

# Formation and Sources P13

## Correlation of Chlorine Input and PCDD/PCDF Emissions at a Full-Scale Hazardous Waste Incinerator

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### Abstract

Data from a full-scale hazardous waste incinerator show that PCDD/F emissions are dependent on chlorine input at a chlorine concentration as low as 0.031 percent. In addition, mass balance data indicate that hazardous waste incinerators may be achieving destruction efficiencies that are orders of magnitude below those achieved by other destruction technologies. The performance standard commonly used for incinerators, Destruction and Removal Efficiency (DRE), entails the comparison of inputs of selected chemicals to their emissions in stack gases. Since stack emissions are only one of several forms of incinerator output (e.g., fly ash, bottom ash, scrubber and quench water, etc.), some of which may carry significant concentrations of undestroyed chemicals, the DREs of incinerators cannot be meaningfully compared to the destruction efficiencies achieved by other technologies.

### Introduction

PCDD/F output, or some fraction thereof, has been found to increase with rising chlorine input in a number of studies with laboratory- and pilot-scale combustors (1,2,3,4,5,6,7,8,9,10) as well as full-scale incinerators (11,12,13,14,15,16,17) and home heating systems (18). These findings support the premise that PCDD/PCDF output can be reduced by materials policies directed toward reducing or eliminating chlorine sources, such as polyvinyl chloride (PVC), from materials destined for burning in incinerators and other combustion system. Such materials policies have been enacted, acknowledged and/or proposed by various national and international entities (19,20,21,22,23,24,25).

The appropriateness of such materials policies has been brought into question by Wikstrom et al. (1996) who reported that decreased chlorine content of the materials burned in their laboratory-scale combustor was associated with reduced PCDD/F emissions only when chlorine levels were 0.5-1 percent or greater (26). The first to postulate such a threshold theory, these researchers suggest that materials policies addressing PVC will not achieve a significant reduction in PCDD/F emissions from well-controlled waste incinerators, since Swedish municipal waste contains only 0.7 percent chlorine of which 40 percent or less stems from PVC. They did not address the implications for total dioxin output or for wastes containing higher

levels of chlorine and/or PVC. E.g., Japanese municipal solid waste carries an average PVC content of 12.2 percent, with a maximum of 25.3 percent (27), while PVC contributes 2/3 of the total chlorine content of Danish municipal waste (14).

In this report, we discuss the results of a trial burn at a full-scale, mobile hazardous waste incinerator in which the chlorine content of the materials burned in each of three tests was 0.031, 0.052 and 0.1 percent, respectively.

### Materials and Methods

The trial burn was conducted from January 24, 1995 through January 26, 1995 using contaminated soils from the Baird & McGuire Superfund Site, Holbrook, Massachusetts, USA. The soils were spiked with three chemicals designated as Principal Organic Hazardous Constituents (POHCs) – naphthalene, chlorobenzene and 1,2,4,5-tetrachlorobenzene. The objectives of the trial burn included demonstrating the ability of the facility to meet the performance criteria of the Resource Conservation and Recovery Act, e.g., adequate DREs with the POHCs (28).

The treatment process at this facility was as follows: First, water was removed from feed soils in a direct-fired rotary dryer equipped with a 10.5 MMBTU/hr dual fuel burner. Organic contaminants were then removed from soils and at least partially destroyed in a direct-fired rotary kiln consisting of a ¾-inch thick, 40-foot long carbon steel cylinder lined with 9-inch thick refractory and equipped with a 32 MM Btu/hr dual fuel burner. Kiln ash was quenched in a water bath and discharged to a storage area. Kiln flue gas was directed to an air pollution control (train consisting of a baghouse, quench tower, wet scrubber and secondary combustion chamber. Fly ash removed by the baghouse underwent separate thermal treatment in an indirect-fired rotating chamber. Ash and flue gas were discharged from this chamber. This ash stream was also quenched and discharged to the storage area. Flue gas from this process was returned to the baghouse.

General characteristics of the materials fed into the system and selected operating parameters are shown in Tables 1 and 2, respectively, as derived from the trial burn report.

Table 1: Waste Feed Characteristics

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
Moisture, %	8.39	7.71	10.0
Heat content, Btu/lb	96.7	97.2	95.4
Ash, %	96.7	97.2	95.4
Chlorine, %	0.031	0.052	0.100

Table 2: Process Operating Parameters

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
Waste feedrate, kg/min	383.6	399.5	394.9
Kiln Discharge Temperature, ° F	1234	1251	1213
Stack flowrate, dscm/min	518.3	530.4	487.7

Stack gas samples for PCDD/F and the POHCs were collected using the U.S. Environmental Protection Agency's Method 0010/23 sampling train and analyzed by Method 23 and Method 8270, respectively. Method 0050 was used for hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>).

### Results and Discussion

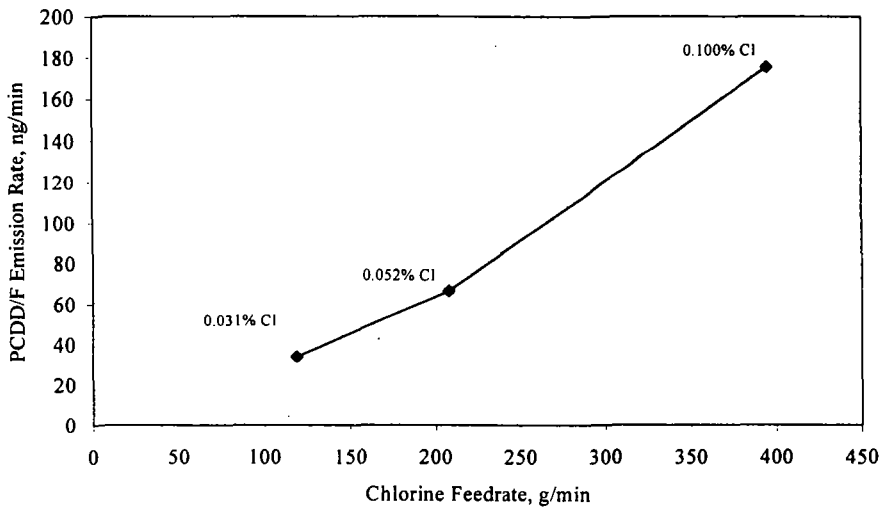
Chlorine feedrates and the concentrations in stack gases as well as emission rates of PCDD/F and HCl/Cl<sub>2</sub> are presented in Table 3.

Table 3: Chlorine Feedrates and PCDD/F and Stack Gas Concentrations and Emission Rates

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
Chlorine feedrate, g/min	118.9	207.7	394.9
H HCl/Cl <sub>2</sub> , □g/min	2075.3	6189.8	4184.5
PCDD/F, ng/min	34.16	66.83	175.57

As illustrated in Figure 1, PCDD/F concentrations in stack gases increased as the chlorine content rose from 0.031 to 0.10 percent. These data indicate that PCDD/F emissions continue to be dependent on chlorine content at chlorine concentrations as low as 0.031 percent. I.e., these findings do not support the theory that a threshold exists in the relationship between PCDD/F emissions and the chlorine content of materials burned. It should also be noted that HCl/Cl<sub>2</sub> emissions do not correlate well with chlorine feedrates, as has been assumed by some assessments of full-scale incinerators, e.g., Rigo et al.(29).

Figure 1: Chlorine Feedrate and PCDD/F Emission Rate, Baird & McGuire Superfund Site Incinerator, Holbrook, Massachusetts, USA



Based on feedrates and rates of release in stack emissions, DREs ranging from 99.99978 to 99.99995 percent were calculated for the three POHCs, as shown in Table 4. However, when releases in other residues (e.g., fly ash, bottom ash, quench water from baghouse, scrubber and secondary combustion chamber blowdown) were also considered, the destruction efficiencies achieved with the three POHCs and three other chemical contaminants ranged from 97.49 to 99.93 percent.

Table 4: Destruction Efficiencies (DEs) and Destruction and Removal Efficiencies (DREs) Achieved by Baird & McGuire Superfund Site Incinerator, Holbrook, Massachusetts, USA

	Chloro- benzene	Xylenes	Naphthalene	2-Methyl- naphthalene	1,2,4,5- Tetrachloro- benzene	4,4'-DDD
Run 1						
DE, %	99.82	99.71	97.90	97.49	98.17	98.76
DRE, %	>99.99977		99.999972		99.9999950	
Run 2						
DE, %	99.93	99.92	99.51	99.55	99.48	99.57
DRE, %	99.99978		99.999929		99.999989	
Run 3						
DE, %	99.88	99.91	99.48	99.56	99.48	99.83
DRE, %	>99.99981		99.999953		99.999989	

It is also important to note that the destruction efficiencies were achieved by a chain of thermal devices, not just the primary kiln and secondary combustion chamber. In addition, the fly ash, which is commonly a major repository of any unburned chemicals and those newly formed within the system, was subjected to further high temperature treatment prior to analysis.

In summary, this study found no evidence of a threshold in the relationship between chlorine input and PCDD/F emissions at chlorine concentrations as low as 0.031 percent. The mass balances calculated in this trial burn also indicate that the destruction efficiencies of hazardous waste incinerators are several orders of magnitude lower than those achieved by other technologies, e.g., gas-phase hydrogenation (30), molten metal (31) and electrochemical oxidation (32).

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