# Formation and Sources II

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

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#### Introduction

Considerable uncertainty exists in the inventory of polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) emissions from uncontrolled combustion sources such as Abackyard@ burning of domestic waste. The contribution from these sources to the worldwide PCDD/F balance may be significant, but few quantitative sampling programs have yet assessed the potential for emission from these sources.

The EPA=s inventory of PCDD/F sources in 1998 (U.S. EPA, 1998) based its estimate of the backyard barrel burn emission factor [140 ng PCDD/F toxic equivalency (TEQ)/kg waste] on limited available sampling data (Lemieux, 1997) and on an activity level (8 x 10<sup>9</sup> kg waste burned/year) derived from assumptions regarding the frequency and number of backyard barrel burns in the U.S. The contribution from backyard barrel burn sources was estimated to be 1,000 g TEQ/y, making this one of the potentially largest sources in the U.S. In order to begin the process of more adequately characterizing this source, a series of barrel burn tests using domestic waste was conducted with the intent of developing an understanding of the causal factors behind barrel burn emissions.

## **Experimental**

Combustion studies were performed at the EPA=s Open Burning Test Facility or Aburn hut@ (see Lemieux, 1997) to provide an initial determination of the impact of limited variation in waste composition on combustion conditions and PCDD/F emissions from a simulated domestic, backyard barrel burn. A composition representative of domestic household waste was prepared for testing based on the typical percentages of various materials characterized and quantified by the New York Department of Environmental Conservation=s Division of Solid Waste (see Lemieux, 1997). This synthesized domestic household waste primarily consisted of actual unshredded house waste. Each batch was constructed of the same specific waste types combined together such that each test had the same composition with the exceptions noted below. Each test consisted of 15 kg of waste, randomly mixed in a concrete mixer and dumped en masse into the test container. Variation from the baseline composition (0.2 % by weight polyvinyl chloride, PVC) consisted of testing at three different PVC levels (0.0, 1.0, and 7.5 % by wt) using pipe forms. PVC levels were effected through substitution of high density polyethylene (HDPE) and iron conduit (both also in pipe form), in an effort to approximate consistent physical and energy properties of the waste across all batches while varying chlorine (Cl). Inorganic Cl levels were derived by soaking a portion of the waste in a calcium chloride (CaCl<sub>2</sub>)-based deicer followed by drying.

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To represent the most common practice for residential waste burning, the test container consisted of an aged, 208 L (55 gal) steel barrel with twelve 2 cm diameter ventilation holes around the base. Prior to testing, the barrel was sandblasted to remove residual paint and any remaining contents that might affect emissions. The barrel was placed on an electronic scale platform to allow the mass consumed by combustion to be continuously monitored. An aluminum skirt was placed around the outer circumference of the barrel to minimize the potential for reburning of combustion gases. High volume air handlers provide metered dilution air into the burn hut. Additional fans were set up inside the burn hut to enhance recirculation within the hut. The hut is lined with Tedlar7. Type K thermocouples (TC1-6) were inserted into the barrel at regularly spaced heights and radial locations from the bottom, within and above the waste.

Before the initiation of each test, the material to be combusted was placed in the barrel, air flow through the facility was initiated, and 15 min of background data were obtained. These data came from continuous emission monitors (CEMs) which sampled for oxygen ( $O_2$ ), carbon dioxide ( $CO_2$ ), and carbon monoxide ( $CO_3$ ) from the gas stream of the exhaust gas duct. Particulate matter (PM) with an aerodynamic diameter < 2.5  $\mu$ m (PM<sub>2.5</sub>) was measured using a dichotomous sampler placed inside the burn hut. Sampling for PCDD/Fs and PCBs (the latter not covered in this paper) was completed via an ambient air Graseby PS-1 sampler located within the test facility and operated for about 1.5 h (2.2 - 2.5 ft³/min). The PCDD/F/PCB train consisted of an open-faced filter holder followed by a polyurethane foam (PUF)-sandwiched XAD-27 bed vapor trap. The combined filter and vapor-phase module was analyzed using high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). Sampling and analytical methods follow those of Lemieux (1997).

The material to be combusted was lit for a short period (<3 min) using a propane torch inserted into a hole midway up the side of the barrel. Sampling was initiated at least 2 min after the removal of the propane flame. Samples were collected over the course of the active burn, and sampling was terminated when the burn mass did not change over an extended period. Blank tests (tests without waste combustion) were also sampled to ensure that the sampling and analysis methods as well as the feed air were not biasing the test. Estimated emissions of PCDD/Fs per unit mass burned were calculated using the concentration of the pollutant in the sample, the flow rate of dilution air into the burn hut, the run time, and the mass of waste burned. When analyzing and reporting the results, all non-detects (NDs) and incidences of questionable analytes were set to equal zero. TEQ values were calculated using toxic equivalent factors (TEFs) from EPA=s interim procedures for assessing PCDD/F risk (U.S. EPA, 1989).

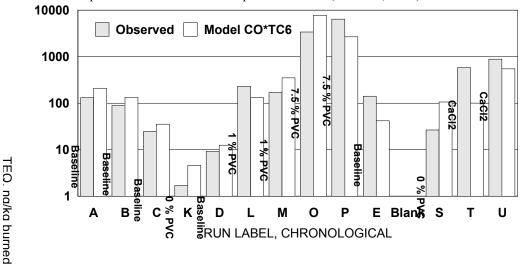
## **Results and Discussion**

Measured PCDD/F values for various fuel compositions are shown in Fig. 1 (shaded bars) on a logarithmic scale. The emissions from the five Baseline runs (constant composition, 0.2 % PVC) varied over 1 order of magnitude and averaged 79 ng TEQ/kg burned (std dev = 60). The average emissions from the 0.0, 1.0, and 7.5% PVC are, respectively, 14, 201, and 4916 ng TEQ/kg burned. Two tests with inorganic Cl ( CaCl<sub>2</sub>) at the same level of Cl found in the 7.5% PVC sample and without any PVC averaged 734 ng TEQ/kg burned. Qualitative comparisons suggest that the runs with higher Cl, both PVC and CaCl<sub>2</sub>, result in a substantial increase in TEQ values.

Tetra-CDF dominated the homologue profiles, the isomers 1,2,3,4,7,8-hexa-CDF and 1,2,3,4,6,7,8-hepta-CDF were the most prevalent of the 2,3,7,8-Cl-weighted isomers, and the TEF-weighted 2,3,4,7,8-penta-CDF dominated the TEQ value.

Only one run (K) resulted in TEQ values for which inclusion of NDs and EMPCs had any substantial effect. In many of the runs, ND and EMPC values had no effect on the TEQ because all of the TEQ compounds were unambiguously detected.

Comparison of these results with previous results (Lemieux, 1997) is tenuous due to some



differences in composition and experimental procedures. Nonetheless, for purposes of examining the ability of discrete testing to determine ranges of emissions factors, the average of the 1 and 7.5% by wt PVC results for total PCDD [sum, tetra- to hepta-CDD since the OCDD blank values for Lemieux (1997) were unreliable] and PCDF (sum, tetra- to octa-CDF) is 0.017 mg PCDD/kg burned and 0.099 mg PCDF/kg burned. These compare well with values from Lemieux (1997) of 0.041 mg PCDD/kg burned and 0.220 mg PCDF/kg burned (for the average 4.5% PVC, Arecycler@ wastes).

Analyses were conducted to discern the significance of monitored run condition parameters in predicting run-specific TEQ values. Predictive models for TEQ (ng/kg burned) were constructed by choosing among continuous measured parameters, and their logarithms and products, of average thermocouple temperatures (TC1 to TC6); average CEM values including CO, CO<sub>2</sub>, and O<sub>2</sub>; PM<sub>2.5</sub>, the time and rate when the waste is at maximum burn rate; composition parameters of Cl wt %, CaCl<sub>2</sub> wt %, and PVC wt %; and values derived from time-weighted temperature intervals (TS1 = 250 to 450 °C and TS3 = 300 to 400 °C) approximating the PCDD/F formation Awindow.@ Due to the limited sample size (N=13), analyses were carried out in sequential procedures, adding and evaluating predictors to determine those that were most significant in predicting log(TEQ). Results of the statistical analyses on these limited data suggest

that the logarithm of waste Cl content (LOGCL), the CO concentration, and the cross product of CO\*TC6 (or TC5) represent some of the best available (highest  $R^2$ ), single-term models of TEQ emissions. Increases in each of these terms result in higher predicted TEQ values. Additional criteria of predictor significance (p values), semi-partial correlations ( $R^2_{SP}$ ), and predictor minimization suggest selection of CO\*TC6 as an optimal model for TEQ values. This suggests that burn condition parameters are better indicators of emissions than composition parameters (Cl) alone. The  $R^2_{SP}$  = 0.834 suggests that over 83% of the variance in the observed TEQ values are predicted by varying CO and TC6 throughout their experimentally observed range. Figure 1 shows the run-specific predictions of the model. More work will be necessary to understand how variables, such as waste composition and waste packing, affect burn condition parameters and, hence, PCDD/F emissions.

### **Conclusions**

Total PCDD/F emissions are approximately within a factor of 2 of earlier, more limited results (Lemieux, 1997), providing general confirmation of the potential emissions from these sources. TEQ values ranged over 3 orders of magnitude, from less than 10 ng TEQ/kg to over 6000 ng TEQ/kg, bracketing the 140 ng TEQ/kg predicted in the EPA source inventory document (U.S. EPA, 1998).

Cl concentration alone, whether from PVC or CaCl<sub>2</sub>, adequately predicted emissions from both Cl sources. Nonetheless, the five Baseline runs, at constant waste composition (Cl content) and with careful duplication of procedures, resulted in over an order of magnitude variation in emissions. Differences in monitored burn conditions, which could have occurred either as a result of Cl composition changes and/or random variation, were better predictors of emission levels than Cl content. The product of CO and an above-waste temperature value (TC6) result in a better predictive model of PCDD/F TEQ values than Cl concentration. Higher values of CO, TC6, and Cl result in higher TEQ values.

Additional research is necessary to understand the causal factors that affect emissions, the common composition and its effects, the typical burning procedures, and the activity level of this burning practice for an adequate characterization of PCDD/F emissions from barrel burning sources.

#### References

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