Emissions of PCDD/F from uncontrolled, domestic waste burning

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Abstract

Emissions of polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) result from inefficiencies of combustion processes, most typically waste combustion. Uncontrolled combustion, such as occurs during so-called "backyard burning" of domestic waste, may therefore produce optimal conditions for formation and emission of PCDD/F. However, few assessments of PCDD/F emissions are available from these sources. This work describes the first known comprehensive assessment of PCDD/F emissions from uncontrolled, domestic waste burning. Emissions were copious, but highly variable, ranging over several orders of magnitude. The potential for emissions appears to be related primarily to combustion parameters and concentrations of various gas-phase species, the latter which may be affected by changes in waste composition, waste orientation, and/or combustion conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dioxin; Household waste; Barrel burns; Combustion; Air pollution; Persistent organic pollutants

1. Introduction

Considerable uncertainty exists in the inventory of polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) emissions from uncontrolled combustion sources such as "backyard" 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 draft inventory of PCDD/F sources (US EPA, 1998) attempted to make a national emissions estimate for backyard burning of domestic waste in barrels, using an emission factor of 140 ng PCDD/F toxic equivalency (TEQ)/kg waste (based on Lemieux, 1997) and an estimated activity level of 8×10^9 kg waste burned/year. The national emissions from backyard barrel burn sources was estimated to be greater than 1000 g TEQ/y although the uncertainty in this estimate was too great for it to be included in the EPA's quantitative inventory of PCDD/F sources. This preliminary estimate is sufficient, however, to demonstrate that backyard barrel burning of waste has the potential of being a major PCDD/F source in the US. To reduce the uncertainty associated with estimating emissions from this source, a better understanding of the causal factors controlling barrel burn emissions is needed. This understanding will help both in developing more representative emission factors and in better characterizing

activity levels. This paper presents results from an expanded series of barrel burn tests designed to elucidate these causal factors.

2. Experimental

Combustion studies were performed at the EPA's Open Burning Test Facility 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). Table 1 presents the composition of the baseline domestic household waste. This synthesized domestic household waste primarily consisted of actual unshredded house waste. Each batch was constructed of the same specific waste types combined such that each test had the same composition with the exceptions noted below. Each test consisted of typically 6.8 kg of this waste, randomly mixed in a concrete mixer and dumped en masse into the test container. Variations to the

baseline tests included both changes in waste composition and in burning conditions. Variation from the baseline composition consisted of testing at four different levels (0.0%, 0.2%, 1%, and 7.5% by weight) of polyvinyl chloride (PVC) 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 the newsprint in a calcium chloride ($CaCl_2$)-based deicer followed by drying. One test was conducted with the waste (baseline composition) compressed piston-like by the application of a technician's weight on a disk of diameter just less than that of the barrel. A test with additional copper (Cu) was conducted by increasing the fraction of Cu wire while reducing ferrous metals and glass/ceramics. A "wet" test to simulate high moisture burns was conducted by soaking half of the newsprint in 1 l of water.

To represent the most common practice for residential waste burning, the test container consisted of a 208 l (55 gal) steel barrel with 2 cm diameter ventilation holes around the base. Prior to testing by (Lemieux et al. 1997), the barrel was sandblasted to remove residual paint and any potential remaining contents that might

Table 1
Baseline waste composition[a]

Waste category	Waste description	Target wt%
Paper	Newpaper, books, office paper	32.8
	Magazines and junk mail	11.0
	Corrugated cardboard, kraft paper	7.6
	Paperboard, milk cartons, drink boxes	10.3
Plastic resin	PET #1, soda bottles	0.6
	HDPE #2,detergent bottles, pieces	6.6
	PVC #3, schedule 40 pipe	0.2
	PS #6, food trays	0.1
	Mixed #7, Poly-Fil polyester	0.1
Food waste	Frozen processed potatoes	5.7
Textile/leather	Rubber and leather sneakers	3.7
Wood	Chipboard, plywood	1.1
Glass/ceramics	Bottles, jars	9.7
	Broken ceramics, flower pots	0.4
Metals (ferrous)	Iron (cans), dog food cans	7.3
Metals (non-ferrous)	Aluminum cans, foil, soda cans	1.7
	Wire, copper pipe, batteries	1.1
Total		100

[a] Inorganic chlorine tests were conducted with calcium chloride ($CaCl_2$)-saturated newspapers (using Prestone Driveway Heat[TM]) such that [Cl] = 7.5 wt%. HDPE #2 = 3.3 wt%, 224.53 g; PVC = 0 wt%, 0 g; iron cans = 3.3 wt%, 224.53 g; The 0 wt% PVC test consisted of HDPE #2 = 6.7 wt%, 455.86 g; PVC = 0 wt%, iron cans = 7.4 wt%, 503.49 g; The high Cu mix test consisted of bottles/jars = 8.7 wt%, 591.94 g; iron cans = 6.4 wt%, 435.45 g; wire, copper pipe, batteries = 3 wt%, 204.12 g.

bias emission measurements. 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 through the barrel. High volume air handlers provided metered dilution air into the burn hut, resulting in 2.5 volume changes per min. Additional fans were set up inside the burn hut to enhance recirculation within the hut. The hut is lined with Tedlar®. Type K thermocouples were inserted at prescribed heights and radial locations from the bottom to the top of the waste-filled barrel, labelled TC1 to TC6, respectively, for data collection throughout each run.

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) from the gas stream of the exhaust gas duct. Emissions of hydrogen chloride (HCl) and Cu were sampled and analyzed in general accordance with EPA Methods 26 (40 CFR, 1994) and 101A (40 CFR, 1991), respectively, except that isokinetic sampling procedures were not utilized since measurements were not made in a stack. Particulate matter (PM) with an aerodynamic diameter <2.5 μm ($PM_{2.5}$) was measured using a dichotomous sampler placed inside the burn hut (40 CFR, 1993). Sampling for PCDD/Fs and polychlorinated biphenyls (PCBs) (the latter not covered in this paper) was completed via an ambient air Graseby™ PS-1 sampler located within the test facility. This train, designed to comply with EPA's ambient sampling method TO-9 (Winberry et al., 1988), consists of an open-faced filter holder followed by a polyurethane foam (PUF)-sandwiched XAD-2 bed vapor trap. Because this sampler does not have a particulate size separation device, fairly low flow rates can be used. Given the expected high concentrations of analytes in these tests, this sampler was operated at approximately 62–71 l/min (2.2–2.5 ft³/min) for approximately 1.5 h. To cool the PUF cartridge during sampling, a copper cooling coil was fabricated to enclose the exterior of the PUF module. The combined filter and vapor-phase module was analyzed using high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) using EPA Test Method 8290 (US EPA, 1994).

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 several minutes. After the tests, the ash was removed and archived but not analyzed in this paper. This was the only method of cleaning the barrel between tests. Blank tests (tests without waste combustion) were also sampled to ensure that the sampling and analysis methods as well as the feed air are not biasing the test. Estimated emissions of PCDD/Fs per unit mass burned were calculated using

$$E = (C_{sample} Q_{hut} t_{run})/(m_{burned}),$$

where E is the estimated emissions in mg/kg burned; C_{sample} the concentration of the pollutant in the sample in mg/m³, Q_{hut} the flow rate of dilution air into the burn hut in m³/min, t_{run} the run time in min, and mf_{burned} is the mass of waste burned over the run in kg. These estimated emissions express a mass of analyte produced per mass of solid waste consumed in the combustion process. [Since m_{burned} is fairly constant for each run (70.8%, 1.8 σ), emissions calculated based on waste charge mass will have similar relative values.] When analyzing and reporting the results, all non-detects (NDs) and peaks that did not meet ion ratio criteria are set to equal zero. TEQ values were calculated using I-TEF values in (Barnes, 1989).

3. Results and discussion

Measured, chronological results of PCDD/F values for various fuel compositions and combustion conditions are shown in Fig. 1 (unshaded bars) on a logarithmic scale. The average baseline emissions (constant composition, 0.2% PVC) varied over 1 order of magnitude and averaged 79 ng TEQ/kg burned (S.D., $\sigma = 49$). The average emissions from the 0.0%, 1.0%, and 7.5% PVC are, respectively, 14, 201, and 4916 ng TEQ/kg burned. The two tests with added inorganic Cl averaged 734 ng TEQ/kg burned. Qualitative comparisons suggest that the runs with higher Cl, via PVC or $CaCl_2$, result in substantial increase in TEQ values.

The tetra-CDF homologue 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-substituted isomers, and the toxic equivalent
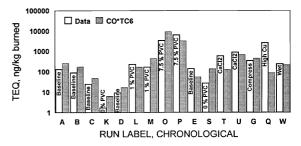

Fig. 1. PCDD/F emissions: measured data (unshaded bars) and modelled by CO*TC6 (shaded bars).

factor (TEF)-weighted 2,3,4,7,8-penta-CDF dominated the TEQ value.

Only one run (K) resulted in TEQ values where inclusion of NDs and EMPC values 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.

Analyses were conducted to discern the significance of monitored run condition parameters in predicting run-specific TEQ values. It was hoped that these models would enable determination of the most critical factors that effect and, hence, limit, emissions. Predictive models for TEQ (ng/kg burned) were constructed by choosing among continuously measured parameters of average thermocouple temperatures (TC1 to TC6); sampled HCl, average CEM values including CO, CO_2, and O_2; $PM_{2.5}$, Cu emissions, the time (MAXTIME) and rate (MAXBURN) when the waste is at maximum burn rate; composition parameters of Cl wt% [Cl] [based on Cl in PVC ($\approx$60%) and in $CaCl_2$ ($\approx$64%)], $CaCl_2$ wt%, and PVC wt%; and the duration (in min) that in-barrel thermocouple temperatures were within the common formation window temperature (TS1 = 250°C to 450°C and TS3 = 300°C to 400°C). Analyses consisted of fitting multiple regression models using SAS® procedure REG/SELECTION = RSQUARE (SAS, 1990) 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 the probability, $P \leqslant 0.05$. 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.

Due to the limited sample size ($N = 16$) and large number of potential predictors, analyses were carried out in sequential procedures, adding and evaluating predictors to determine those that were most significant in predicting log(TEQ). Table 2 shows the results for select one- to three-predictor models, illustrating the effect of choice and number of predictors upon loss or gain of R^2. The most significant one-predictor model actually contains an interactive term, CO*TC6, which is the product of the CO emissions and the temperature at the uppermost portion of the barrel. This model explains over 71% of the observed variation in log(TEQ) and is shown as the shaded bars in Fig. 1. CO alone is the best, one-predictor, one-term model, explaining almost 60% of the log(TEQ) variation. The logarithm of Cu emissions or waste Cl content is also significant (based on its $P < 0.05$), but considerable loss of R^2 indicates that it is not as effective at predicting emissions as the aforementioned models. Inclusion of additional parameters can often result in significant improvement in model R^2, albeit with P values indicating that the predictors are not significantly distinct from zero (for example, TS2 and CO*TC6, where $P_{TS2} > 0.05$). A select, two-predictor model [log(Cl), log(Cu)] indicates that waste Cl content and emissions of Cu result in a slightly better model than CO alone.

Results of the statistical analyses of these limited data indicate that combustion measurements such as emissions of CO, Cu, and HCl in conjunction with temperature (TC6) and waste Cl content are among the most significant predictors of TEQ emissions. Among the compositional variables, the fuel chlorine content [log(Cl)] rather than the form (PVC or $CaCl_2$), is more significant. Emissions of HCl are easily related to variation in waste composition, while emissions of Cu, whose

Table 2
One- to three-predictor models of log(TEQ)

No. of predictors	PRESS R^2	R^2	Predictor(s)	P value(s)
1	0.638	0.718	CO*TC6	<0.0001
1	0.494	0.591	CO	0.0005
1	0.369	0.559	log(Cu)	0.0009
1	0.322	0.468	log(Cl)	0.0035
2	0.652	0.779	TS2, CO*TC6	0.0783, <0.0001
2	0.633	0.762	MAXBURN, CO*TC6	0.1447, <0.0001
2	0.525	0.723	log(Cl), log(Cu)	0.0043, 0.0159
2	0.446	0.751	log(Cu), log(HCl)	0.0052, 0.0848
3	0.607	0.848	TS3, log(Cu), log(HCl)	0.0536, 0.0011, 0.0342

waste level differed for only one run (Run Q), are related to measurements of combustion characteristics, such as CO and temperature. These combustion measurements are only weakly correlated with the composition variation and appear more likely to be affected by unmeasurable variables of waste orientation and proximity.

4. Conclusions

Total PCDD/F emissions are within a factor of approximately 2 of earlier, more limited results (Lemieux, 1997), providing general confirmation of the potential emissions from backyard barrel burn sources. TEQ values 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 (US EPA, 1998).

These limited results suggest that barrel burn PCDD/F emissions (ng TEQ/kg burned) are dependent on both composition and burn condition variables. Variation of two compositional variables, PVC content and Cl type (organic and inorganic), shows that their effects on TEQ values both can be represented by a single parameter of total Cl concentration. The tests also indicate that in the absence of any added Cl source (PVC or $CaCl_2$), PCDD/F emissions (Run S) are within the range of the baseline results (Runs A to E). Burn conditions appear also to affect yields, in a manner that may be independent of Cl content. This limited work shows that these conditions are best predicted by terms indicative of combustion characteristics, CO*TC6, which provide the best predictive model of PCDD/F TEQ emissions. Gas-phase emissions of Cu, a known catalyst for organohalogen synthesis, were a predictor for TEQ values, implicating the role of combustion conditions in affecting emissions. Variation in combustion conditions appears to be only weakly related to composition changes and is more likely related to the random orientation of waste and waste proximity factors in the barrel. These phenomena are likely responsible for the order of magnitude variation observed in baseline composition TEQ results.

Additional research is necessary to understand the causal factors that affect emissions, the common waste 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.

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