

**Appendix 1: Laboratory- and Pilot-Scale Combustion Systems/Processes: Studies Relevant to the Relationship of Chlorine Input and Dioxin Formation<sup>a</sup>**

Kasai et al. (2001) <sup>1</sup>	<p>“Three series of sinter pot tests have been conducted by the addition of PVC, NaCl, oil, mill scale, anthracite and dusts. ... Comparing the results between series A and B, it is consistent that the addition of oil as an organic carbon source gives little effect and the addition of chlorine sources lead to increases in the discharged amount of PCDD/Fs. However, large differences are found in the effect of chlorine sources, i.e. PVC and NaCl. [Note: PVC caused much higher dioxin formation]</p> <p>Addition of chlorine sources to the raw materials lead to increases in the amount of PCDD/Fs discharged in the outlet gas of the sintering process.”</p>
Wikstrom and Marklund (2001) <sup>2</sup>	<p>“The formation of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and the three coplanar polychlorinated biphenyls (pPCBs) was studied during lab-scale fluidized bed combustion of eight artificial municipal solid waste (MSW) fuel mixtures. ... Four different chlorine sources were studied, viz, an inorganic (NaCl) and three organic sources, pure PVC plastic and two products (floor and cable) and the total chlorine level varies between 0.28% and 1.1%. ... A correlation between the total chlorine in the fuel and the formation of hepta- and octa-chlorinated PCDD/F homologues was found. ... A separate PCA evaluation .. of the ten samples taken during good combustion conditions showed as well a significant positive correlation between the Total Cl level in the fuel, HCl, hepta- and octa-chlorinated PCDD/Fs in the flue gas ...”</p>
Yasuhara et al. (2001) <sup>3</sup>	<p>“Exhaust gases from the combustion of newspaper alone, from branches of London plane tree alone, and from newspapers mixed with sodium chloride (NaCl), polyethylene, or poly(vinyl chloride) (PVC) were collected.... Samples with a higher chloride content produced more dioxins, and there is a clear correlation between dioxin formation and chloride content.”</p>
Hatanaka et al. (2000) <sup>4</sup>	<p>“Artificial wastes containing organic (polyvinyl chloride, PVC) or inorganic (NaCl) sources of chlorine at several levels and copper chloride (CuCl<sub>2</sub> · 2H<sub>2</sub>O) as a catalyst were prepared to define the waste composition and make it constant. The experimental setup had been carefully planned to suppress the effects of experimental conditions except the waste composition. Results of combustion experiments revealed that no PCDD/Fs were detected in the absence of Cl sources and copper chloride, but PCDD/Fs formation was recognized in the cases with Cl and a catalyst. In our experimental conditions, both organic and inorganic chlorines affect PCDD/Fs formation obviously. As Cl content in the waste was increased, CO concentration in flue gas became higher, and more PCDD/Fs were formed in both series of experiments with PVC or NaCl. ... As Cl content was increased, PCDFs show a rapid rise, and PCDDs slowly increase in both series of the wastes with PVC or NaCl. These results show that PVC is obviously one of Cl sources for PCDD/Fs formation.. ...It is a fact that Cl contents in wastes play the role of a Cl source and exert a direct influence on PCDD/Fs formation.”</p>

<sup>a</sup> This compilation of studies is not a fully comprehensive collection of all such studies on this topic.

Katami et al. (2000) <sup>5</sup>	<p><i>“The calculated contents of chloride in the samples were less than 0.005% for heavy oil A, 0.0064% for the blank newspaper. 3.1% for NaCl-impregnated newspaper, and 5.1% for newspaper with PVC. It is obvious that the samples with a higher chloride content produced more dioxins. ... Samples with inorganic chloride (NaCl) or with organic chloride (PVC) produced significantly higher amounts of dioxins as compared with the blank newspaper.”</i></p>
Takasuga et al. (2000) <sup>6</sup>	<p><i>“Simplified thermal formation experiments have been conducted using dioxin-free fly ash as a catalyst with many kinds of combustible samples such as newspaper, kerosene, paraffin, PE ( polyethylene), PP (polypropylene) and PVC. Chlorine sources were PVC, NaCl and HCl. The combustion of samples containing chlorine in the absence of dioxin-free fly ash produced dioxins at a low level although HCl was present in the gas stream. On the other hand, the combustion of samples without chlorine with dioxin-free fly ash increased dioxins formation to a level around 10 times higher than that upon heating dioxin-free fly ash alone. This result is considered to be due to the presence of metal chloride in the fly ash and hydrocarbons in the gas stream. The combustion of samples containing either an organic or inorganic chlorine source or using a HCl stream with dioxin-free fly ash increased dioxin level dramatically. ... It was revealed clearly that fly ash catalyzed dioxin formation although there was a limit to dioxin formation when active chlorine in dioxin-free fly ash was the only chlorine source. The formation was limited by the available amount of chlorine.”</i></p>
Wikstrom et al. (2000) <sup>7</sup>	<p><i>“... PCDD/F yields do in fact increase with increasing Cl radicals. ... the presence of Cl radicals could be a critical influencing factor on chlorination and PCDD/F formation.”</i></p>
Hatanaka et al. (1999) <sup>8</sup>	<p><i>“Polyvinyl chloride (PVC) and sodium chloride (NaCl) were mixed in the artificial waste as organic and inorganic Cl sources respectively. ... As the Cl contents increase, PCDFs show a rapid rise and PCDDs slowly increase in both series of fuel with PVC or NaCl. ... It seems that PCDD/Fs in the experiments with NaCl are slightly more than those with PVC ... However, it is difficult to decide that more PCDD/Fs are formed in the combustion of fuel with NaCl than that with PVC from this result. For there is a possibility that increase of sodium component declines the melting point of ash in the fluidized bed. This may result in the change of a fluidized condition in the reactor followed by the change of combustion state.”</i></p>
Tagashira et al. (1999) <sup>9</sup>	<p><i>“Many kinds of waste fuels such as municipal waste, waste plastics, refuse derived fuel (RDF) and so on were burned experimentally, using the test facility having a combustor of almost the same height and gas residence time as that of the industrial scaled CFBC [circulating fluidized-bed furnace]. The objectives of these tests were, firstly to investigate the combustion characteristics of the waste fuels listed above, and secondly to grasp the formation and decomposition behavior of dioxins in the combustor, the cyclone, the convection part and the dust collector, in terms of the isomers of dioxins, respectively, in which the number of chlorine is different from one another. ... Fig. 10 shows the relation between HCl concentration and dioxin concentration in the flue gas. Though it has been said that there is not so much correlation between the concentrations of the hydrogen chloride and dioxin, this result indicates that there is a positive correlation between the two when burned under the same condition in</i></p>

	<i>the same combustor.”</i>
Xie et al. (1999) <sup>10</sup>	<i>“Since MSW in the US generally consists of notable quantities of PVC, Saran and other chlorinated polymers, the yield of HCl from combustion of MSW will be significant. Chlorine gas is a key intermediate in the formation of chlorinated dioxin compounds. It is generally thought that it is molecular chlorine, and not HCl, that reacts with aromatic compounds such as phenols to produce chlorinated aromatic compounds, including chlorophenols and polychlorophenols, which are precursors of PCDDs and PCDFs. ... As expected, HCl emission in the flue gases increased with an increase in the amount of PVC added to the fuel.”</i>
Klyuev et al. (1998) <sup>11</sup>	<i>“We studied PCDD/PCDF and PAH forming from combustion of uncombined PVC, mixtures PVC with some plastifiers commonly using dibutylphthalate (DOP) and a new one EDOS-A-386 (a mixture of polyfunctional compounds with oxygen containing cycles, hydroxy and ester groups) and samples of lineolum plastified with these plastifiers. ... Plastified lineolum gave more abundant yield of PCDD/PCDFs than mechanical mixture of PVC with plastifier. ... Linoleum plastified with DOP evolved more PCDD/PCDFs than one plastified with EDOS (84.2 and 46.0 micg/kg of the combusted material in TEQ, respectively).”</i>
Pandompatam et al. (1997) <sup>12</sup>	<i>“A pilot-scale incinerator with a nominal capacity of 50 kg/h was successfully used to simulate PCDD and PCDF emissions from hog fuel boilers processing NaCl contaminated bark. With 0.76 wt. % chlorine in the bark, about 50 and 100 ng/m<sup>3</sup> of total PCDD, total PCDF were detected. The corresponding PCDD and PCDF values for the uncontaminated control bark were 0.3 and 0.3 ng/m<sup>3</sup>. The Toxicity Equivalent (TEQ) for the 0.76 wt. % salt contaminated bark combustion was 3 ng/m<sup>3</sup> as compared to the control value of 0.02 ng/m<sup>3</sup>.”</i>
Gullett et al. (1997) <sup>13</sup>	<i>“Effects of fly ash loading; ash-borne, extractable organics; sulfur dioxide (SO<sub>2</sub>) and hydrogen chloride (HCl) concentration; and combustion quality on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F) were evaluated in pilot scale tests simulating municipal waste combustion and coal/waste co-combustion testing. ... The apparent absence of PCDD/F from coal combustion processes may be due to a number of factors including lack of appropriate catalysts, lack of organic products of incomplete combustion, insufficient chlorine, and the presence of catalyst-poisoning sulfur as SO<sub>2</sub>. ... In this current work, reduction of PCDD/F formation at an S/Cl of 1/1 shows that, at HCl concentrations used in Tests G and H (440 ppm), the presence of an available chlorinating species may be reaction-limiting. Because we have also seen an effect of combustion conditions, it is clear that both available Cl and organics are limiting PCDD/F formation. ... Formation of PCDD/F in these tests was limited by extra-particle factors, likely the concentration of organic and chlorine reactants.”</i>
Kanters et al. (1996) <sup>14</sup>	<i>“For efficiently operating MSW incinerators with a minimum of dioxin emissions, it is important to control the chlorine load ... A variety of precursors, including chlorophenols, promote the formation of PCDDs via fly ash-catalyzed reactions at ca. 300 °C. ... Upon pyrolysis/combustion, PVC smoothly eliminates most of its chlorine as HCl. ... PVC acts as a source of HCl, but its degradation may also</i>

	<p>lead to the formation of suitable precursors [of PCDD/Fs]. ... [When] conditions are in better agreement with those in a real MWI [municipal waste incinerator] where HCl is present throughout the continuous combustion process ... [t]he HCl concentration in the gas flow was varied, and already with 0.1 g of HCl/Nm<sup>3</sup> ... led to a doubling of the CP [chlorophenol] formation. ... [T]he relation between the CP emission .. and the HCl emission under standard conditions is shown. Samples with a higher chlorine content give a higher CP emission but tend to reach a plateau value. ... [W]ith added HCl .. it appears that the CP emission increases quite regularly if not linearly with [HCl].”</p>
<p>Wikstrom et al. (1996)<sup>15</sup></p>	<p>Using a lab-scale apparatus, Wikstrom et al. combusted an artificial waste with varying levels of chlorine contributed by either PVC or CaCl<sub>2</sub>·6H<sub>2</sub>O. They concluded, “The results from this study indicate no correlation between the quantities of formed PCDDs/PCDFs and PCBzs [polychlorobenzenes] in the combustion process and the level of chlorine in the fuel, when the chlorine level is below 1%. However, when the level of chlorine in the fuel exceeds 1%, an increased formation rate was noted. No distinction in the formation rate of the chlorinated micropollutants was noticed between the two different chlorine sources.”</p> <p>It is important to note, however, that they also offered another, somewhat different conclusion: “[N]o correlation is shown between PCDD/PCDF and PCBz formation and chlorine content when the total chlorine amount in the fuel is 0.5% or lower. The results from this study do not support the opinion that an elimination of only PVC will contribute to a considerable reduction of PCDD/PCDF emissions if the combustion process is well controlled, as in this study.”</p> <p>[Note: This study and the studies described by its authors as supporting their finding of a positive correlation between chlorine input and dioxin output were reviewed and this finding was corroborated. However, the studies cited do not support the authors’ conclusion that the positive correlation between chlorine input and dioxin formation no longer exists when the chlorine content of the combustor feedstock falls below 1 percent.]</p>
<p>Halonen et al. (1996)<sup>16</sup></p>	<p>“Two series of catalyzed incineration tests were performed in a 32 kW laboratory pilot plant to study the effects of metal catalysts on the formation of chlorobenzenes, chlorophenols and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). ... Sodium chloride, representing inorganic chlorine, and tetrachloroethylene representing organic chlorine, were used as chlorine sources in the basic fuel with the different catalysts. Metals and chlorine accounted for 0.5 weight-% of the total fuel flow. ... “Organic chlorine with the catalyst promoted the formation of particle-bound PCDD/Fs, whereas inorganic chlorine was observed to promote the formation of PCDD/Fs more effectively in the gas phase than in the particle phase. ... The highest concentrations of chlorobenzene were observed with all the metals when organic chlorine was used as the additive chemical, the chlorobenzene concentrations in particles being especially high relative to the situation with inorganic chlorine. ... The addition of organic chlorine increased the chlorophenol concentration more than did inorganic chlorine, this being especially the case in the gas phase (Fig. 6).”</p>

Sinkkonen et al. (1995) <sup>17</sup>	<p><i>“Peat, wood chips, refuse derived fuel and liquid packaging board in different combinations were burned at a temperature of at least 850 C. Fly ash samples from these combustions were analyzed for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzothiophenes (PCDBTs) ... The concentrations of tri- and tetrachlorodibenzothiophenes and tri, tetra- and pentachlorodioxins were highest when mixtures of wood chips and refuse derived fuel (RDF) were burned. The fly ash from the combustion of pure peat pellets did not contain any polychlorinated dibenzothiophenes. When wood chips and RDF were burned the concentrations of chlorinated compounds in fly ash were found to increase with increasing concentration of chlorine in the fuel. ... In the combustion of wood chips and RDF the concentrations of chlorinated compounds were found to be increasing with the increasing concentration of chlorine in the fuel. In the combustion of peat no correlation was found between the formation of chlorinated organic compounds and the concentration of chlorine in the peat. The different chlorine/sulphur ratio in peat may be one reason.”</i></p>
Sonnenberg and Nichols (1995) <sup>18</sup>	<p><i>“Small additions of chlorine-containing bleach plant waste to normal black liquor feed stock did not result in detectable HCl emissions during incineration. Large additions (&gt;10% by weight of solids) increased HCl emissions, possibly as a direct result of organochlorine combustion. The total PCDD/F in flue gas increased by a factor of ten with a 1% addition of bleach plant concentrate to black liquor.”</i></p>
Kanters and Louw (1994) <sup>19</sup>	<p><i>“In our study we concentrate on the formation/emission of (poly)chlorophenols, CPs, as a measure for (the risk of) ‘dioxin’ production. ... [T]he following conclusions were drawn:</i></p> <p>...</p> <ul style="list-style-type: none"> <li>• Lowering the chlorine load – by leaving out compostables and PVC -, lowers the CP-level.</li> <li>• Accepting CPs as a surrogate, the same will hold for the chance of ‘dioxin’ emission from the primary combustion process.”</li> </ul>
Ruuskanen et al. (1994) <sup>20</sup>	<p><i>“The purpose of the tests was to examine the effects of sulphur-rich coal on the formation of chlorinated hydrocarbons like PCDD/PCDFs. ... A strong correlation between HCl in flue gas and PCDFs in fly ash samples was found. ... The correlation analysis [for flue gas samples] confirmed that HCl was not a key component in the formation of PCDD/PCDFs. A possible explanation may be that the HCl concentration is not a limiting factor for the conversion of HCl to Cl<sub>2</sub> in the Deacon process. There is always enough HCl for that conversion. ... No correlation between HCl and furans and dioxins was found [in gaseous emissions]. On the other hand, in fly ash samples the significant correlation of HCl and furans was obvious.”</i></p>
Burns (1993) <sup>21</sup>	<p><i>“The chloride concentration in the waste with PVC was approximately 6 wt%, while the waste without PVC contained 1.5 wt% chloride. ... The measured offgas HCl concentrations ranged from 63% to 1% of the theoretical HCl emissions. The difference is most likely due to the chlorinated metal compound formation in the kiln. The HCl sampling method is not isokinetic, thus particles with condensed metal chloride compounds would not have been collected. Also, chlorine from volatilized chlorinated metal compounds in the sample would not be detected unless the chlorine dissociated from the metal. ... The data in</i></p>

	<p><i>Table 13 shows the most significant variable influencing PCDD/PCDF emissions is waste chloride concentration.”</i></p> <p>[Note: This study also showed that increased chlorine caused an increase in submicron particulate concentration, suggesting that the more PVC burned, the higher the concentrations of submicron particles in offgases and, consequently, the poorer the capture efficiency of APCDs. Higher chlorine also caused higher VOC emissions.]</p>
Halonen et al. (1993) <sup>22</sup>	<p><i>“Biosludge mixtures were incinerated in a pilot scale circulating fluidized bed incineration plant. ... In fly ash ... [c]orrelation was present only between the isomers of PCDD/PCDFs and the concentrations of sulphur and chlorine content in the fuel.”</i></p> <p>[Note: This conclusion was based on principal component analysis.]</p>
Halonen et al. (1993) <sup>23</sup>	<p><i>“PCDD/PCDF formation at 850 °C was observed to depend on chlorine content in the fuel. ... The results of the three fuel mixture incineration tests (fig. 2) show that increased chlorine content in the fuel produced higher PCDD/PCDF concentrations formed at 850 °C (AHC), but similar correlation at 200 °C (ABH) was not seen in combustion tests of biosludge. ... It is obvious that variables other than the chlorine and PCDD/PCDF input contents in the fuel have an influence on formed PCDD/PCDF levels. ... The chlorine content of fuel materials had the most effect on PCDD/PCDFs formation at the high temperature region of the flue gas. When the flue gas temperature decreased the correlation of the chlorine content in fuel with the formation of PCDD/PCDF compounds disappeared.”</i></p>
Wagner and Green (1993) <sup>24</sup>	<p><i>“We find several statistically significant relationships between HCl emissions (a surrogate for PVC in the waste) and the emissions of a number of chlorinated organic compounds. ... These results, contrary to the prevailing opinion [1], lead to the physically reasonable conclusion that decreases in the levels of organically bound chlorine in the input leads to decreases in chlorinated organic emissions. ... In final summary the CCTL's experimental, phenomenological, and theoretical studies of toxic emissions from incineration all support the physically intuitive hypothesis that reduction of chlorinated plastics in the input waste stream results in reduction of aromatic chlorinated organic emissions [21]. ... While the CCTL's measurements have been limited to volatiles and light semi-volatiles these results are expected to apply to other chlorinated aromatic hydrocarbons emissions such as phenols, dioxins, and furans, which we have not measured. A number of other publications support a PVC-PCDD association [22-26]. Bulley has also found experimentally that reduction of PVC input leads to reduced chlorinated dioxins and furans [27]. Thus we are convinced that, when all other factors are held constant, there is a direct correlation between input PVC and output PCDD/PCDF and that it is purposeful to reduce chlorinated plastics inputs to incinerators”</i></p>
Altwickler et al. (1993) <sup>25</sup>	<p><i>“As the Cl/C [chlorine/carbon] ratio increases the concentration of potential chlorinated agents can be expected to increase thus increasing the concentration of CBs [chlorobenzenes] (cf. table 5).”</i></p>
Fangmark et al. (1993) <sup>26</sup>	<p><i>“There are also a few other significant main effects, although just above the 95% confidence level. For PCDFs, PCBz, and PCBs the addition of HCl is such an effect and for PCDDs it is the H<sub>2</sub>O</i></p>

	concentration in the fuel. Although the variable HCl is free of confoundings, the effect is too small to make any further conclusions.”
Gullett et al. (1993) <sup>27</sup>	“[HCl] is a significant parameter ... Increases in [HCl] always lead to increases in [PCDD], within the range of our data and model, which should hold for [Cl <sub>2</sub> ] < 100 ppm. This should always be the case in field operations. [Cl <sub>2</sub> ] is a significant predictor for all three models. ... Test without addition of Cl as HCl or Cl <sub>2</sub> also show large increases in PCDD and PCDF, indicating that sufficient Cl precursors are also present on the fly ash to produce PCDD and PCDF. The effect of additional HCl and Cl <sub>2</sub> is, within statistical limits, always to dramatically increase the levels of PCDD and PCDF from those of undoped baseline runs. Thus, both in situ, on-particle Cl and gaseous Cl lead to increased yields, although the yield from the latter is generally over twice that of the former.”
Hassel et al. (1992) <sup>28</sup>	“Both PE/PP[polyethylene/polypropylene] products produced about 10 grams of HCl per kilogram of plastic. The EVA produce about three times more, and the PVC samples produced roughly thirty times more HCl than the PE/PP samples. ... The significance of the chlorine content in a waste stream has been reported with conflicting conclusions. In a study involving municipal solid waste incinerators, formation of PCDD/PCDF was not shown to have any correlation to either the concentration of chlorine in the waste or the concentration of HCl in the combustion gases (6). On the other hand, a broader study indicated that both organic and inorganic chlorine in a waste have "a statistically significant influence on the dioxin formation" (7). The parenteral plastics data apparently indicate that chlorine is an important but not overriding factor in PCDD/PCDF formation. Comparison of the data from the two PE/PP products points to the significance of the catalytic effect of copper. Comparison of the data from the PE/PP bottle and the two PVC products points to the significance of chlorine. Comparison of the EVA data to all the other products can be construed to signify the importance of certain products of incomplete combustion.”
McGrath et al. (1992) <sup>29</sup>	“This test program was designed to study the formation and emission of PCDD/PCDF during Refuse Derived Fuel combustion. Tests were conducted in a pilot scale RDF incinerator. ... Surrogate RDF ...[m]ain components were shredded corrugated cardboard and water. PVC pellets were included as a chlorine source and copper oxide powder as a source for copper ... The data show a decrease in PCDD/PCDF emissions with a reduction in RDF feed rate. A 15% load reduction resulted in reductions of PCDD/PCDF emissions ranging from 5 to 35% from full load operation. The reduction in emissions is likely due in part to the lessening of precursors available for PCDD/PCDF formation as the fuel load is decreased.”
Fangmark et al. (1991) <sup>30</sup>	“In contradiction to what was reported earlier (Vikelsøe, 1990), our experiments show that when increasing the HCl concentration in the flue gases from what can be formed from the 1% PVC (8 g/h) to an additional 10 g/h, which is more than doubling, no measurable effect on the PCDD/PCDF emission could be observed. ...It is also interesting to note that although we are burning a fuel with a constant amount of PVC we find a large range of dioxins and dibenzofurans emitted. The highest value in table 5 is more than 150 times the lowest value, primarily due to different conditions in the cooling

	<p>section.”</p> <p>[Note: An examination of the data in this report show that, for sample 1, all experiments at the high HCl value had an overall average emission of dioxins of 66.1 ng TEQ /Nm<sup>3</sup> and, at the low HCl level, an average of 42.2 ng TEQ/Nm<sup>3</sup>. For sample 2, the high HCl values were associated with an average emission of 62 ng TEQ/Nm<sup>3</sup>; for low HCl, 47.3 ng TEQ/Nm<sup>3</sup>. This shows an overall average increase in dioxin emissions of 42 percent when HCl levels were doubled.]</p>
Lenoir et al. (1991) <sup>31</sup>	<p>Lenoir et al. studied the formation of dioxin during combustion with two chlorine sources (NaCl and PVC) in a pilot-scale combustor, finding as follows: “<i>The investigated fuel types varied in the chlorine content which, in some experiments, was increased by adding NaCl or polyvinylchloride (PVC). Only the addition of 3 % PVC to polyethylene resulted in an increase in PCDD/F concentrations. ... [A]ddition of 3 % PVC to PE increased PCDD/F levels by a factor of 3 compared to the mean value for pure PE combustion. ... [S]tatements about the influence of incinerator operating conditions and fuel types on PCDD/F emission might have to be modified if the total PCDD/F concentration in the flue gas, rather than the PCDD/F fraction attributed to coarse and fine fly ash, had been considered.</i>”</p>
Yasuhara and Ito (1991) <sup>32</sup>	<p>Combustion of PVC (from clear PVC gloves) in the laboratory: “<i>Main combustion products of poly(vinyl chloride) were polynuclear aromatic hydrocarbons. Formation of chlorine-containing compounds was little. Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans was confirmed. Temperature of maximum PCDDs and PCDFs formation was 600 C. Essential profiles of PCDDs and PCDFs formation at various temperatures were similar. Formation amounts of PCDFs were more than those of PCDDs.</i>”</p>
Bruce et al. (1991) <sup>33</sup>	<p>On the basis of results obtained using a lab-scale combustor, the authors of this study concluded, “<i>It is clear from the data that increasing Cl<sub>2</sub> concentration results in increased formation of PCDD/PCDF.</i>”</p>
Gullett et al. (1990) <sup>34</sup>	<p>“<i>The formation mechanisms of the precursors of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) were examined in a laboratory reactor. Both homogeneous and heterogeneous reactions were studied between 200 and 800 °C. with HCl, Cl<sub>2</sub>, and phenol as reactants in a simulated flue gas containing oxygen. Analysis of the reactor effluent showed the homogeneous phase production of chlorophenols and non-chlorinated dioxin and dibenzo-p-dioxin and dibenzofuran, potential precursors to PCDD and PCDF, was related to HCl concentration, reaching a maximum formation level around 650 °C. However, Cl<sub>2</sub> produced a greater variety of chlorinated aromatics at levels over three orders of magnitude greater than with HCl, with product concentrations reaching maximum formation levels around 350 °C. Heterogeneous tests at 450 °C using a CuCl catalyst increased formation of chlorinated organics and PCDDs and identified the major chlorinating reactant to be Cl<sub>2</sub>.</i>”</p>
Gullett et al. (1990) <sup>35</sup>	<p>“<i>Therefore, reducing the amount of Cl<sub>2</sub> present in the PCDD/PCDF formation region should decrease the levels of these highly toxic compounds found in municipal waste combustors.</i>”</p>
Oudhuis et al. (1990) <sup>36</sup>	<p>“<i>The emission levels of flexible PVC are an order of magnitude higher</i></p>

	<i>than those of virgin PVC. ... This result confirms that the formation of PCDDs and PCDFs is due to secondary reactions of organics with HCl. These results are in contrast with the work of Giugliano et al. (3), where no detectable amounts of PCDDs and PCDFs were found during incineration of waste containing PVC, but in agreement with the work of Tyksklind et al. (4) and Theisen et al. (5) in which more or less the same complex patterns were reported.”</i>
Christmann et al. (1989) <sup>37</sup>	<i>“During combustion and pyrolysis of pure polyvinylchloride (PVC) and PVC-cable sheathings in air atmosphere, PCDD/PCDF are formed in significant amounts up to the ppm range. ... Obviously, in many incineration and pyrolysis processes as well as fires, PVC can be considered a main source for the formation of dioxins and furans. ... In the experiment with the soldering iron, we could show that even at temperatures around 350 °C dioxins and furans are formed by the charring of cable coatings in amounts that exceed the German statutory regulation for dangerous substances considerably. ... Also, neither in combustion nor in pyrolysis experiments with chlorine-free polyethylene samples could dioxins or furans be detected.”</i>
Gullett et al. (1989) <sup>38</sup>	Gullett et al. observed that while the presence of HCl is not likely to be directly responsible for PCDD/PCDF formation, at elevated temperatures 650 °C (1202 °F) it promotes the formation of chlorobenzenes and dibenzofurans and furans (PCDD/PCDF precursors).
De Fre and Rymen (1989) <sup>39</sup>	De Fre and Rymen (1989) found as follows when carrying out experiments with HCl concentrations ranging from 150 ppm to 4.5 percent: <i>“The relationship between the HCl concentration and the generated PCDD/PCDF concentration under fixed combustion conditions appears to be exponential ... [with] PCDD and PCDF formation ... found over a temperature range from 900 C to 240 C. ... Since HCl is the combustion product of all organochlorine compounds it follows that any of these compounds is a potential dioxin precursor in combustion. Furthermore, any industrial process where HCl is allowed to contact flue gases is a possible source of PCDDs and PCDFs.”</i>
Yasuhara and Morita (1988) <sup>40</sup>	From the pyrolysis under an airstream of two kinds of vinylidene chloride polymers used for food wraps, Yasuhara and Morita found as follows: <i>“...[M]any chlorinated aromatic compounds were produced by pyrolysis even at 200 °C. ... Particularly, chlorinated aromatic compounds were detected in large quantities. These compounds were divided into several groups, that is, chlorinated benzenes, chlorinated styrenes (PCSs), chlorinated phenols, chlorinated phenylacetylenes, PCNs [polychlorinated naphthalenes], PCBs [polychlorinated biphenyls], and chlorinated benzofurans (PCBFs).”</i>
Eklund et al. (1988) <sup>41</sup>	<i>“Hydrogen chloride will have a large exponent on its concentration in the equilibrium equations. The emission [of dioxins] should therefore be strongly influenced by reduction of hydrogen chloride in the incinerator. This is substantiated by laboratory results and large scale emission studies ...”</i>
Vogg et al. (1987) <sup>42</sup>	Vogg et al. found that the formation of dioxins and furans in MWC fly ash at low temperatures is enhanced by the presence of HCl, SO <sub>2</sub> , and H <sub>2</sub> O. They also found that high chloride concentrations in fly ash

	apparently favor the formation of PCDD/Fs.
Marklund et al. (1986) <sup>43</sup>	<i>“The laboratory pyrolysis of PVC and Saran clearly shows that PVC and other organochlorine polymers can be precursors to the PCDDs and PCDFs found in various incinerators. This is a very important observation because the New York Department of Sanitation recently claimed “PVC has never been shown to be a precursor of PCDF/PCDD. ... A recent German pamphlet arrives at the same erroneous conclusion.”</i>
Eklund et al. (1986) <sup>44</sup>	<i>“We now report the synthesis of a large number of chlorinated environmental pollutants in a simple high-temperature experiment. The results show that phenol and HCl are the most likely precursors of the chlorinated dibenzodioxins and dibenzofurans formed in the combustion of wastes. The dependence of the reaction on the concentration of HCl indicates a way of controlling the formation of these toxic compounds during incineration.”</i>
Liberti et al. (1983) <sup>45</sup>	<i>“The analysis of various vegetables showed the presence of polyphenols but no phenols have been identified. From the analysis carried out on vapours and particulates obtained from the combustion of the vegetable materials both phenols and polyphenols have been identified and measured. ... Nor chlorophenols neither chlorinated species have been however identified in the emissions. ... When the combustion is performed either in the presence of chlorine mixed to the air stream or PVC added to the material, noticeable amounts of chlorophenols are found in emissions: dichloro-, trichloro-, tetrachloro and pentachloro-phenols have been identified in the concentration range of microgram par g of examined material. As a consequence also appreciable amounts of PCDD and PCDF have been identified and the relative concentration reported in table 2. ... It is evident that either the lack of chlorine donors or phenolics in the material to be submitted to incineration prevents such reaction [PCDD/F formation]. According to this mechanism it is possible to explain why for long time vegetable materials have been incinerated without any damage to the environment in spite of the large amounts of plant phenolics present. ... The separation of material, as PVC, eliminates the precursor which contributes to the chlorine donation in the pyrolytic synthesis.”</i>
Tiernan et al. (1983) <sup>46</sup>	<i>“In a laboratory study intended to assess the importance of the combustion of conventional fuels as a source of CDDs/CDFs, pine wood and other fuels were pyrolyzed in air and in air containing a chlorine source (such as HCl) ... The experiments in which pine was combusted in normal air produced no detectable CDDs/CDFs ... However, the detection limits achieved in the analyses for CDDs/CDFs were in the range from 30-500 pg/g of wood combusted. It is possible, of course, that still lower quantities of CDDs/CDFs are formed. When pine wood was combusted in the presence of air saturated with HCl vapor, however, relatively large quantities of the entire series of CDDs/CDFs were detected [<math>&gt;3000</math> ng/g of wood burned].”</i>
Mahle and Whiting (1980) <sup>47</sup>	<i>“The current study was undertaken to see whether or not chlorodioxins could be formed from a naturally occurring organic starting material such as coal. ... [T]his study does represent the first attempt to observe the formation of chlorodioxins from a nonman-made starting material under controlled laboratory conditions. ... First, analysis of the National Bureau of Standards bituminous coal ...</i>

	<p><i>showed no detectable levels of chlorodioxins ... Analysis of the coal for total inorganic and organic chlorine gave 808 +/- 40 ppm ... [A]nalysis of the reaction of coal with air at high temperatures ... gave positive signals barely above the detection limits for H<sub>7</sub>CDD and OCDD. ... The reaction of coal and sodium chloride with air ... does not indicate real differences in chlorodioxin levels when compared to the coal with air experiment. Substantial amounts of all analyzed chlorodioxin species were observed in the chlorination experiment involving coal, air, and hydrogen chloride ... "</i></p> <p>[Note: The trapping system used by these Dow Chemical scientists was very primitive, consisting of two ambient temperature glass wool traps and one ice-water chilled glass bead trap, and the analytical method was quite insensitive. Nonetheless, the experimental data clearly show that concentrations of tetra, hexa-, hepta- and octadibenzodioxins generally increased as follows: coal + air &lt; coal + air + NaCl &lt;&lt; coal + air + HCl &lt;&lt;&lt; coal + air + Cl<sub>2</sub>.]</p>
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