Open burning of household waste: Effect of experimental condition on combustion quality and emission of PCDD, PCDF and PCB

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ABSTRACT

Open burning for waste disposal is, in many countries, the dominant source of polychlorinated dibenzo-dioxins, dibenzofurans and biphenyls (PCDD/PCDF/PCB) release to the environment. To generate emission factors for open burning, experimental pile burns of about 100 kg of household waste were conducted with emissions sampling. From these experiments and others conducted by the same authors it is found that less compaction of waste or active mixing during the fire – "stirring" – promotes better combustion (as evidenced by lower CO/CO_2 ratio) and reduces emissions of PCDD/PCDF/PCB; an intuitive but previously undemonstrated result. These experiments also support previous results suggesting PCDD/PCDF/PCB generation in open burning – while still highly variable – tends to be greater in the later (smoldering) phases of burning when the CO/CO_2 ratio increases.

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1. Introduction

Among other requirements, parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) must develop, maintain and update an inventory of national releases of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). One of the largest sources of PCDD/PCDF in many countries is open burning of waste (Fiedler, 2007).

A national inventory is created by multiplying the amount of a specific activity taking place (activity factor) by the releases of PCDD/PCDF and polychlorinated biphenyls (PCBs) to air or land per unit of activity (emission factor, EF_{air}, EF_{land}) and summing over all sources. The UNEP Toolkit ("Toolkit") (United Nations Environment Programme, 2005) is a collection of emission factors for many processes and is a major resource for national reporting. For the Toolkit, all EF_{air} and EF_{land} are calculated using toxic equivalency factors (TEFs) (Van den Berg et al., 2006), and are recorded

as toxic equivalents (TEQ), For open burning, they are expressed as micrograms TEQ per ton ($\mu g\ TEQ\ t^{-1}$) of waste.

In a recent compilation of 61 national inventories, most of which represent developing countries, three-quarters of the countries reported that open burning processes contribute more than 28% of their total national PCDD/PCDF release (Fiedler et al., 2010). For 25% of the countries, open burning contributed over 80%. Even in some developed, urbanized and industrialized countries, there is still significant combustion of domestic waste in open piles, barrels, fireplaces, household heating stoves, or primitive incinerators as a primary mode of regular waste disposal, especially in rural areas.

Open combustion/open burning of waste – burning outside any device which might mitigate emissions – is highly variable and difficult to characterize. Early in the process leading to the Stockholm Convention, few emission factors had been determined for open burning; most of those were obtained by laboratory simulation. Only recently has domestic waste burning been studied in larger-scale experimentation (Ikeguchi and Tanaka, 1999; Lemieux et al., 2003, 2004; Hedman et al., 2005; Collet and Fiani, 2006; Zhang et al., 2009; Gullett et al., 2010).

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In its document on Best Available Techniques and Best Environmental Practices, the Stockholm Convention Expert Group notes, "With respect to the burning process: Supply sufficient air; maintain steady burning or rate of mass loss; minimize smouldering, possibly with direct extinguishment; ... limit burning to small, actively turned, well-ventilated fires, rather than fires in large poorly ventilated dumps or containers." (United Nations Environment Programme, 2007) While intuitively good advice, there is little or no confirmation in the technical literature of the efficacy of such advice.

Two previous campaigns of open burning experimentation were conducted in Mexico and one in China (Fiedler et al., 2010; Gullett et al., 2010; Zhang et al., 2011). These campaigns were conducted under different conditions of waste composition, burning sample compaction and moisture, and sample treatment during combustion. Some have argued that varying waste composition generally explains much of the variability in open burning experiments (Ikeguchi and Tanaka, 1999; Yasuhara et al., 2001). In these campaigns, however, waste composition explained very little, so another experimental campaign was planned to expand understanding of the effects of the other variables. Herein we report the results of the third Mexico campaign and we compare process parameters and results with those of the earlier campaigns in Mexico (Fiedler et al., 2010; Gullett et al., 2010; Zhang et al., 2011) and China (Fiedler et al., 2010; Zhang et al., 2011).

2. Material and methods

2.1. Waste

A single waste composition, derived from studies of municipal waste burned in previous campaigns, was used in order to minimize variability (Fiedler et al., 2010; Gullett et al., 2010; Zhang et al., 2011). This recipe is reproduced herein (Supporting information).

Samples for burning (45–50 kg) were assembled from categories of waste according to this composition from available materials deposited at the waste site (San Martin de las Pyramides, DF, Mexico) during normal municipal waste collection. The waste was then bagged in polyethylene and trucked to the burn site. For each experiment, two bagged samples (about 90–100 kg) were placed on tared sheets of 1.20 m × 2.43 m corrugated fiber cement board and set on a load cell (Model L-EQM 500/1000; Tor-Rey, Houston, TX, USA). The bags were cut open and waste was exposed. Two kg water was added to compacted samples (those naturally compacted in the bagging and transport process, and not otherwise loosened) to preserve moisture and simulate the condition of earlier burn piles (see Table 1). Samples were covered with a polyethylene sheet after water was added to minimize drying.

Experiments 1, 6, and 6B have light compaction and added moisture. Experiments 2 and 5 consisted of loose waste but no added moisture. Experiment 3 was moistened, but also stirred – the only stirred experiment in this campaign. Lightly compacted waste sat covered for 2–12 h after assembly and prior to ignition; loosened waste was manipulated at the time of ignition to minimize compaction. In one experiment the burning material was turned regularly to promote combustion in a process called "stirring." The other five experiments were untouched during combustion.

Ignition was accomplished by application of a propane torch at a number of sites on the pile, which continued until, in the judgment of the experimenters, sustainable combustion had been initiated. Experiments were allowed to proceed until mass loss had largely ceased. No reignition was required of any fire.

2.2. Collection and quantitation of combustion gases

Combustion gases were analyzed for water, carbon monoxide (CO), carbon dioxide (CO_2), hydrogen chloride (HCl), PCDD/PCDF and PCB. Continuous emission monitoring for CO_2, CO, H_2O and HCl analysis was undertaken using a Fourier Transform Mid-Region Infrared Spectrometer (Model DX 4000, Gasmet Technologies Oy, Helsinki, Finland). Sampled gases were transported from the outlet of the high-volume sampler to the FTIR Analyzer using a Teflon line heated to 180 °C in order to prevent moisture condensation. Sampling procedures followed USEPA NSPS Reference Methods 3A and 10 (USEPA; USEPA) and ASTM D 6348-03, (ASTM International, 2010).

At the beginning of each day, the CO and CO_2 analyzer was calibrated using zero-, low-, mid- and high-level calibration gases. For H_2O and HCl, previous reference spectra developed with the same instrument were used for calibration. Measurement system bias tests were performed before the beginning and at the end of each testing day, and system drift was also tested each day. Baseline values for the sampled gases were determined based on measured concentration of ambient gases immediately pre- and post-experiment. The digital data logging system registered gas concentration every 21 s through the entire testing period, except for one 8-min period in Experiment 6B where data were logged every 61 s.

A thermocouple measured the temperature of the gases entering the gas sampling train, and this temperature was recorded by the data logger, one data point per minute. In Experiment 1, the sampling train thermocouple was rendered inactive for about 90 min during the execution of the experiment, and gas temperature for that period, which varied between 37 °C and 45 °C was interpolated.

The basic apparatus for gas collection has been described previously in detail (Fiedler et al., 2010; Gullett et al., 2010). A high-volume (nominally 1 m³ min⁻¹) sampler (TE-PNY1123 ACCUVOL,

Table 1
Experimental conditions, reaction parameters and gas sampling results.

Experiment	Condition	Mass loss, %	Carbon sampled, g	Carbon burned, kg[a]	Plume fraction sampled, %[b]	COF, %[c]	CO/CO₂[d]	HCl sampled, g	HCl release, kg
1	Compacted/moistened	49.8	35.1	15.70	0.223	72	0.162	0.265	0.119
2	Loosened	42.4	15.9	15.81	0.113	75	0.141	0.097	0.085
3	Compacted/moistened/ stirred	61.8	15.8	19.20	0.075	88	0.128	0.169	0.224
5	Loosened	56.3	23.5	17.34	0.135	82	0.110	0.244	0.180
6	Compacted/moistened	45.7	10.2	15.63	0.064	74	0.125	0.114	0.177
6B	Compacted/moistened	49.6	24.0	16.41	0.151	76	0.191	0.092	0.061

[a] Burned carbon from mass balance.
[b] Sampled carbon as percent of burned carbon.
[c] Carbon oxidation factor.
[d] Mass ratio of CO to CO_2 expressed on the basis of mass of carbon.

Tisch Environmental, Cleves, OH, USA), installed with its intake oriented toward the ground, was used to collect combustion gases. A metal support was installed beneath the sampler to protect it and its sample lines from direct heat and also to act as a platform so it could be rested on a surface when not in use. The metal support was held away from the sampler approximately 25 cm by rigid rods; this gap was sufficient to allow for free intake of combustion gases.

PCDD/PCDF and PCB were captured on a 20 cm × 25 cm quartz microfiber filter (Whatman QMA, Clifton, NJ, USA), followed by 7.5 cm diameter × 7.5 cm high polyurethane foam (PUF) sorbent contained within a glass cartridge (Tisch Environmental). The filter mount, PUF cartridge, and high-volume samplers were hung from a 6.4-m long, 5-cm diameter cast iron pipe boom supported by a quadripod pivot. This pivot enabled the samplers to be moved laterally or vertically and extended or retracted to follow and collect sample from the visible combustion plume, capturing emissions while minimizing exposure of the sampler systems to excessive heat; generally about 1–1.5 m above the combustion zone (see photos in Supporting information).

For four of the six experiments a single PUF was used. In the other two experiments (Experiments 6 and 6B) PUFs were changed twice allowing for collection of three samples of PCDD, PCDF and PCB as the combustion progressed. Filter changes were timed to divide each 3- or 4-h experiment into three approximately equal carbon samples. Quartz filters were changed as needed in all experiments when they were sufficiently obstructed to cause a decrease in airflow of about 10%, approximately once per hour. A filter change typically required about 5 min, during which there was no sampling. All quartz filters associated with a PUF were combined with that PUF for analysis.

Raw data were obtained as ppmv from the analyzers, bias corrected and averaged to yield one sample per minute, converted to ppm by mass, then normalized for baseline concentrations. Baseline-corrected values were multiplied by the mass of air drawn through the high-volume sampler to obtain incremental analyte mass.

It is assumed that, as a practical matter, all combusted carbon goes to CO and CO_2 rather than methane, hydrocarbons or PAHs. Most material mass is burned under well-oxygenated conditions, and other experiments conducted under similar conditions show little THC compared with CO and CO_2 (Aurell et al., 2009). Incremental masses of CO and CO_2 were converted to yield the total mass of carbon collected by the sampling train during the experiment. Incremental masses of HCl and H_2O were determined in a similar way and summed.

The fraction of total carbon burned captured by the sampling train (plume fraction sampled) and the fraction of carbon combusted (carbon oxidation factor, COF) were calculated by a mass balance method. Mass loss was recorded during the experiment. Water and carbon in the initial sample were calculated from the waste composition data. Material left after combustion consisted of unburned remainder and ash. Much of the combustible unburned remainder was dense, wet material such as rolled-up

disposable diapers and bulky fruit; thus, its composition was assumed to be the average of that of disposable diapers and organic matter. Noncombustible unburned material (glass bottles, metal cans, clay dust, etc.) was assumed to be unchanged with the exception of evaporation of its laboratory-determined water content. After the experiment, unburned remainder was separated from ash and weighed, allowing calculation of the ash mass by difference. Ash was stirred to homogenize, then sampled and analyzed for carbon, PCDD/PCDF and PCBs.

2.3. Chemical analysis and determination of emission factors

Analytical procedures for extraction, clean-up, and analysis of PCDD, PCDF, and PCB samples have been described previously (Gullett et al., 2010). The average recovery of ^{13}C-labeled PCDD/PCDF pre-extraction and pre-sampling spikes was 89.8% and 110%, respectively, and 74.3% and 75.6% for ^{13}C-labeled Cl_4 through Cl_8 PCB, respectively. Airborne PCDD/PCDF and PCB were quantified by analyzing for these compounds on the combined filter and PUF sorbent.

Emission factors to air were calculated as ng TEQ per kg of carbon burned (ng TEQ kg^{-1} C_{burned}). TEQ data are reported using the World Health Organization 2005 TEFs (WHO_{2005}). C_{burned} is calculated from the carbon content of CO and CO_2 resulting from combustion and are assumed to comprise the totality of airborne carbon, with other forms negligible by comparison. Emission of PCDD/PCDF per ton of waste (μg TEQ t^{-1} waste) is calculated by multiplying EF_{air} (ng TEQ kg^{-1} C_{burned}) by the carbon content of the waste and the experimental carbon oxidation factor (COF) (Fiedler et al., 2010).

EFs are reported on the basis of PCDD/PCDF, and not including PCB, unless otherwise noted. For calculation, non-detects were treated as their detection limit values. Full congener and homolog profiles for combustion gases and ash may be found in Supporting information.

Statistical analysis was conducted by means of JMP 8 (SAS Institute, Inc., Cary, NC). EF_{air} are analyzed as their logarithms to create a more normal distribution of data (Box et al., 1978). All significance testing is conducted at 95% confidence levels. Unless otherwise noted, EF_{air} values as ng TEQ kg^{-1} C_{burned} are used when comparing experiments. EF_{air} and Emission Factor to land; i.e., ash (EF_{land}) as μg TEQ t^{-1} waste (UNEP Toolkit units) are also provided for these experiments.

3. Results

Tables 1 and 2 show the experimental design and sampling results. Carbon mass in grams is the sum of the carbon content of sampled CO and CO_2; the ratio CO/CO_2 is the ratio of the carbon mass of those gases. HCl in grams is the mass drawn through the air sampler. PCB and ash each comprise a minority fraction of TEQ.

Despite calibration, baselines varied. CO_2 baselines ranged from a low of 305 ppmv (Experiment 2) to a high of 419 ppmv (Experi-

Table 2
Concentrations of PCDD/PCDF and PCB in ash, EF_{air} and EF_{land}.

Experiment	EF_{air}, ng TEQ kg^{-1} C_{burned}	EF_{air} (PCB), ng TEQ kg^{-1} C_{burned}	EF_{air}, μg TEQ t^{-1} waste	EF_{air} (PCB), μg TEQ t^{-1} waste	PCB fraction of TEQ, air, %	EF_{land}, μg TEQ t^{-1} waste	EF_{land} (PCB), μg TEQ t^{-1} waste	Ash% of PCDD/PCDF TEQ, %
1	14000	1000	2300	170	6.9	8.1	0.39	0.4
2	660	50	120	8.9	7.0	6.3	0.40	5.0
3	290	28	62	5.7	8.7	2.0	0.36	3.3
5	870	49	180	9.5	5.3	8.1	0.65	4.5
6	950	13	170	12	6.8	8.0	0.72	4.7
6B	950	48	170	19	10.4	1.2	0.12	0.7

ment 3), with the average for the six experiments 378 ppmv. CO baseline was generally 0–1 ppmv, as was HCl. Water concentration in sampled air was highly variable around 1% by mass and so similar to ambient humidity that a water mass balance calculation yielded no meaningful information.

Peak CO_2 concentration for each experiment ranged from approximately 1500 ppmv to 4000 ppmv, although the average concentration was somewhat lower. CO ranged from zero to peaks in the low hundreds of ppmv, and again, the average concentration was somewhat lower. HCl concentrations as high as 40 ppmv were recorded for a short period in Experiment 5, but were more typically in the range of 1–3 ppmv.

Included in Table 1 is the ratio of carbon recovered through the air sampler to total carbon emitted in the experiment (plume fraction sampled), which ranges from 0.064% to 0.223%. Average HCl sampled is ca. 0.015 g which, when divided by the plume fraction sampled, results in calculated releases of 0.06–0.22 kg from combustion of 38 kg waste to 58 kg waste, respectively. Chlorine recovery on the order of a few tenths of a percent is consistent with the material composition, which contained approximately 0.6% PVC (approximately 0.3% Cl) and presumably inorganic chloride of about the same magnitude (Domalski et al., 1986). HCl concentration above background was far less than that for CO or CO_2, so this mass balance should be considered approximate.

Experiment 1 is very high in PCDD/PCDF and PCB, and comparison of indicators from other runs (particularly replicates 6 and 6B) provides no explanation. The ratio of PCB to PCDD/PCDF and emission of HCl per kg waste are not atypical; CO/CO_2 is not the highest of the runs. It seems more likely, especially as it is a compacted, moistened experiment, that this result is indicative of the variability of open burning. At the very least, Experiment 1 shows the potential for anomalous generation of PCDD/PCDF and PCB, and the potential importance of open burning as a source of these materials.

4. Discussion

4.1. Stirring, compaction and moisture effects on EF_{air}, and CO/CO_2

Two previous experimental campaigns using Mexico waste – MEX-1 (Gullett et al., 2010) and MEX-2 (Fiedler et al., 2010) – were conducted under variable conditions of waste compaction and moisture. There were also three waste compositions: rural, semiurban and urban-industrial. In MEX-1, the first three experiments were conducted on recently assembled waste piles; thus, any waste compaction was loosened just before ignition. The final experiment of MEX-1 was conducted on the remainder of a large pile from which waste had been taken to construct the third experiment. That pile appeared wetter and somewhat more compacted by inspection, having stood undisturbed for some time. The experiments were not actively stirred.

In MEX-2, EF_{air} spanned over two orders of magnitude, but only rural waste was significantly different (higher) than others. Postexperiment review of procedures revealed that the first two experiments were not stirred; the second four only lightly stirred and the final four more aggressively stirred to promote combustion and reduce experiment time. Additionally, rural waste, which comprised the first two experiments, appeared wetter than the others. These observations suggested that compaction, moisture and stirring might explain a large part of the variability of the PCDD/PCDF results, because waste composition alone did not (Fiedler et al., 2010; Zhang et al., 2011).

Experiments and analyses in the current campaign (MEX-3) were designed to test the hypothesis that better combustion efficiency generates lower and more consistent PCDD/PCDF emission.

It was hoped to elucidate the effects of stirring by including a number of experiments where no stirring at all occurred. Additionally, some unstirred experiments were allowed to compact lightly for a time under their own weight, and water was added to keep the waste from drying out, to better understand the impact of compaction/moisture. A summary of experimental conditions for all campaigns appears in Table 3.

The single stirred experiment (Experiment 3) yielded the lowest EF_{air} and loosened experiments were next lowest. An unstirred, compacted experiment with added moisture (Experiment 1) yielded the highest. Compacted and moistened experiments in MEX-3 averaged higher emission factors than loose or stirred experiments.

Previously it has been reported that EF_{air} for the China experiments (CHN) was statistically significantly lower than those conducted in Mexico, but the three China waste compositions did not yield significantly different emission factors (Fiedler et al., 2010; Zhang et al., 2011). Stirring levels for China were not considered because the level of stirring did not vary among the experiments and as a result, stirring is confounded with the country effect.

Campaign is tested as a block for these data.[1] There is not sufficient statistical power to discern a significant difference in EF_{air} among the three campaigns conducted in Mexico, [Geometric averages: MEX-1, 510 ng TEQ kg^{-1} C_{burned} ($N = 4$); MEX-2, 680 ng TEQ kg^{-1} C_{burned} ($N = 10$); MEX-3, 1100 ng TEQ kg^{-1} C_{burned} ($N = 6$)] and when campaign is tested as a block for log EF_{air} it is similarly found not to be significant ($F = 0.444$, prob > $F = 0.6489$), and is thus dropped from the model. On the other hand, CO/CO_2 ratios were compared for the current experiments and those of the previous campaigns. Average CO/CO_2 in MEX-3 (0.143, $N = 6$) and MEX-1 (0.121, $N = 4$) were significantly higher than that of MEX-2 (0.057, $N = 10$) and thus campaign was included as a block.

Statistical analysis was conducted on data in MEX-1, -2 and -3 by defining a Stirring Surrogate Value: No stirring = 0, light stirring/loosened material = 0.5 and stirring = 1.0 (Table 3).

For CO/CO_2 least squares regression of the data against Stirring Surrogate Value and campaign yields highly significant effects for both (stirring effect, s: $F = 8.38$, prob > $F = 0.0105$; campaign effect: $F = 26.61$, prob > $F = <0.0001$).

- *Model*: CO/CO_2 = intercept + s ∗ Stirring Surrogate Value + campaign effect + residual.
- *Results*: Intercept = 0.123; $s = -0.0374$; campaign effect: MEX-1 = 0.121; MEX-2 = −0.0442; MEX-3 = 0.0321.

For EF_{air}, least squares regression of the log of the data against Stirring Surrogate Value is highly significant ($t = -5.51$, prob > $t < 0.0001$).

- *Model*: Log EF_{air} = intercept + s ∗ Stirring Surrogate Value + residual.
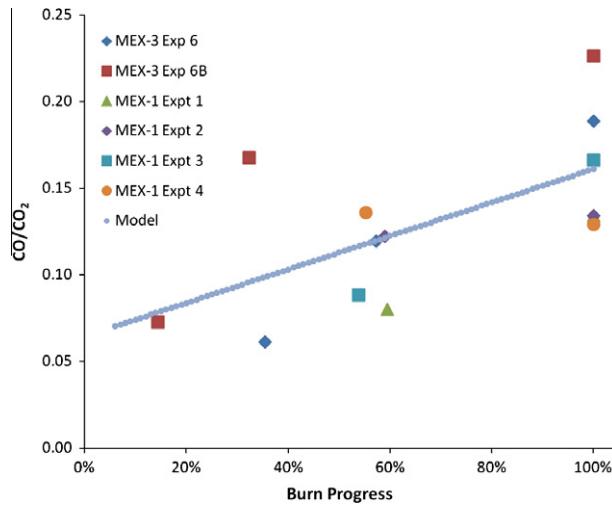- *Results*: Intercept = 3.30; $s = -0.985$.

The negative coefficient s in each case means that both CO/CO_2 and EF_{air} decrease with increased stirring. In fact, Gullett has suggested that a higher ratio of CO to CO_2 correlates with higher PCDD/PCDF emission (Gullett et al., 2010), a similar observation. For both CO/CO_2 and EF_{air} the residuals appeared normally distributed, with no correlation to the magnitude of the response, suggesting no other important variable was unaccounted for. There

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[1] A block is a portion of an experiment that is expected to be more homogenous than the aggregate. Blocks (day, site, equipment, etc.) may constitute unintended assignable causes within an experimental design (Box et al., 1978).
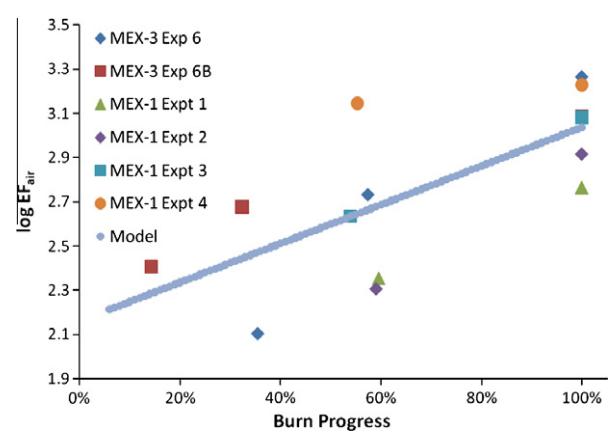
Table 3
Summary of experiments for Mexico and China campaigns.

Campaign	Experiment	Waste[a]	Initial condition	Stirring/moisture	Stirring Surrogate Value	EF_{air}, ng TEQ kg^{-1} C_{burned}	CO/CO_2
MEX-1[b]	Soy 1/2	Semi-urb	Loose	No/no	0.5	370	0.103
MEX-1	Soy 3/4	Semi-urb	Loose	No/no	0.5	460	0.127
MEX-1	San 1/2	Urb-ind	Loose	No/no	0.5	790	0.122
MEX-1	San 3/4	Urb-ind	Compacted	No/moist	0	1500	0.133
MEX-2[c]	RR-1	Rural	Lightly compacted	No/moist	0	2400	0.071
MEX-2	RR-2	Rural	Lightly compacted	No/moist	0	2800	0.102
MEX-2	UIBS-1[d]	Urb-ind	Loose	Light/no	0.5	370	0.054
MEX-2	UIBS-2[d]	Urb-ind	Loose	Light/no	0.5	250	0.079
MEX-2	UI-1	Urb-ind	Loose	Light/no	0.5	1400	0.043
MEX-2	UI-2	Urb-ind	Loose	Light/no	0.5	560	0.035
MEX-2	SU-1	Semi-urb	Loose	Yes/no	1	200	0.059
MEX-2	SU-2	Semi-urb	Loose	Yes/no	1	150	0.063
MEX-2	UIEW-1[e]	Urb-ind	Loose	Yes/no	1	180	0.021
MEX-2	UIEW-2[e]	Urb-ind	Loose	Yes/no	1	460	0.039
MEX-3[f]	Experiment 1	Urb-ind	Lightly compacted	No/water add	0	14000	0.162
MEX-3	Experiment 2	Urb-ind	Loose	No/no	0.5	660	0.141
MEX-3	Experiment 3	Urb-ind	Lightly compacted	Yes/water add	1	290	0.128
MEX-3	Experiment 5	Urb-ind	Loose	No/no	0.5	870	0.110
MEX-3	Experiment 6	Urb-ind	Lightly compacted	No/water add	0	950	0.125
MEX-3	Experiment 6B	Urb-ind	Lightly compacted	No/water add	0	950	0.191
CHN	No wall[g]	Urb		[h]		42	0.091
CHN	No wall	Urb		[h]		220	0.119
CHN	Wall	Urb		[h]		110	0.081
CHN	Wall	Urb		[h]		74	0.062
CHN	No wall	Semi-urb		[h]		13	0.071
CHN	No wall	Semi-urb		[h]		33	0.070
CHN	Wall	Semi-urb		[h]		24	0.081
CHN	Wall	Semi-urb		[h]		110	0.103
CHN	No wall	Rural		[h]		120	0.085
CHN	No wall	Rural		[h]		40	0.095

[a] While the same abbreviations are used, Mexico and China urban, Semi-urban and rural waste are not equivalent.
[b] Gullett et al. (2010).
[c] Fiedler et al. (2010) and Zhang et al. (2011).
[d] Urban-industrial before separation of recyclables.
[e] One kilograms consumer electronics waste added.
[f] Current campaign.
[g] Common China practice is to partially enclose the burn with a block wall.
[h] Reported to be lightly stirred, however since no variation, confounded with country effect.

Fig. 1. Relationship between mass CO/CO_2 and burn progress for multi-sample unstirred experiments: Model $p < 0.02$.

Fig. 2. Relationship between log EF_{air} and burn progress for multi-sample unstirred experiments: Model $p < 0.005$.

was a single outlier: the residual for EF_{air} for MEX-3 Experiment 1 deviated significantly from the normal distribution, which might be expected given the high absolute magnitude of the result, noted previously. Apparently replicate procedures conducted in all campaigns and both countries appear to yield different results characteristic of those campaigns and countries. This observation can be accounted for statistically, but not satisfactorily explained at this time.

4.2. Relationship of CO/CO_2 and EF_{air} to the extent of burn progress

In MEX-1 and MEX-3 some unstirred experiments were conducted while gathering multiple sequential PCDD/PCDF samples over the duration of the experimental burn. Burn Progress, a mea-

sure of the completion of the experiment, is defined as the carbon sampled during the period of PCDD/PCDF sampling divided by the total carbon collected by the end of the burn experiment.

CO/CO_2 is significantly positively correlated with Burn Progress (Fig. 1). EF_{air} is positively correlated with Burn Progress in each experiment and a statistically significant correlation emerges when the experiments are considered together (Fig. 2). Higher EF_{air} and higher CO/CO_2 occurs late in the burn when the pile is still hot but little mass loss is occurring, which might be characterized as a "smoldering" phase.

This observation is important both for experimenters and those who practice open burning. For experimenters, it implies that allowing the experiment to proceed to its natural end where the rate of mass loss approaches zero is critical to an accurate evaluation of the emission potential for PCDD/PCDF and PCB for any given scenario. For those who practice open burning, it implies that unattended, smoldering, poorly oxygenated burns have the highest emissions.

The idea that better combustion, induced by stirring, gives rise to less-polluting open burning is consistent with Stockholm Convention recommendations on Best Available Techniques–Best Environmental Practices (United Nations Environment Programme, 2007). At the same time, only small combustion piles could be stirred in this way. Large scale open burning – entire landfills as an example – may be more analogous to the unstirred experiments in this dataset. Recognizing this potential difference, while these were not experiments on landfill fires, *per se*, the results support the Toolkit approach of having two classes and two different EF_{air} for the subcategory open burning of waste (Household Waste Burning *vs*. Dump Fires). Promoting good combustion is a solid, basic operational principle; however, considerable additional work should be done to fully understand the mechanistic factors that impact emissions from the wide range of open burning practices.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.11.038.

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