

### TRANSIENT PCDD AND PCDF CONCENTRATIONS IN AN MWC

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#### Introduction

Time-resolved evaluations of municipal waste combustor (MWC) performance have shown that concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) and related pollutants undergo significant changes as a response to transient events: startups, shutdowns, and other upset combustion conditions. During and after transient combustion conditions, PCDD/F raw gas levels have been shown to increase by one to two orders of magnitude.<sup>1,2</sup> The consensus holds that the dominant formation mechanism during steady state operation of waste combustors is *de novo* synthesis due to oxychlorination reactions of carbonaceous deposits. However, during transient conditions, the mechanism appears to change, at least in part: the PCDD to PCDF ratio increases,<sup>2-4</sup> the homologue profile shifts to lower chlorinated congeners,<sup>4,5</sup> and the isomer patterns change.<sup>6</sup> Transient conditions, typically indicated by elevated CO, lead to soot formation which has been shown to be active for PCDD/F formation in the presence of metal-catalyst-containing fly ash.<sup>7</sup> The rapidity and duration of the increased PCDD/F concentration response to these transients is largely undocumented but is likely a function of combustor geometry and operating conditions.

Increases in other pollutants, including tri- to pentachlorophenols and tri- to hexachlorobenzenes, have also been observed in multi-hour samples after startups.<sup>3</sup> Online measurements of polycyclic aromatic hydrocarbon (PAH) emissions at a hazardous waste incinerator show significant increases within 60 s in response to a container charge.<sup>8</sup> Likewise, PAHs and other compounds including benzene, phenol, naphthalene, xylene, toluene, DD, and DF, were sampled during and 1 h after a malfunction transient in a waste wood combustor and showed significant, time-dependent increases.<sup>9</sup>

Some evidence<sup>2-4</sup> suggests that the elevated levels of PCDD and PCDF observed from these transients may carry over into the emissions after the air pollution control system (APCS). This suggests that transient-induced increases in PCDD and PCDF formation are not completely mitigated by the APCS, and hence, the elevated emissions may be released to the environment. The higher level of PCDDs and PCDFs during transient combustor operation suggests that attention be given to mitigation of formation potential during startups, shutdowns, and other upset conditions. Understanding and controlling the temporal aspects of the pollutant concentrations requires application of newly developing real time monitors for trace pollutants, although others argue that the transient, lagged nature of the emissions does not easily lend itself to process control.<sup>1,10</sup>

This work examines the changing concentrations of PCDDs/Fs and related compounds in a waste combustor by employing a series of short duration samples in parallel with conventional sampling and with jet resonance-enhanced multiphoton ionization (jet REMPI) for on-line, trace monitoring. Boiler operating scenarios sampled included steady state, pre-shutdown, shutdown, startup, and extended post-startup. These results will be examined to understand the implications for monitoring the combustion process, sampling for compliance purposes, and preventing PCDD/F formation.

#### Materials and Methods

A municipal waste combustor with multiple refuse-derived-fuel (RDF) fired boilers (>400 Mg/day) was sampled over a 9 day period for PCDD/F and other combustion by-products. Samples were drawn from the flue gas duct prior to the flue gas cleaning system; hence, concentrations do not represent stack emissions. Over the course of nine days, 23 sampling periods were completed, five on boiler A and 18 on boiler B (unscheduled maintenance on boiler A led to the switch to boiler B). Five operational scenarios were distinguished to categorize the samples: steady state (SS), periods of high CO (HCO, typically followed by a shut down to

correct waste feed problems), shut down (SD), start up (SU, typically within 1 h of a SD), and late startup (LSU, usually within 2-3 h of a SU). Sampling for PCDD/F included 1 h Method 0023a<sup>11</sup> (M23) samples and 5 min CALUX<sup>12</sup> samples. Three 5-min duration CALUX samples (denoted A, B, and C) were taken every 20 min over the approximately 1 h M23 sampling duration. Sampling for semivolatiles was accomplished with an on-line, laser based technique, jet REMPI with time-of-flight mass spectrometry,<sup>13</sup> and supported by standard extractive sampling via Method 0010<sup>14</sup>(M10). Plant data consisted of continuous CO and CO<sub>2</sub> monitoring. Concentration data are reported as dry values but are uncorrected for O<sub>2</sub> concentrations in order to appropriately reflect the concentrations during the range of sampled combustion conditions.

### Results and Discussion

Average PCDD/F concentrations for boiler B (for which there are more samples) are shown in Table 1. Periods of operational upsets, indicated by high or fluctuating CO levels (HCO), have slightly elevated PCDD/F values above that of the SS. However, the largest concentrations are observed during startups and are likely a result of lower temperatures and incomplete waste burnout resulting in more reactive soot formation. The plant can fire #2 fuel oil during startups but did not do so during these tests since the startups were less than 2 h from the shutdowns.

Run Type	Avg. PCDD/F (ng TEQ/dscm)	No. Runs	Rel. Std. Dev. (%)	PCDD/PCDF Ratio
SS	25.5	3	37	0.18
HCO	39.9	3	33	0.37
SD	39.6	2	40	0.56
SU	198.9	2	14	0.45
LSU	40.4	3	30	0.28

Table 1. PCDD/F sampling results, boiler B.

The PCDD/F concentrations changed rapidly due to these different boiler operating conditions. Results from M23 sampling showed that the greatest rates of increase occurred during boiler startups: 67.3 and 50.8 ng TEQ/m<sup>3</sup>/h; the greatest rates of decrease occurred during late startup periods -49.5, -70.3, -92.5 ng TEQ/m<sup>3</sup>/h. Here the denominator is

the time period between the end of two consecutive sampling periods; actual rates may be more extreme since, typically, over an hour occurs between consecutive samples, and these are 1 h cumulative samples. These rates of increase imply that PCDD/F concentrations can change rapidly: an 8-fold increase occurs from SS to SU scenarios in about 3 h. Conversely, rates appear to decline as quickly or, perhaps, even quicker. These results confirm that high PCDD/F formation occurs during operational transients such as startups but also indicate rapid decline to levels approaching steady state. The time history approach to steady state values was not fully documented due to frequent changes in boiler operating conditions; however, a SS concentration of 14.5 ng TEQ/m<sup>3</sup>/h was sampled about 23 h after SU conditions.

Three 5-min CALUX samples were taken throughout each of three 1-h M23 sampling runs on boiler A to provide additional insight into the rapidity of the TEQ value change during various operating scenarios. The averages of the three 5-min CALUX values for each of the three runs (and two subsequent 1-h CALUX samples) followed the trend of the M23 values ( $R^2=0.88$  for  $N=5$ ) but were about 6 times higher (Table 2). This likely reflects the presence of additional pollutants other than PCDDs/Fs that bind to the Ah receptor and possible inaccuracies in the CALUX TEF calibration for incinerator sample matrices. The CALUX values in Series I decline with time by 7-fold, likely reflecting increased departure from SU conditions (sample A was taken 83 min after startup) and approach to SS conditions. These results refine the rate of PCDD/F change determined from M23 results (above), indicating a potential 7-fold change in the TEQ value over a 60 min period.

Run	Run Type	PCDD/F (ng TEQ/dscm)				
		CALUX				M23
		A	B	C	Avg.	
Series I	LSU	646	214	97	319	36.7
Series II	HCO	713	200	ns	457	127.1
Series III	SU	1713	746	1034	1164	194.7

Table 2. CALUX and M23 results, boiler A. ns = not sampled.

## Thermal processes

During Series I, the average CO values were 202, 212, and 290 ppm during samples A, B, and C, respectively. The relative steadiness of the CO values underscores the inability of CO to predict PCDD/F TEQ values (in this case, CALUX values). The HCO operating conditions resulted in CO values of 280 and 643 ppm corresponding to the A and B CALUX samples, respectively (C was not sampled). The relatively high CO values are accompanied by high CALUX TEQ values, but they don't follow the same trend, again suggesting that CO is a poor indicator of current PCDD/F formation potential. Series III is a SU condition with high CALUX and M23 values. CO concentrations during CALUX samples A, B, and C were 917, 937, and 387 ppm, respectively, reflecting approach to SS conditions. Again, CO values don't correspond with simultaneous CALUX values.

The rapidity of apparent PCDD/F concentration changes was often matched by the semi-volatiles. On-line measurements of jet REMPI during the 5 min HCO and SU CALUX samples (Series II, and III) indicated at least 12-fold changes in average naphthalene over the course of an hour (Figure 1). Less drastic changes and more inconsistent responses were observed for phenanthrene, fluorine (not shown), and pyrene (not shown). Figure 1 also shows that naphthalene responds rapidly during CO peaks, whereas phenanthrene's response is slower and more muted.

The predominant mechanism of PCDD/F formation in waste incinerators is believed to proceed from oxychlorination of carbonaceous structures ("de novo" synthesis). The large surface area for soot and fly ash deposits provides sufficient reactants for continued, or "inertial," reactivity leading to the observation of continued PCDD/F emissions long after cessation of waste feeding (i.e., the "memory" effect). The rapid increases and decreases in PCDD/F concentrations observed in this work imply a rapid reactivity response that belies the notion that long times and large reactant concentrations (deposits) are necessary for PCDD/F formation. At the least, the results imply some alteration of the formation mechanism. This is supported by the increased PCDD:PCDF ratio observed during transient conditions and its eventual return to SS values after continued operations (see Table 1). The transient, upset conditions tend to promote PCDD formation. 52% of the TEQ value is due to PCDDs during startups, versus 39% during steady state operation.

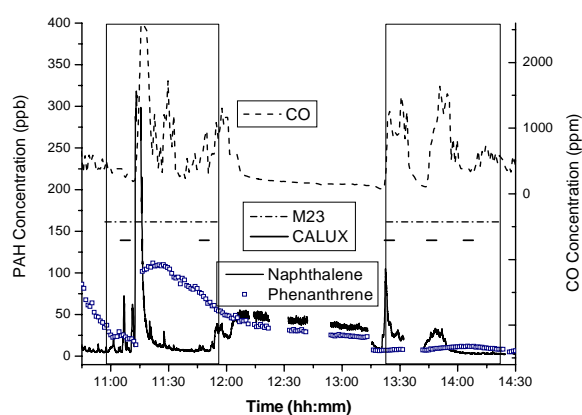


Figure 1. Jet REMPI real-time measurements of naphthalene and phenanthrene matched with plant CO during M23 and CALUX sampling: Series II, HCO (left box) and Series III, SU (right box).

Sampling during steady state conditions in boiler A resulted in PCDD/F concentrations of 130.7 ng TEQ/dscm, while three samples from boiler B had values of 28.6, 33.0, and 14.9 ng TEQ/dscm. This large range in steady state concentrations between boilers A and B exists despite similar waste firing and the same boiler type. The two boilers may be at different stages in their maintenance schedule, resulting in different propensities for PCDD/F formation. Regardless of the explanation, these differences suggest that even steady state conditions are amenable to process monitoring and control in order to minimize conditions that lead to PCDD/F formation.

Pre-APCS concentrations of PCDDs and PCDFs changed rapidly in response to transient operations such as startups, with at least 7-fold increases and decreases within 1 h. The extent to which these transients affect short- and long-term stack emissions was not determined. Large differences exist in PCDD/F levels in identical, parallel boilers. Rapid concentration changes for PAHs, particularly naphthalene, were also observed. The rapidity of the response of PCDDs, PCDFs, and other co-pollutants to transients and the distinctions between similar boilers suggest that rapid on-line monitoring will be necessary to effect changes in operating conditions that will reduce or prevent favorable PCDD/F formation conditions. However, variation in the response time of

pollutants to these transients and facility-specific differences suggest that such measures will require a time-lagged correlation between PCDD/F and monitorable surrogate compounds that is statistically established for each particular facility.

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