,000 °C at a retention time of 0.5 sec, 1,227 °C at a retention time  
17 of 4 msec, and 1,727 °C at a retention time of 5 µsec (Schaub and Tsang, 1983). Thus,  
18 CDDs/CDFs would have to be in concentrations of parts per million in the feed in the combustor  
19 to be found in the parts-per-billion or parts-per-trillion level in the stack gas emissions (Schaub and  
20 Tsang, 1983). However, it cannot be ruled out that CDDs/CDFs in the waste or fuel may  
21 contribute (up to some percentage) to the overall concentration leaving the stack. The only other  
22 possible explanation for CDD/CDF emissions from high-temperature combustion of organic  
23 material is formation outside and downstream of the furnace.

24 The above studies point to formation mechanisms other than simple pass through of  
25 noncombusted feed contamination. These formation mechanisms are discussed and reviewed in  
26 the following sections.

## 28 **2.2. MECHANISM 2 (PRECURSOR): FORMATION OF CDDs/CDFs FROM** 29 **PRECURSOR COMPOUNDS**

30 The second mechanism involves the formation of CDDs/CDFs from aromatic precursor  
31 compounds in the presence of a chlorine donor. This mechanism has been elucidated by

1 laboratory experiments involving the combustion of known precursors in quartz ampules under  
2 starved-air conditions and in experiments that investigated the role of combustion fly ash in  
3 promoting the formation of CDDs/CDFs from precursor compounds. The general reaction in this  
4 formation pathway is an interaction between an aromatic precursor compound and chlorine  
5 promoted by a transition metal catalyst on a reactive fly ash surface (Stanmore, 2004; Dickson and  
6 Karasek, 1987; Liberti and Brocco, 1982). Examples of well-studied precursor compounds  
7 include chlorobenzenes, chlorophenols, phenol, and benzene (Esposito et al., 1980). Gaseous  
8 hydrogen chloride (HCl), free chlorine ( $\text{Cl}_2$ ), and chlorine radicals ( $\text{Cl}\cdot$ ) are the chlorinating agents  
9 within the combustion gases. CDD/CDF formation results from heterogeneous gas-phase  
10 reactions involving chlorinated precursor compounds and a source of chlorine. Chlorophenol and  
11 chlorobenzene compounds are measured in flue gases from MWCs (Dickson and Karasek, 1987).  
12 Precursors are carried from the furnace to the flue duct as products of incomplete combustion.  
13 These compounds can adsorb on the surface of combustion fly ash or entrain in the gas phase  
14 within the flue gases. Thus, there are two formation pathways from precursor compounds:  
15 heterogeneous solid-phase reactions and homogeneous gas-phase reactions. In the post-  
16 combustion region outside the furnace, heterogeneous reactions on the surface of reactive fly ash  
17 can ensue to form CDDs/CDFs from the precursor compounds. This occurs at the cool down  
18 temperatures of 200 to 400 °C. The heterogeneous gas-phase reactions occur from the breakdown  
19 and molecular rearrangement of precursor compounds followed by condensation and chlorination  
20 at the higher temperatures of 500 to 800 °C. Both reaction pathways are catalyzed by copper  
21 chloride ( $\text{CuCl}_2$ ) or another transition metal.

22 Laboratory experiments involving the controlled combustion of precursor compounds have  
23 caused the breakdown of the precursor reagent and the subsequent appearance of CDDs/CDFs as  
24 products of the reaction. For example, Jansson et al. (1977) produced CDDs through the pyrolysis  
25 of wood chips treated with tri-, tetra-, and pentachlorophenol (PCP) in a bench-scale furnace  
26 operated at 500 to 600 °C. Stehl and Lamparski (1977) combusted grass and paper treated with  
27 the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in a bench-scale furnace at 600 to 800  
28 °C and generated ppm<sub>v</sub> levels of TCDD. Ahling and Lindskog (1982) reported CDD formation  
29 during the combustion of tri- and tetrachlorophenol formulations at temperatures of 500 to 600  
30 °C. Decreases in oxygen during combustion generally increased the CDD yield.

1 Ahling and Lindskog (1982) noted that adding copper salts to the tetrachlorophenol  
2 formulation significantly enhanced the yield of CDDs. This may have been an early indication of  
3 copper's role in catalyzing the condensation of chlorophenol to dioxin. Combustion of PCP  
4 resulted in low yields of CDDs. However, when PCP was burned with an insufficient supply of  
5 oxygen in the presence of copper, the investigators noted the formation of tetra- through  
6 octachlorinated congeners. Buser (1979) generated CDDs/CDFs on the order of 0.001 to 0.08%  
7 (by weight) by heating tri-, tetra-, and pentachlorobenzenes at 620 °C in quartz ampules in the  
8 presence of oxygen. It was noted that chlorophenols formed as combustion byproducts; Buser  
9 (1979) speculated that these chlorophenols were acting as reaction intermediates in the formation  
10 of CDDs/CDFs.

11 The second condition postulated to regulate the synthesis of CDDs/CDFs from the  
12 aromatic precursor compound is the adsorption and interaction with the reactive surface of  
13 combustion-generated fly ash (PM) entrained in the combustion plasma and the presence of a  
14 transition metal catalyst ( Stanmore, 2004; Dickson et al., 1992; Bruce et al., 1991; Cleverly et al.,  
15 1991; Gullet et al., 1990a; Commoner et al., 1987; Dickson and Karasek, 1987; Vogg et al.,  
16 1987). These are heterogeneous solid-phase reactions that occur at temperatures below 450 °C.  
17 The molecular precursor leaves the gas phase and condenses onto the fly ash particle. This  
18 condition, which places greater emphasis on heterogeneous surface reactions and less emphasis on  
19 homogeneous gas-phase reactions, was first postulated by Shaub and Tsang (1983) using thermal-  
20 kinetic models based on the temperature of the heat of formation, adsorption, and desorption.  
21 Shaub and Tsang modeled CDD production from chlorophenols and concluded that solid-phase  
22 formation of CDDs/CDFs was of greater importance than gas-phase formation within an  
23 incineration system. The temperature of the combustion gases is a critical factor in the formation  
24 of CDDs/CDFs from aromatic precursor compounds (Weber and Hagenmaier, 1999; Fangmark et  
25 al., 1994; Vogg et al., 1987, 1992; Oberg et al.,1989). Vogg et al. (1987) found that formation  
26 probably occurs outside and downstream from the combustion zone of a furnace in regions where  
27 the temperature of the combustion offgases has cooled within a range of 200 to 450 °C.

28 After carefully removing organic contaminants from MWC fly ash, Vogg et al. (1987)  
29 added known concentrations of isotopically labeled CDDs/CDFs to the matrix. The MWC fly ash  
30 was then heated for 2 hr in a laboratory furnace at varying temperatures. The treated fly ash was  
31 exposed to temperatures increasing in 50 °C increments within a temperature range of 150 to 500

1 °C. Table 2-1 summarizes these data. Because the relative concentration of CDDs/CDFs  
2 increased while exposed to varying temperatures, it was concluded that the temperature of the  
3 combustion gas is crucial to promoting the formation of CDDs/CDFs on the surface of fly ash.  
4 Within a temperature range of 200 to 450 °C, the concentration of CDDs/CDFs increases to some  
5 maxima; outside this range, the concentration diminishes.

6 The region of cooler gas temperature is often referred to as the “post-combustion zone.”  
7 The heat loss may be inherent to the conduction and transfer through the combustion gas metal  
8 ducting system or related to adsorbing/exchanging heat to water in boiler tubes. This region  
9 extends from near the exit of the furnace to the point of release of the combustion gases at stack  
10 tip.

11 Fangmark et al. (1994) found that CDDs/CDFs exhibit a similar dependence at a  
12 temperature range of 260 to 430 °C, with maximum formation occurring around 340 °C. Using a  
13 pilot-scale combustor, Behrooz and Altwicker (1996) found that the formation of CDDs/CDFs  
14 from the precursor 1,2-dichlorobenzene rapidly occurred within the post-combustion region in a  
15 temperature range of 390 to 400 °C, with residence times of only 4 to 5 sec. On the other hand,  
16 CDD/CDF formation from 1,2-dichlorophenol seemed to require higher temperatures.

17 Oberg et al. (1989) examined the role of temperature in the formation kinetics using a full-  
18 scale hazardous waste incinerator (HWI) operating in Sweden. The investigators observed that  
19 maximum CDD/CDF formation transpired in the boiler used to extract heat for cogeneration of  
20 energy. In this study, significant increases in total concentration of I-TEQ<sub>DF</sub> occurred between 280  
21 and 400 °C, and concentrations declined at temperatures above 400 °C. Weber and Hagenmaier  
22 (1999) showed that in gas-phase reactions, chlorophenols react in the presence of oxygen at  
23 temperatures above 340 °C to form CDDs/CDFs. Phenoxyradicals were formed, which in turn  
24 caused the formation of CDDs. Polychlorinated dihydroxybiphenyls were identified as reaction  
25 intermediates in the gas-phase dimerization of chlorophenols, and these intermediates could form  
26 CDFs.

27 Konduri and Altwicker (1994) proposed that rate-limiting factors were the nature and the  
28 concentrations of the precursors, the reactivity and availability of the fly ash surface, and the  
29 residence time in the post-combustion zone. Dickson and Karasek (1987) investigated fly ash  
30 reactivity with <sup>13</sup>C<sub>6</sub>-chlorophenol compounds. Several samples of fly ash from MWCs, copper  
31 smelters, and a variety of combustion fuels were heated at 300 °C in quartz tubes under conditions

1 known to catalyze the conversion of chlorophenols to CDDs/CDFs. The MSW fly ashes included  
2 a sample from a poorly operated mass burn refractory incinerator and a sample from a well-  
3 operated fluidized-bed combustor. The MWC fly ashes proved to be the most active catalytic  
4 medium, despite similarities with respect to specific surface area and average pore diameters. The  
5 fly ash from the refractory MWC generated about seven times more mass of dioxin-like  
6 compounds than the fluidized-bed MWC. In the MSW fly ashes, all CDD/CDF congener groups  
7 were formed from labeled chlorophenols; however, only trace amounts of heptachloro- and  
8 octachlorodioxin were formed with the copper smelter/refiner. X-ray photoelectron spectroscopy  
9 revealed the presence of chlorine adsorbed to the surface of the MWC fly ash but an absence of  
10 chlorine sorbed to the copper smelter fly ash.

11 CDD congener groups have been postulated to form from the labeled PCP precursors by  
12 (1) first forming octachlorodioxin by the condensation of two PCP molecules, and (2) forming  
13 other less-chlorinated dioxins through dechlorination of the more highly chlorinated isomers.  
14 These steps seemed to proceed by an increased reactivity of the chemisorbed precursor molecule  
15 caused by the removal of one or more hydrogen or chlorine atoms along the ring structure  
16 (Dickson and Karasek, 1987), an observation consistent with the kinetic model of Shaub and  
17 Tsang (1983).

18 In related experiments, Dickson and Karasek (1987) more specifically reported on forming  
19 CDDs/CDFs from condensation reactions of chlorophenols on the surface of MWC fly ash heated  
20 in a bench-scale furnace. Their experiment was designed to mimic conditions of MSW  
21 incineration, to identify the step-wise chemical reactions involved in converting a precursor  
22 compound into dioxin, and to determine whether MWC fly ash could promote these reactions.  
23 MWC fly ash was obtained from facilities in Canada and Japan. The fly ash was rinsed with  
24 solvent to remove any organic constituents prior to initiating the experiment. Twenty grams of fly  
25 ash were introduced into a bench-scale furnace (consisting of a simple flow-tube combustion  
26 apparatus) and heated at 340 °C overnight to desorb any remaining organic compounds from the  
27 matrix.  $^{13}\text{C}_{12}$ -labeled PCP and two trichlorophenol isotopes ( $^{13}\text{C}_{12}$ -2,3,5-trichlorophenol and  
28 3,4,5-trichlorophenol) were added to the surface of the clean fly ash matrix and placed in the oven  
29 for 1 hr at 300 °C. Pure inert nitrogen gas (flow rate of 10 mL/min) was passed through the flow  
30 tube and a constant temperature was maintained.

1 Tetra- through octa-CDDs were formed from the labeled PCP experiment; more than 100  
2  $\mu\text{g/g}$  of total CDDs were produced. The congener pattern was similar to that found in MWC  
3 emissions. The 2,3,5-trichlorophenol experiment primarily produced HxCDDs and very small  
4 amounts of tetra- and octa-CDDs. The 3,4,5-trichlorophenol experiment mainly produced OCDD  
5 and 1,2,3,4,6,7,8-HpCDD.

6 Dickson and Karasek (1987) proposed that CDDs on fly ash surfaces may result from  
7 chlorophenol undergoing molecular rearrangement or isomerization as a result of dechlorination,  
8 dehydrogenation, and transchlorination before condensation occurs. These reactions were  
9 proposed as controlling the types and amounts of CDDs that are ultimately formed. Born et al.  
10 (1993) conducted experiments on the oxidation of chlorophenols with fly ash in a quartz tube  
11 reactor heated to about 300 °C. The MWC fly ash mediated the oxidation of chlorophenols to  
12 produce carbon dioxide ( $\text{CO}_2$ ) and carbon monoxide (CO) as major products and polychlorinated  
13 benzenes, monobenzofurans, and nonhalogenated dibenzo-*p*-dioxins as trace species. Formation  
14 of these trace aromatic species occurred after residence times of only 7 to 8 sec, which was  
15 consistent with the later experimental result of Behrooz and Altwicker (1995), which showed the  
16 potential for rapid formation from a precursor.

17 Milligan and Altwicker (1996) fitted experimental flow-tube reactor data to classical  
18 catalytic reaction models to empirically explain the interaction of 2,3,4,6-tetrachlorophenol (as a  
19 model precursor) with reactive MWC fly ash during MSW incineration. The precursor was found  
20 to be highly adsorptive on the surface of fly ash, with a first-order dependence on gas-phase  
21 precursor concentration to CDD formation. The investigators concluded that chlorophenol's  
22 dependence on gas-phase concentration to form CDDs on fly ash reflects the highly heterogeneous  
23 nature of the fly ash surface. Moreover, the estimated  $6 \times 10^{18}$  adsorption sites per gram of fly ash  
24 suggested the presence of highly energetic sites, which may be important in the surface-catalyzed  
25 reactions forming CDDs. An interesting observation by Milligan and Altwicker (1996) was that  
26 precursor molecules appeared to compete with oxygen molecules for the reactive sites; therefore,  
27 chlorophenols are expected to adsorb less readily to the fly ash surface in the presence of oxygen.

28 Experimental evidence suggests that condensation to CDD of chlorophenol compounds  
29 via isomerization and the "Smiles" rearrangement on reactive MWC fly ash surfaces is a proven  
30 pathway for the formation of dioxins from a precursor compound (Addink and Olie, 1995).

1 However, no detailed mechanisms have been presented for CDD/CDF formation from other  
2 precursors such as chlorobenzenes under conditions simulating incineration.

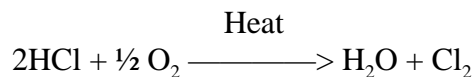
3 A condition in the synthesis of CDDs/CDFs from aromatic precursor compounds is that  
4 the presence of a transition metal catalyst promotes the chemical reaction on the surface of fly ash.  
5 Copper chloride ( $\text{CuCl}_2$ ) is a strong catalyst for promoting surface reactions on particulate matter  
6 to convert aromatic precursor compounds to CDDs/CDFs (Vogg et al., 1987).  $\text{CuCl}_2$  promotes  
7 ring condensation reactions (of the chlorophenols) on fly ash to form CDDs/CDFs (Addink and  
8 Olie, 1995) via the Ullman reaction (Born et al., 1993). In the Ullman reaction, copper catalyzes  
9 the formation of diphenyl ethers by the reaction of halogenated benzenes with alkali metal  
10 phenolates (Born et al., 1993), with copper participating in a nucleophilic aromatic substitution  
11 reaction. Thus, Born et al. (1993) proposed a similar mechanism in catalyzing the formation of  
12 dioxin-like compounds. Using the Ullman reaction as a model, the authors proposed that the  
13 copper-catalyzed condensation of two ortho-substituted chlorophenol molecules form chlorine-  
14 free dibenzo-*p*-dioxins.

15 Vogg et al. (1987) proposed an oxidation reaction pathway, giving rise to the formation of  
16 CDDs/CDFs in the post-furnace regions of the incinerator in the following order: (1) HCl is  
17 thermolytically derived as a product of the combustion of heterogeneous fuels containing  
18 abundant chlorinated organic chemicals and chlorides; (2) oxidation of HCl, with  $\text{CuCl}_2$  as a  
19 catalyst, yields free gaseous chlorine via the Deacon reaction; (3) phenolic compounds (present  
20 from combustion of lignin in the waste or other sources) entrained in the combustion plasma are  
21 substituted on the ring structure by contact with the free chlorine; and (4) a chlorinated precursor  
22 to dioxin (e.g., chlorophenol) is further oxidized (with  $\text{CuCl}_2$  as a catalyst) to yield CDDs/CDFs  
23 and chlorine.

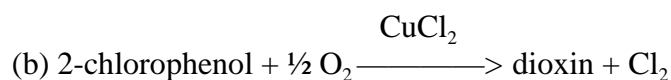
24 Gullett et al. (1990a, b, 1991a, b, 1992) studied the formation mechanisms through  
25 extensive combustion research at EPA and verified the observations of Vogg et al. (1987). It was  
26 proven that CDDs/CDFs could ultimately be produced from low-temperature (i.e., 350 °C)  
27 reactions between dichloride ( $\text{Cl}_2$ ) and a phenolic precursor combining to form a chlorinated  
28 precursor, followed by oxidation of the chlorinated precursors (catalyzed by a copper catalyst such  
29 as  $\text{CuCl}_2$ ), as shown below.

30 1. The initial step in dioxin formation is the formation of chlorine from HCl in the  
31 presence of oxygen (the Deacon process) as follows (Bruce et al., 1991; Vogg et al., 1987):

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2. Phenolic compounds adsorbed on the surface of fly ash are chlorinated to form the dioxin precursor, and the dioxin is formed as a product from the breakdown and molecular rearrangement of the precursor. The reaction is promoted by  $\text{CuCl}_2$  acting as a catalyst (Vogg et al., 1987; Dickson and Karasek, 1987; Gullett et al., 1992):



Eklund et al. (1986) observed the high-temperature formation of a large variety of chlorinated toxic compounds, including CDDs/CDFs, from precursors during a simple experiment in which phenol was oxidized with HCl at 550 °C. One milligram of phenol was placed in a quartz tube reactor with an aqueous solution (10  $\mu\text{L}$ ) of HCl and heated at a temperature of 550 °C for 5 min. Trichlorobenzene, dichlorophenol, dichlorobenzofuran, tetrachlorobenzene, trichlorophenol, and tetrachlorophenol were identified as major products formed. Monochlorobenzene, chlorophenol, dichlorobenzene, tetrachloropropene, pentachloropropene, trichlorobenzofuran, tetrachlorodibenzofuran, trichlorodibenzo-*p*-dioxin, tetrachlorodibenzo-*p*-dioxin, hexachlorodibenzo-*p*-dioxin, hexachlorodibenzofuran, pentachlorobenzene, pentachlorobiphenyl, and pentachlorodihydroxycyclohexane were observed as minor products. Trace species formed included monochlorodibenzofuran, pentachlorodibenzofuran, pentachlorodibenzo-*p*-dioxin, octachlorodibenzofuran, and octachlorodibenzo-*p*-dioxin.

Eklund et al. (1986) hypothesized that chlorinated organic compounds can be produced from phenols, acids, and any chlorine source in the hot post-combustion region (just beyond the exit to the furnace). The reaction was seen as very sensitive to HCl concentration. No chlorinated compounds could be detected when HCl concentrations were  $<10^{-3}$  mol.

Nestrick et al. (1987) reported that the thermolytic reaction between benzene (an unsubstituted precursor) and iron (III) chloride on a silicate surface yielded CDDs/CDFs at temperatures  $\geq 150$  °C. The experimental protocol introduced 100 to 700 mg benzene and  $^{13}\text{C}_6$ -

1 benzene into a macroreactor system consisting of a benzene volatilization chamber connected to a  
2 glass tube furnace. The investigators noted the relevance of this experiment to generalizations  
3 about combustion processes because benzene is the usual combustion byproduct of organic fuels.  
4 Inert nitrogen gas carried the benzene vapor to the furnace area. The exit from the glass tubing to  
5 the furnace was plugged with glass wool, and silica gel was introduced from the entrance end to  
6 give a bed depth of 7 cm to which ferric trichloride ( $\text{FeCl}_3$ ) was added to form an  $\text{FeCl}_3$ /silica  
7 reagent. The thermolytic reaction took place in a temperature range of 150 to 400 °C at a  
8 residence time of 20 min. Although di- through octa-CDDs/CDFs were formed by this reaction at  
9 all temperatures studied, the percent yields were extremely small. Table 2-2 summarizes these  
10 data.

### 11 12 **2.3. MECHANISM 3: *DE NOVO* SYNTHESIS OF CDDs/CDFs DURING** 13 **COMBUSTION OF ORGANIC MATERIALS**

14 The third mechanism, *de novo* synthesis, promotes CDD/CDF formation in combustion  
15 processes from the oxidation of carbon particulate catalyzed by a transition metal in the presence  
16 of chlorine. As in the precursor mechanism (mechanism 2), synthesis is believed to occur in  
17 regions outside of the furnace zone of the combustion process, where the combustion gases have  
18 cooled to a range of temperatures considered favorable to formation chemistry. A key component  
19 to *de novo* synthesis is the production of intermediate compounds (either halogenated or  
20 nonhalogenated) that are precursors to CDD/CDF formation. Research in this area has produced  
21 CDDs/CDFs directly by heating carbonaceous fly ash in the presence of a transition metal catalyst  
22 without the apparent generation of reactive intermediates. Thus, the specific steps involved in the  
23 *de novo* process have not been fully and succinctly delineated. However, laboratory  
24 experimentation has proven that MWC fly ash itself is a reactive substrate, and the matrix can  
25 actually catalyze the *de novo* formation chemistry. Typically, fly ash is composed of an alumina-  
26 silicate construct, with 5 to 10% concentrations of silicon, chlorine (as inorganic chlorides),  
27 sulfur, and potassium (NATO, 1988). Twenty percent of the weight of fly ash particles is carbon,  
28 and the particles have specific surface areas in the range of 200 to 400  $\text{m}^2/\text{kg}$  (NATO, 1988).

29 The *de novo* synthesis essentially is the oxidative breakdown of macromolecular carbon  
30 structures, and CDDs/CDFs are formed partially from the aromatic carbon-oxygen functional  
31 groups embedded in the carbon skeleton (Huang et al., 1999). The distinguishing feature of the *de*

1 *de novo* synthesis over the precursor synthesis is the oxidation of carbon in particulate at the start of  
2 the process to yield precursor compounds. In mechanism 2, the precursor compound is the  
3 starting molecule of the condensation reactions forming CDDs/CDFs (Dickson et al., 1992). By  
4 this distinction, however, one could argue that mechanism 3 is really an augmentation of  
5 mechanism 2 because the production of CDDs/CDFs may still require the formation of a  
6 CDD/CDF precursor as an intermediate species. Nevertheless, a distinction is presented here to  
7 describe additional pathways suggested for the thermal formation of these compounds.

8 To delineate the *de novo* synthesis of CDDs/CDFs, Stieglitz et al. (1989a) conducted  
9 experiments that involved heating particulate carbon containing adsorbed mixtures of magnesium-  
10 aluminum (Mg-Al) silicate in the presence of CuCl<sub>2</sub> (as a catalyst to the reaction). The authors  
11 described heating mixtures of Mg-Al silicate with activated charcoal (4% by weight), chloride as  
12 potassium chloride (7% by weight), and CuCl<sub>2</sub> (1% in water) in a quartz flow tube reactor at 300  
13 °C. The retention time was varied at 15 min, 30 min, and 1, 2, and 4 hr to obtain differences in  
14 the amounts of CDDs/CDFs that could be formed. The results are summarized in Table 2-3. In  
15 addition to the CDDs/CDFs formed as primary products of the *de novo* synthesis, the investigators  
16 observed precursors formed at the varying retention times during the experiment. In particular,  
17 similar yields of tri- through hexachlorobenzenes, tri- through heptachloronaphthalenes, and tetra-  
18 through heptachlorobiphenyls were quantified; this was seen as highly suggestive of the role these  
19 compounds may play as intermediates in the continued formation of CDDs/CDFs.

20 Stieglitz et al. (1989a) made the following observations:  
21

- 22 • The *de novo* synthesis of CDDs/CDFs via the oxidation of carbonaceous particulate  
23 matter occurred at a temperature of 300 °C. Additionally, the experiment yielded  
24 parts-per-billion to parts-per-million concentrations of chlorinated benzenes,  
25 chlorinated biphenyls, and chlorinated naphthalenes through a similar mechanism.  
26 When potassium bromide was substituted for potassium chloride as a source of  
27 halogen for the organic compounds in the reaction, polybrominated dibenzo-*p*-dioxins  
28 and dibenzofurans formed as reaction products.
- 29 • The transition metal compound CuCl<sub>2</sub> catalyzed the *de novo* synthesis of CDDs/CDFs  
30 on the surface of particulate carbon in the presence of oxygen, yielding CO<sub>2</sub> and  
31 chlorinated/brominated aromatic compounds.
- 32 • Particulate carbon, which is characteristic of combustion processes, may act as the  
33 source for the direct formation of CDDs/CDFs, as well as other chlorinated organics.  
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More recently, Stieglitz et al. (1991) investigated the role that particulate carbon plays in the *de novo* formation of CDDs/CDFs from fly ash containing appreciable quantities of organic chlorine. The investigators found that the fly ash contained 900 ng/g of bound organic chlorine. Only 1% of the organic chlorine was extractable. Heating the fly ash at 300 to 400 °C for several hours caused the carbon to oxidize, leading to a reduction in the total organic chlorine in the matrix and a corresponding increase in the total extractable organic chlorine (5% extractable total organic chlorine at 300 °C and 25 to 30% at 400 °C). From this, the authors concluded that the oxidation and degradation of carbon in fly ash are the sources of the formation of CDDs/CDFs; therefore, they are essential in the *de novo* synthesis of these compounds.

Addink et al. (1991) conducted a series of experiments to observe the *de novo* synthesis of CDDs/CDFs in a carbon fly ash system. In this experiment, 4 g of carbon-free MWC fly ash were combined with 0.1 g of activated carbon and placed into a glass tube between two glass wool plugs. The glass tube was then placed into a furnace at specific temperatures ranging from 200 to 400 °C. This protocol was repeated for a series of retention times and temperatures. The investigators observed that CDD/CDF formation was optimized at 300 °C and at the furnace retention times of 4 to 6 hr. Figure 2-2 displays the relationship between retention time, temperature, and CDD/CDF production from the heating of carbon particulate.

Addink et al. (1991) also investigated the relationship between furnace temperature and CDD/CDF production from the heating of carbonaceous fly ash. Figure 2-3 displays this relationship. In general, the concentration began to increase at 250 °C and crested at 350 °C, with a sharp decrease in concentration above 350 °C. The authors also noted a relationship between temperature and the CDD/CDF congener profile: at 300 to 350 °C, the less chlorinated tetra- and penta-CDD/CDF congeners increased in concentration, whereas hexa-, hepta-, and octa-CDD/CDF congeners either remained the same or decreased in concentration. The congener profile of the original MWC fly ash (not subject to *de novo* experimentation) was investigated with respect to changes caused by either temperature or residence time in the furnace. No significant changes occurred, leading the authors to propose an interesting hypothesis for further testing: after formation of CDDs/CDFs occurs on the surface of fly ash, the congener profile remains fixed and insensitive to changes in temperature or residence time, indicating that some form of equilibrium is reached in the formation kinetics.

1 Gullett et al. (1994) used a pilot-scale combustor to study the effect of varying combustion  
2 gas composition, temperature, residence time, quench rate, and sorbent (Ca[OH]<sub>2</sub>) injection on  
3 CDD/CDF formation. The fly ash loading was simulated by injecting fly ash collected from a  
4 full-scale MWC. Sampling and analysis indicated that CDDs/CDFs formed on the injected fly ash  
5 at levels representative of those observed at full-scale MWCs. A statistical analysis of the results  
6 showed that, although the effect of combustor operating parameters on CDD/CDF formation is  
7 interactive and very complicated, substantial reduction in CDD/CDF formation can be realized  
8 with high-temperature sorbent injection to reduce HCl or Cl<sub>2</sub> concentrations, control of excess air  
9 (also affects the ratio of CDDs to CDFs formed), and increased quench rate.

10 Milligan and Altwicker (1995) found that increases in the carbon gasification rate caused  
11 increases in the amounts of CDDs/CDFs formed and gave further evidence linking the oxidation  
12 of carbon to the formation of CDDs/CDFs. Neither the gas-phase CO<sub>2</sub> or CO (products of carbon  
13 oxidation) act as precursors to chlorobenzenes or CDDs/CDFs from reactions with carbon  
14 particulate (Milligan and Altwicker, 1995). Activated carbon, with its high surface area and  
15 excellent adsorptive characteristics, also has the highest gasification rate of all residual carbon  
16 (Addink and Olie, 1995).

17 Experimental evidence suggests the following factors for the *de novo* synthesis of  
18 CDDs/CDFs from carbon: (a) carbon consisting of imperfect and degenerated layers of graphite,  
19 (b) the presence of oxygen, (c) the presence of chlorine, (d) catalyzed reactions by CuCl<sub>2</sub>  
20 or some other transition metal, and (e) temperatures in the range of 200 to 350 °C (Huang and  
21 Buekens, 1995). The oxidation of carbon in fly ash is apparently inhibited at temperatures below  
22 200 °C, thus indicating the lower temperature limit for the thermal inertization of *de novo*  
23 synthesis (Lasagni et al., 2000).

24 Lasagni et al. (2000) determined that at a temperature of 250 °C, the primary product of  
25 the gasification of carbon in fly ash is CO<sub>2</sub>, but in a temperature range of 250 to 325 °C, organic  
26 compounds are formed as products of the oxidation of the carbon. Addink and Olie (1995) raised  
27 the possibility that the molecular backbone of CDDs/CDFs may be present in carbon. If this is the  
28 case, the generation of dioxins and furans from the oxidation of carbon would not require the  
29 formation of intermediate aromatic ring structures. More work is needed to confirm these  
30 possibilities.

1           The *de novo* synthesis of CDDs/CDFs also involves the possibility that aromatic  
2 precursors are formed within the post-combustion zone in the following manner: (1) fuel  
3 molecules are broken down into smaller molecular species (e.g., C<sub>1</sub> and C<sub>2</sub> molecules) during  
4 primary combustion, and (2) these simple molecules recombine in the post-combustion zone to  
5 form larger-molecular aromatic species (i.e., chlorobenzenes and chlorophenols) (Altwicker et al.,  
6 1993). Thus, small molecular products that evolve in the hot zone of the furnace as a  
7 consequence of incomplete fuel or feed material combustion may be important foundation  
8 molecules to the subsequent formation of precursor compounds in the cooler, post-combustion  
9 region.

10           Eklund et al. (1988) reported formation of a wide range of chlorinated organic compounds,  
11 including CDDs, CDFs, and PCBs, from the oxidation of methane with HCl at temperatures of  
12 400 to 950 °C in a quartz flow tube reactor. No active catalysts or reactive fly ashes were added  
13 to the combustion system. From these experimental results, the authors hypothesized that  
14 chlorocarbons, including CDDs/CDFs, are formed at high temperatures via a series of reversible  
15 reactions starting with chloromethyl radicals. The chloromethyl radicals can be formed from the  
16 reaction of methyl radicals and HCl in a sooting flame. Methane is chlorinated by HCl in the  
17 presence of oxygen at high temperatures, forming chlorinated methanes, which react with methyl  
18 radicals at higher temperatures (e.g., 800 °C) to form aromatic compounds. In an oxidative  
19 atmosphere, chlorinated phenols are formed, but alkanes and alkenes are the primary products.  
20 The chlorinated phenols then act as precursors for the subsequent formation of CDDs/CDFs.

21           Aliphatic compounds are common products of incomplete combustion, and they may be  
22 critical to the formation of simple ring structures in the post-combustion zone (Weber et al., 1999;  
23 Sidhu, 1999; Froese and Hutzinger, 1996a, b; Jarmohamed and Mulder, 1994). The aromatic  
24 precursor compounds may be formed in a potentially rich reaction environment of aliphatic  
25 compounds, reactive fly ash particles, HCl, and oxygen. Sidhu (1999) noted that combustion of  
26 acetylene on carbon (a common combustion effluent) in the presence of gaseous HCl and CuCl<sub>2</sub>  
27 (as a catalyst) at 300 °C led to the formation of intermediate precursors and, subsequently,  
28 CDDs/CDFs.

29           Propene oxidized at 350 to 550 °C when in contact with reactive MWC fly ash in a flow  
30 tube reactor formed a wide range of chlorinated aromatic compounds when the resulting  
31 combustion gases were mixed with HCl (Jarmohamed and Mulder, 1994). Although the

1 conversion was low (1 to 3%), the oxidation of propene on fly ash in the presence of HCl can  
2 yield chlorinated benzenes and monobenzofurans. Incorporating an oxygen atom into the  
3 monobenzofuran structure then leads to the formation of monodibenzofuran. The HCl contributes  
4 chlorine to the aromatic ring through the Deacon reaction, and cyclization on the fly ash surface  
5 can yield cyclohexadienyl-substituted benzenes, which in turn can be further oxidized into CDFs.

6 Froese and Hutzinger (1996a) investigated the heterogeneous combustion reactions of the  
7 nonchlorinated C<sub>2</sub> aliphatics. Acetylene, as a model aliphatic compound, was allowed to react  
8 with precleaned MWC fly ash in a tube flow reactor at approximately 600 °C. Metal oxides  
9 (SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CuO)—rather than the metal chlorides used in other precursor  
10 experiments—were added separately as catalysts. The reactants were put into contact with HCl  
11 vapor, which was introduced at a constant flow rate. The acetylene flow was set at 1.1 mL/min  
12 and constantly fell to near 0.9 mL/min over 30 min. Regulated air flow maintained homeostatic  
13 oxidation conditions.

14 Chlorobenzenes and chlorophenols were formed, with isomer patterns generally resembling  
15 isomer patterns of chlorobenzene and chlorophenol emissions from MWCs. CuO was seen as  
16 catalyzing condensation and chlorination reactions under heterogeneous conditions to form the  
17 chlorinated CDD/CDF precursor compounds. Other more volatile compounds formed were short-  
18 chain aliphatic products, such as chloromethane, dichloromethane, and chloro- and  
19 dichloroacetylene. Chlorobenzene congeners were not the major products formed; perchlorinated  
20 aliphatic compounds dominated as gas-phase reaction products.

21 Froese and Hutzinger (1997) noted that perchlorinated aliphatic compounds (e.g.,  
22 hexachloropropene, hexachloro-1,3-butadiene, and hexachlorocyclopentadiene) are important  
23 intermediates in aromatic ring formation; they concluded that the catalytic reaction of C<sub>2</sub> aliphatic  
24 compounds at 600 °C dramatically contributes to the formation of chlorinated and nonchlorinated  
25 aromatic compounds during combustion. Thus, aliphatic compounds can form CDD/CDF  
26 precursor compounds. Variable temperature effects were observed in the formation of  
27 CDDs/CDFs in the same reactions. Maximal OCDD formation occurred at 400 °C, and the tetra-  
28 hepta homologue groups were maximally formed at 600 °C. For CDFs, production of more  
29 highly chlorinated homologues occurred at 400 °C, and the formation of tetrachlorodibenzofurans  
30 occurred at 500 °C. Froese and Hutzinger (1996a) noted a 100-fold increase in  
31 tetrachlorodibenzofuran formation at 500 °C when compared with formation at 400 °C. An

1 explanation for this increase is that the higher temperature maximized the formation of the  
2 CDD/CDF precursor (chlorophenol) from the aliphatic starting compound.

3 Froese and Hutzinger (1996b) produced polychlorinated benzene and phenol compounds at  
4 a temperature range of 300 to 600 °C. This was caused by the heterogeneous combustion  
5 reactions of ethylene and ethane over fly ash in the presence of HCl, oxygen, and a metal catalyst.  
6 No chlorobenzene congener precursors were formed from ethylene and ethane at 300 °C;  
7 however, the formation rate increased with temperature until a maximum production was  
8 achieved at 600 °C. No definitive temperature dependence was observed for the formation of  
9 chlorophenols from the aliphatic starting compounds. However, at 500 °C, 2,4,6-trichlorophenol  
10 dominated the reaction products; at 300 °C, PCP was initially produced.

11 Froese and Hutzinger (1996b) also investigated the effects of elemental catalysts on  
12 potentiating the heterogeneous combustion reactions by measuring the amount of chlorobenzene  
13 and chlorophenol product formed from the reactions of ethylene/HCl over each catalyst at  
14 600 °C. The reaction with SiO<sub>2</sub> did not have a catalytic effect. Al<sub>2</sub>O<sub>3</sub> catalytic action showed  
15 high intensity for the dichlorobenzene isomers and decreasing intensity for the higher chlorinated  
16 isomers. Comparison of the amount of dichlorobenzene product formed indicated that an equal  
17 quantity was produced with either Al<sub>2</sub>O<sub>3</sub> or fly ash; however, Al<sub>2</sub>O<sub>3</sub> formed four to five times  
18 more product than did the CuO catalyst. For tri- to hexachlorobenzene congeners, MWC fly ash  
19 reactions produced 5 to 10 times more product than did the metal catalysts. However, the  
20 presence of the CuO catalyst in these reactions produced a chlorobenzene congener pattern  
21 comparable to the fly ash reactions. With regard to chlorophenol production, Al<sub>2</sub>O<sub>3</sub> also produced  
22 a unique dichlorophenol pattern, suggesting that Al<sub>2</sub>O<sub>3</sub> has a unique catalytic effect in the high-  
23 temperature reactions of C<sub>2</sub> aliphatic compounds.

24 Reactions with CuO produced additional products, including chlorinated methyl  
25 compounds, chlorinated C<sub>2</sub> aliphatics, and perchlorinated C<sub>3</sub>–C<sub>5</sub> alkyl compounds. The authors  
26 noted that these perchlorinated alkyl groups, formed by reacting ethylene and ethane over fly ash  
27 in the presence of the CuO catalyst, are key intermediate compounds to the formation of first  
28 aromatic rings in typical combustion systems. This emphasizes the importance of copper's  
29 catalytic effects in a combustion fly ash system. Al<sub>2</sub>O<sub>3</sub> catalyzed reactions produced  
30 nonchlorinated naphthalene and alkylbiphenyl compounds. Furthermore, the organic chlorine in

1 aliphatic compounds may also act as a direct source of chlorine for the formation of CDDs/CDFs  
2 in a carbon fly ash system (Weber et al., 1999).

3 In an earlier experiment using a similar flow tube apparatus, Froese and Hutzinger (1994)  
4 formed chlorinated benzenes and phenols in fly ash catalyzed reactions with trichloroethylene at  
5 temperatures of 400 to 500 °C. In this case, metal oxides (CuO, FeO<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>) were used as  
6 catalysts, but no HCl was added for oxychlorination of product compounds. Under combustion  
7 conditions, temperature-dependent formation of chlorinated aromatics occurred from the  
8 trichloroethylene starting compound. Reaction with fly ash at 600 °C formed hexachlorobenzene  
9 in concentrations that were about 1,000 times greater than at 400 and 500 °C, with similar results  
10 for chlorophenols. The authors hypothesized that key aromatic precursors for CDDs/CDFs are  
11 formed in the higher-temperature region of a post-combustion zone (about 600 °C) and are then  
12 carried to the cooler post-combustion region (about 300 °C), where the precursors form  
13 CDDs/CDFs.

#### 14 15 **2.4. THE ROLE OF CHLORINE IN THE FORMATION OF CDDs/CDFs IN** 16 **COMBUSTION SYSTEMS**

17 The formation of CDDs/CDFs in the post-combustion region of combustion systems via  
18 either the precursor or *de novo* synthesis mechanisms requires the availability of a source of  
19 chlorine (Luijk et al., 1994; Addink et al., 1995; Stanmore, 2004; Wikstrom et al., 2004 ).  
20 Chlorine concentration in this region is related somehow to the chlorine content of combustion  
21 fuels and feed materials in incineration/combustion systems because there can be no other source.  
22 The main question regarding the role of chlorine in forming CDDs/CDFs is whether or not a  
23 positive and direct correlation exists between the amount of chlorine in feeds and the amount of  
24 CDDs/CDFs formed and emitted from the stack of a combustion system. If a direct relationship  
25 appears to exist, then reductions in the chlorine content of fuels/feeds prior to combustion should  
26 result in a corresponding reduction in the concentrations of CDDs/CDFs formed after combustion.  
27 If the oxychlorination reactions require a number of steps, then the relationship between chlorine  
28 in uncombusted fuels and CDDs/CDFs formed after combustion may not be linear, although it  
29 may still be dependent in some nonlinear association. The main question can best be addressed by  
30 examining both formation mechanisms revealed in laboratory-scale combustion experiments and  
31 correlations between chlorine inputs with CDD/CDF outputs in commercial-scale combustors.

### 2.4.1. Review of Laboratory-Scale Studies

A wide body of experimental evidence has elucidated the direct and indirect associations between chlorine in feeds and fuels and the potential formation of CDDs/CDFs during combustion. The *de novo* synthesis of CDDs/CDFs requires two basic reactions: the transfer of chlorine to residual carbon particulate with subsequent formation of carbon-chlorine bonds and the oxidation of this macromolecular complex to yield CO<sub>2</sub> and volatile and semivolatile organic compounds as side products (Weber et al., 1999). Transition metal compounds, such as CuCl<sub>2</sub>, catalyze these reactions. Gaseous HCl, Cl<sub>2</sub>, and chlorine radicals are the most abundant sources of chlorine available for participating in the formation of CDDs/CDFs and are initially formed as a combustion by-product from the inorganic and organic chlorine contained in the fuel (Wikstrom et al., 2003; Rigo, 1998; Addink et al., 1995; Rigo et al., 1995; Halonen et al., 1994; Luijk et al., 1994; Altwicker et al., 1993; Wagner and Green, 1993; Dickson et al., 1992; Bruce et al., 1991; Gullet et al., 1990b; Commoner et al., 1987; Vogg et al., 1987).

MSW contains approximately 0.45 to 0.90% (w/w) chlorine (Domalski et al., 1986). The most predominant chlorine species formed from MSW combustion is gaseous HCl, which average between 400 and 600 ppm in the combustion gas (Wikstrom et al., 2003; U.S. EPA, 1987a). Chlorine is initially released from the chlorine in the MSW and is rapidly transformed to HCl by the abstraction of hydrogen from reacting with hydrocarbons present in the fuel (Wikstrom et al., 2003). HCl may oxidize to yield free chlorine gas by the Deacon process, and the free chlorine directly chlorinates a CDD/CDF precursor along the aromatic ring structure. Further oxidation of the chlorinated precursor in the presence of a transition metal catalyst (of which CuCl<sub>2</sub> was found to be the most active) yields CDDs/CDFs (Altwicker et al., 1993). Increasing the yield of chlorine in vapor phase from HCl oxidation generally increases the rate of CDD/CDF formation. Formation kinetics are most favored at temperatures ranging from 200 to 450 °C. However HCl is considered a weak chlorinating agent because of the tenacity of the hydrogen to carbon bond of aromatic compounds (Wikstrom et al., 2003).

Chlorine production from gaseous HCl can be reduced either by limiting initial HCl concentration or by shortening the residence time in the Deacon process temperature (Bruce et al., 1991; Gullett et al., 1990b; Commoner et al., 1987). Bruce et al. (1991) observed a general increase in CDD/CDF formation with increases in the vapor-phase concentration of chlorine. Bruce et al. (1991) verified a dependence of the formation of CDDs/CDFs in the post-combustion

1 zone on the concentration and availability of gaseous chlorine. This finding is in agreement with  
2 a simple experiment by Eklund et al. (1986) in which unsubstituted phenol was mixed with HCl at  
3 550 °C in a quartz tube reactor. A wide range of toxic chlorinated hydrocarbons was formed,  
4 including CDDs/CDFs. Eklund et al. (1988) also found a dependence of the amounts of  
5 chlorinated phenol product formed from the nonchlorinated starting material on the increased  
6 amount of HCl introduced into the reaction. Under the conditions of this experiment, no  
7 chlorinated compounds were formed at an HCl concentration of less than  $10^{-3}$  mol, and maximum  
8 chlorophenol concentration occurred at around  $10^8$  mol.

9 Born et al. (1993) also observed that increasing levels of HCl gave rise to increasing rates  
10 of oxychlorination of precursors, with increasing chances for the post-combustion formation of  
11 CDDs/CDFs. However, Addink et al. (1995) observed that an HCl atmosphere and/or chlorine  
12 produced approximately equal quantities of CDDs/CDFs during the *de novo* synthesis from  
13 oxidation of particulate carbon. Such results suggest that chlorine production via the Deacon  
14 process reaction in the *de novo* synthesis may not be the only chlorination pathway and may  
15 indicate that the HCl molecule can be a direct chlorinating agent. In addition, some chlorine is  
16 expected to be formed from the oxidation of metal chlorides (e.g.,  $\text{CuCl}_2$ ), but  $\text{Cl}_2$  formation from  
17 the Deacon process is greater because of the continuous supply of HCl delivered from the  
18 combustion chamber (Bruce et al., 1991). In this case, a first-order dependence of HCl to  $\text{Cl}_2$  is  
19 observed.

20 More recently, however, Wikstrom et al. (2003) have reported on the importance of  
21 chlorine species on the *de novo* formation of CDDs/CDFs. HCl can react with oxidizing radicals  
22 (e.g., hydroxyl radical or OH) to produce chlorine radicals ( $\text{Cl}\cdot$ ).  $\text{Cl}\cdot$  are highly reactive and can  
23 replace hydrogen atoms with chlorine atoms in the H-C bond of the aromatic structure. Thus, HCl  
24 is most likely an indirect chlorinating agent via the formation of chlorine radicals.

25 Experimentally, about 18% of the total chlorine content in fuels can be thermally  
26 converted to chlorine radicals in the post-combustion zone (Procaccini et al., 2003). Although  
27 HCl is the primary chlorine-containing product formed from the combustion of chlorine rich fuels,  
28 HCl may not be the major chlorinating agent in the formation of chloro-organics in the cooled  
29 down region of the combustor. The experiments of Procaccini et al. (2003) indicate that the major  
30 role of HCl in the formation of chloro-organic compounds at cooler temperatures may be that of a  
31 chemical progenitor of chlorine radicals. HCl reacts with the oxidizing radicals OH and O

1 abundantly present in combustion off-gases to reform Cl<sup>·</sup>. Chlorine radicals readily abstract  
2 hydrogen atoms from the H-C bond of aromatic compounds formed as combustion by-products of  
3 organic fuels. By this means, unsubstituted aromatic compounds, e.g., benzene, undergo oxy-  
4 chlorination reactions with the Cl<sup>·</sup> to form chlorobenzenes and chlorophenols. These products are  
5 well defined precursor compounds for the synthesis of CDDs/CDFs.

6 Wagner and Green (1993) investigated the correlation of chlorine content in feed to stack  
7 emissions of chlorinated organic compounds in a pilot-scale incinerator using HCl flue gas  
8 measurements as a surrogate for fuel-bound organic chlorine. In addition to MSW as a fuel,  
9 variable amounts of polyvinyl chloride (PVC) resin were added during 6 of 18 stack test runs.  
10 The resulting data were regressed to determine the coefficient of correlation between HCl  
11 measurements and total chlorobenzene compound emission measurements. In nearly all of the  
12 different regression analyses performed, the relationship between HCl emissions and emissions of  
13 chlorinated organic compounds was positive and well defined. In addition, the investigators  
14 found a direct dependence of HCl emission levels on the level of PVC in the waste, with generally  
15 increasing amounts of HCl formed as increasing amounts of PVC were added. From these  
16 experiments, they concluded that decreased levels of organically bound chlorine in the waste  
17 incinerated led to decreased levels of chlorinated organic compounds in stack emissions.

18 Kanters and Louw (1994) investigated a possible relationship between chlorine content in  
19 waste feed and chlorophenol emissions in a bench-scale thermal reactor. MSW incineration with  
20 a higher content of chlorine in the feed caused higher emissions of chlorophenols via the *de novo*  
21 synthesis pathway. The investigators lowered the chlorine content of the prototype MWC by  
22 replacing chlorine-containing fractions with cellulose. They observed appreciable decreases in the  
23 amounts of chlorophenol formed from combustion and concluded that reductions in the chlorine  
24 content of waste feeds or elimination of PVC prior to municipal waste combustion should result  
25 in a corresponding reduction in chlorophenol and CDD/CDF emissions.

26 In a similar experiment, Wikstrom et al. (1996) investigated the influence of chlorine in  
27 feed materials in the formation of CDDs/CDFs and benzenes in a laboratory-scale fluidized bed  
28 reactor. Seven artificial fuels (composed of 34% paper, 30% wheat flour, 14% saw dust, 7%  
29 polyethylene, and 2% metals), to which varying amounts of organic chlorine and inorganic  
30 chlorine (CaCl<sub>2</sub> · 6H<sub>2</sub>O) were added, were combusted. The chlorine content of these fuels varied  
31 from 0.12 to 2%. All combustion was performed with a high degree of combustion efficiency

1 (99.999%) to avoid the formation of polyvinylidene chloride and naphthalenes as products of  
2 incomplete combustion of pure PVC. With the combustion conditions held constant, only the  
3 chlorine content of the fuel was varied. Flue gases were sampled for CDDs/CDFs and  
4 chlorobenzenes.

5 In these experiments, concentrations of PCB isomers were approximately 1,000-fold  
6 higher than CDDs/CDFs (expressed as concentration of I-TEQ<sub>DF</sub>). Moreover, a correlation was  
7 found between I-TEQ<sub>DF</sub> and PCB levels in the flue gases and the chlorine content of the fuel. A  
8 fivefold increase in both I-TEQ<sub>DF</sub> and PCB concentrations was observed in the flue gases from  
9 combustion of fuels containing 0.5 and 1.7% total chlorine. Furthermore, no differences were  
10 observed in the amount of chlorinated product produced or when the source of chlorine in the fuel  
11 was organic or inorganic. No correlation was observed between total CDD/CDF and PCB  
12 formation and total chlorine in the feed when chlorine levels in feed were or lower (0.5%). The  
13 highest amounts of CDDs/CDFs and PCBs were formed from the fuel with the highest total  
14 chlorine content (1.7%).

15 Under the conditions of this experiment, Wikstrom et al. (1996) observed that a chlorine  
16 fuel content of 1% was a threshold for forming excess CDDs/CDFs and PCBs during combustion.  
17 The authors noted that MSW in Sweden contained about 0.7% chlorine, of which approximately  
18 40% was organic chlorine. They concluded that MSW was below the observed threshold value of  
19 1% chlorine content associated with a general increase in CDD/CDF and PCB formation in the  
20 post-combustion region. They also stated that their study did not support the hypothesis that  
21 elimination of only PVC from waste prior to combustion will cause a significant reduction in  
22 CDD/CDF emissions if the combustion process is well controlled (high combustion efficiency).  
23 Wang et al. (2003) verified the existence of a theoretical chlorine-in-fuel threshold when they  
24 demonstrated *de novo* synthesis combusting fuels with 0.8 to 1.1% chlorine.

25 A primary by-product of PVC combustion is HCl. Paciorek et al. (1974) thermally  
26 degraded pure PVC resin at 400 °C and produced 550 mg/g HCl vapor as a primary thermolysis  
27 product, which was observed as being 94% of the theoretical amount, based on the percent weight  
28 of chlorine on the molecule. Ahling et al. (1978) concluded that HCl can act as a chlorine donor  
29 to ultimately yield chlorinated aromatic hydrocarbons from the thermolytic degradation of pure  
30 PVC and that these yields are a function of transit time, percent oxygen, and temperature. They  
31 observed data from 11 separate experiments conducted with temperatures ranging from 570 to

1 1,130 °C. These data indicated that significant quantities of various isomers of dichloro-,  
2 trichloro-, tetrachloro-, and hexachlorobenzenes could be produced. Choudhry and Hutzinger  
3 (1983) proposed that the radical species Cl· and H· generated in the incineration process may  
4 attack the chlorinated benzenes and abstract hydrogen atoms to produce orthochlorine-substituted  
5 chlorophenol radicals. These intermediate radical species then react with molecular oxygen to  
6 yield ortho-substituted chlorophenols. As a final step, the ortho-substituted chlorophenols act as  
7 ideal precursors to yield CDDs/CDFs with heat and oxygen. The chlorine in aliphatic compounds  
8 has been observed as both yielding high amounts of HCl during combustion and acting as a direct  
9 chlorine source for the *de novo* synthesis of CDDs/CDFs (Weber et al., 1999).

10 In addition to HCl as a by-product of PVC combustion, Kim et al. (2004) determined that  
11 the combustion of pure PVC yielded appreciable amounts of PAHs, PCBs, chlorobenzenes, and  
12 chlorophenols. They suggested that the gas-phase production of PCBs and chlorobenzenes  
13 contributed to the gas-phase formation of CDDs/CDFs through the precursor mechanism.  
14 Chlorophenols, however, contributed to the *de novo* formation. Kim et al. (2004) reported that the  
15 *de novo* synthesis of CDDs/CDFs from chlorophenols was approximately 100 times greater than  
16 formation from PCB and chlorobenzene precursors.

17 Takeo et al. (2002) found a clear correlation between dioxin formation and the chlorine  
18 content of mixed plastics combusted in a laboratory scale incinerator. PVC, polyethylene (PE),  
19 polystyrene (PS), and polyethylene terephthalate (PET) and their various mixtures were burned at  
20 temperatures greater than 600 °C. Average CO concentrations in the exhaust gases were varied  
21 from 2 to 880 ppm as a general indication of the quality of the fire in the combustion chamber.  
22 When incinerated, each type of plastic formed CDDs/CDFs in the exhaust gases. Of the total  
23 CDDs formed, hexa-CDD and tetra-CDD formed in the greatest amounts when PE was  
24 combusted. Mono-CDF was the most abundant CDF formed from PE combustion. Mono-ortho  
25 coplanar PCBs were preferentially formed over nonortho-PCBs. The combustion of PS caused  
26 tetra-CDD to be formed in the greatest abundance of all possible CDDs whereas tetra-CDF was  
27 the most abundant dibenzofuran. Mono-ortho PCBs formed more than nonortho coplanar PCBs  
28 when PS was combusted. The combustion of PET mostly formed mono-CDD and mono-CDF  
29 among the CDDs/CDFs formed. When PVC was combusted with the conditions of high  
30 temperature and low CO (good combustion), a total of 53.5 ng/g of total CDD was formed, with  
31 the hexa-CDD predominating. In addition, good combustion conditions formed a total of 771

1 ng/g of CDFs, with Cl<sub>2</sub> and Cl<sub>3</sub> CDF congeners dominating. When PVC was combusted with the  
2 conditions of low temperature and high CO (poor combustion), the total CDDs and CDFs formed  
3 increased significantly to 429 ng/g and 8,492 ng/g, respectively. Tri-CDD and di-CDF dominated  
4 the congener distributions suggesting that poor combustion of PVC tends to form high levels of  
5 lower chlorinated CDDs/CDFs. The investigators observed that maintaining good combustion  
6 tended to minimize the formation of CDDs/CDFs from the combustion of chlorinated plastics.

7 Shibata et al. (2003) reported on forming CDDs/CDFs from the combustion of PVC in  
8 quartz ampules. Synthesis of CDDs/CDFs proceeded *de novo* in a temperature range of 200 to  
9 400 °C and catalyzed by copper oxide (CuO). Maximum formation occurred at 300 °C. Hepa-  
10 and Octa-CDD were the dominant CDDs observed in the flue gases whereas tetra-, penta-and  
11 hexa-CDFs dominated the CDFs. The ratio of CDFs to CDDs from PVC combustion was greater  
12 than 1, which is typical of MSW combustion (Shabata et al., 2003).

13 Addink and Altwicker (1999) reported on the role of the inorganic chloride ion in the  
14 formation of CDDs/CDFs using the labeled compound Na<sup>37</sup>Cl. The inorganic chloride ion forms  
15 carbon-chlorine bonds on soot particles during combustion. The chlorine in the soot can be  
16 directly inserted into a CDD/CDF molecule during formation or it can exchange with the chloride  
17 ions in the transitional metal catalyst, which promotes CDD/CDF formation. Thus, the inorganic  
18 chlorine ion participates as a chlorine donor to CDD/CDF formation.

19 De Fre and Rymen (1989) reported on the formation of CDDs/CDFs from hydrocarbon  
20 combustion in a domestic gas/oil burner in the presence of 15 and 300 ppm concentrations of HCl.  
21 More than 100 chlorinated organic compounds were detected in the flue gases whenever HCl was  
22 injected into the system. The investigators observed formation of CDDs and CDFs in all  
23 experiments where HCl was injected in a hydrocarbon flame. In this case, CDFs were always  
24 more abundant than CDDs. It was concluded that the relationship between the HCl concentration  
25 and the emitted concentration of CDDs/CDFs under fixed combustion conditions appeared to be  
26 exponential for a wide range of temperatures (240 to 900 °C).

## 2.4.2. Review of Full-Scale Combustion Systems

The review of experimental data clearly indicates an association between chlorine content of feed/fuels and the potential synthesis of CDDs/CDFs. Paradoxically, the review of full-scale operating incineration processes does not yield such unequivocal results, indicating that complex kinetic events make strong associations difficult in full-scale systems. The following is a review of studies of the association between chlorine in feeds and stack releases of CDDs/CDFs in full-scale incineration systems.

In the stack testing of a variety of industrial stationary combustion sources during the National Dioxin Study in 1987, EPA made a series of qualitative observations about the relationship between total chlorine present in the fuel/waste and the magnitude of emissions of CDDs/CDFs from the stack of the tested full-scale combustion facilities (U.S. EPA, 1987a). In general, combustion units with the highest CDD emission concentrations had greater quantities of chlorine in the fuel; conversely, sites with the lowest CDD emission concentrations contained only trace quantities of chlorine in the feed. The typical chlorine content of various combustion fuels was reported by Lustenhouwer et al. (1980) as coal, 1,300  $\mu\text{g/g}$ ; MSW, 2,500  $\mu\text{g/g}$ ; leaded gasoline, 300 to 1,600  $\mu\text{g/g}$ ; and unleaded gasoline, 1 to 6  $\mu\text{g/g}$ .

Thomas and Spiro (1995) also analyzed the relationship between CDD/CDF emissions from combustion and the chlorine content of feed materials. Thomas and Spiro (1996) plotted average CDD/CDF emission factors for a variety of combustion processes (black liquor boilers, unleaded gasoline combustion, leaded gasoline combustion, wire incineration, cigarette combustion, sewage sludge incineration, MWC, PCP-treated wood combustion, hazardous waste incineration, and hospital waste incineration) against the average chlorine concentration of the combusted material. The plot showed that average CDD/CDF emissions of combustion source categories tend to increase with the average chlorine content of the combusted fuel. This analysis indicated that combustion sources with relatively high combustion efficiency and adequate air pollution controls tended to have emissions two orders of magnitude lower than those of poorly operated sources. This suggests that the magnitude of CDD/CDF emissions is strongly dependent on chlorine concentration in fuels in the context of the more poorly controlled and operated combustion sources, and the association becomes less apparent in the well controlled facilities operating with good combustion practices. The slope of the log-log plot was between 1 and 2 for

1 the poorly controlled and operational facilities indicating that the relationship between chlorine  
2 content and CDD/CDF emissions was more than proportional.

3 Costner (1998) reported finding a positive correlation between chlorine content of feed  
4 material and CDD/CDF emissions at a full-scale hospital waste incinerator. Costner concluded  
5 that emissions at this facility were dependent on chlorine input at a concentration as low as  
6 0.031% and that there was no evidence of a threshold in the relationship between chlorine in feed  
7 and CDD/CDF emissions.

8 Rigo et al. (1995) summarized the results of a study commissioned by the American  
9 Society of Mechanical Engineers (ASME, 1995). The study was a statistical evaluation of the  
10 relationship between HCl concentration in flue gases and various combustion systems (i.e.,  
11 MWCs, hospital waste incinerators, HWIs, biomass combustors, laboratory combustors, and  
12 bench-scale combustors) to stack emissions of total CDDs/CDFs. In this study, HCl was used as a  
13 surrogate for total chlorine content in the fuel. The data analysis was sufficient for 92 facilities in  
14 the database that showed both HCl and CDD/CDF emissions. Of the 92 facilities, 72 did not  
15 show a statistically significant relationship between chlorine input and CDD/CDF output in  
16 emissions streams, 2 showed increasing CDD/CDF concentrations with increasing chlorine, and 8  
17 showed decreasing CDD/CDF concentrations with increasing chlorine. AMSE (1995) reports the  
18 following conclusion:

19  
20 The failure to find simultaneous increases in most cases and finding inverse  
21 relationships in a few indicates that any effect chlorine has on CDD/CDF emissions  
22 is smaller than the variability of other causative factors. Whatever effect chlorine  
23 has on CDD/CDF emissions in commercial-scale systems is masked by the effect  
24 of APCS (air pollution control systems) temperature, ash chemistry, combustion  
25 conditions, measurement imprecision, and localized flow stratification.

26  
27 Liberson and Belanger (1995) reported the results of an analysis of the formation and  
28 emission of CDDs/CDFs as a function of total chlorine in combustion feed materials at a rotary  
29 kiln HWI. The data were generated from multiple test series conducted over a 13-month period at  
30 the HWI while operating a carbon injection system specifically designed to control and reduce  
31 CDD/CDF stack emissions. The chlorine feed rates ranged from 0 to 3,300 lb/hr, and the  
32 CDD/CDF emission rates ranged from 0.7 to 39 ng/dscm. The authors noted that multiple series  
33 of CDD/CDF control systems were used on this HWI (i.e., a high temperature secondary

1 combustion chamber, a spray dryer-evaporative quench that further cools the combustion gases,  
2 activated carbon injection to adsorb semivolatile organics, and a cool-side electrostatic  
3 precipitator followed by an acid gas scrubber to collect HCl and Cl<sub>2</sub>). From analyses of the data,  
4 the authors concluded that no correlation exists between CDD/CDF emissions and chlorine feed  
5 in a modern MWC using carbon injection for CDD/CDF control.

6 More recently, Wang et al. (2003) investigated the association between chlorine content of  
7 waste feeds and CDD/CDF emissions from full-scale combustion systems. Previously, Wikstrom  
8 et al. (1996) had discerned a chlorine content in feeds of 1% as being a threshold concentration to  
9 the formation of CDDs/CDFs, i.e., association with the magnitude of CDDs/CDFs formed  
10 occurred only when chlorine content in the feed was  $\geq 1\%$ . Wang et al (2003) confirmed the  
11 apparent existence of a chlorine threshold to the emissions of total CDDs/CDFs after statistically  
12 reviewing input of chlorine in feed versus output of CDDs/CDFs in emissions at two tested  
13 medical incinerators and two tested MWCs. Additionally, the authors examined second-hand data  
14 from 13 other dioxin sources obtained from the literature and found that the formation of CDFs  
15 was greater than the formation of CDDs when the chlorine content of the waste feed exceeded the  
16 threshold. However, when the chlorine content was below the approximate 1% threshold, the  
17 formation of CDDs was greater than the formation of CDFs. The authors proposed that chlorine  
18 content below the threshold formed chlorinated precursors to CDDs rather than forming the  
19 dibenzofuran molecule. Chlorine content above the threshold contributed to deterioration of  
20 combustion conditions causing the formation of PAHs, which, in turn, contributed to the  
21 formation of CDFs.

## 22 23 **2.5. POTENTIAL PREVENTION OF CDD/CDF FORMATION IN COMBUSTION** 24 **SYSTEMS**

25 Given what is currently understood about oxychlorination reactions in the synthesis of  
26 CDDs/CDFs, researchers have identified certain interventions that could be taken to reduce or  
27 impede formation in combustion systems. Rayhunathan and Gullett (1996) demonstrated in a  
28 pilot-scale incinerator that sulfur compounds can combine with the metal catalyst necessary to  
29 stimulate the Deacon reaction of HCl and oxygen to yield Cl<sub>2</sub>, thereby neutralizing the catalyzing  
30 agent and reducing the formation of CDDs/CDFs. The Deacon reaction, which forms free  
31 chlorine in the combustion plasma, is seen as occurring only in the presence of a catalyst. Thus,

1 the sulfur dioxide (SO<sub>2</sub>) molecule (formed when sulfur in the fuel combines with oxygen) can  
2 inhibit the catalytic activity of the fly ash by either combining with a metal-based Deacon catalyst  
3 in the fly ash or depleting the Cl<sub>2</sub> formed. The authors observed that the principal action of sulfur  
4 in inhibiting the formation of CDDs/CDFs in combustion systems is through SO<sub>2</sub> depletion of Cl<sub>2</sub>,  
5 as follows:



6  
7  
8  
9 The relevance of this finding is that the co-combustion of MSW with coal (that contains  
10 sulfur) should lead to dramatic reductions in the amount of CDDs/CDFs formed and emitted, and  
11 it may explain why, in the United States, coal combustion at power plants results in CDD/CDF  
12 emission rates more than a magnitude lower than those at MWCs.

13 Naikwadi and Karasek (1989) investigated the addition of calcium oxide (CaO) and  
14 triethylamine (TEA) to the flue gases of a combustion system as an inhibitor of the catalytic  
15 activity of fly ash. They placed 500 µg <sup>13</sup>C-labeled PCP (a dioxin precursor) in a combustion flow  
16 tube and allowed it to react with organic-extracted MWC fly ash at 300 °C under an air stream.  
17 Under these conditions, CDDs/CDFs were formed at concentrations ranging from 1,660 to 2,200  
18 ng per 100 µg <sup>13</sup>C-PCP. The experimental method was then modified by mixing reactive MWC  
19 fly ash with either CaO or TEA. The results showed that the amount of CDDs/CDFs formed  
20 could be reduced by an order of magnitude from the reaction of PCP with fly ash and the addition  
21 of TEA as an inhibitor. When CaO was mixed with fly ash, the amount of CDDs/CDFs formed  
22 decreased more than 20-fold.

## 23 24 **2.6. THEORY ON THE EMISSION OF PCBs**

25 Air emissions of PCBs from MSW incineration is less well studied. Probably the  
26 formation mechanisms that apply to CDDs/CDFs would also apply to PCBs. Mechanism 1 (pass  
27 through) is implicit in the Toxic Substances Control Act rule, which requires 99.9999%  
28 destruction in HWIs. When this occurs, 0.0001% of the initial amount of PCBs fed into the HWI  
29 may be emitted from the stack. This may indicate that some small fraction of the PCBs present in  
30 the fuel fed into an incineration process may result in PCB emissions from the stack of the  
31 process.

1 PCBs have been measured as contaminants in raw refuse prior to incineration in an MWC  
2 (Choudhry and Hutzinger, 1983; Federal Register, 1991a). Using this information, it is possible  
3 to test mechanism 1 for CDD/CDF emissions: that the PCB contamination present in the fuel is  
4 mainly responsible for emissions from the stack. The mass balance of total PCBs, beginning with  
5 measurement in the raw refuse and ending with measurement at the stack of an RDF MWC  
6 (Federal Register, 1991a), can be used to calculate the destruction rated efficiency (DRE) of  
7 incineration of the PCB-contaminated MSW. Using results from test number 11 at the RDF  
8 facility (Federal Register, 1991a), a computation of DRE can be made using the following  
9 equation (Brunner, 1984):

$$DRE = \frac{W_I - W_O}{W_I} \times 100\% \quad (2-1)$$

10  
11  
12  
13  
14  
15 where:

16  $W_I$  = mass rate of contaminant fed into the incinerator system

17  
18  $W_O$  = mass rate of contaminant exiting the incinerator system

19  
20 In test 11, 811 ng total PCBs/g refuse were measured in the MSW fed into the incineration  
21 system, and 9.52 ng/g were measured at the inlet to the pollution control device (i.e., outside the  
22 furnace region but preceding emission control). From these measurements, a DRE of 98.8% can  
23 be calculated. Therefore, it appears that PCB contamination in the raw MSW fed into this  
24 particular incinerator may have accounted for the PCB emissions from the stack of the MWC.

25 PCBs can be thermolytically converted into CDFs (Choudhry and Hutzinger, 1983;  
26 U.S. EPA, 1984). This process occurs at temperatures somewhat lower than those typically  
27 measured inside the firebox of an MWC. Laboratory experiments conducted by EPA indicate that  
28 the optimum conditions for CDF formation from PCBs are near a temperature of 675 °C in the  
29 presence of 8% oxygen and a residence time of 0.8 sec (U.S. EPA, 1984). This resulted in a 3 to  
30 4% efficiency of conversion of PCBs into CDFs. Because 1 to 2% of the PCBs present in the raw  
31 refuse may survive the thermal stress imposed in the combustion zone of the incinerator (Federal  
32 Register, 1991a), it is reasonable to presume that PCBs in the MSW may contribute to the total  
33 mass of CDF emissions released from the stack of the incinerator.

1           Although it appears that contamination of waste feed with PCBs may be an important  
2 factor in detecting PCBs in stack emissions from combustion processes, recent research has  
3 indicated that these compounds may also be formed in the post-combustion zone, either from *de*  
4 *nov*o synthesis or from precursor compounds. Zheng et al. (1999) observed the formation of  
5 PCBs in the post-combustion zone from the pyrolysis of chlorobenzenes using a laboratory-scale  
6 furnace. The investigators observed that PCBs were optimally formed from less-chlorinated  
7 chlorobenzenes (e.g., 1,3-dichlorobenzene) catalyzed by CuCl<sub>2</sub>. In this experiment, maximum  
8 PCB production occurred at a temperature of 350 °C. Wikstrom et al. (1998) reported secondary  
9 formation of PCBs in the post-combustion zone similar to the *de novo* synthesis of CDDs/CDFs,  
10 albeit PCBs were formed in only small amounts relative to CDDs/CDFs.

11           Fangmark and coworkers (1994) postulated that formation of PCBs and CDDs/CDFs in  
12 the post-combustion zone may occur through the same mechanisms. On the other hand,  
13 Blumenstock et al. (1998) produced results in a pilot-scale furnace that were inconsistent with the  
14 *de novo* formation of CDDs/CDFs in the post-combustion zone (i.e., PCBs seemed to be  
15 optimally formed at high temperatures in oxygen-deficient atmospheres). Shin and Chang (1999)  
16 noted a positive correlation between PCB concentrations on MSW incineration fly ash and fly ash  
17 concentrations of CDDs/CDFs, suggesting that high PCB levels in fly ash may be a contributory  
18 cause of the post-combustion formation of CDDs/CDFs (i.e., PCBs are precursors to  
19 CDDs/CDFs). Nito et al. (1997) noted the formation of CDFs and CDDs from the pyrolysis of  
20 PCBs in a fluidized bed system, indicating that PCBs in feeds may account for CDFs formed in  
21 MSW incineration. More combustion-related research needs to be conducted to firmly establish  
22 whether or not PCB contamination in feeds or post-combustion formation (or both) may explain  
23 the presence of PCBs in combustion flue gases.

## 24 25 **2.7. SUMMARY AND CONCLUSIONS**

### 26 **2.7.1. Mechanisms of Formation of Dioxin-Like Compounds**

27           There are three primary mechanisms for CDD/CDF emissions from combustion sources.  
28 **Mechanism 1 (pass through).** This mechanism involves CDDs/CDFs contained in the feed  
29 passing through the combustor intact and being subsequently released into the environment. For  
30 most systems, this is not thought to be a major contributor to CDD/CDF emissions for three  
31 reasons. First, for commercial systems with good combustion controls, the temperatures and

1 residence times should result in the destruction of most CDDs/CDFs in the feed. Second, mass  
2 balance studies of a number of combustion systems show that more CDDs/CDFs can be detected  
3 in the cool down region downstream of the furnace than in the feed. Third, the CDD/CDF  
4 congener profile in the feed differs from the congener profile in the stack emissions.  
5 Consequently, synthesis appears to be a more important mechanism than pass through. The  
6 concentration of CDDs/CDFs in the flue gases of any particular combustion system will  
7 ultimately be derived as a result of the balance between reactions leading to formation and  
8 reactions leading to destruction of these compounds.

9 **Mechanism 2 (precursor).** This mechanism involves the formation of CDDs/CDFs from  
10 the thermal breakdown and molecular rearrangement of aromatic precursors either originating in  
11 the feed or forming as a product of incomplete combustion. Actual synthesis of CDDs/CDFs  
12 occurs in the post-combustor environment. Gaseous benzene is the most abundant aromatic  
13 compound associated with products of incomplete combustion of waste. Benzene reacts with  
14 chlorine radicals within the combustion gas plasma causing aromatic H abstraction and the  
15 subsequent formation of chlorobenzenes and chlorophenols. Homogeneous gas-phase formation  
16 of CDDs/CDFs occurs from these precursor compounds at temperatures  $>500$  °C, catalyzed by the  
17 presence of copper compounds. In addition, the CDDs/CDFs can form from gas-phase  
18 precursors as heterogeneous, catalytic reactions with reactive fly ash surfaces. This reaction has  
19 been observed to be catalyzed by the presence of a transition metal sorbed to the fly ash. The  
20 most potent catalyst is  $\text{CuCl}_2$ . Relatively low temperatures in the range of 200 to 450 °C has been  
21 identified as a necessary condition for these heterogeneous reactions to occur, with either lower or  
22 higher temperatures inhibiting the process. Because these reactions involve homogeneous gas-  
23 phase and heterogeneous solid-phase chemistry, the rate of emissions is less dependent on reactant  
24 concentration than on conditions that are favorable to formation, such as temperature, retention  
25 time, source and species of chlorine, and the presence of a catalyst.

26 **Mechanism 3 (*de novo* synthesis).** This mechanism involves the heterogeneous solid-  
27 phase formation of CDDs/CDFs in the post-combustion environment on the surface of fly ash.  
28 Such heterogeneous chemistry occurs in two ways: (1) Directly from the oxidation of carbon  
29 within the fly ash and subsequent reactions with organic and inorganic chlorine, and (2) The  
30 oxidative breakdown of macromolecular carbon structures (e.g., graphite), and oxychlorination  
31 reactions of aromatic precursors (such as chlorobenzenes and chlorophenols) on fly ash surfaces

1 leading to CDD/CDF formation. In either case, formation kinetics is most favored at temperatures  
2 in the range of 200 to 450 °C and is promoted by the catalytic properties of either the fly ash or  
3 the presence of a transition metal compound. Mechanisms 2 and 3 can occur simultaneously,  
4 share a number of common reaction pathways, and occur in the same physical environment, and  
5 they are controlled by many of the same physical conditions. In well-designed and well-operated  
6 combustion systems, the precursor species needed for mechanism 2 are reduced; consequently *de*  
7 *novo* synthesis can become the dominant pathway for formation. In systems with incomplete  
8 combustion, it is difficult to sort out the relative contribution of these two mechanisms to total  
9 emissions. Both mechanisms, however, can be curtailed if steps are taken to minimize the  
10 physical conditions needed to support formation (i.e., time, temperature, and reactive surface).

11 The combustion formation chemistry of PCBs is less well studied than that of  
12 CDDs/CDFs, but it is reasonable to assume that these same three mechanisms would apply. For  
13 waste incineration, PCBs can exist in significantly higher concentrations in the feed than do  
14 CDDs/CDFs. Consequently, mechanism 1 may play a more prominent role in the origin of PCB  
15 emissions than CDD/CDF emissions.

### 16 17 **2.7.2. Role of Chlorine**

18 From the various analyses on the role and relationship of chlorine to CDD/CDF formation  
19 and emissions, the following observations and conclusions are made.

20 1. Although chlorine is an essential component in the formation of CDDs/CDFs in  
21 combustion systems, the empirical evidence indicates that, for commercial-scale incinerators,  
22 chlorine levels in feed are not the dominant controlling factor for the amount of CDDs/CDFs  
23 released in stack emissions. Important factors that can affect the rate of CDD/CDF formation  
24 include overall combustion efficiency, post-combustion flue gas temperatures and residence  
25 times, and the types and designs of air pollution control devices employed on combustion  
26 systems. Data from bench-, pilot-, and commercial-scale combustors indicate that CDD/CDF  
27 formation can occur by three principal mechanisms. Some of these data, primarily from bench-  
28 and pilot-scale combustors, have shown direct correlation between chlorine content in fuels and  
29 rates of CDD/CDF formation. Other data, primarily from commercial-scale combustors, show a  
30 weaker relationship between the presence of chlorine in feed and fuels and rates of CDD/CDF  
31 released from the stacks of combustion systems. The conclusion that the amount of chlorine in

1 feed is not a strong determinant of the magnitude of CDD/CDF stack emissions applies to the  
2 overall population of commercial-scale combustors. For any individual commercial-scale  
3 combustor, circumstances may exist in which changes in chlorine content in feed could affect  
4 CDD/CDF emissions. For uncontrolled combustion, such as open burning of household waste,  
5 chlorine content of wastes may play a more significant role in levels of CDD/CDF emissions than  
6 the one observed in commercial-scale combustors.

7 2. Both organic and inorganic forms of chlorine in combustion fuels yields abundant  
8 gaseous HCl in the post-combustion region. It has been shown that chlorine radicals are the most  
9 potent chlorinating agent in the formation of chloro-organic compounds from combustion. HCl  
10 may be the dominant chemical progenitor of chlorine radicals participating in oxychlorination  
11 reactions to CDD/CDF synthesis. Formation of chlorine radicals from HCl occurs in the cool  
12 down zone via the oxidation of HCl in the presence of a transition metal catalyst (the Deacon  
13 reaction). Although the preponderance of scientific evidence suggests that this is an important  
14 pathway for producing chlorinated compounds in emissions, it is still unclear whether HCl can  
15 also directly chlorinate aromatics or whether it must first be oxidized to yield free chlorine.

16 3. Laboratory-scale experiments have examined correlations between chlorine content of  
17 feeds and total CDDs/CDFs formed in combustion systems. These experiments suggested that for  
18 feeds containing <1% chlorine, the amount of CDDs/CDFs formed is independent of the chlorine  
19 content of the feed. For feeds with a chlorine content >1%, a direct correlation is observed. The  
20 existence of an apparent threshold to the chlorine content of waste has been verified in full-scale  
21 combustion systems. It has not been determined, however, whether these relationships are  
22 relevant to poorly controlled combustion of wastes and biomass such as backyard barrel burning,  
23 landfill fires, and agricultural burning.

24 4. The combustion of PVC can contribute to the formation of CDDs/CDFs in two ways.  
25 Firstly, gaseous HCl is a primary product formed from the combustion of PVC. We have seen  
26 that HCl is a major contributor of chlorine radicals necessary for the formation of CDDs/CDFs.  
27 Thus, PVC indirectly contributes to dioxin synthesis. Secondly, the combustion of PVC directly  
28 forms benzene which is followed by oxychlorination reactions that further form chlorinated  
29 benzenes and chlorinated phenols; these compounds then act as precursors to CDD/CDF  
30 formation.

1           5. The most critical factors associated with minimizing CDD/CDF formation in  
2 combustion systems are (a) Achieving nearly complete combustion of the feed through the  
3 application of good combustion practice (i.e., time, temperature, and turbulence), and (b) Assuring  
4 that combustion gases are quenched to below the temperature range for heterogeneous solid-phase  
5 formation chemistry in the post-combustion region of the system, i.e. reduce the temperature to  
6 below 200 °C.

### 7 8 **2.7.3. General Conclusion**

9           Although the formation chemistry of CDDs/CDFs is more complicated and less  
10 understood than the relatively simple constructs described in this review, the current weight of  
11 evidence suggests that the formation mechanisms outlined above describe the principal pathways  
12 of most CDDs/CDFs formed and emitted from combustion sources.

**Table 2-1. Concentration of CDDs/CDFs on municipal incinerator fly ash at varying temperatures**

Congener	CDD/CDF concentration on fly ash (ng/g)				
	Temperature				
	200 °C	250 °C	300 °C	350 °C	400 °C
CDD					
Tetra	15	26	188	220	50
Penta	40	110	517	590	135
Hexa	65	217	1,029	550	110
Hepta	100	208	1,103	430	60
Octa	90	147	483	200	15
CDF					
Tetra	122	560	1,379	1,185	530
Penta	129	367	1,256	1,010	687
Hexa	61	236	944	680	260
Hepta	48	195	689	428	112
Octa	12	74	171	72	12

Source: Adapted from Vogg et al. (1987).

**Table 2-2. CDDs/CDFs formed from the thermolytic reaction of 690 mg benzene + FeCl<sub>3</sub> silica complex**

<b>Congener</b>	<b>Mass produced (ng)</b>	<b>Number of mols produced</b>	<b>Percent yield<sup>a</sup></b>
DiCDD	4.9	0.019	4.3 e-7
TriCDD	54	0.019	4.3 e-6
TCDD	130	0.4	9.0 e-6
PeCDD	220	0.62	1.4 e-5
HxCDD	170	0.44	9.9 e-6
HpCDD	98	0.23	5.2 e-6
OCDD	20	0.04	9.0 e-7
Total CDDs	696.9	1.94	4.4 e-5
DiCDF	990	4.2	9.5 e-5
TriCDF	7,800	29	6.6 e-4
TCDF	12,000	39	8.8 e-4
PeCDF	20,000	59	1.3 e-3
HxCDF	33,000	88	2.0 e-3
HpCDF	40,000	98	1.1 e-3
OCDF	74,000	167	3.8 e-3
Total CDFs	187,000	484.2	1.1 e-2

percent yield = (number of mols of CDD or CDF/mols benzene) x 100.

Source: Nestruck et al. (1987).

**Table 2-3. *De novo* formation of CDDs/CDFs after heating Mg-Al silicate, 4% charcoal, 7% Cl, 1% CuCl<sub>2</sub> in H<sub>2</sub>O at 300 °C**

Congener	Concentration of CDD/CDF (ng/g)				
	Reaction time (hr)				
	0.25	0.5	1	2	4
TCDD	2	4	14	30	100
PeCDD	110	120	250	490	820
HxCDD	730	780	1,600	2,200	3,800
HpCDD	1,700	1,840	3,500	4,100	6,300
OCDD	800	1,000	2,000	2,250	6,000
Total CDDs	3,342	3,744	7,364	9,070	17,020
TCDF	240	280	670	1,170	1,960
PeCDF	1,360	1,670	3,720	5,550	8,300
HxCDF	2,500	3,350	6,240	8,900	14,000
HpCDF	3,000	3,600	5,500	6,700	9,800
OCDF	1,260	1,450	1,840	1,840	4,330
Total CDFs	8,360	10,350	17,970	24,160	38,390

Source: Stieglitz et al. (1989a).

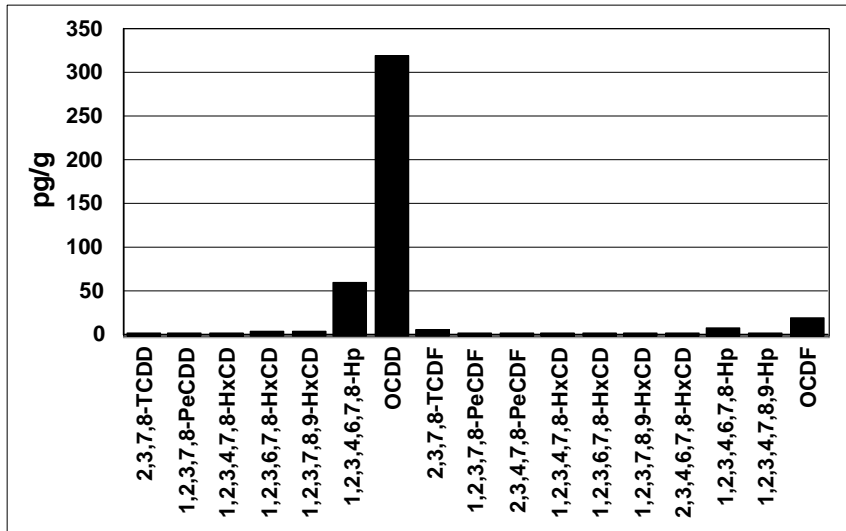
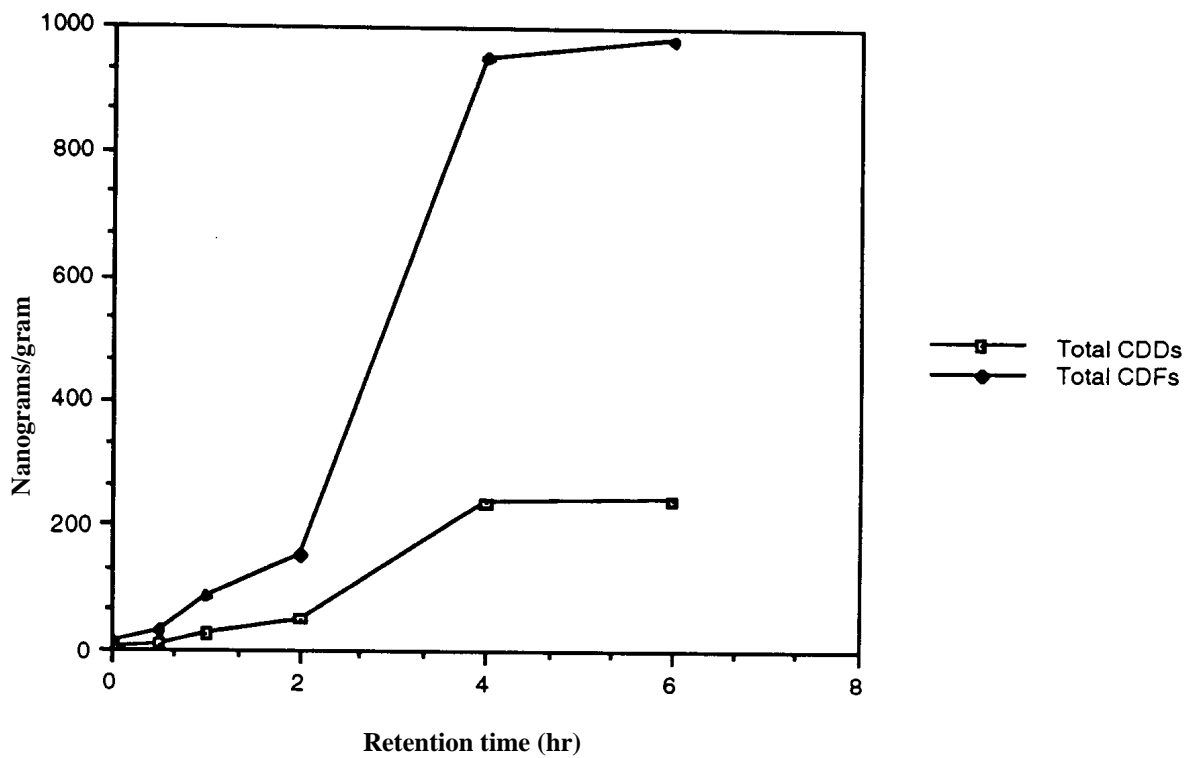


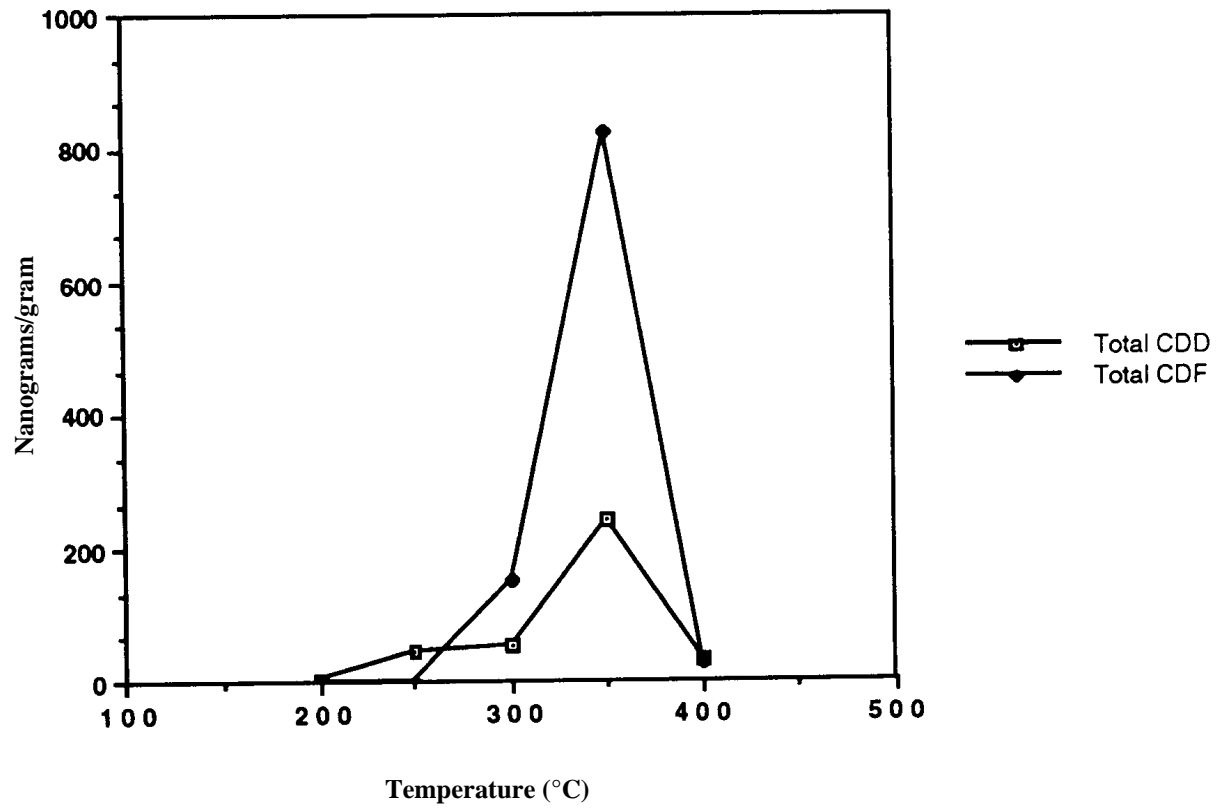
Figure 2-1. Typical CDD and CDF congener distribution in contemporary municipal solid waste (MSW).

Source: Adapted from Abad et al. (2002).



**Figure 2-2. The *de novo* synthesis of CDDs/CDFs from heating carbon particulate at 300 °C at varying retention times.**

Source: Addink et al. (1991).



**Figure 2-3. Temperature effects on CDD/CDF formation.**

Source: Addink et al. (1991).