# Emissions of Chlorinated Dibenzodioxins and Dibenzofurans from Waste Combustion Plants in the UK

P. W. Cains+ and P. Dyke*

+*Technical Products Division, Harwell Laboratory, Oxon, OX11 0RA, UK.*
**ETSU, Harwell Laboratory, Oxon, OX11 0RA, UK.*

**Abstract.**

Measurements of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) emissions from a variety of small-scale waste combustion plants have been analyzed. Simple global correlations against parameters such as CO, HCl, feedstock composition, combustion or boiler exit temperature do not provide any guide to PCDD/F emission levels. Complex interactions between fuel types and properties and process design features indicate that a greater understanding of fundamental mechanisms is required to prescribe effective control measures against PCDD/F emissions.

**Acknowledgement:** The authors are grateful to the UK Department of Trade and Industry for funding this work.

## Introduction

Intensive laboratory studies have identified a range of factors important to the formation of PCDD/F in municipal solid waste (MSW) incineration, particularly the role of fly ash in the formation processes. There have also been a large number of tests on operating incinerators. It has been difficult to draw definitive conclusions from these data, largely because of the incomplete nature of much field test work, and the extreme difficulties encountered in attempting to simulate the conditions of real plant in the laboratory. Sparingly little data has been published on PCDD/F formation in combustion plants burning waste feedstocks other than MSW.

The UK Department of Trade and Industry funded Warren Spring Laboratory to test PCDD/F emissions from small incinerators burning a range of waste types , along with operational characteristics including feed rates, boiler performance, temperature profiles, and emissions of combustion and acid gases, particulates, heavy metals, and other trace organics. Feedstock and residue macro-compositions were also analysed, together with trace organic contamination of the latter. We have assessed the PCDD/F assays in the light of the latest understanding of PCDD/F formation mechanisms, as identified from a literature survey and from contact with other active researchers.

## Feedstocks and Combustion Conditions

Table 1 summarizes the measured mass totals of toxic PCDD and PCDF isomers (characterized by non-zero Toxic Equivalency Factors) and the corresponding Toxic Equivalents (TEQs), downstream of grit arrestors, classified according to feedstock in the approximate order of emission levels per kg feedstock incinerated. On the basis of mass totals, refuse derived fuel (RDF) yields the highest levels;

scrap tyres, coal and clinical wastes also give relatively high totals. The totals for the other feedstocks are considerably lower. Table 1 also shows the consistency and variability of the PCDD/F data within individual processes. Tests in cases [3], [4], and [6] were conducted over comparatively short time intervals (days), and all show fairly consistent totals and TEQs despite the fact that operating conditions (particularly feed rate and firing conditions) are altered. On the other hand, case [13] includes replicated results for two sets of measurements taken 6 months apart on the same plant with nominally constant operating conditions and feedstock composition. A substantial variation has occurred: to both dioxin and furan levels. For the second run [13]/2 they are factors of 3-5 higher than the corresponding values for run [13]/1. It is possible that deposits collecting inside the incinerator may contribute to PCDD/F formation or retention.

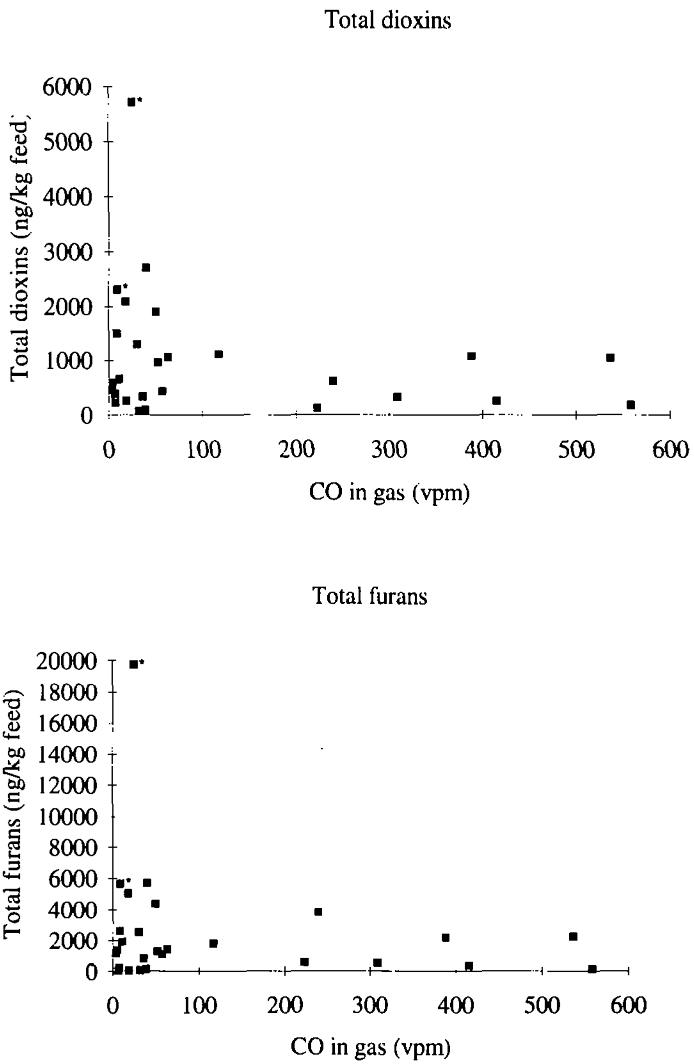
**Table 1. Mass Total and Toxic Equivalent (TEQ) Dioxin and Furan Yields.**

| Feedstock | Plant[ ] / Operating Conditions+ | Dioxins (ng/kg feed) Total* | Dioxins (ng/kg feed) TEQ (I-TEF) | Furans (ng/kg feed) Total* | Furans (ng/kg feed) TEQ (I-TEF) |
|---|---|---|---|---|---|
| RDF | [2]/L # | 4550 | 115 | 18570 | 616 |
| | [2]/H | 1925 | 46.4 | 5006 | 196 |
| | [13]/1 | 426 | 3.71 | 1095 | 60.7 |
| | [13]/1 | 654 | 7.99 | 1910 | 118 |
| | [13]/2 | 2080 | 24.7 | 5030 | 210 |
| | [13]/2 | 1900 | 24.1 | 4360 | 163 |
| | [13]/2 | 2700 | 21.5 | 5690 | 200 |
| Scrap tyres | [3]/L | 871 | 84.1 | 1130 | 104 |
| | [3]/H | 828 | 117 | 1065 | 111 |
| Coal | [4]/L | 1034 | 23.8 | 1703 | 77.8 |
| | [4]/H | 802 | 23.8 | 1900 | 85.2 |
| Clinical waste | [5]/L | 810 | 40.4 | 1328 | 98.5 |
| | [5]/H | 620 | 30.8 | 624 | 57.7 |
| | [7]/G | 1510 | 50.2 | 2630 | 218 |
| | [7]/P | 614 | 147 | 3820 | 556 |
| | [8] | 361 | 24.1 | 1642 | 166 |
| | [8] | 976 | 38.5 | 1566 | 122 |
| | [10] | 592 | 22.7 | 1390 | 104 |
| | [10] | 460 | 16.4 | 1198 | 67.5 |
| | [11] | 44.8 | 0.17 | 64.0 | 6.32 |
| | [11] | 34.1 | 0.44 | 31.3 | 2.96 |
| Straw | [1] | 328 | 35.0 | 794 | 80.5 |
| Wood waste | [6]/C | 231 | 6.91 | 324 | 12.4 |
| | [6]/I | 124 | 4.25 | 87.6 | 5.00 |
| Sewage sludge | [9] | 143 | 0.51 | 36.1 | 2.24 |
| | [9] | 179 | 1.69 | 252 | 26.3 |
| | [9] | 272 | 2.32 | 45.1 | 3.84 |
| | [14] | 218 | 20.3 | 224 | 22.7 |

+L = Low fire; H = high fire; C = continuous firing; I = Modulated firing; G = good combustion; P = poor combustion; 1,2 = two separate runs under nominally identical operating conditions. Other replicated results represent repeat measurements.
*Mass totals of isomers with non-zero Toxic Equivalency Factors (I-TEF).
# contaminated sample affected results by an unquantified amount
Cases [9] & [14] are fitted with ESPs, [13], [10] [9]& [11] are fitted with wet scrubbers; the unabated emissions are not available in these cases (all other plants had simple grit arrestors only).

Analysis of plant data can be carried out globally or locally. Global comparisons are made across a range of different plant and feedstock types. Local comparisons are made on a specific plant and feedstock, where changes in conditions are relatively minor. Generally, global comparisons have not identified clear causal effects, for example Fig. 1 plots dioxin and furan totals against CO levels in the exhaust gases. Similar plots against HCl levels and nominal combustion chamber temperature also show no clear correlations, although there is a generalized tendency for higher PCDD/F levels to correspond to lower recorded temperatures.

**Fig. 1. Total PCDD and PCDF in gaseous emissions vs CO level**




*Dioxin/furan levels for asterisked points may be slightly overestimated because of sampling error.

Poor combustion generally correlates with higher relative proportions of lower chlorinated congeners, as shown in Fig. 2 for a single plant [7] incinerating clinical waste. The lower chlorinated species have the higher toxic equivalency factors, giving higher TEQs where combustion conditions are poor.

**PCDD/F Formation on Particulates in Flue Gases.**

In view of the extensive evidence of heterogeneous PCDD/F formation, measured PCDD/F levels in flue gases and on entrained particulates have been examined in relation to particulate loadings and compositions. No unequivocal global correlations were evident. Fig. 3 shows the PCDD and PCDF totals in the gaseous emissions against the Cu content of particulate matter remaining in the flue gas downstream of grit arrestor devices: there are indications that high PCDD/F levels accompany high Cu levels. A similar trend was found in plots of PCDD/F versus the Cu contents of grit ashes, and less markedly for plots against the Cl contents of entrained particulates.

**Heat Recovery and Particulate Removal Devices.**

Comparisons of PCDD/F levels from plants [2] and [5] fitted with heat recovery boilers with [8] and [12] without heat recovery showed no indications that heat recovery enhances PCDD/F emission levels. More generally, we also find no evidence of correlation between heat recovery boiler exit temperature and PCDD/F levels. Further investigations are required on a single plant and feedstock that take account of fouling and cleaning cycles.

Electrostatic precipitators can create high PCDD/F levels if operated in an unfavourable temperature regime, 250° - 400°C. In our study, however, the two plants employing ESPs, [9] and [14], gave very low PCDD/F yields, even though both operated around the most unfavourable temperature of 300°C. Both processes incinerated sewage sludge, and we infer that, in this case at least, the feedstock exerts a greater effect on PCDD/F formation than the process operating conditions.

We conclude that for plants burning a range of wastes further work is required to provide a more thorough understanding of the formation and destruction mechanisms, and on an ability to relate this to the operating conditions of incineration plant. This will lead to a more successful strategy of PCDD/F abatement and control.

Note: The views expressed in this paper are those of the authors and do not necessarily represent those of ETSU or the Department of Trade and Industry.

**Fig. 2. PCDD/F isomer distributions in gaseous emissions from a clinical waste incinerator.**

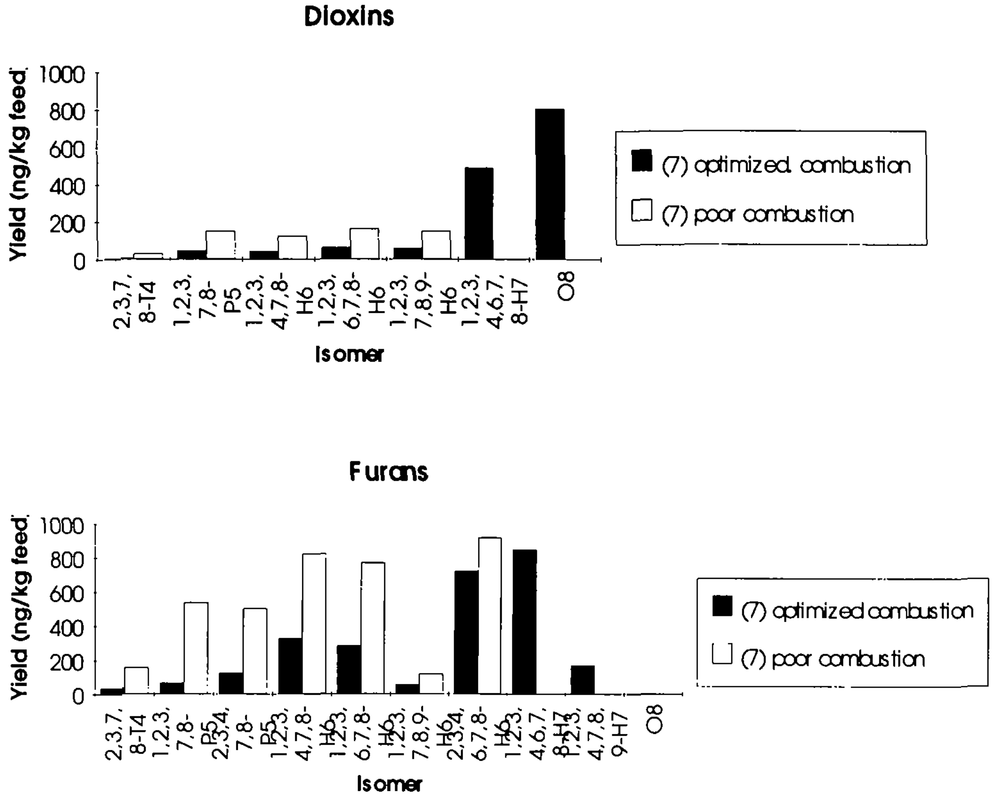


**Fig. 3. PCDD and PCDF in gaseous emissions vs quantity of copper in entrained particulate downstream of grit arrestors.**