

PCDD/F, PBDD/F, and PBDE Emissions from Open Burning of a Residential Waste Dump

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This work reports on the first known field study determining emission factors for polychlorinated and polybrominated dibenzodioxins/dibenzofurans (P[C/B]DDs/Fs) and polybrominated diphenyl ethers (PBDEs) from open burning of domestic waste. Two burning waste dump sites in Mexico were sampled using high-volume samplers mounted to a mobile sampling boom. Concurrent measurements of CO and CO₂ allowed determination of emission factors via the carbon balance method. PCDD/F emission factors averaged 823 ng toxic equivalency (TEQ)/kg C_{burned} (*N* = 8, 68% relative standard deviation, RSD), a value at least five times higher than those from previous tests with domestic waste burned in barrels and approximately 2000 times higher than those from stacks of modern municipal waste combustors. These emission factors appear to be related to combustion quality, as conditions conducive to smoldering combustion, rather than flaming combustion, resulted in higher emission factors. Emissions of 40 PBDE congeners, likely originating from brominated flame retardants, averaged 724 μg/kg C_{burned} (RSD = 96%) and had congener patterns similar to those of reported atmospheric sampling. Emissions of PBDDs/Fs were similar in magnitude to their chlorinated counterparts, averaging 470 ng TEQ/kg C_{burned} (RSD = 105%), and may originate as reaction products of PBDE combustion or as thermally desorbed impurities from the PBDE flame retardant.

Introduction

For developing countries or locations without centralized waste collection and treatment, burning domestic waste at the domicile or local dump is a common, albeit sometimes illegal, practice to minimize volume and vector hazard. The

potential mix of refuse, hazardous household wastes (plastic bags, paints, solvents, discarded electronic wastes), and discarded tires can be problematic when combined with poor combustion conditions, resulting in significant levels of trace pollutant formation. Emissions from open, uncontrolled burning of domestic waste in dumps are believed to be a significant, if not dominant, source of global polychlorinated dibenzodioxins and furans (PCDDs/Fs). In the past decade, these sources of PCDD/F have been increasingly documented in national inventories as required of signatories to the Stockholm Convention on Persistent Organic Pollutants (1). Combustion of domestic products containing common brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) may also lead to concurrent emissions of PBDEs (2, 3) and polybrominated dibenzodioxins and furans (PBDDs/Fs). The PBDEs and PBDDs/Fs are of growing concern due to the increased use of brominated flame retardants in consumer goods. Their release from combustion processes represents an additional exposure pathway to the commonly cited indoor air/ingestion route. PBDE levels in breast milk have been rising at alarming rates in the last ten years (4, 5), have been linked with health effects (2), and various PBDE technical formulations have been consequently banned or restricted from use (6). Impurities of commercial technical mixes of BFRs and their potential thermal breakdown products include PBDDs/Fs (7, 8). PBDDs/Fs reportedly have toxicities (9, 10) and persistence similar to PCDDs/Fs and have been found in human tissue, blood, and milk samples (11–14), but remain virtually undocumented from combustion sources.

Significant uncertainty exists with trace pollutant emission factors for open burning of domestic waste. Despite this, limited measurements to determine PCDD/F emission factors from burning dumps have been made. PCDD/F concentrations were measured in the air of a burning landfill (15) and estimations of the plume size, wind velocity, and waste amount resulted in an approximate emission factor of 3.5–7.5 ng (Eadon)/kg of waste burned. Ruokojärvi et al. (16) also sampled a burning landfill fire but their concentrations could not be related to the amount of waste burned to determine emission factors. Persson and Bergström (17) measured PCDD/F emissions from experimental fires designed to simulate surface landfill fires and deep landfill fires using 9-month-old domestic waste. For both simulations, the average PCDD/F emission factor was reported to be 1000 ng TEQ (Nordic)/kg waste burned. PCDD/F emission factors for burning dumps have also been extrapolated from laboratory studies burning assimilated domestic waste (18). Previous simulation studies using a constant composition of domestic waste in a metal barrel found that PCDD/F emission factors averaged 77 ng TEQ per kg of waste burned but varied over a range of 24, likely reflecting the effect of random waste orientation on PCDD/F production (19). Similarly, work of Hedman et al. (20) found a 10-fold variation in repeats of garden and household waste emissions. The potential for PCDD/F formation appears to be affected by both variations in waste composition and burn conditions, such as bulk density and moisture. Uncertain variation of combustion conditions and waste composition typically exist in burning dumps, making PCDD/F emission factors for burning dumps likely to have even a wider range of values than observed in simulation studies.

There are virtually no data on PBDD/F emissions from open burning and, in general, data on emissions of PBDDs/Fs from combustion are very limited. PBDDs/Fs in stack gases from a U.S. waste combustor ranged from 1.41 to 16.5 pg

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Nm⁻³ (sum of 17 tri- to octa-BDDs/Fs) (21). Wang et al. (22) reported PBDDs/Fs from municipal and industrial incinerators in Taiwan at a mean value of 2.28 and 18.2 pg Nm⁻³, respectively (sum of seven 2,3,7,8-Br-substituted tetra- to hexa-BDDs/Fs). Numerous studies confirmed the expected release of PBDDs/Fs during real fire accidents (PBDFs were found in almost all samples, and PBDDs were not regularly detected) (14). The PBDF levels of accidental fire residues were on the order of several μg/kg, with maximum values reaching 107 mg/kg (3). Li et al. (23) have reported severe contamination of ambient air with PBDDs/Fs around an electronic waste dismantling area in China with concentrations ranging from 1.6 to 2104 pg TEQ Nm⁻³ (only eight 2,3,7,8-substituted congeners).

Due to the importance of domestic waste burning to national inventories and the global balance of PCDD/F, there is a need to determine emission factors from open burning dumps. Emerging awareness of PBDE releases and the toxicity of PBDDs/Fs suggest that these contaminants should also be quantified. More accurate emission factor values will allow global efforts to reduce persistent organic pollutants, spearheaded by the Stockholm convention on persistent organic pollutants, to sufficiently prioritize sources and, hence, efforts to reduce risks. This paper reports on efforts to undertake field sampling for determination of emission factors from uncontrolled burning of waste dumps.

Methods

Two mixed rural/urban sites north of Mexico City were selected for the study. Soyaniquilpan de Juárez has a population of approximately 10,000 and is located approximately 55 km north-northwest from Mexico City (N 20° 00.570', W 099° 29.267'; altitude 2400 m). The dump site is located in farmland approximately 2 km from the main road and receives about 8 Mt/day of residential waste. San Martín de las Pirámides (San Martín), which also has some light industry (shoes and toothpaste products), is located about 60 km northeast of Mexico City (N 19° 42.270', W 098° 42.267'; altitude 2332 m). Approximately 21,000 residents are served by this dump, including the nearby city of Otumba, resulting in approximately 25 Mt/day. The site is located approximately 1 km from a main highway, surrounded by agricultural cactus (*Opuntia ficus-indica* or Indian Figure *Opuntia*, "Nopal") fields. In this site only, the local municipality appears to spread a dirt cover over the waste on a weekly basis. In each of these sites, scavengers separate out plastic bottles, aluminum, corrugated cardboard, and glass for sale to local recyclers. The segregated plastics were primarily polyethylene terephthalate (PET) and high density polyethylene (HDPE). There was little apparent poly(vinyl)-chloride (PVC) and, hence, recycling. In both sites there is some evidence of burning, which is believed to be initiated by the scavengers, to create more room in the dump. However, this practice appears to have been virtually eliminated, potentially in response to a site visit 18 months earlier and the accompanying sensitivity of the municipality.

Four air samples were taken from each site (total = 8) during the 3-day sampling campaign. At both sites two piles of approximately 5 m³ of waste were constructed and segregated from the rest of the dump to avoid fire-spread hazard. All of the waste piles were lit rather easily and quickly with a propane torch. Two samples were taken consecutively ("First" and "Second") from each of the piles. Three days of testing resulted in pairs of consecutive samples from two pile burns at both sites for a total of eight samples.

Sampling for PCDD/F was accomplished with two parallel, high-volume (nominally 1 m³/min) samplers (Tisch Environmental, TE-PNY1123 ACCUVOL (<http://www.tisch-env.com/tisch/tegnpy1123.asp>)). The use of parallel samplers

allowed for verification of sampling methods and sample backups. The high-volume samplers were modified to allow remote control of the blower. Flow measurements based on pressure drop across an orifice were monitored and recorded in real time using a data acquisition system (IOtech Personal Daq/56 USB, <http://www.iotech.com/catalog/daq/persdaq.html>) and a laptop computer. Each sampler consisted of a 20 cm × 25 cm (8 in. × 10 in.) stainless steel filter holder, a 15 cm (6 in.) long cylindrical container for the polyurethane foam (PUF) media, and an aluminum-casing blower motor. The filter consisted of a 20 cm × 25 cm (8 in. × 10 in.) quartz microfiber filter (Whatman QMA). The 7.5 cm diameter × 7.5 cm high (3 in. × 3 in.) PUF media were contained within glass cartridges obtained from Tisch Environmental (<http://www.tisch-env.com/tisch/filtermedia.asp>). Prior to sampling, each PUF was precleaned for over 12 h by sequential Soxhlet extraction with toluene and then acetone. The PUF was then dried under flowing nitrogen and spiked with five tetra- to octa-CDD/CDF ¹³C-labeled standards (except for the tetra-CDD, which was ³⁷Cl-labeled), three ¹³C-labeled mono- to tri-CDD/CDF standards, and 15 ¹³C-labeled PBDD/F and PBDE standards. In each site, replicate samples were taken.

The filter mount, PUF cartridge, and high-volume samplers were hung from a 7-m long, 5-cm diameter cast iron pipe boom supported by a quadripod pivot (see Supporting Information (SI), Figure S1). This pivot enabled the samplers to be moved laterally and vertically to follow and sample from the plume, capturing more of the emissions while minimizing exposure of the sampler systems to excessive heat. The boom could also be slid through the pivot to extend the distance of the samplers, while adjusting counterweights. Thermocouples (type K) positioned on the samplers enabled the temperature to be monitored. Teflon tubing connected to a stainless steel line (both 6.4 mm, or 0.25 in.) positioned between the two samplers conveyed sampled gas to an NDIR CO/CO₂ continuous emission monitor (California Analytical model A20599). Other Teflon lines allowed for differential pressure measurements and flow rate measurements. The Teflon lines ran through the center of the sampling boom back to the monitors. Observation of CO/CO₂ concentrations during the burn ensured that their values were high enough above ambient to ensure proper placement of the sampling equipment in the fire plume. The monitors were calibrated using a zero and high span gas (800 ppm CO₂ and 160 ppm CO) prior to measurements, followed by a leak check of the sampling system. The IOtech Personal Daq/56 data acquisition system recorded the temperature, differential pressure for flow volume, and CO/CO₂ concentrations. Power was provided by a 3.75 kJ s⁻¹ gas-powered generator located nominally downwind from the samplers and as distant from the fire as possible.

The sampling duration was set by an estimate of the amount of time (sampled volume) necessary to ensure detectable levels (based on HRGC/HRMS) of each of the 17 toxic equivalence factor (TEF) compounds that comprise the PCDD/F toxic equivalency quotient (TEQ) value. This time was based on prior experience from waste burning experiments in which carbon evolution was measured and compared to PCDD/F TEQ emission factors. The latter was assumed to be 20 ng PCDD/F TEQ/kg of waste burned, corresponding to the minimum emission factor obtained from uncontrolled, domestic waste burning (19).

Emission factors were determined by the ratio of the sampled PCDD/F mass to the cocollected carbon mass (CO₂ and CO) in the same sample volume. Other carbon emissions from combustion, such as elemental carbon and organic carbon, are assumed minimal compared to the mass of CO plus CO₂. When ambient air background CO and CO₂ are

TABLE 1. Sampling Details

site	test	sample order ^a	duration (min)	volume (Nm ³)	ΔCO avg (ppm)	ΔCO ₂ avg (ppm)	ΔCO/ΔCO ₂ (%)	C collected (g)
Soyaniquilpan	1	F	72	42.62	26.5	369.2	7.2	8.83
	2	S	113	71.39	21.2	151.1	14.0	6.02
	3	F	89	62.47	25.1	207.3	12.1	7.76
	4	S	89	51.73	28.3	175.8	16.1	5.38
San Martín	5	F	74	49.11	23.1	226.7	10.2	7.14
	6	S	120	97.57	16.8	101.4	16.6	6.11
	7	F	90	66.99	19.4	142.7	13.6	5.78
	8	S	41	24.68	40.6	308.6	13.2	4.67
average			88	60.56	25.1	210.3	12.9	6.46

^a F - first, S -second.

subtracted, the accumulated C represents the combusted material in the sample. This “carbon balance” method allows calculation of the emission factor in terms of PCDD/F ng TEQ/kg carbon burned (C_{burned}). The C_{burned} mass collected by the CO and CO₂ CEMS can be related to the initial mass of the waste through the carbon concentration of the original waste, the carbon burnout efficiency, and the moisture content of the waste. The carbon concentration was determined from a reconstituted sample, based on a compositional study (24) at multiple dump sites near Mexico City. The principal distinction between sites characterized as rural, semiurban, urban, and industrial (and combinations thereof) wastes was the quantity of organic matter. The composition study showed that the average waste was approximately 33% organic matter, 21% plastics, and 18% paper and diapers. The ultimate analysis for carbon concentration showed 38.4% by mass C in the samples.

Presampling standards were spiked on the PUF prior to sampling to ensure adequate extraction recovery (between 70 and 130%). Internal standards of ¹³C₁₂-labeled PCDD and PCDF internal standards were added to every sample prior to extraction. The internal standards allowed quantification of the native PCDDs and PCDFs in the sample. Recoveries of the presampling ¹³C₁₂-labeled PCDD/PCDF standards are measured relative to the pre-extraction standards and are a measure of the sampling train collection efficiency.

Extraction of PCDDs/Fs, PBDDs/Fs, and PBDEs from train samples was performed by means of sequential Soxhlet extraction with methylene chloride (3.5 h) with restricted exposure to light, followed by 16 h extraction with toluene to ensure removal of PCDDs/Fs from the carbonaceous matrix. All raw extracts were concentrated using the three-ball Snyder columns, filtered, and concentrated further with nitrogen to 1 mL using an automated evaporator, TurboVap II Concentration Workstation (Caliper Technologies, USA). For determination of PCDDs/Fs and PBDDs/PBDFs/PBDEs, one-half and one-quarter of the extract was cleaned and fractionated using an automated liquid chromatography multicolumn (multilayer silica, basic alumina and, in the case of PCDDs/Fs, also a carbon column) Power Prep Dioxin System (FMS Fluid Management Systems, Inc., USA). The volumes and concentrations of elution solvents used for PCDDs/Fs, PBDDs/Fs, and PBDEs analysis are published elsewhere (25). The remaining one-quarter of the extract was archived. Concentrations of PCDDs/Fs, PBDD/F, and PBDEs were determined by the HRGC/HRMS analysis using a Hewlett-Packard gas chromatograph 6890 Series equipped with a CTC Analytics Combi PAL autosampler (CTC Analytics, Switzerland) and coupled to a Micromass Premiere (Waters Inc., UK) double-focusing high-resolution mass spectrometer. The HRMS was operated in an electron impact (35 eV and 650 μA current) selective ion recording (SIR) mode at resolution $R > 10000$ MU (5% valley). For analysis of mono-through octa- CDDs/Fs, a 60-m DB-Dioxin (J&W Scientific, USA) GC column was used (0.15 μm film thickness × 0.25

mm i.d.). For analysis of mono- through deca-BDEs and tetra-through octa-BDD/Fs, the GC was equipped with 15 m DB-5 (0.25 μm film thickness × 0.25 mm i.d.) (J&W Scientific, USA). The MonoBDEs have not been reported due to quantitative interferences observed at SIR QA trace. The GC oven temperature for PBDEs and PBDDs/Fs analysis was programmed from 130 to 320 °C at 10 °C min⁻¹ (10 min hold). The temperature program for PCDDs/Fs was from 130 to 260 °C at 6 °C min⁻¹ with a final hold time of 50 min. The carrier gas (helium) flow rate was 1 mL min⁻¹ for brominated compounds analysis and 0.9 mL min⁻¹ for chlorinated compounds. Two μL and 1 μL of the extract were injected under splitless mode for PCDDs/Fs and PBDDs/PBDFs/PBDEs, respectively. The injection port temperature was set at 270 and 300 °C for chlorinated and brominated target analysis, respectively.

PCDD/F TEQ values were calculated based on World Health Organization (WHO) toxic equivalency factors (TEFs) (16) and PBDD/F TEFs were assigned as those of their PCDD/F equivalents (14). This latter assumption was based, in part, on recently published *in vitro* bio- and immuno-assay assessments of PBDD/F aryl hydrocarbon (AhR) agonist properties and dioxin-like toxicity (9, 10, 26). The International Programme on Chemical Safety (IPCS) of WHO suggested that until TEFs for PBDD/PBDF are established, the preliminary use of the same TEF values as described for the chlorinated analogues appears to be justified (14). Initially, filters and PUFs were extracted separately to determine the distribution of the targets. Since virtually all of the target analytes were found on the filter, subsequent analyses were done with combined filters and PUFs. This also minimized the impact of copious nondetects on the PUF and their effect on the emission factor calculation when nondetects were set to the detection limit.

Results and Discussion

Table 1 contains the sampling data for the eight samples. Sampling times from 41 to 120 min resulted in sample volumes collected ranged from 24.7 to 97.6 m³. Measurement of CO + CO₂ resulted in collection of 4.67 to 8.83 g of carbon above ambient levels. The run-specific PCDD/F emission factors ranged from 202 to 1700 ng TEQ/kg C_{burned} (Table 2), averaging 823 ng TEQ/kg C_{burned} (SD = 562 ng TEQ/kg C_{burned}). PBDD/F emission factors ranged from 87.2 to 1580 ng TEQ/kg C_{burned} and were of magnitude similar to those of their chlorinated counterparts. For calculation of PBDD/F TEQ values, the toxic equivalency factors for the corresponding PCDDs/Fs were applied, resulting in an average emission factor of 470 ng TEQ/kg C_{burned} (SD = 494 ng TEQ/kg C_{burned}). Under these assumptions, the TEQ contribution from the PBDDs/Fs averages about 60% of that of the PCDDs/Fs. Emissions of 40 PBDE congeners (including two coeluting pairs) ranged from 42.4 μg/kg C_{burned} to 1840 μg/kg C_{burned} with an average of 724 μg/kg C_{burned} (SD = 692 μg/kg C_{burned}).

TABLE 2. PCDD/F, PBDE, and PBDD/F Emission Factors

site	test	sample order ^a	PCDD/F ^b (ngTEQ/kg C _b) ^c	PCDD/FND = 0/ND = DL (unitless)	PBDE ^d (μg/kg C _b)	PBDD/F ^e (ngTEQ/kg C _b)	PBDD/FND = 0/ND = DL (unitless)
Soyaniquilpan	1	F	226	1.00	117	87.2	0.79
	2	S	584	0.99	243	171	0.67
	3	F	202	1.00	42.4	178	0.85
	4	S	826	1.00	176	299	0.64
San Martín	5	F	432	1.00	983	775	0.71
	6	S	1210	1.00	1840	1580	0.59
	7	F	1400	1.00	1530	370	0.91
	8	S	1700	1.00	856	299	0.93
average EF (SD)			823 (562 SD)		724 (692 SD)	470 (494 SD)	

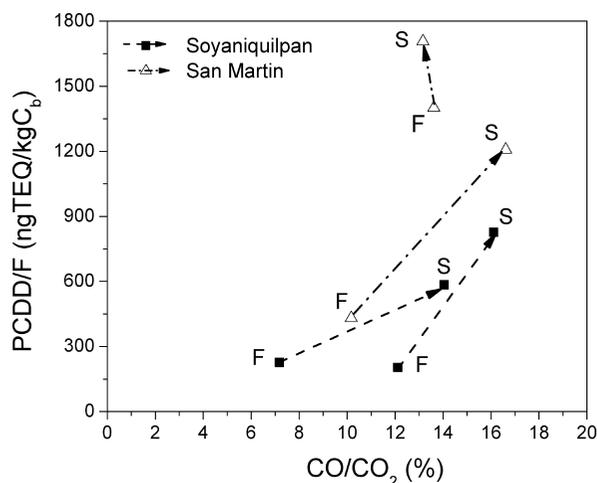
^a F - first, S -second. ^b 17 2,3,7,8-Cl-substituted tetra- to octa-CDD/F. ^c kg C_b - kg carbon burned. ^d 40 di- to deca-BDE congeners (see SI Table S2). ^e 13 2,3,7,8-Br-substituted tetra- to octa-BDD/F (see SI Table S3).

PCDD/F was analyzed with virtually no impact of non-detectable (ND) 2,3,7,8-Cl-substituted congeners on the concentration. Seven of the eight samples showed no distinction between the PCDD/F concentration at ND = 0 and ND = detection limit (DL); one sample was at a ratio of 0.99/1.0.

The PCDD/F emission factors reported here significantly exceed published values for combustion of domestic waste under a variety of realistic burn compositions and conditions (19, 20, 27). Published values for domestic waste combustion in barrels are on the order of 160 ng TEQ/kg C_{burned} (19) and for mixed domestic and yard waste in barrels are 40 ng TEQ/kg C_{burned} (20). These values compare with our average value of 823 ng TEQ/kg C_{burned}. Note that the emission factors reported here in terms of mass of carbon burned can be related to the initial waste mass with the carbon mass percentage, the carbon combustion efficiency, and the initial waste moisture. Our PCDD/F emission factors are approximately 2000 times higher than from stacks of high-technology, modern municipal waste combustor with sophisticated air pollution control systems (data from ref 28).

The two sites had overlapping ranges of PCDD/F emission factors, although the San Martín site had a higher average emission factor by about 2×. This is possibly due to a compositional difference between the sites. Emission factors were generally repeatable at each site; the San Martín site saw the largest variation, about 2×, between its samples. Given the inability to control composition, sample wetness, and combustion quality, this range does not seem particularly surprising.

In all four test cases, the initial, or first ("F"), samples had the lower emission factor and the subsequent second ("S") sample had a higher emission factor, up to 4× (see Figure 1). Compositional differences were expected to be minor within the same pile, suggesting that these changes in the emission factors are due to different combustion conditions between the F and S samples. A possible explanation is that the latter stage of the fire is more represented by smoldering combustion, which may have a greater propensity for PCDD/F formation. In addition, the latter stages of the burn may have a higher overall waste pile temperature due to the insulating ash layer. These temperatures may be more conducive to PCDD/F formation, as the active flame front recedes into the pile. The first possibility is supported by plotting the emission factors versus the run-averaged CO/CO₂ ratio, a measure of combustion quality. Figure 1 shows that, in general, higher CO/CO₂ ratios are present in the S samples, which have higher emission factors. One sample, 8S (see Table 2), reports higher PCDD/F levels at a slightly lower CO/CO₂ ratio. This might be due to the shorter sampling time and volume necessitated by an oncoming lightning storm. These results are consistent with published data (19) on waste combustion in barrels showing that five of six


FIGURE 1. PCDD/F emission factors and combustion quality, CO/CO₂.

samples increased in emission factor throughout the burn while one, a wetted sample, decreased through the burn.

The 2,3,7,8-Cl-substituted congener patterns (SI Figure S2) and the homologue profiles from the eight field burns (SI Figure S3) are comparable to those from published measurements in municipal solid waste combustors (29, 30) and refuse-derived fuel in a pilot plant (data shown from ref 31). Despite likely distinctions in fuel composition and combustion conditions, the congener patterns are quite similar between our field sampling at a waste dump and the cited references. Notably, however, these congener patterns are also quite similar to those seen in iron and steel sinter plants (33), suggesting that the patterns are not necessarily fuel- and process-specific but dictated by some thermodynamic constraints. The homologue profiles (shown in SI Figure S3) are very similar, declining in molar fraction from tetra- to octa- for both PCDDs and PCDFs. The hepta- and octa-PCDDs (SI Figure S2) tend to dominate the PCDD profile while the PCDFs are more equivalent in concentration across the range of Cl substitution. These trends are similar to those in earlier barrel burn studies with domestic waste (20, 32), and in reported municipal solid waste emissions ((31)(data shown), (34)).

PBDE emissions were observed, consistent with landfill fire simulation results (18). In our study, total PBDE concentrations ranged from 42.4 to 1840 μg/kg C_{burned} with an average of 724 μg/kg C_{burned} (SD = 692 μg/kg C_{burned}). In three of the four sampling pairs, the PBDE emission factors increased for the S samples. The one exception was the last sample, which was truncated due to weather.

More than 50 wt % of our observed PBDE congeners reflect the major congeners of the technical PentaBDE (TeBDE-47,

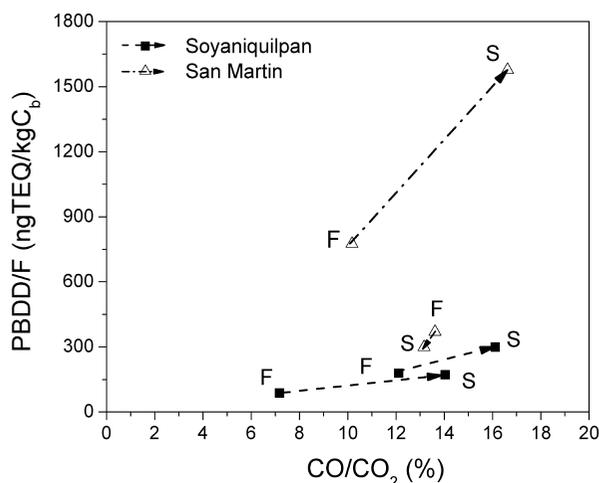


FIGURE 2. PBDD/F emission factors and combustion quality, CO/CO₂.

PeBDE-99, -100), OctaBDE (HpBDE-183, -196, -197), and DecaBDE (NoBDE-206, -207, -208, DcBDE-209) mixtures. Their presence is likely due to volatilization of flame-retarded consumer products during combustion. The presence of numerous other congeners, such as the lowly brominated congeners DiBDE-7, TrBDE-30, and TeBDE-79 which have not yet been reported in technical mixes (35), suggests reactive changes of the technical PBDEs during combustion such as debromination. The congener patterns of PBDE emissions in our study (SI Table S2) were similar to those of reported atmospheric sampling, with lowly brominated congeners being more abundant than the highly brominated (36–41), suggesting that open burning of domestic waste may be a contributing global source.

PBDD/F emission factors (Table 2) were similar in magnitude to their chlorinated counterparts, ranging from 87 to 1578 ng TEQ/kg C_{burned} (when applying the toxic equivalency factors for the corresponding PCDDs/Fs) for an average value of 470 ng TEQ/kg C_{burned} (SD = 494 ng TEQ/kg C_{burned}). The PBDDs/Fs likely originate as contaminants of brominated flame retardants in consumer products (7) and as combustion byproducts of the PBDEs (8). Fewer 2,3,7,8-Br-substituted PBDD/F congeners were detected than their chlorinated counterparts. The ratio of the average PBDD/F TEQ concentration ratio for ND = 0.0 and ND = DL was 0.76 (range from 0.59 to 0.93), mostly due to nondetects among the PBDDs (Table S-3). Only one sample, 3F, had detectable PBDD compounds.

Similar to the PBDE emission factors, the PBDD/F emission factors increase for all pairs of the F to the S samples, except for the last pair where the sampling was truncated due to weather. The PCDD/F trend of increasing emission factors with poor combustion quality (higher CO/CO₂ ratio) is observed in all four PBDD/F sample pairs, but with less prominence (Figure 2). These results, combined with those from the PCDDs/Fs, suggest that higher emission factors can be expected when combustion conditions are poorer and smoldering combustion predominates. This observation supports the possibility of reactive formation of PBDDs/Fs over that of simple volatilization.

The molar-averaged bromination levels of the PBDEs and detected PBDFs are quite similar, 69.4 and 71.2% Br, respectively. This supports the hypothesis that PBDEs may be a potential source of PBDFs through a thermal desorption or formation pathway. The bromination pattern observed for PBDFs is similar to that of PBDEs. This is consistent with findings of Hanari et al. (ref 7) on profiles of PBDF impurities in PBDE technical formulations, where more highly brominated mixtures of PBDEs (DecaBDE and OctaBDE) contained

heavily brominated PBDF homologues, and lower brominated formulations (PeBDE) had side-impurities of lower brominated furans.

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Supporting Information Available

Three figures and three tables contain information on the sampling apparatus, the PCDD/F homologue profiles and congener patterns, and the run-specific PCDD/F, PBDD/F, and PBDE data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Fiedler, H. National PCDD/PCDF release inventories under the Stockholm Convention on Persistent Organic Pollutants. *Chemosphere* **2007**, *67*, S96–S108.
- Sakai, S.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* **2001**, *42*, 519–531.
- IPCS-WHO. *Brominated Diphenyl Ethers*; Environmental Health Criteria 162; International Program on Chemical Safety, World Health Organization: Geneva, 1994; <http://www.inchem.org/documents/ehc/ehc/ehc162.htm>.
- Schecter, A.; Johnson-Welch, S.; Kuang, C.; Harris, T. R.; Pöpke, O.; Rosen, R. J. Polybrominated diphenyl ether (PBDE) levels in the livers of U.S. human fetus and newborns. *Toxicol. Environ. Health A* **2007**, *70*, 1–6.
- Mazdai, A.; Dodder, N. G.; Abernathy, M. P.; Hites, R. A.; Bigsby, R. M. Polybrominated diphenyl ethers in maternal and fetal blood samples. *Environ. Health Perspect.* **2003**, *111* (9), 1249–1252.
- BSF, Bromine Science Forum, 2009; <http://www.bsef.com/regulation/international-regulations/>.
- Hanari, N.; Kannan, K.; Miyake, Y.; Okazawa, T.; Kodavanti, P.; Aldous, K.; Yamashita, N. Occurrence of polybrominated biphenyls, polybrominated dibenzo-p-dioxins, and polybrominated dibenzofurans as impurities in commercial polybrominated diphenyl ether mixtures. *Environ. Sci. Technol.* **2006**, *40*, 4400–4405.
- Weber, R.; Kuch, B. Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environ. Int.* **2003**, *29* (6), 699–710.
- Behnisch, P. A.; Hosoe, K.; Sakai, S. Brominated dioxin-like compounds: in vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **2003**, *29*, 861–877.
- Samara, F.; Gullett, B.; Harrison, R.; Chu, A.; Clark, G. Determination of relative assay response factors for toxic chlorinated and brominated dioxins/furans using an enzyme immunoassay (EIA) and a chemically-activated luciferase gene expression cell bioassay (CALUX). *Environ. Int.* **2009**, *35*, 588–593.
- Choi, J.-W.; Fujimaki, S.; Kitamura, K.; Hashimoto, S.; Ito, H.; Suzuki, N.; Sakai, S.-I.; Morita, M. Polybrominated dibenzo-p-dioxins, dibenzofurans, and diphenyl ethers in Japanese human adipose tissue. *Environ. Sci. Technol.* **2003**, *37*, 817–821.
- Kotz, A.; Malisch, R.; Kypke, K.; Oehme, M. PBDE, PBDD/F, and mixed chlorinated-brominated PXDD/F in pooled human milk samples from different countries. *Organohalogen Compd.* **2005**, *67*, 1540–1544.

- (13) Ohta, S.; Okumura, T.; Nakao, T.; Aozasa, O.; Miyata, H. Contamination levels of organic bromine compounds (BFRs, dioxins) in mother's milk and daily milk products. *Organohalogen Compd.* **2005**, *67*, 562–564.
- (14) IPCS-WHO. *Polybrominated Dibenzop-Dioxins and Dibenzofurans*; Environmental Health Criteria 205; International Program on Chemical Safety, World Health Organization: Geneva, 1998; <http://www.inchem.org/documents/ehc/ehc/ehc205.htm>.
- (15) Pettersson, K. Boström, C.-A. *Bränder på avfallsupplag*; Institutet för Vatten-Och Luftvårdsforskning: Stockholm, Sweden, February 1996.
- (16) Ruokojärvi, P.; Ettala, M.; Rahkonen, P.; Tarhanen, J.; Ruuskanen, J. Polychlorinated dibenzo-p-dioxins and -furans (PCDDs and PCDFs) in municipal waste landfill fires. *Chemosphere* **1995**, *30* (9), 1697–1708.
- (17) Persson, P. E.; Bergström, J. Emission of chlorinated dioxins from landfill fires. In *Proceedings of the Sardinia 91: Third International Landfill Symposium*, 1991; Vol. 1, pp 1635–1645.
- (18) Hirai, Y.; Kida, A.; Sakai, S. Emission factors of PCDD/DF and PBDE by landfill fire simulation. *Organohalogen Compd.* **2005**, *67*, 2246–2249.
- (19) Lemieux, P.; Gullett, B.; Lutes, C.; Winterrowd, C.; Winters, D. Variables affecting emissions of PCDDs/Fs from uncontrolled combustion of household waste in barrels. *J. Am. Waste Manage. Assoc.* **2003**, *53*, 523–533.
- (20) Hedman, B.; Näslund, M.; Nilsson, C.; Marklund, S. Emissions of polychlorinated dibenzodioxins and dibenzofurans and polychlorinated biphenyls from uncontrolled burning of garden and domestic waste (backyard burning). *Environ. Sci. Technol.* **2005**, *39* (22), 8790–8796.
- (21) Wyrzykowska, B.; Gullett, B. K.; Tabor, D.; Touati, A. Levels of brominated diphenylether, dibenzo-p-dioxin, and dibenzofuran in flue gases of a municipal waste combustor. *Organohalogen Compd.* **2008**, *70*, 62–65.
- (22) Wang, L.-C.; Chang-Chien, G.-P. Characterizing the emissions of polybrominated dibenzo-p-dioxins and dibenzofurans from municipal and industrial waste incinerators. *Environ. Sci. Technol.* **2007**, *41*, 1159–1165.
- (23) Li, H.; Yu, L.; Sheng, G.; Fu, J.; Peng, A. Severe PCDD/F and PBDD/f pollution in air around an electronic waste dismantling area in China. *Environ. Sci. Technol.* **2008**, *41*, 5641–5646.
- (24) IASA. *Ingeniería Aplicada y Sustentabilidad Ambiental, Muestreo y caracterización de residuos sólidos urbanos en tres sitios tipo de disposición final en México; Distrito Federal, Mexico*, 2008.
- (25) Wyrzykowska, B.; Tabor, D.; Gullett, B. Same-sample determination of ultratrace levels of polybromodiphenylethers, polybromodibenzo-p-dioxins/furans, and polychlorodibenzo-p-dioxins/furans from combustion flue gas. *Anal. Chem.* **2009**, *81*, 4334–4342.
- (26) Van den Berg, M.; Birnbaum, L. S.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; Rose, M.; Safe, S.; Schrenk, D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R. E. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. *Toxicol. Sci.* **2006**, *93*, 223–241.
- (27) Gullett, B. K.; Lemieux, P. M.; Lutes, C. C.; Winterrowd, C. K.; Winters, D. L. Emissions of PCDD/F from uncontrolled, domestic waste burning. *Chemosphere* **2001**, *43*, 721–725.
- (28) UNEP. *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*; United Nations Environment Programme: Geneva, Switzerland, 2001.
- (29) Giugliano, M.; Cernuschi, S.; Grosso, M.; Aloigi, E.; Miglio, R. The flux and mass balance of PCDD/Fs in a MSW incineration full scale plant. *Chemosphere* **2001**, *43*, 743–750.
- (30) Chen, T.; Gu, Y. L.; Yan, J. H.; Li, X. D.; Lu, S. Y.; Dai, H. F.; Cen, K. F. Polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas emissions from municipal solid waste incinerators in China. *J. Zhejiang Univ. Sci. A* **2008**, *9*, 1296–1303.
- (31) Jansson, S.; Fick, J.; Tysklind, M.; Marklund, S. Post-combustion formation of PCDD, PCDF, PCBz, and PCPh in a laboratory-scale reactor: Influence of dibenzo-p-dioxin injection. *Chemosphere* **2009**, *76* (6), 818–825.
- (32) Lemieux, P.; Lutes, C.; Abbott, J.; Aldous, K. Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels. *Environ. Sci. Technol.* **2000**, *34* (3), 377–384.
- (33) Wang, L.-C.; Lee, W.-J.; Tsai, P.-J.; Lee, W.-S.; Chang-Chien, G.-P. Emissions of polychlorinated dibenzo-p-dioxins from stack flue gases of sinter plants. *Chemosphere* **2003**, *50*, 1123–1129.
- (34) Aurell, J.; Jansson, S.; Marklund, S. Effects of quench time profiles on PCDD/F formation in the postcombustion zone during municipal solid waste incineration. *Environ. Eng. Sci.* **2009**, *26* (3), 541–550.
- (35) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-BDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247–6254.
- (36) Hites, R. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.
- (37) Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. *Environ. Sci. Technol.* **2001**, *35*, 1078–1083.
- (38) Venier, M.; Hites, R. Flame retardants in the atmosphere near the Great Lakes. *Environ. Sci. Technol.* **2008**, *42*, 4745–4751.
- (39) Wurl, O.; Potter, J. R.; Durville, C.; Obbard, J. P. Polybrominated diphenyl ethers (PBDEs) over the open Indian Ocean. *Atmos. Environ.* **2006**, *40*, 5558–5565.
- (40) Su, Y.; Hung, H.; Sverko, E.; Fellin, P.; Li, H. Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. *Atmos. Environ.* **2007**, *41*, 8725–8735.
- (41) Hoh, E.; Hites, R. A. Brominated flame retardants in the atmosphere of the East-Central United States. *Environ. Sci. Technol.* **2005**, *39*, 7794–7802.

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