

# Chlorine , Combustion and Dioxins: Does Reducing Chlorine in Wastes Decrease Dioxin Formation in Waste Incinerators?

By Pat Costner  
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## Executive Summary

Does the chlorine content of materials that are burned affect dioxin formation?

Since every molecule of dioxin<sup>a</sup> contains two or more atoms of chlorine, chlorine is an absolute necessity for dioxin formation. Therefore, when no chlorine is present, no dioxins are formed.

Can dioxin formation be reduced by restricting the chlorine content of the materials that are burned?

Lower chlorine input has been found to correlate with reduced dioxin formation in studies carried out in

- ▶ laboratory- and pilot-scale combustion systems (see Appendix 1),
- ▶ small-scale combustion systems (see Appendix 2), and
- ▶ full-scale combustion systems. (see Appendix 3)

In the specific case of full-scale waste incinerators, some studies have found decreased dioxin formation with reduced chlorine input, while others have not. This has led many policymakers and others to surmise that, for this particular category of combustion systems, chlorine input has little or no influence on dioxin formation.

No scientific theory has been advanced to explain how or why the chlorine/dioxin relationship in full-scale waste incinerators should differ from that in other combustion systems. However, a very practical explanation for the inconsistent findings among studies of waste incinerators can be found among the various factors that are known to weaken and confound the results of such studies (e.g., study design flaws; sampling and analytical methods that yield highly uncertain data; delayed release of dioxins, and high variability of waste contents and incinerator operating conditions).

Along with other extraneous elements, these factors create a background of experimental 'noise' too great to allow consistent characterization of the relationship of chlorine input and dioxin formation in full-scale waste incinerators. Taking that background noise into account, the many studies that have been conducted in a variety of different combustion systems, including full-scale waste incinerators, constitute a compelling body of evidence that dioxin formation in waste incinerators decreases when chlorine input is reduced.

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<sup>a</sup> In this paper, the terms 'dioxin' and 'dioxins' are used to include both the polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs).

## 1. Chlorine: An Integral Part of Every Dioxin Molecule

It is a scientific certainty that chlorine must be present for dioxin formation to take place in any combustion process. However, one of the critical questions with regard to dioxin formation during combustion is whether increased availability of chlorine enhances dioxin formation or, conversely, whether reducing the availability of chlorine lessens dioxin formation.

Many studies have been carried out in a wide variety of combustion systems with the aim of answering this question. As discussed below, most studies of laboratory-, pilot-, and small-scale combustors and some studies of full-scale combustors show that lower chlorine input results in less dioxin formation. Scientific consensus on the positive relationship between chlorine input and dioxin formation is strong enough that national governments and parties to regional and global treaties make recommendations and enact policies to restrict chlorine input to several types of small- and full-scale combustion systems, including full-scale waste incinerators, with the aim of reducing dioxin formation.

## 2. Laboratory- and Pilot-Scale Combustion Systems: Most Studies Show Positive Chlorine/Dioxin Relationship

Numerous studies of laboratory- and pilot-scale combustion systems have found that dioxin formation decreases with reduced chlorine input. The U.S. Environmental Protection Agency (2000) acknowledged this to be the case in their recent review of such studies:<sup>1</sup>

*"[R]eview of experimental data clearly indicates an association between chlorine content of feed/fuels and ... synthesis of CDDs and CDFs."*

Key findings of more than 45 laboratory- and pilot-scale studies are presented in Appendix 1. The overwhelming majority of these studies show that low chlorine input is associated with reduced dioxin formation, as indicated by dioxin concentrations in gaseous emissions and/or fly ash. For example, Katami et al. (2000) found less dioxin output in gaseous emissions with lower chlorine input during the combustion of newspaper with PVC or sodium chloride, as shown in

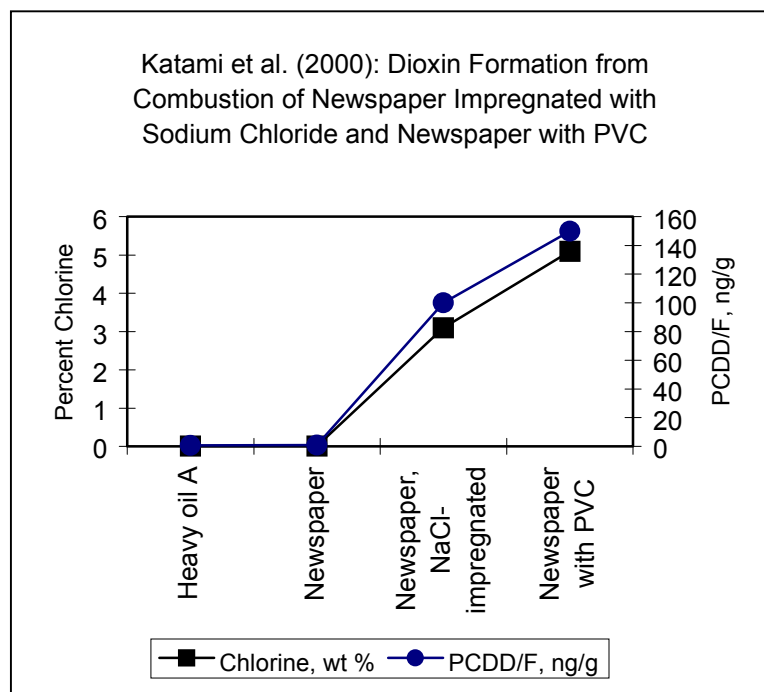


Figure 1: Katami et al. (2000)

Figure 1.<sup>2</sup>

In another series of laboratory experiments, Wikstrom et al. (1996) varied the chlorine content of an artificial waste by spiking it with PVC or calcium chloride, obtaining the results illustrated in Figure 2.<sup>3</sup>

Hatanaka et al. (1999) also found that lower chlorine input reduced dioxin formation when PVC and sodium chloride were used as chlorine source. In addition, their results showed that polychlorinated dibenzo-p-dioxins (PCDDs) were formed much more slowly than the polychlorinated dibenzofurans (PCDFs), as shown in Figure 3.<sup>4</sup> The latter finding is important in evaluating the results of other studies since many studies have compared chlorine input with total PCDD/Fs, while in older studies, often only PCDDs were considered.

These are only three among the many studies that have found that decreased dioxin formation is associated with reduced chlorine input, such as the majority of those presented in Appendix 1. Appendix 1 also contains excerpts and comments on several frequently cited studies that have reported finding no correlation between chlorine input and dioxin formation.

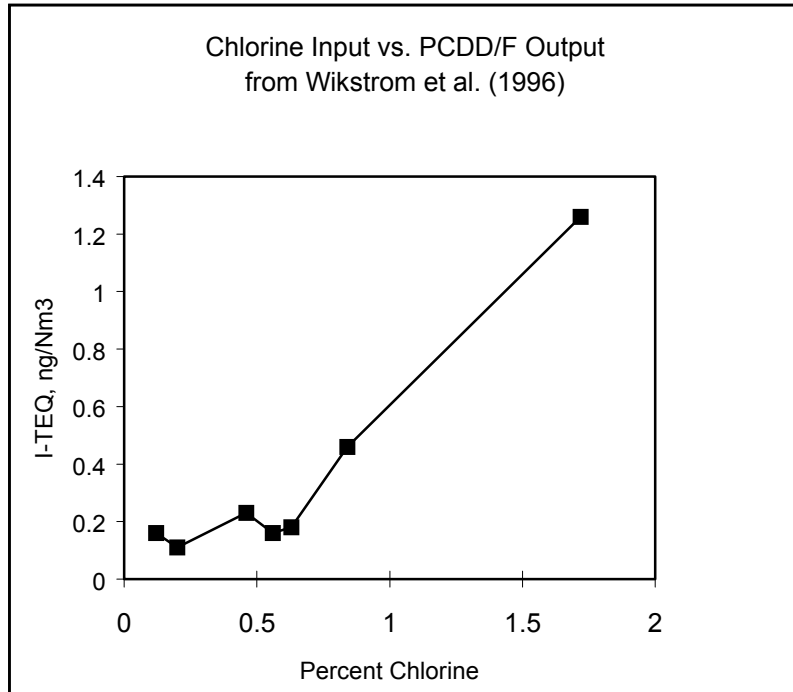


Figure 2: Wikstrom et al. (1996)

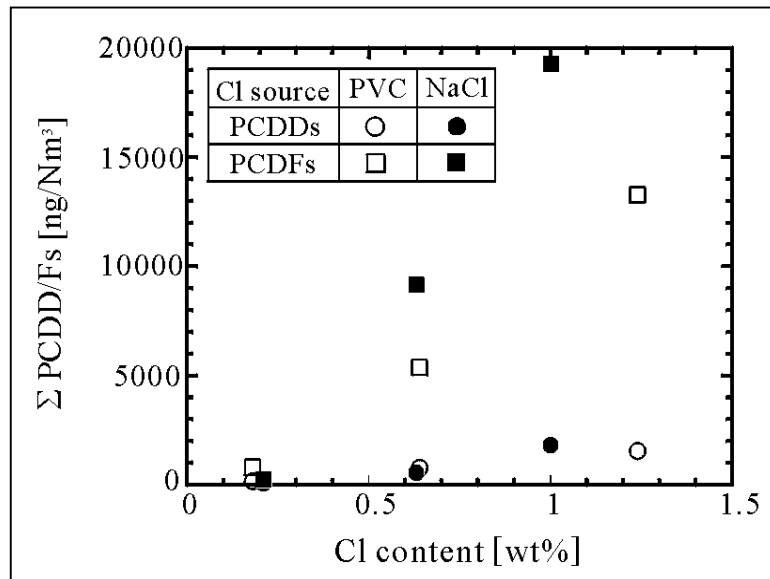


Figure 3: Hatanaka et al. (1999)

### 3. Small-Scale Combustion Systems: Most Studies Show Positive Chlorine/Dioxin Relationship

Lower chlorine input is also associated with reduced dioxin formation in domestic heating systems and internal combustion engines, as well as during the combustion of domestic waste in open barrels, waste piles, and other open fires. Appendix 2 lists key findings of twelve such studies, all of which found that lower chlorine input was correlated with reduced dioxin formation. Based on such evidence, some national governments, e.g., Germany and Austria, have banned or proposed to ban combustion of chlorine-containing materials in these systems (see Appendix 4).

For example, Gullett et al. (2000) carried out a series of experiments in which simulated domestic waste

with varied quantities of PVC was burned in open barrels and, in one case, in a waste pile. As illustrated in Figure 4, dioxin formation decreased with lower PVC content. In the one test with a waste pile, they found considerably lower dioxin formation than with the open barrel burns.<sup>5</sup> Another interesting finding in a related study was the marked impact of recycling on the PVC content of the simulated domestic waste: *“the percentage of PVC for the avid recycler rose from 0.7% to 4.5%.”*<sup>6</sup> The latter

finding suggests that increased recycling rates may result in a PVC content in domestic waste that is as much as six times greater than the generally accepted value.

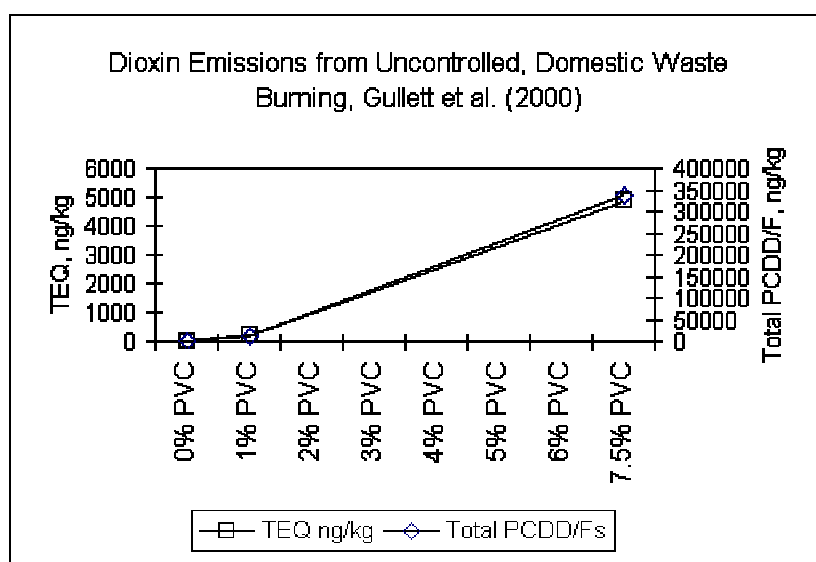


Figure 4: Gullett et al. (2000)

### 4. Full-Scale Combustion Systems: Is the Chlorine/Dioxin Relationship Different?

Policies of restricting chlorine input for the purpose of reducing dioxin formation in combustion systems have been adopted or recommended by national governments, professional associations, and advisory bodies as well as international treaties, as described in Appendix 4. For example, the Parties to the Convention on Long-Range Transboundary Air Pollution have agreed that reducing inputs of plastics, e.g., PVC and other chlorine-containing materials, is an effective and often low-cost method for reducing dioxin formation in full-scale combustion systems including iron/steel production, sinter plants, primary and secondary copper production, secondary

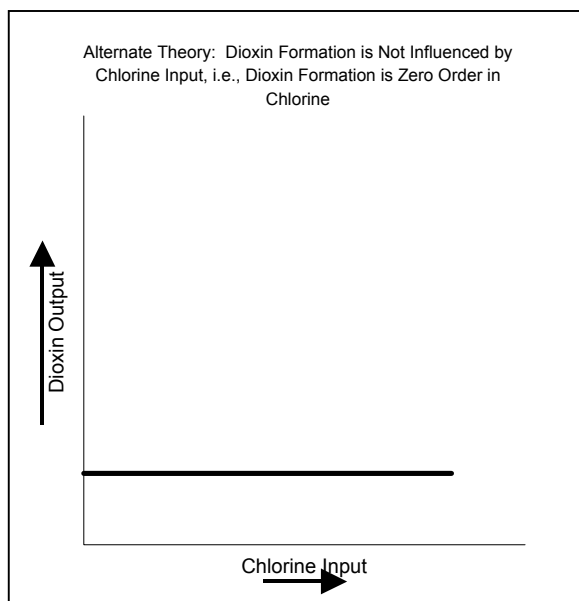
aluminum production, utility and industrial boilers, motor vehicles and domestic appliances.<sup>7</sup> In a more specific example, the U.S. Environmental Protection Agency attributed reduced dioxin releases from lead smelters to the phase-out of PVC separators in lead batteries which are processed in such smelters,<sup>8</sup> while the United Nations Environment Programme (UNEP) suggested a ten-fold higher dioxin emission factor when PVC is present in the materials sent to lead smelters than when the materials are PVC-free.<sup>9</sup>

Other examples include attribution by the UK Environment Agency's of significant reductions in emissions of dioxins and hydrogen chloride from a full-scale waste incinerator not only to upgraded pollution control but also to *"reduc[ing] the amount of chlorine containing waste accepted;"*<sup>10</sup> the recent recommendation by the Austrian Federal Environment Agency for *"the reduction of chlorine in fuels"* for small and small-firing combustion systems;<sup>11</sup> USEPA's suggestion that the health care industry *"use plastics such as polyethylene and polystyrene in place of polyvinyl chloride";*<sup>12</sup> and the German Office of the Environment's conclusion that *"[C]hlorine-free plastics such as polyethylene and polypropylene, which may be used as PVC substitutes in the packaging industry, seem to be ecologically sounder than PVC; the environmental damage caused by PVC (release of dioxin from uncontrolled fires, ... increased chlorine input in incinerators) is generally not present ..."*<sup>13</sup>

#### 4.1 Full-Scale Waste Incinerators: A Focus of Controversy

Waste incinerators are at the center of the chlorine/dioxin controversy, perhaps because they currently receive the bulk of discarded PVC and other chlorine sources that are deliberately burned. This means that the economic and political consequences of restricting chlorine input to waste incinerators are much more far-reaching than restricting chlorine inputs to other combustion systems, such as lead smelters.

As shown in Appendix 3, many studies of waste incinerators have found that lower



chlorine input is associated with decreased dioxin formation. These evaluations of data from the Danish network of municipal waste incinerators,<sup>14</sup> more than 80 full-scale combustion systems in the U.S.,<sup>15</sup> a dozen combustion facilities in the U.K.,<sup>16</sup> and other full-scale systems have all shown a positive relationship between chlorine input and dioxin formation. However, not all studies have found such an association. The apparent lack of agreement among such studies has, in recent years, been increasingly regarded as evidence that, for this one particular

Figure 5: Alternate Theory: Dioxin Formation is Zero Order in Chlorine

class of combustors, reducing chlorine input does not lessen dioxin formation. In other

words, it is contended that, in full-scale waste incinerators, dioxin formation is not affected by changes in chlorine input. If this were true, dioxin formation would, in effect, be zero order in chlorine, as illustrated in Figure 5.

However, the lack of consistency in waste incinerator studies can be more readily understood when consideration is given to the wide variety of extraneous factors that influence study results (see Section 4.2 below). For example, Rigo et al. (1995) point out that their failure to find a positive relationship between chlorine input and dioxin formation can be attributed to such factors:<sup>17</sup>

*“Any effect chlorine has on PCDD/F concentrations in commercial scale systems is masked by the effect of air pollution control system [APCS] temperature, ash chemistry, combustion conditions, measurement imprecision, and localized flow stratification.”*

Takeshita and Akimoto (1992) found that lower levels of hydrogen chloride (HCl), an indicator for chlorine input, were associated with decreased dioxin concentrations in the stack gases of a municipal waste incinerator.<sup>18</sup> In an earlier related study, Takeshita and Akimoto (1989) had similar findings, as shown in Figure 6. In addition, they reported that PCDFs were formed more rapidly than PCDDs,<sup>19</sup> a finding recently corroborated by Hatanaka et al. (2000) in a small-scale combustor.<sup>20</sup>

When Kopponen et al. (1992) examined fly ash collected during the combustion of coal and bark spiked with PVC in a district power plant, they found lower dioxin concentrations in the ash with reduced chlorine input, as shown in Figure 7.<sup>21</sup>

Analyzing data from a full-scale hazardous waste incinerator, Costner (1998) found that reduced chlorine feedrates were associated with lower dioxin concentrations in the stack gases, as shown in Figure 8. In this study,

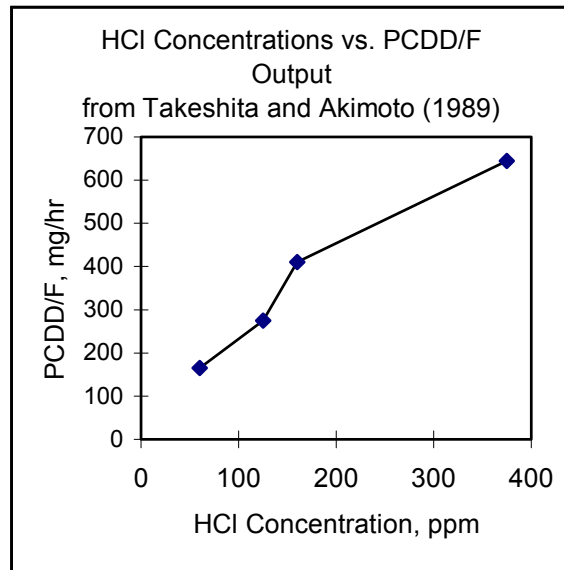
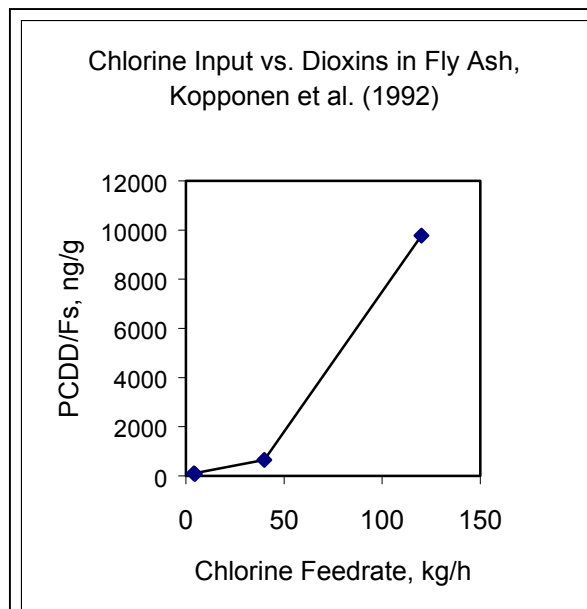


Figure 6: Takeshita and Akimoto (1989)



another interesting finding that bears on negative results by other researchers was the lack of correlation of chlorine feedrates with concentrations of HCl and Cl<sub>2</sub> in the stack gases.<sup>22</sup>

Some scientists who agree that dioxin formation correlates with chlorine input nonetheless oppose policies restricting chlorine input. They contend that, even though restricting chlorine input reduces dioxin formation, other factors have far greater influence. For example, while Wikstrom and Marklund (2001) found a positive chlorine/dioxin relationship, they concluded that *“the most important variable for changes in the PCDDs/Fs [dioxins] ... formation was disturbance in the combustion condition and not the variation in chlorine content of the fuel”*.<sup>23</sup>

While this assertion may well be true, it is comparable to saying that the quantity of fuel in an airplane’s tank is not the most important factor in determining how far the plane can fly: *“The most important variable for changes in the distance the airplane flies is disturbance in the combustion condition, e.g., engine failure, and not the variation in the amount of fuel in its tank.”* The truth of this statement does nothing to negate the fact that, when an airplane is functioning normally, the distance it can travel depends on the quantity of fuel in its tanks: less fuel, less distance. In a similar fashion for waste incinerators the weight of evidence suggests that, under normal conditions, the quantity of dioxins formed depends on the amount of chlorine in the feed: less chlorine, less dioxin.

As noted above, some researchers have reported finding no correlation between chlorine input and dioxin formation in full-scale waste combustion systems, e.g., Rigo et al. (1995),<sup>24</sup> Mark (1994),<sup>25</sup> Giugliano et al. (1989),<sup>26</sup> and Gottesman et al. (1988).<sup>27</sup> These negative studies have been used to dissuade many national and international policymakers

from pursuing policies for replacing chlorine-containing materials, such as PVC, with chlorine-free materials or segregating chlorine-containing materials from wastestreams slated for incineration. Consequently, it is very important to examine the factors that may have contributed to their supposedly negative findings.

In one of the more frequently-cited negative studies, (Rigo et al., 1995), sometimes referred to as the “ASME report”, the authors’ conclusions are not supported by their own statistical analyses. For example, their analyses show a predominance of positive correlations between chlorine input or its indicator and dioxin concentrations in the stack gases of municipal and medical waste incinerators.<sup>28,29</sup> This study as well as others with negative studies suffer from a variety of commonly-shared difficulties as discussed

Figure 8: Costner (1998)

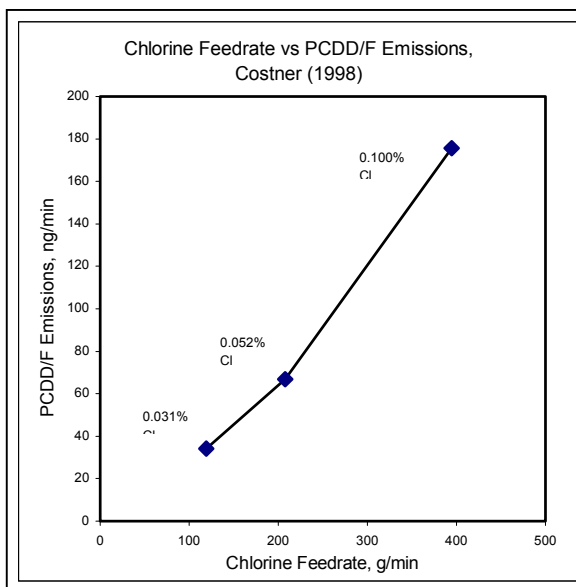


Figure 7: Kopponen et al. (1992)

below.

#### 4.2 Difficulties in Studies of Full-Scale Combustion Systems.

Defining the relationship between chlorine input and dioxin formation in modern, full-scale waste combustors is admittedly a very difficult task. Various factors contribute to the difficulties of obtaining data that are sufficiently robust for evaluating the relationship of chlorine input and dioxin output in full-scale incinerators:

- **Imprecision of dioxin measurements.** Dioxins in incinerator stack gases are the smallest (< 0.1 to 1 percent of total dioxin output),<sup>30,31</sup> most highly manipulated and most difficult-to-measure of an incinerator's primary dioxin releases (stack gases, fly ash, bottom ash, scrubber water filter cake, etc.). The difficulties in obtaining representative samples of stack gases for dioxin analysis and carrying out such analyses are well known. Nonetheless, dioxin concentrations in stack gases are the most commonly used indicators for dioxin formation, despite the fact that the values are known to be highly uncertain. For example, a survey by a research group in the U.K., APARG (1995), found a margin of error of 50 percent for such measurements.<sup>32</sup> This high uncertainty stems in large part from the difficulties of obtaining representative samples of a large, high-velocity stream of hot gases and in analyzing such samples with sufficient precision and accuracy.<sup>b</sup>
- **Delayed release of dioxins.** The "memory effect", which has been documented in a number of studies (e.g., Gullett et al. (2000)<sup>33</sup>; Blumenstock et al. (2000)<sup>34</sup>; Zimmerman et al. (2001)<sup>35</sup>; Hunsinger et al. (2000)<sup>36</sup>) occurs when dioxins are adsorbed onto the walls of incinerator stacks, ducts, etc., and then slowly released. This results in underestimation of the dioxin emissions that might otherwise correlate with a specific rate of chlorine input. Delayed release presents a formidable barrier to evaluating the relationship between chlorine input and dioxin releases in stack gases since the dioxin concentration in a given sample of stack gas has only a very weak relationship to the amount of dioxins that was produced as the sample was taken. Moreover, this phenomenon has seldom been taken into consideration in studies of the dioxin/chlorine relationship in full-scale systems. As a result, the methodology most commonly used to evaluate the chlorine/dioxin relationship – comparison of the dioxin concentration in stack gas with the chlorine input during the stack sampling period – cannot be expected to show a strong relationship between chlorine input and dioxin formation.
- **Interferants in characterizing the chlorine/dioxin relationship.** Bromine effectively obscures the relationship of chlorine input and dioxin output. I.e., evaluations of the chlorine/dioxin relationship carried out using municipal waste or other materials that contain bromine sources, such as brominated flame retardants, are less likely to define the chlorine/dioxin relationship appropriately due to interference by bromine. As pointed out by Lemieux and Ryan (1996), when

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<sup>b</sup> See Costner (1997) for a more thorough discussion of the limitations of measurements of stack gas concentrations of dioxins and HCl.



bromine is present in the wastes fed into an incinerator, polybrominated dioxins as well as mixed bromochloro- dioxins are formed “*at the expense of PCDDs/PCDFs*”.<sup>37</sup>

- **Unreliability and uncertainty of hydrogen chloride measurements.** Hydrogen chloride (HCl) concentrations in stack gases are commonly regarded as reliable indicators of chlorine input. However, at one full-scale hazardous waste incinerator, Costner (1998) found that HCl emissions showed no correlation with chlorine input, while Sonnenberg and Nichols (1995) determined that only 5 percent of the chlorine input was released as HCl in stack gas at another full-scale waste incinerator.<sup>38</sup> In another study, Kanters et al. (1996) found that about 25 percent of the chlorine fed into the combustor remained in the ash.<sup>39</sup> Further, the values obtained for HCl concentrations in stack gases are highly uncertain. For example, in one closely controlled study, HCl measurements had a standard deviation of +/- 28 percent.<sup>40</sup> Moreover, Rigo (1998) found a margin of error of 36 percent for measurements of HCl concentrations in stack gases.<sup>41</sup> <sup>c</sup>

The factors described above are only a few of those that are known to influence the results of studies of the chlorine/dioxin relationship in full-scale waste incinerators.

## 5.0 Conclusion

A positive chlorine/dioxin relationship has been documented in studies of laboratory- and pilot-scale combustion systems, small-scale combustion systems, and full-scale combustion systems, including some studies involving numerous waste incinerators. Given the many extraneous factors affecting the study of full-scale waste incinerators, these numerous studies constitute a compelling body of evidence that dioxin formation in waste incinerators decreases when chlorine input is reduced.

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<sup>c</sup> See Costner (1997) for a more thorough discussion of the limitations of measurements of stack gas concentrations of dioxins and HCl.

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- <sup>40</sup> Lenoir, D., Jaune, A., Hutzinger, O., Mutzenich, G., Horch, K., **1991**. Influence of operating parameters and fuel type on PCDD/F emissions from a fluidized bed incinerator. *Chemosphere* 23: 1491-1500.
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**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 (Vikelseo, 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 [&gt;3000 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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**Appendix 2: Small-Scale and Other Combustion Systems/Processes: Studies Relevant to the Relationship of Chlorine Input and Dioxin Formation<sup>a</sup>**

Combustion System or Process	Source	Key Excerpts and Notes
Internal combustion engine	Broz et al. (2000) <sup>1</sup>	<p><i>“The effect of synthetic and mineral oils on the formation of polyaromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) in emissions from a spark ignition engine was studied on a Skoda Favorit engine fueled with leaded gasoline. ... The restriction of PCB and PCDD/F in emissions can be achieved by exclusion of the presence of halogens, especially of chlorine in the reaction system, regardless of whether it is organic- or inorganic-bond.”</i></p>
Open barrel	Gullett et al. (2000) <sup>2</sup>	<p><i>“... the test container consisted of a 208 L (55 gal.), steel, precleaned barrel with 24 2 cm diameter ventilation holes around the base. ... The last two baseline tests had values of 429 and 609 ng TEQ/kg. ... One open burn (waste pile) test ... with the baseline waste composition resulted in emission of 59 ng TEQ/kg. This suggests that open burning produces less PCDDs/Fs than containerized barrel burning, but this remains to be verified by replicate tests. ... PCDD/F emissions increase with higher amounts of Cl, whether organic or inorganic, and higher amounts of Cu catalyst.”</i></p>
Domestic furnace	Launhardt and Thoma (2000) <sup>3</sup>	<p><i>“Various herbaceous biofuels (straw, whole plant cereals and set aside hay) and spruce wood were tested .... The trials were conducted in an automatically charged multi-fuel furnace for domestic applications (50 KW<sub>th</sub>). Both flue gas and the different ash fractions were analysed. However, for the PCDD/F, PCPh and PCBz increased emissions were detected when herbaceous fuels were applied. This may be attributed to their higher chlorine concentration and the high ash content, which is responsible for increased dust emissions during combustion. Similar observations were also found for the</i></p>

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

		<i>PCDD/F-concentrations in the ashes. ... Investigations on modern biomass combustion plants in Bavaria (Huber and Friess 1998) showed, that PCDD/F emissions are slightly higher for straw and whole crops, compared to wood. A dependence of PCDD/F-emissions on the chlorine content in the fuel can also be found for the biomass tested here ..."</i>
Open barrel	Lemieux et al. (2000) <sup>4</sup>	<i>"This study measured the emissions of several pollutants, including polychlorinated dibenzo- p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), from burning mixtures designed to simulate waste generated by a "recycling" and a "nonrecycling" family in a 208-L (55-gal) burn barrel at the EPA's Open Burning Test Facility. ... . Emissions of PCDDs/PCDFs appear to correlate with both copper and hydrochloric acid emissions. ... the percentage of PVC for the avid recycler rose from 0.7% to 4.5%. ... In general, PCDDs/PCDFs emissions were higher for the avid recycler than for the nonrecycler. ... These data suggest that increases in emissions of either copper or HCl may be associated with increases in PCDD/PCDF emissions."</i>
Semi-open household waste burner	Ikeguchi et al. (2000) <sup>5</sup>	<i>"Levels of dioxins in the flue gas ranged widely, from 0.3 ng-TEQ/Nm<sup>3</sup> to 4500 ng-TEQ/Nm<sup>3</sup>, reflecting a kind of waste and a combustion condition ... Especially corrugated paper mixed with polyvinyl chloride (PVC) recorded higher value, more than 100 ng-TEQ/Nm<sup>3</sup> while corrugated paper mixed with polyethylene (PE) and polystyrene (PS) accounted dioxins level below 50 ng-TEQ/Nm<sup>3</sup>, as similar as in the cases of wood chip, newspaper, and garden waste. ... As shown dioxins [sic] level increases as chlorine concentration in waste increases irrespective with the type of chlorine, i.e., organic or inorganic chlorine."</i>
Small waste incinerator	Nakao et al. (2000) <sup>6</sup>	<i>In "a small incineration with a combustion capacity of 50 kg/hr .... On the other hand, a mixture of combustions of chloric plastic (No. 7) and electric wire (No. 8) gave a remarkably high concentration [of dioxins]. From these results, it is clear that generation of dioxin analogues increased by a mixture of combustion with chloric plastic. "</i>

Simulated house fire	Ruokojarvi et al. (2000) <sup>7</sup>	<p><i>“Simulated apartment fires were arranged in the two floor block of flats normally used for fire fighting practice. Pieces of chipboards and old furniture were used as fire loads. ... Adding PVC plastic material to the fire (samples G5 and G7) did not increase the PCDD/F concentrations in combustion gas samples, even though the concentrations of CPhs, which have been regarded as PCDD/F precursors, did seem to increase. The highest PCDD/F concentrations were in samples 5, 6 and 7, however, and no PVC had been added to the fire in the case of sample 6. ... The highest PCDD/F concentrations in the wipe samples were in sample W4, collected during the fires with additional PVC, but the concentrations in sample W1 were nearly as high, so that it cannot be concluded that the extra PVC was responsible for the increase.”</i></p> <p>[Note: No attempt was made to determine either the chlorine content or the PVC content in the materials burned in these experiments. The materials contained in each of the seven `fireloads' were highly variable. However, additional PVC was included in two of the seven `fireloads'. Among the three `fireloads' that resulted in the highest air concentrations of dioxins, in TEQs, two had added PVC. Also, as the authors noted, the wipe samples having the highest dioxin concentrations were those from the two PVC-augmented `fireloads'.]</p>
House heating systems	Launhardt et al. (1998) <sup>8</sup>	<p><i>“The PCDD/F-concentrations in fluegases using untreated wood were in the range of 2-25 pg I-TE/m<sup>3</sup>. The combustion of paper, cartons, painted wood and wood with 2-5% PVC gave PCDD/F-concentrations from 38 to 952 pg I-TE/m<sup>3</sup> and 380 to 2,240 ng I-TE/kg (chimney soot). ... Analogous to the emission the concentration in the chimney soot increases with the content of chlorine (up to 2 240 ng I-TE/kg). The PCDD/F-concentrations in chimney soot using natural wood were on a low level of 32 ng I-TE/kg.”</i></p>
House-heating stove – tile with air circulation	Thuss et al. (1997) <sup>9</sup>	<p><i>“Lignite briquettes with different salt contents (“normal”-coal, 300 ppm w/w, “salt”-coal, 2000 ppm w/w) were burned in a common type of a house heating facility. The content of polychlorodibenzodioxins and furans (PCDD/F) in</i></p>

		<p><i>the flue gas and in the bottom ash were determined. The values calculated from the homologue sums were significantly higher for the "salt"-coal briquettes regarding their flue gas concentrations and slightly increased in respect to the bottom ashes. Taking into account a wide variety of additional analytical parameters and considering mechanistic aspects, our assumption was proved that the higher chlorine content of the "salt"-coal briquettes is responsible for the increased values. ... From the discussion of the single parameters it can be deduced that the higher PCDD/F-emission of the "salt"-coal combustion is caused by the higher chlorine content of the "salt"-briquettes. All other alternative approaches to explain this difference were found to be non-relevant ... The only plausible explanation for the higher PCDD/F content of the "salt"-coal bottom ash is the higher chlorine content as well."</i></p>
Open barrel	Lemieux (1997) <sup>10</sup>	<p><i>"It is probable that the fraction of PVC in the refuse contributes significantly to the total amount of PCDDs/PCDFs produced. ... [E]missions of PCDDs/PCDFs are significantly higher for the avid recycler. This phenomenon is likely due to several factors, including the higher mass fraction of PVC in the avid recycler's waste, a different temperature profile, and possibly a different mix of metallic catalysts"</i></p>
House-heating stove – tile with air circulation	Thuss and Popp (1995) <sup>11</sup>	<p><i>"Investigations of emissions of PCDD/F from lignite domestic heating were performed. ... Two sorts of lignite briquettes were investigated: "salt" coal briquettes from the former open cast mine Merseburg-Ost (chlorine content: 2000 ppm w/w) which belonged to the preferred fuels in the GDR and "normal" coal briquettes from the open cast mine Profen (chlorine content: 300 ppm w/w) which have been widely used in the eastern part of Germany. It is shown that the PCDD/F concentrations of the flue gases of the "salt" coal combustion are about 7- fold higher than the corresponding values of the "normal" coal. The patterns of the congeners and the homologue profiles are nearly the same. ... From this investigation, we deduced that the higher PCDD/F emission of the salt coal combustion can be</i></p>

		<i>correlated with the higher chlorine content of the "salt" briquettes. All other alternative approaches to explain this difference were found to not be relevant because the corresponding parameters do not differ significantly ... Various investigations with synthetic coals under defined conditions produced the result that PCDD/F-formation during coal combustion processes is strongly dependent on the chlorine supply originating from the used feed stock."</i>
Open fire	Merk et al. (1995) <sup>12</sup>	<i>In the fire experiment 500 kg wood and 40 kg PVC were completely incinerated. The fumes dispersed throughout the closed hall ... The concentrations of PCDD/F in the fumes of PVC fire (about 5 ng TE/m<sup>3</sup>) are in the same range as the concentrations of PCDD/F in stack gas of municipal waste incinerators. ... These results show that incineration of PVC in open fires result on considerable amounts of PCDD/F, which demonstrate the toxic potential of these industrial material in accidental fires.</i>

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### Appendix 3: Full-Scale Combustors: Studies Relevant to the Relationship of Chlorine Input and Dioxin Output<sup>a</sup>

<p>Hunsinger et al. (2000)<sup>1</sup></p>	<p><i>“Further experiments burning different fuels showed that inside the combustion chamber the formation of PCDD/F depends significantly on the fuel composition. Especially the content of halogens (and metals) play an important role. Burning bio mass fractions like natural wood chips or straw pellets resulted only in trace amounts of PCDD/F above the fuel bed. In contradiction to the measurements inside the combustion chamber the concentrations of PCDD/F found in the raw gas downstream of the boiler showed no influence of the fuel composition. The explanation of these results must be attributed to memory effects from fly ash deposits in the boiler section. They influence significantly the PCDD/F formation inside the boiler over a very long time.”</i></p>
<p>Yamamura et al. (1999)<sup>2</sup></p>	<p><i>“The furnace H emitted the lowest dioxin of 0.012ng-TEQ/m<sup>3</sup>N. This is due to not only the property of the waste, which are chemical residues with high volatile content, but also the characteristics of the furnace, which is easy to have stable combustion condition. Compared with E with the highest dioxin of 160ng-TEQ/m<sup>3</sup>N and F, although F emits 2.5 times higher CO than E, F emits much lower dioxins of 2.9ng-TEQ/m<sup>3</sup>N than E. One of the main reasons for this significant difference is due to the wastes incinerated. E incinerated plastics including medical waste, which contains plastic bags and tubes mainly made of PVC, and wood chips, while F incinerated demolition waste such as wood chips.”</i></p>
<p>Costner (1998)<sup>3</sup></p>	<p>Findings in this evaluation of a hazardous waste incinerator (rotary kiln) in the U.S. are as follows: <i>“Data ... show that PCDD/F emissions are dependent on chlorine input at a chlorine concentration as low as 0.031 percent. In addition, mass balance data indicate that hazardous waste incinerators may be achieving destruction efficiencies that are orders of magnitude below those achieved by other destruction technologies. ... PCDD/F concentrations in stack gases increased as the chlorine content rose from 0.031 to 0.10 percent. ... HCl/Cl<sub>2</sub> emissions do not correlate well with chlorine feedrates as has been assumed by some assessments of full-scale incinerators, e.g., Rigo et al.”</i></p>
<p>Manninen et al. (1997)<sup>4</sup></p>	<p><i>“A one- year co-combustion of RDF with peat and coal was carried out in a 65 MW circulating fluidized-bed (CFB) boiler power plant.... HCl emissions increased when the chlorine</i></p>

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

	<i>content of the fuel mixture increased, because limestone injection was not used.</i>
Manninen et al. (1996) <sup>5</sup>	Results of seventeen test runs in a circulating fluidized bed boiler are as follows: <i>“Because a mixture of packaging materials can contain metals from foils and printing inks, chlorine from PVC, and food contaminants, a question has emerged: How do these metals and chlorine affect PCDD/F formation? On the other hand, does the combustion of packaging material with sulphur containing coal have an inhibiting effect on the formation? The objective of this study was to find answers to these questions by evaluating the full-scale combustion results from 17 test runs carried out in a multifuel circulating fluidized-bed boiler (CFB). Multivariate projection methods such as Principal Component Analysis (PCA) and Partial Least Squares Projections to Latent Structures (PLS) were used. ... The results of the PLS calculations (-&gt; Fig. 2 and regression coefficients) show that a lower heating value (LHV in dry solids) or the amount of volatile components in the fuel mixture, or the temperature of the bed did not correlate significantly with the PCDD/F values. Pb, Cu, Cr and Cl contents of the fuel and polychlorinated phenols (PCPhs) in the flue gas correlated most closely with the PCDFs in the flue gas and fly ash. ... The chlorine content of the fuel correlated with PCDFs and there was an inverse correlation between the S/Cl ratio and PCDFs.”</i>
Wanke and Vehlow (1996) <sup>6</sup>	This study at the TAMARA facility found that <i>“an additional input of Br [bromine] into the incinerator does obviously promote the specific formation of mixed halogenated [dioxin] congeners significantly. In Fig. 2 the sum of the Br containing dioxins [in raw gas] is plotted as a function of the Br input into the incinerator for all test trials except of those with poor combustion conditions. As a first approach the graph can be interpreted as a straight correlation between both parameters. The data, however, are very low and suffer from high analytical uncertainties.”</i>
Huotari and Vesterinen (1996) <sup>7</sup>	In experiments performed with three commercial fluidized bed combustors and one lab-scale FBC, Huotari and Vesterinen (1996) found: <i>“The chlorine content of fuel rose up to 0.35% as a measured dry base (db). The emissions of the toxic PCDD/F compounds were found to follow fuel-Cl content trendwise, as expected. However quantitatively the relative emission levels varied with the factor of 10<sup>3</sup> at the same Cl- content in fuel. ... The PCDD/F-emissions are related to fuel-Cl content. ... The PCDD/F-concentrations in flue gas (ng/m<sup>3</sup><sub>n</sub>) tended to follow fuel Cl-content, but PCDD/F contents in separated ash (ng/g)</i>



	<p>was mainly influenced by combustion conditions, like the furnace temperature. ... The increase in concentrations of chlorinated benzenes, chlorophenols and PCB in flue gas, fuel-Cl and fuel-Cl/S and Cu in fly ash increased PCDD/F contents in flue gas. ”</p>
<p>Vesterinen and Flyktman (1996)<sup>8</sup></p>	<p>“Refuse derived fuel (RDF) has been burned with wood chips and milled peat in a 4 MW bubbling fluidized bed boiler. ... In co-combustion of RDF [refuse derived fuel] with wood chips the clear correlation was seen between the chlorine content of the fuel mixture and the PCDD/F concentration in flue gas. A similar correlation was also seen between the fuel chlorine and chlorophenol concentration in flue gas.” [Note: the chlorine content of the fuels to ranged from 0.03 to 0.33%]</p>
<p>Moller et al. (1995)<sup>9</sup></p>	<p>In their review of data from some of the 33 full-scale combustors in Denmark, Moller et al. (1995) concluded as follows: “The hydrochloric acid content in the stack fume is dependent on the content of PVC and other chlorine sources in the waste. It is calculated that 2/3 of the chlorine in the Danish incinerator plants originates from PVC in the waste and thus also the hydrogen chloride formed. Burning PVC also yields a large amount of soot-containing smoke. ... The presence of chlorine in the material [PVC] gives the potential for contribution to the formation of polychlorinated dioxins and furans during the fire. If formed, it seems that these substances have the highest tendency to be present in the soot. The amount will depend on the fire conditions such as oxygen available, temperature, catalyst available such as copper and the amount of chlorinated material, e.g., PVC involved in the fire. However, the content of PVC in the waste also contributes to the emission of dioxins and heavy metals. ... There seems to be a relationship between HCl emissions and the emissions of a number of chlorinated organic compounds including dioxins. However, the relationship is a 2nd or 3rd order relationship... . It is most likely that the reduction of the chlorine content in the waste can contribute to the reduction of the dioxin formation, even though the actual mechanism is not fully understood. The influence on the reduction is also expected to be a 2nd or 3rd order relationship.”</p>
<p>Thomas and Spiro (1995)<sup>10</sup></p>	<p>In their study, Thomas and Spiro (1995) reviewed data from more than 80 full-scale combustion systems/processes in the U.S., concluding as follows: “Nevertheless, the data presented in section 4 will show that dioxin emission factors from combustion of similar fuels, with broadly similar combustion</p>

	<p><i>systems and pollution control devices, typically vary by less than an order of magnitude. This holds true, for example, for hospital waste incinerators, sewage sludge incinerators, and industrial wood boilers. Thus, for most processes dioxin emissions can be categorized by the combustion activity. Exceptions are the incineration of municipal and hazardous waste, for which different types of combustion systems can have dioxin emission factors that differ by more than an order of magnitude.”</i></p> <p><i>“While a dependence on chlorine content might seem to be a foregone conclusion, there has in fact been doubt on this point since limited data, on test-burns at municipal waste incinerators, for example, have shown no correlation. There are, of course, many variables besides chlorine content, especially the operating conditions of the combustion system, and the application of pollution control technology. Figure 1 shows that favorable operating conditions (open symbols) can lower emissions by as much as two orders of magnitude. But under poorly controlled conditions (closed symbols), there is a clear dependence on chlorine content. Moreover, the relationship is more than proportional since the slope of the loglog plot is somewhere between one and two. Since dioxin molecules contain more than one chlorine atom, a higher order dependence is not unexpected.”</i></p>
<p>Rigo et al. (1995)<sup>11</sup></p>	<p>This study is described as examining data from a total of 169 full-, lab-, bench- and pilot-scale facilities. “A general review ... found no statistically significant relationship between chlorine input and PCDD/F stack gas concentrations for the majority (80 percent) of the 90 facilities which had sufficient simultaneous data ... Eleven percent displayed an increase; 9 percent displayed decreasing PCDD/F concentration with increasing chlorine.”</p> <p>[Note: The lack of agreement between the conclusions presented in this report and the results of the authors’ statistical analyses as well as many other limitations are addressed in detail in Costner (1997)<sup>12</sup> and, specifically with respect to municipal and medical waste incinerators, in Costner (1997).<sup>13</sup> As documented in these reviews, statistical analyses by Rigo et al. (1995) actually show a positive association between HCl and dioxin concentrations in stack gases at 15 of 22 municipal waste incinerators and 10 of 15 medical waste incinerators as well as a positive association between chlorine federates and dioxin concentrations in stack gases at 14 of 23 cement kilns.]</p>

<p>Cains and Dyke (1994)<sup>14</sup></p>	<p>An examination of data from more than a dozen combustion facilities in the U.K. led to the following conclusions: <i>“Simple global correlations of dioxin and furan levels against general parameters such as the CO or HCl concentration in the flue gas, Cu, Cl or S levels in the feedstocks, grit ashes or particulates entrained in the flue gas, combustion or boiler exit temperatures are not sufficiently robust to characterize the conditions that promote formation in a general or universal way. Specific correlations of PCDD/F levels against the copper and chlorine contents of entrained particulates tentatively support results of laboratory studies on the role of Cu and Cl in fly ash in promoting PCDD/F formation.”</i></p>
<p>Mark (1994)<sup>15</sup></p>	<p>This study was commissioned and published by the Association of Plastics Manufacturers in Europe and carried out at the TAMARA mass burn incinerator in Germany. <i>“In order to categorise the relative effects of polymers on the combustion of MSW the project studied three test cases:</i></p> <ul style="list-style-type: none"> <li>• <i>combustion of MSW containing an average level of polymers - base case</i></li> <li>• <i>combustion of MSW containing an added 7.5 per cent by weight of mixed plastics waste - medium polymer case</i></li> <li>• <i>combustion of MSW containing an added 15 per cent by weight of mixed plastics waste - high polymer case.”</i></li> </ul> <p><i>... APME estimates the European average content of PVC in MSW to be approximately 10 per cent weight, so to match this figure the PVC element of mixed waste polymers used for testing was increased by the addition of post-use articles such as PVC pipes and flooring products. This meant that the addition of plastics, with an average heat of combustion three times higher than standard MSW, caused the total feed to the combustor to be reduced accordingly.</i></p> <p><i>... soot blowing was carried out two hours before, and at the end of every six hour sampling period. Change over times from one condition to another - ie A to C - were a minimum period of 12 hours to ensure stable boiler conditions. ... Two types of additives - lime, with or without carbon - were used during the test to confirm the effectiveness of carbon in removing dioxins and furans. ... HCl concentration in the flue gas rose as expected because of the addition of PVC to the waste plastics, although this was subsequently reduced to amounts found in normal clean gas by the emission control system. ... Peaks in raw gas concentrations were only two to three times the normal value of 1.5 g HCl/m<sup>3</sup>. ... There was no increased formation of chlorinated dibenzodioxin/furans (PCDD/F) in the raw gas when adding mixed waste plastics.”</i></p>

	<p>[Note: The data presented are not sufficient for assessing the relationship between chlorine and/or PVC input and dioxin output: 1) neither the chlorine content nor the actual PVC content of the incinerator feedstock was reported; 2) waste feedrates were apparently decreased as plastics content was increased; 3) additives were used -- lime with and without carbon -- that are commonly used to reduce dioxin formation by reacting with the available HCl and Cl<sub>2</sub> and/or reduce dioxin levels in the flue gas through adsorption; and 4) the frequency of soot blowing combined with abbreviated stabilization times (as little as 12 hours) can be expected to have considerable influence on dioxin formation as well as measured dioxin values.]</p>
<p>Wilken et al. (1994)<sup>16</sup></p>	<p>At the Bielefeld-Herford municipal solid waste incinerator in Germany, reductions in PCDD/F emissions were achieved as follows: “... [T]he average of 2.73 ng I-TEQ/m<sup>3</sup> and the median of 2.81 ng I-TEQ/Nm<sup>3</sup> of the actual routine performance lie distinctly below former emission concentrations, which ranged from 2.9 to 4.2 ng I-TEQ/Nm<sup>3</sup>. The same trend can be observed for PCB, but not for chlorobenzenes and chlorophenols ... Since the measurement in December 1991 effective emission reduction means like</p> <ul style="list-style-type: none"> <li>• exclusion of PVC and computer scrap in the input,</li> <li>• optimizing combustion operation,</li> <li>• installation of a high-performance quasi-dry flue gas purification system in 1993 have been realized at this plant.”</li> </ul>
<p>Jager et al. (1993)<sup>17</sup></p>	<p>In experiments at three full-scale combustors in Germany, Jager et al. found as follows: “At MWI A, addition of polyvinylchloride resulted in a slight but not significant increase in PCDD/PCDF in clean gas, while concentrations of chlorobenzenes, PCB and hydrogen chloride increased rapidly. Nevertheless, the chlorine content in the input must have had an influence on the dioxin emission, as has been observed at MWI C at the summer and winter campaign. Lenoir et al. also observed a significant increase in PCDD/PCDF emission after addition of 3% PVC to the waste input. ... At MWIs A and D, the raise of the bromine content in the input material resulted in a significant rise of mixed-halogenated dioxins and furans, especially monobromo-polychloro compounds, and in increase of chlorinated dioxins and furans too (Fig. 5).”</p> <p>“Recommendations concerning waste input</p> <ul style="list-style-type: none"> <li>• Reduce halogen availability in the combustion chamber by excluding certain materials from MWI input.</li> </ul>

	<ul style="list-style-type: none"> <li>• Exclude brominated compounds (e.g., electronic scrap) from your MWI.</li> <li>• Exclude polyvinylchloride (PVC) from combustion in order to reduce halogen offer and PCB, chlorobenzene and hydrogen chloride emissions.”</li> </ul>
Frankenhaeuser et al. (1993) <sup>18</sup>	<p>This study was performed with a bubbling fluidized bed boiler. “The objectives of this study were to examine the extent to which mixed plastics (4 % Cl) can be burned in a modern boiler together with coal (0.5% S), and to check the influence of the sulphur/chlorine ratio in the fuel on emissions. ... No clear correlation to increased mixed plastics feed could be seen [in flue gas emissions of PCDD/F]. PCDD/F in fly ash increased significantly with increased mixed plastics feed ... It is probable that the sulphur contained in the primary fuel poisoned the catalysts responsible for the formation of PCDD/F in all the plastics/coal blends.”</p>
Thomas (1992) <sup>19</sup>	<p>“... [C]hlorine is not the only determinant of dioxin emissions. However, for larger variations in chlorine content, the data indicate a relationship between chlorine content and dioxin emissions. While there are sources with high chlorine content and low dioxin emissions, there are no known sources of low chlorine content and high dioxin emissions.”</p>
Takeshita et al. (1992) <sup>20</sup>	<p>At a full-scale municipal waste combustor, Takeshita et al. found as follows: “The simultaneous control of combustion, hydrogen chloride (HCl) concentration level in the flue gas and the gas temperature proved very effective in the control of PCDD/Fs formation ... [W]ith increasing gas temperature or HCl level in the gas except for exp. 4, the PCDDs/Fs concentrations tended to increase, and at any of similar gas temperature, the concentrations tended to increase at higher HCl levels. However, the PCDDs/Fs concentrations in the EP ash samples were closely related to the amount of injected slaked lime. ... At any of similar gas temperature, the amounts of PCDDs/Fs formed at the high HCl level were higher than those measured at the middle HCl level, and at similar middle and high levels of HCl, the amounts of PCDDs/Fs formed at higher gas temperatures were higher than those formed at lower gas temperatures. At a gas temperature of 300 °C, HCl in the flue gas markedly increased the formation of PCDDs/Fs. ... The PCDDs/Fs concentrations in the gas when the gas temperature was 300 °C were at higher levels in proportion to the HCl concentration levels. When the gas temperatures were 200 and 240 °C, the PCDDs/Fs concentrations at the lowest HCl level in the gas were remarkably higher than at</p>

	<i>other HCl levels. This phenomenon indicates that the PCDDs/Fs formation was linked to some other factors increasing the amount of dust in the gas as shown in Fig. 8.”</i>
Johnke and Stelzner (1992) <sup>21</sup>	In their study of 15 full-scale municipal waste combustors in Germany, Johnke and Stelzner found as follows: <i>“The addition of PVC (1% wt) to the waste resulted in a marked increase in HCl levels in the raw gas, but in no significant change in PCDD/PCDF concentrations. However, it cannot be concluded from this that PCDD/PCDFs do not form in the incineration of PVC. ... Tests involving an increased supply of bromine in the waste have also been performed; here, a distinct increase in polyhalogenated dioxin/furan levels and a slight increase in the concentrations of the chlorinated PCDD/PCDFs as well as benzenes, was ascertained.”</i>
Matilla et al. (1992) <sup>22</sup>	In their study using a full-scale combustor, Mattila et al. reported as follows: <i>“Our results prove the evidence for conversion of chlorinated plastic material to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). ...[T]he total amount of PCDD/Fs correlates closely with the formed HCl concentration in tests 1 to 3, but in test 4 the yield of PCDD/Fs was ten times higher than expected. ... This full scale study showed that the formation of PCDDs and PCDFs is connected with the total chlorine content in the fuel mixtures. The results give a strong support to the PCDD/F formation mechanism involving chlorinated plastics as the identified chlorine source. The second major implication of the PCDD/F formation is its relationship to the concentration of HCl formed during combustion.”</i>
Kopponen et al. (1992) <sup>23</sup>	At a 60 megawatts district power plant, Kopponen et al. (1992) combusted a mixture of coal and bark mixture with the addition of PVC and non-chlorinated plastics. <i>“... the total PCDD/PCDF concentrations were over 100 times higher in the fly ash from combustion of chlorine containing material (combustion 4) than those of basic fuel (coal and bark materials).”</i>
Manscher et al. (1990) <sup>24</sup>	<i>From their analysis of data from 10 municipal solid waste incinerators and two hospital incinerators in Denmark, Manscher et al. concluded as follows: “For models that, in addition to the block effects, contain the parameters of load and excess air, it is found that among the rest of the parameters considered, only the hydrogen chloride becomes significant [for dioxin emissions]. ... [They found] ... a 14 % increase in the dioxin emissions when the HCl emission is doubled. This relation is valid in the range of 100 to 1000 mg/m<sup>3</sup> of HCl.”</i>

<p>Vikelsee et al. (1990)<sup>25</sup></p>	<p>In experiments at a full-scale combustor, Vikelsee et al. found as follows: <i>“The results showed increased dioxin emission at high levels of PVC and NaCl, and decreased emission at high lime levels.”</i></p> <p>[Note: When the PVC content of municipal solid waste was doubled, dioxin emissions (only PCDDs were measured) increased by 32 percent and HCl emissions by 64 percent. Doubling NaCl concentrations led to a 17 percent increase in dioxin emissions (PCDDs only) and a 9 percent increase in HCl. When HCl concentrations were doubled, dioxin emissions (PCDDs only) increased by 42 percent.]</p>
<p>Aittola and Wihersaari (1990)<sup>26</sup></p>	<p>In this study, wood chips, wood chips with 65% crushed municipal waste, and wood chips with 85% crushed municipal waste were converted into gases in a 5 MW gasification unit and the gases were burned in a conventional boiler. The wood chips contained 0.3 percent by weight chlorine and the MSW, 12 percent by weight chlorine. Among the findings were <i>“the concentration of hydrochloric acid in the flue gases follows the mixing ratio of MSW.”</i> Similarly, dioxin concentrations in the flue gases also increased with rising MSW content in the materials burned.</p>
<p>National Environmental Protection Agency, Denmark, (1989)<sup>27</sup></p>	<p>In their study of full-scale combustors, the Danish EPA noted a 14 percent increase in dioxin emissions from municipal waste combustors and a 25 percent increase from medical waste incinerators when HCl concentration doubled.</p>
<p>Takeshita and Akimoto (1989)<sup>28</sup></p>	<p>A study with a fluidized bed incinerator in Japan found as follows: <i>“PCDDs and PCDFs in the boiler and the EP [electrostatic precipitator] ash samples and in the gas samples were found at lower levels in proportion to the decrease of levels of hydrogen chloride in the gas. ... [L]evels of PCDDs in the EP outlet gases tended to decrease in proportion to the decrease in levels of hydrogen chloride in the flue gases. ... At higher levels of hydrogen chloride in the gases, PCDFs were increasingly formed.... From the relationship between hydrogen chloride levels in the gases at the EP outlet and the total amounts of PCDDs and PCDFs as shown in Figure 11, it is clear that the control of hydrogen chloride levels by the supply of Dolomite to the furnace controlled the formation of PCDDs and PCDFs successfully.”</i></p>
<p>Giugliano et al. (1989)<sup>29</sup></p>	<p>Tests in a <i>“non-conventional system”</i>, an industrial rotary kiln with an afterburner led to the following conclusions: <i>“The incineration of urban wastes with added PVC, up to 10% by</i></p>

	<p><i>weight, did not produce the emission of detectable concentrations of polychlorinated dibenzodioxins and -furans upstream flue gas cleaning equipment. ... The tests were conducted in a 1.5 t h<sup>-1</sup> industrial rotary kiln/afterburner combustion chamber, equipped with a fuel oil burner of high heat output that makes the unit a nonconventional system particularly interesting for the thermal destruction of organic micropollutants. ... Sampling was performed upstream the air pollution control equipment ... For organic micropollutants, 3.5 to 5 m<sup>3</sup> of gas at normal conditions were collected in duct with an allglass isokinetic probe followed by a glass wool filter for particulate matter retention, two consecutive water cooled flasks at 2 °C and a final C-18 adsorbent cartridge. ... Detection limits of the analytical procedure employed are 0.5 ng for 4- to 7-CDDs and -CDFs, 2.5 ng for 8-CDDs and -CDFs, ...”</i></p> <p>[Note: The failure to detect any PCDDs can be attributed to reliance on an analytical procedure which, by today’s standards, had unusually high detection limits, as shown above. Also PCDFs were not analyzed.]</p>
<p>Gottesman et al. (1988)<sup>30</sup></p>	<p>This study, entitled “Vinyl Industry Response to Environmental Concerns About PVC in Municipal Solid Waste,” had the following findings: <i>“As expected, the amount of PVC in the waste being incinerated does increase the amount of HCl in the combustion gases. ... In this, and the Prince Edward Island Study, the data show that the amount of dioxin that finally came out of the incinerator in these test runs was approximately the same amount as that that came in with the MSW. In other words, there was no net increase in environmental dioxins as a result of the incineration process. ... At the tertiary duct and the boiler outlet, none of the contrasts associated with the amount of PVC were significant at the 5% level for either PCDDs and PCDFs.”</i></p> <p>[Note: This study has been cited by some authors as having found no correlation between chlorine input and dioxin output. Since the authors do not present actual input or output data, their findings cannot be reviewed. However, their last statement shown above leaves open the possibility that a positive correlation was found between the amount of PVC combusted and dioxin concentrations at the tertiary duct and boiler outlet but that this positive correlation was significant at some level below 95 percent.]</p>
<p>Karasek and Viau (1983)<sup>31</sup></p>	<p>This study was carried out with an energy recovering incinerator in France. <i>“Data shown here are the result of addition of 300% the usual level of PVC to a municipal</i></p>



	<p><i>incinerator. No significant differences in the concentrations of these substances [PCDDs] on the fly ash were found.... it is evident that in these experiments the addition of PVC to the feedstock had no observable effect on the levels of PCDD, and other compounds generated in the incineration process. ... Unspiked garbage was found to contain 1% PVC of the total feed by laboratory analysis. ... It is striking that there is a distinctive lack of hydrocarbons and polycyclic aromatic hydrocarbons ... ”</i></p> <p>[Note: The analytical method used was, as expected, primitive with high detection limits. Also PCDFs were not determined.]</p>
<p>U.S. Environmental Protection Agency (1984)<sup>32</sup></p>	<p><i>“The chlorine content of fuel is obviously an important parameter affecting the formation of PCDD’s and PCDF’s. However, it can be generally stated that chlorine must be present for the formation of PCDD, and general trends indicate that increased chlorine concentrations in the feed improve the possibilities of PCDD emissions. ... Shih et al. developed a ranked priority list of conventional combustion systems emitting polycyclic organic matter including PCDDs and PCDFs. The rationale presented for source ranking is based on fuel characteristics and combustion conditions. Shih’s work places great emphasis on both the chlorine content of the feed and the concentration of aromatics in the feed.”</i></p>
<p>Olie et al. (1977)<sup>33</sup></p>	<p><i>“During our investigation of the environmental loading with organic pollutants by waste products of municipal incinerators we detected a large number of organochlorine compounds in fly ash ... [The most abundant chlorinated compounds in all fly ash samples were highly chlorinated benzenes ... The amount of chlorodibenzodioxins and chlorodibenzofurans entering the atmosphere via flue gases is probably quite small. However, due to the extreme toxicity of some of the components and the fact that most incineration plants are located in densely populated areas extensive monitoring of such facilities might be advisable.”</i></p> <p>[Note: Table 1 of this report shows all tetra- through octa-PCDDs and PCDFs were detected in the fly ash of the Arnheim incinerator, while Table 2 shows that all tetra- through octa-PCDDs were detected in the flue gas of the Alkmaar incinerator.]</p>

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**Appendix 4: Dioxin Abatement Measures Adopted and/or Recommended by National, International and Advisory Bodies<sup>a</sup>**

Combustion system/process	Source	Dioxin abatement measure
Small and small-firing combustion systems	Hubner et al. (2000) <sup>1</sup>	<i>“An important measure to reduce dioxin emissions is the reduction of chlorine in fuels used for small and smallest firing installations. Dioxin emissions of domestic households and the agriculture and forestry sector can be reduced primarily by the use of “clean” fuels such as untreated wood, oil and gas together with modern firing installations. Therefore, the joint combustion of different types of waste in such installations should be banned in the view of the Austrian Federal Environment Agency.”</i>
Incinerators and other thermal processes	Air Pollution Abatement Review Group (1995) <sup>2</sup>	<i>“One of the more obvious primary ways of minimising TOMPS [toxic organic micropollutants, e.g., dioxins] in incinerators and in other thermal processes is to try to avoid (or reduce) TOMPS, their precursors or fundamental species (such as chlorine or bromine) being included in the feedstock.”</i>
Internal combustion engines, e.g., vehicles	Convention on Long Range Transport of Air Pollutants <sup>3</sup>	<i>“Avoiding halogenated additives in fuels and lubricants.”</i>
	Schulz (1993) <sup>4</sup>	In 1992, the German Federal Government enacted a prohibition against using chlorinated and brominated compounds as petrol additives to reduce dioxin release via car exhausts.
Iron ore sintering	Convention on Long Range Transport of Air	<i>“Halogenated compounds may result in the formation of PCDD/F if they enter sinter plants in the feed materials (coke breeze, salt content in the ore) and in added recycled material ...”</i>

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

	Pollutants <sup>5</sup>	<i>ore) and in added recycled material ...”</i>
Domestic heating systems	Convention on Long Range Transport of Air Pollutants <sup>6</sup>	<i>“The emissions from residential combustion appliances can be reduced by restricting the input materials to good-quality fuel and avoiding the burning of waste, halogenated plastics and other materials.”</i>
Utility and Industrial Boilers	Convention on Long Range Transport of Air Pollutants <sup>7</sup>	<i>“It should be noted that PCDD/F emissions could increase significantly if waste material (sewage sludge, waste oil, rubber wastes, etc.) is added to the fuel.”</i>
Copper production, primary and secondary	Convention on Long Range Transport of Air Pollutants <sup>8</sup>	<i>“Pretreating scrap, for example stripping of plastic or PVC coatings ...”</i>
Aluminum production, secondary	Convention on Long Range Transport of Air Pollutants <sup>9</sup>	<i>“Avoidance of halogenated material (hexachloroethane) [and] chlorine-containing lubricants (for instance chlorinated paraffins) ...”</i>
Non-ferrous metal production	Convention on Long Range Transport of Air Pollutants <sup>10</sup>	<i>“Pre-sorting scrap, avoidance of feed material like plastics and PVC-contaminated scrap ...”</i>
Steel production	Convention on Long Range Transport of Air Pollutants <sup>11</sup>	<i>“General primary measures for PCDD/F reduction can be sorting, de-oiling and decoating of scraps, which may contain plastics, rubber, paints, pigments and vulcanizing additives.”</i>
Medical waste incinerators	U.S. Environmental	<i>“Plastics and metal-containing components of the waste, such as sharps, could be segregated: this could result in lower HCl [hydrogen chloride],</i>

	Protection Agency (1988) <sup>12</sup>	<i>polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans, and trace metal emission rates. ... Another approach to possibly lowering HCl and PCDD/PCDF emission rates would be to have hospitals use low chlorine content plastics. This could be accomplished if the health care industry were to use plastics such as polyethylene and polystyrene in place of polyvinyl chloride, which contains over 45 weight percent chlorine.”</i>
Recovery of nonferrous metals from scrap and residues, secondary aluminium production, production of electrosteel from scrap metal, burning of derived timber product wastes, of packaging materials, and of hospital wastes, domestic stoves, landfill fires	German Federal Office of the Environment (1992) <sup>13</sup>	“Non-halogenated plastics, which will not cause the creation of dioxins and furans, are as rule technically available for packaging purposes. Therefore, a substitution of PVC is required in this field to make consequent use of all means to minimize PCDD/PCDF pollution. ... [L]andfilling of PVC wastes should be eliminated as far as possible ... Apart from other plastics, timber, stone or metal may be regarded as major potential substituted for PVC in the construction sector. From the ecological point of view, the non-halogenated plastics polyethylene and polypropylene are generally more favourable than PVC. ... [C]hlorine-free plastics such as polyethylene and polypropylene, which may be used as PVC substitutes in the packaging industry, seem to be ecologically sounder than PVC; the environmental damage caused by PVC (release of dioxin from uncontrolled fires, migration into food or rooms, increased chlorine input in incinerators) is generally not present ...”
Dioxin sources	Stockholm Convention (2001) <sup>14</sup>	<i>“Promote the development and, where it deems appropriate, require the use of substitute or modified materials, products and processes to prevent the formation and release of the chemicals listed in Annex C [byproducts, including dioxins] ...</i>
Dioxin sources	Air Pollution Abatement Review Group	<i>“General release reduction measures: When considering proposals to construct new facilities or significantly modify facilities using processes that release chemicals listed in this Annex [Annex C – byproducts], priority</i>

	(1995) <sup>15</sup>	<i>should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of such chemicals."</i>
PVC	Swedish Chemical Policy Committee (1997) <sup>16</sup>	<i>"Taking into consideration the precautionary principle and the present limited knowledge of its long-term health and environmental effects, PVC plastic materials do not belong in the future ecocycle society. As soon as possible, and no later than 2007, PVC plastic materials should be substituted by materials that are environmentally compatible in the long term"</i>
PVC	Ecocycle Commission (1994) <sup>17</sup>	<i>"PVC contains 57 percent chlorine. The presence of chlorine in the waste that is incinerated can give rise to the formation of dioxins and other chlorinated hydrocarbons, as well as the formation of hydrogen chloride, which is acidifying and highly corrosive. ... The chlorine content of incinerated waste poses risks of dioxin formation. Due to the chlorine content of the waste, special treatment stages for the flue gases and corrosion-resistant equipment in the incineration plants are required. ... High chloride concentrations in the waste also make it difficult to stabilize the ashes prior to landfilling. ... The importance of PVC for the formation of dioxins and other chlorinated hydrocarbons in connection with incineration is debated. ... Other dioxin emissions where PVC may be the source are uncontrolled fires on waste landfills, illicit incineration of cable and remelting of PVC-covered steel sheet. ... One way to prevent environmental impact from PVC is to phase out its use. ... A phase-out through the active employment of the substitution principle can be effective in sectors where alternative materials exist or can be developed, which applies to a large portion of PVC usage. Such a phase-out should also apply to imported products. ... The Ecocycle Commission is of the opinion that the strategy decided on by the Riksdag of phasing out short-lived PVC products by substitution can and should be implemented at once. ... The Ecocycle Commission recommends that today's plasticized</i>

		<i>PVC and rigid PVC with environmentally harmful additives be phased out as soon as possible.”</i>
PVC	Central Pollution Control Board of India (1996) <sup>18</sup>	Polyvinyl chloride (PVC) can no longer be burned in medical waste incinerators.

<sup>1</sup> Hübner, C., Boos, R., Bohlmann, J., Burtscher, K., Wiesenberger, H., **2000**. State-of-the-art measures for dioxin reduction in Austria. (In Österreich eingesetzte Verfahren zur Dioxinminderung - Deutsche Zusammenfassung) Wien, 2000. (Monographien; Band 116)

<sup>2</sup> Air Pollution Abatement Review Group. **1995**. Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995. Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK.

<sup>3</sup> LRTAP, ANNEX VII, RECOMMENDED CONTROL MEASURES FOR REDUCING EMISSIONS OF PERSISTENT ORGANIC POLLUTANTS FROM MOBILE SOURCES. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants.

<sup>4</sup> Schulz, D. 1993. PCDD/PCDF - German policy and measures to protect man and the environment, Chemosphere 27 (1-3): 501-507.

<sup>5</sup> LRTAP, ANNEX V, BEST AVAILABLE TECHNIQUES TO CONTROL EMISSIONS OF PERSISTENT ORGANIC POLLUTANTS FROM MAJOR STATIONARY SOURCES. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants.

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<sup>14</sup> Stockholm Convention on Persistent Organic Pollutants, 2001. Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants, Appendix II, UNEP/POPS/Conf/4, 5 June 2001.



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