IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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THE EFFECT OF 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D) ON PCDD/F EMISSIONS FROM OPEN BURNING OF BIOMASS

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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. Field sampling and laboratory simulations of open burning ⁴⁻⁶ without addition of pesticide have measured PCDD/F emissions to the atmosphere. 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 ⁷, combustion conditions ⁸, biomass fuel properties ^{9,10}, and the presence of pesticides adsorbed onto the leafy surfaces ¹¹. Several studies reported high levels of organochlorine compounds in pine needles ^{11, 12}, including organochlorine pesticides ¹³⁻¹⁵. Formation of PCDD/F may also be tied to the combustive conversion of adsorbed pesticides or their trace byproducts. Precursors found in the soil ⁴ 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 ^{16, 17}. The compound 2,4-dichlorophenoxyacetic acid (2,4-D) is a widely used pesticide which has a chemical structure readily amenable to reaction to form PCDD/F. 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. 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 ¹⁸.

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-D at one and ten 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.

Materials and Methods

Materials

Locally available loblolly pine trees (*Pinus taeda*) were used as a biomass fuel for all the experiments. The pine forest floor was recreated with pine needles and duff collected from beneath the tree. Selection of 2,4-D, C₈H₆Cl₂O₃, CAS 94-75-7, 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, USA).

Test Facility description

Biomass was burned in an open burn test facility: an air-ventilated and enclosed facility used to simulate small-scale open burning conditions. It consists of a 2.9 x 3.5 m base and a sloped ceiling height of 2.8 m at the apex and 2.2 m at the walls. 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. Thermocouples were placed on different positions. 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, carbon dioxide and oxygen. Flow measurements based on pressure drop were monitoring in real time.

Test Procedure

Approximately 8 kg of pine biomass and 1 m² of duff material was collected. The biomass was sprayed with a hand sprayer and left overnight for drying outside under shelter. The pine biomass branches were sprayed with the manufacturer's recommended concentration of the pesticide for woody plants and non-cropland biomass. This concentration, termed, C1, was increased ten-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. Emissions were gathered from three or four burns to create a single composite sample in an effort to collect sufficient sample to avoid non-detects for the PCDD/F congeners. Emission samples to characterize PCDD/F were collected with a high volume sampler (Tisch Environmental, TE-PNY1123 ACCUVOL) and PCDD/F were adsorbed in the filter and PUF. The PUF is pre-spiked with five isotopically-labeled tetra-through octa-CDD/F standard compounds prior to the sampling to determine the overall efficiency of sample collection and retention. The combined PUF and filter were Soxhlet-extracted overnight with toluene and then concentrated. The extract was cleaned and fractionated using an automated liquid chromatography multicolumn system (Power Prep Dioxin System, FMS Fluid Management Systems, Inc., Watertown, MA, USA). 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 17 PCDD/F congeners were analyzed using the isotope dilution method¹⁹, 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. 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. Raw material and ashes were also analyzed.

Results and discussion

Emission factors were determined using the "carbon balance" method in terms of ng PCDD/F TEQ/ kg carbon burned (C_b) and also as Total PCDD/F values (ng/kg C_b). Experimental results are presented in Table 2 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. All non-detects (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, while reporting data as ND=0 provides for a lower bound of the values. Regarding TEQ values, ANOVA analysis performed on data showed that the only significant differences were between C10 and all other conditions.

Total PCDD/F values (sum of tetra- to octa- congeners) demonstrate a high increase in the non-toxic congeners in C10 experiments compared to C0 confirmed also by ANOVA test. Considering the chemical structure of 2,4-D with chlorine atoms in non-consecutive positions, the probability of forming toxic congeners seems to be lower than forming the non-toxic. PCDD/F emission factors show the dominance of Total PCDF vs. Total PCDD emissions agreeing the literature. 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.

Table 1. 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 0.20 0.08	0.22	58	1.08 0.78 0.78	0.88	16	66 60 29	52	31
C ₁	0.09 0.08 0.02	0.06	49	1.57 1.13 0.85	1.2	25	1100 750 940	940	16
C ₁₀	1.40 1.10 0.84	1.14	22	2.2 2.0 2.3	2.2	5	6400 7010 10020	7800	20
	ng TEQ/kg C _i								
Raw Pine branches	0.01 0.01	0.01	15	0.94 0.39	0.67	34	11 9	10.1	10
Ash	0.00 3·10 ⁻⁴ 0.00	8·10 ⁻⁵	140	0.44 0.23 0.86	0.51	52	4 2 34	13	109

Conclusions

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 (C10) resulted in a statistically significant increase in the TEQ-PCDD/F emissions relative to the control (pine branches sprayed with water). C10 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.

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