2.0. 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 and CDFs emitted from combustion sources. Current understanding of the conditions necessary to form CDDs and CDFs were primarily derived from studying full-scale municipal solid waste incinerators (MSWIs), augmented with observations involving the experimental combustion of synthetic fuels and feeds within the laboratory. However, the formation mechanisms elucidated from these studies are generally relevant to most combustion systems in which organic material is burned with chlorine. Intensive studies have examined MSWIs from the perspective of identifying the specific formation mechanism(s) that occur within the system. This knowledge may lead to methods that prevent the formation of CDDs and CDFs and their release into the environment. Although much has been learned from such studies, how to completely prevent 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 forming CDDs and CDFs can be identified by evaluating emission test results from MSWIs in combination with laboratory experiments.

CDD/CDF emissions from combustion sources can potentially be explained by three principal mechanisms, which should not be regarded as being mutually exclusive. The first is that CDDs and CDFs are present as contaminants in the combusted organic material, and pass through the furnace and are emitted unaltered. This mechanism is discussed in Section 2.1. The second is that CDD/CDFs ultimately form from the thermal breakdown and molecular rearrangement of precursor ring compounds, which are defined as chlorinated aromatic hydrocarbons with a structural resemblance to the CDD and CDF molecules. Ringed precursors emanated 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, similar to the second and described in Section 2.3, is that CDD/CDFs are synthesized *de novo*. *De novo* synthesis describes a pathway of forming CDD/CDFs from heterogeneous reactions on fly ash involving carbon, oxygen, hydrogen, chorine, and a transition metal catalyst. With these reactions, intermediate compounds having an aromatic ring structure are formed. Studies in this area suggest that aliphatic compounds, which arise as products of incomplete combustion, may play a critical role in initially forming simple ring molecules, which later evolve into complex aromatic precursors. CDD/CDFs are then formed from the intermediate compounds. In both mechanisms (2) and (3), formation occurs outside the furnace, in the so-called post-combustion zone. Particulate bound carbon is suggested as the primary reagent in the *de novo* syntheses pathway.

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

Section 2.5 discusses the generation and formation of coplanar PCBs. The presence of coplanar PCBs in stack emissions to combustors is an area in need of further research. Evidence to date suggests that PCB emissions are mostly attributed to PCB contamination in waste feeds, and that emissions are related to mechanism (1). However, newly published research has also indicated that it is possible to form PCBs in much the same way as described in mechanisms (2) and (3) identified in the formation of CDD/CDFs within the post-combustion zone.

Section 2.7 provides a closing summary of the three principal formation mechanisms and the role of chlorine. From the discussion in this chapter, it should be evident that no clear distinction exists between the precursor and de novo synthesis mechanisms for forming CDDs and CDFs. Both formation pathways depend on the evolution of precursors within combustion gases, the interaction of reactive fly ashes, a generally oxidative environment, the presence of a transition metal catalyst, the presence of gaseous chlorine, and a favorable range of temperature. Temperature of the combustion gases (i.e., flue gases) is perhaps the single most important factor in forming dioxin-like compounds. Temperatures between 200° and 450° Celsius (C) are most conducive to forming CDD/CDFs, with maximum formation occurring at around 350°C. If temperature falls outside this range in temperature, the amount of CDD/CDFs formed is minimized.

2.1. MECHANISM 1: CDD/CDF CONTAMINATION IN FUEL AS A SOURCE OF COMBUSTION STACK EMISSIONS

The first mechanism involved in the stack emission of CDDs and CDFs is the incomplete destruction of CDD/CDF contaminants present in the fuel or feeds delivered to the combustion chamber. Not all of these molecules are destroyed by the combustion system, thus allowing trace amounts to be emitted from the stack. Most work in this area has involved the study of municipal solid waste incineration (MSWI), where CDDs and CDFs were analytically measured in the raw refuse fed into the incinerator.

As discussed in Volume 2 to this report, CDD/CDFs are ubiquitous in the environment (air, water, soil) and in foods and paper. Therefore, CDD/CDFs are clearly present in municipal waste. Tosine et al. (1983) first reported detecting trace amounts of HpCDD and OCDD in the MSW fed into an MSWI in Canada. HpCDD ranged in concentration from 100 ppt to 1 ppb, and OCDD ranged from 400 to 600 ppt. Wilken et al. (1992) separated the various solid waste fractions of MSW collected from municipalities in Germany and analyzed them for the presence of CDD/CDFs and other organochlorine compounds. Total CDD/CDFs were detected in all MSW fractions in the following range of concentrations: paper and cardboard = 3.1 to 45.5 ppb; plastics, wood, leather, and textiles combined = 9.5 to 109.2 ppb; vegetable matter = 0.9 to 16.9 ppb; and "fine debris" (defined as particles < 8 mm) = 0.8 to 83.8 ppb. Ozvacic (1985) measured CDD/CDFs in the raw MSW fed into two MSWIs operating in Canada. In one MSWI, CDDs were detected in the refuse; concentration ranged from 10 to 30 ppb, but no CDFs were detected (detection limit: 1 pg/g). In the MSW fed to the second MSWI, CDDs were detected in a range of 75 to 439 ppb, and CDFs were detected only in one of three samples at a total concentration of 11 ppb. EPA has reported detecting CDD/CDFs in refuse derived fuel (RDF) burned in a large urban MSWI (Federal Register, 1991a). CDDs were detected in 13 MSW samples taken prior to incineration at concentrations ranging from 1 to 13 ppb; CDFs ranged from not detected to 0.6 ppb. In these samples, OCDD predominated; the lower chlorinated congeners were not detected. Clement et al. (1988) performed a mass balance involving an input versus output of CDD/CDFs at two operational MSWIs in Canada. The mass balance showed that the mass of CDDs and CDFs emitted at the stack point was much greater than the mass of CDD/CDFs in the raw MSW fed into the incinerator, and that the profiles of the distributions of CDD/CDF congeners were strikingly different. Primarily, higher chlorinated congeners were detected as contaminants in the waste; whereas, the total array of tetra - octa CDD/CDFs could be detected in the stack gases.

CDDs/CDFs present in the waste feeds may account for some fraction of the CDD/CDFs released from the stack. However, mass balance studies have clearly shown that more CDD/CDF can be detected downstream of the furnace than what is detected in the feed, indicating that CDD/CDFs are being synthesized after the feed has been combusted (Commoner et al., 1984, 1985, 1987; Clement et al., 1988; Hay et al., 1986; Environment Canada, 1985). Moreover, it is expected that the conditions of thermal stress imposed by high temperatures reached in typical combustion would destroy and reduce the CDDs and CDFs present as contaminants in the waste feed to levels that are 0.0001 to 10 percent of the initial concentration, depending on the performance of the combustion source and the level of combustion efficiency. Stehl et al. (1973) demonstrated that the moderate temperature of 800°C enhances the decomposition of CDDs at a rate of about 99.95 percent, but that lower temperatures result in a higher survival rate. Theoretical modeling has shown that unimolecular destruction of CDDs/CDFs at 99.99 percent can occur at the following temperatures and retention times within the combustion zone: 977°C with a retention time of 1 second; 1,000°C at a retention time of ½ second; 1,227°C at a retention time of 4 milliseconds; and 1,727°C at a retention time of 5 microseconds (Schaub and Tsang, 1983). Thus, CDDs and CDFs would have to be in parts per million concentration in the feed to the combustor to be found in the part per billion or part per trillion level in the stack gas emission (Shaub and Tsang, 1983). However, it cannot be ruled out is that CDDs/CDFs in the waste or fuel may contribute (up to some percentage) to the overall concentration leaving the stack. This leaves the only other possible explanation for CDD/CDF emissions from high temperature combustion of organic material, formation outside and downstream of the furnace. These studies point to formation mechanisms other than simple pass through of non-combusted feed contamination. These formation mechanisms are discussed and reviewed in the sections which follow.

2.2. MECHANISM 2: FORMATION OF CDD/CDFs FROM PRECURSOR COMPOUNDS

The second mechanism involves the formation of CDDs and CDFs from aromatic precursor compounds in the presence of a chlorine donor. This mechanism has been elucidated from laboratory experiments involving the combustion of known precursors in quartz ampules under starved-air conditions, and in experiments that investigate the role of combustion fly ash in promoting the formation of CDD/CDFs from precursor compounds. The general reaction in this formation pathway is an interaction between an aromatic precursor compound and chlorine promoted by a transition metal catalyst on a reactive fly ash surface (Dickson and Karasek, 1987; Liberti and Brocco, 1982). Examples of well studied precursor compounds include chorobenzenes, chlorophenols, phenol, and benzene (Esposito et al., 1980). Examples of diverse chlorine donor compounds are polyvinyl chloride (PVC), and gaseous hydrogen chloride (HCl). CDD and CDF formation results from heterogeneous gas-phase reactions involving chlorinated precursor compounds and a source of chlorine. Chlorophenol and chlorobenzene compounds are measured in flue gases from MSWIs (Dickson and Karasek, 1987). Precursors are carried from the furnace to the flue duct as products of incomplete combustion. These compounds can adsorb on the surface of combustion fly ash, or entrain in the gas phase within the flue gases. In the post-combustion region outside the furnace, heterogeneous reactions ensue to form CDD/CDFs. Laboratory experiments involving the controlled combustion of precursor compounds have caused the breakdown of the precursor reagent and the subsequent appearance of CDD/CDFs as products of the reaction. For example, Jansson et al. (1977) produced CDDs through the pyrolysis of wood chips treated with tri-, tetra-, and pentachlorophenol in a bench-scale furnace operated at 500-600°C. Stehl and Lamparski (1977) combusted grass and paper treated with the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in a bench-scale furnace at 600-800°C and generated ppm_v levels of TCDD. Ahling and Lindskog (1982) reported CDD formation during the combustion of tri- and tetrachlorophenol formulations at temperatures of 500-600°C. Decreases in oxygen during combustion generally increased the CDD yield.

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

Temperature of the combustion gases is, perhaps, the most dominant factor in the formation of CDDs and CDFs from aromatic precursor compounds (Fangmark et al., 1994; Vogg et al., 1987, 1992; Oberg et al.,1989; Weber and Hagenmaier, 1999). Vogg et al. (1987) found that formation probably occurs <u>outside</u> and downstream from the combustion zone of a furnace to a combustion source in regions where the temperature of the combustion offgases has cooled within a range of 200° to 450°C.

After carefully removing organic contaminants from MSWI fly ash, Vogg et al. (1987) added known concentrations of isotopically labeled CDD/CDFs to the matrix. The MSWI fly ash was then heated for 2 hours in a laboratory furnace at varying temperatures. The treated fly ash was exposed to increasing temperatures in 50°C increments in a temperature range of 150^0 to 500°C. Table 2-1 summarizes these data. Because the relative concentration of CDD/CDFs increased while exposed to varying temperature, it was concluded that the temperature of the combustion gas is crucial to promoting the formation of CDD/CDFs on the surface of fly ash. Within a temperature range of 200° to 450°C, the concentration of CDD/CDFs increases to some maxima; outside this range, the concentration diminishes.

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

Fangmark et al. (1994) found that CDD/CDFs exhibit a similar dependence on temperature and residence times between 260° and 430°C, with maximum formation occurring around 340°C. Using a pilot-scale combustor, Behrooz and Altwicker (1996) found the formation of CDD/CDFs from the precursor 1,2-dichlorobenzene rapidly occurred within the post-combustion region in a temperature range of 390° to 400°C, with residence times of only 4-5 seconds. On the other hand, CDD/CDF formation from 1,2-dichlorophenol seemed to require higher temperatures; still outside the furnace, but likely in the exit to the furnace where gas temperatures are >400°C.

Oberg et al. (1989) investigated the role that temperature plays in the formation kinetics using a full-scale hazardous waste incinerator operating in Sweden. Oberg et al. (1989) observed that maximum CDD/CDF formation transpired in the boiler used to extract heat for co-generation of energy. In this investigation, significant increases in total concentration of I-TEQ$_{DF}$ occurred between temperatures of 280° to 400°C, and concentrations declined at temperatures above 400°C. Weber and Hagenmaier (1999) showed that in gas phase reactions chlorophenols react in the presence of oxygen at above 340°C to form CDDs and CDFs. Phenoxyradicals were formed which, in turn, caused the formation of CDDs. Polychlorinated dihydroxybiphenyls were identified as reaction intermediates in the gas phase dimerization of chlorophenols, and these intermediates could form PCDFs.

Other conditions postulated to regulate the synthesis of CDDs and CDFs from the aromatic precursor compound are adsorption and interaction with the reactive surface of combustion generated fly ash (particulate matter) entrained in the combustion plasma, and the presence of a transition metal catalyst (Vogg et al., 1987; Bruce et al., 1991; Cleverly et al., 1991; Gullet et al., 1990a; Commoner et al., 1987; Dickson and Karasek, 1987; Dickson et al., 1992). The molecular precursor leaves the gas-phase and condenses to the fly ash particle. This places greater emphasis on heterogeneous surface reactions and less emphasis on homogeneous gas-phase reactions. This condition was first postulated by Shaub and Tsang (1983) using thermal-kinetic models based on heats of formation, adsorption, and desorption. Shaub and Tsang (1983) modeled CDD production from chlorophenols and concluded that gas-phase formation within an incineration system is likely to be of low probability and importance given the short (i.e., seconds) residence time of the combustion gases. Konduri and Altwicker (1994) proposed that rate limiting factors were the nature and the concentrations of the precursors, the reactivity and availability of the fly ash surface, and the residence time in the post-combustion zone. Dickson and Karasek (1987) investigated fly ash reactivity with $^{13}C_6$-chlorophenol compounds. Several fly ashes from a variety of combustion fuels were heated at 300°C in quartz tubes under conditions known to catalyze the conversion of chlorophenols to CDD/CDFs (i.e., MSWI, and copper smelter fly ashes). The MSW ashes included a sample from a poorly-operated mass burn refractory incinerator and a sample from a well-operated fluidized bed combustor. The MSWI fly ashes proved to be the most active catalytic medium, despite similarities with respect to specific surface area and average pore diameters. The ash from the refractory MSWI generated about seven times more mass of dioxin-like compounds than the fluidized-bed MSW incinerator. In the MSW ashes, all CDD/CDF congener groups were formed from labeled chlorophenols; however, only trace amounts of heptachloro- and octachlorodioxin were formed with the copper smelter/refiner. X-ray photoelectron spectroscopy revealed the presence of chlorine adsorbed to the surface of the MSWI fly ashes, but an absence of chlorine sorbed to the copper smelter fly ash.

CDD congener groups were postulated to form from the labeled pentachlorophenol precursors by: (1) first forming octachlorodioxin by the condensation of two pentachlorophenol molecules, and (2) forming other lower chlorinated dioxins through dechlorination of the more highly chlorinated isomers. These steps seemed to proceed by an increased reactivity of the chemisorbed precursor molecule caused by the removal of one or more hydrogen or chlorine atoms along the ring structure (Dickson and Karasek, 1987), an observation consistent with the kinetic model of Shaub and Tsang (1983). In related experiments, Dickson and Karasek (1987) more specifically reported on forming CDD/CDFs from condensation reactions of chlorophenols on the surface of MSWI fly ash heated in a bench-scale furnace. Their experiment was designed to mimic conditions of MSW incineration, to identify the step-wise chemical reactions involved in converting a precursor compound into dioxin, and to determine if MSWI fly ash could promote these reactions. MSWI fly ash was obtained from facilities in Canada and Japan. The MSWI fly ash was rinsed with solvent to remove any organic constituents prior to initiating the experiment. Twenty grams of fly ash were introduced into a bench-scale oven (consisting of a simple flow-tube combustion apparatus) and heated at 340°C overnight to desorb any remaining organic compounds from the matrix. $^{13}C_{12}$ -labeled pentachlorophenol (PCP) and two trichlorophenol isotopes ($^{13}C_{12}$- 2,3,5-Trichlorophenol and 3,4,5-Trichlorophenol) were added to the surface of the clean fly ash matrix and placed into the oven for 1 hour at 300°C. Pure inert nitrogen gas (flow rate of 10 mL/min) was passed through the flow tube to maintain constant temperatures. Tetra- through octa- CDDs were formed from the labeled pentachlorophenol experiment; over 100 μg/g of total CDDs were produced. The congener pattern was similar to that found in MSWI emissions. The 2,3,5-Trichlorophenol experiment primarily produced HxCDDs and very small amounts of tetra- and octa-CDD. The 3,4,5-Trichlorophenol experiment mainly produced OCDD and 1,2,3,4,6,7,8-HpCDD. Dickson and Karasek (1987) proposed that CDDs on the fly ash surface may result from chlorophenol undergoing molecular rearrangement or isomerization as a result of dechlorination, dehydrogenation, and trans-chlorination before condensation occurs. These reactions were proposed as controlling the types and amounts of CDDs that are ultimately formed. Born et al. (1993) conducted experiments on the oxidation of chlorophenols with fly ash in a quartz tube reactor heated to about 300°C. The MSWI fly ash mediated the oxidation of chlorophenols to produce carbon dioxide and carbon monoxide as major products, and polychlorinated benzenes, monobenzofurans, and nonhalogenated dibenzo-p-dioxins as trace species. Formation of these trace aromatic species occurred after residence times of only 7 - 8 seconds which was consistent with the later experimental result of Behrooz and Altwicker (1995) which showed the potential for rapid formation from a precursor. Milligan and Altwicker (1996) fitted experimental flow-tube reactor data to classical catalytic reaction models to empirically explain the interaction of 2,3,4,6-tetrachlorophenol (as a model precursor) with reactive MSWI fly ash during MSW incineration. The precursor was found to be highly adsorptive on fly ash, with a first-order dependence on gas-phase precursor concentration to CDD formation. Milligan and Altwicker (1996) concluded that chlorophenol's dependence on gas-phase concentration to form CDD on fly ash reflects the highly heterogeneous nature of the fly ash surface. Moreover the estimated 6×10^{18} adsorption sites per gram of fly ash suggest the presence of highly energetic sites, which may be important in the surface-catalyzed reactions forming CDDs. An interesting observation of Milligan and Altwicker (1996) was that precursor molecules appeared to compete with oxygen molecules for the reactive sites; therefore, chlorophenols are expected to adsorb less readily to the fly ash surface in the presence of oxygen. Experimental evidence suggests that condensation to CDD of chlorophenol compounds via isomerization and the Smiles rearrangement on reactive MSWI fly ash surfaces is a proven pathway for forming dioxins from a precursor compound (Addink and Olie, 1995). However, no detailed mechanisms have been presented for CDD/CDF formation from other precursors, such as chlorobenzenes under conditions simulating incineration.

A condition to the synthesis of CDD/CDFs from aromatic precursor compounds is that the presence of a transition metal catalyst promotes the chemical reaction on the surface of fly ash. Copper chloride is a strong catalyst for promoting surface reactions on particulate matter to convert aromatic precursor compounds to chlorinated dioxins and dibenzofurans (Vogg et al., 1987). Copper chloride promotes ring condensation reactions (e.g., chorophenols) on fly ash to form CDD/CDFs (Addink and Olie, 1995) via the Ullman reaction (Born et al., 1993). In the Ullman reaction, copper catalyzes the formation of diphenyl ethers by the reaction of halogenated benzenes with alkali metal phenolates (Born et al., 1993), with copper participating in a nucleophilic aromatic substitution reaction. Thus, Born et al. (1993) proposes a similar mechanism in catalyzing the formation of dioxin-like compounds. Using the Ullman reaction as a model, Born et al. (1993) proposed that the copper-catalyzed condensation of two ortho-substituted chlorophenol molecules form chlorine-free dibenzo-p-dioxins. Vogg et al. (1987) proposed an oxidation reaction pathway, giving rise to the formation of CDDs and CDFs in the post-furnace regions of the incinerator in the following order: (1) hydrogen chloride gas (HCl) is thermolytically derived as a product of the combustion of heterogeneous fuels containing abundant chlorinated organic chemicals and chlorides; (2) oxidation of HCl, with copper chloride ($CuCl_2$) as a catalyst, yields free gaseous chlorine via the Deacon reaction; (3) phenolic compounds (present from combustion of lignin in the waste or other sources) entrained in the combustion plasma are substituted on the ring structure by contact with the free chlorine; and (4) the chlorinated precursor to dioxin (e.g., chlorophenol) is further oxidized (with copper chloride as a catalyst) to yield CDDs and CDFs and chlorine.

Gullett et al. (1990a; 1990b; 1991a; 1991b; 1992) studied the formation mechanisms through extensive combustion research at EPA, and verified the observations of Vogg et al. (1987). It was proven that CDDs and CDFs could be ultimately produced from low temperature reactions (i.e., 350°C) between Cl_2 and a phenolic precursor, combining to form a chlorinated precursor, followed by oxidation of the chlorinated precursors (catalyzed by a copper catalyst such as copper chloride) as in examples (1) and (2), below.

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

$$2HCl + \frac{1}{2} O_2 \xrightarrow{\Delta} H_2O + Cl_2$$

(2) Phenolic compounds adsorbed on the fly ash surface 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 copper chloride acting as a catalyst (Vogg et al., 1987; Dickson and Karasek, 1987; Gullett et al., 1992):

(a) phenol + $Cl_2 \longrightarrow$ chlorophenol (dioxin precursor)

(b) 2-chlorophenol + $\frac{1}{2} O_2 \xrightarrow{CuCl_2}$ dioxin + Cl_2

On the other hand, Eklund et al. (1986) observed the high temperature formation of a large variety of chlorinated toxic compounds, including CDDs and 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 (10μL) of HCl and heated at 550°C for 5 minutes. Trichlorobenzene, dichlorophenol, dichlorobenzofuran, tetrachlorobenzene, trichlorophenol, and tetrachlorophenol were identified as major products formed. Monochlorobenzene, chlorophenol, dichlorobenzene, tetrachloropropene, pentachloropropene, trichlorobenzofuran, tetrachlorodibenzofuran, trichlorodibenzodioxin, tetrachlorodibenzodioxin, hexachlorodibenzodioxin, hexachlorodibenzofuran, pentachlorobenzene, pentachlorobiphenyl, and pentachlorodihydroxycylohexane were seen as minor products. Trace species formed included: monochlorodibenzofuran, pentachlorodibenzofuran, pentachlorodibenzodioxin, octachlorodibenzofuran, and octachlorodibenzodioxin. 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 (e.g., just exit to the furnace). The reaction was seen as very sensitive to HCl concentration. At HCl $< 10^{-3}$ moles, no chlorinated compounds could be detected. Nestrick et al. (1987) reported that the thermolytic reaction between benzene (an unsubstituted precursor) and iron (III) chloride on a silicate surface yielded CDD/CDFs at temperatures $\geq 150°C$. The experimental protocol introduced 100 - 700 mg of native and $^{13}C_6$-benzene into a macro-reactor system, consisting of a benzene volatilization chamber connected to a glass tube furnace. The investigators noted the relevance of this experiment to generalizations about combustion processes because benzene is the usual combustion byproduct of organic fuels. Inert nitrogen gas carried the benzene vapor to the furnace area. The exit from the glass tubing to the furnace was plugged with glass wool, and silica gel was introduced from the entrance end to give a bed depth of 7 cm to which the $FeCl_3$ was added to form a $FeCl_3$/silica reagent. The thermolytic reaction took place in a temperature ranging from 150-400°C, at a residence time of 20 minutes. Although di- through octa-CDD/CDF were formed by this reaction at all the temperatures studied, the percent yields were extremely small. Table 2-2 summarizes these data.

2.3. MECHANISM 3: THE *DE NOVO* SYNTHESIS OF CDDS/CDFS DURING COMBUSTION OF ORGANIC MATERIALS

The third and last mechanism, *de novo* synthesis, promotes CDD/CDF formation in combustion processes from the oxidation of carbon particulate catalyzed by a transition metal in the presence of chlorine. As in mechanism 2, synthesis is believed to occur in regions outside of the furnace zone of the combustion process, where the combustion gases have cooled to a range of temperatures considered favorable to formation chemistry. A key component to *de novo* synthesis is the production of intermediate compounds (either halogenated or nonhalogenated) that are precursors to CDD/CDF formation. Research in this area has produced CDD/CDFs directly by heating carbonaceous fly ash in the presence of a transition metal catalyst, without the apparent generation of reactive intermediates. Thus, the specific steps involved in the *de novo* process have not been fully and succinctly delineated. However, laboratory experimentation has proven that MSWI fly ash, itself, is a reactive substrate, and the matrix can actually catalyze the *de novo* formation chemistry. Typically, fly ash is composed of an alumina-silicate construct, with 5-10 percent concentrations of silicon, chlorine (as inorganic chlorides), sulfur, and potassium (NATO, 1988). Twenty percent of the weight of fly ash particles are carbon, and the particles have specific surface areas in the range of 2-4 m^2 (NATO, 1988). The *de novo* synthesis essentially is the oxidative breakdown of macromolecular carbon structures, and CDD/CDFs are formed partially from the aromatic carbon-oxygen functional groups embedded in the carbon skeleton (Huang et al., 1999). The distinguishing feature of the *de novo* synthesis over the precursor synthesis is the oxidation of carbon in particulate at the start of the process to yield precursor compounds. In mechanism 2, the precursor compound is the starting molecule to the condensation reactions forming CDD/CDFs (Dickson et al., 1992). By this distinction, however, one could argue that mechanism 3 is really an augmentation to mechanism 2, because the production of CDD/CDFs <u>may</u> still require the formation of a CDD/CDF precursor as an intermediate species. Nevertheless, a distinction is presented here to describe additional pathways suggested for the thermal formation of these compounds.

To delineate the *de novo* synthesis of CDD/CDFs, Stieglitz et al. (1989a) conducted experiments that involved heating particulate carbon containing adsorbed mixtures of Mg-Al silicate in the presence of copper chloride (as a catalyst to the reaction). The authors described heating mixtures of Mg-Al silicate with activated charcoal (4 percent by weight), chloride as potassium chloride (7 percent by weight), and 1 percent copper chloride ($CuCl_2$) (in water) in a quartz flow tube reactor at 300°C. The retention time was varied at 15 minutes, 30 minutes, and 1, 2, and 4 hours to obtain differences in the amounts of CDD/CDFs that could be formed. The results are summarized in Table 2-3. In addition to the CDD/CDFs formed as primary products of the *de novo* synthesis, the investigators observed precursors formed at the varying retention times during the experiment. In particular, similar yields of tri- though hexa-chlorobenzenes, tri- through hepta-chloronaphthalenes, and tetra- through hepta-chlorobiphenyls were quantified; this was seen as highly suggestive of the role these compounds may play as intermediates in the continued formation of CDD/CDFs. Stieglitz et al. (1989a) made the following observations:

- The *de novo* synthesis of CDD/CDFs via the oxidation of carbonaceous particulate matter occurred at a temperature of 300°C. Additionally, the experiment yielded ppb to ppm concentrations of chlorinated benzenes, chlorinated biphenyls, and chlorinated naphthalenes through a similar mechanism. When potassium bromide was substituted for potassium chloride as a source of halogen for the organic compounds in the reaction, polybrominated dibenzo-p-dioxins and dibenzofurans formed as reaction products.

- The transition metal compound copper chloride catalyzed the *de novo* synthesis of CDD/CDFs on the surface of particulate carbon in the presence of oxygen, yielding carbon dioxide and chlorinated/brominated aromatic compounds.
- Particulate carbon, which is characteristic of combustion processes, may act as the source for the direct formation of CDD/CDFs, as well as other chlorinated organics.

More recently, Stieglitz et al. (1991) investigated the role that particulate carbon plays in the *de novo* formation of CDD/CDFs from fly ash containing appreciable quantities of organic chlorine. Stieglitz et al. (1991) found that the fly ash contained 900 μg/g of bound organic chlorine. Only 1 percent of the organic chlorine was extractable. Heating the fly ash at 300-400°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 (TOX) (e.g., 5 percent extractable TOX at 300°C and 25-30 percent extractable total organic chlorine at 400°C). From this, Stieglitz et al. (1991) concluded that the oxidation and degradation of carbon in the fly ash are the source for the formation of CDD/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 CDD/CDFs in a carbon-fly ash system. In this experiment, 4 grams of carbon-free MSWI fly ash were combined with 0.1 gram of activated carbon and placed into a glass tube between two glass wool plugs. The glass tube was then placed into a furnace at a specific temperature, ranging from 200 to 400°C. This 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 4-6 hours. Figure 2-1 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 2-2 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°C to 350°C, the lower chlorinated tetra- and penta-CDD/CDF congeners increased in concentration, while hexa-, hepta-, and octa-CDD/CDF congeners either remained the same or decreased in concentration. The congener profile of the original MSWI 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 CDD/CDFs occurs on the surface of fly ash, the congener profile remains fixed and insensitive to changes in temperature or residence time, indicating some form of equilibrium is reached in the formation kinetics.

Gullett et al. (1994) used a pilot-scale combustor to study the effect of varying the combustion gas composition, temperature, residence time, quench rate, and sorbent ($Ca[OH]_2$) injection on CDD/CDF formation. The fly ash loading was simulated by injecting on fly ash collected from a full-scale MSWI. Sampling and analysis indicated CDD/CDF formed on the injected fly ash at levels representative of those observed at full-scale MSWIs. A statistical analysis of the results showed that, although the effect of combustor operating parameters of CDD/CDF formation is interactive and very complicated, substantial reduction in CDD/CDF formation can be realized with high temperature sorbent injection to reduce HCl or Cl_2 concentrations, control of excess air (also affects ratio of CDDs to CDFs formed), and increased quench rate.

Several steps may be involved in the copper-catalyzed formation of CDDs and CDFs, with residual carbon on fly ash at 300°C (Addink and Olie, 1995). Copper initially reacts with chlorine to form $CuCl_2$, and then the ligand transfers the halide to a carbon atom of an organic macromolecule. The chlorinated macromolecular structure oxidizes into small compounds. Milligan and Altwicker (1995) found that increases in the carbon gasification rate caused increases in the amounts of CDDs and CDFs formed, and gave further evidence linking the oxidation of carbon to the formation of CDD/CDFs. Neither the gas-phase CO_2 nor CO (products of carbon oxidation) act as precursors to chlorobenzenes or CDD/CDF from reactions with carbon particulate (Milligan and Altwicker, 1995). Activated carbon, with a high surface area and excellent adsorptive characteristics, also has the highest gasification rate of all residual carbon (Addink and Olie, 1995). Experimental evidence suggest that the conditions for the *de novo* synthesis of CDDs and CDFs from carbon are: (a) the carbon consists of imperfect and degenerated layers of graphite; (b) oxygen must be present; (c) chlorine must be present; (d) the reactions are catalyzed by copper chloride or some other transition metal; and (e) temperatures in the range of 200°C to 350°C (Huang and Buekens, 1995). The oxidation of carbon in fly ash is apparently inhibited at temperatures below 200°C, thus indicating the lower temperature limit for the thermal inertization of *de novo* synthesis (Lasagni et al., 2000). Lasagni et al. (2000) determined that at a temperature of 250^0 C, the primary product of the gasification of carbon in fly ash is CO_2 , but in a temperature range of 250-325°C, organic compounds are formed as products of the oxidation of the carbon. Addink and Olie (1995) raised the possibility that the molecular backbone of CDDs and CDFs may be present in carbon. If this is the case, the generation of dioxins and furans from the oxidation of carbon would not require the formation of intermediate aromatic ring structures. More work is needed to identify these possibilities.

The *de novo* synthesis of CDD/CDFs also involves the possibility that aromatic precursors could be formed within the post-combustion zone as in the following manner: (1) fuel molecules are broken into smaller molecular species (e.g., C_1, C_2 molecules) during primary combustion; and (2) these simple molecules recombine in the post-combustion zone to form larger molecular aromatic species (i.e., chlorobenzenes and chlorophenols) (Altwicker et al., 1993). Thus, small molecular products that evolve in the hot-zone of the furnace as a consequence of the incomplete fuel or feed material combustion may be important foundation molecules to the subsequent formation of precursor compounds in the cooler, post-combustion region. Eklund et al. (1988) reported formation of a wide range of chlorinated organic compounds, including CDDs, CDFs, and PCBs, from the oxidation of methane with HCl at temperatures of 400° to 950°C in a quartz flow tube reactor. No active catalysts nor reactive fly ashes were added to the combustion system. From these experimental results, Eklund et al. (1988) hypothesized that chlorocarbons, including CDDs and CDFs, are formed at high temperatures via a series of reversible reactions starting with chloromethyl radicals. The chloromethyl radicals can be formed from the reaction of methyl radicals and hydrogen chloride in a sooting flame. Methane is chlorinated by HCl in the presence of oxygen at high temperatures, forming chlorinated methanes, which react with methyl radicals at higher temperature (e.g., 800°C) to form aromatic compounds. In an oxidative atmosphere, chlorinated phenols are formed, but alkanes and alkenes are the primary products. The chlorinated phenols then act as precursors for the subsequent formation of CDD/CDFs.

Aliphatic compounds are common products of incomplete combustion, and may be critical to the formation of simple ring structures in the post-combustion zone (Weber et al., 1999; Sidhu, 1999; Froese and Hutzinger, 1996a; Froese and Hutzinger, 1996b; Jarmohamed and Mulder, 1994). The aromatic precursor compounds may be formed in a potentially rich reaction environment of aliphatic compounds, reactive fly ash particles, HCl, and oxygen. Sidhu (1999) noted that combustion of acetylene on carbon (a common combustion effluent) in the presence of gaseous HCl and copper chloride (as a catalyst) at 300°C formed intermediate precursors, and subsequently, CDDs and CDFs. Propene oxidized at 350° to 550°C in contact with reactive MSWI fly ash in a flow tube reactor forms a wide range of chlorinated aromatic compounds, when the resulting combustion gases are mixed with hydrogen chloride gas (Jarmohamed and Mulder, 1994). Although the conversion was low (i.e., 1-3 percent), the oxidation of propene on fly ash in the presence of HCl can yield chlorinated benzenes and monobenzofurans. Incorporating an oxygen atom into the monobenzofuran structure leads then to the formation of monodibenzofuran. The HCl contributes chlorine to the aromatic ring through the Deacon reaction, and cyclization on the fly ash surface can yield cyclohexadienyl-substituted benzenes, which, in turn, can be further oxidized into CDFs (Jarmohamed and Mulder, 1994). Froese and Hutzinger (1996a) investigated the heterogeneous combustion reactions of the nonchlorinated C_2 aliphatics. Acetylene, as a model aliphatic compound, was allowed to react with pre-cleaned MSWI fly ash in a tube flow reactor at ca. 600°C. Metal oxides (e.g., SiO_2, Fe_2O_3, and CuO) were added separately as catalysts, instead of the metal chlorides used in other precursor experiments. The reactants were put into contact with HCl vapor, introduced at a constant flow rate. The acetylene flow was set at 1.1 mL/min and constantly fell to near 0.9 mL/min over 30 minutes. Regulated air flow maintained homeostatic oxidation conditions. Chorobenzenes and chlorophenols were formed, with isomer patterns generally resembling isomer patterns of chlorobenzene and chlorophenol emissions from MSWIs. CuO was seen as catalyzing condensation and chlorination reactions under heterogeneous conditions to form the chlorinated CDD/CDF precursor compounds. Additional more volatile compounds formed were short-chain aliphatic products, such as chloromethane, dichloromethane, and chloro-and dichloroacetylene. Chlorobenzene congeners were not the major products formed; perchlorinated aliphatic compounds dominated as gas-phase reaction products. Froese and Hutzinger (1997) noted that perchlorinated aliphatic compounds (e.g., hexachloropropene, hexachloro-1,3-butadiene, and hexachlorocyclopentadiene) are important intermediates in aromatic ring formation; they concluded that the catalytic reaction of C_2 aliphatic compounds at 600°C dramatically contributes to formation of chlorinated and nonchlorinated aromatic compounds during combustion. Thus, aliphatic compounds can form CDD/CDF precursor compounds. Variable temperature effects were observed in the formation of CDD/CDF in the same reactions. Maximal OCDD formation occurred at 400°C, and the tetra-hepta homologue groups were maximally formed at 600°C. For CDFs, production of higher chlorinated homologues occurred at 400°C, and 500°C favored the formation of tetrachlorodibenzofurans. Froese and Hutzinger (1996a) noted a 100-fold increase in TCDF formation at 500°C, when compared to formation at 400°C. An explanation for this is that the higher temperature of 500°C maximized the formation CDD/CDF precursor (chlorophenol) from the aliphatic starting compound; whereas, at the lower temperature of 300°C, practically no ring structures were observed. Froese and Hutzinger (1996b) have produced polychlorinated benzene and phenol compounds from the high temperature (i.e., 300° to 600°C) heterogeneous combustion reactions of ethylene and ethane over fly ash in the presence of HCl, oxygen, and a metal catalyst in a combustion flow tube. No chlorobenzene congener precursors were formed from ethylene and ethane at 300°C; however, the formation rate increased with temperature, until a maximum production was achieved at 600°C. No definitive temperature dependence was observed for the formation of chlorophenols from the aliphatic starting compounds. However, at 500°C, 2,4,6-trichlorophenol dominated the reaction products; at 300°C, pentachlorophenol was initially produced. Froese and Hutzinger (1996b) also investigated the effects of elemental catalysts on potentiating the heterogeneous combustion reactions by measuring the amount of chlorobenzene and chlorophenol product formed from the reactions of ethylene/HCl over each catalyst at 600°C. The reaction with SiO_2 did not have a catalytic effect. Al_2O_3 catalytic action showed high intensity for the dichlorobenzene isomers, and decreasing intensity for the higher chlorinated isomers. Comparison of the amount of dichlorobenzene product formed indicated that an equal quantity was produced with either Al_2O_3 or fly ash; however, Al_2O_3

formed four to five times more product than the CuO catalyst. For tri- to hexa-chlorobenzene congeners, MSWI fly ash reactions produced 5 to 10 times more product that the metal catalysts. However, the presence of the CuO catalyst in these reactions produced a chlorobenzene congener pattern comparable to the fly ash reactions. With regard to chlorophenol production, Al_2O_3 also produced a unique dichlorophenol pattern, suggesting that Al_2O_3 has a unique catalytic effect in the high-temperature reactions of C_2 aliphatic compounds. Reactions over CuO produced additional products, including chlorinated methyl compounds, chlorinated C_2 aliphatics, and perchlorinated C_3 - C_5 alkyl compounds. Froese and Hutzinger (1996b) noted that these perchlorinated alkyl groups, formed by reacting ethylene and ethane over fly ash in the presence of the CuO catalyst, are key intermediate compounds to the formation of first aromatic rings in typical combustion systems. This emphasizes the importance of copper's catalytic effects in a combustion fly ash system. Al_2O_3 catalyzed reactions produced nonchlorinated naphthalene and akyalbiphenyl compounds. Furthermore, the organic chlorine in aliphatic compounds may also act as a direct source of chlorine for the formation of CDDs, CDFs in a carbon fly ash system (Weber et al., 1999).

In an earlier experiment using a similar flow-tube apparatus, Froese and Hutzinger (1994) formed chlorinated benzenes and phenols in fly ash catalyzed reactions with trichloroethylene at temperatures of 400° to 500°C. In this case, metal oxides (CuO, FeO_3, Al_2O_3) were used as catalysts, but no HCl was added for oxychlorination of product compounds. Under combustion conditions, a temperature dependent formation of chlorinated aromatics occurred from the trichloroethylene starting compound. Reaction with fly ash at 600°C formed hexachlorobenzene in concentrations that were about 1,000 times greater than at 400° and 500°C, with similar results for chlorophenols. Froese and Hutzinger (1994) hypothesized that key aromatic precursors for CDD/CDFs are formed in the higher temperature region of a post-combustion zone (ca. 600°C), which are then carried to the cooler post-combustion region (ca. 300°C), where the precursors form CDDs and CDFs.

2.4. THE ROLE OF CHLORINE IN THE FORMATION OF CDDS AND CDFS IN COMBUSTION SYSTEMS

The formation of CDDs and CDFs in the post-combustion region of combustion systems via either the precursor or *de novo* synthesis pathways requires the availability of gaseous chlorine (Luijk et al., 1994; Addink et al., 1995). Chlorine concentration in this region is related somehow to the chlorine content of combustion fuels and feed materials in incineration/combustion systems, because there can be no other source. The central question of the role of chlorine in forming CDDs and CDFs is whether or not their exists a positive and <u>direct</u> correlation between the amount of chlorine in feeds and the amount of CDDs and CDFs formed and emitted from the stack. If a direct relationship appears, then reductions in the chlorine content of fuels/feeds prior to combustion should result in a corresponding reduction in the concentrations of CDDs and CDFs formed after combustion. If the oxychlorination reactions require a number of steps, then the relationship between chlorine in uncombusted fuels and CDD/CDFs formed after combustion may not be linear, although still dependent in some nonlinear association. The central question can best be addressed by examining both formation mechanisms revealed in laboratory scale combustion experiments and correlations between Cl 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 and CDFs during combustion. The *de novo* synthesis of CDDs and 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 carbon dioxide and volatile and semivolatile organic compounds as side products (Weber et al., 1999). Transition metal compounds, such as copper chloride, catalyze these reactions. Hydrogen chloride gas is the major direct source of chlorine available for participating in the formation of CDD/CDFs, which is initially formed as a combustion by-product from the inorganic and organic chlorine contained in the fuel (Vogg et al., 1987; Bruce et al., 1991; Gullet et al., 1990; Commoner et al., 1987; Addink et al., 1995; Luijk et al., 1994; Dickson et al., 1992; Wagner and Green, 1993; Halonen et al., 1994; Rigo et al., 1995; Rigo, 1998; Altwicker et al.,1993). MSW contains approximately 0.45-0.90 percent (by weight) chlorine (Domalski et al., 1986). If left uncontrolled, MSW incinerators are a major stationary combustion source of HCl air emissions, which average between 400 to 600 ppm in the combustion gas (U.S. EPA, 1987a). In the presence of oxygen, 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 copper chloride was found to be the most active) yields CDDs and 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 between 200°C to 450°C. Chlorine production 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 and CDF formation, with increases in the vapor phase concentration of chlorine. Figure 2-3 shows the apparent dependence of the extent of formation of CDDs and CDFs upon chlorine concentration in the vapor phase. Bruce et al. (1991) verified a dependence on the concentration and availability of gaseous chlorine in the formation of CDD/CDFs in the post-combustion zone. This is in agreement with a simple experiment of Eklund et al. (1986) in which unsubstituted phenol was mixed with HCl at 550°C in a quartz tube reactor and formed a wide range of toxic chlorinated hydrocarbons, including CDDs and CDFs as reaction products. Eklund et al. (1988) also found a dependence of the amounts of chlorinated phenol product formed from the nonchlorinated starting material with the increased amount of HCl introduced into the reaction. Under the conditions of this experiment, no chlorinated compounds were formed at an HCl concentration of less than 10^{-3} moles, and maximum chlorophenol concentration occurred at ca. 10^{+8} M. Born et al. (1993) also observed that increasing levels of HCl give rise to increasing rates of oxychlorination of precursors, with increasing chances for the post-combustion formation of CDDs and CDFs. However, recently Addink et al. (1995) observed that an HCl atmosphere and/or chlorine produced approximately equal quantities of CDD/CDFs during the *de novo* synthesis from oxidation of particulate carbon. These experimental results suggest that chlorine production via the Deacon process reaction in the *de novo* synthesis may not be the only chlorination pathway, and may indicate that the HCl molecule can be a direct chlorinating agent. In addition, some chlorine is expected to be formed from the oxidation of metal chlorides (e.g., $CuCl_2$), but Cl_2 formation from the Deacon process is greater because of the continuous supply of HCl delivered from the combustion chamber (Bruce et al., 1991). In this case, a first order dependence of HCl to Cl_2 is observed.

Wagner and Green (1993) investigated the correlation of chlorine content in feed to stack emissions of chlorinated organic compounds in a pilot-scale incinerator, using HCl flue gas measurements as a surrogate for fuel-bound organic chlorine. In addition to MSW as a fuel, variable amounts of PVC resin were added during 6 of 18 stack test runs. The resulting data were regressed to determine the coefficient of correlation between HCl measurements and total chlorobenzene compound emission measurements. In nearly all of the different regression analyses performed, the relationship between HCl emission and emissions of chlorinated organic compounds was positive and well-defined. In addition, Wagner and Green (1993) found a direct dependence of HCl emission levels to the level of PVC in the waste, with generally increasing amounts of HCl formed as increasing amounts of PVC were added. From these experiments, Wagner and Green (1993) concluded that decreases in the levels of organically bound chlorine in the input to an incinerator led to decreases in chlorinated organic compound stack emissions. Kanters and Louw (1994) investigated a possible relationship of chlorine content in waste feed to chlorophenol emissions in a bench-scale thermal reactor. MSWI, with a higher content of chlorine, caused a higher emission of chlorophenols via the *de novo* synthesis pathway. Kanters and Louw (1994) lowered the chlorine content of the prototype MSWI by replacing Cl-containing fractions with cellulose. They observed appreciable decreases in the amounts of chlorophenol formed from combustion. Kanters and Louw (1994) concluded that reductions in the chlorine content of waste feeds or elimination of PVC prior to MSWI combustion should result in a corresponding reduction in chlorophenol and CDD/CDF emissions.

In a similar experiment, Wikstrom et al. (1996) investigated the influence of chlorine in feed materials to the formation of CDDs, CDFs, and benzenes in a laboratory-scale fluidized bed reactor. An artificial fuel (composed of 34 percent paper, 30 percent wheat flour, 14 percent saw dust, 7 percent polyethylene, and 2 percent metals) to which varying amounts of organic chlorine (PVC) and inorganic chlorine ($CaCl_2 \cdot 6H_2O$) were added, was combusted. Seven fuels were studied, and the chlorine content was varied from 0.12 to 2 percent. Flue gases were sampled for CDDs, CDFs, and chlorobenzenes. All combustion was performed with a high degree of combustion efficiency (e.g., 99.999 percent) to avoid forming polyvinylidene chloride and naphthalenes as products of incomplete combustion of pure PVC. With the combustion conditions held constant, only the chlorine content of the fuel was varied. From these experiments, about 1,000-fold higher concentrations of PCB isomers were produced, as compared to CDD/CDF (expressed as concentration of I-TEQ$_{DF}$). Moreover, a correlation was found between I-TEQ$_{DF}$ and PCB levels in the flue gases and the chlorine content of the fuel. A 5-fold increase in both I-TEQ$_{DF}$ and PCB concentration was observed in the flue gases from combustion of fuels containing 0.5 and 1.7 percent total chlorine. Moreover, no differences were observed in the amount of chlorinated product produced or whether the source of chlorine in the fuel was organic or inorganic. No correlation was observed between total CDD/CDF and PCB formation and total chlorine in the feed when chlorine levels in feed were 0.5 percent or lower. Highest amounts of CDD/CDFs and PCBs were formed from the fuel having the highest total chlorine content (1.7 percent). Under the conditions of this experiment, Wikstrom et al. (1996) observed that a chlorine fuel content of 1.0 percent was a threshold for forming excess CDDs, CDFs, and PCBs during combustion. The authors noted that Swedish MSW contains about 0.7 percent chlorine, of which approximately 40 percent are organic chlorine. They concluded that Swedish MSW is below the observed threshold value of 1.0 percent chlorine associated with a general increase in CDD, CDF, and PCB formation in the post-combustion region. Wikstrom et al. (1996) stated that their study does not support the thesis that elimination of only PVC from the waste prior to combustion will cause a significant reduction of CDD/CDF emissions if the combustion process is well controlled (high combustion efficiency).

A primary byproduct of combusting PVC is the generation of HCl. Paciorek et al. (1974) thermally degraded pure PVC resin at 400°C and produced 550 mg/g HCl vapor as a primary thermolysis product, which was observed as being 94 percent of the theoretical amount based on the percent weight chlorine on the molecule. Ahling et al. (1978) concluded that HCl can act as a chlorine donor to ultimately yield chlorinated aromatic hydrocarbons from the thermolytic degradation of pure PVC, and that these yields are a function of transit time, percent oxygen, and temperature. They observed data from 11 separate experiments, conducted with a range of temperatures from 570 to 1,130°C. These data indicated that significant quantities of various isomers of dichloro-, trichloro-, tetrachloro-, and hexachlorobenzenes could be produced. Choudhry and Hutzinger (1983) proposed that the radical species Cl· and H· generated in the incineration process may attack the chlorinated benzenes thus formed, and abstract hydrogen atoms to produce ortho-chlorine substituted chlorophenol radicals. These intermediate radical species then react with molecular oxygen to yield ortho-substituted chlorophenols. As a final step, the ortho-substituted chlorophenols act as ideal precursors to yield CDD/CDFs with heat and oxygen. The chlorine in aliphatic compounds has been observed as both yielding high amounts of HCL during combustion, and also acting as a direct chlorine source for the *de novo* synthesis of CDDs/CDFs (Weber et al., 1999).

Recently Addink and Altwicker (1999) have reported on the role of the inorganic chloride ion in the formation of CDD/CDFs using the labeled compound, $Na^{37}Cl$. The inorganic chloride ion forms carbon-chlorine bonds on soot particles during combustion. The chlorine in the soot can both be directly inserted into a CDD/CDF molecule during formation, or can exchange with the chloride ions in the transitional metal catalyst which promotes CDD/CDF formation. Thus, the inorganic chlorine ion participates as a chlorine donor to CDD/CDF formation.

De Fre and Rymen (1989) reported on forming CDDs and CDFs from hydrocarbon combustion in a domestic gas/oil heating burner in the presence of 15 and 300 ppm concentrations of HCl. Over 100 chlorinated organic compounds were detected in the flue gases whenever HCl was injected into the system. De Fre and Rymen (1989) observed formation of CDDs and CDFs in all experiments where HCl was injected in a hydrocarbon flame. In this case, CDFs were always more abundant that CDDs. De Fre and Rymen (1989) concluded that the relationship between the HCl concentration and the emitted concentration of CDD/CDF under fixed combustion conditions appeared to be exponential for a wide range in temperature (e.g., 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 and 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 CDD/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 on the relationship between total chlorine present in the fuel/waste and the magnitude of emissions of CDDs and CDFs from the stack of the tested 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 μg/g; MSW: 2,500 μg/g; leaded gasoline: 300-1,600 μg/g; and unleaded gasoline: 1-6 μg/g.

Thomas and Spiro (1995) also analyzed the relationship of CDD/CDF emissions from combustion to 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, MSWI, 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. The analysis clearly indicated that combustion sources with relatively high combustion efficiency and adequate air pollution controls tended to have two order of magnitude lower emissions than poorly operated sources. This suggested a strong dependence on chlorine concentration in fuels and the magnitude of CDD/CDF emissions in the more poorly controlled combustion sources. The slope of the log-log plot was between 1 and 2, indicating that the relationship of chlorine content to CDD/CDF emissions was more than proportional.

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

Rigo et al. (1995) summarized the results of a study commissioned by the American Society of Mechanical Engineers (ASME, 1995). The study was a statistical evaluation of the relationship of HCl concentration in flue gases to various combustion systems (i.e., MSWI, hospital waste incineration, hazardous waste incineration, biomass combustors, laboratory and bench-scale combustors) to the stack emission of total CDDs and CDFs. HCl was a surrogate for total chlorine feed content in this study. The data analysis was sufficient for 92 facilities in the data base that showed both HCl and CDD/CDF emissions. From the 92 facilities, 72 did not show statistically significant relationship between chlorine input and CDD/CDF output in emissions streams; 2 facilities showed increasing CDD/CDF concentrations with increasing chlorine; and 8 facilities showed decreasing CDD/CDF concentrations with increasing chlorine. AMSE (1995) concluded that:

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

Liberson and Belanger (1995) reported the results of an analysis of the formation and emission of CDDs and CDFs as a function of total chlorine in combustion feed materials at a rotary kiln hazardous waste incinerator (HWI). The data were generated from multiple test series conducted over a 13-month period at the HWI, while operating a carbon injection system specifically designed to control and reduce CDD and CDF stack emissions. The chlorine feed rates ranged from 0 to 3,300 pounds per hour, while the CDD/CDF emission rates ranged between 0.7 and 39 ng/DSCM. The authors noted that multiple series of CDD/CDF control systems were employed on this HWI (e.g., a high temperature secondary combustion chamber, a spray dryer-evaporative quench that further cools the combustion gases, activated carbon injection to adsorb semi-volatile organics, and a cool-side electrostatic precipitator followed by an acid gas scrubber to collect HCl and Cl_2). From the analyses of data, Liberson and Belanger (1995) concluded no correlation exists between CDD/CDF emissions and chlorine feed in a modern MWI, using carbon injection for CDD/CDF control.

2.5. POTENTIAL PREVENTION OF CDD/CDF FORMATION IN COMBUSTION SYSTEMS

Given what is currently understood about oxychlorination reactions in the synthesis of CDDs and CDFs, researchers have identified certain interventions that could be taken to reduce or impede formation in combustion systems. Recently, Haghunathan and Gullett (1996) demonstrated in a pilot-scale incinerator that sulfur compounds can combine with the metal catalyst necessary to stimulate the Deacon reaction of HCl and O_2 to yield Cl_2, thereby, neutralizing the catalyzing agent and reducing the formation of CDDs and CDFs. The Deacon reaction, which forms free chlorine in the combustion plasma, is seen as only occurring in the presence of a catalyst. Thus, the SO_2 molecule (formed when sulfur in the fuel combines with oxygen) can either inhibit the catalytic activity of the fly ash by combining with a metal-based Deacon catalyst in the fly ash, or by depleting the Cl_2 formed. Haghunathan and Gullett (1996) observed that the principal action of sulfur for inhibiting the formation of CDDs and CDFs in combustion systems is through SO_2 depletion of Cl_2, as follows:

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_2$$

The relevance of this finding is that the co-combustion of municipal solid waste with coal (that contains sulfur) should lead to dramatic reductions in the amount of CDDs and CDFs formed and emitted, and may explain why, in the United States, coal combustion at power plants results in over a magnitude lower CDD/CDF emission rate than MSWIs.

Naikwadi and Karasek (1989) investigated the addition of calcium oxide (CaO) and triethylamine (TEA) to the flue gases of a combustion system as an inhibitor of the catalytic activity of fly ash. They placed 500 μg C-13-labeled pentachlorophenol (a dioxin precursor) in a combustion flow tube and allowed it to react with organic-extracted MSWI fly ash at 300°C under an air stream. Under these condition, CDD/CDFs were formed at concentrations ranging from 1,660 ng to 2,200 ng per 100 μg ^{13}C-PCP. The experimental method was then modified by mixing reactive MSWI fly ash with either CaO or TEA. The results showed that the amount of CDD/CDF formed could be reduced by an order of magnitude from the reaction of PCP with fly ash and the addition of TEA as an inhibitor. When CaO was mixed with fly ash, the amount of CDD/CDFs formed decreased by over 20 times.

2.6. THEORY ON THE EMISSION OF POLYCHLORINATED BIPHENYLS

The air emission of PCBs from MSW incineration is less well studied. Probably the formation mechanisms that apply to CDDs/CDFs would also apply to PCBs. Mechanism 1 (pass through) is implicit in the TSCA rule which requires 99.9999 percent destruction in hazardous waste incinerators. When this occurs, 0.0001 percent of the initial amount of PCBs fed into the hazardous waste incinerator may be emitted out the stack. This may indicate that some small fraction of the PCBs present in the fuel fed into an incineration process may result in PCB emissions from the stack of the process.

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

$$\mathrm{DRE} = \frac{W_I - W_o}{W_I} \times 100\%$$

Where:

W_I = mass rate of contaminant fed into the incinerator system

W_o = mass rate of contaminant exiting the incinerator system

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

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

Although it appears that contamination of waste feeds with PCBs may be an important factor to detecting PCBs in stack emissions from combustion processes, recent research has indicated the possibility that these compounds may also be formed in the post-combustion zone either from *de novo* synthesis or from precursor compounds. Zheng et al. (1999) observed the formation of PCBs in the post-combustion zone from the pyrolysis of chlorobenzenes using a laboratory scale furnace. Zheng and coworkers (1999) observed that PCBs were optimally formed from lower chlorinated chlorobenzenes (i.e., 1,3-dichlorobenzene) catalyzed by copper chloride. In this experiment, maximum PCB production occurred at a temperature of 350°C. Wikstrom et al. (1998) reported secondary formation of PCB in the post-combustion zone similar to the *de novo* synthesis of CDDs and CDFs, albeit, PCBs were formed in only small amounts relative to CDD/CDFs. Fangmark and coworkers (1994) have postulated that formation of PCBs, CDDs, and CDFs in the post-combustion zone may occur either from a common precursor, or by side reactions affected in a similar way by temperature and residence time. On the other hand, Blumenstock et al. (1998) produced results in a pilot-scale furnace that were inconsistent with the *de novo* formation of CDDs and CDFs in the post-combustion zone (i.e., PCBs seemed to be optimally formed at high temperatures in oxygen deficient atmospheres). Shin and Chang (1999) have noted a positive correlation between PCB concentrations on MSW incineration fly ash and fly ash concentrations of CDDs and CDFs, suggesting that high PCBs levels in fly ash may be a contributory cause to the post-combustion formation of CDDs and CDFs (i.e., PCBs are precursors to CDD/CDFs). Nito et al. (1997) noted the formation of CDFs and CDDs from the pyrolysis of PCBs in a fluidized bed system indicating that PCBs in feeds may account for CDFs formed in municipal solid waste incineration. More combustion related research needs to be conducted to firmly establish whether or not PCB contamination in feeds or post-combustion formation (or both) may explain the presence of PCBs in combustion flue gases.

2.7. SUMMARY AND CONCLUSIONS

2.7.1. Mechanisms of Formation of Dioxin-Like Compounds

There are three primary mechanisms for CDD/CDF emissions from combustion sources:

Mechanism 1: This refers to CDD/CDFs contained in the feed which pass through the combustor intact and are subsequently released to the environment. For most systems, this is not thought to be a major contributor to CDD/CDF emissions for two reasons. First, for commercial systems with good combustion controls, the temperatures and residence times should result in the destruction of most CDD/CDFs in the feed. Second, mass balance studies of a number of combustion systems show that more CDD/CDFs can be detected downstream of the furnace than in the feed. Consequently synthesis appears to be a more important mechanism than pass through.

Mechanism 2: This is the formation of CDD/CDFs from the thermal breakdown and molecular rearrangement of aromatic precursors either originating in the feed or forming as a product of incomplete combustion. Actual synthesis of CDD/CDF occurs in the post-combustor environment. The CDD/CDFs form when the precursors sorb onto binding sites on the surface of fly ash particles. This reaction has been observed to be catalyzed by the presence of a transition metal sorbed to the particulate. The most potent catalyst is copper chloride. Heat in a range of 200 to 450°C has been identified as a necessary condition for these reactions to occur, with either lower or higher temperatures inhibiting the process. Since these reactions involve heterogenous chemistry, the rate of emissions is less dependent on reactant concentration than conditions that promote formation such as temperature, retention time and availability of catalytic surfaces. For this mechanism to be significant, two broad conditions are needed.

Mechanism 3: This is the formation of CDD/CDFs in the post-combustion environment in the absence of aromatic precursors. This *de novo* synthesis involves the oxidative breakdown of macromolecular carbon structures (e.g., graphite) leading to the formation of aromatic CDD/CDF precursors. These precursors then undergo the transformations associated with mechanism 2 to form CDD/CDFs. As with mechanism 2, since this mechanism involves heterogenous chemistry, the rate of emissions is dominated by the same physical conditions as discussed in mechanism 2. Mechanisms 2 and 3 can occur simultaneously, share a number of common reaction pathways, occur in the same physical environment and are controlled by many of the same physical conditions. In well designed and operated combustion systems, the precursor species needed for mechanism 2 are not in abundant supply; consequently *de novo* synthesis can become the dominant pathway for formation. In systems with incomplete combustion, it is difficult to sort out the relative contribution of these two mechanisms to total emissions. Both mechanisms, however, can be curtailed if steps are taken to minimize the physical conditions needed to support formation (i.e., time, temperature and reactive surface).

The combustion formation chemistry of PCBs is less well-studied than for CDD/CDFs, but it is reasonable to assume that these same three mechanisms would apply. For waste incineration, PCBs can exist in significantly higher concentrations in the feed than CDD/CDFs. Consequently, mechanism 1 may play a more prominent role in PCB emissions from some forms of waste combustion.

2.7.2. Role of Chlorine

From the various analyses on the role and relationship of chlorine in feeds to CDD/CDF formation and emissions, the following observations and conclusions are made:

1. Although chlorine is an essential component for the formation of CDD/CDFs in combustion systems, the empirical evidence indicates that, for commercial scale incinerators, chlorine levels in feed are not the dominant controlling factor for rates of

CDD/CDF stack emissions. Important factors which can affect the rate of CDD/CDF formation include the overall combustion efficiency, post-combustion flue gas temperatures and residence times, and the availability of surface catalytic sites to support CDD/CDF synthesis. Data from bench, pilot and commercial scale combustors indicate that CDD/CDF formation can occur by a number of mechanisms. Some of these data, primarily from laboratory and pilot scale combustors, have shown direct correlation between chlorine content in fuels and rates of CDD/CDF formation. Other data, primarily from commercial scale combustors, show little relation with availability of chlorine and rates of CDD/CDF formation. The conclusion that chlorine in feed is not a strong determinant of CDD/CDF emissions applies to the overall population of commercial scale combustors. For any individual commercial scale combustor, circumstances may exist in which changes in chlorine content of feed could affect CDD/CDF emissions. For uncontrolled combustion, such as open burning of household waste, chlorine content of wastes may play a more significant role in affecting levels of CDD/CDF emissions than observed in commercial scale combustors.

2. Both organic and inorganic chlorine in combustion fuels yield HCl in the post-combustion region. HCl vapor is the dominant source of chlorine leading to the formation of CDD/CDFs. The reaction proceeds via the oxidation of HCl in the presence of an inorganic chloride catalyst (the Deacon reaction). Although the preponderance of scientific evidence suggest that this is a dominant pathway for producing chlorinated compounds in emissions, it is still unclear if HCl can also directly chlorinate aromatics, or must first be oxidized to yield free chlorine.

3. Laboratory scale experiments have examined correlations between chlorine content of feeds with total CDD/CDF formation. These experiments have suggested that for feeds containing less than 1% Cl, the rate of CDD/CDF formation is independent of Cl. For feeds with Cl content greater than 1%, a positive correlation is seen. Although this relationship is observed at the laboratory scale, it has been shown not to apply to commercial scale combustors (see 1 above). It has not been determined, however, if these relationships are relevant to other types of combustion such as backyard barrel burning, landfill fires and agricultural burning.

2.7.3. General Conclusion

The trace chemistry of combustion appears to involve a wide variety of formation pathways indicating that the chemistry of CDD/CDF formation is more complicated than the relatively simple constructs described in this review. Despite this complexity, the current weight of evidence would suggest that the role of chlorine and the formation mechanisms outlined above will account for most of the CDD/CDF emissions associated with combustion.

Table 2-1. Concentration of CDD/CDFs on Municipal Incinerator Fly Ash at Varying Temperatures

Congener	CDD/CDF Concentration on Fly Ash (ng/g)				
	Temperature (°C)				
	200°	250°	300°	350°	400°
CDD					
Tetra	15	26	188	220	50
Penta	40	110	517	590	135
Hexa	65	217	1029	550	110
Hepta	100	208	1103	430	60
Octa	90	147	483	200	15
CDF					
Tetra	122	560	1379	1185	530
Penta	129	367	1256	1010	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. CDD/CDFs Formed from the Thermolytic Reaction of 690 mg Benzene + $FeCl_3$Silica Complex

Congener	Mass Produced (ng)	Number of Moles Produced	Percent Yield[a]
DiCDD	4.9	0.019	4.3 E-7
TriCDD	54	0.019	4.3 E-6
TCDD	130	0.400	9.0 E-6
PeCDD	220	0.620	1.4 E-5
HxCDD	170	0.440	9.9 E-6
HpCDD	98	0.230	5.2 E-6
OCDD	20	0.040	9.0 E-7
Total CDDs	696.9	1.940	4.4 E-5
DiCDF	990	4.200	9.5 E-5
TriCDF	7,800	29.00	6.6 E-4
TCDF	12,000	39.00	8.8 E-4
PeCDF	20,000	59.00	1.3 E-3
HxCDF	33,000	88.00	2.0 E-3
HpCDF	40,000	98.00	1.1 E-3
OCDF	74,000	167	3.8 E-3
Total CDFs	187,790	484.2	1.1 E-2

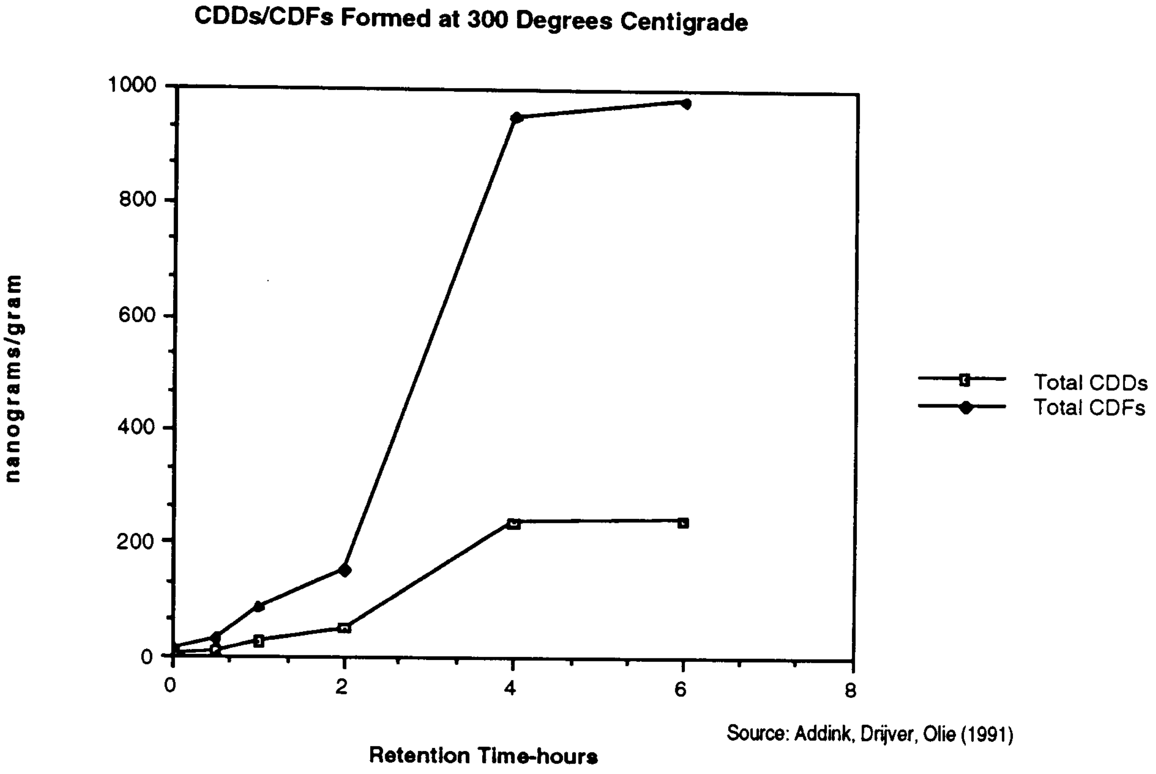
[a] Percent yield = (number of moles of CDD or CDF/moles benzene) x 100.

Source: Nestrick et al. (1987)

Table 2-3. *De Novo* Formation of CDDs/CDFs after Heating Mg-Al Silicate, 4% Charcoal, 7% Cl, 1% $CuCl_2.2H_2O$ at 300°C

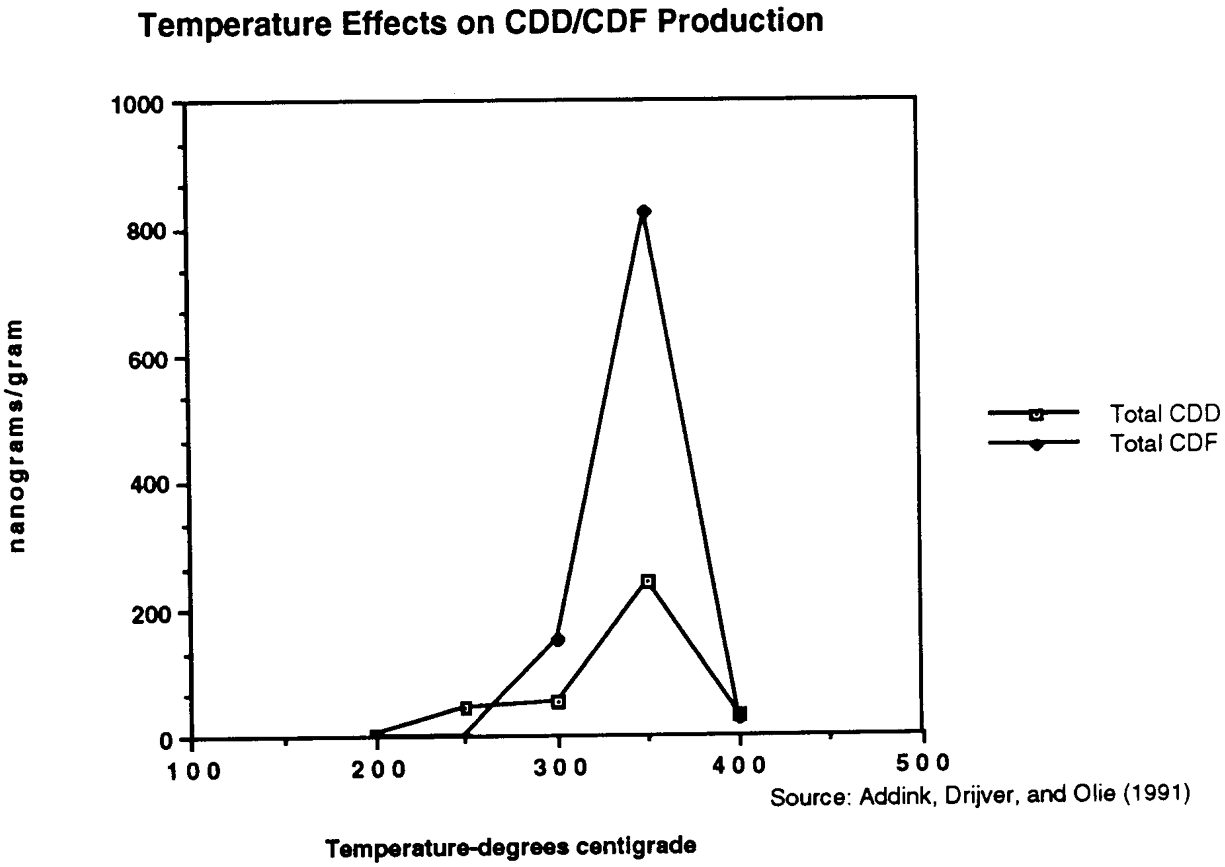
Congener	Concentrations of CDD/CDF (ng/g)				
	Reaction Time (hrs)				
	0.25	0.5	1	2	4
TCDD	2	4	14	30	100
PeCDD	110	120	250	490	820
HxCDD	730	780	1600	2200	3800
HpCDD	1700	1840	3500	4100	6300
OCDD	800	1000	2000	2250	6000
Total CDD	3342	3744	7364	9070	17020
TCDF	240	280	670	1170	1960
PeCDF	1360	1670	3720	5550	8300
HxCDF	2500	3350	6240	8900	14000
HpCDF	3000	3600	5500	6700	9800
OCDF	1260	1450	1840	1840	4330
Total CDF	8360	10350	17970	24160	38390

Source: Stieglitz et al. (1989a).



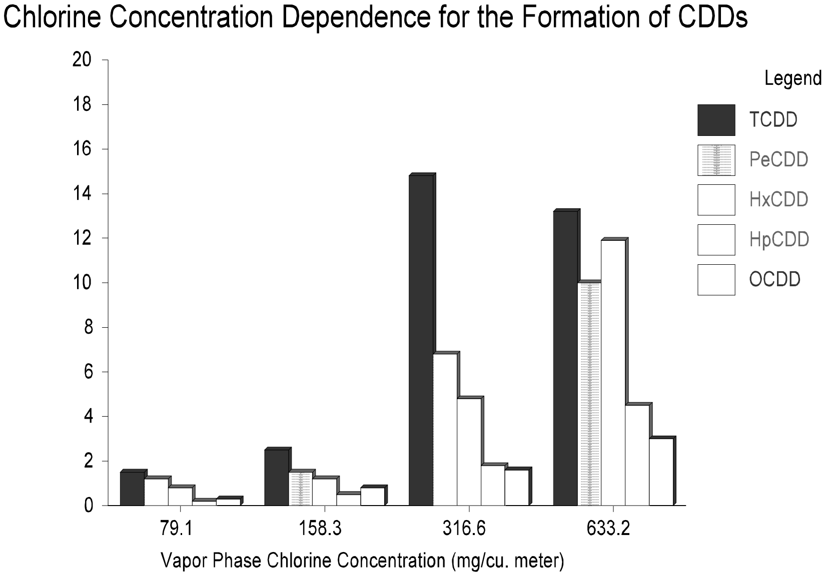
Source: Addink, Drijver, Olie (1991)

Figure 2-1. The *de novo* Synthesis of CDD/CDFs from Heating Carbon Particulate at 300°C at Varying Retention Times



Source: Addink, Drijver, and Olie (1991)

Figure 2-2 Temperature Dependence on CDD/CDF Formation



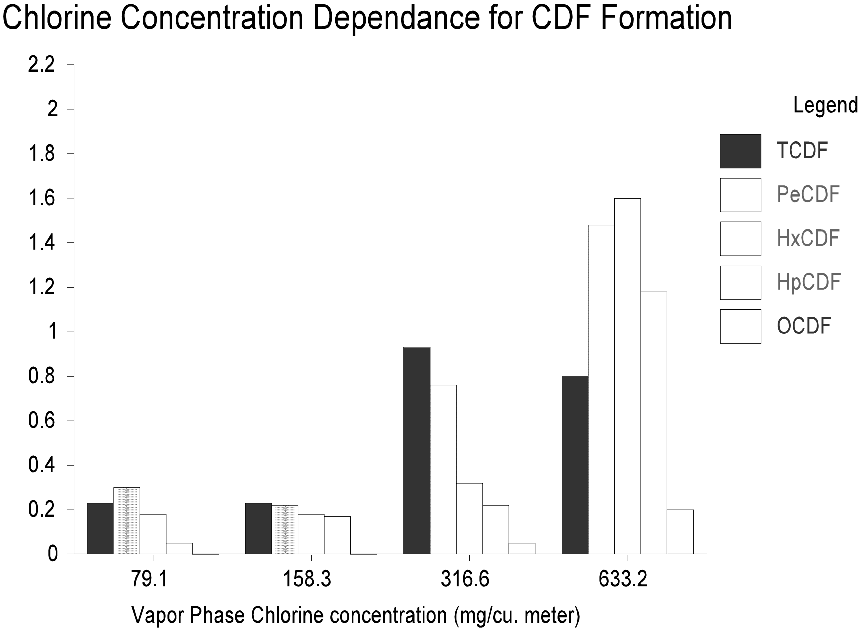


Figure 2-3. The Association Between Vapor Phase Cl_2 and the Formation of CDDs/CDFs