

DETERMINATION AND COMPARISON OF PERSISTENT ORGANOCHLORINE
COMPOUNDS IN SOIL REFERENCE MATERIALS

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Introduction

Approximately 250 soil samples have been submitted for analysis to investigate the levels of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), co-planar polychlorinated biphenyls (Co-PCBs) and mono-ortho polychlorinated biphenyls (MO-PCBs) in urban soils. With each process batch of samples, additional quality control (QC) or reference soil samples have been submitted to monitor ongoing precision and accuracy. The reference soil samples have been used historically on a large number of studies but have only been classified for PCDD/PCDF concentration. These reference soils, however, have not previously been classified for either Co-PCBs or MO-PCBs. This paper will present the relative levels of the PCDDs/PCDFs and PCBs found in the reference soils.

Materials and Methods

Soil samples were collected, sieved to 250- μm and delivered to the laboratory. All samples were prepared and analyzed according to isotope dilution quantitation specified in a method based on the techniques presented in US EPA Method 8290¹, 1613B², and Method 1668³.

Approximately 20-g of each sample is fortified with a mixture of ¹³C-labeled PCDD/PCDF/PCB internal quantitation standards (IQS), extracted by soxhlet for 16 hours with toluene, and then concentrated. Each extract is then spiked with a cleanup standard (³⁷Cl₄-2,3,7,8,-TCDD) to monitor efficiency through the remainder of extract cleanup. The extracts are then processed through a concentrated acid shake and silica cleanup. Following silica, each extract is split with one portion reserved for PCDD/PCDF/Co-PCB analysis and the other for MO-PCB analysis. The MO-PCB extracts are fortified with ¹³C-labeled recovery standards and concentrated to a final volume of 20- μL in tridecane. The PCDD/PCDF/Co-PCB extracts are further processed through alumina and carbon columns, fortified with ¹³C-labeled recovery standards and concentrated to a final volume of 10- μL in tridecane.

All HRGC/HRMS analyses are conducted using a Hewlett-Packard 5890 gas chromatograph interfaced to a VG-70S-250 double focusing/dual sector high resolution mass spectrometer. A DB-5ms gas chromatography column (60 meter, 0.25 mm ID, 0.25 μm film thickness) is used. Mass spectrometer acquisition is performed at 10,000 resolution in the selected ion monitoring mode (SIM) and sensitivity of 10:1 signal-to-noise is routinely achieved for all calibration standards.

For extract analysis, all qualitatively identified peaks above the level of 2.5:1 signal-to-noise are quantified using isotope dilution. A six-point initial calibration curve (I-CAL) for PCDD/PCDF is performed using a 0.25-200 pg/ μ L range for tetra-substituted isomers, 1.25-1000 pg/ μ L range for penta- through hepta-substituted isomers and 2.5-2000 pg/ μ L range for octa-substituted isomers. The Co-PCB and MO-PCB I-CAL is also a six-point curve using a 2.5-500 pg/ μ L range for all isomers.

For toxic equivalency quotient (TEQ) calculations, concentrations detected in samples are multiplied by the corresponding toxic equivalency factor (TEF) presented in Table 1. For analytes that are not detected, including interference values (e.g., polychlorinated diphenyl ethers), a value of one-half the reporting limit is used for the TEQ calculation.

Results and Discussion

A comparison of concentrations (expressed in pg/g) and Total TEQ is presented in Table 2. This table also breaks out the contribution for PCDD/PCDF and for PCBs separately. Results compare well between the known PCDD/PCDF TEQ and the determined PCDD/PCDF TEQ for all reference soils. The general trend is that PCBs (specifically MO-PCBS) are found at higher concentrations than are the PCDDs/PCDFs in the same sample. Based on the TEFs used, however, the percent contribution to the total TEQ from PCBs can be significant but is usually lower than the PCDD/PCDF contribution percentage.

This information is significant because it is demonstrated that PCBs be measured in the same extract with PCDDs/PCDFs and they can also cause interference and reporting of false positive results. For example, there are hexa-PCB congeners that elute within the quantitation window of the penta-CDDs. If these are not removed during sample cleanup, they may be identified as Penta-CDDs (which have a higher TEF value) and cause an elevation of the Total TEQ. This can be mitigated instrumentally by monitoring of additional (different) mass ions than those specified in the standard methodologies.

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References

1. USEPA Method 1613, "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B." Oct. 1994.
2. USEPA Method 8290, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography / High Resolution Mass Spectrometry (HRGC/HRMS), Revision 0." September 1994.
3. Draft Method 1668 for the Measurement of Toxic PCB Congeners by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry. Draft Revision. March, 1997.
4. Van den Berg et al., Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife, *Environmental Health Perspectives* 106:775-792, 1998.

Table 1 Analytes Measured and Toxic Equivalency Factors Used

Compound	TEF
PCDDs and PCDFs	QATS-TEF ¹
2,3,7,8-TCDF	0.1
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
1,2,3,4,6,7,8-HpCDD	0.01
OCDF	0.001
OCDD	0.001
Coplanar PCBs	I-TEF ²
3,3',4,4'-TCB (PCB 77)	0.0001
3,4,4',5-TCB (PCB 81)	0.0001
3,3',4,4',5-PeCB (PCB 126)	0.1
3,3',4,4',5,5'-HxCB (PCB 169)	0.01
Mono- Ortho-PCBs	I-TEF ²
2,3,3',4,4'-PeCB (PCB 105)	0.0001
2,3,4,4',5-PeCB (PCB 114)	0.0005
2,3',4,4',5-PeCB (PCB 118)	0.0001
2',3,4,4',5-PeCB (PCB 123)	0.0001
2,3,3',4,4',5-HxCB (PCB 156)	0.0005
2,3,3',4,4',5'-HxCB (PCB 157)	0.0005
2,3',4,4',5,5'-HxCB (PCB 167)	0.00001
2,3,3',4,4',5,5'-HpCB (PCB 189)	0.0001

¹ USEPA QATS TEFs used for D/Fs

² World Health Organization (Van den Berg et al., 1998⁴) used for PCBs

Table 2 Concentration and TEQ Comparison Results

Sample	Description	Known D/F TEQ	Concentration (pg/g)			TEQ (pg/g) ¹			% of Total Concentration		% of Total TEQ	
			D/F	PCB	Total	D/F	PCB	Total	D/F	PCB	D/F	PCB
1001			337	3410	3750	4.23	8.76	13.0	9	91	33	67
1002			1090	38900	40000	94.2	29.7	124	3	97	76	24
1003			204	1160	1360	4.32	2.59	6.92	15	85	62	37
1004	PEL-R	35.5	535	1680	2210	35.2	1.22	36.4	24	76	97	3
1005	CIL-R	<5	844	194	1040	4.59	1.41	6.00	81	19	77	24
1006			841	2110	2950	56.0	1.73	57.7	29	72	97	3
1007			289	28700	29000	30.6	69.7	100	1	99	31	70
1008			877	2260	3140	56.5	5.24	61.8	28	72	91	8
1009			688	1800	2480	49.5	4.72	54.2	28	73	91	9
1010			318	449	767	4.59	1.69	6.28	41	59	73	27
1011	RMA-S	Blank	20.6	82.7	103	1.59	0.599	2.19	20	80	73	27
1012			333	1380	1710	26.0	5.04	31.0	19	81	84	16
1013	RMA-F	Blank	22.9	90.1	113	2.32	0.434	2.75	20	80	84	16
1014			414	22500	22900	45.6	16.8	62.3	2	98	73	27
1015			115	329	445	2.80	1.51	4.30	26	74	65	35
1016	PEM-R	59.1	520	26200	26700	60.9	19.3	80.2	2	98	76	24
1017			891	35600	36500	96.1	117	214	2	98	45	55
1018	RMA-B	Blank	19.4	82.6	102	2.09	0.792	2.89	19	81	72	27

¹ QATS TEFs used for D/Fs and World Health Organization (Van den Berg et al., 1998⁴) used for PCBs.