

ANALYSIS OF POLYCHLORINATED DIBENZOFURANS
AND POLYCHLORINATED DIBENZODIOXINS: I - AN
INTER- AND INTRA-LABORATORY EVALUATION OF
VARIOUS PROTOCOLS FOR CONGENER SPECIFIC
ANALYSES OF SEDIMENTS AND RESIDUES

by

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Analytical data form the basis for expensive and far-reaching decisions in hazardous waste management and site remediation. The analytical data initially define the type and extent of the contamination, and, ultimately, assess the success of the implemented remedial program. Chemical analyses of samples with low levels of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) can prove difficult, especially in heterogeneous, weathered matrices. The presence of interfering organic compounds, such as oils, may further complicate the analyses needed to serve as the basis for these important decisions.

The site of this work was multi-building plastics manufacturing facility in the Northeastern United States. The facility ceased production in 1980.

Because of the difficulties possible in the analyses required and the importance of the analytical results in this particular effort, extreme care was afforded the selection of the primary and QA/AC laboratories for PCDF-PCDD analyses. The first part of the study was designed to compare various analytical protocols on both an inter- and intra-laboratory basis. At the time of this and associated studies, there were no

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USEPA standard procedures for many of the matrices of interest (i.e. materials of construction - brick, concrete, wood, etc.) nor were there formal protocols for high resolution GC/MS procedures. In an effort to reduce inherent inhomogeneities in the distribution of constituents of interest, the first phase of the protocol evaluation testing was performed on weathered sediments and residues from raceways. These raceways are underground waterways beneath the facility which were designed to generate hydroelectric power for the facility. The media, sediments and residues, could (theoretically) be better mixed prior to division into replicate samples for distribution to the participating laboratories. Analysis was to be performed for total homologous series of PCDF/PCDD and 2,3,7,8 congeners.

The protocols tested varied both in extraction techniques and in the GC/MS analytical approach employed. Specifically these included jar (shake) vs Soxhlet extraction; benzene vs methanol/hexane vs acetone/hexane vs toluene; high vs low (extended) resolution mass spectrometry. This study also investigated protocol precision via the reinjection of the same extract using different protocols. The analytical results of the various combinations and permutations were then compared to each other as well as the results from the closest matrices studied by the USEPA in their document, "Performance of RCRA Method 8280 for the Analysis of Dibenzo-p-Dioxins and Dibenzofurans in Hazardous Waste Samples" as well as the 1986 ASTM report on inter- and intra-laboratory precision in TCDD measurements using EPA Method 8280.

This paper presents the results of the sediment/residue analyses from the raceways. The results are summarized in two tables, comparing the means and ranges of concentrations of the data to the data from the USEPA. The USEPA data were derived from soils and sludges (the two closest media to sediment and residues) extracted/analyzed via an approved procedure (USEPA Method 8280). The raceway samples performance appeared to exceed the USEPA results (i.e., lower relative standard deviations, narrower ranges, etc.), although the results incorporate all the various extraction/analytical procedures tested.

TABLE I

COMPARISON OF THE RANGES OF RESULTS OBTAINED FROM THE
PCDD/PCDF ANALYSES OF SAMPLES OF VARIOUS MATRICES FROM
USEPA STUDIES AND THE GENCORP,
LAWRENCE, MASSACHUSETTS FACILITY RACEWAY QA/QC PROGRAM

Analyte	USEPA Results ^a				GenCorp, Lawrence, Massachusetts Facility Raceway Results ^b		
	Soil A	Soil B	Sludge A	Sludge B	North Sediment	Exterior Sediment	North Residue
	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)
TCDD	345-764	ND-2	ND-6	ND-10	ND	ND	ND-3.4
PeCDD	ND-14	ND-7.2	ND-431	ND-42.5	ND	ND	ND-2.2
HxCDD	ND	230-260	768-6,970	216-708	ND-0.40	ND-034	ND-1.5
HpCDD	ND-27	194-4,500	337-15,743	110-2,460	0.21-6.9	0.38-1.7	4.3-9.1
OCDD	ND-141	ND-45,174	421-52,912	253-11,408	1.2-16	0.95-5.2	12-18
TCDF	31-54	ND-22	ND-23	ND-933	0.033-12	0.042-0.69	8.4-168
PeCDF	ND-41	ND-715	ND-671	ND-148	0.036-4.1	ND-0.40	ND-23
HxCDF	ND	308-777	48-622	9.7-744	ND-1.4	ND-0.52	1.6-3.9
HpCDF	ND-2.6	67.2-2,750	ND-400	40.8-830	ND-5.7	0.12-1.1	1.7-6.4
OCDF	ND-7.1	7.9-1,205	ND-271	7.8-260	ND-5.9	ND-1.9	1.4-6.7

^aRCRA Method 8280 USEPA.

^bIncludes values from both the primary and QA/QC laboratories.

TABLE 2
 COMPARISON OF THE MEAN CONCENTRATIONS AND PERCENT RELATIVE
 STANDARD DEVIATIONS FOR USEPA STUDIES AND THE
 GENCORP, LAWRENCE, MASSACHUSETTS FACILITY RACEWAY QA/QC PROGRAM

Analyte	USEPA Results				GenCorp, Lawrence, Massachusetts Facility Raceway Results		
	Mean Concentrations ^a ppb (\pm percent RSD) ^b				Mean Concentrations, ppb (\pm percent RSD) ^c		
	Soil A	Soil B	Sludge A	Sludge B	Residue	Sediment	Sediment
TCDD	503(26.1)	2(0)	6(--)	10(--)	3.1(8.1)	ND(--)	ND(--)
PeCDD	14(--)	3.9(47.1)	230(79.2)	36(24.3)	1.8(21)	ND(--)	ND(--)
HxCDD	ND(--)	363(26.0)	2,609(86.1)	399(39.7)	1.1(40)	0.16(75)	0.24(46)
HpCDD	24(18.7)	3,463(68.2)	8,605(76.3)	1,426(69.7)	6.7(25)	0.90(48)	3.3(64)
OCDD	72(108.7)	12,235(121.7)	19,545(90.7)	3,741(77.4)	15.0(15)	2.6(58)	9.6(63)
TCDF	39.4(25.3)	7.6(89.9)	15(73.6)	61(45.7)	117(54)	0.33(91)	4.6(104)
PeCDF	4.1(1.7)	118(169.0)	34(98.1)	61(77.6)	20(18)	0.22(64)	1.1(127)
HxCDF	ND(--)	484(32.5)	190(120.2)	402(55.9)	3.0(30)	0.23(78)	0.56(79)
HpCDF	2.6(--)	805(85.0)	237(64.5)	467(52.4)	3.4(53)	0.46(83)	2.1(95)
OCDF	7.1(--)	649(61.5)	126(66.0)	91(81.8)	3.0(73)	0.73(119)	2.5(80)

^aRCRA Method 8210 (USEPA).

^bRSD = Relative Standard Deviation.

^cIncludes values from both the primary and QA/QC laboratories.