

PCDDs/PCDFs IN AMBIENT AIR (< 1fg/m³) – LONG TERM SAMPLING (30 DAYS) WITH HRGC/HRMS – METHOD PERFORMANCE DATA

Gary T Hunt & Melita F Lihzis

TRC Environmental Corporation 650 Suffolk St. Lowell, MA USA 01854

Introduction

The state of Connecticut (CT) has established an Ambient Air Quality Standard (AAQS) for PCDDs/PCDFs expressed as 2,3,7,8-TCDD equivalents on an annualized basis of 1.0 pg/m³ TEQ. This AAQS represents the maximum concentration permitted in ambient air from all known sources of PCDDs/PCDFs including background contributions. Atmospheric concentrations of PCDDs/PCDFs are currently monitored at a single site located in Hartford, Connecticut. The data collected at this site are compared annually to the AAQS and ultimately used to demonstrate compliance with the AAQS. The Connecticut Department of Environmental Protection (CT DEP) commenced monitoring to evaluate compliance with the AAQS in 1987. Initial efforts were comprised of monitoring in the vicinity of a number of municipal waste combustors or resource recovery facilities (RRF) located in the state. During the period Fall 1993 to Spring 2002 quarterly monitoring campaigns using the long duration approach (30 day composite samples) were conducted using a single monitoring location in the vicinity of each of the RRFs. Commencing in the winter of 2002-03, CT DEP performed monitoring only in Hartford and only during winter months. Winter time was selected on the basis of its having the highest measured concentrations of PCDDs/PCDFs in ambient air based upon data collected previously by CT DEP. CT DEP adopted the modified high volume air sampling approach in concert with HRGC/HRMS for the purposes of enhancing sensitivity to allow for measurement of PCDDs/PCDFs isomers typically present in fg/m³ concentrations in ambient air. This approach over time has proven to be a highly sensitive and reliable technique for monitoring of PCDDs/PCDFs isomers at near molecular levels in ambient air. The precision and accuracy of the enhanced method has been demonstrated through use of isotopically labeled field applied surrogates in concert with collocated samplers. The paper presented here provides a summary of the quality control data collected during the past six years of monitoring at the Hartford, CT site. These data serve to demonstrate method performance under actual field monitoring conditions.

MATERIALS AND METHODS

Sampling Location and Methods

PS-1 samplers manufactured by General Metal Works were modified to collect ambient air samples for subsequent PCDDs/PCDFs analysis. The PS-1 samplers for this program were modified to accept an 8" x 10" rectangular filter in lieu of the standard 10.14" diameter circular filter. This modification accommodated the high particulate filter loading expected during the extended 30-day sampling period. The PS-1 sampler accepts a Teflon-coated glass fiber filter and polyurethane foam plug (density of 0.024 grams/cm³) for collection of particulate-associated and vapor phase PCDDs/PCDFs, respectively. The sample collection procedures are consistent with the approach prescribed in modified EPA Method TO-9 and prior ambient PCDDs/PCDFs monitoring programs performed in the state of Connecticut under the direction and sponsorship of the CT DEP. Samples were collected on the property of Brainard Airport situated in Hartford, CT. The site is believed to be similarly representative of the urban environment. Each of the wintertime sample sessions consisted of two consecutive 30-day sampling periods. Each sample collection event consisted of two collocated sampling systems. The calendar dates for each of the six (6) sampling periods are listed in Table 4. PCDDs/PCDFs analyses were conducted by Vista Laboratory, formerly Alta Laboratory (Eldorado Hills, CA) employing EPA Method TO9A modified for use with CT DEP ambient air samples.

Analytical Methods

Laboratory methods followed procedures prescribed in EPA Method TO9A. After collection, the filter and PUF were combined for sample preparation, spiked with labeled PCDD/PCDF internal standards, and soxhlet extracted in

toluene for 16 hours. The extracts were then spiked with Clean-Up Recovery standard and tetradecane, exchanged to hexane and concentrated to the tetradecane. The extracts were subjected to an Acid Base Silica Gel cleanup on column using hexane, discarding all eluates. Next the extracts were eluted through a Florisil column with hexane and the eluate discarded. Finally, the florisil column was rinsed with dichloromethane and the eluate collected. The eluate was concentrated and transferred to a vial containing Recovery Standard and tetradecane for HRMS analysis. The analytes were separated by high resolution capillary gas chromatography with subsequent analyses by high-resolution mass spectrometry. Two exact m/z s were monitored for each analyte. An individual 2,3,7,8-substituted congener was identified by comparing the GC retention time and ion-abundance ratio of two exact m/z s with the corresponding retention time of an authentic standard and the theoretical ion-abundance ratio of the two exact m/z s. The instrument was tuned to the minimum required resolving power of 10,000 and the mass resolution check achieved before any analysis was performed for each 12-hour analytical session. An initial calibration curve was analyzed to demonstrate the linearity of the HRMS system over the calibration range and verified with a continuing calibration verification standard per analytical batch. Quantitative analysis was performed using selected ion current profile (SICP) areas.

QUALITY CONTROL RESULTS

Field Blanks

Field blank samples exposed to field conditions were analyzed to assess possible contamination throughout the sample collection and analysis process. Unlike method blanks, field blanks are sensitive to field-derived sample contamination, contributed by passive deposition and sample handling. Field blanks were open to the atmosphere for the duration of the sample set-up and recovery periods. Analytical results reported for actual program samples were corrected using the corresponding field blanks. Twelve (12) field blanks, one per each of twelve 30-day sampling sessions, were collected during the course of the 2002-2008 field program. The majority of the analytes in the field blanks were either non-detected (< 2 - 6 pg/isomer; average values reported in Table 1) or measured less than 4-10 pg/sample (maximum values reported in Table 1). The only analytes observed greater than 10 pg/sample on a consistent basis were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF. With the exception of these four (4) isomers as shown in Table 1 average quantities for the balance of the 2378-substituted isomers found in field blanks ranged from 2.3-5.6 pgs. Based upon an average air volume of 7,659 m^3 detection limits of < 1 fg/m^3 ($< 10^{-15}$ g/m^3) for these isomers were routinely achievable. In all instances quantities found in field blanks were the major determinant in establishing method sensitivity/ detection limits on an isomeric specific basis. Note that all average quantities reported in Table 1 treated both measured values and detection limits as measured values and hence represent conservative estimates.

Field Surrogates

Prior to sample collection, PUF sorbent cartridges were fortified with five isotopically labeled field surrogate compounds. The surrogate compounds were spiked just below the inlet surface of the PUF plug at the laboratory following completion of the cleanup procedure and prior to disposition to the TRC field team. This procedure allowed for an assessment of the accuracy of the combined sampling and analysis regime. Accuracy is assessed as the average field-applied surrogate recovery (observed vs. applied) in program samples. All recoveries fell within the acceptable ranges established for use of EPA Method TO9A[1] (50-120 % for tetra – hexa substituted, and 40-120% for hepta – octa substituted) As shown in Table 2 average recoveries of field applied labeled PCDDs/PCDFs representing the twenty-three (23) field samples ranged from 97.7-104.2 %. These data represent near complete quantitative recovery of each of the field applied surrogate compounds and are significantly better than method performance goals established for use of EPA Method TO9A. These data demonstrate quantitative retention of all field applied surrogate compounds in all 23 samples over the course of a 30 day sampling period during which an average air volume of 7659 m^3 was collected. Data resulting from use of this sampling and analyses method as a result can be regarded as reliable and of known accuracy.

Collocated Sampler Precision

A single collocated sampler pair was included in each PCDDs/PCDFs 30 day sampling period. Collocated samplers were operated for the same duration at near identical flow rates and were in close proximity to each other so as to represent near identical air space. The data resulting from analyses of the collocated samplers pairs was used to define the precision of the combined sample and collection and analyses scheme.

Precision was determined by the collection and analysis of replicate samples and is expressed as the relative percent difference (RPD). The collocated sampler data for the eleven (11) pairs collected as part of the winter 2002-2008 sampling period are summarized in Table 4. Results are provided for each of the analytes measured in the sampler pair in units of pg/m^3 . The relative percent difference data shown are consistent with expected values from other CT DEP sponsored programs that employed the long-term monitoring approach (2,3,4 and 5) including the 12% average precision result reported by Maisel and Hunt previously (4). These data demonstrate that precision of the combined sampling and analyses method is acceptable for individual 2378-substituted isomers and congeners. Although congener values represent sums of all isomers present in each congener class, the precision results are comparable. For example the TCDD congener concentration may represent up to 22 positional isomers of TCDD while 2378-TCDD represents but a single isomer concentration. Since method quality control measures are directed at individual 2378-substituted isomers the precision and accuracy of concentrations reported for the congeners exceeds expectations.

Internal Standards

Internal standards are added to all samples prior to extraction in the laboratory. These standards consisting of a suite of ten (10) isotopically labeled PCDDs/PCDFs (one per each of ten congeners) are used for quantifying of native species present in field samples. The absolute recoveries of the internal standards are monitored to insure that concentrations reported for native species are accurate and that method performance goals are satisfied. Average recoveries for each of the ten (10) isotopically labeled internal standards representing the population of twenty-three (23) field samples are summarized in Table 3. All recovery data exceed method performance goals listed in EPA Method TO9A[1].

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Table 1

2002 - 2008^a WINTER SAMPLING CAMPAIGNS AT BRAINARD AIRPORT

Field Blank Data Summary^b

Average Sample Air Volume (m3) 7,659

Parameter	Average FBB Conc		Minimum FBB Conc		Maximum FBB Conc	
	pg/sample	pg/m3	pg/sample	pg/m3	pg/sample	pg/m3
2,3,7,8-TCDD	2.30	0.0003	1.42	0.0002	4.13	0.0005
1,2,3,7,8-PeCDD	3.96	0.0005	2.11	0.0003	7.07	0.0009
1,2,3,4,7,8-HxCDD	4.16	0.0005	2.55	0.0003	6.18	0.0008
1,2,3,6,7,8-HxCDD	4.99	0.0007	3.03	0.0004	6.95	0.0009
1,2,3,7,8,9-HxCDD	5.60	0.0007	2.94	0.0004	8.06	0.0011
1,2,3,4,6,7,8-HpCDD	43.63	0.0057	3.21	0.0004	112	0.0146
OCDD	320.16	0.0418	9.39	0.0012	776	0.1013
2,3,7,8-TCDF	2.67	0.0003	1.73	0.0002	4.53	0.0006
1,2,3,7,8-PeCDF	3.93	0.0005	2.15	0.0003	7.6	0.0010
2,3,4,7,8-PeCDF	4.64	0.0006	2.6	0.0003	8.82	0.0012
1,2,3,4,7,8-HxCDF	4.15	0.0005	1.14	0.0001	8.79	0.0011
1,2,3,6,7,8-HxCDF	3.84	0.0005	1.05	0.0001	8.24	0.0011
2,3,4,6,7,8-HxCDF	4.15	0.0005	1.14	0.0001	9.14	0.0012
1,2,3,7,8,9-HxCDF	2.45	0.0003	0.841	0.0001	6.97	0.0009
1,2,3,4,6,7,8-HpCDF	15.71	0.0021	1.24	0.0002	33.4	0.0044
1,2,3,4,7,8,9-HpCDF	3.28	0.0004	1.39	0.0002	7.13	0.0009
OCDF	21.97	0.0029	4.66	0.0006	65.3	0.0085
N = 12						

Notes:

a - Samples collected at Sheldon St. site in downtown Hartford, CT during the 2002-03 sampling event only.

All other sampling events (2003-2008) took place at Brainard Airport site.

b - Average, minimum and maximum quantities (pg/sample) and corresponding air concentrations include both measured values as well as nondetect (ND) values. ND values were considered as max measured value in the calculation of all averages reported.

Table 2

2002 - 2008^a WINTER SAMPLING CAMPAIGNS AT BRAINARD AIRPORT

Field Surrogate Recovery Summary

Labeled Standard	Average % Recovery	Standard Applied (pg)	Standard Applied Concentration (pg/m3) ^b	SD
37Cl-2,3,7,8-TCDD	98.50	1000	0.131	4.34
13C-2,3,4,7,8-PeCDF	97.49	4000	0.522	5.23
13C-1,2,3,4,7,8-HxCDD	103.59	4000	0.522	7.48
13C-1,2,3,4,7,8-HxCDF	103.36	4000	0.522	6.66
13C-1,2,3,4,7,8,9-HpCDF	104.16	4000	0.522	10.39
N = 23				

Notes:

a - Samples collected at Sheldon St. site in downtown Hartford, CT during the 2002-03 sampling event only.

All other sampling events (2003-2008) took place at Brainard Airport site.

b - The concentration of the standard applied was calculated using quantity for each isotopic standard applied (pg) in combination with an average air volume of 7,659 cubic meters for 23 field samples.

Table 3
2002 - 2008^a WINTER SAMPLING CAMPAIGNS AT BRAINARD AIRPORT
Internal Standard Recovery Summary

Labeled Standard ^b	Average % Reco	SD
13C-2,3,7,8-TCDD	92.35	7.99
13C-1,2,3,7,8-PeCDD	88.75	8.64
13C-1,2,3,6,7,8-HxCDD	87.77	8.69
13C-1,2,3,4,6,7,8-HpCDD	93.77	11.04
13C-OCDD	80.92	18.81
13C-2,3,7,8-TCDF	95.47	9.54
13C-1,2,3,7,8-PeCDF	92.03	10.34
13C-1,2,3,6,7,8-HxCDF	83.94	11.35
13C-1,2,3,4,6,7,8-HpCDF	84.42	10.57
13C-OCDF	76.97	17.13
N = 23		

Notes:

a - Samples collected at Sheldon St. site in downtown Hartford, CT during the 2002-03 sampling event only.

All other sampling events (2003-2008) took place at Brainard Airport site.

b - 4000 picograms of each labeled standard were applied to each sample; equivalent to 0.533 pg/m³ (based upon average air volume of 7,659 cubic meters for 23 field samples).

Table 4
2002 - 2008^a WINTER SAMPLING CAMPAIGNS AT BRAINARD AIRPORT
COLLOCATED SAMPLERS PRECISION - Relative Percent Difference (RPD)^b

SAMPLING PERIOD	12/30/02 - 1/29/03	1/29/03 - 2/28/03	12/30/03 - 1/17/04	1/27/04 - 2/26/04	12/12/04 - 1/20/2005	1/20/05 - 2/18/05	12/12/05 - 1/11/06	1/11/06 - 2/10/06	12/18/06 - 1/17/07	12/17/07 - 1/16/08	1/16/08 - 2/15/08	Average
Parameter	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)	RPD (%)
2,3,7,8-TCDD	30.18	0.88	6.46	10.26	0.02	7.81	4.03	7.36	0.49	5.04	14.58	7.92
TOTAL TCDD	7.13	11.31	14.14	6.56	4.45	4.40	7.85	0.51	6.52	10.91	16.30	8.19
1,2,3,7,8-PeCDD	3.60	17.66	28.06	29.79	5.92	7.60	5.70	8.42	21.77	1.32	11.02	12.80
TOTAL PeCDD	15.98	14.12	3.56	21.29	2.89	3.91	0.09	1.19	15.53	6.90	1.80	7.93
1,2,3,4,7,8-HxCDD	2.94	15.61	18.10	43.79	11.66	3.44	7.28	6.81	3.30	6.05	3.20	11.11
1,2,3,6,7,8-HxCDD	4.76	16.98	39.96	49.62	0.10	0.25	7.49	1.19	11.67	0.61	7.19	12.71
1,2,3,7,8,9-HxCDD	6.52	14.07	41.16	58.61	1.16	0.70	6.59	4.03	8.23	2.82	3.20	13.37
TOTAL HxCDD	2.64	15.35	22.50	35.26	4.40	4.20	19.32	3.35	8.62	2.22	2.26	10.92
1,2,3,4,6,7,8-HpCDD	1.48	5.51	43.54	56.92	9.43	5.67	5.23	0.64	6.56	5.12	2.92	13.00
TOTAL HpCDD	4.22	9.15	41.04	55.47	8.55	4.67	2.72	0.07	8.06	3.52	3.25	12.79
OCDD	5.04	2.48	48.75	64.29	11.56	6.85	2.66	1.26	1.48	4.35	5.26	14.00
2,3,7,8-TCDF	1.86	14.62	15.29	6.32	11.87	1.26	2.55	1.61	13.02	15.74	8.24	8.40
TOTAL TCDF	2.69	18.49	0.45	4.22	5.94	2.84	2.10	0.10	8.52	8.70	1.58	5.06
1,2,3,7,8-PeCDF	8.10	26.83	0.22	4.62	4.91	3.94	6.44	4.06	13.30	2.20	1.09	6.88
2,3,4,7,8-PeCDF	10.46	19.30	0.87	13.11	2.18	7.04	5.87	1.21	1.94	6.41	9.53	7.08
TOTAL PeCDF	3.85	24.18	2.04	9.83	6.92	3.85	3.93	2.11	2.52	6.85	1.76	6.17
1,2,3,4,7,8-HxCDF	22.80	33.28	1.23	12.75	6.62	6.53	2.25	2.73	16.23	4.75	5.13	10.39
1,2,3,6,7,8-HxCDF	19.52	28.64	3.13	19.01	8.26	7.83	3.84	0.54	9.09	4.76	0.73	9.58
2,3,4,6,7,8-HxCDF	12.41	23.52	5.00	15.92	12.21	6.02	0.60	3.90	9.68	6.83	1.52	8.87
1,2,3,7,8,9-HxCDF	32.13	31.00	1.01	20.10	17.12	0.04	0.69	7.34	15.66	7.75	0.99	12.17
TOTAL HxCDF	12.89	28.16	7.73	17.71	8.61	5.44	3.51	1.74	10.34	5.92	2.47	9.50
1,2,3,4,6,7,8-HpCDF	6.74	25.70	5.14	16.62	7.03	7.42	2.31	0.65	7.78	3.61	2.41	7.76
1,2,3,4,7,8,9-HpCDF	24.17	40.35	7.63	3.48	0.93	1.05	1.15	2.81	3.89	8.62	2.19	8.75
TOTAL HpCDF	1.28	28.36	7.43	12.55	5.48	4.81	0.65	0.92	6.37	3.16	2.08	6.64
OCDF	18.05	11.19	8.75	22.14	0.05	3.92	3.93	4.44	5.28	1.85	4.22	7.62

Notes:

a - Samples collected at Sheldon St. site in downtown Hartford, CT during the 2002-03 sampling event only. All other sampling events (2003-2008) took place at Brainard Airport site.

b - $RPD = \frac{Abs(X1 - X2)}{[(X1 + X2)/2]}$

Sampler No 1 Was discontinued during the Jan 17, 2007 - Feb 20, 2007 due to damage sustained from vehicle traffic. Therefore there are no RPD results for that sampling event.