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Dioxin Formation: The Burn Barrel Study

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ABSTRACT

The uncontrolled burning of household waste in barrels has recently been implicated as possibly being a major source of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs). In addition to PCDDs/Fs, other similar pollutants such as coplanar polychlorinated biphenyls (PCBs) are also emitted from burn barrels. This paper reports results from tests that were designed to examine some of the factors influencing the emissions of PCDDs/Fs from burn barrels. Results from PCDDs/Fs and PCBs are reported, along with results from statistical analyses of the influence of waste compositional and combustion variables on their emissions.

Introduction

Previous Results

The uncontrolled burning of household waste in barrels is a common activity in rural areas of the U.S. and is a primary waste management technique in many parts of the developing world. This activity typically consists of a household's placing their garbage in a 208 L (55 gal.) drum called a "burn barrel," and after a period of time when a sufficient quantity of garbage has accumulated in the burn barrel, the waste is ignited and burned over a period of several hours.

The EPA's Control Technology Center (CTC) received numerous requests from state and local agencies requesting information on emissions from burn barrels. In response to these requests, the CTC funded a study performed by EPA's Air Pollution Prevention and Control Division (APPCD), in collaboration with the New York State Department of Health (NYSDOH), to characterize the emissions of many pollutants from a limited number of burn barrels. Pollutants measured during this study included fixed combustion gases (e.g., carbon monoxide [CO] and nitrogen oxides [NO_x]), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), particulate matter (PM), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs). The results from this study were published in an EPA report in 1997 [1]. Emissions of many pollutants were significant. Initial observations suggested that emissions of PCDDs/Fs were significant enough that burn barrels could potentially be a major national source of airborne PCDDs/Fs, given moderate estimates of frequency of this practice.

Lemieux et al. performed further data analyses on the PCDD/F data from the 1997 report, in an attempt to see if any trends could be observed that may suggest a causal relationship between waste composition and burn conditions and emissions of PCDDs/Fs [2]. Although apparent relationships between PCDD/F emissions and airborne hydrochloric acid (HCl) and copper (Cu) emissions were observed, there were not sufficient data points available to make rigorous statistical analyses. In addition, the 1997 report showed significant variability between duplicate runs. Finally, the study reported in the 1997 report utilized low resolution mass spectrometry (LRMS) to perform the analyses, which resulted in some of the individual PCDD/F isomer concentrations falling below the lowest analytical calibration point. This made it difficult to reliably estimate the emissions of PCDDs/Fs in terms of toxic equivalency units (TEQs), which is a weighted measure of the biological behavior of PCDDs/Fs in living organisms [3]. High resolution mass spectrometry (HRMS) could be used to improve measurement sensitivity so that TEQs could be accurately calculated.

The limited amount of data and high degree of variability confounded efforts to incorporate burn barrels into the U.S. dioxin inventory [3]. In an effort to reduce the uncertainty in the emissions estimation, EPA's Office of Pesticides, Prevention, and Toxic Substances (OPPTS) funded additional testing on burn barrels so that the emissions of PCDDs/Fs can be characterized as a function of waste composition, burn conditions, and other physical properties of the waste in the barrels (e.g., degree of compaction and wetness). Initial results from these follow-on tests were reported by Gullett et al., [4,5], who found that waste composition parameters (e.g., chlorine [Cl] content, Cu emissions) and combustion conditions (e.g., barrel temperature distributions, and CO concentrations) can statistically account for the variability of PCDDs/Fs between runs. This paper will discuss those results in light of additional data on emissions of PCBs from burn barrels and will discuss the contributions of the PCBs to the TEQ emissions.

PCDD/F and PCB Formation Mechanisms

Extensive research has been conducted to investigate the formation mechanisms of PCDDs/Fs in the years since PCDDs/Fs were first discovered in the exhaust gases from municipal waste combustors (MWCs) in 1977 [6]. Since then, multiple formation mechanisms have been proposed [7-13]. Field studies on MWCs have shown that the amount of flyash (and its accompanying metallic catalysts) and organic precursors that pass through the temperature window between 250 and 700 °C, as well as the amount of time spent in that optimal temperature window, are the primary variables affecting PCDD/PCDF emissions [14]. Field studies have been unable to clearly demonstrate a correlation between Cl input and PCDD/F emissions in full-scale combustion systems, probably because other variables (PM carryover, PM control device temperature, and combustion efficiency) dominate [15]. It is the authors' view that Cl is present in excess relative to the other reactants in these systems. Based on current PCDD/PCDF formation theories, a "worst-case scenario" for formation of PCDDs/Fs from combustion systems would combine:

- poor gas-phase mixing,
- low combustion temperatures,
- oxygen-starved conditions,
- high PM loading,
- PM-bound Cu,
- presence of HCl and/or Cl, and
- significant gas-phase residence time in the 250-700 °C temperature range.

Barrel burning is a combustion source that appears to fit the requirements for such a worst-case scenario for production of PCDDs/Fs.

There are data in the literature to support the hypothesis that in combustion systems, along with PCDDs/Fs, other similar chlorinated organic compounds are produced through a similar heterogeneous mechanism. These additional compounds include PCBs and polychlorinated naphthalenes (PCNs) [16,17]. Certain of the PCBs -- the coplanar isomers -- exhibit behavior in biological systems similar to PCDDs/Fs, and are termed the "dioxin-like" PCBs and have associated toxic equivalency factors (TEFs) that are used to calculate the contribution of coplanar PCBs to the TEQ estimate [18].

This paper will focus on waste composition and combustion variables that affect emissions of PCDDs/Fs from burn barrels, and examine the relative contribution of coplanar PCBs to the TEQ. In addition, this paper will investigate whether the waste combustion variables that influence emissions of PCDDs/Fs also influence PCB emissions.

EXPERIMENTAL

Combustion studies were performed at the EPA's Open Burning Test Facility or "burn hut" [1] 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 State Department of Environmental Conservation's Division of Solid Waste [1]. This synthesized domestic household waste primarily consisted of actual unshredded household waste. Each batch was constructed of the same specific waste types combined such that each test had the same composition, except as noted in Table 1. Each test consisted of 15 lb (6.8 kg) of waste, randomly mixed for a brief time 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 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 Cl. Inorganic Cl levels were derived by soaking a portion of the waste in a calcium chloride ($CaCl_2$)-based deicer followed by drying. Additional plastic components included polystyrene (PS) and polyethylene terephthalate (PET).

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 the testing described in Reference [1], 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 recirculation of combustion gases back through the air inlet holes. 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 was lined with Tedlar®. Type K thermocouples 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 CO from the gas stream of the exhaust gas duct.

PM with an aerodynamic diameter < 2.5 μm ($PM_{2.5}$) was measured using a dichotomous sampler placed inside the burn hut. Sampling for PCDD/Fs and PCBs was completed via an ambient air Graseby™ PS-1 sampler located within the test facility and operated for about 1.5 h at between 0.062 and 0.071 m^3/min (2.2 and 2.5 ft^3/min). The PCDD/F/PCB train consisted of an open-faced filter holder followed by a polyurethane foam (PUF)-sandwiched XAD-2® 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 previously reported [4].

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 and PCBs 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 the World Health Organization (WHO) [18].

RESULTS AND DISCUSSION

Table 2 lists the PCDD/F data from 18 runs (runs are listed in chronological order not alphabetical order). PCB data are also included in Table 2 for the 10 runs which analyzed for PCBs. The data are represented in nanograms per kilogram waste consumed. Data are also presented in TEQ units of nanograms per kilogram waste consumed, both with and without including PCBs in the TEQ calculations. The PCDD/F emission values range over many orders of magnitude.

Analyses were conducted to discern the significance of monitored run condition parameters in predicting run-specific TEQ values. Predictive models for TEQ (ng/kg consumed) were constructed by choosing among continuous measured parameters of average thermocouple temperatures (TC1 to TC6); average CEM values including CO, HCl, CO_2, and O_2; $PM_{2.5}$, Cu emissions, the time (MAXTIME) and rate (MAXBURN) when the waste is at maximum burn rate (in kilograms per hour); composition parameters of Cl wt %, $CaCl_2$ wt %, and PVC wt %; and values derived from time-weighted temperature intervals (TS2 = 250 to 450 °C and TS3 = 300 to 400 °C; TS2 and TS3 represent the number of TC samples in the barrel that were within the listed temperature range over the entire run). Analyses consisted of fitting multiple regression models using SAS® procedure REG/SELECTION=RSQUARE [19] using single, paired, and logarithmic values of these parameters in order to arrive at a prediction of log(TEQ). Use of logarithms was thought necessary to compensate for the highly skewed distributions of actual yields. Due to the limited number of runs and compositional variations, only models with up to three predictors were considered. The principal criterion for model selection was maximization of 1) PRESS R^2, which equals 1 - PRESS/SST, where PRESS is the predicted residual sum of squares obtained by cross-validation (calculated by excluding the observation from the prediction calculation), and SST is the residual sum of squares corrected for the mean only and 2) the model squared multiple correlation coefficient (R^2). In addition, the effect of each selected predictor was required to be significant in the model, ideally requiring p 0.05. Exclusion of potential predictors from these models suggests that, at least under the test conditions explored here, these variables were not sufficient to significantly alter overall model R^2, and hence were relatively less important in suggesting mechanisms of formation. Table 3 lists the variables that were found to be statistically significant predictors of log(TEQ) [4].

There were not sufficient PCB data to conduct as rigorous a statistical analysis. However, it is useful to visualize how emissions of PCBs track with emissions of PCDDs/Fs. Figure 1 shows the homologue profile of the PCBs, and Figure 2 shows the homologue profile for the PCDDs/Fs for a typical run (Run A). Both profiles are consistent in that the emissions decrease as the number of substituted chlorines increase. In fact, for the PCBs, only the two cases with 7.5% PVC showed any nona- and deca-substituted PCBs, and only one of the baseline cases showed low levels of octa-PCB.

Figure 3 shows how emissions of total PCBs track with total emissions of PCDDs/Fs. As PCDDs/Fs increase, a resulting increase in PCBs is observed. This is consistent with current theories that postulate the simultaneous formation of an entire class of chlorinated organic compounds, which contain PCDDs/Fs, PCBs, and PCNs [16,17]. In these experiments, PCNs were not targeted as analytes. This observation suggests that the same independent variables that control PCDD/F formation could also control PCB formation.

Figure 4 plots emissions of PCBs vs. emissions of PCDDs/Fs in TEQ units. A similar trend is observed that tracks with total emissions. However, a major difference between Figures 3 and 4 is that, although emissions of total PCBs are significantly higher than total emissions of PCDDs/Fs, the contribution to the TEQ from PCBs is significantly lower than for PCDDs/Fs. Table 2 shows that the TEQ contribution due to PCBs ranged from 0.02 to 7.4% of the TEQ due to PCDDs/Fs. This is because the PCB isomers that have been assigned TEFs by the WHO were not formed in significant concentrations from barrel burning. Based on the observation that the concentrations of the coplanar PCBs were very low relative to the total PCBs within each homologue group, by difference, the remainder must be the non-planar PCBs. The non-planar PCBs that were formed in much more significant concentrations are not included in TEQ calculations, which utilize a cancer endpoint based on Ah-receptor activity [18]. The low emissions of coplanar PCBs is probably due to a mechanistic effect resulting from the combination of chlorinated organic precursors in such a way as to promote asymmetric distribution of chlorines around the PCB molecule.

CONCLUSIONS

A series of tests were performed to investigate emissions of PCDDs/Fs from open burning of household waste in barrels. These tests were systematically performed so that emissions could be characterized as a function of waste composition, physical properties, and combustion-related parameters, and so that variability could be measured between duplicate test conditions. A subset of those tests included sampling and analysis for PCBs.

Statistical analysis of the PCDD/F data relative to the waste composition parameters, physical preparation parameters, and measured combustion variables yielded models that were able to successfully explain the variability in the PCDD/F data. The resulting predictors could be grouped into two classes: variables related to the waste composition and experimental setup; and variables related to the combustion occurring in the barrel. Both types of variables were necessary to include in the statistical model to maximize the model fit. Important variables include barrel temperatures, CO, Cu, and HCl concentrations, and waste Cl content (independent of the form of the waste Cl).

Emissions of PCBs showed the same general trends as emissions of PCDDs/Fs. Total PCB emissions were significantly higher than PCDD/F emissions; however, TEQs due to PCBs were much lower than TEQs due to PCDDs/Fs. TEQs due to PCBs ranged from 0.02 to 7.4% of those of PCDDs/Fs. Although emissions of PCBs as a chemical class were significant, barrel burning did not result in the formation of significant levels of the coplanar, or dioxin-like PCBs. This phenomenon is likely due to a mechanistic effect that promotes the formation of the non-planar PCBs.

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