## PCDD/F EMISSIONS FROM UNCONTROLLED, DOMESTIC WASTE BURNING

Brian K. Gullett<sup>1</sup>, Paul M. Lemieux<sup>1</sup>, Chris K. Winterrowd<sup>2</sup>, Dwain L. Winters<sup>3</sup>

 <sup>1</sup>U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA, gullett.brian@epa.gov
<sup>2</sup>ARCADIS Geraghty & Miller, P.O. Box 13109, Research Triangle Park, NC 27709, USA
<sup>3</sup>U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, D.C. 20460, USA

### Introduction

Emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) from "backyard, barrel burning" of domestic waste have been shown to have significant, yet highly variable levels.<sup>1-3</sup> PCDD/F toxic equivalency values (TEQs) ranged across 3 orders of magnitude, from less than 10 to over 6000 ng TEQ/kg, bracketing the 140 ng TEQ/kg used in the EPA source inventory document.<sup>4</sup> The national emissions from backyard barrel burn sources were estimated to be greater than 1,000 g TEQ/y although the uncertainty in this estimate was too great for it to be included in the EPA's quantitative inventory of PCDDs/Fs.<sup>4</sup> These results suggest that backyard burning of domestic waste could be a major source of PCDD/F emissions in the U.S. Extrapolation to global waste combustion practices is difficult, but emissions from these sources to the worldwide PCDD/F balance may be significant.

To reduce the uncertainty associated with estimating emissions from this source, a better understanding of the causal factors controlling barrel burn emissions is needed. Through variation of waste composition while monitoring burn parameters, the initial studies related the potential for emissions primarily to combustion parameters (e.g., temperature) and concentrations of various gas-phase species (e.g., carbon monoxide, CO).<sup>3</sup> These species may be affected by changes in waste composition, waste orientation, and/or combustion conditions. To develop a better understanding of what factors affect emissions, additional tests were conducted varying burn practices and composition factors.

#### Experimental

Studies were performed at the EPA's Open Burning Test Facility to further define the impact of variation in combustion practices and waste composition on PCDD/F emissions from a simulated domestic, backyard barrel burn. A composition representative of domestic household waste (6.8 kg) was prepared (see Refs. 2,3) which consisted of actual unshredded house waste. Variations to the baseline tests included both changes in charge size [6.8 kg ("Baseline") and 13.9 kg ("Double")], waste moisture levels ("Wet"), waste compression ("Compress"), and waste composition [0.07 wt. % added copper (Cu) in Baseline vs. 2.0 % Cu ("High Cu")]. Previous tests' used three different levels (0.0, 1.0, and 7.5 wt. %) of polyvinyl chloride (PVC) to vary the baseline composition (0.2 % PVC), 7 wt. % inorganic chlorine (Cl) as calcium chloride (CaCl<sub>2</sub>), a compressed waste burn, a wet test, and a high Cu test. This paper reports on the combined previous and current tests.

To simulate common practice for residential waste burning, the test container consisted of a 208 L (55 gal.), steel, precleaned barrel with 24 2 cm diameter ventilation holes around the base. High volume air handlers provided metered dilution air into the enclosed burn hut, resulting in 2.5 volume changes per minute. Additional fans were set up inside the burn hut to enhance circulation within the hut. Type K thermocouples were inserted at prescribed heights and radial locations from the bottom to the top of the waste-filled barrel, labeled TC1 to TC6, respectively, for data collection throughout each run. Continuous emission monitors (CEMs) sampled for common gases, while PCDD/F sampling was completed via ambient sampling methods. Samples were

**ORGANOHALOGEN COMPOUNDS** 

Vol. 46 (2000)

collected over the course of the active burn, and sampling was terminated when the burn mass did not change over several minutes. When analyzing and reporting the results, all non-detects (NDs) and peaks that did not meet ion ratio criteria were set to equal zero. Emissions were reported as nanograms TEQ per kilogram of waste burned. TEQ values were calculated using International Toxic Equivalency Factor (I-TEF) values in Barnes (Ref. 5). Further experimental, sampling, and analytical details are available elsewhere.<sup>2,3</sup>

### **Results and Discussion**

The composite, 24-barrel tests resulted in PCDD/F total emissions ("Totals," tetra- to octa-CDD/F) ranging from 306 to 425,247 ng/kg burned. International TEQ (I-TEQ) values ranged from 1.7 to 6,433 ng I-TEQ/kg burned. The High Cu condition had the largest variability (N=2) with values of 18 to 2,594 ng TEQ/kg. When grouped by similar run conditions, Fig. 1 shows considerable variability in the normally distributed log(TEQ) means and the 95% confidence intervals. The TEQ and PCDD/F totals are included in Table 1.

Seven Baseline tests (five reported in Ref. 3) had emissions from 9 to 609 ng TEQ/kg, a range of about 2 orders of magnitude. The mean and median emissions were 204 and 131 ng TEQ/kg, respectively. The large variation in baseline emissions, despite careful attention to standardized composition and procedures, suggests that random factors, such as waste orientation, may have a significant impact on PCDD/F emissions. The last two baseline tests had values of 429 and 609 ng TEQ/kg. The difference between the previous five and the two most recent baseline tests is statistically significant at the p = 0.05 level. The reason for the increase in subsequent baseline tests is not clear. However, comparison of other repeat data shows mixed trends for

PCDD/F emissions between previous<sup>3</sup> and current tests, suggesting that no temporal Log(TEQ) trends influenced the data. One open burn (waste pile) test ("Open") with the baseline waste composition resulted in emissions of 59 ng TEQ/kg. This suggests that open burning produces less PCDDs/Fs than containerized barrel burning, but this remains to be verified by replicate tests.



Figure 1. PCDD/F log(TEQ) values by run condition. The center line across each diamond represents the group mean. The height of each diamond represents the 95% confidence interval for each group.

ORGANOHALOGEN COMPOUNDS Vol. 46 (2000)

Run Type	N	TEQ	SD	Total	SD
		(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
0 % PVC	2	14	18	1549	1758
1 % PVC	2	201	43	11518	817
7.5 % PVC	2	4916	2146	336642	125306
Baseline	7	204	227	5801	5270
7 % CaCl <sub>2</sub>	2	734	216	67471	17082
Compress	2	190	220	14388	7807
Double	3	386	341	9822	7887
High Cu	2	1306	1821	126982	177560
Wet	2	1130	1260	35196	23359
Open	1	59	NA	4760	NA

Table 1. PCDD/F Means and Standard Deviations by Run Type (N = no. of runs, SD = std. dev., NA = not applicable).

Comparison of runs (N=14) in which burn condition factors (Double, Compress, Wet, Baseline) were changed, but the composition was held constant, resulted in PCCD/F emissions that ranged from 9 to 2,020 ng TEQ/kg. Table 1 shows the means and standard deviations for these runs. Excluding the one high TEO (and Total) value for Wet, analysis of variance testing on the mean TEQs and Totals for these factors shows no statistically significant differences, likely due to the limited number of runs and the wide variability in emissions. To determine whether this variability could be accounted for by combustion characteristics, the normally distributed log(TEQ) data were modeled by choosing among continuously measured parameters of average and maximum thermocouple temperatures (TC1 to TC6); sampled hydrogen chloride (HCl) and Cu emissions; average CEM values including CO, carbon dioxide (CO<sub>2</sub>), and oxygen (O<sub>2</sub>); the time (MAXTIME) and mass loss rate (MAXBURN) when the waste is at maximum burn rate; and the duration (in minutes) that in-barrel thermocouple temperatures were within the common formation window temperature [TS2 = 250 to 450 °C (excluding TC1 and TC2) and TS3 = 300 to 400 °C]. An optimal model ( $R^2 = 0.81$ ,  $Q^2 = 0.60$ ) for log(TEQ) of these 14 baseline composition runs consisted of three, significant ( $\alpha < 0.05$ ), linear predictors: TC4MAX, TS2, and MAXBURN. Selection of these predictors suggests that temperature and burn rate parameters provided the best predictive capability of TEQ emissions.

Comparison of 15 runs in which only Cl levels were changed [PVC (60 wt % Cl), Baseline (0.2 wt % Cl), CaCl<sub>2</sub> (64 wt % Cl)] shows significant differences (? = 0.05) between TEQ values for the 7.5 % PVC runs with all other runs. Comparison of log(TEQ) values maintains this distinction only for Baseline/7.5% PVC and 0% PVC/7.5% PVC. Distinctions in these runs are clearly related to level of Cl content of the waste: log(TEQ) can be modeled with log(Cl) ( $R^2$  = 0.57,  $Q^2$  = 0.43). With a more rigorous statistical algorithm, no distinction is observed in log(TEQ) for inorganic (7% Cl in CaCl<sub>2</sub>) versus organic (7.0 % Cl in PVC) Cl sources. These 15 runs were well modeled for log(TEQ) ( $R^2$  = 0.90,  $Q^2$  = 0.84) by TC2MAX, TC5MAX, and CO. Selection of these parameters indicates the importance of temperature trends as well as CO emissions in predicting PCDD/F emissions, supporting earlier results<sup>3</sup>. Comparison of log(Total) means suggests significant differences for 7.5% PVC versus 1.0 % PVC, Baseline, and 0 % PVC as well as for CaCl<sub>2</sub> versus Baseline, and 0 % PVC. A model of log(Total) for this group results in predictors selected quite similar to those already mentioned: TC5MAX and CO ( $R^2$  = 0.75,  $Q^2$  = 0.57).

### **ORGANOHALOGEN COMPOUNDS**

Vol. 46 (2000)

The tetra-CDD homologue dominated the PCDD ng/kg values (tetra- to octa-chlorinated) with few exceptions. The 2,3,7,8,-TeCDD isomer dominated the PCDD I-TEQ value. The tetra-CDF homologue dominated the PCDF ng/kg values (tetra- to octa-chlorinated) without exception. The isomer 2,3,4,7,8-PeCDF contributed approximately 50% of the PCDF I-TEQ value. The PCDF/PCDD ratio is always > 1. Only one run (0 % PVC) resulted in TEQ values where inclusion of NDs and estimated maximum potential concentration (EMPC) values had any substantial (< 10 %) effect, likely due to this run's low PCDD/F emissions. In all other runs, the TEQ compounds were unambiguously detected.

The results indicate that a high degree of PCDD/F emission variation can be expected due to factors not wholly related to waste composition or burning practice. Random factors, such as waste orientation, likely play a significant role in affecting combustion conditions (as observed, for example, by thermocouple variations) and, hence, emissions. Statistical modeling of the results offers support for this possibility, through selection of temperature-related predictors. The lower emissions from the Open burn, as compared to the same-composition Baseline runs, underscore the role of burning practice and/or waste orientation effects. While the wide variation in PCDD/F emissions and limited number of runs preclude unambiguous determinations of differences due to composition and burn condition factors, several trends seem apparent. PCDD/F emissions increase with higher amounts of Cl, whether organic or inorganic, and higher amounts of Cu catalyst. Test runs at alternative burn conditions (Compress, Wet, Double) resulted in higher mean PCDD/F emissions (543 ng TEQ/kg) and a 3-fold increase in the standard deviation of the TEQ value from that of the Baseline runs. These results, coupled with that of the lower-emitting Open burn, suggest widely variant PCDD/F emissions from uncontrolled domestic waste burning. These emissions are partially dependent on practice- and composition-related factors as well as random waste orientation.

### References

- Lemieux, P. (1997) Evaluation of Emissions from the Open Burning of Household Waste in Barrels, Vol. 1. Technical Report, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC. EPA/600/R-97-134a (NTIS PB98-127343).
- 2. Lemieux, P., Lutes, C., Abbott, J., and Aldous, K. (2000) Environ. Sci. Technol. (in press).
- 3. Gullett, B., Lemieux, P., Lutes, C., Winterrowd, C., and Winters, D. (2000) Chemos. (in press).
- U.S. EPA (1998) The Inventory of Sources of Dioxin in the United States, Review Draft, EPA/600/P-98-002Aa (NTIS PB98-137037), National Center for Environmental Assessment, Washington, D.C.
- Barnes, D. (1989) Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, D.C. EPA/625/3-89-016 (NTIS PB90-145756).

ORGANOHALOGEN COMPOUNDS Vol. 46 (2000)