PCDD/F EMISSIONS FROM AGRICULTURAL FIELD BURNING

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Introduction

This paper presents the first known values for emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) from seasonal agricultural field burning. Post-harvest field burning is a common practice to remove residues, control weeds, and release nutrients for the next crop cycle. While there appear to be no PCDD/F emission data relating to agricultural field burns, air sampling during forest fires[1] did indicate elevated total PCDD/F concentrations (20 pg/m^3) over negligible background levels. The potential similarity of forest and agriculture residue biomass sources and the ubiquity of agricultural field burning suggest that agricultural field burning should be examined for its role in contributing to the global PCDD/F balance.

The difficulty of obtaining relevant and accurate PCDD/F emission measurements relating to agricultural field burns has led to laboratory simulations and soil sampling. Laboratory pyrolytic experiments (2 L/min air, 700 ^{o}C) with rice straw showed PCDD/F emissions at 6 and 22 ng I-TEQ/kg of raw biomass[2]. Efforts to measure PCDD/F soil and ash concentrations before and after forest fires and wheat straw field burn events[3-6] have found little evidence for significant changes in concentrations, although shifts to higher homologue profiles were observed[5,6]. These methods, however, do not account for air emissions and cannot be expected to result in emission factors.

The objective of this work was to generate initial PCDD/F emission factors from the combustion of agricultural biomass in a manner representative of actual burn conditions.

Methods and Material

Two sampling campaigns of biomass burns were conducted in an open burn simulation facility (described more fully elsewhere[7,8]) consisting of an enclosed, ventilated facility with a sample weighing platform, high volume air handlers (2.5 volume changes per minute to simulate open burn conditions), interior recirculation fans, and gas sampling equipment. PCDD/F measurements were made using a Graseby™ PS-1 sampler by EPA's ambient method[9]. This sampler consists of an open-faced filter holder followed by polyurethane foam (PUF) surrounding an XAD-2 sorbent. The combined filter and PUF/XAD-2 module was analyzed using high resolution gas chromatography and mass spectrometry (HRGC/HRMS) for PCDD/F (in this paper, all references to PCDD/F concentrations include tetra- to octa-homologues only). Emission factors were calculated in terms of pollutant mass/mass of biomass burned:

$$E = (C_{sample}\ Q_{hut}\ t_{run})/\ (m_{burned})$$

where E is the estimated emissions in pg/kg burned, C_{sample} is the concentration of the pollutant in the sample in pg/m^3, Q_{hut} is the flow rate of dilution air into the burn hut in m^3/min, t_{run} is the run time in min, and m_{burned} is the mass in kg of biomass burned over the run. Toxicity equivalency factors[10] were

used to derive the toxic equivalence emission factor (TEQ). All non-detects (NDs) were set either to zero or the detection limit (DL), as specified. Blank tests (sampling from the facility without biomass combustion) were conducted throughout the two sampling campaigns to ensure that the sampling and analysis methods, potential facility contamination, and ambient air PCDD/F concentrations were not biasing the test results.

The biomass tested include wheat straw (*Triticum aestivum L.*, variety Madsen) from Washington State University's Lind Dryland Research Station in Lind, WA, in the arid (<25 cm rainfall/year), central part of the state, and rice straw from Sutter County, CA. The first campaign consisted of winter wheat straw [0.08 % chlorine, Cl (dry), 8.89 % moisture] and the second consisted of spring wheat straw [0.82 % Cl (dry), 8.80 % moisture]. A single test on rice straw (variety M202, a popular CA medium grain rice) stubble [0.33 % Cl (dry), 9.10 % moisture] was done at the end of the second campaign. Wheat straw stubble was gathered from irrigated wheat fields. The rice straw had been baled and placed in covered storage. The biomass was placed on a burn platform grid in the manner and density observed in the field: 30 % lying flat, 45 % upright, about 12.5 % semi-upright, and the balance was partially decomposed wheat. The moisture content was maintained in the field-sampled condition. Each burn consisted of about 0.75 kg; about 3.5 kg of biomass was used in each day's burns. Consecutive burns were compiled into a single sample media to limit the possibility of non-detects, such that sampling time ranged from 75 to about 500 min.

Results and Discussion

PCDD/F emission factors are illustrated in Figure 1, showing wheat straw emission factors ranging from about 337 to 602 pg TEQ/kg and the one rice straw burn at 537 pg TEQ/kg (ND=0). Due to the emission concentrations and extended sampling time, no NDs were found for the wheat burns– all 2,3,7,8-Cl-substituted isomers were greater than the DL. The rice straw burn emission factor increased to 725 pg TEQ/kg when ND = DL. Sample/background TEQ ratios were about 2/1 and 8/1 for the three winter wheat straw emissions (WW1-3) and for the two parallel-sampled spring wheat straw emissions (SW1-A, -B), respectively. No apparent distinction is observed between background-corrected emission factors for winter and spring wheat burns. This occurs despite a 10-fold difference in Cl content between the winter and spring wheat stubble, 0.08 % and 0.82%, respectively.

While PCDD/F TEQ values seem equivalent between the winter and spring wheat stubble, there is a noticeable, and surprising, difference between the winter and spring wheat homologue profiles and isomer patterns. The winter wheat stubble homologue profiles (not shown) were very high in octachlorodibenzodioxin (OCDD), while those for the spring stubble and rice straw (not shown), were high in tetrachlorodibenzodioxin (TCDD) and tetrachlorodibenzofuran (TCDF). The 2,3,7,8-Cl-substituted congeners are dominated by the OCDD (values of 18,580; 8,270; and 6,740 pg/kg) and octachlordibenzofuran (OCDF) in both wheats, but more so for the winter versus spring wheat stubble. The 2,3,7,8-TCDF has a strong presence in the spring wheat stubble, but is minimal in the winter stubble. As with the homologue profile, the rice straw isomer pattern most similarly reflects that of the spring wheat. These observed differences in the wheat samples are surprising, especially for the isomer patterns, as the same fuel type and combustion scenario are generally expected to have similar results. These differences may be related to seasonal variations in Cl content,[11,12] although the limited number of tests were not meant to discriminate this factor. Principal Component Analysis (PCA) of the normalized homologue profiles and isomer patterns (not shown) confirms the distinctiveness of each of the three biomass types, despite reasonably similar emission factors.

The PCDD/F data ranges for the wheat and rice straw stubble preliminarily suggest that the 2000 pg TEQ/kg value used for biomass in recent inventories[13] overestimates emissions from these specific biomass sources. Based on published agricultural data[14] and methods for calculating field burning

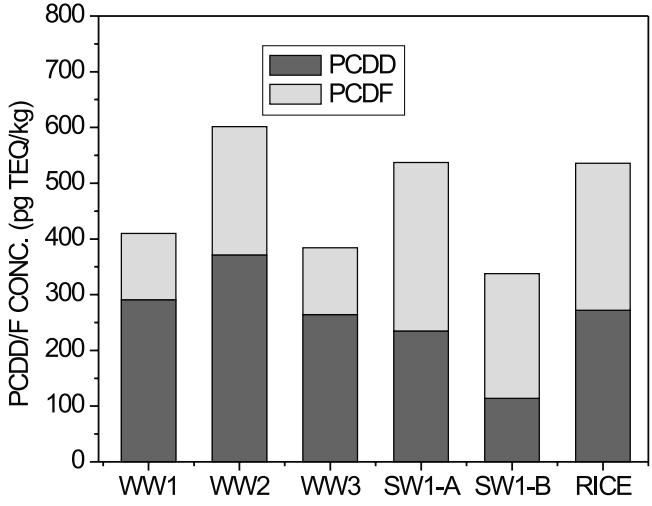

Figure 1. PCDD/F Emission Factors (pg TEQ/kg of biomass burned) for winter wheat (WW), spring wheat (SW), and rice straw stubble (RICE). Values shown as ND = 0 (no difference for wheat burns when ND = DL).

emissions,[15] the estimated annual emissions from burning 1.65 million metric tonnes of wheat stubble and 254,700 tonnes of rice stubble, using an emission factor of 0.5 ng TEQ/kg burned, results in about 0.8 and 0.1 g TEQ/year, respectively. This value preliminarily suggests that wheat and rice field burning are only minor sources of PCDD/F to the U.S. emission inventory.

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References

1. Clement, R., Tashiro, C. (1991) 11th International Symposium on Chlorinated Dioxins and Related Compounds, Research Triangle Park, NC, September 23-27, 1991, Abs. # S34.
2. Muto, H., Saitoh, K., Takizawa, Y. (1993) Bull. Environ. Contam. Toxicol. 50:340.
3. Buckland, S., Dye, E., Leathem, S., Taucher, J. (1994) Organohalogen Compds. 20:85.
4. Van Oostdam, J., Ward, J. (1995) Dioxins and Furans in the British Columbia Environment, Victoria, British Columbia: BC Environment, Environmental Protection Department.
5. Walsh, P., Brimblecombe, P., Creaser, C., Olphert, R. (1994) Organohalogen Compds. 20:283.
6. Kim, E.-J., Oh, J.-E., Chang, Y.-S. (2001) Organohalogen Compds. 50:386.
7. Lemieux, P., Lutes, C., Abbott, J., Aldous, K. (2000) Environ. Sci. Technol. 34(3):377.
8. Gullett, B., Lemieux, P., Lutes, C., Winterrowd, C., Winters, D. (2001) Chemos. 43:721.
9. Winberry, W., Murphy, N., Riggan, R. (1988) Compendium Method TO-9: Method for the Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) in Ambient Air Using High-

Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) in: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/600/4-89-017 (NTIS PB90-127374), U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, June 1988.

10. Van den Berg, M., Birnbaum, L., Bosveld, A., Brunstrom, B., Cook, P., Feeley, M., Giesey, J., Hanberg, A., Hasegawa, R., Kennedy, S., Kubiak, T., Larsen, J., van Leeuwen, F., Liem, A., Nolt, C., Peterson, R., Poeelinger, L., Safe, S., Schrenk, D., Tillit, D., Tysklind, M., Younes, M., Warn, F., Zacharewski, T. (1988) Environmental Health Perspectives, 106:775.
11. Burvall, J. (1997) Biomass and Bioenergy 12(3):149.
12. Hadders, G., Olsson, R. (1997) Biomass and Bioenergy 12(3):171.
13. U.S. EPA (2001) Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-P-Dioxin (TCDD) and Related Compounds, Part I, Vol. 1: "Source of Dioxin-Like Compounds in the United States," Office of Research and Development, EPA/600/P-00/001Cb, Washington, DC, October 2001.
14. U.S.D.A. (2001) Department of Agriculture, Agricultural Baseline Projection Tables (94005), http://usda.mannlib.cornell.edu/data-sets/baseline/2001/, Washington, DC, February 2001.
15. U.S. EPA (1999) Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1997, EPA 236-R-99-003, http://www.epa.gov/globalwarming/publications/emissions/us1999/index.html, Office of Policy, Washington, DC, April 1999.