



POPS and Emerging Contaminants Symposium

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Measuring Trace Levels of Polychlorinated Dibenzo-p-dioxins and
Polychlorinated Dibenzofurans (PCDDs/PCDFs) in Ambient Air

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ThermoFisher
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Presented by
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Topics of Discussion

- CTDEEP (formerly CTDEP) Method History
- Method Summary
- Performance Data
- Applications
- Data Analyses

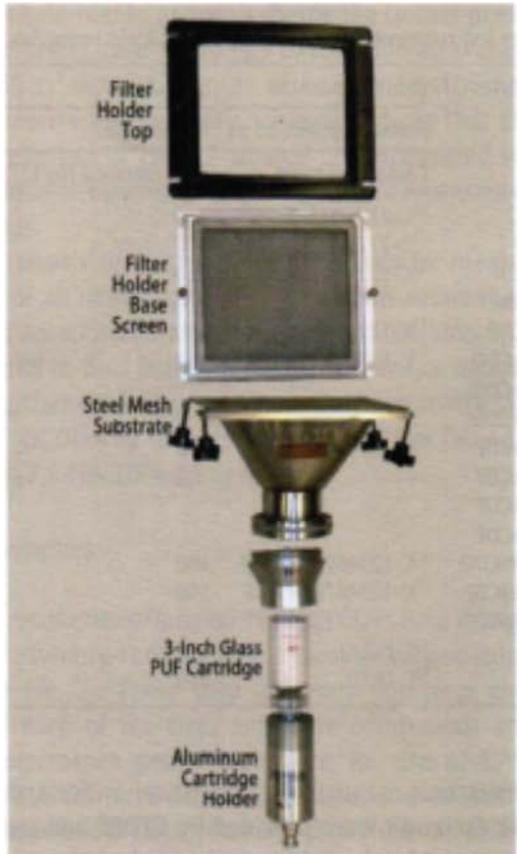
CTDEEP – Ambient Dioxin Monitoring History

- Purpose to demonstrate compliance with Ambient Air Quality Standard (AAQS) for PCDDs/PCDFs (1.0 pg/m³ TEQ).
- CTDEEP sponsored method validation (1987).
- Method predates EPA Method TO-9/TO-9A.
- Commenced monitoring in 1987 (48-hour samples) – at multiple Municipal Solid Waste (MSW) facilities.
- 1993 – Adopted 30-day sampling events to enhance representativeness of data and detection limits.
- 1993-2002 Multiple locations at MSW facilities.
- 2002-2012 30-day sampling events at a single location.

CTDEEP Method Summary

- Samples collected in winter months only (historically highest levels from combustion source influences).
- Sampling locations considered to be representative of the urban environment.
- Each session consisted of two (2) consecutive 30-day sampling events, each consisting of collocated sampling systems.
- PS-1 (General Metal Works) high volume samplers were modified to accept an 8" x 10" rectangular filter in lieu of the standard 10.14 cm diameter circular filter.
- Polyurethane Foam (PUF) sorbent cartridge (density = 0.024 g/cm³).
- PUF and filter combined for Soxhlet extraction and HRGC/HRMS analyses.
- Average air volume collected ≈ 7,700 m³.
- Laboratory methods followed procedures outlined in EPA Method TO-9A (HRGC/HRMS).

Filter Collection Apparatus



Method Performance Features – Quality Control Measures

- Field Blank – one per sampling event.
- Collocated Sampler Pair – one per sampling event.
- Internal Standards – ten C₁₃ labeled isomers – all samples.
- Field Surrogates – all samples (five labeled isomers).
- Flow Checks (weekly).
- Flow Audits (CTDEEP Staff).

Flow Audits

- Flow audits were performed by agency staff using an independent critical orifice provided by the agency.
- Pre and post sampling event audit results were within compliance limits ($\pm 10\%$ D).
- These data confirmed the accuracy of the sampler calibration established using the primary critical orifice.

Critical Orifice



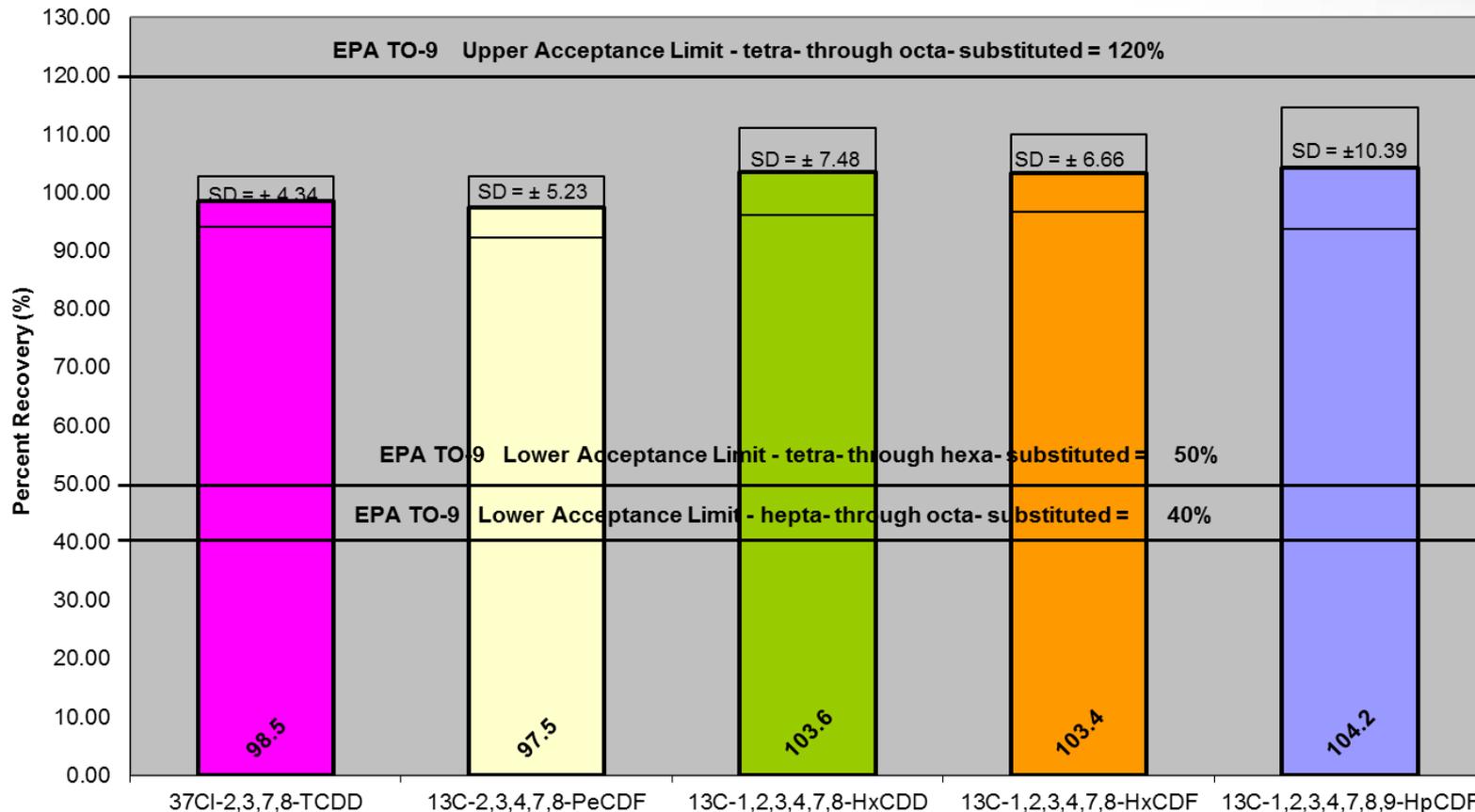
CTDEEP Flow Audit



Field Surrogates

- Prior to sample collection, PUF sorbent cartridges were fortified in the laboratory with five isotopically labeled surrogate compounds.
- Data serves to define accuracy of the combined sample collection and analysis method.
- Data assures that “breakthrough” (loss) of native PCDDs/PCDFs has not taken place during each 30-day sampling event ($\sim 7,000 \text{ m}^3$).

Field Surrogate Recovery Data Summary
Actual % Recovery Data (Mean and SD; N = 23 samples)
and Comparison to EPA Method TO-9A Acceptance Limits



The Surrogate fortifications were adjusted to account for the increased sample volume; 1,000 pg (0.31 pg/m³) of 37Cl-2378-TCDD were applied to each sample and 4,000 pg (0.522 pg/m³) of each of the other four surrogates were applied to each sample.

Field Surrogates

- Surrogate Recoveries ranged from 97.5 – 104.2%.
- Recovery data exceed all EPA Method TO-9A data quality objectives (performance goals).
- Quantitative retention (30 days/7,000 m³) of all surrogates and native PCDDs/PCDFs is demonstrated.
- This feature, first introduced in development of the CTDEEP method in 1987, was later adopted by US EPA in revisions to sampling methods for PCDDs/PCDFs in ambient air (EPA Method TO-9A), as well as development of EPA Reference Method 23 for measurement of PCDDs/PCDFs in stationary source emissions.

Collocated Sampler Precision

- A single collocated sampler pair was included in each 30-day sampling event.
- Data resulting from analyses of the collocated sampler pairs was used to define the precision of the combined sample collection and analyses scheme.
- Precision is expressed as the relative percent difference (RPD) between measured concentrations in each of the two (2) samples.

Sampling Locations

CTDEEP Sampling Site
Collocated Samples (30 Day Event)



Collocated Samples – Gulf Shore
Monitoring Site - 2010



2002-2008^a Winter Sampling at Brainard Airport Collocated Samplers Precision – Relative Percent Difference (RPD)^b (11 sampler pairs).

PCDDs Parameter	Average RPD (%)	PCDFs Parameter	Average RPD (%)
2,3,7,8-TCDD	7.92	2,3,7,8-TCDF	8.40
TOTAL TCDD	8.19	TOTAL TCDF	5.06
1,2,3,7,8-PeCDD	12.80	1,2,3,7,8-PeCDF	6.88
TOTAL PeCDD	7.93	2,3,4,7,8-PeCDF	7.08
		TOTAL PeCDF	6.17
1,2,3,4,7,8-HxCDD	11.11	1,2,3,4,7,8-HxCDF	10.39
1,2,3,6,7,8-HxCDD	12.71	1,2,3,6,7,8-HxCDF	9.58
1,2,3,7,8,9-HxCDD	13.37	2,3,4,6,7,8-HxCDF	8.87
TOTAL HxCDD	10.92	1,2,3,7,8,9-HxCDF	12.17
		TOTAL HxCDF	9.50
1,2,3,4,6,7,8-HpCDD	13.00	1,2,3,4,6,7,8-HpCDF	7.76
TOTAL HpCDD	12.79	1,2,3,4,7,8,9-HpCDF	8.75
		TOTAL HpCDF	6.64
OCDD	14.00	OCDF	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 - $RPD = \text{Abs}(X1-X2)/[(X1+X2)/2]$

Collocated Sampler Precision Results

Data for the eleven (11) pairs collected during the Winter 2002-2008 sampling period.

- % RPD data (N=11) for PCDDs: 8 – 14% and PCDFs: 5 – 12%.
- % RPD data relies exclusively on measured concentrations. All 2,3,7,8 PCDDs/PCDFs were detected in all field samples (no ND values).

Method Performance – Some Findings

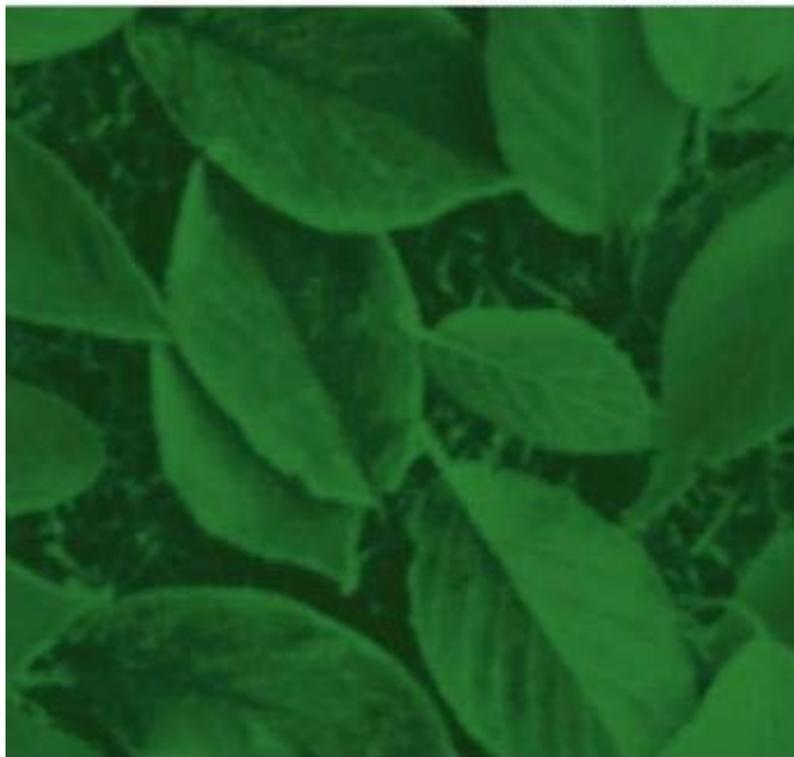
- Method insures collection of high quality data with a high degree of precision and accuracy.
- Method performance consistently exceeds EPA Method TO-9A data quality objectives/goals (internal standards/field surrogates).
- Highly sensitive method; detection limits $<1 \text{ fg/m}^3$ demonstrated for all isomers (with exception of OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF).
- Method sensitivity below PCDD/PCDF concentrations typically found in ambient air. Measured concentrations should be expected if isomers are present at 1 fg/m^3 (ND = non-existent).
- Results allow for advanced data analyses and more meaningful comparison of data sets (such as congener profile analyses).

CTDEEP Method Published (Chemosphere, Dec. 2011)



PERSISTENT ORGANIC POLLUTANTS AND DIOXINS

Editors H. Fiedler and G. Yu



PCDDs/PCDFs in ambient air ($<1 \text{ fg m}^{-3}$) – The CTDEP long term sampling (30 d) method

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ABSTRACT

The Connecticut Department of Environmental Protection (CTDEP) commenced monitoring for PCDDs/PCDFs (polychlorinated dibenzodioxins and polychlorinated dibenzofurans) in ambient air in 1987 and adopted the long term (30 d) sampling approach in 1993. The CTDEP method represents the first use of isotopically labeled PCDDs/PCDFs as field surrogates to monitor the behavior of native PCDDs/PCDFs present in actual ambient air samples. This feature first introduced in 1987 was later adopted by US EPA in revisions to sampling methods for PCDDs/PCDFs in ambient air (EPA Method TO9A) as well as development of EPA Reference Method 23 for measurement of PCDDs/PCDFs in stationary source emissions. Results are provided here for a total of twenty-three (23) samples (reported as pairs) representing twelve (12) 30 d sampling events conducted at a site located in metropolitan Hartford CT. Samples were collected in winter months during calendar years 2002–2008. PCDDs/PCDFs concentration data (pg m^{-3}) are reported as both congener sums (Cl_x , Cl_y) and 2378 substituted congeners. Total PCDDs/PCDFs concentrations for these twelve (12) sampling events ranged from 0.68 pg m^{-3} (2003) to 4.18 pg m^{-3} (2004) with a mean concentration of 2.04 pg m^{-3} .

Method performance was monitored through use of collocated samples, in field isotopically labeled compounds, isotopically labeled laboratory applied internal standards and field blank samples. Method performance consistently exceeded goals established in USEPA Method TO9A for these same parameters. Average recoveries of in field labeled PCDDs/PCDFs ranged from 97.5% to 104.2%. Average (mean) recoveries for each of the ten (10) isotopically labeled internal standards ranged from 77.0% (^{13}C -OCDF) to 95.5% (^{13}C -2,3,7,8-TCDF). Method precision defined as % RPD data for collocated sampler pairs ranged from 8% to 14% for PCDDs and from 5% to 12% for PCDFs. The mean RPD for all PCDDs/PCDFs combined is 9.6%. Field monitoring results demonstrate method sensitivity for all PCDDs/PCDFs congeners and 2378-substituted congeners to be well below concentrations typically found for these compounds in ambient air (all reported data represent measured concentrations). Quantities (pg) found in field blanks represent the major determinant to achieving further enhancements in method sensitivity for selected congeners (OCDF = 42 fg m^{-3} ; 1,2,3,4,6,7,8-HpCDD = 5.7 fg m^{-3} ; and 1,2,3,4,6,7,8-HpCDF = $<2.1 \text{ fg m}^{-3}$). The CTDEP method represents a highly sensitive and reliable technique for monitoring of PCDDs/PCDFs congeners and other persistent organic pollutants (POPs) at ultra trace levels in ambient air (fg m^{-3}).

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1. Introduction

The Connecticut Department of Environmental Protection (CTDEP) initiated dioxin monitoring 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.

The programs conducted from 1987 through 1992 relied on 48-h sampling periods representing air volumes in the range of 550–850 m^3 to measure ambient PCDDs/PCDFs levels. Beginning in fall 1993, CTDEP adopted a long duration sampling approach to both enhance method detection limits and meet the requirements of CCS 22a-191 (State of CT, 1988). This long duration approach utilized a 30-d continuous sampling period in lieu of 48-h sampling sessions. Air volumes collected during 30 d sampling periods were in the range of 7500–8000 m^3 .

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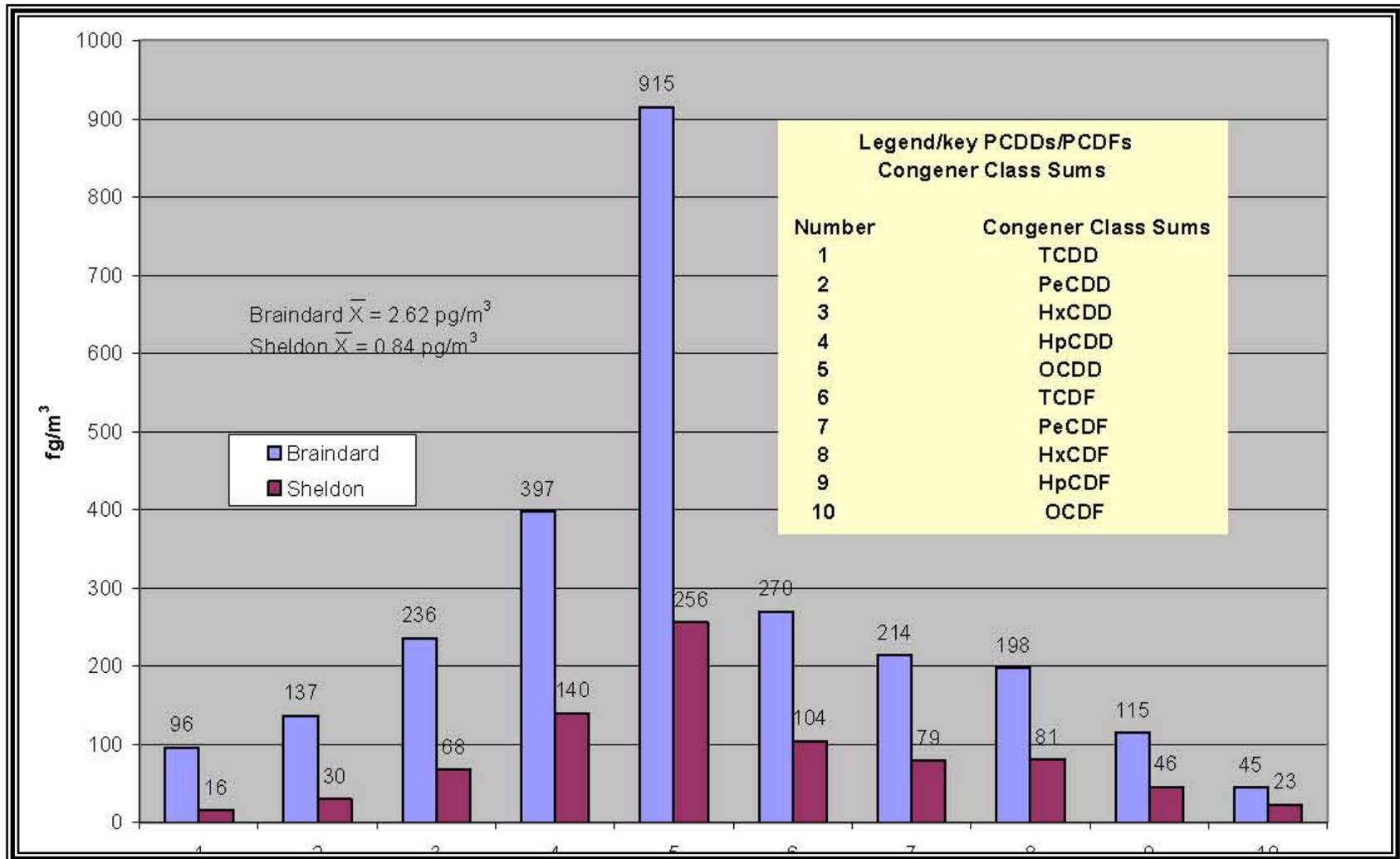
Total PCDDs/PCDFs (Cl₄ – Cl₈) in Ambient Air – Comparison of US Cities Rural and Remote Locations

	Location	pg/m ³
Urban US Cities	Hartford, CT	2.6
	Los Angeles, CA	7.4
	Phoenix, AZ	27
	Fresno, CA	51
	Bridgeport, CT	1.9
	Bloomington, IN	1.8
Rural Locations	TeWera, NZ	0.88
	Culverden, NZ	0.48
	Mohawk Mountain, CT (winter)	0.58
	Mohawk Mountain, CT (fall)	0.53
	Burlington, CT (winter)	0.68
	Burlington, CT (fall)	0.41
Remote Locations	Baring Head, NZ	0.14
	Nelson Lakes, NZ	0.04
	Bermuda (1993-1994)	0.11
	Bermuda (1996-1997)	0.04
	Barbados	0.02
MCRR F 2015	Lucketts 2015	3.70
	Beallsville 2015 (mean)	1.05
MCRR F 2008	Lucketts 2008	1.86
	Beallsville 2008 (mean)	1.40

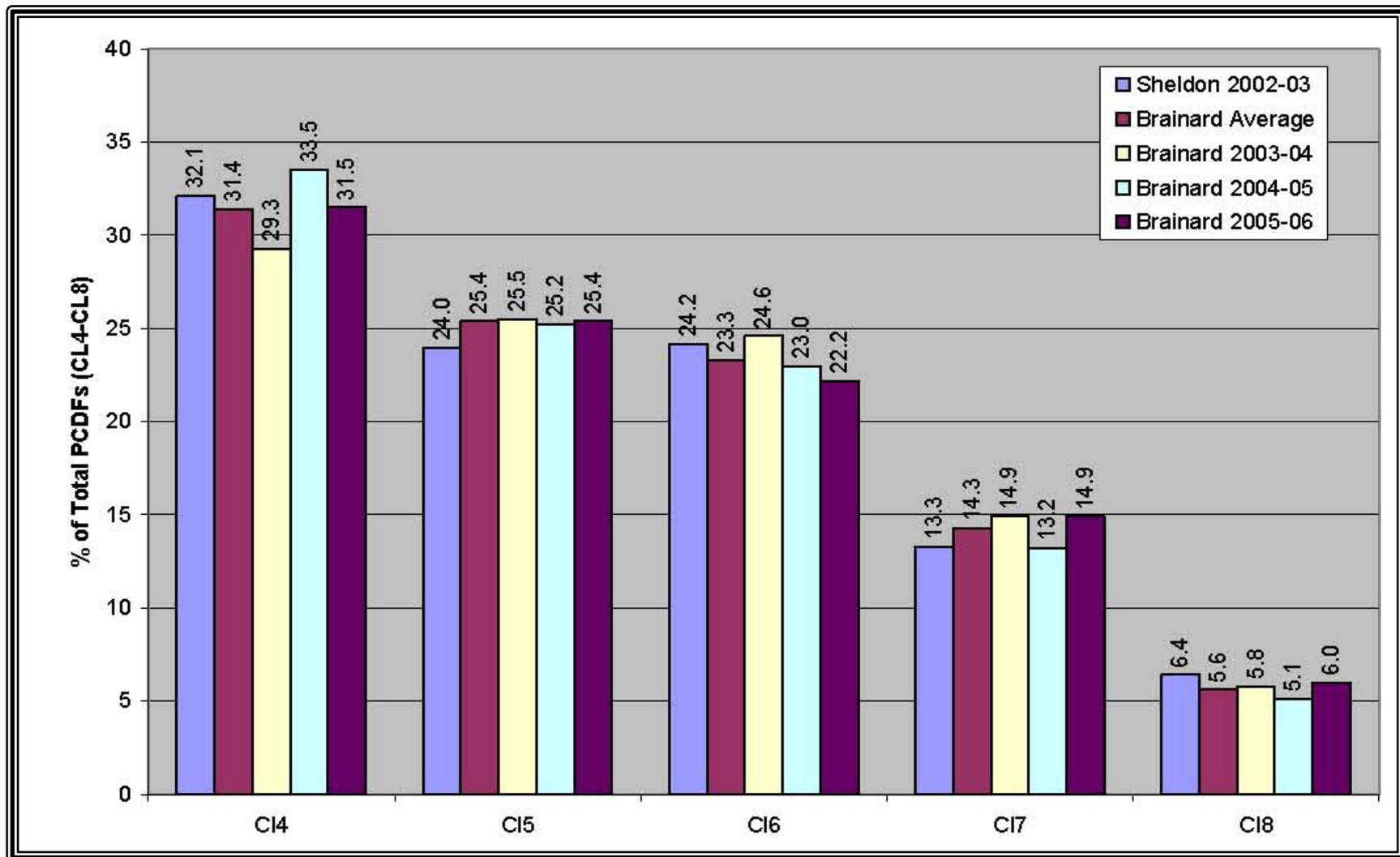
Profile Analyses – Some Tips

- % Contributions Relative to Totals.
- NOT Concentrations.
- NOT Mass Units.
- NOT TEF/TEQ Weighted.
- For Comparisons Only.
- DNA-Like Forensics.

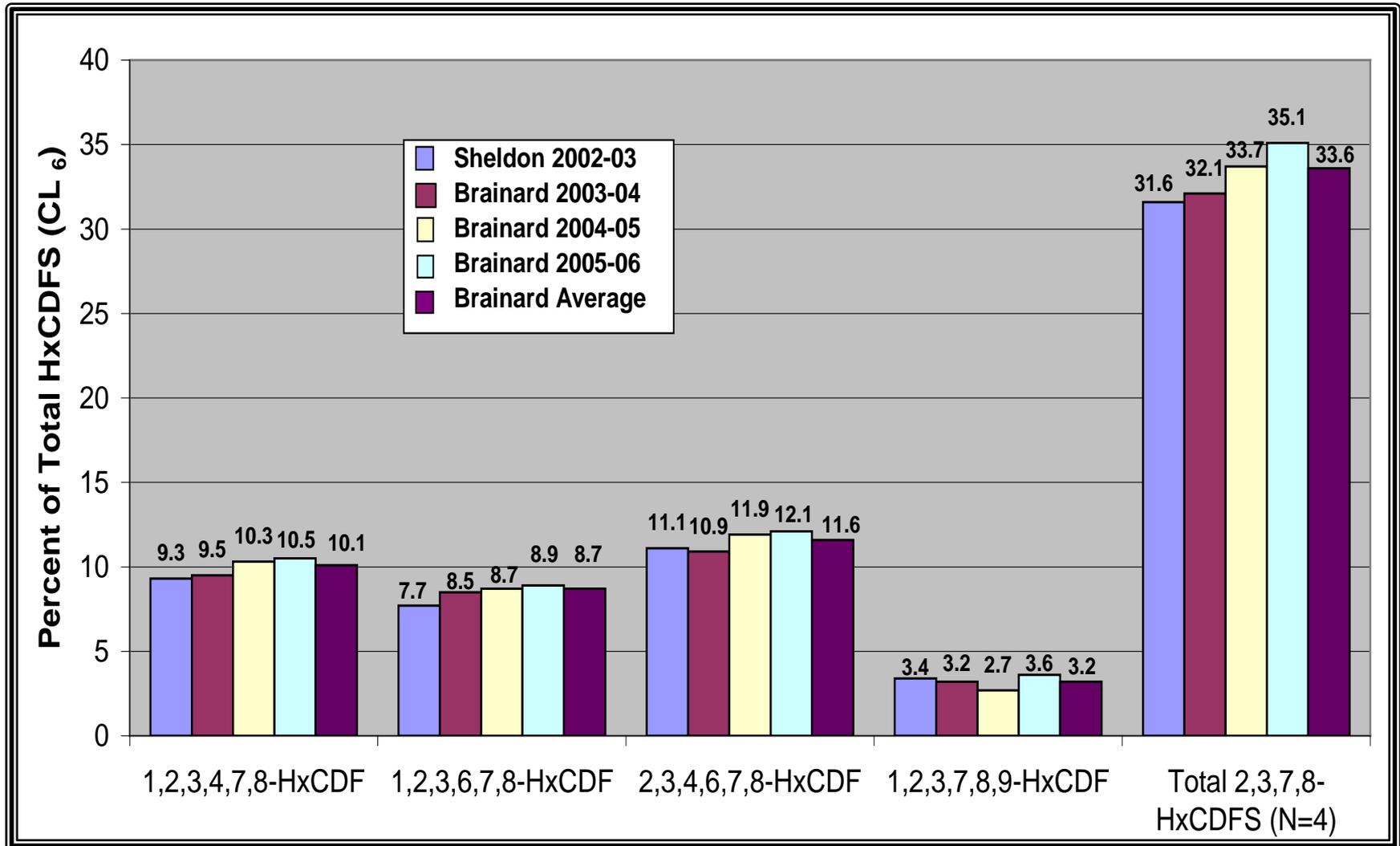
PCDDs/PCDFs Congener Classes – 2003-2006 Winter Campaigns at Brainard Airport and 2002-2003 Campaign at Sheldon Street Ambient Profile Comparison (fg/m³)



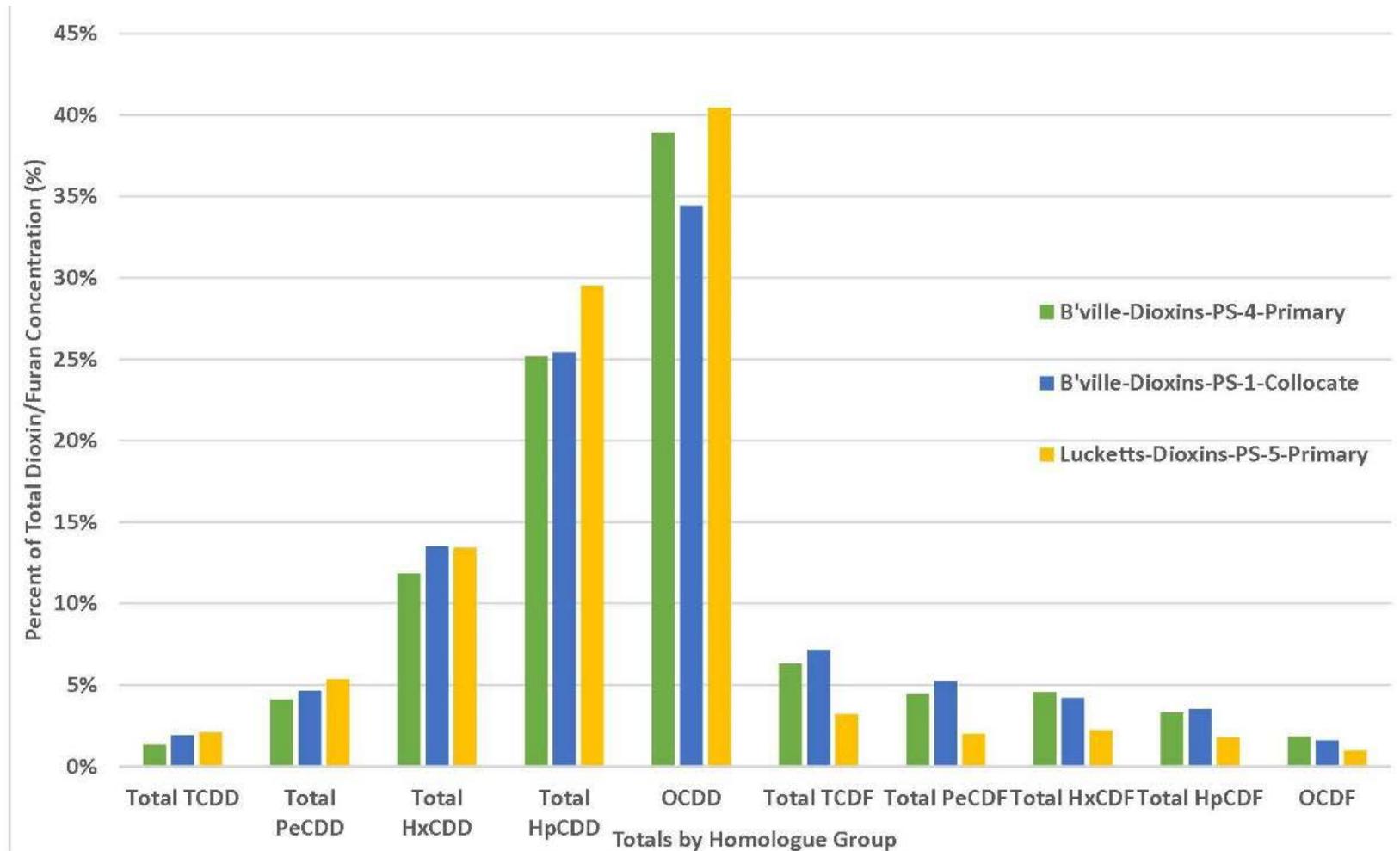
PCDFs Weight Percent of Total PCDFs – Comparison of Brainard (2003-2006) and Sheldon (2002-2006) Ambient Air Profiles



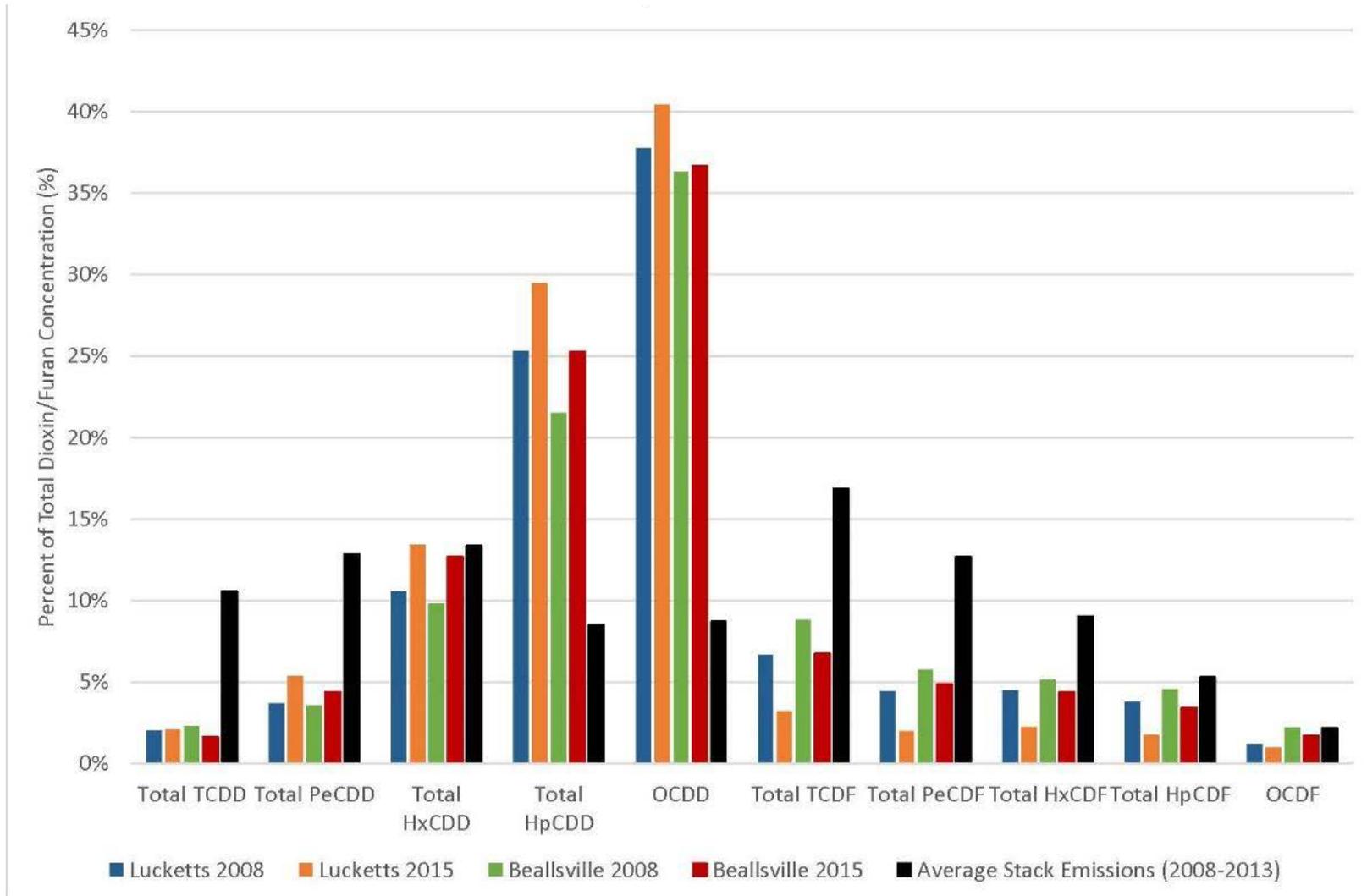
2,3,7,8-HxCDFs – Weight Percent of Total HxCDFs Air Profiles (4 of 16 congeners)



Dioxin/Furan Homologue Profile 30-day Ambient Air – Winter 2015 MCRRF



Dioxin/Furan Profile Comparison 2008 & 2015 Ambient Samples vs. 2008-2013 Stack Emissions



PCDDs/PCDFs Homologue Profiles – Findings

- MCRRF emissions are not measurably impacting levels at either sampling location*.
- Monitoring sites are not impacted by a dominant local emission source*.
- Regional background sources represent largest contributors to concentrations measured at both sites*.
- PCDDs/PCDFs profile results suggest a blend of combustion sources at both sites.
- MCRRF emissions differ significantly from ambient samples.
- Ambient OCDD (35-40% of Total) > MCRRF OCDD (<10% of Total).

* Supported by dispersion modeling of stack emissions using AERMOD.

Questions?

Thank you

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