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Effect of Moisture, Charge Size, and Chlorine Concentration on PCDD/F Emissions from Simulated Open Burning of Forest Biomass

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S *Supporting Information*

ABSTRACT: Loblolly pine (*Pinus taeda*) was combusted at different charge sizes, fuel moisture, and chlorine content to determine the effect on emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) as well as copollutants CO, PM, and total hydrocarbons. The experiments were performed in an enclosed chamber under conditions simulating open, prescribed burns of forest biomass. Burn progress was monitored through on line measurement of combustion gases and temperature while PCDD/F concentrations were determined by ambient sampling methods. PCDD/F toxic equivalency (TEQ) and total (tetra- to octa-CDD/F) emission factors were independent of charge size ($1-10$ kg) and moisture content ($7-50\%$). However, the lower chlorinated, mono- to tri-CDD/F compounds were increased by poor combustion conditions: combustion efficiency lower than 0.919 was generally found when the moisture content was higher than 30%. The increase of fuel matrix chlorine from 0.04% to 0.8% using a brine bath resulted in about a 100-fold increase of PCDD/F to about 90 ng TEQ/kg of carbon burned, C_b. These emission factors were linearly dependent on Cl concentration in the biomass. PCDD 2,3,7,8-Cl-substituted congeners and homologue patterns were also influenced by the addition of chlorine resulting in emissions with a higher abundance of the most toxic congeners (TeCDD and PeCDD). When both chlorine and moisture content were increased in the fuel, a simultaneous effect of the two parameters was observed. The increased TEQ values expected from higher Cl concentrations were mitigated by the presence of water, giving MCE = 0.868, promoting formation of mono- to tri-PCDD/F, and lowering the TEQ value. Open burn simulations were used to study PCDD/F formation in different combustion conditions providing a mathematical correlation between PCDD/F emissions and chlorine and moisture content in the fuel.
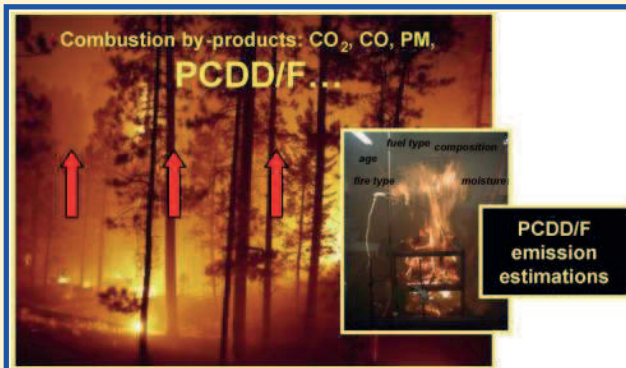
INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) are unintentional byproducts of a wide range of combustion activities including among others, waste combustion, diesel vehicles, and biomass sources. Because of their toxicity, protection of human health and the environment requires identification and quantification of PCDD/F sources. In particular, the Stockholm Convention on Persistent Organic Pollutants has required from signatories the development of national inventories on PCDD/F emissions.[1,2]

Table 1. Experimental Conditions and Fuel Characteristics. A Carbon Content Value of 50% on Dry Basis Was Used for the Calculations

name	number of burn replicates	experiment type	biomass composition	mass charge per burn (kg)	water content (%)	Cl content (%)[a]
1 kg	1	biomass charge size	67% green + 33% dry	0.7	44	0.05 ± 0.01
2 kg	4			1.9 ± 0.3	38 ± 2	0.05 ± 0.01
4 kg	3			3.8 ± 0.3	37 ± 3	0.05 ± 0.01
10 kg	3			10.2 ± 0.6	41 ± 4	0.05 ± 0.01
50% H$_2$O	3	moisture	biomass at established water	3.6 ± 0.2	49 ± 3	0.05 ± 0.01
30% H$_2$O	3		content and 10−15% dry fuel	3.6 ± 0.5	31 ± 4	0.05 ± 0.01
17% H$_2$O	2			3.1 ± 0.6	17 ± 1	0.05 ± 0.01
7% H$_2$O	1			2.01	7	0.05 ± 0.01
0.04% Cl	2	chlorine	green soaked in brine and then dried	2.3 ± 0.3	6 ± 2	0.04 ± 0.02
0.18% Cl	1			2.7	10	0.18 ± 0.02
0.25% Cl	1			2.13	7	0.251 ± 0.006
0.39% Cl	1			2.25	7	0.393 ± 0.004
0.44% Cl	1			2.25	7	0.437 ± 0.009
0.54% Cl	1			2.76	10	0.545 ± 0.006
0.73%Cl	1			2.04	7	0.73 ± 0.03
0.8% Cl	1			2.80	12	0.8 ± 0.1
1.1% Cl	1			2.08	7	1.13 ± 0.09
0.8% Cl − 24% H$_2$O	1	moisture/chlorine	[b]	2.54	24	0.8 ± 0.1

[a] Cl content expressed as dry basis. [b] Prepared as the samples with increased Cl content and dried in the open air to 24% of moisture content.

According to the latest Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States,[3] the total air releases included in the inventory were almost 1500 g I-TEQ/yr (international toxicity equivalents). The largest source was estimated to derive from the open burning of domestic waste, which has been the object of many recent studies[4−6] and has been categorized with sufficient confidence to be used for quantitative purposes. Emission factors were determined from combustion test of a model waste whose composition was derived from surveys. The release from domicile waste burning has been determined to be 473 g I-TEQ/yr, or about 35% of the total releases from known, reliably quantified sources (categories A−C, ref 3). Other open burning activities, such as landfill fires, postharvest field burning, and forest wildfires have not been included in the inventory because their emission factors have been considered nonrepresentative due to the limited data available. However, these sources can potentially exceed by more than a factor of 4 the releases actually taken into consideration in the inventory. Forest open burning alone is likely to be a much higher source. It was estimated that in the United States, 244 million metric tons of biomass were consumed by prescribed and wild burning in 2000.[3] Recent estimations of emission factors from forest burning simulations have been given with average values of 34 ng/I-TEQ/kgC$_b$,[7] 5.8 ngTEQ/kgC$_b$,[8] 18.6 ng I-TEQ/kg burned.[9] Using this last value, the total annual release in the U.S. can be estimated to exceed 4500 g I-TEQ. This estimation is likely to significantly increase in other countries, where open burning is even more important: it has been estimated that most of the open fires occur in Africa (40%) and South America (25%), while the remaining 35% is distributed over the rest of the world.[10]

Given that open burning of biomass has the potential to be the most significant source of PCDD/F, it is important to provide a better emission estimates for inventories. PCDD/F measurements need to take into account variables such as combustion quality and biomass species, combustible fuel composition, fuel dimensions,[11] conditions (dry versus wet, piled versus scattered) and density and fire type (crown fires versus understory and duff fires,.[12]

Research has begun to examine some of these biomass and combustion variables. Different PCDD/F emissions have been found when burning brown versus green pine needles[8] in open burning simulations.[9] Increased emissions have been found burning biomass or salt-laden waste wood with various chlorine contents in a pilot-scale fluidized bed combustor[13] and chlorine content of different combusted materials has been linearly correlated with PCDD/F emissions.[14] Environmental variables such as wind speed, atmospheric relative humidity, fire direction, fuel size, and fuel moisture have also shown significant impact in burn properties and efficiency.[10] Laboratory studies indicated that moisture content affects waste burning rate, CO, and hydrocarbon concentrations[15] but no indication is reported on PCDD/F emissions.

Other difficulties in the determinations of reliable emission factors are uncertainties due to the field sampling process and the ability of laboratory simulations to represent actual fires. Good agreement between field and simulated fire measurements was found for many organic compounds.[16,17] However, the agreement has not yet been demonstrated for PCDD/F emission estimations: field studies on bushfires in Australia resulted in emission factors 10 times lower than those from laboratory tests. This difference was attributed to sampling method limitations, the challenge of

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quantifying the amount of biomass burning, or differences in the formation mechanism during the burns[18,19] caused by an inability to simulate the field condition in the laboratory.

Determination of the effects of burn and fuel source variables on PCDD/F emission factors requires controlled conditions to be able to reproduce both the fire and the biomass characteristics. Laboratory simulations provide the possibility to control burn conditions and to sample larger fractions of the smoke than in the field thereby minimizing the chance of analytical nondetects. However, because significantly smaller amounts of fuel are used in laboratory simulations the representativeness of the tests to the field situation needs to be assessed. It is necessary to better understand charge size effects on PCDD/F formation before applying laboratory simulation results to research on the determination of the emission factors.

This work provides a preliminary examination of PCDD/F emission factor variability during open burning of biomass, testing correlations between mass charge size, moisture content, and chlorine content with PCDD/F emissions. The results can be used to develop more accurate and reliable emission factors estimates and provide guidance on prescribed burn practices that can minimize PCDD/F emissions.

■ EXPERIMENTAL SECTION

Materials. A single biomass source, Loblolly pine (*Pinus taeda*), was used as fuel in all the experiments. Loblolly pine is a common species in North Carolina and trees of similar dimension (2−6 m tall) were easily and locally accessible. Branches, twigs (diameter <1 cm), and pine needles from live, fresh trees were used for the tests. After collection the biomass was pretreated to obtain different fuel properties in order to evaluate the effect of three burn scenarios (Table 1) varying (1) mass charge size; (2) moisture contents; and (3) chlorine contents

To evaluate the effect of charge size, freshly cut and dry branches or twigs were mixed at proportions of 67 and 33% by weight, respectively. The freshly cut green biomass had a water content between 50 and 60% per wet fuel mass depending on the season. The dry biomass was produced from the freshly cut biomass by being stored indoors or outdoors (depending on ambient weather conditions) for about 7−15 days and oven-dried for more than 48 h at 35 °C to obtain a final moisture content <10%. After mixing the dry biomass with the freshly cut branches, the final water content of the fuel mixture used in the charge size experiments was about 40%.

To study the effect of biomass moisture content, fuels at intermediate water contents were obtained by placing freshly cut biomass indoors or outdoors for several days until the desired moisture levels were reached. The moisture content was measured by oven drying (105 °C) and weight loss measurements.

The biomass was also modified to obtain fuels at different chlorine contents: 3.5 kg of fresh branches and twigs were soaked in 75 L of a sodium chloride water solution at concentrations of 0.25, 0.5, 1.0, and 1.5% w/w for 5 days. Subsequently, the biomass was drained and laid on paper towels, then exposed to the outdoor or indoor air for several days until a moisture content of around 10% was reached. This final treatment was necessary to ensure that fuels at equal water content yet varying chlorine

content were tested. In addition to these treatments, a single biomass sample was prepared in a brine solution at 1.5% w/w sodium chloride and dried to a final water content of 24%. The resulting biomass chlorine content was determined by oxygen bomb calorimetry (PARR 1341) using methods based on ASTM Method D2361 (see Supporting Information (SI) Section S1). To obtain replicate fuels, two batches of brine solutions at various chlorine contents were prepared in late summer and spring. Table 1 reports the chlorine content of the biomass determined on a dry basis for each treatment in brine. Of the total chlorine, 20% was determined to be superficial (i.e., it could be removed washing the biomass three times in deionized water). These chlorine concentrations are representative of natural concentrations. Although wood chlorine content generally ranges around 0.005%, some biomass such as hog fuels,[13] sugar cane,[20] and reed canary grass[21] can reach concentrations as high as 0.9%.

The amount of biomass burned in each test was bounded by the necessity to maintain open burn conditions with minimal oxygen depletion, while at the same time having sufficient PCDD/F production to surpass method detection limits. Previous experiments on biomass burning[9,20] indicated that sampling about 30 g of combusted carbon (determined as the sum of CO_2 and CO emissions) resulted in detectable PCDD/F. Accordingly, emissions from multiple burns were combined into a single sample (common filter and PUF) to obtain sufficient C for analysis.

Setting. Burn simulations have been carried out in an open burn test facility (SI Figure S1). The test facility consists of a 3.9 × 3.9 × 4.6 m structure with concrete block walls that are covered with metal sheets for ease of cleaning. In order to ensure open burn conditions (high ambient air dilution with minimal depletion of the oxygen concentration) air was pulled by a high volume blower through an opening (0.7 × 0.7 m) at the side of the facility. The flow rate could be adjusted between 20 and 100 m3/min and was metered into the duct (18 cm radius) exiting the facility using a Pitot tube. Fans and flow deflectors within the test facility were used to enhance air circulation, whereas the incoming air was prevented from directly impinging on the flames. Biomass was placed on a stainless steel stand that allowed positioning the branches and twigs in an upright position. The scale plate was covered with certified (ASTM B-479) clean aluminum foil (Ultra High Vacuum) purchased from All Foils, which was replaced after each burn. Thermocouples were placed on the scale, in the middle and atop the biomass assembly, downstream from the sampling sorbent, and next to the walls of the facility.

Sampling Procedure. Samples to characterize PCDD/F air emissions were taken inside the burn hut facility via a high volume sampler: Tisch Environmental TE-PNY1123 Accuvol Modified PUF Sampler (http://www.tisch-env.com/tegpny1123.asp) using EPA's ambient TO9A method[22] which consists of an open-faced filter holder, followed by polyurethane foam (PUF), prespiked with eight presampling surrogates.[23] The filters (Whatman, TE-QMA Micro-Quartz Filter Media 8" x 10") were preweighed in a weighing chamber after conditioning for at least 48 h at 22 °C and relative humidity of 35%. Lines to the continuous emission monitors (CEMs) were positioned next to or at the exit of the sampler to monitor for oxygen (O_2, model 755, Rosemount Analytical, Solon, OH), carbon dioxide (CO_2, model VIA510, Horiba, Irvine, CA), carbon monoxide (CO, model VIA510, Horiba, Irvine, CA), and total hydrocarbon (THC, model 300HFID, California Analytical, Anaheim, CA). CEM data together with measurements of sampling

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Table 2. Combustion Characterization and Emission Factors for on-Line Monitored Emission, PM and PCDD/F (Te−Oc)[a]

name	total C from emissions per sample (g)	C burn rate, k (t^{-1})	EF_{CO_2} g/km fuel	EF_{CO} g/kg fuel	EF_{THC} g/kg fuel	EF_{PM} g/kg fuel	MCE	PCDD/F (nmol/kgC$_b$)	PCDF:PCDD (Te−Oc)	PCDD/F (ng TEQ/kgC$_b$)
1 kg	30	0.22	1523	106	na	52	0.90	0.17	4	0.95
2 kg [b]	79 ± 48	0.3 ± 0.1	1413 ± 44	136 ± 14	48 ± 7	44 ± 8	0.87 ± 0.01	0.29 ± 0.17	10 ± 8	1.53 ± 0.83
4 kg	37 ± 12	0.5 ± 0.1	1486 ± 97	106 ± 19	39 ± 8	40 ± 12	0.90 ± 0.02	0.27 ± 0.25	11 ± 14	0.92 ± 0.86
10 kg [b]	19 ± 5	0.22 ± 0.02	1453 ± 47	125 ± 17	36	55 ± 15	0.88 ± 0.02	0.33 ± 0.24	8 ± 6	1.6 ± 0.5
50% H$_2$O	33 ± 9	0.38 ± 0.01	1258 ± 42	152 ± 3	67 ± 14	77 ± 24	0.841 ± 0.003	0.29 ± 0.12	4 ± 3	0.75 ± 0.49
30% H$_2$O	52 ± 23	0.50 ± 0.01	1577 ± 42	95 ± 6	33	23 ± 12	0.914 ± 0.007	0.29 ± 0.12	12 ± 12	3.2 ± 1.6
17% H$_2$O[b]	59 ± 22	0.52 ± 0.02	1681 ± 3	60 ± 8	11.3 ± 0.2	7 ± 2	0.943 ± 0.001	0.19	4	0.99
7% H$_2$O	33.47	0.55	1720	50	na	12	0.956	0.39	20	2.09
0.04% Cl	32 ± 5	0.64 ± 0.01	1726 ± 18	52 ± 1	5	7 ± 2	0.955 ± 0.002	0.10 ± 0.04	14 ± 7	0.46 ± 0.21
0.18% Cl	50	0.58	1675	65	12	8	0.943	0.50	15	2.9
0.25% Cl	33	0.51	1703	67	na	9	0.942	1.6	24	8.8
0.39% Cl	37	0.47	1675	69	9	na	0.940	3.9	25	22.05
0.44% Cl	42	0.44	1696	65	na	13	0.943	2.6	28	13.7
0.54% Cl	54	0.52	1640	86	13	8	0.924	2.8	20	18.0
0.73% Cl	31	0.59	1667	74	na	18	0.935	6.5	33	33.3
0.8% Cl	28	0.47	1649	80	11	10	0.929	11.9	22	91.5
1.1%	29	0.56	1641	96	na	15	0.916	5.6	23	32.7
0.8% Cl − 24% H$_2$O	10	0.43	1442	137	46	na	0.868	4.0	46	19.1

[a] C burn rate is carbon burn rate; MCE is modified combustion efficiency; EF is emission factor. See Supporting Information for definition of these derived quantities. na is not available. EF $_{THC}$ is reported as g CH$_4$/kg fuel, that is, an average molecular weight of 16 per carbon atom. [b] For these experiments, one replicate has not been included in the PCDD/F quantification since it was done just after an experiment at high Cl content, without cleaning the open burn test facility.

flow 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).

The fire was started with a propane torch at multiple locations of the biomass pile, typically for less than 20 s. Combustion was easily initiated due to selection of a ratio of dry to fresh biomass that allowed for self-sustained combustion. Sampling was initiated when combustion progressed unaided. Times to terminate the sampling were established based on temperature readings, visual analysis of the final product remaining on the burn platform, and when no significant emission of C above ambient levels was registered by the continuous emission monitors (CO$_2$ < 5 ppm).

In tests with reduced moisture content and higher charge size the temperature of the gases close to the sampler was >60 °C during the flaming phase of the burns. When this temperature was reached presampling spike recoveries did not meet quality criteria (70−130%, ref 23) and most likely target compounds were lost (Table 1). To avoid this situation, the sampling system was modified by addition of a dilution flow (50−60 L/min) of cold (around −10 °C) nitrogen that resulted in sampled gas temperatures lower than 60 °C in all of the remaining tests. (see SI Section S2 and Figure S2 for more detailed information).

Analysis. The 17 toxic PCDD/Fs and total mono- to octa-PCDD/Fs were analyzed using the isotope dilution method.[23] PUFs and filters from multiple burns conducted under the same conditions were combined and analyzed together to avoid nondetects and obtain more accurate TEQ values.[24] Before extraction, filters from each burn were weighed after 48 h conditioning time at 22 °C and a relative humidity of 35%, in order to determine the mass of collected particulate matter (PM). The samples were Soxhlet extracted for 17 h with toluene after addition of 14 carbon-labeled PCDD and PCDF internal standards, representing the mono- through octa-chlorinated homologues. The high levels of interferents (around 1000 times

higher than targets) required modification of the standard clean up procedure, including concentration of the extract to 30−50 mL and overnight refrigeration after the addition of around 300 mL of hexane. This procedure allowed the precipitation of nonhexane-soluble compounds. The solution was then filtered, concentrated to around 3 mL, and stored. Half of the sample was then cleaned using an automated system (Fluid Management System Inc., FMS, Watertown, MA) with the use of high volume silica columns prewetted with sulfuric acid. This clean up procedure reduced the levels of undesired compounds while maintaining acceptable recovery levels for the mono- to octa- congeners (more details in the SI). The samples were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC-HRMS) with a DB-Dioxin Column (J&W Scientific, Santa Clara, CA) as reported elsewhere.[25]

■ RESULTS AND DISCUSSION

Combustion and emission characteristics for the 31 experiments are shown in Table 2. Of 31 total experiments, 28 experiments were conducted for PCDD/F analyses and three additional experiments were conducted only for the CEM. When experiments were repeated, the average and the respective standard deviation are reported. Variation of the three test parameters resulted in PCDD/F emission factors (EFs) ranging from 0.46 to 91.5 ng TEQ/kgC$_b$, CO$_2$ EF from 1258 to 1726 g/kg fuel, CO EF from 50 to 152 g/kg fuel, EF THC from 5 to 67 g/kg fuel, and modified combustion efficiency (MCE) from 0.841 to 0.956. Field blanks resulted in PCDD/F air concentrations at least 1 order of magnitude lower than the lower emission factors from the combustion experiments. Laboratory blanks resulted in nondetects except for 1,2,3,4 TeCDD; this value was excluded from the evaluation of total concentrations and does not enter into the TEQ calculations.

Emission Factors of Online Monitored Species. Table 1 reports test parameters related to burn quality. Oxygen concentrations during the burns averaged between 20.70% and 20.93%, ensuring that burn conditions represented open-air combustion.
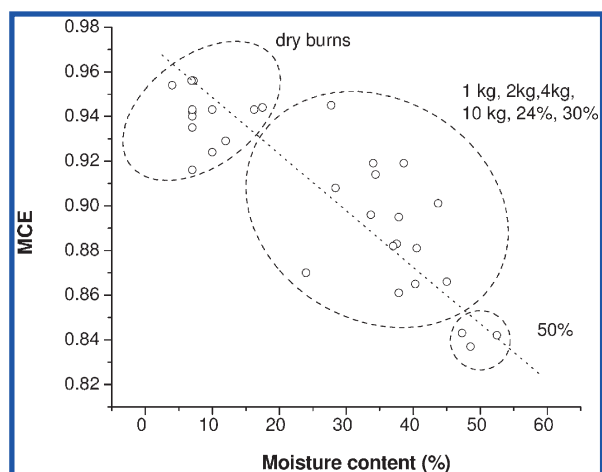
Figure 1. Relation between time-averaged modified combustion efficiency (MCE) and moisture content for all 31 experiments. In the circles are highlightened three data subsets, representative of the experiments at higher water content and lower MCE values, medium water contents and MCE values, and low water contents and higher MCE values.

Mass balances comparing fuel C loss as CO and CO_2 were compared to scale weight measurements, showing agreement with ±15%, except for one test where the mass balance was off 30%.

Burn durations varied, depending on the type of the fuel, between 30 and 60 min. The shorter burns were those with lower moisture content and lower mass charge size. Carbon burn rate and MCE (for calculations of these parameters see SI) were also characteristic of the experiment type. Burns with higher moisture content (1−10 kg charge size and >24% moisture content) had a significantly (at the 99% confidence level) lower carbon burn rate, k, than all the other burns. MCE varied throughout the burns: in our tests it was higher than 0.9 at the beginning of the burns (0−1 min). Subsequently MCE dropped to about 0.7 before slowly increasing until the end of the tests (SI Table S1). Variation of the MCE throughout burns is an important parameter since it is used to monitor different phases of the burns (i.e., flaming vs smoldering) and it is related to variation in the emission factors.[26,27] Flaming phases are characterized by higher MCE (see SI) and lower PCDD/F emissions per C burned than smoldering phases.[8] The time integrated averaged MCE (Table 2) gives global information of the combustion conditions of the burns and it appears to be well correlated to moisture content as shown in Figure 1 ($R^2 = 0.703$).

Emission factors for CO, THC, and PM vary similarly with experimental conditions and are linearly related (positively) (SI Figures S4 and S5) to each other. Generally the experiments with biomass at higher water content (also considering experiments at different charge sizes, containing 37−44% water content) reported the highest emission factors (Table 2, SI Figure S5): for CO the average EF in the experiments with water content >17% resulted in 119 ± 27 g/kg fuel, compared to 68 ± 14 g/kg fuel for experiments with water content ≤17%. Regarding THC and PM, the experiments with water content >17% resulted in average EFs equal to 44 ± 17 and 54 ± 20 g/kg fuel, respectively, while for experiments with water content ≤17% their values were 10 ± 3 and 10 ± 4 g/kg fuel, respectively.

The emission factors estimated in our experiments agree with EFs determined for the flaming and smoldering of pine needles in reported studies.[28,29] CO_2, CO, THC, and PM for loblolly pine

with water content <17% are comparable to those of laboratory burn simulations for pine species at similar water contents.[28] On the other hand, emission factors similar to those assessed for burning biomass at higher water contents have been found in prescribed burns of pine-dominated forest in flaming and smoldering conditions.[29] This comparison indicates that our tests at different charge sizes and 30−40% water content should be a better representation of the conditions of field burns, which is important to take into account, since these tests are characterized by a significant smoldering phase (determined from temperature measurements, MCE calculations, and visual observation) and increased emissions of products of incomplete combustion.

PCDD/F. PCDD/F results are reported in SI Table S1. Relative standard deviations (RSD) for total Te-OCDD/F both in nmol/kgC_b and in ng TEQ/kgC_b in repeated experiments averaged around 60%, with minimum values for the experiments at 0.04% Cl and 10 kg (around 40%) and higher values for the 4 kg burns (up to 90%). These RSDs are not unusual[8] and are associated with variations in the fuel used in the burns (e.g., seasonal differences, plant chemical and physical composition), changes in the experimental setting (e.g., different orientation of the biomass on the rack and the fire lighting procedure), and uncertainties in analyses near detection limit concentrations. Means of the detection limits in the samples are reported for each homologue in the SI (Table S2) and average 0.05 ± 0.04 ng TEQ/kgC_b and 0.001 ± 0.001 nmol/kgC_b per single congener.

Apart from Te-OCDD/F, Mo-TrCDD/F homologues were determined in all the samples. However, due to low recoveries of the presampling spikes, when the sampling gas temperature was >60 °C and the sample was particularly difficult to clean up, some values needs to be considered only approximate (see SI, section S2). Table 2 reports only data relative to Te-OCDD/F. Complete results of total PCDD/F and their homologue profiles are reported in SI Table S1 and Figures S6−S8, which are discussed below.

Mass Charge Size. Experiments ranging a factor of 10 in mass charge size resulted in a 2-fold variation of the Te-OCDD/F from 0.17 to 0.39 nmol/kgC_b (Table 2). The concentrations did not show any trend with biomass charge size and the variations were of the same order of magnitude as the experimental error. The same lack of correlation is also shown between mass charge size and TEQ values (ranging from 0.92 to 1.9 ng/kgC_b). Moreover, no significant variations in the 2,3,7,8 isomer pattern and homologue distributions could be noted (SI Figure S6a and S7a). PCDF contribution to the TEQ was 40−70% and the PCDF molar concentrations were always 80−90% of the totals. The most important isomer was 2,3,7,8 TeCDF and the contribution of the isomers generally decreased with the chlorination degree, with exception of 1,2,3,4,6,7,8 HpCDF and OCDF. For PCDD, the isomer pattern was dominated by OCDD (>50% on a molar basis) followed by HpCDD (15−20% on a molar basis) (SI Figure S6a). Regarding the homologues, TeCDF were also the most abundant group within the PCDFs, comprising around 70% of the Te-OCDF, followed by PeCDF. For PCDD all five homologue groups had similar abundance with TeCDD and OCDD somewhat higher than 20% (SI Figure S7a).

Water. Emission factors for biomass at four different water contents varied between 0.19 and 0.39 nmol/kgC_b and from 0.75 to 3.2 ng TEQ/kgC_b with no dependence on moisture content (Table 2). The isomer and homologue patterns were comparable with those of the experiments at different charge sizes (SI Figures S6b and S7b). Only a slight increase in abundance of PeCDD (from around 10% to 20%) and OCDD (from around 10% to

30%) homologues could be noted in the samples at 48% water content as compared to the samples at lower water contents.

TEQ values, homologue and isomer distributions found in this work were similar to previously reported values of *Pinus taeda* simulated pile burns (0.63 ngTEQ/kgC_b, relative standard deviation = 69%, 8). However, in the previous work PCDD were comparable to PCDF concentrations (average value for PCDD = 258 ng/kgC_b and for PCDF = 300 ng/kgC_b), whereas our burns showed a marked predominance of PCDF (in average 8 times higher, as ng/kgC_b) over PCDD. This result may be related to differences in the experimental setting (standing biomass for all our tests instead of pile burns and no added dirt) but the reasons for this discrepancy remain uncertain.

Chlorine. All the burns with pine needles at high chlorine contents resulted in significantly increased PCDD/F emissions. The emission factors ranged from 0.5 to 11.9 nmol/kgC_b and from 2.9 to 91 ng TEQ/kgC_b, whereas the baseline fuel, pine needles soaked in water without salt addition, resulted in 0.1 ± 0.04 nmol/kgC_b and 0.46 ± 0.21 ngTEQ/kgC_b. These emission factors were in the same range of the values for burns at different mass charge size and moisture content. Isomer and homologue patterns are reported in SI Figures S6c and S7c.

Isomers and homologue distributions for PCDF were similar to those of the experiments at different mass charge size and moisture content. In all these experiments 2,3,7,8 isomers and total homologues decreased from lower to higher chlorinated congeners. However, PCDD emissions showed a different behavior from experiments without chlorine addition (including the sample with 0.04% Cl). 2,3,7,8 TeCDD and 1,2,3,7,8 PeCDD were the most abundant isomers, each constituting 40% of the totals. The other isomers increased from HxCDD to OCDD, resembling the patterns of the samples with biomass at lower chlorine contents. The homologues also presented a different pattern with the TeCDD and PeCDD as the major contributors. The PCDF:PCDD ratio (molar basis, Table 2) was on average 24 ± 5 times higher than the value found for the emissions of the burns with low chlorine (on average $9:1 \pm 5$). This observation is in agreement with laboratory scale experiments[30] where the presence of chlorine affected the formation mechanism by favoring mainly PCDF and shifting the PCDD homologue and isomer patterns.

Chlorine and Water. The biomass sample prepared with 0.8% of chlorine and 24% of moisture content resulted in TEQ equal to 19.1 ngTEQ/kgC_b, and Te-OCDD/F totals equal to 4.0 nmol/kgC_b. These values were significantly higher than those for the samples at comparable water content (17% H_2O and 30% H_2O) and no chlorine addition. This indicates that the chlorine content has a major effect on the emission factors also when burning biomass with a certain moisture level. However, this burn presented lower emissions than those of the corresponding burns of dry biomass with similar chlorine content (0.73% Cl and 0.8% Cl). PCDF homologue and isomer patterns were comparable to the burns of dry biomass at high chlorine and similarly PCDD homologue and isomer patterns presented high TeCDD and PeCDD contribution. However, OCDD was around 50% of the toxic isomers and 19% of the Te-Octa homologues, similarly to the emissions of burns with biomass at high water content (48%) and no addition of chlorine. These observations can indicate that to some extent water content affected PCDD/F formation, reducing TEQ value and Te-OCDD/F. However, this effect of water could be noted only when emission factors were significantly higher than the detection limit.

A regression for TEQ and the three variables of this study, as well as their cross products, indicated that the only significant correlation was with chlorine concentration. The determination coefficient (R^2) for the regression between the logarithm of TEQ and chlorine concentration was equal to 0.72 and P value < 0.0001 (Figure 2). The relationship followed the equation:

$$\log[(\text{TEQ}\,(\text{ng/kgC}_b)] = (1.9 \pm 0.2) \times \text{Cl}(\%)$$

This relationship explains some of the differences found in previously reported studies from biomass burning when the fuel had different chlorine contents. Burns of sugar cane with chlorine contents of 0.06% and 0.87% resulted in a 10-fold higher TEQ for the latter.[20] Emission factors from forest burning were also somewhat increased (taking into account data variability) when the chlorine content of the fuel was about 0.16% instead of about 0.03%.[9] However, it was not possible to associate the results on the chlorine effect, since many other parameters where involved in the burns.

Our data, in which we used only one type of biomass burned in consistent experimental conditions, indicate that there is a linear relationship between chlorine content in the fuel and PCDD/F emissions. This relationship, however, could vary depending on the biomass species burned, biomass characteristics (such as moisture content), and combustion quality.

M-OCDD/F Estimations. M-OCDD/F data are extensively reported in SI Table S1. These compounds are important as an index of combustion efficiency, as they increase in concentration during poor combustion. Moreover, in the presence of appropriate conditions (such as catalyst and chlorine and 300−500 °C) they can act as precursors for higher chlorinated compounds and therefore may increase TEQ emissions.[31,32]

As indicated previously (and described in the SI), in some experiments Mo-TrCDD/F determination was less accurate, and steps were taken in order to improve their determination. For all 31 runs, the Mo-TrCDD/F accounted for 70−80 molar percentage of the total yields (SI Figure S8). The experiments with charge sizes 1−4 kg resulted in similar total emissions with an average of 38 ± 16 nmol/kgC_b (RSD = 42%). However, with 10 kg of biomass burned total emissions were significantly higher and equal to 137 ± 30 nmol/kgC_b (RSD = 22%). When the biomass water content was changed the emission factors showed 20-fold variation within the range studied, from 5 to 96 nmol/kgC_b. Total emissions of the burns with increased chlorine contents varied from 5.4 to 125 nmol/kgC_b. The emissions of the burn of biomass at 0.8% chlorine and 24% water content resulted in the highest total PCDD/F level, 284 nmol/kgC_b.

PCDD/F emissions appeared to be related to moisture content (P value = 0.014) as shown in SI Figure S9. Since high moisture contents resulted in a decrease in the burns efficiency (Figure 1), PCDD/F total emissions are also somehow related to MCE (P value = 0.024). The use of multiple regression analysis indicated no dependence of totals with mass charge size and allowed us to model the logarithm of the total emissions as a function of moisture and chlorine content, following the equation:

$$\begin{aligned}\log[\text{M} &- \text{OCDD/F(nmol/kgC}_b)] \\ &= (0.9 \pm 0.2) + (1.2 \pm 0.2) \times \text{Cl}(\%) + (0.017 \pm 0.004) \\ &\quad \times H_2O(\%)\end{aligned}$$

The determination coefficient (R^2) is equal to 0.5 and P value is 0.00015. This preliminary model confirms that chlorine is the main
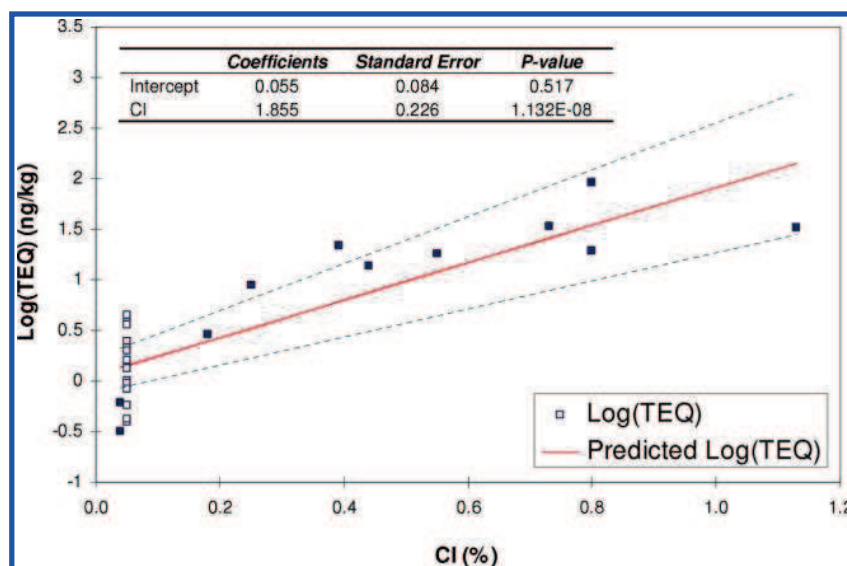
Figure 2. Regression analysis and line for the trend between biomass chlorine content and logarithm of TEQ using all the 28 data points. $R^2 = 0.72$. Filled squares represent data from experiments varying chlorine content; open squares represent data from experiments varying mass charge size and moisture content and have no significance in the shown relationship. Dashed lines represent the 95% confidence interval.

parameter affecting the total emissions but that water can play a significant role depending on its percentage. A model describing more accurately the result of high chlorine when also water is present in the biomass burned could be calculated including in the experimental matrix additional experiments using biomass with both chlorine and water present at various concentrations.

The main outcome of this study is that PCDD/F emission factors (as log TEQ) are linearly related with chlorine content of the fuel. The presence of chlorine also influences the chlorination degree of the isomers mainly favoring chlorination of PCDD and increasing the abundance of toxic compounds such as 2,3,7,8 TeCDD and 1,2,3,7,8 PeCDD. Burns resulting in poor combustion conditions, such as those with biomass at increased water content, lead to a significant increase of total PCDD/F emissions, while no variation was shown in TEQ and Te-OCDD/F emissions.

PCDD/F in Ash Samples and Raw Biomass. Analysis of raw material and two ash samples (experiments with 50% H_2O C and 0.73% Cl in SI Table S1) was performed to quantify M-OCDD totals and homologue profiles (see SI Section S4 and Table S3). In the raw biomass the total PCDD and PCDF were about 0.50 nmol/kgC and the PCDF were 10 times higher than PCDD. This concentration is around $^1/_{10}$ of our lowest emission factor, which confirms previous results[9] suggesting that PCDD/F emissions are not simply a result of vaporization of surface-bound PCDD/F but are formed during the combustion process. The ash samples contained higher PCDD/F concentrations per mass of initial carbon than the raw biomass, consisting mainly of PCDF. The ash of the test with 0.73% Cl, contained PCDD/F concentrations of 64.6 pmol/g dry basis and 2.4 pg TEQ/g dry basis, values seven times higher than those of the ashes of the experiment at 50% H_2O. Considering the amounts of ash remaining after the burns, these reported TEQ values per mass of carbon burned are 10 and 130 times lower than air emissions (SI Table S3). SI Figure S10 reports the homologue profiles of these three samples. The two ash samples have homologue profiles similar of those of the air emissions, with around 80−90% of MCDD and MCDF. In contrast, the raw biomass showed a different pattern: higher chlorinated dioxins were more abundant than in the ash samples and lower chlorinated furans were less important than in the

ash samples. This observation is another indication that new compounds are formed during the burns.

■ ASSOCIATED CONTENT

ⓢ Supporting Information.   Sampling and analytical modified methods and data quality are described together with complete results of M-OCDD/F, their homologue and isomers profiles, detection limits, and concentrations in raw biomass and two ash samples. Schematics of the experimental setting, explanation of calculations of modified combustion efficiency (MCE), emission factors (EF) and carbon burn rate (k), relationships between EF of on line monitored species, MCE, and k and total PCDD/F emission factors as a function of moisture content are also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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