

**ANNOTATED BIBLIOGRAPHY**

# **Studies of Chlorine Input Versus Dioxin Output from Combustors**

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## The Relationship Between Chlorine Input to Combustors and Dioxin Output: An Annotated Bibliography

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### Introduction

Chlorine is the limiting element for dioxin<sup>a</sup> formation in waste combustion systems. This circumstance suggests that the total dioxin output<sup>b</sup> from these systems can be reduced and/or eliminated by curbing chlorine input, i.e., the implementation of materials policies for chlorine-containing materials.

Such materials policies were acknowledged almost a decade ago by the U.S. Environmental Protection Agency. For example, the Agency outlined two approaches for reducing dioxin output from hospital waste incinerators: 1) replacement of polyvinyl chloride (PVC) by other low-chlorine plastics; and 2) segregating PVC from incinerator inputs:<sup>1</sup>

*"Plastics and metal-containing components of the waste, such as sharps, could be segregated: this could result in lower HCl, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans, and trace meal 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."*

Similarly, in 1995, an advisory group for the U.K. Department of the Environment discussed the applicability of such materials policies for thermal processes in general.<sup>2</sup>

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<sup>a</sup> In this paper, the terms "dioxin" and "dioxins" include all of the polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs).

<sup>b</sup> Dioxin output is the quantity of dioxins released in all combustor residues - stack emissions, fly ash, bottom ash, scrubber water, etc.

*"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."*

Some of the materials policies that have been formally incorporated into dioxin abatement efforts as well as others that are recommended or proposed are as follows:

- A 1996 report from the Intergovernmental Forum on Chemical Safety (IFCS) concluded that it was appropriate and important to consider materials policies in developing strategies to minimize and/or eliminate releases of both the polychlorinated and polybrominated dioxins and furans;<sup>3</sup>
- The Governing Council of the United Nations Environmental Programme adopted the recommendations of the IFCS report on Feb. 7, 1997, as part of the process of achieving a global, legally binding agreement to eliminate or reduce persistent organic pollutants in the global environment;<sup>4</sup>
- On November 22, 1996, the American Public Health Association adopted a resolution urging health care facilities and suppliers to reduce or eliminate their use of PVC and other chlorinated plastics that are currently disposed of in medical waste incinerators;<sup>5</sup>
- The Central Pollution Control Board of India ruled in July 1996 that polyvinyl chloride (PVC) can no longer be burned in medical waste incinerators;<sup>6</sup>
- In 1994, the International Joint Commission (IJC) between the U.S. and Canada recommended that "...the Parties ... alter production processes and feedstock chemicals so that dioxin, furan and hexachlorobenzene no longer result as byproducts" and "... develop timetables to sunset the use of chlorine and chlorine-containing compounds as industrial feedstocks and that the means of reducing or eliminating other uses be examined."<sup>7</sup> This followed the IJC's 1992 conclusion: "We know that when chlorine is used as a feedstock in a manufacturing process, one cannot necessarily predict or control which chlorinated organics will result and in what quantity. Accordingly, the Commission concludes that the use of chlorine and its compounds should be avoided in the manufacturing process;"<sup>8</sup> and
- 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.<sup>9</sup>

There is ample scientific support for materials policies that require 1) replacement of chlorine-containing materials in products destined for disposal in incinerators or interactions in other thermal processes or 2) segregation of chlorine-containing materials from wastes and other inputs to incinerators and other thermal processes. This is evidenced by the findings and conclusions of a majority of related studies published in the peer-reviewed scientific literature. Listed below are many of these studies, in addition to some of the more frequently-cited studies showing negative findings.

Reports and papers are presented in reverse chronological order. To present a brief but accurate synopsis of each study, annotations are composed primarily of direct excerpts, which are printed in italics, in addition to some general descriptions and comments, which appear in standard print.

### 1997

**Thuss, U., Herzschuh, R., Popp, P., Ehrlich, C., Kalkoff, W.-D. 1997. PCDD/F in flue gas and in bottom ash of lignite domestic combustion and the role of the salt content of the burned briquettes. *Chemosphere* 34 (5-7): 1091-1103.**

*"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 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."*

*"A house-heating facility (tiled stove with air circulation) with a heating power of 9 kW was chosen to carry out the investigations."*

*"It is easily understood why chlorine, as a atom, which is multiple incorporated in the PCDD/F-molecules, is of high importance for the PCDD/F formation."*

*"A comparison of both coal sorts shows that the chlorine content is approximately seven times higher for the "salt" briquettes and their bottom ash (Table 2). The bottom ashes amount has approximately twice as much chlorine than is present in the briquettes. These chlorine values are in good accordance to the PCDD/F-emission concentrations."*

"Concerning the ITE-concentrations the "salt"-coal flue gas emissions are approximately seven times higher, regarding to the homologue sums a four fold increase was determined."

"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."

"Lastly, our own results show that even a relatively small surplus of chlorine causes a significantly higher PCDD/F-emission. Such a surplus could be realized by admixtures of chlorine containing waste."

**Pandompatam, B., Kuman, Y., Guo, I., Liem, A.J. 1997. Comparison of PCDD and PCDF emissions from hog fuel boilers and hospital waste incinerators. Chemosphere 34 (5-7): 1065-1073.**

"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>."

"In the pulp and paper industry, "hogged fuel," consisting of saw dust and bark is usually burnt for energy recovery purposes. Recent field studies [2,3,4] showed that PCDD and PCDF are formed from combustion of sodium chloride (NaCl) contaminated hog fuel. The salt contamination occurs during the sea transportation of logs to the coastal pulp mills. The concentration of salt in the hog fuel can vary up to 1% dry weight while the typical moisture level is approximately 50%."

From Table 1. Summary of Operating Conditions During Sampling

Operating Variables	Control	Salted Bark
Chloride in Feed, wt%dry	0.007	0.760
HCl (grab sampling), ppm dry*	1.4	55.3

\* Corrected to 11% Oxygen

Table 2. Total PCDD, PCDF and TEQ Comparison of Salt-Contaminated to Control Tests

TEST	Total PCDD*	Total PCDF*	TEQ*
Salted Bark**	54 +/- 11	106 +/- 12	3.2 +/- 0.6
Control	0.3	0.3	0.02

\* ng/dsm<sup>3</sup> Corrected to 11% Oxygen TEQ = Toxicity Equivalent

\*\* Average +/- Standard Deviation

**Gullett, B., Raghunathan, K. 1997. Observations on the effect of process parameters on dioxin/furan yield in municipal waste and coal systems. Chemosphere 34 (5-7): 1027-1032.**

"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."

## 1996

**Manninen, H., Perkio, A., Vartiainen, T., Ruuskanen, J. 1996. Formation of PCDD/PCDF: Effect of fuel and fly ash composition on the formation of PCDD/PCDF in the cocombustion of refuse-derived and packaging-derived fuels. Environ. Sci. & Pollut. Res. 3 (3): 129-134.**

Manninen et al. (1996) concluded that "...the correlation of the fuel Cl content and PCDD/Fs was significant...."

Their study was carried out "... in a normal multi-fuel power plant by co-combustion of packaging-derived fuel (PDF) or refuse-derived fuel (RDF) with fossil fuels, such as coal or peat. This work includes the results of 17 co-combustion tests and an evaluation of the results by the Principal

*Component Analysis (PCA) and the Partial Least Squares Projections to Latent Structures (PLS)."*

"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 co-combustion tests were carried out in a 65 MW CFB multifuel boiler having an ESP for flue gas cleaning. Operation parameters were kept constant during every 24 hour test run. Temperature in the bed was 850-877 °C and 133-140 °C in the sampling point after the ESP. Residence time in the hot zone was >2s and the oxygen content was 4.5-5.5% (wet) in the furnace."

"Total PCDD and PCDF concentrations in the flue gas after the ESP, including gaseous phase and particles, and in the fly ash were small in all tests. They were on the same level as in normal power plant combustion and much lower than PCDD/F concentrations in waste incineration."

"The results of the PLS calculations (-> 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 calcium content of the fly ash correlated closely with the Cl content. This shows that part of the chlorine was bound by Ca into the fly ash, thereby decreasing HCl emission in the flue gas. The correlation of higher chlorinated PCDDs and PCDFs with Ca, Cl and PCBz in the fly ash is seen from the results."

"The chlorine content of the fuel correlated with PCDFs and there was an inverse correlation between the S/Cl ratio and PCDFs."

**Wanke, T., Vehlow, J. 1996. The influence of flame retarded plastic foams upon the formation of Br containing dibenzo-p-dioxins and dibenzofurans in a MSWI. *Organohalogen Compounds* 28: 530-535.**

In this study at the TAMARA facility, Wanke and Vehlow (1996) found that "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."

"The same relationship for the bromine containing dibenzofurans is shown in Fig. 3. This indicates a correlation at low and approximately constant furan concentrations at high Br input. This behaviour could be explained by assuming a similar de novo synthesis for the Br containing compounds as has been found for the formation of chlorinated dioxins and furans."

"According to the de novo synthesis mechanism the inventories of active carbon, halogenides and copper in the fly ashes control the formation potential. Hence the relationship of Br containing species and the bromide concentration in the fly ashes should be regarded as has been done in Fig. 4 for the furans. This graph demonstrates that the furan levels show about the same dependence upon the bromide concentration in both test campaigns."

**Kanters, M., Van Nispen, R., Louw, R., Mulder, R. 1996. Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste. *Environ. Sci. Technol.* 30 (7): 2121-2126.**

Kanters et al. (1996) concluded, "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 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]."

Huotari, J., Vesterinen, R. 1996. PCDD/F emissions from co-combustion of RDF with peat, wood waste, and coal in FBC boilers. *Haz. Waste & Haz. Materials* 13(1): 1-9.

In experiments performed with combustors ranging from small to full-scale, Huotari and Vesterinen (1996) found as follows: "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  $10^3$  at the same Cl- content in fuel. ... The PCDD/F-emissions are related to fuel-Cl content."

Vesterinen, R., Flyktman, M. 1996. Organic emissions from co-combustion of RDF with wood chips and milled peat in a bubbling fluidized bed boiler. *Chemosphere* 32(4): 681-689.

In their study of a full-scale combustor, Vesterinen and Flyktman (1996) concluded as follows: "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."

Wikstrom, E., Lofvenius, G., Rappe, C., Marklund, S. 1996. Influence of level and form of chlorine on the formation of chlorinated dioxins, dibenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor. *Environ. Sci. Technol.* 30(5): 1637-1644.

Using a lab-scale apparatus, Wikstrom et al. combusted an artificial waste with varying levels of chlorine contributed by either PVC or  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . 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."

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."

"To avoid these mechanisms influenced by the uncontrolled formation of precursors, all experiments were performed with a high combustion efficiency (CE). The only variation between the experiments were the form and content of chlorine in the fuel."

"This study shows that the emission is not influenced by the form of chlorine in the fuel, either organic or inorganic. .... Figures 5 and 6 show that approximately 1% chlorine in these fuels is a threshold value for the formation of excess PCDD/PCDF and PCBz during combustion. ... Thus, the chlorine content in a normal MSW is below the threshold value of 1% for an increase in PCDD/PCDF and PCBz formation. ... 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."

[Note: This study and those 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, neither the data presented by Wikstrom et al. (1996) nor any of the other studies cited support the contention that this positive correlation ceases to exist when the chlorine content of the combustor feedstock falls below 1 percent.]

#### 1995

Moller, S., Larsen, J., Jelnes, J.E., Faergemann, H., Ottosen, L.M., Knudsen, F.E. "Environmental Aspects of PVC." Environmental Project No. 313. Denmark: Ministry of the Environment, Danish Environmental Protection Agency, 1995.

In their review of data from full-scale combustors, 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 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 (Tromp et al. 1994, Shepherd, 1993, Miljostyrelsen, 1989A; Boerekamps-Kanters, Louw, 1992; Mark, 1994). 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."*

**Thomas, V.M., Spiro, T.G. 1995. An estimation of dioxin emissions in the United States. Toxicol. and Environ. Chemistry 50:1-37.**

*In their study, Thomas and Spiro (1995) reviewed data from a broad array of combustion systems, 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 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."*

*"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."*

**Halonen, I., Tarhanen, J., Ruikojarvi, P., Tuppurainen, K., Ruuskanen, J. 1996. Effect of catalysts and chlorine source on the formation of organic chlorinated compounds. Chemosphere 30 (7): 1262-1273.**

*"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)."*

#### **1994**

**Cains, P., Dyke, P. 1994. Chlorinated dibenzodioxin and dibenzofuran emissions from waste combustion plants in the UK. Chemosphere 28(12): 2101-2119.**

*"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."*

**U.S. Environmental Protection Agency. "Combustion Emissions Technical Resource Document (CETRED)." Draft. EPA 530-R-94-014, Washington, D.C. May 1994.**

*"The absence of any apparent trends in the PCDD/PCDF emission data versus either HCl or THC does not preclude these as important parameters in characterizing dioxin/furan emissions. It does suggest, however, that the scatter in the data set combined with other potential dominant trends can mask smaller effects that might be anticipated."*

**Mark, F. "Energy recovery through co-combustion of mixed plastics waste and municipal solid waste," Association of Plastics Manufacturers in Europe (APME), June 1994.**

"In order to categorise the relative effects of polymers on the combustion of MSW the project studied three test cases:

- \* combustion of MSW containing an average level of polymers - base case
- \* combustion of MSW containing an added 7.5 per cent by weight of mixed plastics waste - medium polymer case
- \* combustion of MSW containing an added 15 per cent by weight of mixed plastics waste - high polymer case."

"The total polymer content in residual MSW ranged from 8.5 to 12 per cent weight, depending on collection sites."

"Analysis of the mixed waste plastics used as fuel in the test programme was undertaken by ... Three 230 kilogram bale samples of representative mixed waste were hand sorted to show the following contents:..."

"Use of identification codes on sample items showed the split by polymer to be ... polyvinyl chloride 4% wt."

"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."

"... 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." [No data were given for uncontrolled HCl levels. I.e., HCl measurements were taken following treatment for acid gas removal.]

"Increased hetero atom content was recorded only for the Cl concentrations in the raw gas." [No raw gas data were given]. "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."

"No correlation between polymer content and increased occurrence of PCDD/Fs can be derived from the results of these tests. This was true even when the higher concentrations of PVC were present."

[Note: As the above description of this study show, the results are of limited usefulness in assessing the relationship between chlorine (or PVC) input and dioxin output: 1) no direct determinations of either the chlorine or PVC content of the incinerator feedstock were undertaken; 2) waste feedrates were apparently decreased as plastics (including PVC) content was increased; 3) the use of additives, lime with and without carbon, obscures data interpretation; 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.]

**Ruuskanen, J., Virtainen, T., Koja, I., Manninen, H., Oksanen, J., Frankenhaeuser, M. 1994. Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in co-combustion of mixed plastics with coal, exploratory principal component analysis. Chemosphere 28: 1989-1999.**

"The purpose of the tests was to examine the effects of sulphur-rich coal on the formation of chlorinated hydrocarbons like PCDD/PCDFs. ...No correlation between HCl and furans and dioxins [in flue gas] was found. On the other hand, in fly ash samples the significant correlation of HCl and furans was obvious."

**Wilken, M.; Boske, J.; Jager, J.; Zeschmar-Lahl, B. 1994. PCDD/F, PCB, chlorobenzene and chlorophenol emissions of a municipal solid waste incineration plant (MSWI) - variation within a five day routine performance and influence of Mg(OH)<sub>2</sub>-addition. Chemosphere 29 (9-11): 2039-2050.**

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

- exclusion of PVC and computer scrap in the input,
- optimizing combustion operation,

- installation of a high-performance quasi-dry flue gas purification system in 1993 have been realized at this plant."

### 1993

Jager, J., Wilken, M., Beyer, A., Rakel, H., Zeschmar-Lahl, B., Jager E. 1993. Practical concepts to minimize the emission of halogenated organic compounds from municipal solid waste incinerators. *Chemosphere* 27 (1-3): 141-148.

In experiments with full-scale combustors, 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)."

Burns, D.B. "Final Report Consolidated Incineration Facility Metals Partitioning Test (U)," WSRC-TR-93-623, U.S. Department of Energy, Savannah River Technology Center, Aiken, SC, August 31, 1993

"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 Table 13 shows the most significant variable influencing PCDD/PCDF emissions is waste chloride concentration."

[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.]

Jager, J., Wilken, M., Beyer, A., Rakel, H., Zeschmar-Lahl, B., Jager, E. 1993. Practical concepts to minimize the emission of halogenated organic compounds from municipal solid waste incinerators. *Chemosphere* 27 (1-3): 141-148.

"Recommendations concerning waste input

- Reduce halogen availability in the combustion chamber by excluding certain materials from MWI input.
- Exclude brominated compounds (e.g., electronic scrap) from your MWI.
- Exclude polyvinylchloride (PVC) from combustion in order to reduce halogen offer and PCB, chlorobenzene and hydrogen chloride emissions."

Halonen, I., Tarhanen, J., Oksanen, J., Vilokki, H., Vartiainen, T., Ruuskanen, J. 1993. Formation of organic chlorinated compounds in incineration of pulp and paper mill biosludges. *Chemosphere* 27(7): 1253-1268.

"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."

[Note: This conclusion was based on principal component analysis.]

Halonen, I., Tarhanen, J., Kopsa, T., Palonen, J., Vilokki, H., Ruuskanen, J. 1993. Formation of polychlorinated dioxins and dibenzofurans in incineration of refuse derived fuel and biosludge. *Chemosphere* 26 (10): 1869-1880.

"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."

Wagner, J., Green, A. 1993. Correlation of chlorinated organic compound emissions from incineration with chlorinated organic input. *Chemosphere* 26 (11): 2039-2054.

*"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"*

Frankenhaeuser, M., Manninen, H., Kojo, I., Ruuskanen, J., Vartiainen, T., Vesterinen, T.R., Virkki, J. 1993. Organic emissions from co-combustion of mixed plastics with coal in a bubbling fluidized bed boiler. *Chemosphere* 27 (103): 309-316.

*"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."*

Altwickler, E., Konduri, R., Lin, C., Milligan, M. 1993. Formation of precursors to chlorinated dioxins/furans under heterogeneous conditions. *Combust. Sci. Technol.* 88: 349-368.

*"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)."*

Fangmark, I., van Bavel, B., Marklund, S., Stromberg, B., Berge, N., Rappe, C. 1993. Influence of combustion parameters on the formation of polychlorinated dibenzo-p-dioxins, dibenzofurans, benzenes, and biphenyls and polyaromatic hydrocarbons in a pilot incinerator. *Environ. Sci. Technol.* 27 (8): 1602-1610.

*"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 concentration in the fuel. Although the variable HCl is free of confoundings, the effect is too small to make any further conclusions."*

Gullett, B., Lemieux, P., Kilgroe, J., Dunn, J. 1993. Formation and prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran during waste combustion: The role of combustion and sorbent parameters. Presented at the 1993 Conference on Municipal Waste Combustion, Williamsburg, Virginia, March 30-April 3, 1993.

In experiments with a pilot-scale combustor, Gullett et al. found as follows: *"[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."*

## 1992

Thomas, V. "Total PCDD and PCDF Emissions from Known Combustion Sources and the Relationship of Chlorine Content to PCDD and PCDF Emissions." PU/CEES Working Paper No. 129, Princeton University, July 1992.

*"... [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."*

**Takeshita, R., Akimoto, Y., Nito, S. 1992. Relationship between the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans and the control of combustion, hydrogen chloride level in flue gas and gas temperature in a municipal waste incinerator. Chemosphere 24(5): 589-598.**

*At a full-scale combustor, Takeshita et al. found as follows: "The control of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) formation was investigated in a municipal waste incinerator equipped with the electrostatic precipitator (EP). 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, reducing the concentration levels of PCDDs/Fs in the flue gas at the EP outlet to 0.2 ng/Nm<sup>3</sup> as 2,3,7,8-tetrachlorodibenzo-p-dioxin when evaluated by the international toxicity equivalent factors."*

#### *"PCDDs/Fs Concentrations in EP Ash*

*As shown in Fig. 5, with 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."*

#### *"PCDDs/Fs Concentrations in EP Outlet Gas*

*... 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 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."*

**Johnke, B., Stelzner, E. 1992. Results of the German dioxin measurement programme at MSW incinerators. Waste Management & Research 10: 345-355.**

*In their study with full-scale combustors, Johnke and Stelzner found as follows: "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."*

**Mattila, H., Virtanen, T., Vartianinen, T., Ruuskanen, J. 1992. Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas from co-combustion of mixed plastic with coal and bark. Chemosphere 25 (11):1599-1609.**

*In their study using a full-scale combustor, Mattila et al. reported as follows: "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."*

**Hassel, G.R., Rizeq, R.G., Barton, R.G., and McGrath, T.P. 1992. Emissions assessments from incineration of large volume parenteral plastic containers. In Proceedings of the 1992 Incineration Conference: Thermal Treatment of Radioactive, Hazardous Chemical, Mixed and Medical Wastes, Albuquerque, New Mexico, May 11-15, 1992, pp. 483-488.**

*"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."

**Kopponen, P.; Torronen, R.; Ruuskanen, J.; Tarhanen, J.; Vartiainen, T.; Karenlampi, S. 1992. Comparison of cytochrome P4501A1 induction with the chemical composition of fly ash from combustion of chlorine containing material. Chemosphere 24 (4): 391-401.**

"PVC-containing material is a source of PCDDs/PCDFs because of the chlorine it contains. There is direct evidence of the conversion of PVC to PCDDs and PCDFs in pyrolysis (Marklund et al. 1986). During combustion and pyrolysis of pure PVC and PVC-containing materials in the atmospheric air, significant amounts of PCDDs/PCDFs have been reported to be produced in both laboratory experiments (ppm range) and in fires (ppb range) (Christmann et al. 1989; Theisen et al. 1989). Furans were the predominant compounds detected."

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. The chlorine content and PCDD/F concentrations in fly ash for each experiment was as follows:

Experiment	Added Material	Total Chlorine Content	PCDD/F in Fly Ash, pg/g
1	None	0.04 % (w/w)	77.1
2	Non-chlorinated Plastic	0.04 % (w/w)	109
3	PVC + Non-chlorinated Plastic	0.4 % (w/w)	654
4	PVC	1.2 % (w/w)	9,768

"... 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)."

### 1991

**Fangmark, I., Marklund, S., Rappe, C., Stromberg, B., Berge, N. 1991. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, Part II. Chemosphere 23 (8-10): 1233-1243.**

"In contradiction to what was reported earlier (Vikelsee, 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 section."

[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.]

**Lenoir, D., Kaune, A., Hutzinger, O., Mutzenich, G., Horch, K. 1991. Influence of operating parameters and fuel type on PCDD/PCDF emissions from fluidized bed incinerator. Chemosphere 23: 1491-1500.**

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: "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."

**Yasuhara, A., and Ito, H. 1991. Combustion of poly (vinyl chloride). J. Environ. Chem. 1: 525-528.**

"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."

Combustion of PVC (from clear PVC gloves) gave the following yields of PCDD/Fs:

Temperature, °C	PCDD/Fs, ng/g PVC
300	3.22
400	5.753
500	12.212
600	20.466
700	17.633
800	12.267

**Pasek, R., Chang, D. 1991. Potential benefits of polyvinyl chloride and polyvinylidene chloride reductions on incinerator emissions. Air Waste Manag. Assoc. 1991, 91-33.1.**

[Note: This study is cited as shown above by Wikstrom et al. (1996) and described as showing a positive correlation between chlorine input and dioxin output. However, we are, as yet, unable to locate this paper.]

**Karanen, E., Aittola, J.-P., Lappanen, A. 1991. Combustion of wood and plastic waste from packaging industry in residential furnaces. Energy Environ. D: 517-531.**

[Note: This study is described by Wikstrom et al. (1996) as showing a positive correlation between chlorine input and dioxin output. However, we are, as yet, unable to locate this paper.]

**Kevin, R., Beach, B., Beach, L.O., Gullett, B.K. 1991. The role of the gas-phase Cl<sub>2</sub> in the formation of PCDD/PCDF during waste combustion. Waste Manage. 11: 97-102.**

[Note: This study is described by Wikstrom et al. (1996) as showing a positive correlation between chlorine input and dioxin output. However, we are, as yet, unable to locate this paper.]

## **1990**

**Manscher, O., Heidam, N., Vikelsoe, J., Nielsen, P., Blinksbjerg, P., Madsen, H., Pallesen, L., Tiernan, T. 1990. The Danish Incinerator Dioxin Study. Part 1. Chemosphere 20 (10-12): 1779-1784.**

From their analysis of data from 10 municipal solid waste incinerators and two hospital incinerators, 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. ... [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."

**Vikelsoe, J., Nielsen, P., Blinksbjerg, P., Madsen, H., Manscher, O. 1990. Significance of chlorine sources for the generation of dioxins during incineration of MSW. Organohalogen Compounds 3: 193-196.**

In experiments at a full-scale combustor, Vikelsoe et al. found as follows: "The results showed increased dioxin emission at high levels of PVC and NaCl, and decreased emission at high lime levels."

[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.]

**Gullett, B.K., Bruce, K., Beach, L.O. 1990. Formation of chlorinated organics during solid waste combustion. Waste Manage. Res. 8: 203-214.**

"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>."

**Gullett, B.K., Bruce, K., Beach, L. 1990. The effect of metal catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. Chemosphere 20 (10-12): 1945-1952.**

"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."

Oudhuis, A., Tromp, P., Olie, K., Moulijn, J. 1990. Formation of PCDDs and PCDFs during low-temperature pyrolysis of PVC in an inert and oxidative atmosphere. *Organohalogen Compounds* 3: 303-305.

*"The emission levels of flexible PVC are an order of magnitude higher 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."*

#### **1989**

National Environmental Protection Agency, Denmark. "Dioxin emission ved affaldsforbrænding." (in Danish, English summary available). Miljøprojekt nr. 117, 1989.

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.

Christmann, W., Hasiske, D., Kloppel, K.D., Partscht, H., Rotard, W. 1989. Combustion of polyvinylchloride - an important source for the formation of PCDD/PCDF. *Chemosphere* 19: 387-392.

*"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."*

Takeshita, R., Akimoto, Y. 1989. Control of PCDD and PCDF formation in fluidized bed incinerators. *Chemosphere* 19 (1-6): 345-352.

*"...levels 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."*

Giugliano, M., Cernuschi, S., Ghezzi, U. 1989. The emission of dioxins and related compounds from the incineration of municipal solid waste with high contents of organic chlorine (PVC). *Chemosphere* 19: 407-411.

*"The incineration of urban wastes with added PVC, up to 10% by 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, ..."*

[Note: The failure by Giugliano et al. to detect any dioxins may well be attributed to reliance on an analytical procedure which, by today's standards, had unusually high detection limits.]

Gullett, B., Bruce, K., Beach, L. 1989. Formation mechanisms of chlorinated organics and impacts of sorbent injection. Presented at the International Conference on Municipal Waste Combustion, U.S. EPA/Environment Canada, Hollywood, FL, April 1989.

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, R., Ryman, T. 1989. PCDD and PCDF formation from hydrocarbon combustion in the presence of hydrogen chloride. *Chemosphere* 19: 331-336.

De Fre and Rymen (1989) found as follows when carrying out experiments with HCl concentrations ranging from 150 ppm to 4.5 percent: "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."

### 1988

**Yasuhara, A., Morita, M. 1988. Formation of chlorinated aromatic hydrocarbons by thermal decomposition of vinylidene chloride polymer. Environ. Sci. Technol. 22 (6): 646-650.**

From the pyrolysis under an airstream of two kinds of vinylidene chloride polymers used for food wraps, Yasuhara and Morita found as follows: "...[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)."

**Gottesman, R., Carroll, W., Fishbein, L. 1988. Vinyl industry response to environmental concerns about PVC in municipal solid waste. Energy Prog. 8: 148-153.**

"... the prime objective of this study was to determine whether dioxins and furans, PCDDs and PCDFs are generated when PVC is incinerated. PVC users were concerned about dioxin because: incinerators do emit dioxin; chlorine is needed to make it; PVC is a source of chlorine; and, dioxin found in lake sediments only postdates commercialization of PVC. ... 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."

[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.]

### 1987

**Karasek, F., Dickson, L. 1987. Model studies of polychlorinated dibenzo-p-dioxin formation during municipal refuse incineration. Science 237: 754-756.**

"The chromatograms show the similarity in the isomer distribution of dioxins formed from labeled pentachlorophenol and from PVC combustion products with that of dioxins extracted from fly ash collected from the municipal incinerator."

**Vogg, H., Metzger, M., Stieglitz, L. 1987. Recent findings on the formation and decomposition of PCDD/PCDF in solid municipal waste incineration. Presented at the seminar: "Emissions of Trace Organics from Municipal Solid Waste Incinerators," Copenhagen, January 1987.**

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.

### 1986

**Marklund, S., Kjeller, L.-O., Hansson, M., Tysklind, M., Rappe, C., Ryan, C., Collazo, H., and Dougherty, R. Determination of PCDDs and PCDFs in incineration samples and pyrolytic products, in Rappe, C., Choudhary, G., and Keith, L. (eds), "Chlorinated Dioxins and Dibenzofurans in Perspective; Lewis Publishers: Chelsea, MI, 1986.**

"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. ... From this table it is clear that the inhalation exposure is marginal compared to the exposure via food, especially fish and other foodstuffs from the aquatic food chain."

### 1983

**Liberti, A., Goretti, G., Russo, M.V. 1983. PCDD and PCDF formation in the combustion of vegetable wastes. Chemosphere 12(4-5): 661-663.**

"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 per 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."

**Tiernan, T., Taylor, M., Garrett, J., Van Ness, G., Solch, J., Deis, D., Wagel, D. 1983. Chlorodibenzodioxins, chlorodibenzofurans, and related compounds in the effluents from combustion processes. Chemosphere 12 (4-5): 595-606.**

"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 [ $>3000$  ng/g of wood burned]."

**Karasek, F., Viau, A., Guiochon, G., Gonnord, M. 1983. Gas chromatographic-mass spectrometric study on the formation of polychlorinated dibenzo-p-dioxins and polychlorobenzenes from polyvinyl chloride in a municipal incinerator. J. Chromatog. 270: 227-234.**

"Data shown here are the result of addition of 300% the usual level of PVC to a municipal incinerator. No significant differences in the concentrations of these substances 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."

### 1980

**Shih, C. et al. "POM Emissions from Stationary Conventional Combustion Sources, Exposure, Transport, and Control." EPA-600/2-80-156, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1980.**

[Note: When this original study is received, we will provide appropriate excerpts. In the interim, the results of this study were described in "National Dioxin Study Tier 4 - Combustion Sources: Initial Literature Review and Testing Options," EPA-450/4-84014b. Research Triangle Park, NC: U.S. Environmental Protection Agency, October 1984, as follows: "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."]

**Mahle, N., Whiting, L. 1980. The formation of chlorodibenzo-p-dioxins by air oxidation and chlorination of bituminous coal. Chemosphere 9: 693-699.**

"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 ... 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 ... "

## 1977

Olie, K., Vermeulen, P., Hutzinger, O. 1977. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere* 8: 455-459.

*"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."*

[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.]

## References - Introduction

<sup>1</sup> U.S. Environmental Protection Agency, "Hospital Waste Combustion Study: Data Gathering Phase." EPA-450/3-88-017, Washington, D.C., December 1988.

<sup>2</sup> Air Pollution Abatement Review Group, "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, 1995.

<sup>3</sup> Intergovernmental Forum on Chemical Safety, "IFCS Ad Hoc Working Group on Persistent Organic Pollutants Meeting: Final Report," Geneva: IFCS Secretariat, c/o World Health Organization, 21-22 June 1996.

<sup>4</sup> United Nations Environmental Programme, "International Action to Protect Human Health and the Environment Through Measures Which Will Reduce and/or Eliminate Emissions and Discharges of Persistent Organic Pollutants, Including the Development of an International, Legally-Binding Instrument," Decision Taken By Nineteenth Session of the UNEP Governing Council, Nairobi, 7 February, 1997, Geneva: United National Environmental Programme, February 1997.

<sup>5</sup> American Public Health Association, Resolution Adopted at the 124th Annual Meeting, New York City, New York, 20 November 1996.

<sup>6</sup> Central Pollution Control Board, Ministry of Environment and Forests, Government of India, "Environmental Standards and Guidelines for Management of Hazardous Waste," New Delhi, India, 12 July 1996.

<sup>7</sup> International Joint Commission, "Seventh Biennial Report on Great Lakes Water Quality," ISBN 1-895085-74-8, Washington, D.C.: International Joint Commission, 1994.

<sup>8</sup> International Joint Commission, "Sixth Biennial Report on Great Lakes Water Quality," ISBN 1-895085-36-5, Washington, D.C.: International Joint Commission, 1992.

<sup>9</sup> Schulz, D., PCDD/PCDF - German policy and measures to protect man and the environment, *Chemosphere* 27 (1-3): 501-507 (1993).