Atmospheric PCDDs/PCDFs in Hartford Connecticut- Current Levels, Time Trends and Profile Comparisons

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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 this site during winter months in calendar years 2003-04, 2004-05 and 2005-06 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. Results available for a prior Sheldon Street site representing the period 1994-2002 are compared to the Brainard data set. Trends in total PCDDs/PCDFs measured at each of these two (2) sites are examined. Lastly, congener/isomeric profiles characteristic of each of the two sites are compared in an attempt to identify types of combustion sources contributing to atmospheric concentrations of PCDDs/PCDFs present in winter time at each site.

Materials and Methods

Sample collection and laboratory analyses methods were described previously (1,2) 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 six (6) sampling periods are listed in Table 1.

Results and Discussion

Results are provided for a total of twelve (12) samples (reported as pairs) representing a total of six (6) 30 day sampling events. PCDDs/PCDFs concentration data (pg/m3) as congener sums (Cl4-Cl8) and 2378-substituted isomers are summarized in Table 1. All results reported here and in figures to follow represent values corrected with the corresponding field blank.

Comparison of 2003-06 Brainard Data to Historical Levels in Connecticut (1993-2002)

Total PCDDs/PCDFs concentrations for the twelve (12) sample set are listed in Table 1. The mean concentration for the Brainard Airport Site of 2.52 pg/m3 is higher than winter and fall mean concentrations shown in Figure 1 for

other 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 (2.52 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 shown in Figure 1. 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 Figure 1. This location was deemed representative of the Hartford Metropolitan area and an urban exposure setting during these prior monitoring programs. 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 (1). 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 shown in Figure 1 with the exception of the background sites at Cornwall/Mohawk Mountain and Burlington.

Trends in Total PCDDs/PCDFs Concentrations

All of the available data for Hartford sites collected during calendar years 1994-2006 are plotted graphically in Figure 2. These data expressed as total PCDDs/PCDFs concentrations (Cl4-Cl8) on a per annum basis indicate a great deal of variability for measured concentrations at the Sheldon Street Site while the Brainard Site data is less variable and consistently higher than the majority of the Sheldon yearly average values. The mean concentration for the Sheldon data set (1994-2002) is 1.58 pg/M3 in contrast to the mean concentration for the Brainard Site (2003-2006) of 2.53 pg/M3. The latter data set again suggests that the Brainard location may be more influenced by combustion source contributions during winter months than the Sheldon site.

PCDDs/PCDFs Profile Analyses- Congener Class Sums

Composite PCDDs/PCDFs profiles (Cl4-Cl8 congener sums) for both the Brainard Road (n=8) and Sheldon Street (n=4) sample sets are shown in Figure 3. While the average concentrations for each of the congener classes in comparison of the two sites differ significantly (Brainard > Sheldon) the profiles themselves are virtually identical. An examination of the composite PCDDs/PCDFs congener (Cl_4 – Cl_8) sum profiles shown in Figure 3 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<Cl_5<Cl_6<Cl_7<Cl_8). 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 composite profiles for both the Brainard Road and Sheldon Street sites are indicative of combustion source emissions. The composite profiles for the two locations were further examined on a weight % or concentration % basis. This consisted of expressing concentrations for each of the PCDFs congener classes as a % of total PCDFs (Cl4-Cl8 Total) and each of two PCDDs congener classes (Cl5 and Cl6) as a % of total PCDDs (Cl4-Cl7). OCDD was not included in the PCDDs total due to highly variable reported concentrations attributable to its ubiquity, high concentrations in ambient air samples and persistence as a laboratory contaminant. Comparison of these weighted profiles for both PCDDs and PCDFs using average concentrations measured at each of the two sites is shown in Figure 4. As shown the contributions for each of the PCDFs congener classes as a % of total PCDFs is identical for the two sites. This is also the case in examining the contributions of PeCDDs and HxCDDs as a % of total PCDDs concentrations for each of the two sites. These data illustrate that the composite profiles measured at each of the two sites in winter months are virtually identical. It is further suggested that the PCDDs/PCDFs profiles at both sites are attributable to primarily combustion source influences and that the composition and types of combustion sources emissions present at the two sites as represented by 30 day composite samples are the same.

Acknowledgments

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References

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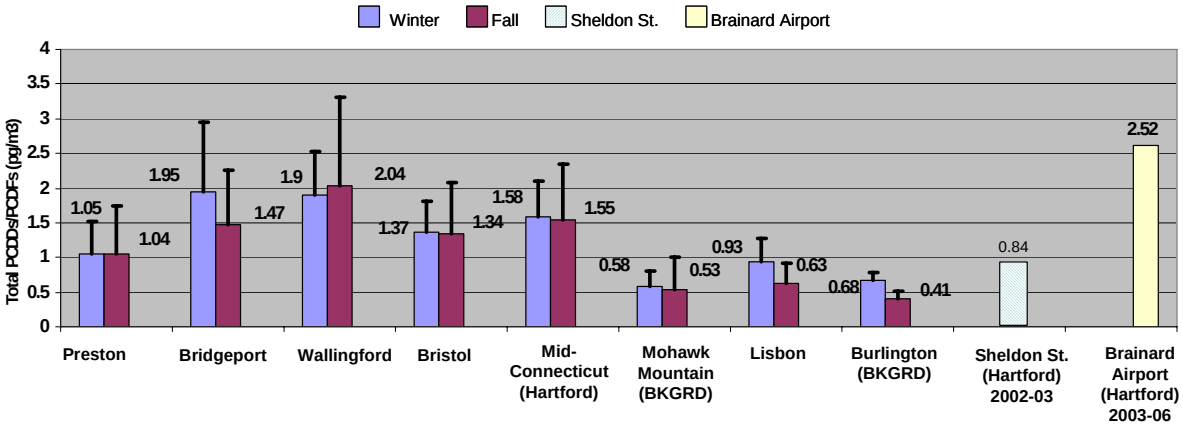
2) Ambient Monitoring for PCDDs/PCDFs in Connecticut- The Winter 2002-03 Sampling Campaign. Final Report Prepared for CTDEP by Gary Hunt TRC Environmental Corporation (TRC Project # 36641) August 2004.
3) Proceedings of Dioxin 2005, Toronto Canada August 2005.
4) The Inventory of Sources of Dioxin in the United States, United States Environmental Protection Agency Office of Research and Development, EPA/600/P-98/002Aa, April 1998.

TABLE 1.
AMBIENT MONITORING FOR PCDDs/PCDFs
ACTUAL CONCENTRATIONS
2003-04, 2004-05 AND 2005-06 WINTER CAMPAIGN AT BRAINARD AIRPORT

SAMPLING PERIOD	Dec 30 - Jan 27, 2004		Jan 27 - Feb 26, 2004		Dec 12 - Jan 20, 2005		Jan 20 - Feb 18, 2005		Dec 12, 2005 - Jan 11, 2006		Jan 11 - Feb 10, 2006		Average
SAMPLER ID	Sampler 1	Sampler 2	Sampler 1	Sampler 2	Sampler 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	7,819	7,949	7,690	7,992	
Parameter	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
2,3,7,8-TCDD	0.001	0.001	0.002	0.001	0.002	0.002	0.002	0.002	0.001	0.001	0.003	0.002	0.002
TOTAL TCDD	0.044	0.050	0.049	0.046	0.098	0.103	0.183	0.192	0.049	0.045	0.084	0.084	0.089
1,2,3,7,8-PeCDD	0.006	0.005	0.009	0.007	0.006	0.006	0.009	0.010	0.006	0.006	0.007	0.007	0.007
TOTAL PeCDD	0.075	0.072	0.102	0.082	0.137	0.141	0.237	0.246	0.090	0.090	0.145	0.143	0.135
1,2,3,4,7,8-HxCDD	0.009	0.007	0.013	0.008	0.008	0.009	0.012	0.013	0.009	0.009	0.009	0.010	0.010
1,2,3,6,7,8-HxCDD	0.018	0.012	0.026	0.016	0.015	0.015	0.022	0.022	0.016	0.015	0.019	0.019	0.018
1,2,3,7,8,9-HxCDD	0.018	0.012	0.025	0.014	0.013	0.013	0.017	0.018	0.016	0.015	0.017	0.018	0.016
TOTAL HxCDD	0.184	0.147	0.252	0.177	0.217	0.227	0.336	0.350	0.158	0.192	0.258	0.250	0.233
1,2,3,4,6,7,8-HpCDD	0.233	0.150	0.356	0.198	0.131	0.144	0.153	0.162	0.182	0.173	0.198	0.199	0.186
TOTAL HpCDD	0.477	0.315	0.732	0.414	0.275	0.300	0.325	0.341	0.361	0.352	0.405	0.405	0.384
OCDD	1.316	0.800	2.365	1.214	0.381	0.428	0.396	0.424	0.610	0.626	0.769	0.779	0.799
2,3,7,8-TCDF	0.004	0.005	0.006	0.006	0.007	0.008	0.011	0.011	0.009	0.008	0.009	0.008	0.008
TOTAL TCDF	0.165	0.166	0.184	0.177	0.277	0.294	0.441	0.454	0.282	0.276	0.272	0.272	0.281
1,2,3,7,8-PeCDF	0.006	0.006	0.008	0.008	0.010	0.010	0.016	0.016	0.011	0.010	0.010	0.011	0.011
2,3,4,7,8-PeCDF	0.010	0.010	0.015	0.013	0.017	0.017	0.027	0.029	0.019	0.017	0.019	0.019	0.018
TOTAL PeCDF	0.137	0.134	0.177	0.160	0.208	0.223	0.329	0.342	0.227	0.218	0.223	0.218	0.223
1,2,3,4,7,8-HxCDF	0.012	0.012	0.017	0.015	0.020	0.021	0.030	0.032	0.021	0.021	0.019	0.020	0.021
1,2,3,6,7,8-HxCDF	0.011	0.010	0.016	0.013	0.016	0.018	0.025	0.028	0.018	0.017	0.017	0.017	0.018
2,3,4,6,7,8-HxCDF	0.014	0.013	0.020	0.017	0.022	0.025	0.035	0.037	0.024	0.024	0.023	0.023	0.024
1,2,3,7,8,9-HxCDF	0.004	0.004	0.006	0.005	0.005	0.006	0.008	0.008	0.008	0.008	0.006	0.006	0.006
TOTAL HxCDF	0.130	0.120	0.184	0.154	0.195	0.213	0.287	0.303	0.208	0.201	0.181	0.184	0.203
1,2,3,4,6,7,8-HpCDF	0.049	0.046	0.070	0.060	0.077	0.083	0.100	0.108	0.078	0.076	0.076	0.077	0.077
1,2,3,4,7,8,9-HpCDF	0.006	0.005	0.008	0.007	0.009	0.009	0.009	0.009	0.010	0.010	0.010	0.010	0.009
TOTAL HpCDF	0.083	0.077	0.091	0.103	0.121	0.128	0.154	0.161	0.127	0.126	0.133	0.134	0.123
OCDF	0.030	0.028	0.045	0.036	0.052	0.052	0.055	0.057	0.051	0.049	0.054	0.057	0.049
TOTAL [a]	2.64	1.91	4.18	2.56	1.96	2.11	2.74	2.87	2.16	2.18	2.52	2.52	2.52

Data has been blank-corrected using corresponding field blank results.
( ) = parameter not detected at the indicated detection limit.
[a] "Total" entries for pg/m^3 include summation of tetra through octa congener class totals.

Figure 1. Comparison of Brainard Airport Data to Historical Data at Other Connecticut Sites (Fall/Winter 1993-2002)



Hartford, CT Monitoring Sites
Figure 2. Winter Time PCDDS/PCDFS Concentrations Over Time

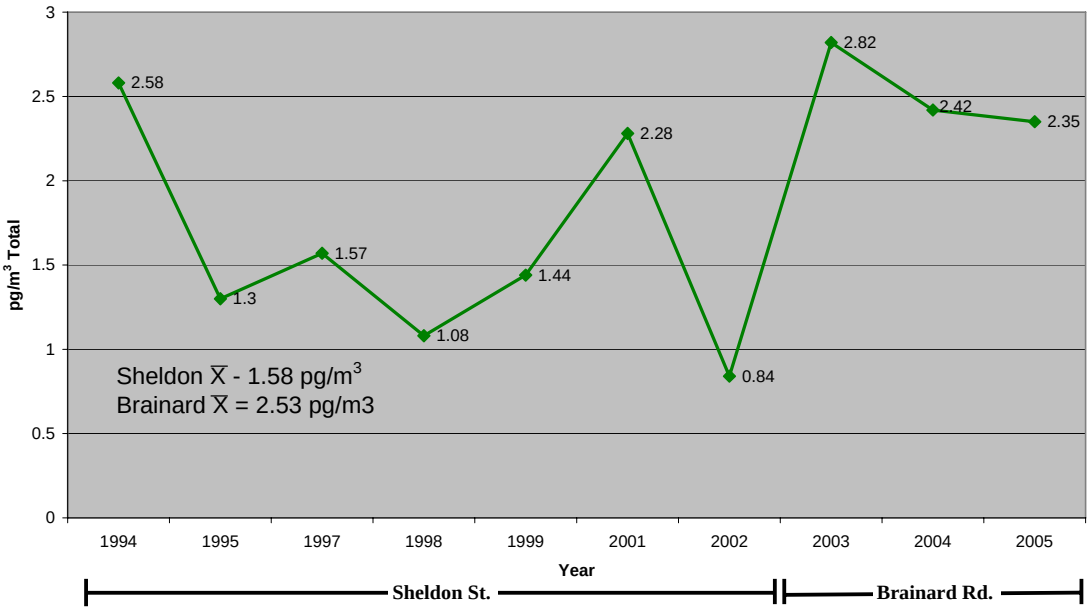


Figure 3. PCDDs/PCDFs Congener Classes - fg/m^3
2003-05 Winter Campaigns at Brainard Airport and 2002-03 Campaign at Sheldon Street
Profile Comparison

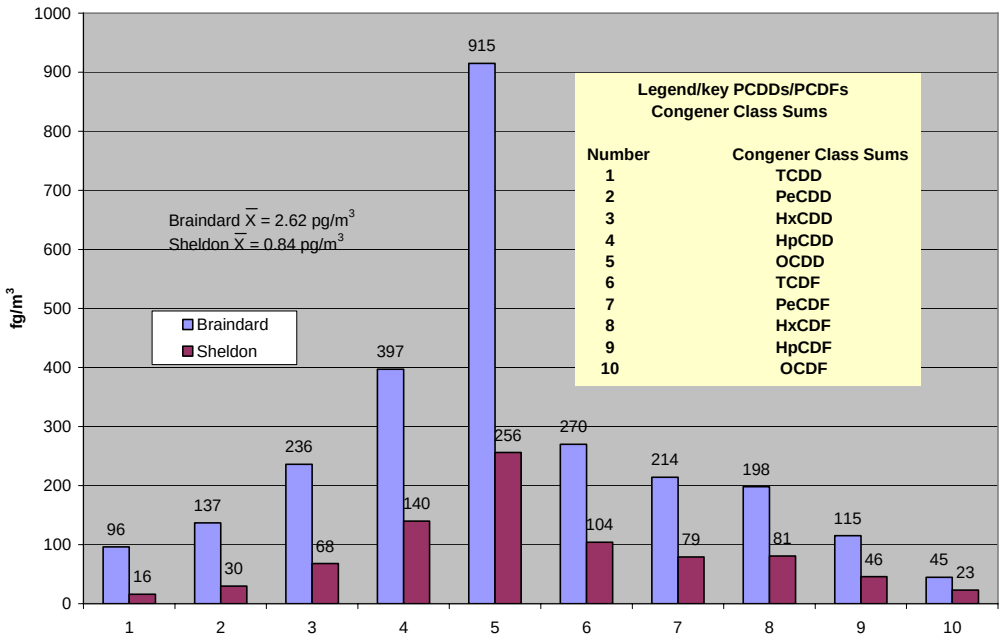


Figure 4 - PCDFs Congener Class Profile (Cl4-Cl8) Weight
- % of Total PCDFs Concentrations
- Comparison of Brainard (2003-2006) and Sheldon (2002-2003)