Atmospheric Concentrations of PCDDs/PCDFs in Metropolitan Hartford Connecticut- Current Levels and Historical Data

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Introduction

Historical Evolution of Monitoring Programs in Connecticut

The Connecticut Department of Environmental Protection (CT DEP) commenced monitoring for PCDDs/PCDFs in ambient air 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. These programs were conducted on both a pre-operational and post-operational basis employing multiple station networks in the vicinity of the following RRFs: Mid-Connecticut (Hartford), Bristol, Wallingford, Bridgeport, Lisbon and Preston. In addition background monitoring was conducted at a site in Mohawk Mountain (Cornwall CT). This background monitoring station was relocated to Burlington in the summer of 2000.

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 still included in the study (Mid-Connecticut, Bristol, Wallingford, Bridgeport, Preston, and Lisbon) as well as Mohawk Mountain and Burlington. 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.

Results are provided here for a single monitoring site in the vicinity of Brainard Airport situated in the Hartford Connecticut metropolitan area. The Brainard Site is the only location currently used by the CTDEP for ambient monitoring of PCDDs/PCDFs. Data collected at the site during winter months in calendar years 2003-04 and 2004-05 were examined. These data are compared to historical data collected at a number of sites in the State of Connecticut including sites in the Hartford Metropolitan area.

Materials and Methods

PS-1 samplers manufactured by General Metals 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/cm^3) 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 sampling 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 four (4) sampling periods are listed in Table 1. Other information pertinent to each of the sampling periods including collection flows, duration and sample volumes are also summarized in Table 1.PCDDs/PCDFs analyses were conducted by Alta Laboratory (Eldorado Hills CA) employing EPA Method TO9A modified for use with CTDEP ambient air samples.

Results and Discussion

Results are provided for a total of eight (8) samples (reported as pairs) representing a total of four (4) 30 day sampling events. PCDDs/PCDFs concentration data (pg/m^3 as congener sums (Cl4-Cl8) and 2378-substituted isomers are summarized in Table 2. All results reported here and in figures to follow represent values corrected with the corresponding field blank.

TEF Data

The state of Connecticut 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/m^3 TEQ. This AAQS represents the maximum concentration permitted in ambient air from all known sources of PCDDs/PCDFs including background contributions. The eight sample data set expressed on the basis of TEF weighted concentrations is plotted graphically in Figure 1.The highest values were observed during the January 20-February 18 2005 sampling event (0.0193 and 0.0204) while the lowest TEQ values were observed during the December 21 2004-January 20 2005 sampling event (0.0124 and 0.0127).The mean concentration for the eight sample set of 0.013 pg/m^3 TEQ represents 1.4 % of the CT DEP AAQS guideline of 1.0 pg/m^3 TEQ. The TEQ data reported here are significantly lower than data reported previously by Hunt and Maisel [1] for monitoring in the State of Connecticut (0.092 pg/m^3).

Comparison of 2003-05 Data to Historical Levels in Connecticut (1993-2002)

Total PCDDs/PCDFs concentrations for the eight (8) sample set are listed in Table 2. Session average concentrations (average of pair of samples) were as follows: B (3.37 pg/m3) > D (2.81 pg/m3) > A (2.28 pg/m3) > C (2.04 pg/3).(Session letter identification codes are listed in Table 1). The mean concentration for the eight sample set was 2.62 pg/m^3

This first data set for the Brainard Airport Site, can be compared to historical data collected at other sites in the State of Connecticut and in particular data collected during comparable seasonal conditions found in Fall and Winter months. The largest data set of long term monitoring results is contained in the draft Dioxin Data Evaluation Report: 1993-2002 prepared by ENSR in April 2003 [2]. A summary of data for each of eight (8) sites in use during this period is provided in Table 3. Average concentrations (and one standard deviation) are provided representing the Fall and Winter seasons. The mean concentration for the Brainard Airport Site of 2.62 pg/m3 is significantly higher than winter and fall mean concentrations shown for each of the sites in use during the calendar years 1993-2002. These include urban settings in the cities of Bridgeport, Wallingford and Hartford. The Brainard Airport mean concentration (2.62 pg/m3) does fall below the upper limit concentrations reported for Wallingford (Fall = 3.31 pg/m3) and Bridgeport (Winter = 2.94 pg/m3) resulting from the addition of one standard deviation to the reported mean values for each of these sites. The Brainard Airport mean concentration remains higher than the upper limit concentrations similarly calculated for the remaining six locations listed in Table 3. These include average and upper limit Fall and Winter concentrations reported for the Mid-Connecticut site situated in downtown Hartford. This site has been in use since the inception of the Connecticut DEP monitoring program in 1987 and was in continuous use during the calendar period 1993-2002 represented by data in Table 3. This location was deemed representative of the Hartford Metropolitan area and an urban exposure setting during these prior monitoring programs. The Brainard Airport data suggest that ambient concentrations for the Hartford Metropolitan area may be understated by use of historical data. Sufficient data, however, do not exist at present to establish trends at this location or to ascertain the source or sources contributing to elevated concentrations at this location. It is premature to conclude to what extent these data are representative of the Hartford Metropolitan area or of urban exposure or to what extent the concentrations observed during the winters of 2003-2004 and 2004-2005 may be attributable to sources local to the site or site specific biases. Data collected at another Hartford site during the winter months of 2002-2003 by CTDEP suggest that the Brainard site may be influenced by localized sources or site specific biases [3]. These samples were collected on the property of the Sheldon Street North Parking Lot situated in downtown Hartford. Two (2) pairs

of collocated 30 day samples were collected during the calendar period of December 30 2002 through February 28 2003. The total PCDDs/PCDFs concentration for the four (4) sample set expressed as a mean was 0.84 pg/m3. Individual sample concentrations ranged from 0.68-0.97 pg/m3.These data are below the fall and winter averages reported for all of the other ambient sites listed in Table 3 with the exception of the background sites at Cornwall and Burlington. Additional sampling sessions are planned for the Brainard Site during the winter of 2005-2006 so as to assist in responding to these questions regarding site biases and sources of these biases.

PCDDs/PCDFs Profile Analyses- Congener Class Sums

Data reported previously in Table 2 are plotted graphically in Figure 2. Data are expressed in units of fg/m^3 for each of the ten (10) PCDDs/PCDFs congener classes. Results are provided for each of the eight samples as well as an average concentration representing the sample set. For convenience purposes only the average concentration for each of the ten (10) congener classes is displayed in Figure 2. Actual concentrations for the other congener sums (Cl_4 – Cl_8) in individual samples can be found in Table 2.

An examination of the composite PCDDs/PCDFs congener (Cl_4 – Cl_8) sum profiles shown in Figure 2 indicates a predominance of the hexa, hepta and octa PCDDs and the tetra, penta and hexa PCDFs. Within the PCDDs congener classes (Cl_4 – Cl_8) we find increasing concentrations with corresponding increases in chlorine substitution ($Cl_4$5678). Conversely, the PCDFs profile within the Cl_4 – Cl_8 congener classes indicates diminishing concentrations with corresponding increases in chlorine substitution (Cl_4>Cl_5>Cl_6>Cl_7>Cl_8).

The ambient PCDDs/PCDFs profile reported for the Brainard Airport Site is consistent with those typically reported for ambient air on a global basis [4, 5, 6]. This profile is also consistent with profiles typically attributable to combustion sources [7].The Brainard Airport Site PCDDs/PCDFs profile is remarkably similar to profiles observed at the majority of sites used by the State of Connecticut during prior PCDDs/PCDFs monitoring programs. These profiles at the time were also found to be attributable to combustion source emissions [8].

PCDDs/PCDFs – 2,3,7,8-Substituted Isomer Profiles

Data reported previously in Table 2 are plotted graphically in Figure 3. Figure 3 displays concentrations for each of the fifteen (15) 2,3,7,8-substituted PCDDs/PCDFs (Cl_4-Cl_8). Data are expressed in units of fg/m^3 for each of the fifteen (15) PCDDs/PCDFs isomers. Results are provided for each of the eight Brainard Airport samples as well as an average concentration representing the sample set. For convenience purposes only the average concentration for each of the fifteen (15) isomers is displayed in Figure 3. Actual concentrations for all of the isomers in individual samples can be found in Table 2.

The winter 2003-04 monitoring results indicate the 2,3,7,8- substituted PCDDs/PCDFs isomer profile is remarkably similar to profiles observed at the majority of sites used by the State of Connecticut during prior PCDDs/PCDFs monitoring programs. These profiles at the time were also found to be attributable to combustion source emissions profiles.

Acknowledgments

The author wishes to acknowledge the financial support of the State of Connecticut who funded this program and the technical support and guidance provided by CTDEP staff members.

References

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Table 1. CT DEP WINTER 2003-04 and 2004-05 Sampling Sessions
Brainard Airport, Hartford CT

Sample Collection Period	Sampling Unit Sessions	Duration (minutes)	Sampling Rate (LPM)	Sample Volume (m^3)
December 30, 2003 -	1A	40267.4	177.35	7,141
January 27, 2004	2A	40267.8	176.55	7,106
January 27, 2004 -	1B	42985.0	171.20	7,359
February 26, 2004	2B	42992.4	177.25	7,620
December 21, 2004 -	1C	43288.2	180.00	7,792
January 20, 2004	2C	43288.8	181.40	7,853
January 20, 2005 -	1D	41510.4	180.60	7,497
February 18, 2005	2D	41510.0	176.60	7,331

TABLE 2. AMBIENT MONITORING FOR PCDDs/PCDFs

ACTUAL CONCENTRATIONS–2003-04 AND 2004-05 WINTER CAMPAIGNS AT BRAINARD AIRPORT

SAMPLING PERIOD		Dec 30 - Jan 27, 2004		Jan 27 - Feb 26, 2004		Dec 21, 2004 - Jan 20, 2005		Jan 20 - Feb 18, 2005		Average
SAMPLER ID		SAMPER 1	SAMPLER 2	SAMPLER 1	SAMPLER 2	SAMPLER 1	SAMPLER 2	SAMPLER 1	SAMPLER 2	
SAMPLE VOLUME (m^3)		7,141	7,109	7,359	7,620	7,792	7,853	7,497	7,331	
Parameter	TEF	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³
2,3,7,8-TCDD	1	0.001	0.001	0.002	0.001	0.002	0.002	0.002	0.002	0.002
TOTAL TCDD	0.01	0.044	0.050	0.049	0.046	0.098	0.103	0.184	0.192	0.096
1,2,3,7,8-PeCDD	0.5	0.006	0.005	0.009	0.007	0.006	0.006	0.009	0.010	0.007
TOTAL PeCDD	0.005	0.075	0.072	0.102	0.082	0.137	0.141	0.237	0.246	0.137
1,2,3,4,7,8-HxCDD	0.04	0.009	0.007	0.013	0.008	0.008	0.009	0.012	0.013	0.010
1,2,3,6,7,8-HxCDD	0.04	0.018	0.012	0.026	0.016	0.015	0.015	0.022	0.022	0.018
1,2,3,7,8,9-HxCDD	0.04	0.018	0.012	0.025	0.014	0.013	0.013	0.017	0.018	0.016
TOTAL HxCDD	0.0004	0.184	0.147	0.252	0.177	0.217	0.227	0.336	0.350	0.236
1,2,3,4,6,7,8-HpCDD	0.001	0.233	0.150	0.356	0.198	0.131	0.144	0.153	0.162	0.191
TOTAL HpCDD	0.00001	0.477	0.315	0.732	0.414	0.275	0.300	0.325	0.341	0.397
OCDD	0	1.316	0.800	2.365	1.214	0.381	0.427	0.396	0.424	0.915
2,3,7,8-TCDF	0.1	0.004	0.005	0.006	0.006	0.007	0.008	0.011	0.011	0.007
TOTAL TCDF	0.001	0.165	0.166	0.184	0.177	0.277	0.294	0.441	0.464	0.270
1,2,3,7,8-PeCDF	0.1	0.006	0.006	0.008	0.008	0.010	0.010	0.016	0.016	0.010
2,3,4,7,8-PeCDF	0.1	0.010	0.010	0.015	0.013	0.017	0.017	0.027	0.029	0.017
TOTAL PeCDF	0.001	0.137	0.134	0.177	0.160	0.209	0.223	0.329	0.342	0.214
1,2,3,4,7,8-HxCDF	0.01	0.012	0.012	0.017	0.015	0.020	0.021	0.030	0.032	0.020
1,2,3,6,7,8-HxCDF	0.01	0.011	0.010	0.016	0.013	0.016	0.018	0.025	0.028	0.017
2,3,4,6,7,8-HxCDF	0.01	0.014	0.013	0.020	0.017	0.022	0.025	0.035	0.037	0.023
1,2,3,7,8,9-HxCDF	0.01	0.004	0.004	0.006	0.005	0.005	0.006	0.008	0.008	0.006
TOTAL HxCDF	0.0001	0.130	0.120	0.184	0.154	0.195	0.213	0.287	0.303	0.198
1,2,3,4,6,7,8-HpCDF	0.001	0.049	0.046	0.070	0.060	0.077	0.083	0.100	0.108	0.074
1,2,3,4,7,8,9-HpCDF	0.001	0.006	0.005	0.008	0.007	0.009	0.009	0.009	0.009	0.008
TOTAL HpCDF	0.00001	0.083	0.077	0.091	0.103	0.121	0.128	0.154	0.162	0.115
OCDF	0	0.030	0.028	0.045	0.036	0.052	0.052	0.055	0.057	0.044
TOTAL [a]		2.64	1.91	4.18	2.56	1.96	2.11	2.74	2.87	2.622

Data has been blank-corrected using corresponding field blank results.
( ) = parameter not detected at the indicated detection limit.
[a] "Total" entries for pg/m³ include summation of tetra through octa congener class totals.

Table 3. Average Ambient PCDDs/PCDFs Concentrations pg/m3 Fall/Winter: 1993-2002

Site Location	Winter-(pg/m3)		Fall-(pg/m3)	
	AVG.	STD. DEV.	AVG.	STD. DEV.
Preston	1.05	0.47	1.04	0.70
Bridgeport	1.95	0.99	1.47	0.78
Wallingford	1.90	0.63	2.04	1.27
Bristol	1.37	0.45	1.34	0.74
Mid-Connecticut	1.58	0.51	1.55	0.80
Mohawk Mountain	0.58	0.23	0.53	0.48
Lisbon	0.93	0.34	0.63	0.29
Burlington	0.68	0.11	0.41	0.10
Average	1.34	0.72	1.20	0.86

Figure 1: Dioxin Levels as TEQ Concentrations and as % of CT Ambient Air Quality Standard (1 pg/m^3) for 2003 - 2005

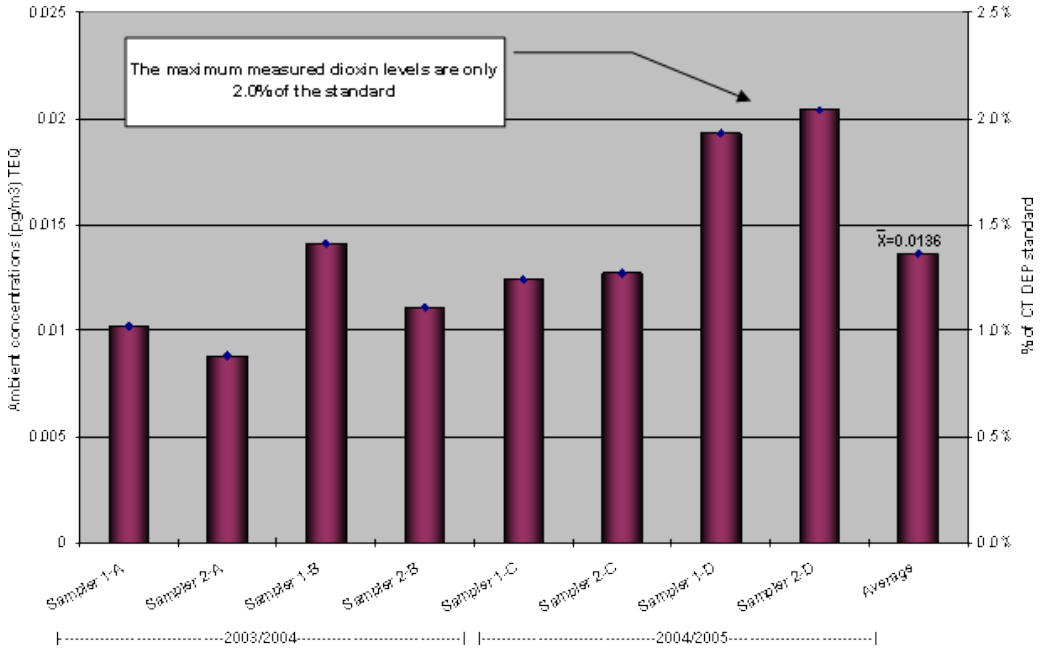

FIGURE 2. PCDDs/PCDFs CONGENER CLASSES -
ACTUAL CONCENTRATIONS -- 2003-04 AND 2004-05 WINTER CAMPAIGNS
AT BRAINARD AIRPORT

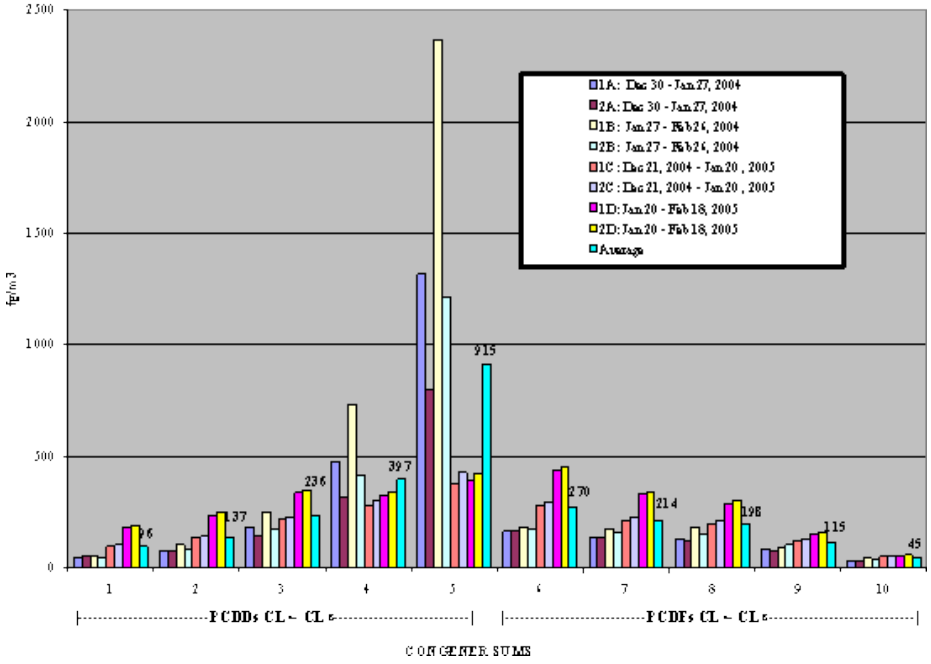

FIGURE 3. 2,3,7,8 - SUBSTITUTED PCDDs/PCDFs ISOMERS - BRAINARD AIRPORT SITE (CONN)
ACTUAL CONCENTRATIONS (fg/m^3) -- 2003-04 and 2004-05 WINTER CAMPAIGNS