1 Introduction

Previous contributions to this series\textsuperscript{1–3} have highlighted the concern over emissions of polychlorinated dibenzo-\textit{p}-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) to atmosphere from waste incineration processes. Regulatory control of these emissions has typically been addressed in two ways:

- By identifying what are believed to be the key design and operational parameters controlling emissions of PCDD/Fs, and stipulating suitable limits within which these parameters should be maintained.
- In addition to the above, imposing emission limits for PCDD/Fs in the stack gas.

For example, the UK’s Chief Inspector’s Guidance to Inspectors \textit{Process Guidance Note IPR 5/3} requires new municipal solid waste incinerators to be designed to the following specifications:

- The combustion gases should be maintained at a temperature of at least 850°C for at least 2 seconds in the presence of at least 6% oxygen.
- PCDD/F emissions should be below 1 ng m\textsuperscript{-3} (expressed as NATO-CCMS Toxic Equivalents, I-TEQ). The aim should be to achieve a guide emission concentration of 0.1 ng I-TEQ m\textsuperscript{-3}.

From an operational and regulatory perspective, the challenge is to develop control strategies which are effective in the field, but which are also practical to implement. For example, from a knowledge of the fundamental chemical and physical mechanisms of PCDD/F formation and their relationships to the prevailing physical and chemical conditions, it is possible to identify through laboratory experiments key operational parameters or surrogate emissions


which can individually be correlated with PCDD/F emissions.\textsuperscript{2-4} Control of these parameters would therefore imply control of PCDD/F emissions. However, in full-scale combustors, variations in feedstock composition and perturbations in operating conditions are often sufficient to mask correlations between measured PCDD/F emission levels and process parameters that tightly controlled bench scale experiments indicate are likely to be important. While some tests on full-scale plant have established correlations between, say, PCDD/F emissions and particulate emissions,\textsuperscript{2,5} other studies have not found this to hold.\textsuperscript{4,6} The lack of consistency in attempts to correlate measured PCDD/F levels globally against parameters identified as important in laboratory studies also indicates that simple, single, key operating parameters are not necessarily identifiable, and that combinations of factors determine PCDD/F formation and emission levels. This has important practical consequences, since it implies that a control strategy based on regulating simple process variables may not be amenable to a generalized prescription of preferred operating conditions.

This chapter commences with a brief review of the current basis for the development of control strategies relating to PCDD/F emissions from waste combustors. There follows a discussion of some of the plant trials undertaken to gain insights into the influence of operating variables on PCDD/F formation. The chapter ends with an analysis of potential control strategies for PCDD/F control in combustors, applying our current knowledge on the fundamentals of PCDD/F formation.

2 Early Investigations

PCDDs and PCDFs were first identified in incinerator stack emissions in the mid-1970s. Emissions of other trace organics (chlorobenzenes, chlorophenols, PAHs \textit{etc}.) were also known to occur, but public and regulatory attention focused on the former compounds owing to their toxicity relative to other organic micropollutants, and highly publicized accidental releases from industrial installations.

Theoretical studies into the mechanisms of formation of PCDD/Fs in combustion systems, with the specific aim of elucidating emission control strategies, commenced in the early 1980s. Seminal contributions\textsuperscript{7-9} examined free radical, homogeneous gas-phase reactions in the hot, combustion zone of municipal solid waste (MSW) incinerators, and concluded that this formation mechanism could not account for measured concentrations of PCDD/Fs in incinerator stack emissions. Measurements taken at various stages of the combustion and gas cleaning train of a MSW incinerator at Tsushima, Japan,
indicated enhanced PCDD/F concentrations as the combustion gases passed through the cooler, post-combustion zone. It was postulated that reactions between phenolic precursors (formed in the combustion zone as products of incomplete combustion, (PICs) and hydrochloric acid on the surface of flyash in the cooler (150–250°C) parts of the incinerator were responsible for the observed elevated levels of PCDD/Fs in the stack gases. Other research teams investigated heterogeneous surface-catalysed reactions operating in the temperature range 250–400°C and confirmed the dominance of this formation mechanism. These studies suggested a mechanistic framework which could provide a basis for the development of PCDD/F emission control strategies:

- Incomplete combustion of organic wastes in the combustion chamber leads to the formation of solid carbon and organic fragments (PICs) which serve as organic precursors to the dioxin/dibenzofuran molecule.
- The waste provides a source of chlorine and of metals. The latter are incorporated into flyash, which carries over to the cooler (250–400°C) post-combustion zone of the incineration system.
- The organic precursors are incorporated into, or adsorb onto the surface of the flyash in the post-combustion zone, and, following a complex sequence of reactions which are catalysed by metals (primarily copper) in the flyash, lead to the formation of PCDD/Fs along with other chlorinated trace organics.

From the early 1980s, pilot and full-scale incineration systems were studied to identify design and operating parameters which correlated with PCDD/F emissions. Pre-1987 investigations emphasized combustion zone design and control, since the importance of post-combustion PCDD/F formation had yet to be fully appreciated. In keeping with the above mechanistic framework, parameters which related to efficient combustion of organic wastes (excess oxygen level, combustion temperature, CO level) were measured and correlated against PCDD/F emissions. However, the ad hoc and poorly controlled conditions under which measurements were generally taken limited the usefulness of these studies. The correlations claimed by some workers were unconvincing when subjected to a rigorous statistical analysis.

### 3 US and Canadian Studies

In the mid-1980s, systematic investigations to determine a set of generalized PCDD/F reduction/emission control strategies were commenced by the US

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US EPA Studies

Much of the early work on the control of organic emissions from combustors was conducted in the US as part of a programme involving the measurement of organic emissions and the formulation of control strategies. The concept of Good Combustion Practice (GCP) was introduced, the term being defined as ‘those combustion conditions which lead to low emissions of trace organic pollutants’. Following a comprehensive study of three types of MSW incinerators (mass burn, RDF-fired and modular starved air units), the US EPA concluded in 1987 that low organic emissions could be achieved in properly designed and operated MSW incinerators, by a combination of good combustion control techniques and appropriate gas cleaning technology.

The rationale for the application of GCP to the control of organic emissions was that the latter were the products of incomplete combustion. Hence, optimization of combustion conditions to approach as closely as possible the theoretical ideal of complete combustion (i.e. combustion to CO\(_2\), water, etc.), coupled with appropriate ‘end-of-pipe’ control strategies, should lead to reductions in trace organic emissions. The US EPA recommendations for GCP fell into three categories:

- Minimization of organic emissions to atmosphere through optimum design of the combustor.
- Operation of the combustor within its design specifications, with control systems to prevent excursions outside of the design envelope.
- Monitoring and verification of combustion performance, with continuous surveillance of key design and operating parameters.

The main design and operational parameters which required control in order to meet the above goals of GCP were identified as follows:

- Furnace temperature
- Underfire air capacity
- Overfire air requirement
- Excess air requirement
- Air distribution and mixing

Table 1 lists the recommendations for GCP to minimize organic emissions from combustors.\(^{17}\)

The implementation of GCP will be discussed in Section 4 below.

Canadian Studies

In 1983, Environment Canada commenced a five-year National Incinerator Testing and Evaluation Program (NITEP) with the following objectives:\(^{18}\)

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G. H. Eduljee and P. Cains

Environmental Protection Agency (US EPA) and by Environment Canada. These studies are described below.
Table 1 US EPA recommendations for Good Combustion Practice (GCP) to minimize trace organic emissions from MSW, RDF and modular starved air combustors

<table>
<thead>
<tr>
<th>Element</th>
<th>Components</th>
<th>Recommendations$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design</td>
<td>Temperature at fully mixed</td>
<td>All: 1800°F (980°C) at fully mixed conditions</td>
</tr>
<tr>
<td></td>
<td>conditions</td>
<td>MB: At least four separately adjustable plenums. One each under the drying and burnout zones and at least two separately adjustable plenums under the burning grate.</td>
</tr>
<tr>
<td></td>
<td>Underfire air control</td>
<td>RDF: As required to provide uniform bed burning stoichiometry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MSA: No recommendations provided</td>
</tr>
<tr>
<td>Overfire air capacity</td>
<td>(not an operating requirement)</td>
<td>MB, RDF: 40% of total air</td>
</tr>
<tr>
<td>Overfire air injector</td>
<td>design</td>
<td>MSA: 80% of total air</td>
</tr>
<tr>
<td>Operation/</td>
<td>Excess air</td>
<td>All: That required for penetration and coverage of furnace cross section</td>
</tr>
<tr>
<td>control</td>
<td></td>
<td>MB, MSA: 6–12% oxygen in flue gas (dry basis)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RDF: 3–9% oxygen in flue gas (dry basis)</td>
</tr>
<tr>
<td>Turndown restrictions</td>
<td>All: 80–110% of design; lower</td>
<td>All: 80–110% of design; lower limit may be extended by verification tests</td>
</tr>
<tr>
<td></td>
<td>limit may be extended by</td>
<td>All: On auxiliary fuel to design temperature</td>
</tr>
<tr>
<td></td>
<td>verification tests</td>
<td>All: On prolonged high CO or low furnace temperature</td>
</tr>
<tr>
<td>Verification</td>
<td>Oxygen in flue gas</td>
<td>MB, MSA: 6–12% (dry basis)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RDF: 3–9% (dry basis)</td>
</tr>
<tr>
<td></td>
<td>CO in flue gas</td>
<td>All: 50 ppm on 4-hour average corrected to 12% CO$_2$</td>
</tr>
<tr>
<td></td>
<td>Furnace temperature</td>
<td>All: Minimum of 1800°F (980°C) [mean] at fully mixed conditions</td>
</tr>
<tr>
<td></td>
<td>Adequate air distribution</td>
<td>All: Verification tests (adequately low exhaust emission of trace organics or combustion uniformity using in-furnace CO profiles)</td>
</tr>
</tbody>
</table>

$^a$All = all combustors; MB = mass burn combustors; RDF = refuse-derived fuel combustors; MSA = modular-starved air combustors.

- To identify energy-from-waste technologies in Canada.
- To assess relationships among state-of-the-art designs, operations, energy benefits and emissions of organic and inorganic trace chemicals.
- To examine the effectiveness of emission control systems.
- To develop national guidelines for emissions from MSW incinerators.

The study predated the theoretical advances of the mid-1980s which identified post-combustion low-temperature PCDD/F formation reactions as a key
consideration. The programme focused primarily on conventional combustion-related design and operational issues.

**Mass-burn Technology Assessment.** Extensive testing was undertaken on the Quebec Urban Community MSW incinerator in Quebec City, a mass-burn, water-wall combustor equipped with heat recovery boilers and a two-stage electrostatic precipitator. The objective was to determine the design and operational changes necessary to upgrade the incinerator to state-of-the-art, and to minimize emissions of organics and metals. Operating parameters such as MSW feed rate, excess air levels, distribution of underfire and overfire air, combustion temperature, etc., were systematically varied, concurrent with measurements of CO, organics (total hydrocarbons, chlorobenzenes, chlorophenols, PCBs, PAHs, PCDDs and PCDFs), particulate levels, metals and acid gases. A one-sixth scale model of the furnace was constructed to test out possible design changes.

The trials were successful in that design and operating conditions were identified, which provided consistently lower emissions of organics and metals relative to both the original furnace design and operating regime, and to ‘poor’ operating conditions with the new design. Under ‘good’ operating conditions, emissions of each of the organic chemical groups were lowest; conversely, trace organic emissions were highest under conditions indicative of ‘poor’ operation (low furnace temperature, poor air distribution, high MSW feed rate, etc.). PCDD/F and particulate emissions were reduced by the same degree under the new design and operating conditions, suggesting a direct operational and mechanistic link.

Simple and multiple regression analysis provided relationships between organic and inorganic emissions and operating parameters. The most important of these were as follows:

- PCDD/F emissions were strongly correlated with primary gas flow, CO emissions, particulate emissions, copper emissions, chlorobenzene emissions and chlorophenol emissions. Primary airflow was the most influential operational setting for control of trace organic emissions.
- Particulate emissions correlated with CO emissions and primary gas flow.
- As a class, emissions of trace organics were minimized by a combination of control on CO, oxygen and furnace temperature. The best control models used three of the following four operational settings:
  - total airflow
  - primary/secondary air ratio
  - steam rate or refuse feed rate
  - secondary air front/rear ratio
- CO was the best single surrogate for the prediction of PCDD/F emissions. PAH and PCB emissions did not correlate well with CO emissions.
- The results of NITEP mirrored that of the 1987 US EPA recommendations for GCP (see Table 1). Using the modified design and control models identified in the study, 10- to 100-fold reductions in trace organic, particulate and metals emissions were achieved on a consistent basis.

**Gas Cleaning Technology Assessment.** In a second series of tests, two pilot-scale air pollution control systems were tested on the Quebec City MSW incinerator: a
Control of PCDD and PCDF Emissions from Waste Combustors

dry scrubber/fabric filter and a wet-dry (spray dryer) scrubber/fabric filter. Three sampling points were positioned on the pilot plant to determine gas characteristics and trace organics/metal composition at the inlet, pre-fabric filter and post-fabric filter. Operating parameters such as inlet temperature, pressure drop across the filter, particulate, CO and oxygen concentration, etc., were measured.

For PCDD/F removal, overall removal efficiency across the scrubber unit was determined, masking any catalytic effect of trapped flyash. However, the tests did identify an increase in PCDD/F concentration in the flue gas with an increase in gas temperature, in the region 100–200°C.

4 Implementation of Good Combustion Practice

Introduction

From a regulatory standpoint, the most appropriate means of implementing GCP for minimization and control of trace organic emissions is to frame a set of general rules which can be applied to all combustors of a particular type. Five classes of criteria can be identified:

- Design criteria (for example, requiring a minimum gas-phase residence time of 2 seconds in the combustion zone).
- Operational criteria (for example, requiring a minimum furnace temperature of 850°C, or maintenance of a minimum excess oxygen level in the combustion gas).
- Measurement and control of surrogates such as CO and particulate emissions (for example, maintaining CO emission below 50 mg m⁻³).
- Control regimes (restrictions of waste feeds; failsafe, interactive control systems; automatic shutdown procedures, etc.).
- Monitoring regimes (measurement and recording of combustion temperature; continuous monitoring of excess oxygen, CO emissions and combustion efficiency, etc.).

HMIP’s Chief Inspector’s Guidance Notes and European Union Directives on incineration provide examples of regulatory requirements and/or guidance which incorporate aspects of the above five types of criteria for GCP.

It has been noted that the imposition of specific GCP requirements (for example, maintaining a minimum furnace temperature, or maintaining CO levels of less than 50 mg m⁻³) on small-scale commercial combustors has not been universally successful in ensuring low PCDD/F emissions.¹⁹ This observation is in line with the comments in Section 1 above regarding the lack of consistency in regulating PCDD/F emissions through simple, single operating variables in isolation from other broader considerations.

In the sections below a few correlations suggested by the mechanistic model for PCDD/F formation are reviewed in the light of tests conducted on a wider range of pilot-scale and large-scale systems.

**Particulate Emissions and PCDD/F Emissions**

The NITEP study indicated a strong correlation between particulate emissions and PCDD/F emissions, suggesting that one emission control strategy would involve improving particulate collection efficiency in the gas cleaning train. In regulatory terms, this requirement of GCP would be achieved by specifying more stringent particulate emission limits. However, other studies have shown the absence of a correlation between particulate and PCDD/F emissions in small-scale combustion systems located in the UK. A broader survey of the literature indicates more positive correlations, but also indicates the lack of a consistent pattern. Some recent studies are discussed below.


The tests were conducted with the knowledge of the importance of post-combustion, low-temperature reactions, and represented an advance on the 1987 GCP study. The results of the trials on cement kilns, lightweight aggregate kilns, hazardous waste incinerators, liquid injection incinerators, fluidized bed incinerators, fixed hearth incinerators and hazardous waste boilers were summarized as follows:

> ‘While the [discussion on low-temperature reactions] emphasizes the role of particulate matter [PM] in the post-combustion production and capture of PCDD/PCDF, it is important to note that other parameters can dominate the production of PCDD/PCDF, and tight post-combustion control of PM emissions without attention to these other parameters can lead to higher, not lower, dioxin/furan emissions. It is also important to note that the above discussion does not imply that low PM emissions are necessarily accompanied by low dioxin emissions … it is possible to minimize post-combustion formation of dioxin by limiting [air pollution control device] inlet temperatures (for example, by rapidly quenching combustion gases). When this occurs, low dioxin/furan emissions can be achieved without significant PM control … it appears to be quite possible for [hazardous waste] burning facilities with moderate or even no PM control to exhibit low PCDD/PCDF emissions. Similarly, facilities can exhibit extremely high dioxin/furan emissions in the presence of very low PM emissions.’

The US EPA defined Best Current Operating Practice (BOP) as being the use of GCP combined with a temperature limitation of 350°F (approximately 175°C) on the inlet to post-combustion control devices. Rapid quenching of the combustion gases to below 175°C was also regarded as BOP.

However, it does not follow that on an individual plant basis, consistent correlations between particulate emissions and PCDD/F emissions cannot be
found. For example, an analysis of the US EPA test programme on clinical waste incinerators indicated the following.\textsuperscript{5}

- PCDD/F emissions were strongly correlated with both particulate and CO emissions. In newer facilities with better combustion control, the strongest correlation was with CO, while in older facilities the strongest correlation was with particulate matter.

- There was evidence of interdependencies between individual operating parameters on a particular facility. For example, primary chamber temperature was also strongly correlated with PCDD/F emissions through its influence on CO and particulate emission levels.

These correlations have also been observed in other full-scale incinerator studies, for example in the NITEP programme.

\textit{Dutch Studies}. In a study examining emissions from MSW incinerators operating in the Netherlands, a number of emission types were measured: acid, gases, organics, particulates, CO, etc.\textsuperscript{20} The relationship between particulate and PCDD/F emissions was tested. In presenting a plot of these emissions, the report stated that ‘no really clear correlations emerge.’

The lack of a correlation was also appreciated in a follow-up study in which the data presented in the Dutch report\textsuperscript{20} (particulate concentration, water content, carbon monoxide concentration, furnace temperature, etc.) were compared with the PCDD/F emissions using statistical regression techniques.\textsuperscript{21} The aim was to determine which operating and emission parameters were strongly related to PCDD/F emissions. The data set was divided into two groups on the basis of the type of air pollution control device installed:

- plants equipped solely with electrostatic precipitators (ESP);
- plants fitted with both an ESP and a wet scrubber (so-called ‘Modern installation’).

For the latter type of plant, it was found that the particulate concentration did not correlate with PCDD/F emissions. Only two parameters elicited statistically meaningful correlations: the furnace temperature and the carbon content of the filter dust collected in the ESP.

Negative observations of this nature should be treated with caution in view of the positive correlations obtained by other workers, and also because inter-plant comparisons would not be expected to elicit as consistent a correlation trend as for tests on a single plant.\textsuperscript{4,5}

The Dutch study notes that:\textsuperscript{20} ‘In general, it can be concluded that low dioxin emissions … only occur at low levels of CO, C\textsubscript{x}H\textsubscript{y} and particulates. The converse is not the case, however; low CO, C\textsubscript{x}H\textsubscript{y} and particulate levels by no means guarantee lower dioxin emissions.’ This qualification is important: since low particulate emissions do not guarantee low PCDD/F emissions, it may not be cost-effective to insist on low particulate emissions on a particular plant if tests

show that low PCDD/F emissions are being consistently achieved. However, in terms of establishing the general principles of an overall PCDD/F control strategy, requiring low particulate emissions would appear to constitute a sensible precautionary measure.

German Studies. Independent confirmation of the possibility of high particulate emissions being accompanied by low dioxin emissions is provided by the monitoring data collected on the TAMARA pilot MSW incineration plant at the Karlsruhe Nuclear Research Centre. The pilot plant was fitted with cyclones and a wet scrubber. The particulate and total PCDD/F concentrations in Table 2 are downstream of the cyclones but prior to the wet scrubber. If the reported PCDD/F concentrations are converted to toxic equivalents, values in the region of 1 ng I-TEQ m$^{-3}$ would be obtained. The data indicate that particulate emission concentrations far in excess of present-day regulatory requirements can be accompanied by low PCDD/F emissions.

A further discussion on the influence of particulate emissions on PCDD/F formation and emissions is provided in Section 5.

Operating Conditions and PCDD/F Emissions

Parametric studies on full-scale plant, examining the influence of operating parameters on PCDD/F formation, have been noted in Section 1 and Section 3. There is a remarkable consistency in the conclusions drawn in the studies on operating plants. Two studies are discussed for illustrative purposes.

Parametric tests conducted by US EPA on the Montgomery County South MSW incinerator have been reported. Three tests at each of six different test conditions were conducted to evaluate the effects on PCDD/F emissions of electrostatic precipitator (ESP) inlet temperature, sorbent injection into the furnace and into the duct leading to the ESP, and combustion temperature. The key findings were as follows:

- Poor combustion conditions in the furnace and high ESP temperatures resulted in the highest PCDD/F formation rates as measured in collected flyash.
- Formation of PCDD/Fs within the ESP was strongly dependent on the ESP operating temperature. A reduction in operating temperature from 300°C to 200°C decreased PCDD/F stack emissions by a factor of 10.
- PCDD/F concentrations increased across the ESP, even at a low ESP operating temperature of 149°C.
- Greater removal efficiency of particulates also correlated with lower stack emissions of PCDD/Fs.

Other factors not explicitly accounted for in the tests may also have influenced the findings. For example, introduction of the sorbent into the ESP would have increased the particulate loading in the ESP, potentially increasing the surface

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Control of PCDD and PCDF Emissions from Waste Combustors

<table>
<thead>
<tr>
<th>Test number</th>
<th>Particulates (mg m(^{-3}))</th>
<th>PCDD/Fs (ng m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>T19/1</td>
<td>500</td>
<td>78.5</td>
</tr>
<tr>
<td>T19/4</td>
<td>953</td>
<td>103</td>
</tr>
<tr>
<td>T19/7</td>
<td>1032</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>T19/10</td>
<td>947</td>
<td>&lt; 32</td>
</tr>
</tbody>
</table>

area available for PCDD/F formation. A lower ESP temperature would have lowered the gas velocity through the unit (therefore resulting in higher particulate removal), but would also have resulted in a lower PCDD/F formation rate.

The second study\(^{24}\) describes tests undertaken at four different MSW incinerators under a variety of operating conditions reflecting both good and poor combustion practice. The latter was investigated by measuring operating parameters and emissions during ‘cold blowing’, corresponding to a low production of steam, a low combustion temperature and a high CO release. An interesting aspect of the tests is that the boiler cleaning operation known as ‘soot blowing’ was also investigated. Over the period of soot blowing, a 10-fold increase in particulate emissions was observed.

The outcome of the tests was similar to that of study on the Montgomery County South incinerator, and are summarized below:

- During periods of ‘cold blowing’ arising from the spontaneous reaction of the primary air supply system to a blockage in the feed hopper, an increase in primary air flow led to a fall in combustion temperature, an increase in oxygen concentration and a three-fold increase in PCDD/F emission concentrations. Utilizing supplementary support fuel to maintain constant combustion conditions during periods of cold blowing resulted in a sharp decrease in PCDD/F emissions.
- Cooling the combustion gases post-boiler from 470°C to 265°C resulted in a sharp decrease in PCDD/F emissions. While this is attributed largely to increased adsorption of PCDD/Fs to particulate matter at the lower temperature, material which is subsequently removed from the gas phase by the pollution control device, it is also possible that the reduction is a consequence of the shift to the lower end of the window of PCDD/F formation of 250–400°C.
- During soot blowing, a 10-fold increase in particulate emission concentrations was accompanied by a 30-fold increase in PCDD/F emission concentrations prior to the pollution abatement device. Accounting for particulate removal in the fabric filter, an overall three-fold increase in PCDD/F emission concentrations was observed during periods of soot blowing.

Based on the tests, a number of means by which PCDD/F formation could be minimised were suggested.\(^{24}\) These are listed in Table 3.

Comparisons with the GCP requirements listed in Table 1 and the discussion relating to the NITEP trials indicates an overall consistency of approach to the control of PCDD/F formation in combustors. The efficacy of controlling the halogen content of the waste fuel is examined in Section 5.
Table 3 Recommendations for reducing PCDD/F emissions from MSW incinerators

Recommendations concerning the design of MSW incinerators
- Avoid the risk of cold zones in the combustion chamber by providing:
  - air flow regulation according to demand
  - means for equal distribution of MSW on the combustion grate
  - means for homogenization of input MSW
- Avoid ‘cold blowing’ effects through preheating of combustion air
- Install continuously performing technologies for cleaning boiler surfaces
- Provide for a cooling section for flue gas to enhance adsorption of gaseous PCDD/Fs onto particulates
- Consider a high-performance flue gas purification and abatement system
- Reduce flue gas temperature after the boiler system below 250°C
- Reduce flue gas temperature at the ESP considerably below 250°C

Recommendations concerning operating conditions
- Keep operation conditions constant
- Avoid CO peaks and high oxygen surplus
- Reduce particulate and soot deposition through more frequent cleaning
- Reduce halogen availability in combustion chamber through addition of halogen fixing additives such as limestones and amines
- Increase the transformation of gaseous PCDD/Fs into particulate-bound form by the addition of adsorptive solids such as activated carbon
- Improve general flue gas purification through the addition of limestone and activated carbon

Recommendations concerning waste input
- Reduce halogen availability in the combustion chamber by excluding certain materials from the MSW input
- Exclude brominated compounds (for example, electronic scrap) from the MSW
- Exclude PVC from the MSW in order to reduce halogen input

Source: Jager et al.24

Precursor Emissions versus PCDD/F Emissions

A corollary of the precursor-mediated route to PCDD/F formation is that a reduction in precursor concentrations in gases exiting the combustion chamber will have a beneficial effect in reducing the propensity for PCDD/F formation in downstream equipment. Organic precursors such as chlorobenzenes and chlorophenols can be formed as a result of gas-phase reactions in the primary and secondary combustion chambers of incinerators. These precursors to PCDDs and PCDFs adsorb onto flyash in the cooler parts of the incinerator such as the boiler and gas cleaning units such as ESPs, and are then subjected to catalytic reaction in the presence of copper to form PCDDs and PCDFs. The greater the quantity of precursors formed in the furnace, the greater is the propensity for dioxin formation in downstream equipment (assuming downstream conditions are such that dioxins can be formed).

The formation of precursors is dependent on the temperature at which the waste is combusted (and, in addition, residence time and mixing characteristics), and hence the degree of destruction of the organic constituents in the primary and secondary chambers. Higher combustion temperatures equate to a higher degree
of destruction and hence to lower concentrations of potential precursors leaving
the furnace zone. Since destruction of potential organic precursors is dependent
on the combustion conditions in the furnace, one might also expect interactions
between combustion temperature and precursor emissions, combustion air
control (distribution and oxygen concentration) and precursor concentrations,
and possibly ultimate correlations between some or all of these parameters and
PCDD/F emissions.

A recent study has examined potential correlations between emissions of
organic precursors and PCDD/F emissions. A large number of studies on
full-scale operational plants have observed a proportional relationship between
PCDD/F emissions and emissions of other trace organics such as chlorophenols
and chlorobenzenes. An example of predictions based on such correlation is
shown in Figure 1.

It is important to note that the correlation does not necessarily imply a causal
link between the presence of a precursor and the presence of PCDD/Fs in the
stack gases: the two types of substances may have been formed by different and
unrelated reaction pathways. However, the presence of a correlation does imply
that changes in the combustion process and hence in the underlying reaction
schemes affect both types of emissions to an equal extent.

A number of factors can obscure or destroy a proportional relationship
between precursor and PCDD/F emissions concentrations. For example, the
mixing characteristics of the combustion chamber are equally important, and
represent a key design variable. Poor mixing of wastes and combustion air could
negate the advantage gained by operating at a higher temperature (and hence a
higher propensity for precursor destruction). Another confounding factor is the
relationship between precursor concentrations and the presence of particulate
matter. The reactions leading to the formation of PCDDs and PCDFs are surface
catalysed. Hence their formation will be dependent on the number of active sites
on the surface of the flyash, and therefore on particulate composition/morphology
and particulate concentration. However, to a large extent the formation of
precursors and the generation of particulates are independent processes. It is
possible to envisage a case where poor combustion results in an excess of organic
precursors but (owing to low ash content) low particulate concentrations relative
to the available precursors. The resulting PCDD/F concentrations will also be
low, but it is likely that an increase in particulate concentration will be
accompanied by an increase in dioxin formation, up to the point where the
number of active sites and the number of precursor molecules are in balance.
Beyond this point, a increase in particulate concentration will not result in an
increase in dioxin formation.

Conversely, it is possible to generate very low concentrations of organic
precursors (for example, because of a high furnace temperature) but relatively
high concentrations of particulates owing to a high ash content of the waste. Since
the number of active reaction sites exceeds the number of precursor molecules, a
further increase in particulate concentration will not be accompanied by an
increase in dioxin formation. This may explain the data presented in Table 2 for

Figure 1 Observed and predicted PCDD/F emissions from a MSW incinerator, using chlorobenzenes and chlorophenols as surrogates. (Taken from Öberg and Bergström25)
Control of PCDD and PCDF Emissions from Waste Combustors

the TAMARA facility, Tests T19/1 and T19/7, in which a two-fold increase in particulate concentration (500 mg m\(^{-3}\) to 1032 mg m\(^{-3}\)) is not accompanied by a corresponding increase in PCDD/F concentrations (78.5 ng m\(^{-3}\) to < 50 ng m\(^{-3}\)).

Another variable which will affect the correlation is particle size. Since the reactions of interest are surface catalysed, the quantity of PCDD/Fs formed should strictly be proportional to the available surface area, which in turn will depend on particle size. A greater proportion of small particles in a sample of flyash will result in a greater surface area being available for reaction than another sample of the same weight containing a greater preponderance of larger particles. Inspection of the data on Dutch MSW incinerators\(^{20}\) shows that there is a wide variation in particle size distribution between the various incinerators: ‘Zaanstad B’ has 14% of the flyash below 0.95 \(\mu\)m and 50% above 20 \(\mu\)m, whereas ‘Rosendaal’ has 40% of flyash below 0.95 \(\mu\)m and 10% above 20 \(\mu\)m. Therefore, two identical particulate concentrations from two separate incinerators could well present different surface conditions for the reactions of interest.

Thus, precursor concentrations and their effect on PCDD/F formation cannot be divorced from upstream particulate concentrations.

5 Reaction Fundamentals and Control Strategies

General Principles

The principles of good combustion practice (GCP) in Section 3 can be restated in a manner which better relates to the mechanistic aspects of PCDD/F formation and to field operational and control regimes. Updating GCP to include catalysed heterogeneous reactions in the post-combustion zone, the following goals of GCP can be identified:

- Maximize the destruction of organics in the combustion chamber, so as to prevent the carryover of uncombusted organics or products of incomplete combustion (PICs) into the post-combustion zone. This in turn will reduce the likelihood of PCDD/F formation in the post-formation zone.
- Minimize particulate carryover into the post-combustion zone. Since the dominant PCDD/F formation reactions have been identified as being catalysed by the surface of flyash, reduced carryover should lower the likelihood of PCDD/F formation.
- Minimize the potential for low-temperature catalysed reactions in the post-combustion zone by minimizing the time the gases and particulate matter spend in the temperature region 250–400°C or by suppressing the catalytic activity of flyash.
- Minimize emissions of PCDD/Fs by employing end-of-pipe control strategies.

In terms of developing control strategies relating to the control of PCDD/F formation and emissions, the above goals can be discussed under four headings:

- Control of feedstock
- Control of the combustion process
- Control of the post-combustion process
- End-of-pipe strategies
The combined control of combustion and post-combustion processes constitutes the equivalent of US EPA’s Best Current Operating Practice (BOP) discussed above. In this section, we draw out relevant observations concerning the fundamentals of PCDD/F formation in order to inform the development of potential control strategies.

**Control of Feedstock**

Three issues are discussed under this heading: (1) the effect that different feed materials might have on the propensity for PCDD/F formation in combustors; (2) whether restrictions in feedstock composition are likely to have a beneficial effect in terms of reduced PCDD/F emissions; (3) whether the manner in which the feedstock is presented to the combustor influences PCDD/F formation. Each issue is discussed below.

*Effect of Different Feed Materials.* The question as to whether different waste types have intrinsically different compositional characteristics which impact on the propensity for PCDD/F formation during combustion has not been specifically addressed in this study. The fact that all waste types, and indeed all fuels, including fossil fuels such as coal, generate PCDD/Fs on combustion suggests a common reaction framework which applies to all combustors fired with any type of fuel or waste type. However, studies have indicated that flyash generated from MSW combustion and from the combustion of chemical waste differ in their catalytic activity, the former being more active per gramme of material. This either reflects the compositional variations of different starting materials, or different combustion conditions under which these wastes are treated. For example, it is possible that the breakdown of lignin structures within wastes fed to a MSW incinerator results in a more active flyash than would be generated in a chemical waste incinerator. This issue has yet to be resolved.

In terms of PCDD/F control strategies, an important point is that combustors should be specifically designed to accept the waste in question, so as to ensure that the requirements of GCP and BOP are met regardless of the type of waste. Thus, a designer of a clinical waste incinerator should allow for the fact that medical waste invariably arrives at the facility in sealed bags or containers, that the composition of the waste could vary markedly from bag to bag, and that there is relatively little scope for inspection and equalization of loads. The design of the waste reception and loading equipment, feed regime, and of the combustor will therefore be influenced by these considerations. In the case of the combustion of wood chips, other factors may be more important and result in a different design of the combustion system. The key point is that if GCP and BOP are observed, then the issue of waste type is of secondary importance.

*Restrictions in Feedstock Composition.* There has been considerable debate as to whether removal of chlorine-containing components of MSW (such as PVC) prior to combustion contributes to a lowering of PCDD/F emissions relative to a conventional mass burn operation (see Table 3). The rationale for this suggestion

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is that chlorination reactions at post-combustion temperatures cannot proceed to completion and thus result in maximum yields of PCDD/Fs if HCl delivery to the reaction sites is reduced. In order to achieve the latter, the principal sources of chlorine in the feed material should be removed prior to combustion. PCDD/F formation in combustors is a side-reaction which, in terms of percentage yield, is inconsequential relative to the dominant oxidative reactions between organic matter and chlorine in MSW and oxygen in combustion air. Literature sources indicate that the quantity of HCl in process gases is at best a secondary determinant in influencing PCDD/F yields, and is much less important than the temperature–time window.  

PCDD/Fs are produced in trace quantities, and the demand for HCl participating in the chlorination reactions is correspondingly very small. While removal of materials such as PVC could potentially result in a significant reduction in the total amount of HCl generated by the combustion of MSW in the furnace, this will not necessarily impact on the small quantity required for PCDD/F formation. In other words, there is sufficient chlorine present in the remaining MSW, clinical waste or other waste-based feedstock after removal of PVC to satisfy the requirements of the PCDD/F formation reactions, even under optimum formation conditions. PVC/plastics removal is therefore unlikely to affect emissions of PCDD/Fs, all other operational conditions remaining constant.

Recent trials on laboratory, pilot and full-scale plant have tended to confirm the lack of a beneficial effect on PCDD/F emissions, when chlorine-containing components of MSW and other waste types are withdrawn from the feedstock to a combustor. As a strategy for controlling PCDD/F formation, our view is that removal of chlorine-containing materials such as PVC is unlikely to prove effective.

Similar arguments should apply to the likely effectiveness of strategies based on reducing levels of metals and potential organic precursors in the waste stream, at least with regard to influencing PCDD/F emissions. Removal or control of metals or sources of metals such as mercury and cadmium may still be necessary in order to achieve the required emission concentrations for these chemicals.

Presentation of the Feedstock. Mention was made above of the need to consider the manner in which the waste is presented to the combustor. The aim is to ensure that the requirements of GCP are met, once the waste has been introduced into the combustor.

Combustion is best controlled when the waste is homogeneous, both in physical and compositional terms. Thus, during industrial waste combustion this can be achieved by blending the incoming waste streams to a consistent, controlled composition prior to combustion. Solid material can be shredded

prior to being fed into the incinerator in order to reduce particle size, and ensure increased contact with combustion air, and uniform burning. A graphic illustration of the effect of waste preparation on combustion control has been presented elsewhere. Feeding large items of waste into an incinerator resulted in large excursions in CO levels, with spikes rising to as high as 2000 ppm in the stack gas owing to the difficulty in controlling both the mixing with combustion air and the combustion temperature. Shredding the waste to a smaller and more uniform size ensured better control of combustion conditions, and resulted in a lower and smoothed CO release.

Different types of waste will require different handling techniques. For example, clinical waste is invariably sealed at source, and shredding of this material prior to it being fed into the combustor would not be considered good practice. The principle, that the combustor and associated handling requirements should reflect the type of waste to be treated, remains an important consideration for the control of PCDD/F emissions.

**Control of the Combustion Process**

Conventional control strategies dealing with the combustion process are well summarized by the US EPA’s requirements for good combustion practice (GCP) listed in Table 1, and by the requirements listed in Table 3. There are three issues to be considered: (1) whether current knowledge of the fundamentals of PCDD/F formation provides either a justification for these requirements, or represents a conflict with presently held views on PCDD/F control; (2) whether current knowledge suggests alternative, less costly, means of control; (3) whether some or all of these requirements need to be modified and/or supplemented with new requirements in the light of more recent knowledge.

**Relevance of Current Thinking to Good Combustion Practice.** With respect to issues (1) and (2), current thinking on the mechanistic aspects of PCDD/F formation does not contradict the requirements for GCP as set out in Section 5 and by the US EPA in 1987 (see Table 1), nor does it suggest that any of these requirements are superfluous. Precursor concentrations, temperature regimes, etc., are directly impacted by operational practices which have been demonstrated in both bench-scale and full-scale tests either to reinforce or to negate the goals set out for GCP in a predictable and reproducible manner. This issue is discussed further in Section 6.

As with feedstock preparation, uniform mixing of the waste with combustion air and adequate turbulence in the combustion chamber are important to ensure consistent and controlled combustion conditions. In order to implement GCP on old plant, it may be necessary to examine and redesign, for example, the primary air distribution system and air control regime, and introduce baffles to improve turbulence. Such modifications have been shown to be effective in improving combustion control, and consequently in reducing PCDD/F emissions. These are not novel control strategies, nor are they necessarily inexpensive to implement, but current thinking relating to GCP does reinforce the need for greater customization in incinerator design. The use of computational fluid dynamic (CFD) modelling of incinerator plants is a means of simulating the
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material and energy distribution patterns in an incinerator, and is an excellent tool for visualizing the flow patterns in an incinerator, hence aiding in the design of plant configurations and control systems.\textsuperscript{31,32}

PCDD/F Formation Mechanisms. With regard to issue (3), a recent development is the evidence of in-flight formation of PCDD/Fs. Measured formation rates for in-flight formation have been much higher than those for static formation,\textsuperscript{28,33,34} but they inevitably apply over relatively short residence times of gas–solid contact. Moreover, it has been proposed that the enhanced catalytic activity is associated with freshly produced ash, and that this activity diminishes inherently over periods of the order of 0.1–1 second.\textsuperscript{34}

However, in-flight mechanisms may determine the ultimate PCDD/F emission levels that are achievable in well designed and operated plant, since it is very difficult to envisage a design that does not involve passing combustion gas with some particulate loading through the temperature window of 250–400°C. The application of in-flight calculations could assist in estimating potential limiting formation levels under various post-combustion scenarios.\textsuperscript{28} Since the in-flight formation rate is in units of ng (total PCDD/F) g\textsuperscript{−1} (flyash) min\textsuperscript{−1}, it follows that the current calculation method would prescribe low particulate loading and short residence time in the temperature window 250–400°C as the measures most likely to minimize PCDD/F formation.

Another potential limiting factor relating both to the feed composition and the combustion process is the incomplete destruction of PCDD/Fs present in the incoming waste. For example, if the MSW contained a trace quantity of PCDD/Fs at a concentration of, say, 50 µg I-TEQ tonne\textsuperscript{−1} (wet) and if 99% was destroyed in the combustor, then the uncombusted PCDD/Fs would contribute a concentration of 0.1 ng I-TEQ N m\textsuperscript{−3} in the exit gas, assuming that physical and chemical processes in the post-combustion zone (for example, adsorption on activated carbon) do not alter the composition of the combustion gases during their passage to the stack. This process is not well understood, and requires further elucidation in bench-scale tests.

Control of the Post-combustion Process

Several issues need to be considered in relation to control of the post-combustion stage of a combustor:

- Control of the temperature window in which optimum PCDD/F formation occurs: 250–400°C.
- Minimization of particulate loading.
- Minimization of the time particulate matter spends in the post-combustion zone.
- Inhibition of the catalytic activity on flyash surface.

Each issue is discussed in turn.

Control of the Temperature Window for PCDD/F Formation. Bench-scale and full-scale trials are unequivocal in identifying the post-combustion temperature as a key operation variable influencing the formation of PCDDs and PCDFs. There is now a general consensus that maintenance of post-combustion conditions in the gas cleaning system below about 200°C is desirable.

There will always exist intermediate temperatures in sections of the post-combustion train between the furnace temperature (~900°C) and the conditioner/ESP/fabric filter temperature (~200°C), notably in the boiler and economizer sections, and it therefore follows that PCDD/F formation cannot be entirely suppressed. However, good operating practice as currently recommended by equipment suppliers centres on the need to minimise buildup of particulate matter on equipment surfaces subjected to temperatures within the formation range so that the residence time of particulate matter subjected to these temperatures is minimized (see below).

Minimization of Particulate Loading. Our current appreciation of static and in-flight formation of PCDD/Fs indicates that if all other operational parameters were kept constant, lower particulate concentrations in the post-combustion zone would result in lower PCDD/F formation. Particulate removal prior to the gases entering the post-combustion zone is one control measure that merits examination. Conventional technology has concentrated exclusively on end-of-pipe particulate removal systems (ESPs, fabric filters, carbon filters, etc.), but with the recent development of filtration media capable of operating at high temperatures, the potential exists for the removal of a significant proportion of the particulate matter emanating from the furnace prior to its entry into the boiler and pollution abatement system. Drawing on static and in-flight PCDD/F formation mechanisms, a fall in particulate concentration in the furnace off-gases should be paralleled by a fall in PCDD/F production, assuming that all other requirements of GCP are observed. A recent trial on a fullscale clinical waste incinerator has demonstrated the efficacy of this control technique.³⁵

Minimizing the Residence Time of Particulate Matter. The operation of boilers, economizers, ESPs and other post-combustion equipment at around 3200°C is generally regarded as conducive to the production of high PCDD/F emissions. High formation rates in boilers, ESPs, etc., appear to occur primarily due to high static formation on trapped particulates and, in the case of ESPs, electrostatic enhancement of PCDD/F levels in the gas phase.³⁶ It follows that an important aspect of controlling emissions is the prevention of particulate build-up on plant and pipework operated in the temperature region associated with formation. This should be taken together with the minimization of all gas–particulate contact in the formation temperature window. However, the requirement to cool combustion gases implies that such conditions, and hence some PCDD/F formation, cannot be eliminated entirely.

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Inhibition of Catalytic Activity. The fact that the dominant (i.e. heterogeneous) PCDD/F formation reaction is surface-catalysed offers a means of reducing PCDD/F formation in the post-combustion zone of a combustor. The addition of ammonia to the flue gases suppressed the formation of PCDD/Fs on flyash surfaces.\(^{37}\) Since ammonia is also used as a reactant in the reduction of nitrogen oxides (NO\(_x\)) to nitrogen, the simultaneous control of NO\(_x\) and PCDD/F emissions using conventional de-NO\(_x\) technology has been suggested.\(^{38,39}\) The results of successful pilot scale trials using ammonia injection technology and descriptions of commercial systems have been reported.\(^{40,41}\)

Another approach to the suppression of catalytic activity has been taken by workers at the University of Waterloo.\(^{26,42-44}\) After conducting extensive laboratory trials on flyash obtained from a variety of combustion plants, an amine-based ‘destroyer/inhibitor’ mixture was formulated. This reactant was injected into the boiler of a MSW incinerator in an amount that represented 7–10% of the flyash loading in the flue gas; the ‘destroyer’ in the temperature window 590 ± 50°C, and the ‘inhibitor’ in the temperature window 375 ± 50°C. Overall reductions in PCDD/F formation of 80–94% were claimed. This approach has yet to be made commercially available.

End-of-Pipe Strategies

These include the control of particulate emissions, adsorption of PCDD/Fs by activated carbon or other substrates, and decomposition of PCDD/Fs or catalytic destruction.

Control of Particulate Emissions. As noted above, PCDD/F formation is via a surface-catalysed mechanism. It may therefore be thought that capture and removal of the particulate matter would necessarily result in a corresponding reduction in PCDD/F emission concentrations. If this logic were applied as a control strategy in isolation, it would suggest progressive lowering of particulate emissions as a simple means of PCDD/F emission control. Yet as a large number of parametric studies have shown, it does not follow that a correlation between PCDD/F emissions and particulate emissions is necessarily observed in full-scale incinerators under all operating conditions. The reaction sequence is complex, and a number of variables affect the rate of formation and quantities of PCDD/Fs produced, for example:

\(^{42}\) K. P. Naikwadi and F. W. Karasek, Chemosphere, 1989, 18, 1219.
\(^{44}\) F. W. Karasek and K. P. Naikwadi, Organohalogen Compd., 1994, 19, 315.
G. H. Eduljee and P. Cains

- The type of organic precursors present in the combustion gases, and the concentrations of these precursors.
- The availability of the flyash surface, since other chemicals present in the gases compete for a limited number of adsorption sites, and reactions other than those resulting in PCDD/F formation also occur.
- The reactivity of the flyash surface.
- The amount of carbon and of metals (especially of copper) present in the flyash.
- The residence time of the flyash particles in the temperature zone of interest – whether they are held up on boiler tubes or ESP plates, or whether they pass rapidly through as in the case of a wet scrubber.

Following formation, PCDD/Fs will partition between the solid and the gas phases depending on the temperature and the nature of the solid surface. The efficacy of particulate capture as a means of control of PCDD/F emissions therefore also presupposes conditions under which PCDD/Fs are primarily associated with the solid phase.

For these reasons, particulate removal will not necessarily result in a proportional reduction in PCDD/F emissions. PCDD/F emissions can be controlled by means other than limiting particulate emissions (e.g. by controlling PCDD/F formation).

Adsorptive Processes. The use of activated carbon, sprayed into a dry/semi dry scrubbing unit along with lime or less frequently packed in an adsorption unit positioned after the particulate removal device and prior to the stack, has become a standard component in gas cleaning trains as a means of PCDD/F control on all sizes of plant fed with MSW or clinical waste. Other adsorptive media such as zeolites are also being tested. The inclusion of an adsorptive device in combustion systems fired with wood and agricultural wastes is not normally contemplated, and as noted above, an interesting issue to be resolved is whether different waste types generate flyash of different activities relative to PCDD/F formation.

Catalytic Destruction. It has been reported that catalysts employed for the selective catalytic reduction (SCR) of NOx emissions also demonstrate the ability to decompose organohalogen compounds, including PCDD/Fs.39 Successful pilot trials at MSW and hazardous waste incineration facilities indicated that PCDD/F emission concentrations of <0.1 ng I-TEQ m⁻³ could be achieved in the absence of ammonia when titanium dioxide-based SCR catalysts were maintained between 200–350°C.

6 Summary

Our analysis of PCDD/F formation mechanisms and results from parametric trials on bench, pilot and full scale plant tends to reinforce rather than supplant existing strategies for reduction and control of PCDD/F emissions. Mechanistic considerations supply an underlying rationale for the requirements of Good Combustion Practice, many components of which were formulated before the reaction pathways were elucidated in laboratory experiments. The key to the
**Table 4** Multiple regression analysis for PCDD emissions to the spray drier inlet (SDI): predictive models

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<tr>
<th>$R^2$</th>
<th>Variables in model</th>
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<tr>
<td></td>
<td>CO (corrected)</td>
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<tr>
<td>0.79</td>
<td>X</td>
</tr>
<tr>
<td>0.82</td>
<td>X</td>
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<tr>
<td>0.89</td>
<td>X</td>
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<td>0.93</td>
<td>X</td>
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**Table 5** Multiple regression analysis for PCDD emissions to the spray drier inlet: control models

<table>
<thead>
<tr>
<th>$R^2$</th>
<th>Variables in model</th>
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<tr>
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<tr>
<td>0.39</td>
<td>X</td>
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<tr>
<td>0.59</td>
<td>X</td>
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<td>0.67</td>
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Implementation of GCP has been amply demonstrated in the bench scale parametric studies and in the full scale NITEP trials: because of the inter-dependency of the operating variables and their interaction in terms of the effect on combustion conditions, it is likely that control of only a selection of operational parameters to the exclusion of others will not provide an overall optimum in terms of minimizing PCDD/F formation. All relevant operational parameters need to be controlled in concert in order to achieve the BOP goals outlined in Section 5.

Recent tests provide an excellent example of the control of PCDD/F emissions from MSW combustion facilities.\(^{46}\) Tables 4 and 5 reproduce the results of a multiple regression analysis on operating variables relevant to the combustion system (i.e., before the combustion gases enter the pollution abatement equipment).

In the so-called predictive model illustrated in Table 4, progressively better correlations with PCDD concentrations in flue gas exiting the combustor are obtained as ‘monitoring variables’ comprising the concentrations of CO, NO$_x$ and water and the furnace temperature are successively combined into a single overall control model. When all four monitoring variables are combined, excellent prediction of PCDD concentrations is obtained. However, when ‘control variables’ such as waste moisture content, rear wall air flow, total overfire air flow, and underfire air flow are correlated with PCDD emission concentrations, the overall fit is much less effective (see Table 5). A similar trend was observed.


between plant variables and PCDF emissions.

The improvement in predictive power when ‘monitoring variables’ are combined points to the desirability of optimizing a range of operating variables in concert. Optimising furnace temperature also requires optimization of air flow, which in turn impacts on CO concentrations and NO\textsubscript{x} production. Lack of control on any single operational variable is likely to negate any reduction in PCDD/F formation. The excellent correlation coefficient of $R = 0.93$ in Table 4 also indicates that optimization of all four monitoring variables will result in consistently low PCDD/F emissions from the furnace.

The poor correlation between PCDD/F emissions and ‘control variables’ ($R^2 = 0.31–0.67$) suggests that the mixing and flow characteristics of the furnace play an important role in ensuring optimum combustion conditions, and that it is not sufficient merely to monitor furnace input variables.\textsuperscript{31,32} For example, it is possible to supply an adequate quantity of combustion air to the furnace, but intermittent blockages on the grate, the lack of turbulence in sections of the furnace or a sluggish air supply control system could result in less than optimum combustion conditions, and therefore higher PCDD/F emissions. It is essential that PCDD/F control strategies are underpinned by interactive monitoring of furnace conditions (and by extension, post-combustion operating conditions) if consistently low PCDD/F emissions are to be achieved and maintained.

The implementation of GCP, coupled with control of post-combustion conditions, can affect PCDD/F emissions as summarised in Figure 2 for an MSW incinerator.\textsuperscript{45}
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GCP alone will permit consistent achievement of PCDD/F emissions of 0.5–10 ng I-TEQ m$^{-3}$, as confirmed by the NITEP trials on the modified Quebec Urban Community MSW incinerator. Maintenance of GCP and operation of the pollution abatement equipment below 200°C will help achieve further reductions to 0.1 ng I-TEQ m$^{-3}$ and below. Catalytic oxidation or treatment with activated carbon enables the emission range to be maintained below 0.1 ng I-TEQ m$^{-3}$ with greater consistency.

7 Acknowledgements

The authors are grateful to the Department of Trade and Industry, through the Energy Technology Support Unit (ETSU), for funding this work and granting permission for publication. The views expressed in this chapter are those of the authors and do not necessarily represent those of ETSU or the Department of Trade and Industry. The authors especially wish to thank Mr Patrick Dyke of ETSU for the valuable assistance and advice he has offered throughout the study.