

## Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Coplanar Polychlorinated Biphenyls in Soil and Garden Vegetables from Private Homes Near Times Beach, Missouri, Incineration Sites

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### Introduction

Human exposure to chlorinated dioxins and dioxin-like compounds has been a major worldwide concern over the past two decades. There have been major concerns about the deposition of PCDD/PCDF congeners from incinerators by air particulate and introduction of the toxic compounds into the food chain. (1-4) Specifically, household garden vegetables collected from gardens of private homes near Times Beach were examined in this study. The test vegetation samples in this study included tomatoes, peppers, Swiss chard, cucumber, beets, okra, and carrots. Multiple techniques for the extraction of garden vegetation were examined. A rotary extraction method, which was used previously for the extraction of dioxins and PCBs from blood and blood serum, has proven to be useful for extraction of the dioxins/furans and co-PCBs from vegetation.

### Methods

The samples were treated as food for human consumption, so stems and small rocks were removed, but peels and skins were not. Vegetation samples were cleaned to remove dirt, then ground and homogenized. A 30-g to 50-g sample size (based on wet weight) was used for all vegetation samples. Percent moisture for each sample was determined using the remaining sample homogenates. Each 30-g to 50-g sample was fortified with <sup>13</sup>C<sub>12</sub>-labeled internal quantitation standards at the same concentrations as the soil samples. Vegetation samples were extracted using a mixture of ethanol/saturated ammonium sulfate/hexane by tumbling action in a rotary extractor for 30 min at high speed. After extraction, the sample was centrifuged for 10 min at 2000 rpm, and the hexane layer was collected. This was repeated two more times, and the hexane extracts were combined. Soil samples (10-g sample size based on dry weight) were extracted with toluene using a Soxhlet extractor for a minimum of 16 hrs. Samples were spiked with 20 pg/μL of

<sup>37</sup>Cl<sub>4</sub>-labeled cleanup standard, based on the final extract volume, and were subjected to multiple acid partitioning. Samples were further cleaned through silica and alumina columns. Sample extracts were eluted through an AX-21 carbon column, were concentrated to 1 mL, and spiked with 10 μL of <sup>13</sup>C<sub>12</sub>-labeled recovery standard at a concentration level of 100 pg/μL. Then they were concentrated to a final extract volume of 10 μL. Samples were analyzed on a Fisons Autospec-Ultima high resolution mass spectrometer equipped with a Hewlett Packard 5890 Series II gas chromatograph, operating at 10,000 resolving power in the SIM mode, using a 60m DB-5 capillary fused silica column (0.25mm internal diameter, 0.25 μm film thickness).

### Results and Discussion

- 1) The average recoveries of the <sup>13</sup>C<sub>12</sub>-labeled internal quantitation standards for both soil and vegetation samples are summarized in Table 1. The average recoveries of the internal quantitation standards ranged from 63.8 ± 8.22 to 110 ± 13.5 for soil and 61.3 ± 11.1 to 100 ± 12.4 for vegetation samples. Although the recovery of the internal quantitation standards for the individual samples are not presented here, all of the recoveries for the individual samples met the regulatory guidelines specified in EPA Method 8290 and Draft Method 1668. The experimental precision and reproducibility, as shown by the calculated standard deviations for percent recoveries of the internal quantitation standards for the vegetation samples, indicate that the rotary extraction method can be utilized for extracting garden vegetation.
- 2) Table 2 presents the summary for the percent recovery and relative percent difference from the native sample for all 17 2,3,7,8-substituted congeners of PCDDs/PCDFs and 4 Co-PCBs for the MS/MSD pairs prepared with the two batches of the vegetation samples. Table 2 also includes results for the LCSs processed with each batch of vegetation samples. The recoveries of the native PCDD/PCDF/Co-PCB congeners obtained from the analysis of MS/MSD pairs and LCSs show good overall accuracy for this experimental method.
- 3) Table 3 presents a summary of the results obtained from the analysis of the two soil samples that presented the highest concentration levels for 1,2,3,4,6,7,8-HpCDD and OCDD congeners, as well as a selected number of garden vegetation that showed detectable concentration levels of 1,2,3,4,6,7,8-HpCDD and OCDD far above the levels found in the MB. All soil samples presented elevated concentration levels of hepta and octa dioxin congeners, ranging from 79.4 pg/g to 161 pg/g and 2470 pg/g to 12100 pg/g for 1,2,3,4,6,7,8-HpCDD and OCDD congeners, respectively. The highest detected levels are carrots 22.5 pg/g and 208 pg/g, Swiss chard 21.8 pg/g and 112 pg/g, tomatoes 31.8 pg/g and 130 pg/g, and beets 11.0 pg/g and 102 pg/g, for 1,2,3,4,6,7,8-HpCDD and OCDD congeners, respectively (based on sample dry weight). The results in Table 3 also shows similar congener-specific trends for both soil and vegetation samples. In addition, the results obtained for the soil and vegetation samples show a pattern of contamination that may be compatible with the deposition of PCDD/PCDF congeners by air particulates.

**Table 1. Average percent recoveries of the internal quantitation standards**

Congeners	SOIL (a)		VEGETATION (b)	
	Standard		Standard	
	Average	Deviation	Average	Deviation
13C-2,3,7,8-TCDF	76.3	11.0	74.4	6.41
13C-2,3,7,8-TCDD	73.8	11.4	76.2	7.99
13C-1,2,3,7,8-PeCDF	73.1	10.8	73.5	11.1
13C-1,2,3,7,8-PeCDD	63.8	8.22	61.3	11.1
13C-1,2,3,6,7,8-HxCDF	78.2	10.0	86.4	7.50
13C-1,2,3,6,7,8-HxCDD	88.8	14.3	87.2	7.78
13C-1,2,3,4,6,7,8-HpCDF	75.5	11.9	87.5	10.6
13C-1,2,3,4,6,7,8-HpCDD	109.8	13.5	100.4	12.4
13C-OCDD	91.6	20.0	84.7	12.2
37Cl-2,3,7,8-TCDD	70.4	7.85	83.4	6.57
13C-81-TCB	70.3	6.48	71.9	6.31
13C-77-TCB	67.9	5.93	74.2	5.95
13C-126-PeCB	78.2	6.56	73.7	8.63
13C-169-HxCB	81.9	8.37	73.5	15.3

(a) n = 10; b) n = 35

**Table 2. Results for LCS and MS/MSD pair for the vegetation samples**

Congener	Spike Level pg/g (a)	Batch 1 Vegetation				Batch 2 Vegetation		
		LCS %Recovery	MS/MSD Pair		LCS %Recovery	MS/MSD Pair		
			Average %Recovery	%RPD		Average %Recovery	%RPD	
2,3,7,8-TCDF(a)	4	112	120	2.51	114	109	1.83	
2,3,7,8-TCDD	4	97.0	97.0	2.06	96.3	97.0	6.19	
1,2,3,7,8-PeCDF	20	126	124	2.43	118	117	0.858	
2,3,4,7,8-PeCDF	20	106	113	5.31	113	111	0	
1,2,3,7,8-PeCDD	20	129	137	0.733	138	138	3.64	
1,2,3,4,7,8-HxCDF	20	120	125	0.803	119	119	1.68	
1,2,3,6,7,8-HxCDF	20	116	118	1.69	115	115	0.873	
2,3,4,6,7,8-HxCDF	20	105	119	9.28	104	102	0	
1,2,3,7,8,9-HxCDF	20	106	105	20.1	108	114	2.64	
1,2,3,4,7,8-HxCDD	20	123	128	3.92	118	121	0.830	
1,2,3,6,7,8-HxCDD	20	109	111	3.60	108	107	0	
1,2,3,7,8,9-HxCDD	20	123	114	23.8	121	123	0.816	
1,2,3,4,6,7,8-HpCDF	20	119	119	2.53	115	114	0	
1,2,3,4,7,8,9-HpCDF	20	112	119	6.72	107	108	0	
1,2,3,4,6,7,8-HpCDD	20	89.0	93.5	3.21	89.0	89.5	3.35	
OCDF	40	112	106	10.4	103	104	0.966	
OCDD	40	113	115	2.62	112	114	1.75	
81-TCB	8	92.5	90.0	4.44	95.6	99.5	1.01	
77-TCB	8	101	98.0	2.04	102	100	4.00	
126-PeCB	40	89.5	91.5	1.09	99.0	99	2.02	
169-HxCB	40	86.8	95.0	8.42	92.0	99.5	1.01	

(a) Spike levels are based on the 50-g sample wet weight.

**Table 3. Comparison between results (pg/g; dry weight) of selected soils and garden vegetation**

Congener	Soil	Soil	Tomato	Swiss Chard	Carrot	Beets
2,3,7,8-TCDF(a)	2.31	U(0.600)	0.415	U(0.413)	U(0.423)	U(0.169)
2,3,7,8-TCDD	2.30	0.532	U(0.723EMPC)	U(0.448EMPC)	0.600	0.280
1,2,3,7,8-PeCDF	4.29	U(0.0299)	0.585	U(0.254EMPC)	U(0.136)	0.120
2,3,4,7,8-PeCDF	5.96	U(0.244EMPC)	U(0.631)	U(0.269MPC)	0.533	U(0.240EMPC)
1,2,3,7,8-PeCDD	41.9	1.10	2.75	U(0.373EMPC)	U(0.383EMPC)	U(0.0361)
1,2,3,4,7,8-HxCDF	21.3	U(0.383EMPC)	U(0.923EMPC)	U(0.239EMPC)	0.183	0.147
1,2,3,6,7,8-HxCDF	28.4	U(0.364EMPC)	U(1.57EMPC)	0.224	0.233	U(0.107EMPC)
2,3,4,6,7,8-HxCDF	32.7	U(0.346EMPC)	2.82	1.31	1.37	1.04
1,2,3,7,8,9-HxCDF	U(0.257)	U(0.0345)	U(0.768)	U(0.0942)	U(0.0222)	U(0.00924)
1,2,3,4,7,8-HxCDD	82.0	1.93	1.89	0.433	U(0.383EMPC)	0.213
1,2,3,6,7,8-HxCDD	113	3.75	U(2.80EMPC)	U(1.58EMPC)	1.32	U(0.800EMPC)
1,2,3,7,8,9-HxCDD	153	3.68	3.38	0.761	0.700	U(0.413EMPC)
1,2,3,4,6,7,8-HpCDF	706	U(4.69EMPC)	24.6	2.64	2.82	1.80
1,2,3,4,7,8,9-HpCDF	28.4	U(0.646)	U(1.36)	U(0.531)	U(0.445)	U(0.145)
1,2,3,4,6,7,8-HpCDD	2280	120	31.8	21.8	22.5	11.0
OCDF	1120	11.3	28.0	2.31	41.7	2.44
OCDD	>12100	9480	130	112	208	102
Total TEQs	117	4.72	4.21	0.529	1.28	0.564
Total TCDF	125	U(0.600)	12.8	U(0.413)	U(0.423)	0.200
Total TCDD	27.4	0.532	2.29	0.776	1.85	0.827
Total PeCDF	379	U(0.0307)	38.5	2.43	3.08	1.81
Total PeCDD	280	3.83	15.7	0.373	0.617	U(0.227)
Total HxCDF	944	3.91	34.8	2.88	4.00	4.08
Total HxCDD	1010	19.8	30.0	6.49	11.1	5.41
Total HpCDF	1380	U(0.588)	40.3	2.64	7.87	5.19
Total HpCDD	3340	236	50.6	36.3	46.0	23.5

(a) The calculated concentration of 2,3,7,8-TCDF should be considered as the maximum concentration since the DB-5 column is not 2,3,7,8-TCDF specific.

(b) EMPC represents the estimated maximum possible concentration and is reported as non-detect since the resulting natural isotopic abundance ratio for chlorine does not meet the criteria specified in Method 8290.

(c) EMPC were not included in the calculation of TEQs.

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