LEVELS OF CHLORINATED DIOXIN AND FURAN EMISSIONS FROM PENTACHLOROPHENOL-TREATED WOOD.

Heldur Hakk and Gerald Larsen

United States Department of Agriculture, Agricultural Research Service, Biosciences Research Laboratory, Fargo, ND 58105, USA

Introduction

A recently reported source of polychlorinated dioxins and furans (PCDDs/PCDFs) in beef produced in the United States is through dermal contact, licking, or chewing pentachlorophenol (PCP) treated wood used in production facilities[1-3]. Wild elk contained moderate levels of PCDD/PCDF in the same congener patterns found in PCP- treated wood, presumably due to exposure from winter feeding stations erected for these animals[4]. The extent of PCDD/PCDF contamination in PCP-treated wood at various depths was reported previously[5]. Disposal of aging telephone poles or wood used in pole barns often occurs during recycling or open burning. The purpose of the present study was to quantify the levels of PCDD/PCDF congeners released into the atmosphere following an open burn.

Materials and Methods

Dioxin levels at various depths in wood samples (PCP treated wood, 4.61cm x 15.0cm x 50cm) have been analyzed by using solvent extraction and HR-GC/MS as previously reported[5]. A combustion apparatus was assembled that allowed for the constant flow of emissions upward and through a polyurethane foam (PUF) filter (Supelco, Inc. Bellefonte, PA, USA). All components of the apparatus were subjected to a wash procedure that involved laboratory detergent; 5% bleach soak for 16h, solvent rinses with acetone, toluene, and methylene chloride:hexane prior to assembly. A 125 ml borosilicate glass Ehrlenmeyer flask was heated with a propane torch to produce an air intake hole (15 mm), and a thermocouple hole (6 mm). Disposable stainless steel stands and sample-holding screens were fabricated to hold and contain the wood samples at the optimum height during combustion. A borosilicate glass chimney of 2.5 cm x 14.3 cm was constructed to dissipate the heat produced. At the top was attached a PUF filter in a glass holder using 3M brand tape (#2-0300). Air flows were maintained between 2.5 and 3.0 liters/min using vacuum. Temperatures 1.0 cm above the flame were measured with a thermocouple, and ranged from 580-720°C. Aliquots of wood samples (~ 50 mg) were enclosed in a folded piece of Kimwipe® (5.5 x 5.5 cm). A propane torch inserted into the air intake hole was used to ignite and sustain combustion of the wood samples for 1.0 min. An open flame was observed above each sample indicating that oxidation was being supported. Kimwipe blank values were combusted and used as controls.

The PUF filters were removed, and the chimneys and holders were rinsed with 50:50 hexane:methylene chloride onto the PUF filter. The filter and rinses were placed in an extraction cell of an accelerated solvent extractor (ASE; Dionex, Sunnyvale, CA). The ASE extraction conditions were 100°C, 1500 psi, 30 min, 50:50 hexane:methylene chloride. The ash samples were removed from the flask with 6N HCl, left standing for 30 min, centrifuged at 4000 x g for 5 min, decanted, rinsed 3x with water, and transferred to an ASE extraction cell containing washed Celite 545. The ASE extraction conditions were as above, except 100% toluene was used as the

solvent instead of the 50:50 hexane:methylene chloride. High resolution mass spectra for PUF and ash extracts were obtained with a VG Ultima mass spectrometer (Micromass; Manchester, England) according to EPA Method 1613.

Results and Discussion

1,2,3,4,6,7,8,9-Octachlorodibenzo-*p*-dioxin (OCDD); 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD); 1,2,3,4,6,7,8,9-octachlorodibenzofuran (OCDF); 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF) are the most abundant dioxin/furan congeners associated with technical grade pentachlorophenol[6]. The levels of these compounds in addition to the other 13 EPA Method 1613 congeners in this PCP-treated board were reported previously[5]. To summarize the data: the PCDD/PCDFs were present at highest concentrations (i.e. OCDD 17 ppm) on the surface of the PCP treated wood, decreased to about half the levels at 4.2 mm under the surface (i.e. OCDD 7 ppm), and remained relatively constant through the remaining interior of the wood (i.e. OCDD 7.1 ppm).

Regardless of the depth or original concentration, the percent volatilized for a particular PCDD/PCDF congener was constant, and therefore the emission data for each congener were averaged. From the combustion data it was evident that each of the congeners was present in the emission gases and trapped on the PUF (Figure 1). In general, the lower chlorinated congeners were more readily converted into emissions, while the higher chlorinated congeners were less volatile. The congener pattern of the emission strongly resembled that of a PCB formulation, i.e. OCDD, HxCDD, OCDF, and 1234678-HpCDF were predominant. 2378-TCDF was completely volatilized (109%). 2378-TCDD was present at an average of 1200 ppt at the surface in the wood, and 7% was volatilized under these combustion conditions. A relatively high percentage (15%) of 234678-HxCDF was volatilized (Figure 1), while less than 4% of the other three HxCDF congeners were volatilized. Approximately 2% of the original OCDD content in the wood was converted into OCDD emissions, and less than 0.5% of the OCDF was volatilized.

The relatively high levels of 2378-TCDF and 234678-HxCDF in the PUF may be due to an alternate explanation. Pentachlorophenol is known to contain hexachlorinated diphenyl ethers as contaminants[7], which could serve as pre-dioxins in the low-temperature formation of PCDD/PCDFs. Artifactual formation of OCDD has been observed when nonachloro-2-phenoxyphenol was exposed to thermal, photochemical, or basic conditions[8].

Essentially no PCDD/PCDFs remained associated with the ash. The remaining PCDD/PCDF mass was probably oxidized to hydroxylated dioxins, furans, and/or diphenyl ethers, which would not have been detected by our method.

The concentrations of individual congeners present in the PCP-treated wood sample were very large, and despite the relatively low level of volatilization for many of the congeners after combustion, these results may still represent a significant source of environmental contamination. The tetra- and penta-chlorinated dioxin/furan concentrations in the wood ranged from 4–200 ppb, while the hexa- through octa-chlorinated dioxin/furan concentrations ranged from 160–16,000 ppb (data not shown). Shown in Table 1 is the potential environmental impact of the open burning of this particular PCP-treated board. An average PCDD/PCDF emission for each congener was calculated by dividing the sum of the individual emissions by the number of sampling depths. The total furan pg TEQ/g was over 1700 (Table 1), and the majority of the toxic equivalents (TEQs) were from the HxCDF series[9]. The individual congener with the largest contribution to the total furan TEQs was 123678-HxCDF, i.e. 1076 pg TEQ/g. In the PCDD series, the total pg

TEQ/g was 2034. All PeCDD, HxCDD, and HpCDD congeners were nearly equal contributors to the dioxin TEQ, and ranged from 150-750 pg TEQ/g. 2378-TCDD and OCDD were minor contributors to the total dioxin TEQ, i.e. 20 pg TEQ/g. These data are of a similar magnitude to PCDD/PCDF emissions from open burning of household wastes in barrels. In a combustion test utilizing 7.5% PVC as a chlorine source, Gullet *et.al*[10] measured emissions of 4916 ng TEQ/kg in a representative domestic household waste.

A relatively small 1.0 kg sample of this PCP treated wood burned under similar conditions in an open barrel would emit 21 ng, 743 ng, and 177 μg of 2378-TCDD, 12378-PeCDD, and OCDD, respectively. Therefore, disposal of aged PCP-treated wood by open burning may represent a significant input to worldwide PCDD/PCDFs inventories.

Table 1. Levels of PCDD/PCDFs released as emissions (in ppt) from average PCP-treated wood burned at 580-720° C.

Congener	Ave Conc (ppt)	pg TEQ/g	
2,3,7,8-TCDF	566	56	
1,2,3,7,8-PeCDF	310	15	
2,3,4,7,8-PeCDF	370	185	
1,2,3,4,7,8-HxCDF	1147	114	
1,2,3,6,7,8-HxCDF	1624	162	
2,3,4,6,7,8-HxCDF	10762	1076	
1,2,3,7,8,9-HxCDF	0	0	
1,2,3,4,6,7,8-HpCDF	9233	92	
1,2,3,4,7,8,9-HpCDF	1068	10	
OCDF	9925	10	
Furan TEQ's			1720
2,3,7,8-TCDD	21	21	
1,2,3,7,8-PeCDD	743	743	
1,2,3,4,7,8-HxCDD	1466	146	
1,2,3,6,7,8-HxCDD	2947	294	
1,2,3,7,8,9-HxCDD	2550	255	
1,2,3,4,6,7,8-HpCDD	55871	558	
OCDD	177381	17	
Dioxin TEQ's			2034
Total TEQ's			**3754**

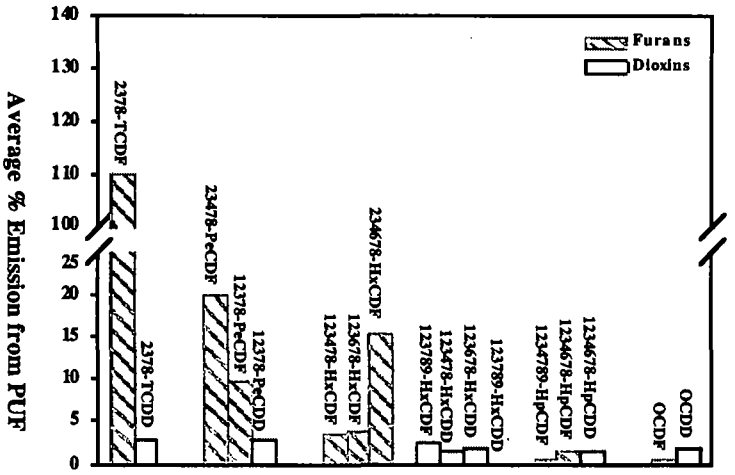

Figure 1. Average percent emissions of dioxin/furan congeners from PCP-treated wood samples after combustion at 580-720° C.

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References

1. Feil, V., Davison, K., Larsen, G. and Tiernan, T. (1995) Organohalogen Cmpds. 26, 117-120.
2. Fries, G., Feil, V. and Davison, K. (1996) Organohalogen Cmpds. 28, 156-159.
3. Feil, V., Davison, K., Larsen, G. and Fries, G. (1997) Livestock Environment V, Volume II 1004-1009.
4. Feil, V.J. and Larsen, G.L. (1998) Organohalogen Cmpds. 39, 113-114.
5. Larsen, G.L. and Feil, V.J. (1999) Organohalogen Cmpds. 41, 223-225.
6. Cleverly, D., Schaum, J., Schweer, G., Becker, J. and Winters, D. (1997) Organohalogen Cmpds. 32, 430-435.
7. Firestone, D., Ress, J., Brown, N.L., Barron, R.P. and Damico, J.N. (1972) J. Ass. Offic. Anal. Chem. 55, 85.
8. Huwe, J.K., Feil, V.J., Zaylskie, R.G. and Tiernan, T.O. (2000) Chemosphere 40, 957-962.
9. Van den Berg, M., Birnbaum, L.S., et.al. (1998) Environ. Health Persp. 106, 775-792.
10. Gullett, B.K., Lemieux, P.M., Lutes, C.C., Winterrowd, C.K. and Winters, D.L. (1999) Organohalogen Cmpds. 41, 157-160