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Effect of 2,4-Dichlorophenoxyacetic Acid (2,4-D) on PCDD/F Emissions from Open Burning of Biomass

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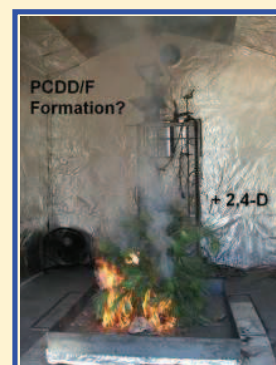
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S Supporting Information

ABSTRACT: To understand the effect of leaf-surface pesticides on emissions of PCDD/F during biomass burns, nine combustion experiments simulating the open burning of biomass were conducted. Needles and branches of *Pinus taeda* (Loblolly pine) were sprayed with the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) at 1 and 10 times the manufacturer's recommended application concentration. The biomass was then dried overnight, burned in an open burn test facility, and emission samples were collected, analyzed, and compared against emission samples from burning untreated biomass. Blank tests and analysis of PCDD/F in the raw biomass were also performed. Emission results from burning a water-sprayed control show a ~20-fold increase in PCDD/F levels above that of the raw biomass alone, implicating combustive formation versus simple volatilization. Results from burns of pine branches sprayed with pesticide showed a statistically significant increase in the PCDD/F TEQ emissions when burning biomass at ten times the recommended pesticide concentration (from 0.22 to 1.14 ng TEQ/kg carbon burned (C_b), both ND = 0). Similarly, a 150-fold increase in the total PCDD/F congener mass (tetra- to octachlorinated D/F) above that of the control was observed (from 52 to 7800 ng/kg C_b), confirming combustive formation of PCDD/F from 2,4-D. More replicate testing is needed to evaluate effects at lower pesticide concentrations.



INTRODUCTION

Combustion of biomass from agricultural practices and forest fires is believed to be a significant source of worldwide releases of polychlorinated dibenzodioxins and dibenzofurans (PCDD/F).^{1–3} Some authors reported an increase of PCDD/F levels in ash-laden soils after a forest fire.⁴ Field sampling⁵ and laboratory simulations of open burning^{6,7} without addition of pesticide have measured PCDD/F emissions to the atmosphere. Emission factors, or the mass of PCDD/F per mass of biomass consumed, range considerably, from less than 0.5 mg toxic equivalency (TEQ)/(t fuel consumed) to greater than 100 mg TEQ/(t fuel consumed).⁶

PCDD/F emissions during biomass burning may be attributed to thermal desorption of these adsorbed species from the waxy cuticle surrounding the leaf. A number of factors have been shown or postulated to affect PCDD/F emissions, including chloride content,⁸ combustion conditions,⁹ biomass fuel properties,^{10,11} and the presence of pesticides adsorbed onto the leafy surfaces.¹² Biomass, particularly pine species, has been shown to adsorb PCDD/F readily onto the leaf surface^{13,14} and could be expected to desorb the compounds readily when heated. However, some authors document up to 100-fold increases in PCDD/F releases from combustion experiments above concentrations found on the raw biomass, indicating that PCDD/F emissions are not derived primarily from vaporization of PCDD/F adsorbed on the leafy surfaces.^{7,11,15} The presence

of PCDD/F in emissions is also due to formation of these compounds in the combustion process.

Several studies reported high levels of organochlorine compounds in pine needles,^{12,16} including organochlorine pesticides.^{17,18} Semivolatile organic compounds (SVOCs) adsorbed on pine needles remain leaf-bound and are not believed to undergo significant natural revolatilization.¹⁹ Formation of PCDD/F may also be tied to the combustive conversion of adsorbed pesticides or their trace byproducts. Precursors found in the soil⁵ such as the fungicide pentachlorophenol (PCP) and highly chlorinated phenoxyphenols (PCPPs) have also been implicated in PCDD/F formation, mainly OCDD, from the combustion process.^{20,21}

Some chlorinated pesticides such as 2,4-dichlorophenoxyacetic acid (2,4-D) are used frequently in the U.S. and Europe for several crops. The global market of 2,4-D is estimated to be over US\$300 million and the main producers are Agrolinz, Atanor, Dow, AH Marks (UK), Nufarm (Australia), Polikemia, Rhône-Poulenc, Sanachem, Sinochem (China), and Ufa, together with four other producers in Turkey.²² According to the U.S. EPA, the annual domestic usage is 46 million pounds

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with 66% used for agricultural and 34% used for nonagricultural purposes.²³ The U.S., South America, Europe, and the countries from the former Soviet Union are major markets for 2,4-D-weed pesticide.²⁴ 2,4-D has a chemical structure (see Figure 1A) readily

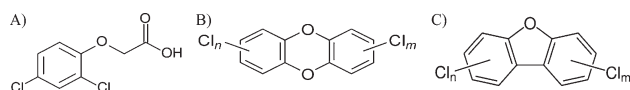


Figure 1. Chemical structures of (A) 2,4-D, (B) PCDD, and (C) PCDF.

amenable to reaction to form PCDD/F. 2,4-D is a chlorinated phenoxy compound, functions as a systemic herbicide, and is used to control many types of broadleaf weeds. The principal use of this pesticide is for the control of broadleaf weeds in cereal crops (including wheat, maize, rice, and sorghum), grassland, and turf areas. 2,4-D is also widely used in mixtures with other herbicides to provide weed control in forestry, orchards and noncrop areas, and for the control of aquatic weeds.^{25,26}

Overspray of pesticides and herbicides has been cited as the cause of halogenated organic emissions to the land from both subsequent biomass combustion²⁷ and vaporization of impurities in their formulations.²⁸ Biomass samples spiked with pesticides and then burned yielded 35- to 270-fold higher values of PCDD/Fs in the ash as compared to the controls.²⁷ Similar studies assessing PCDD/F emissions from experiments with and without addition of pesticide are apparently lacking in the literature.

While combustive formation of PCDD/F from organochlorine pesticide precursors is possible, many pesticides, including 2,4-D, have impurities of PCDD/F in their formulations which could be released during combustion. Some authors reported considerable amounts of PCDD/F in different pesticides.^{28,29} C. Rappe and co-workers³⁰ reported on phenoxyacetic acids and impurities of PCDD/Fs with a focus on occupational exposure to these pesticides however did not look for effects of fire. A recent study found a notable amount of PCDD/F emissions from the combustion of several pesticides.³¹

To understand the effect of 2,4-D on emissions of PCDD/F during biomass burns, combustion experiments were conducted to simulate open burning of biomass. Biomass was sprayed with the selected pesticide, 2,4-D, burned in an open burn test facility, and emission samples were collected, analyzed, and compared against emission samples from untreated biomass.

EXPERIMENTAL SECTION

Emissions were sampled from a total of nine open burns of biomass sprayed with two concentrations of the pesticide and a water-sprayed control sample.

Materials. Locally available loblolly pine trees (*Pinus taeda*) were used as a biomass fuel for all the experiments. While pesticide overspray on forest species is not a common practice, the local abundance of loblolly pine and previous emission data from loblolly combustion experiments made this species a good biomass surrogate. Young trees or branches with a length of ≤ 2 m were used to simulate the open air understory burning environment in a forest. The limbs were supported in an upright position using a 10 cm high metal tree base. The pine forest floor was recreated with pine needles and duff collected from beneath the tree, keeping the same approximate area density.

Selection of 2,4-D (2,4-dichlorophenoxyacetic acid, C₈H₆Cl₂O₃, CAS 94–75–7, Figure 1A) for use in these experiments was based

on its high volume of industry usage, its commercial availability, the presence of Cl in its composition, and its chemical structure. The 2,4-D was purchased from Ag Supply (CA). For more information see Supporting Information (SI).

Open Burn Test Facility. Biomass was burned in an open burn test facility: an air-ventilated, enclosed facility used to simulate small-scale open burning conditions. The facility consists of a 2.9 × 3.5 m base and a sloped ceiling height of 2.8 m at the apex and 2.2 m at the walls. The basic structure is composed of sheet metal fitted to a frame of structural galvanized square tubing. The interior was finished in 1.6 cm thick sheetrock which also forms a backing to which aluminum foil is attached. A second layer of certified (ASTM B-479)³² clean aluminum foil comprises the final wall and ceiling surface. In order to ensure open burn conditions, air was pulled through an opening in the side of the facility by a high volume blower, minimizing oxygen depletion and maintaining an atmosphere at approximately 19% O₂. The air exchange flow rate in the burn hut is about 20 m³/min and this flow rate is measured in all the runs by means of a Pitot tube inserted into the duct (25.4 cm) following EPA Method 1.³³ The air residence time inside the facility is approximately 1.3 min. Fans and flow deflectors within the test facility are used to enhance air circulation. Test material is placed on a burn pan atop an electronic balance for burn rate determination. The floor is made of 30 × 30 cm paving stones surrounding the electronic scale, shielding the scale from direct heat. Thermocouples were placed on the scale, in the middle of the biomass, above the biomass, and in the exhaust duct.

The burn facility is equipped with a continuous emission monitor (CEM) system. Lines to the CEMs were positioned next to or at the exit duct to monitor carbon monoxide (CO, model VIA510, Horiba, Irvine, CA), carbon dioxide (CO₂, model VIA510, Horiba, Irvine, CA, for CO₂ concentrations higher than 1000 ppm and an Infrared Analyzer model 3300A (Fuji Electric Corp., Tokyo, Japan) for CO₂ concentrations lower than 1000 ppm), and oxygen (O₂, model 755, Rosemount Analytical, Solon, OH). Flow measurements based on pressure drop across an orifice, together with CEM data, were monitored and recorded in real time using a data acquisition system (IOtech Personal Daq/56 USB (Measurement Computing Corp., Norton, MA)).

A heated (120 °C) Teflon tube with an in-line heated quartz filter was connected to the exhaust of a high volume sampler and used to sample a portion (~1%) of the gases from the burn facility. An in-line refrigerated gas dryer and silica desiccant was used prior to the CEMs. Three-point calibrations of the CEMs were accomplished using compressed calibration gases, both before and after testing. Potential bias due to losses in the sample transfer line was monitored by injecting the calibration gases both at the point of sampling and at the inlet of the gas analyzer.

Test Procedures. Approximately 8 kg of pine biomass (young trees or branches and needles) and 1 m² of duff material was collected as done previously⁸ and prepared for the next day's testing. The biomass was sprayed with a hand sprayer and left overnight for drying outside under shelter. The duration of the test program was limited to four weeks to minimize any potential seasonal change in the biomass. The pine biomass branches were sprayed with the manufacturer's recommended concentration of the pesticide for woody plants and noncrop-land biomass. One mL of pesticide was diluted in 50 mL of water (as it is said in the specimen label, 1.0 gal/acre or 3.7 lb

2,4-D equivalent per gallon (440 kg/m³), based on typical pine forest area densities). This concentration, termed C₁, was increased 10-fold, termed C₁₀, for the second test variable. The control biomass, C₀, consisted of biomass that was sprayed with water only and went through the same drying and testing procedure as the pesticide-spiked samples.

The fire was started in several places with a propane torch, a process that typically took five seconds, and sampling was initiated upon self-sustained combustion. The nominal flaming burn time was around 3 min, but sampling continued up to 30 min until visible smoldering was no longer observed. Emissions were gathered from three or four burns to create a single composite sample in an effort to collect sufficient sample to avoid nondetects for the PCDD/F congeners.

To avoid any possibility of carryover contamination, the experiments started with the lower concentration tests (therefore, C₀ experiments were done first) and ended with C₁₀.

Sampling, Analytical Methods, and Quality Assurance.

Emission samples to characterize PCDD/F (tetra- to octachlorinated homologues) were collected with a high volume sampler (Tisch Environmental, TE-PNY1123 ACCUVOL (<http://www.tisch-env.com/tegnpy1123.asp>)) operating at 550 L/min following EPA Method TO-9A.³⁴ The high volume sampler consists of a 20 × 25 cm open-faced filter holder which contains a quartz microfiber filter (Whatman QMA, GE Healthcare Life Sciences, Piscataway, NJ). The filter is followed by a 15 cm long cylindrical container holding polyurethane foam (PUF) media and an aluminum casing connected to a blower motor. The 7.5 cm diameter × 7.5 cm high PUF plug is contained within a glass cartridge and is prespiked with five isotopically labeled tetra- through octa-CDD/F standard compounds prior to the sampling. The role of these spiked compounds is to determine the overall efficiency of sample collection and retention.

The combined PUF and filter were Soxhlet-extracted overnight with toluene. The extract was concentrated using a three-ball Snyder column, filtered and concentrated further with nitrogen to 1 mL using an automated evaporator, TurboVap II Concentration Workstation (Caliper Technologies, Hopkinton, MA). The extract was cleaned and fractionated using an automated liquid chromatography multicolumn system (Power Prep Dioxin System, FMS Fluid Management Systems, Inc., Watertown, MA), which consists of multilayer silica, basic alumina, and carbon columns. The final extract is analyzed by HRGC/HRMS using a Hewlett-Packard gas chromatograph 6890 series equipped with a CTC Analytic Combi PAL autosampler (CTC Analytics, Zwingen, Switzerland) and coupled to a Micromass Premiere (Waters, Inc., Manchester, UK) double-focusing high resolution mass spectrometer. The HRMS was operated in an electron ionization mode (35 eV and 650 mA current), selected ion monitoring (SIM) mode at resolution $R > 10000$ MU (5% valley). The HRMS source temperature was 250 °C. A 60 m Rtx-Dioxin 2 (Restek Corp., Bellefonte, PA) GC column was used (0.25 μm film thickness, 0.25 mm i.d.). The GC oven temperature program for the PCDD/F analysis was from 170 to 300 at 10 °C/min with a final hold time of 23 min. The carrier gas (helium) flow rate was a static 1.2 mL/min for 25 min, then ramped to the final flow of 1.5 mL/min. The temperature of the GC injection port was 270 °C.

The 17 PCDD/F congeners were analyzed using the isotope dilution method,³⁵ modified by the use of different internal standards to those specified in the method. Internal standards of nine ¹³C₁₂-labeled PCDDs and PCDFs were added to every

sample prior to the extraction procedure, allowing quantification of the native PCDDs and PCDFs in the sample.

To ensure that the chromatographic peaks unequivocally belong to the corresponding PCDD/F, it is necessary to establish some criteria to confirm their identification. They are as follows:

- Signal to noise ratio greater than 3.
- The retention time of the compound must be within two seconds for both masses and be in the corresponding chromatographic window.
 - The chromatographic peaks corresponding to both ion masses of the same compound must comply with the isotopic ratio with a maximum deviation of 15%.
- 2,3,7,8-substituted congeners are compared to the labeled compounds to identify the retention time.

Background and laboratory blank tests (sampling in the burn facility without combustion and laboratory procedure blank) were conducted to ensure that the sampling and analysis methods, potential facility contamination and ambient feed air were not biasing the tests with PCDD/F.

The biomass as-gathered (raw pine branches without being burned) was also analyzed for levels of PCDD/F by spiking with 14 ¹³C₁₂-2,3,7,8-substituted PCDD/F standards and extracting them with toluene in a Soxhlet extractor. The concentrated extract was solvent-exchanged with hexane following a modified U.S. EPA Method 23³⁵ extraction procedure and cleanup. Injection standards were added prior to GC/MS analysis.

A portion of the ashes for each experimental condition (C₀, C₁, and C₁₀) was similarly analyzed after combustion testing. The same HRGC/HRMS procedure used for the emission sample was also used for both the raw biomass and the ash samples.

The potential for impurities of PCDD/F in the 2,4-D was previously studied³⁶ and those results were used herein.

Calculations. Data are reported as both TEQ and "Total" values, where the latter are defined as the summed mass concentration of all the tetra- to octa-chlorinated congeners, considering not only the toxic ones but also the others. Toxic equivalency factors (TEFs) from the World Health Organization (WHO₂₀₀₅) were used to derive the TEQ value.³⁷ All nondetects (NDs) of the 2,3,7,8-chlorine-substituted congeners were set to both zero and their detection limit (DL) due to the significant difference between the resulting TEQ values. Calculations of emission factors when ND = DL provides for an upper bound of the concentration and emission factor, whereas reporting data as ND = 0 provides for a lower bound of the values. All peaks that met the retention time criterion but not the ion ratio criterion were treated as their estimated maximum potential concentration (EMPC) values determined from the integrated peak area of the smallest ion.

Emission factors were determined using the "carbon balance" method (for example, see ref 38) in terms of ng PCDD/F TEQ/kg carbon burned (C_b) and also as Total PCDD/F values (ng/kg C_b). The emission factor term is determined by the ratio of the sampled PCDD/F mass to cocollected carbon mass (CO₂ and CO), that is, the carbon burned, in the same sample volume. Other carbon emissions from combustion, such as particulate carbon and hydrocarbons, are assumed to be minimal compared to the mass of CO plus CO₂ when the modified combustion efficiency (MCE), defined as $[\text{CO}_2/(\text{CO} + \text{CO}_2)] \cdot 100$, is greater than 90–95%, indicating a high degree of oxidation.

When ambient air background CO and CO₂ are subtracted, the cumulative C represents the combusted material in the sample. A multiplication conversion factor of 0.5 can be applied to express the results per mass of waste burned as previously mentioned (literature has documented the carbon content in biomass sample to be approximately 50%).⁷

RESULTS AND DISCUSSION

Experimental conditions are summarized in Table 1, where the sampling time (minutes), biomass weight (kg), total carbon

Table 1. Experimental Conditions

test condition	sampling time (min)	biomass weight (kg)	total carbon sampled (g)	MCE (%)	max T (°C)	average CO ₂ (ppm)
pine branches spiked with water, C ₀	90	5	31	92	450	1380
	89	5	30	91	310	1290
	89	5	33	92	305	1450
pine branches spiked with 2,4-D, C ₁	118	6	23	91	86	950
	120	6	35	96	308	1300
	120	6	40	96	350	1430
pine branches spiked with 2,4-D, C ₁₀	120	6	32	95	520	1150
	120	6	34	95	330	1100
	120	6	26	95	455	990

sampled (g) and the MCE are reported. The MCE values in these experiments (91–96%) are similar to the MCE values shown in the literature with average values ranging 93–97%³⁹ and 84–96%.⁸ Maximum temperatures were, in general, reached for the thermocouple located above the pan (temperature data are in the SI). Average CO₂ data are also shown in Table 1. Values are quite similar, indicating similar combustion conditions for all experiments.

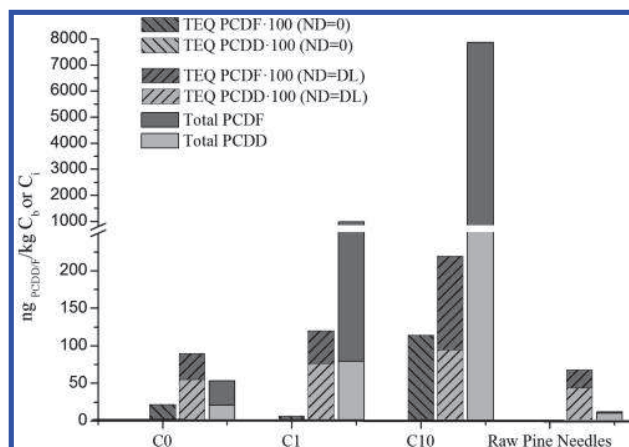


Figure 2. PCDD and PCDF emissions for all the burns and the raw biomass. Total = sum of tetra- to octa-chlorinated for the toxic and nontoxic congeners. C_b is the carbon burned for C₀, C₁, and C₁₀ runs. For the raw pine branches and ash runs, C_i is the carbon content in the initial sample.

Experimental results are presented in Table 2 and Figures 2 and 3 with emission factors expressed as ng TEQ/kg C_b or total ng/kg C_b, and raw biomass and ash concentrations expressed as TEQ/kg C_i or total ng/kg C_i where C_i is the initial carbon content of the as-gathered. Individual emission factor values ranged from 0.02 ng TEQ/kg C_b (when ND = 0 for C₁ experiments) to 2.25 ng TEQ/kg C_b (when ND = DL for C₁₀ experiments). Testing for statistical differences was conducted on the Total PCDD/F and TEQ emission data (both ND = 0 and ND = DL) to determine possible distinctions between PCDD/F emissions from these conditions. Relative standard deviations (RSDs) for the results, in ng TEQ/kg C_b or ng TEQ/kg C_i, in repeated experiments ranged from 5 – 140%. Surrogate/internal standard

Table 2. Emission Factor Data for All of the Experiments

runs	PCDD/F emission factor (ng TEQ/kg C _b)						Total PCDD/F emissions (ng/kg C _b)		
	ND = 0			ND = DL			value	average	RSD(%)
	value	average	RSD (%)	value	average	RSD (%)			
C ₀	0.39	0.22	58	1.08	0.88	16	66	52	31
	0.20			0.78			60		
	0.08			0.78			29		
C ₁	0.09	0.06	49	1.57	1.2	25	1100	940	16
	0.08			1.13			750		
	0.02			0.85			940		
C ₁₀	1.40	1.14	22	2.2	2.2	5	6400	7800	20
	1.10			2.0			7010		
	0.84			2.3			10 020		
raw pine branches	ng TEQ/kg C _i								
	0.01	0.01	15	0.94	0.67	34	11	10.1	10
	0.01			0.39			9		
ash	0.00	8 × 10 ⁻⁵	140	0.44	0.51	52	4	13	109
	3 × 10 ⁻⁴			0.23			2		
	0.00			0.86			34		

^aUnits are in ng TEQ/kg C, where C_b is equal to carbon burned for C₀, C₁, and C₁₀ runs. For the raw pine branches and ash analyses, C_i is the carbon content in the initial sample, assuming that in 1 kg of biomass there is 0.5 kg of carbon content. For the ashes, an approximate weight percentage of ash of 5% was used.⁷

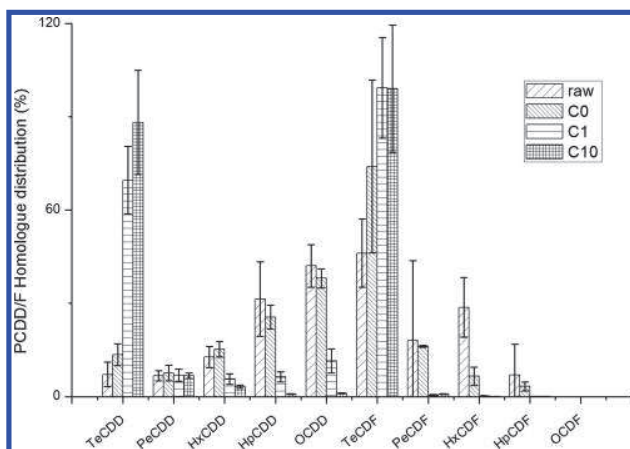


Figure 3. Relative distribution of PCDD/F homologues for all the burning experiments and for the raw biomass. Units are ng of homologue divided by total ng of sum of PCDD for the PCDD homologues and by sum of PCDF for the PCDFs, expressed as a percentage.

recoveries were all within the specified limits of the respective methods.³⁵

PCDD/F TEQ Results. Tables S1–S3 (SI) present the results of a standard Analysis of Variance (ANOVA) test using Tukey's Test (for data of homogeneous variance) at a 95% confidence level to compare the means.^{40,41} For TEQ values, the data show that the only significant differences were between the C₁₀ PCDD/F TEQ and all of the other conditions for both ND = 0 and ND = DL. PCDD/F TEQ values for the raw biomass, ash, and C₀ are statistically similar at the 95% confidence level, suggesting that combustion has no net effect on the concentration of PCDD/F toxic congeners. However, this conclusion is tempered by the minimal sample size ($N = 3$) for each condition. More statistical data and information can be found in SI Tables S1 and S2.

The finding of a significant difference for C₀ from C₁₀ and not C₀ from C₁ implies a threshold pesticide exposure beyond which PCDD/F TEQ yields are influenced by the presence of 2,4-D. However, more likely from a chemical reaction standpoint is that the number of trials of C₁ was insufficient to show distinction with C₀. The potential influence of C₁ can be estimated by assuming a linear regression of the C₀, C₁, and C₁₀ data. At ND = 0, this result is PCDD/F TEQ = 0.10 · Concentration + 0.10 ($R^2 = 0.85$, $F = 39.5$) and at ND = DL the regression is PCDD/F TEQ = 0.12 · Concentration + 0.97 ($R^2 = 0.85$, $F = 46.7$). More replicate data and data at intermediate concentrations could verify this relationship.

No statistical distinctions were observed between C₀ and C₁. Their averaged emission factor (0.14 ng TEQ/kg C_b and at ND = 0) is eight times lower than C₁₀ at ND = 0. Likewise, at ND = DL, their averaged C₀ and C₁ emission factor (1.0 ng TEQ/kg C_b) is a factor of 2 lower than for C₁₀, suggesting that a concentration of 2,4-D ten times the manufacturer's recommended application rate results in a about a 2- to 10-fold increase of PCDD/F TEQ above the average value between C₀ and C₁.

Total PCDD/F Emissions Results. Table 2 and Figure 2 show that the Total PCDD/F values (sum of tetra- to octa-congeners) demonstrate a high increase in the nontoxic congeners in C₁₀ experiments compared to C₀. The ANOVA test also confirms this situation. Tables S4 and S5 in the SI present the results of the test at 92.5% confidence level. Additional statistical analyses are presented in the SI.

Unlike PCDD/F TEQ values, significant differences are now observed between Total PCDD/F and all 2,4-D tests (C₁ and C₁₀) and the raw and ash values. As a consequence, more nontoxic congeners are likely to form under C₁ and C₁₀ conditions. Figure 2 highlights that the magnitude of the Total PCDD/F emission increase is much higher than with the TEQ values. Furthermore, the PCDD/F Total emissions for C₁₀ are approximately eight times greater than C₁ and more than 150 times greater than C₀. This contrasts with the increase of the emission factors expressed as ng TEQ/kg C_b where C₁₀ showed only an 8-fold increase compared to C₀ or C₁. PCDD/F Total emissions in C₁₀ are statistically significant and greater than C₀, as confirmed by an ANOVA test at a 95% confidence level (Table S5, SI).

Considering the chemical structure of the pesticide (2,4-D, Figure 1A) which has the chlorine atoms in nonconsecutive positions (2,4), the probability of forming the toxic congeners (2,3,7,8) seems to be much lower than the probability for forming the nontoxic congeners. On the other hand, more emissions of the nontoxic PCDD/Fs compared to the toxic ones are therefore formed using this pesticide.

In a previous study, analysis of a raw 2,4-D pesticide found its byproduct concentration to be 10 ng TeCDF/g of active 2,4-D.³⁶ In relating this byproduct yield to our tests, simple vaporization alone from C₁ and C₁₀ would have been expected to yield about 18 and 180 ng TeCDF, respectively. Our study, sampling only about 1% of the flue gas, resulted in 21 and 220 ng TeCDF for the C₁ and C₁₀ samples, respectively. This 100-fold increase in TeCDF from that expected from the raw pesticide byproduct concentrations confirms PCDD/F formation rather than simple volatilization of the impurities.

PCDD versus PCDF. PCDD/F emission factors (Figure 2) show the dominance of Total PCDF vs Total PCDD emissions (considering the sum of all toxic and nontoxic congeners), consistent with the literature.^{8,11,42} ANOVA analysis carried out comparing total PCDD and total PCDF values at a 95% confidence level confirmed a significant predominance of total PCDF over the total PCDD for C₁ and C₁₀ conditions. Comparison of the TEQ values for PCDD and PCDF at ND = DL and ND = 0 (SI Tables S7 and S8, respectively) shows no statistical differences for the former. At ND = 0, however, TEQ PCDF is statistically significant and greater than TEQ PCDD for C₁₀.

Figure 3 shows the relative distribution of PCDD/F homologues. The general pattern for the PCDFs is higher yields for the lower chlorinated homologues. This pattern becomes more prevalent as the 2,4-D concentration increases to C₁₀ with the pattern shift indicating a reaction mechanism rather than simple volatilization. Nevertheless, the dominance of Total TeCDD over the Total PCDD and the dominance of Total TeCDF over the Total PCDF can be observed, in accord with previous experiments from forest fire simulations,¹⁵ simulated forest and grassland fires,¹¹ and simulated open burning of forest biomass,⁸ which all indicate a large fraction of the tetrachlorinated congeners. The TeCDD relative yield is high for C₁ and C₁₀ (as mentioned above), agreeing with the hypothesis of a noteworthy formation of TeCDD (largely the nontoxic congeners) from the dimerized 2,4-D, rather than a revolatilization of the impurities.

Similar 2,3,7,8-Cl-substituted congener patterns are obtained for all the burning conditions (See Figure S1, SI). However, the emission patterns for the PCDF congeners differ significantly from the emission patterns obtained for the raw material, unlike the PCDDs that are indistinguishable. Emission samples from all the experiments reported nondetects (below the DL) for the

tetra- to hexa-CDD, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF congeners.

Comparison of the PCDD/F levels in the ash with those in the emissions indicates that ash levels are low and statistically distinct from the emissions. Comparison of the TEQ values (8.0×10^{-5} , 0.06, and 1.10 ng TEQ/kg C_b or C_i in the ash, C_1 , and C_{10} , respectively) for congeners detected in the ash with the C_1 and C_{10} emissions showed that the emissions were between 6 and 100 times higher than the ash. For this source, the partitioning of PCDD/F to the land is apparently minimal compared to the emissions. As Table 1 shows, the ng TEQ/kg C_i for the ash are of the same order of magnitude as for the ng TEQ/kg C_b of C_0 and the as-gathered raw pine branches.

The TEQ value for the raw biomass (0.01 ng TEQ/kg C_i when ND = 0) agrees with literature values (0.02 ng TEQ/kg C_i ⁸). When ND = DL, the TEQ value is 0.67 ng TEQ/kg C_i ; this upper bound compares well with previous experiments from combustion of forest fuels and sugar cane⁶ at 0.58 ng TEQ/kg C_{initial} . In this same study⁶ pine litter emissions of PCDD/F exceeded the PCDD/F present in the raw biomass by a factor of 4. Another study with pine branches resulted in 0.66 ng TEQ/kg C_i for the raw biomass,⁷ showing a 100-fold increase during the combustion of pine branches and confirming PCDD/F formation from combustion rather than simple surface volatilization.

Limited trials in this study showed that only the application of a 2,4-D pesticide concentration 10 times higher than that recommended by the manufacturer (C_{10}) resulted in a statistically significant increase in the TEQ-PCDD/F emissions relative to the control (pine branches sprayed with water). C_{10} resulted in 1.14 ng TEQ/kg C_b when ND = 0, greater than a 100-fold increase in the emissions over the raw biomass (0.01 ng TEQ/kg C_i). When ND = DL, an emission factor of 2.18 ng TEQ/kg C_b is obtained, more than three times higher than the value for the raw biomass (0.67 ng TEQ/kg C_i), showing that emissions could not be due just to the volatilization of adsorbed PCDD/F on the raw biomass, but also to the formation of PCDD/F during the combustion process.

■ ASSOCIATED CONTENT

■ Supporting Information

ANOVA procedures and tables with results of the analysis performed with PASW Statistics 18 Software are displayed in this section. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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