Urban vs. Wildland Wildfires: Implications for Assessing Dioxin & Furan Impacts

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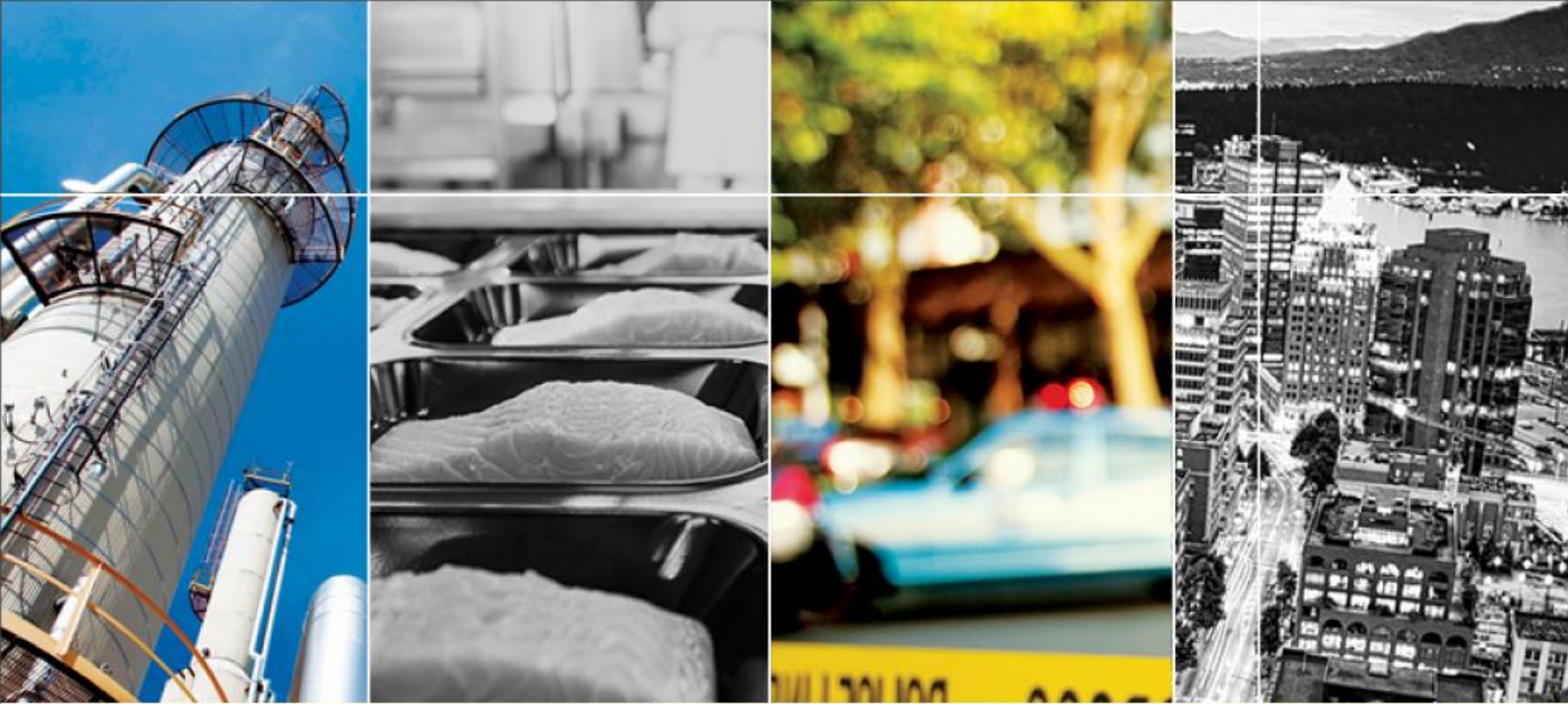
Overview of Presentation

1. Introduction to Dioxins and Furans
2. Dioxin and Furan Levels from Wildland vs. Urban Wildfires
3. Sampling and Analysis Considerations
4. Recommendations



Introduction to Dioxins and Furans

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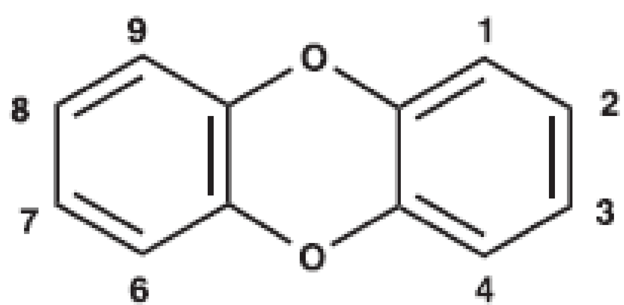
Dioxins & Furans - General Facts

- Polychlorinated, aromatic hydrocarbons
- Toxic, persistent, bioaccumulative, anthropogenic.
- Canadian government is targeting virtual elimination from anthropogenic sources, 80% of (anthropogenic) releases come from:
  - Municipal waste combustion
  - Residential wood combustion
  - Iron sintering
  - Electric arc furnace steel manufacture
  - Burning salt-laden wood in coastal pulp and paper boilers
  - Vehicle fuel combustion (diesel, marine)

Dioxin & Furan Chemistry

Dioxins

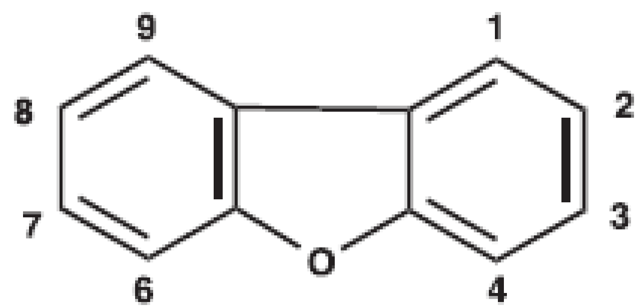
- Dioxin = polychlorinated dibenzo-para-dioxin (PCDD). 75 chemicals in the family
- Varying numbers of chlorine atoms (up to eight) can be attached to the structure.
- Seven toxic dioxin congeners: **2,3,7,8-TCDD is the most toxic.**



Dibenzo-p-dioxin

Furans

- Furan = polychlorinated dibenzofuran (PCDF). 135 chemicals in the family
- Varying numbers of chlorine atoms (up to eight) can be attached to the structure..
- Ten toxic furan congeners: **2,3,4,7,8-penta-CDF is the most toxic.**



Dibenzofuran

Naming Conventions

Abbr.	Homologue Group	No. of Congeners	Toxic Congeners (2,3,7,8-substitted)
MCDD	Monochlorodibenzo-p-dioxin	2	---
DCDD	Dichlorodibenzo-p-dioxin	10	---
TrCDD	Trichlorodibenzo-p-dioxin	14	---
TCDD	Tetrachlorodibenzo-p-dioxin	22	1
PCDD	Pentachlorodibenzo-p-dioxin	14	1
HxCDD	Hexachlorodibenzo-p-dioxin	10	3
HpCDD	Heptachlorodibenzo-p-dioxin	2	1
OCDD	Octachlorodibenzo-p-dioxin	1	1
MCDF	Monochlorodibenzofuran	4	---
DCDD	Dichlorodibenzo-p-dioxin	16	---
TrCDD	Trichlorodibenzo-p-dioxin	28	---
TCDF	Tetrachlorodibenzofuran	38	1
PCDF	Pentachlorodibenzofuran	28	2
HxCDF	Hexachlorodibenzofuran	16	4
HpCDF	Heptachlorodibenzofuran	4	2
OCDF	Octachlorodibenzofuran	1	1

210 congeners

75 Dioxin congeners

135 Furan congeners

7 "toxic" congeners

10 "toxic" congeners

17 "toxic" congeners

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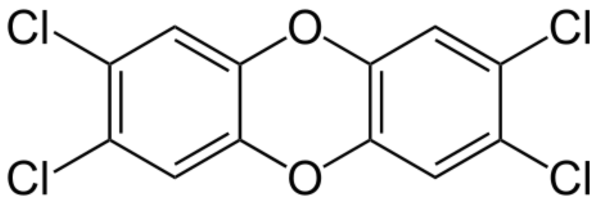
Toxic Equivalency Factors (TEFs)

TEF values allow us to express concentration in terms of Toxic Equivalents (TEQ)

DIOXINS	NATO TEF	WHO TEF
2,3,7,8-Tetra CDD	1	1
1,2,3,7,8-Penta CDD	0.5	1
1,2,3,4,7,8-Hexa CDD	0.1	0.1
1,2,3,6,7,8-Hexa CDD	0.1	0.1
1,2,3,7,8,9-Hexa CDD	0.1	0.1
1,2,3,4,6,7,8-Hepta CDD	0.01	0.01
1,2,3,4,6,7,8,9-Octa CDD	0.001	0.0003



2,3,7,8-Tetrachlorodibenzo-p-dioxin

TEQ =
TEF x concentration in sample

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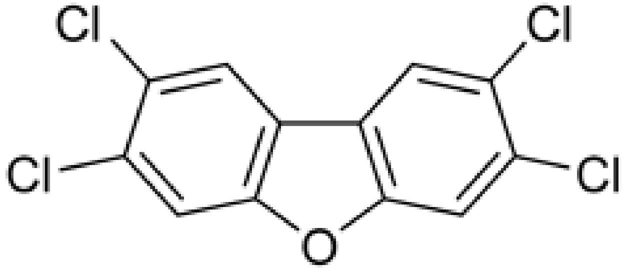
Toxic Equivalency Factors (TEFs)

FURANS	NATO TEF	WHO TEF
2,3,7,8-Tetra CDF	0.1	0.1
1,2,3,7,8-Penta CDF	0.05	0.03
2,3,4,7,8-Penta CDF	0.5	0.3
1,2,3,4,7,8-Hexa CDF	0.1	0.1
1,2,3,6,7,8-Hexa CDF	0.1	0.1
1,2,3,7,8,9-Hexa CDF	0.1	0.1
2,3,4,6,7,8-Hexa CDF	0.1	0.1
1,2,3,4,6,7,8-Hepta CDF	0.01	0.01
1,2,3,4,7,8,9-Hepta CDF	0.01	0.01
1,2,3,4,6,7,8,9-Octa CDF	0.001	0.0003



2,3,7,8-Tetrachlorodibenzofuran

PCDD/F Sources: Canada and USA

CANADA

(PCDD/F g TEQ /yr)	1999	2014
Municipal Waste Incineration	83	20
Residential Wood Burning	**36**	7
Metallurgical Processes	34	4
Pulp and Paper Industry	16	1
Vehicle Fuel Combustion	**9**	23
Residential Oil Combustion	7	0.3
Electric Power Genertion	5	2
Wood Waste Combustion	4	4
Wood Preservation	4	0
Cement and Concrete	3	2
Medical Incinerators	3	3
Industrial Incinerators	1	0.4
Chemical Production	0.3	0.3
Total	**204**	**68**

Area Burned 2015
Canada: 3.9 mm ha
USA: 4.0 mm ha

Wildfires: USA
1987: 940g TEQ
1995: 1300g TEQ
2000: 4600g TEQ

Wildfires in Canada likely produce >10x more PCDD/F than all other sources combined!

USA

(PCDD/F g TEQ /yr)	2000
Residential Wood Burning	**510**
Medical Waste Incinerators	378
Non-incinerated waste	90
Municipal Waste Incinerators	84
Power Generation	88
Vehicle Fuel Combustion	**106**
Metallurgical Processes	44
Cement Kilns	38
Industrial Wood Burning	42
Chemical Production	34
Hazardous Waste Incinerators	6
Petroleum Refining (catalyst)	2
Pulp and Paper	2
Other	2
Total	**1425**

Canada has a lot less people than the US but about the same amount of trees!

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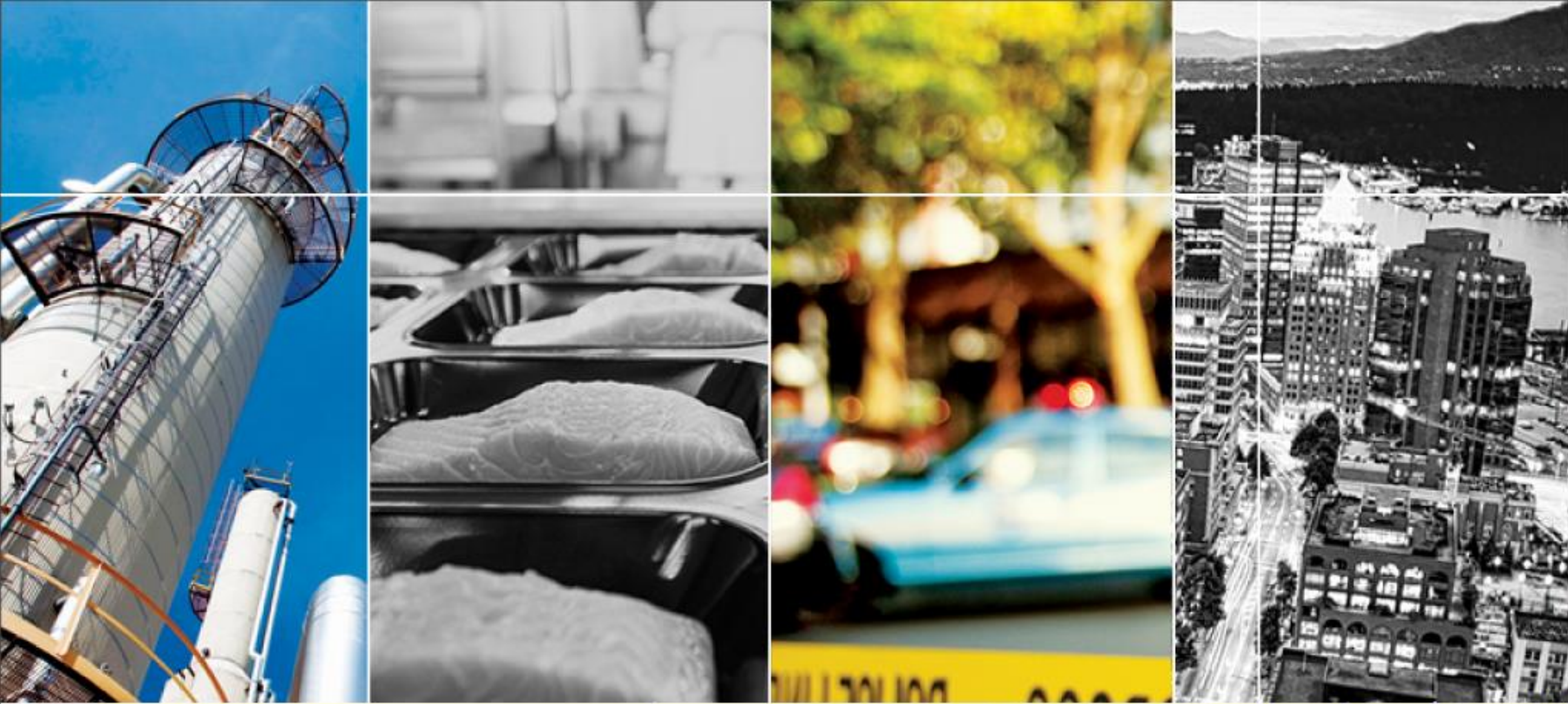
Sources: Environment Canada and US EPA



Dioxin and Furan Levels from Wildland vs. Urban Wildfires

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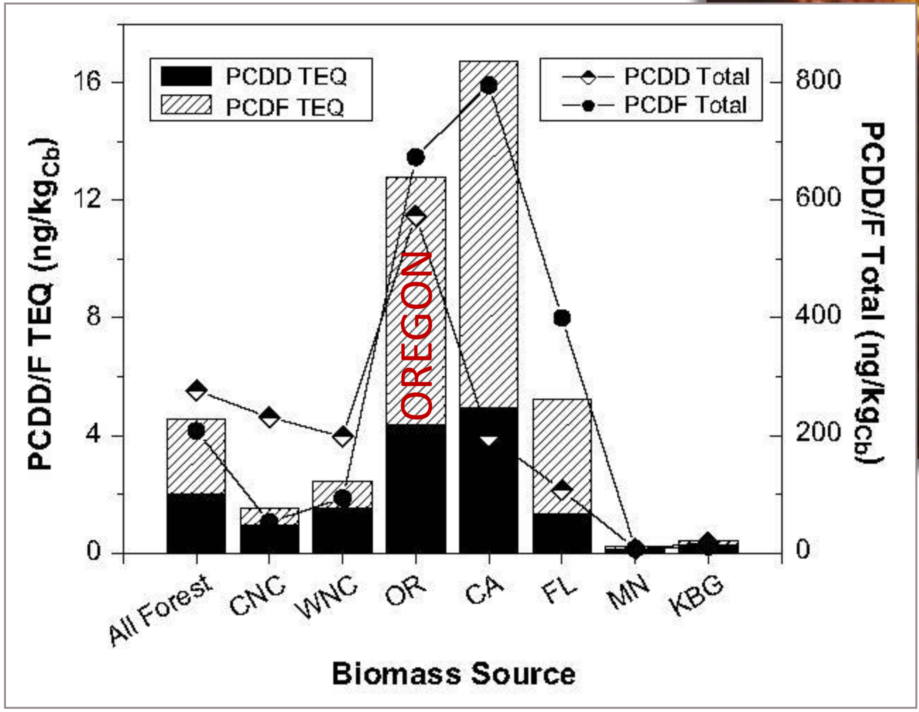
Dioxins & Furans from Forest Wildfires

Dioxins vs. Furans? Toxicity (TEQ)?

Both variable depending on what is being burned



For Oregon forest biomass:

- Equal mass PCDD & PCDF
- TEQ for PDCF 2x that of PCDD.

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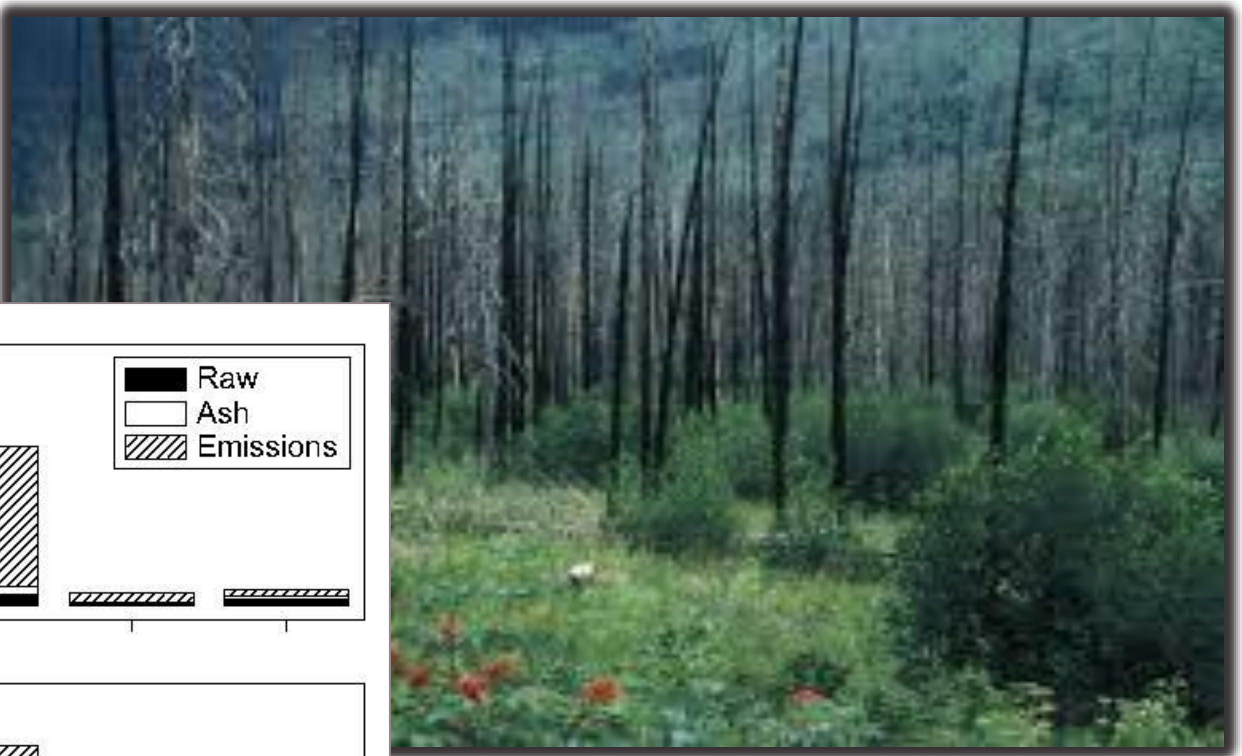
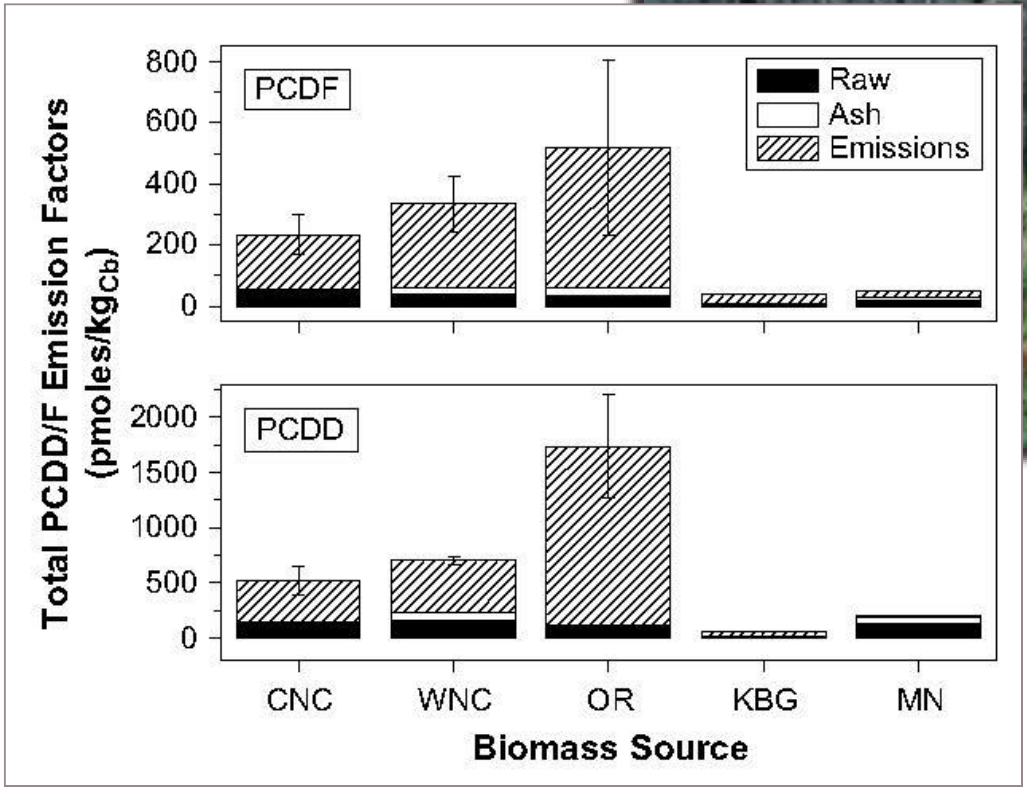
Gullett et al., 2008 Atmospheric Environment

Comparison: Dioxins/Furans from Forest & Grassland Controlled Burns

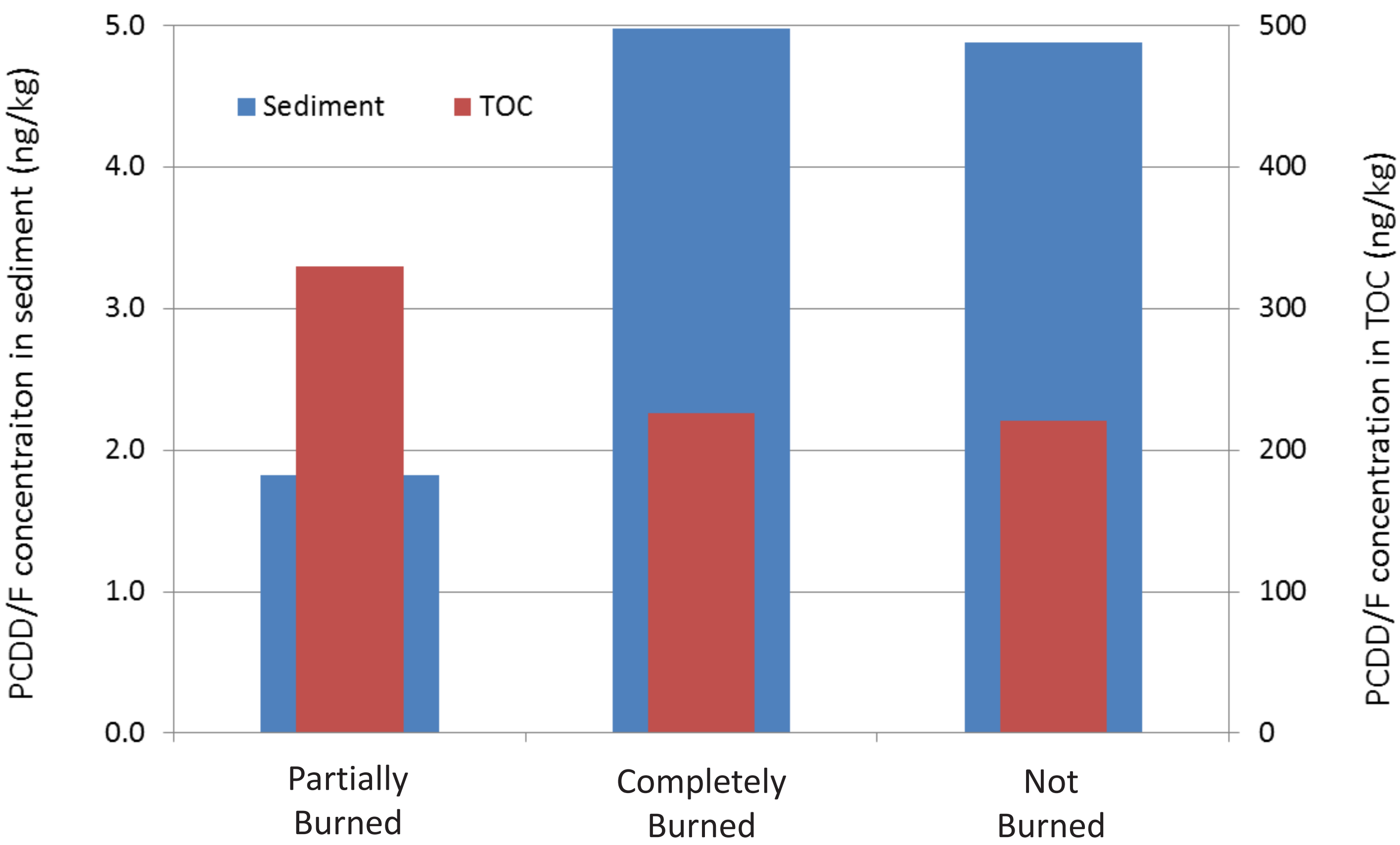




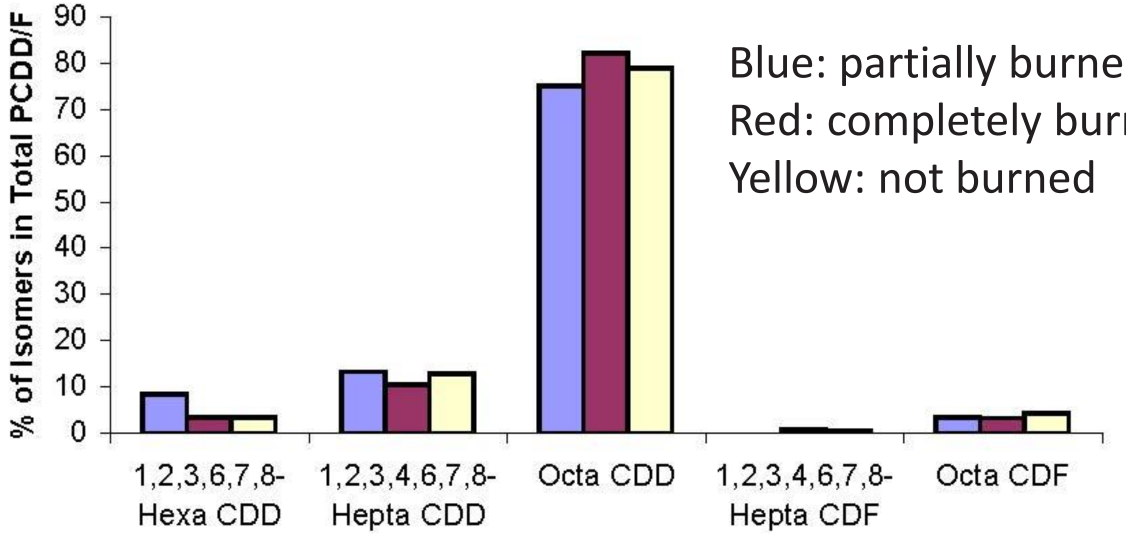
- Amount of PCDD/F produced from forest biomass is >> original content.
- Bulk of PCDD/F go to atmospheric emissions.

Sediment: From a 1998 Northern Alberta Wildfire

- Sediment dioxin/furan levels indistinguishable from background
- True for both total sediment and sediment carbon (TOC)



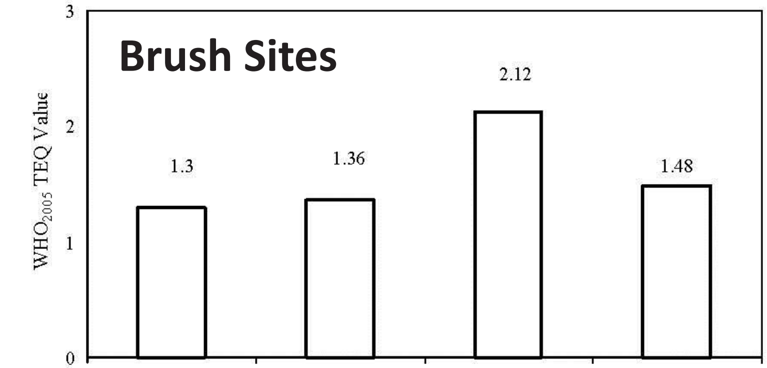
Congener Profiles

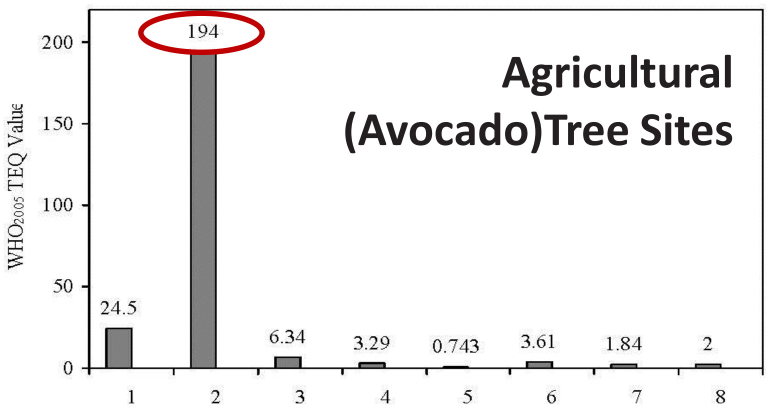


Blue: partially burned
Red: completely burned
Yellow: not burned

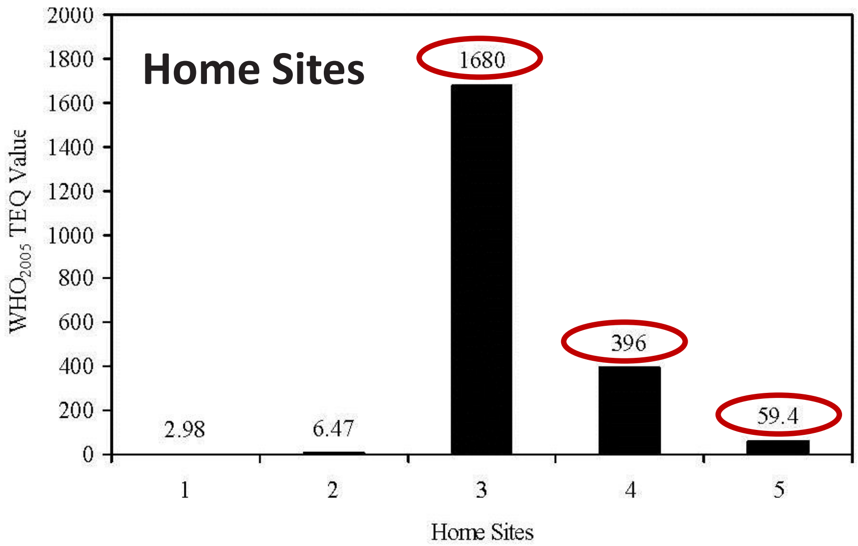
- Dioxins composed primarily of Octa CDD, followed by Hepta CDD
- Furans and other dioxins present at lower levels

2007 California Urban/Wildland Wildfire





All data in PCDD/F ng TEQ/kg in ash or topsoil

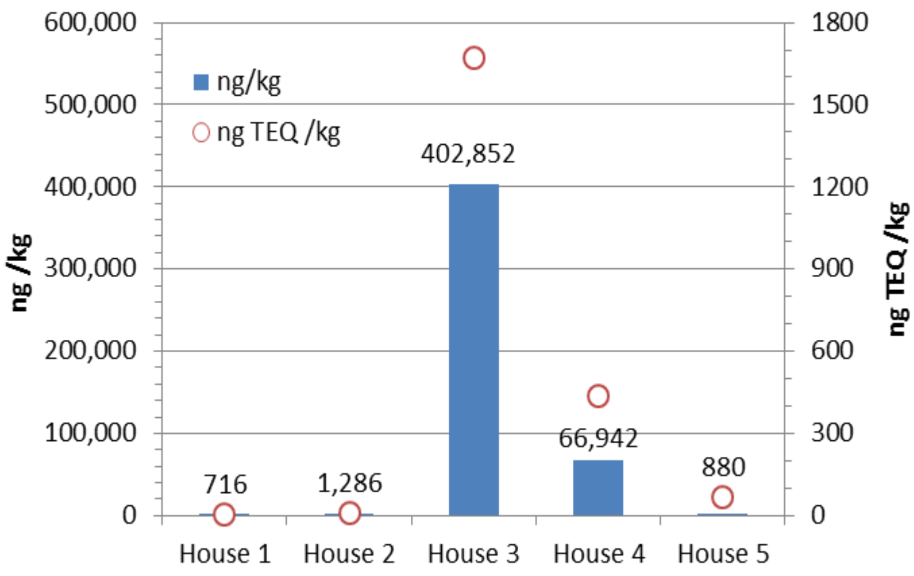


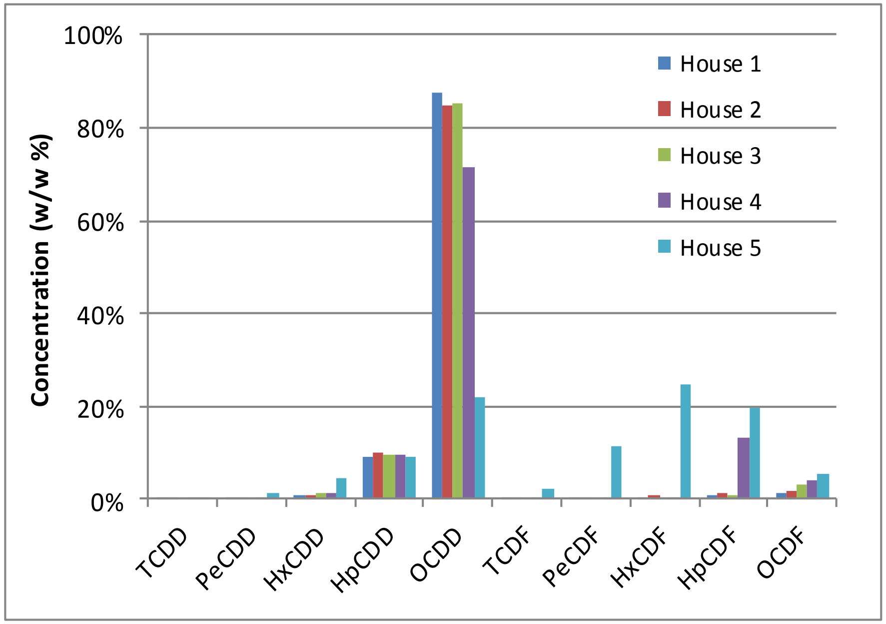
CCME guidelines:
All soil types and uses: 4 ng TEQ/kg

- Highest values found near burned homes.
- PCDD/F significantly exceeded levels reported for forest wildfires in the literature.
- Authors suggest ambient levels could be affected.
  - Danger of interpreting wildfire PCDD/F as industrial contamination.

House Results

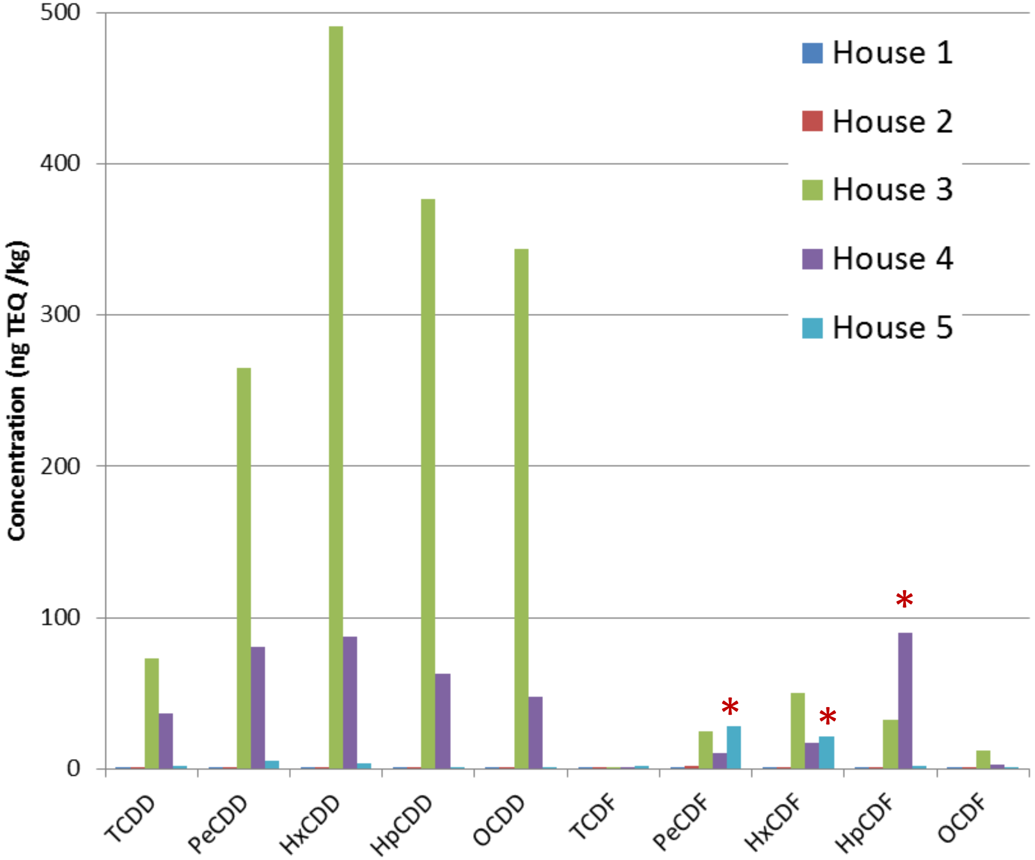
- Low toxicity houses still have 1000x the levels of total PCDD/F per kg soil/ash than seen in N. Alberta wildland wildfires
- Congener proportions for houses 1, 2 and 3 are similar and consistent with N. AB. woodland wildfire profiles
- Congener proportions for houses 4 and 5 are different. Less OCDD, more HxCDD and Furans





Deardorff et al. 2008 Organohalogen Compounds

House Results - Toxicity



Houses 1&2: both mass and toxicity data are low and consistent with wildland fire data

House 3: toxicity due to high mass of total PCDD/F – 400x higher than low toxicity house

House 4: toxicity due to high mass of total PCDD/F (100x) and disproportionate amount of one toxic HpCDF

House 5: toxicity due to disproportionate amounts of a toxic PeCDF and all four HxCDF

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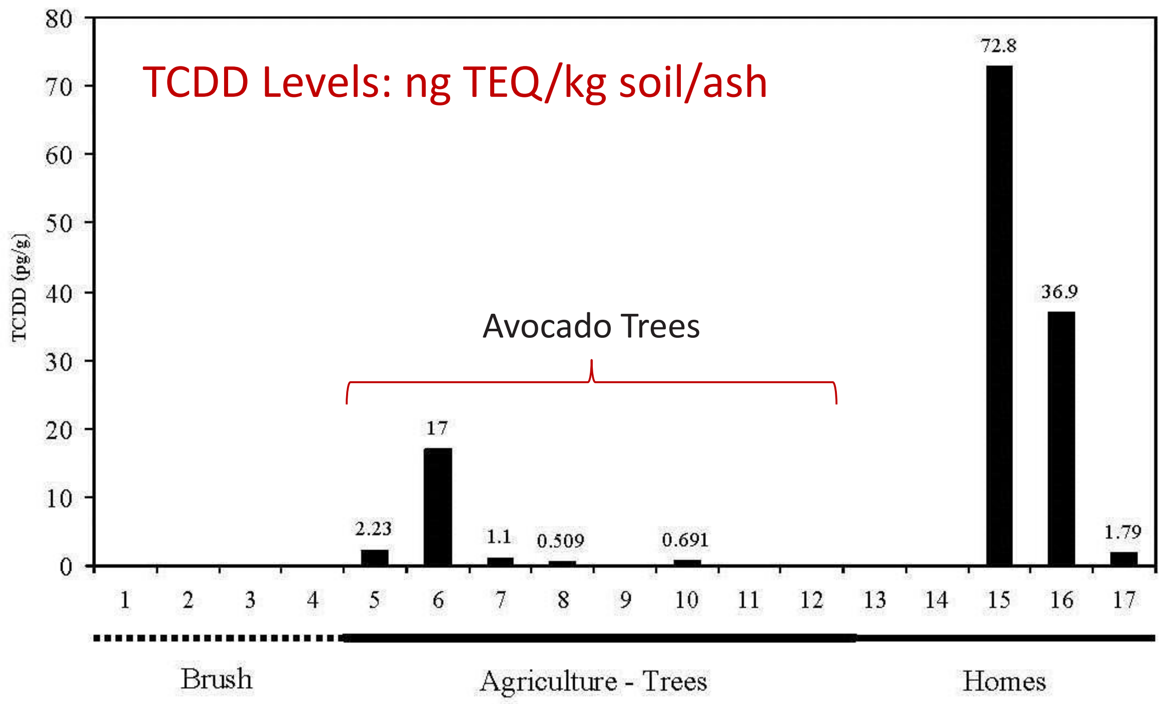
Deardorff et al. 2008 Organohalogen Compounds

2007 California Urban/Wildland Wildfire - Conclusions

- In urban wildfire impacted areas, high concentrations of dioxins/furans including TCDD don't necessarily imply industrial activity.
- Authors suggest ambient levels could be affected, which should be considered in future assessments in the area.



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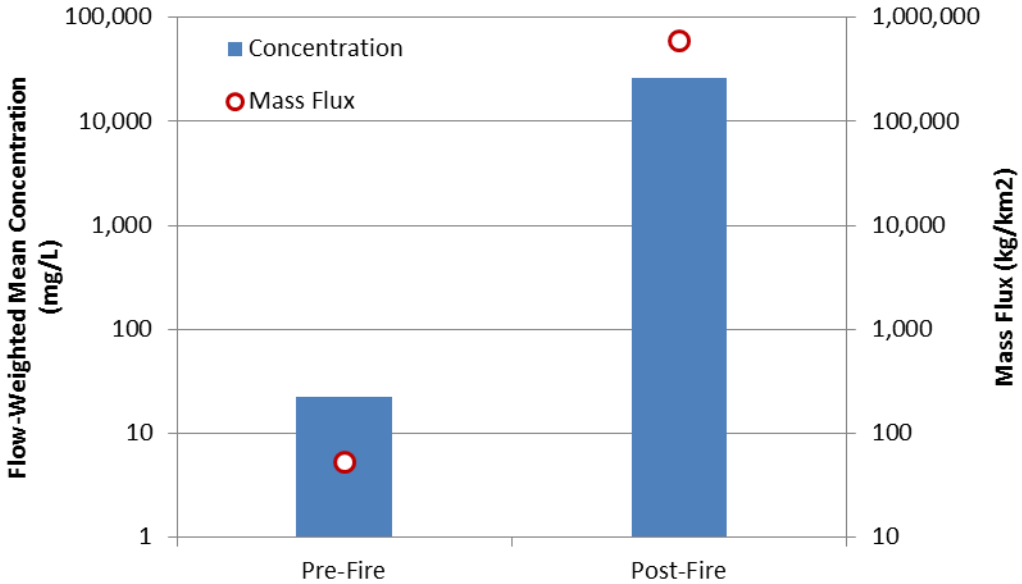
Deardorff et al. 2008 Organohalogen Compounds

Watershed Transport Considerations

Evaluation of sediment movement within a watershed pre- and post-fire



Sediment concentrations and mass flux increased by 3 orders of magnitude post-fire

Loss of vegetation and changes in soil properties greatly increased the magnitude of storm runoff, resulting in sediment-laden stormwater carrying high concentrations of particulate-bound contaminants

Sampling & Analysis Considerations

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Sampling Requirements

Sample Matrix	Sample Container	Minimum Sample Size	Storage
Water (EPA 1613)	2 x 1-L pre-cleaned amber glass bottle; Teflon® lined cap	2 L	<4° C ($Na_2S_2O_3$ if chlorinated; H_2SO_4 if pH >9)
Soil/Ash (EPA 8290)	1 x 250 mL pre-cleaned amber glass bottle; Teflon® lined cap	100 g	<4° C (frozen preferred)
Tissue (EPA 8290)	1 x 250 mL pre-cleaned amber glass bottle[1]; Teflon® lined cap	100 g	Frozen
Air (EPA TO-9/Method 23)	Glass Fibre Filter/PUF Plug (EPA TO-9) XAD Resins/Impinger Fluids (EPA Method 23)	N/A	<4° C

[1] **Sample container may be sample dependent; important to ensure container is "background free"**

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Field Quality Assurance

Ideally, have a documented Quality Assurance Project Plan (QAPP) agreed to by all parties;

At a minimum, flag field contamination

Field QC

- Equipment Rinse Blanks
- Trip Blanks (remain sealed)
- Field Blanks (open at site)

Field Spikes – typically only for water samples

Field Duplicates

- Understand sample heterogeneity
- Typically high for soils

May also want to consider:

Contamination at urban wildfire sites is very uneven:

- Multiple samples per building site
- Composite sampling
- Grid Sampling

Analytical Methods

Sample Submission

No Plastic Containers!

Soil vs. Ash?
Indicate clearly on the COC

Extraction

Ash:
Acid Digestion + Solvent Extract

Soil:
Solvent Extraction Only**

Clean-up

1. **Acid Backwash**
2. **Mixed Bed Column:**

   Possible additional clean-ups:

3. **Alumina Column**
4. **Carbon Column**

Analysis

High Resolution Mass Spectrometry

Maximum assurance of correct parameter identification

**** IF IT IS AN ASH SAMPLE, SPECIFY THAT CLEARLY ON THE COC**
Soil mineralizes during fire, resulting ash traps PCDD/F in its crystalline structure.
Need acid digestion to remove - solvent only elutes from the particle surfaces.

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PCDD/F Clean-up Protocol

Acid Backwash

- Remove oxidizable compounds: lipids, PAHs, some OCPs

Mixed Bed Silica Column

- Acidic – remove additional oxidizable compounds, which are mostly oxidized to acids
- Basic – remove acid species produced above plus phenols
- $AgNO_3$ – remove organic sulphur compounds, & olefins
- possibly additional steps if beds above are overloaded

For heterogeneous samples, different steps or numbers of steps may be performed on different samples in batch.

Alumina Column

- Removes most PCBs

Activated Charcoal Column

- Removes co-planar PCBs

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Laboratory Quality Assurance

- Laboratory Quality Control (QC) Samples
  - Method Blanks
  - Blank Spikes/Blank Spike Duplicate
  - Sample Duplicate
  - Matrix Spike/Matrix Spike Duplicate

Method Blanks & Spikes are processed according to the most strenuous clean-up required for the batch.

Recoveries in any specific sample in a job could be better than shown for spike recoveries in the QA report.

- TCDF Confirmation required
  - 2,3,4,7-TCDF, 2,3,7,8-TCDF, 1,2,3,9-TCDF co-elute in the standard instrument set-up
  - If a positive is seen for 2,3,7,8-TCDF, re-inject with a different instrument set-up to confirm

If 2,3,7,8-TCDF is reported >EDL, ensure you are referring to the 'TCDF Confirmation' data when interpreting the report, contribution from non-toxic congeners can be significant.

Toxic Equivalency – Treatment of EDL Data

		Calculated EDL	Sample Result	NATO TEF	Toxic Equivalency
Dioxins	2,3,7,8- Tetra CDD	1.7	2.3	1	2.3
	1,2,3,7,8- Penta CDD	3.2	<3.2	0.5	1.6
	1,2,3,4,7,8- Hexa CDD	2.8	4.3	0.1	0.43
	1,2,3,6,7,8- Hexa CDD	2.9	<2.9	0.1	0.29
	1,2,3,7,8,9- Hexa CDD	4.6	5.2	0.1	0.52
	1,2,3,4,6,7,8- Hepta CDD	6.6	8.2	0.01	0.082
	1,2,3,4,6,7,8,9- Octa CDD	15	48	0.001	0.048
Furans	2,3,7,8- Tetra CDF	1.9	<1.9	0.1	0.19
	1,2,3,7,8- Penta CDF	2.2	<2.2	0.05	0.11
	2,3,4,7,8- Penta CDF	3.1	<3.1	0.5	1.6
	1,2,3,4,7,8- Hexa CDF	2.9	3.6	0.1	0.36
	1,2,3,6,7,8- Hexa CDF	4.3	6.3	0.1	0.63
	1,2,3,7,8,9- Hexa CDF	4.2	<4.2	0.1	0.42
	2,3,4,6,7,8- Hexa CDF	5	<5	0.1	0.5
	1,2,3,4,6,7,8- Hepta CDF	4.6	<4.6	0.01	0.046
	1,2,3,4,7,8,9- Hepta CDF	3.6	5.3	0.01	0.053
	1,2,3,4,6,7,8,9- Octa CDF	9.2	60	0.001	0.06
Toxic Equivalent Quantity					**9.24**

Units = pg/g

Note that the two toxic penta CDD/F congeners reported at <EDL comprise 1/3 of total sample TEQ

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Toxic Equivalency – Sample Calculation

Example Report:

- All results <EDL were assigned, in this case, at the absolute value of the EDL.

Treatment of <EDL-results need to be set-up ahead of time:

- At EDL: worst case scenario.
- Half DL: typically used for brownfield assessments.
- Zero DL: likely underestimates site toxicity.

Recommendations

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Urban Wildfire Assessments - Recommendations:

1. Urban wildfire sites can sometimes have significantly higher mass loadings and TEQ relative to wildland wildfire sites.

2. Conduct appropriate field QC to avoid biasing data due cross-contamination from PCDD/F hotspots.

3. When submitting ash samples, clearly state this on the COC

4. When testing in burned areas after an urban wildfire, take multiple or composite samples at each property site to get a representative TEQ value – expect variable PCDD/F loadings on the property.

5. Consider the possibility of elevated ambient background in historic urban wildfire sites.

6. Consider sediment flow paths downstream of urban wildfire sites.

7. Understand whether reports are biasing TEQ data low or high, depending on how <EDL data are handled.

Sources

Deardorff, Thomas L.; Karch, Nathan J.; Holm, Stewart E. Dioxin levels in ash and soil generated in southern California fires, Organohalogen Compounds (2008), 70, 2284-2288.

Gullett, B.; Touati, A.; Oudejans, L PCDD/F and aromatic emissions from simulated forest and grassland fires, Atmospheric Environment (2008), 42(34), 7997-8006.

Gabos, S.; Ikonomou, M. G.; Schopflocher, D.; Fowler, B. R.; White, J.; Prepas, E.; Prince, D.; Chen, W. Characteristics of PAHs, PCDD/Fs and PCBs in sediment following forest fires in northern Alberta, Chemosphere (2001), 43(4-7), 709-719.

M. P. Burke, T. S. Hogue, A. M. Kinoshita, J. Barco, C. Wessel, E. D. Stein. Pre- and post-fire pollutant loads in an urban fringe watershed in Southern California, Environmental Monitoring & Assessment (2013) 185:10131–10145

Thank you!

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