



Evaluation of Dioxin Patterns to Apportion Pollution Sources

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Agenda

- Background and clean-up imperative
- Data description
- Methods description
- Mixture analysis results
- Comparisons to other data
- Summary

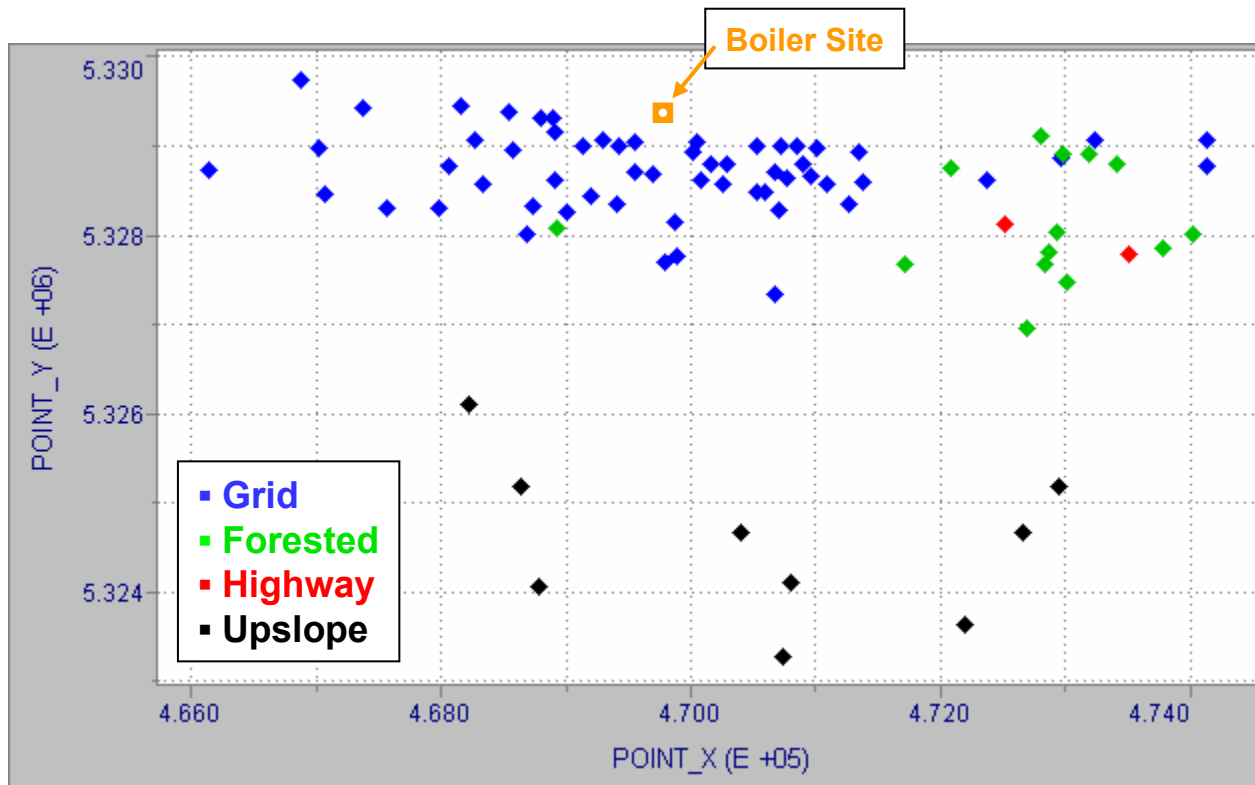
Situation

- Pulp mill using hog-fuel boiler
 - Operated for 60+ years
 - Emission controls upgraded several times
 - Odor complaints history
 - A state clean-up site—status: in process
- Many prior analyses
 - Prior data interpretation not multivariate
 - Different levels of quality in GC work
 - Multiple agencies involved
- Current study objectives
 - Characterize dioxin distribution
 - Apportion sources

Study Plan

- Design sampling plan to cover impacted & not impacted areas
 - Near to site, down and upwind (prevailing)
 - Forested and uncovered sites (fields and yards)
 - Along major highway
 - Upslope, rural areas
- Collect soil samples (box and center), up to top 10 cm
- GC/MS analysis of composited soils, via standard methods for dioxins/furans (EPA Method 1613B)
- Multivariate analysis of dioxin/furan congeners

Sampling Locations

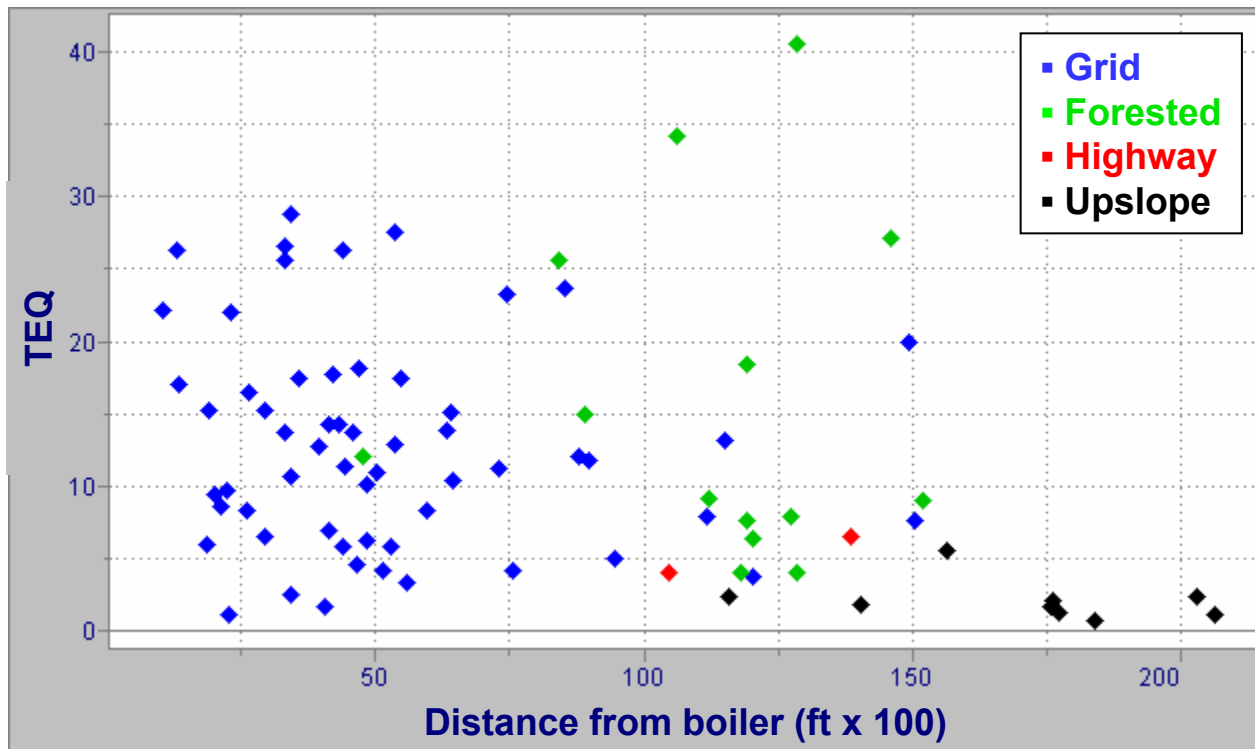


Dioxin and Furan Congeners

Index	Congener	TEF
1	2,3,7,8-TCDD	1
2	1,2,3,7,8-PECDD	1
3	1,2,3,4,7,8-HXCDD	0.1
4	1,2,3,6,7,8-HXCDD	0.1
5	1,2,3,7,8,9-HXCDD	0.1
6	1,2,3,4,6,7,8-HPCDD	0.01
7	OCDD	0.0003
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PECDF	0.03
10	2,3,4,7,8-PECDF	0.3
11	1,2,3,4,7,8-HXCDF	0.1
12	1,2,3,6,7,8-HXCDF	0.1
13	1,2,3,7,8,9-HXCDF	0.1
14	2,3,4,6,7,8-HXCDF	0.1
15	1,2,3,4,6,7,8-HPCDF	0.01
16	1,2,3,4,7,8,9-HPCDF	0.01
17	OCDF	0.0003

Analysis of TEQs

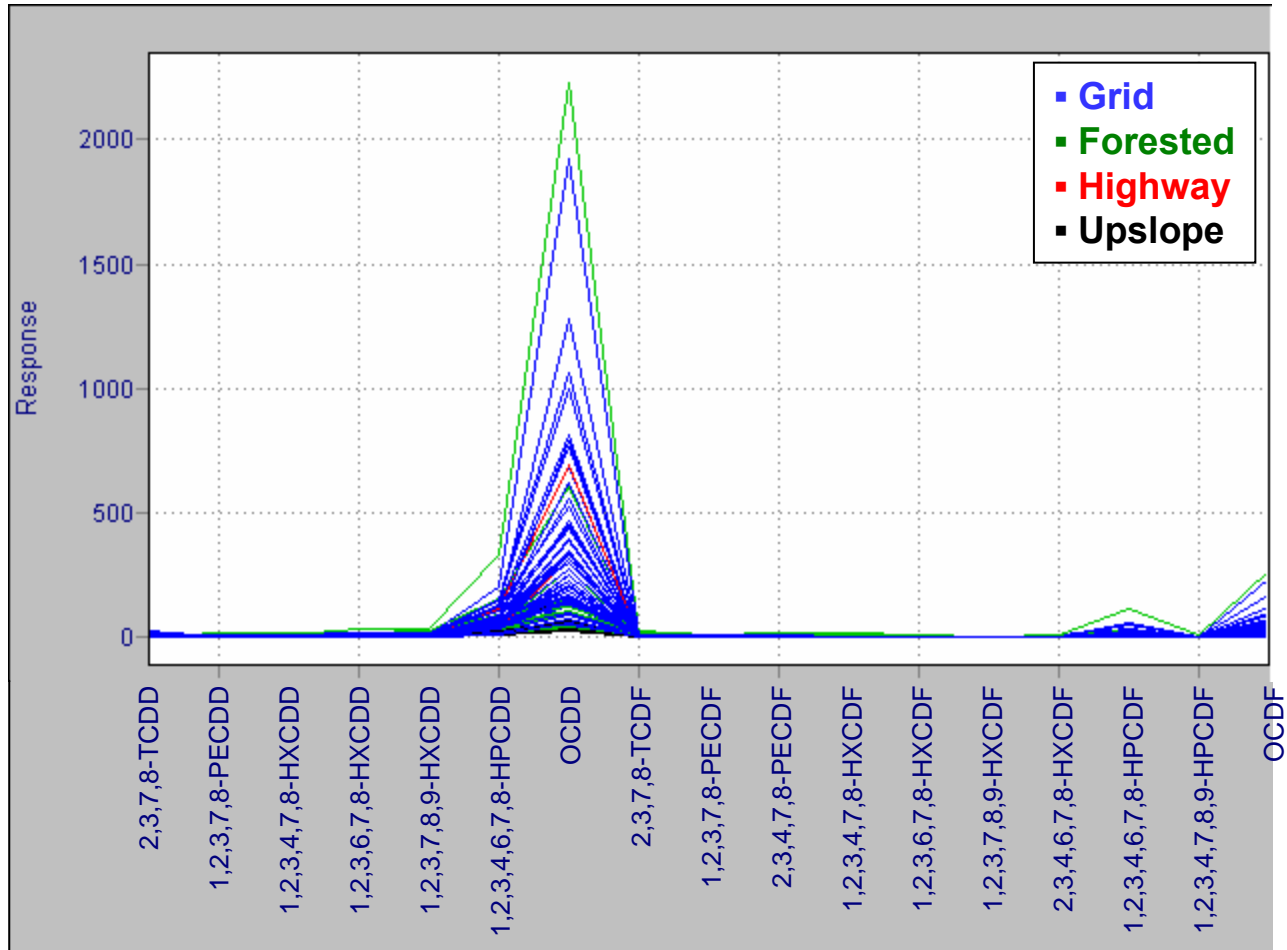
- Sample's TEQ = $\sum([\text{congener}] \bullet \text{TEF})$



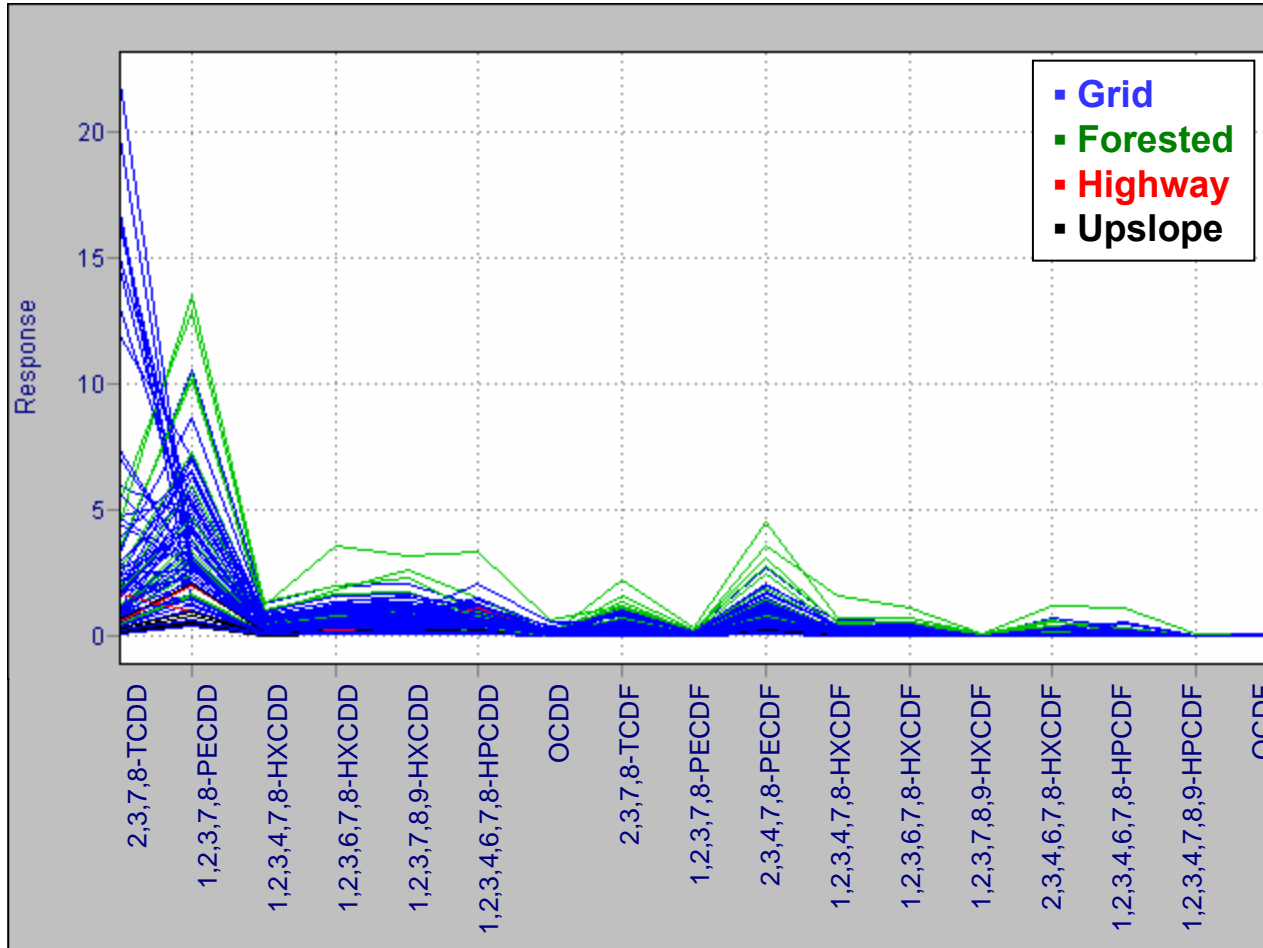
Multivariate Analysis

- Pretreatment
 - Scale by TEF
 - Area % normalization
- HCA (hierarchical cluster analysis)
 - Group average linking
- PCA (principal components analysis)
 - Number of sources by cross-validation
- MCR-ALS (multivariate curve resolution-alternating least squares)
 - Non-negativity in profiles, amounts
- Software
 - Pirouette (from Infometrix)

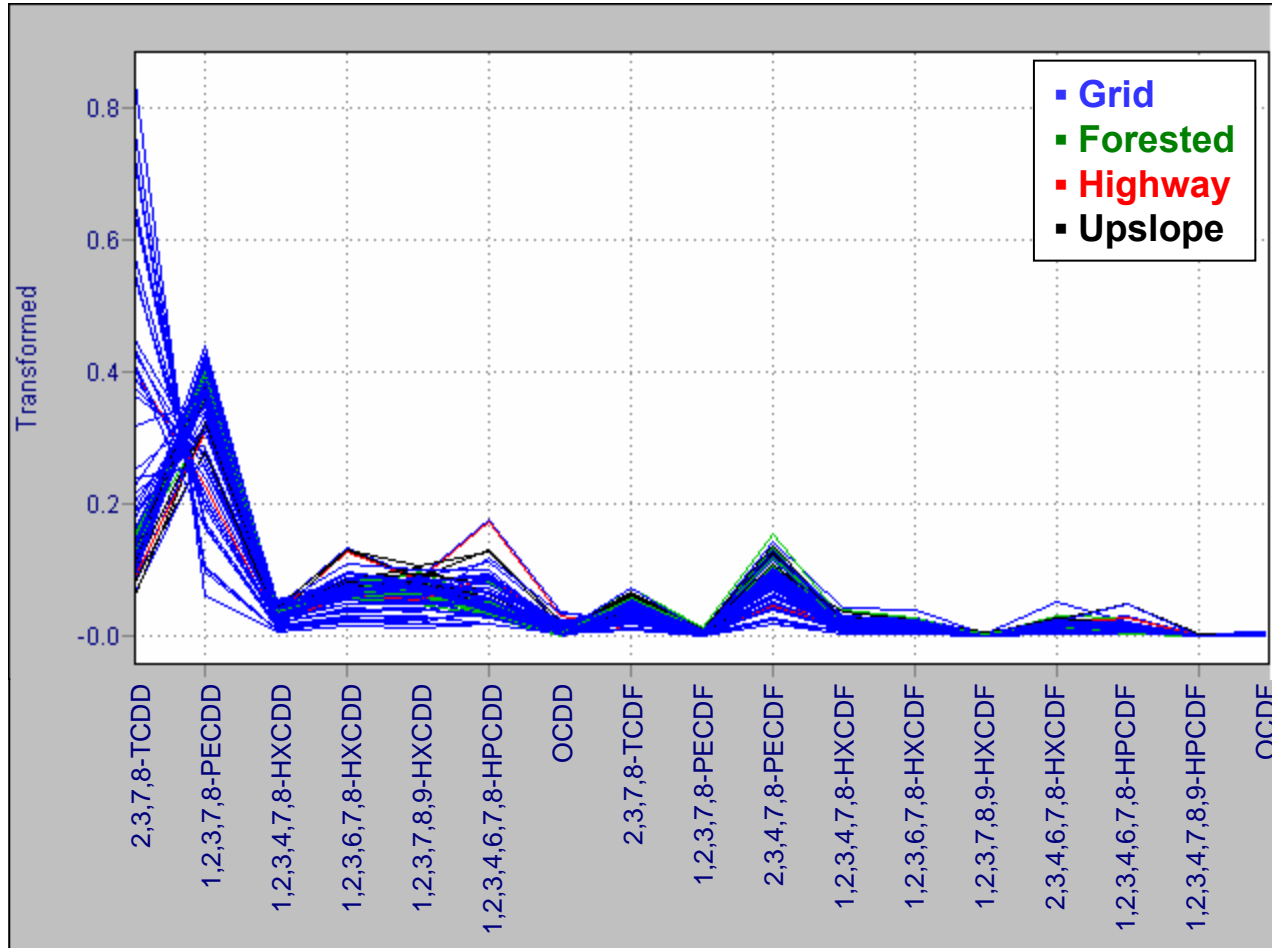
Bulk Congener Data



Congener Data, TEF-scaled



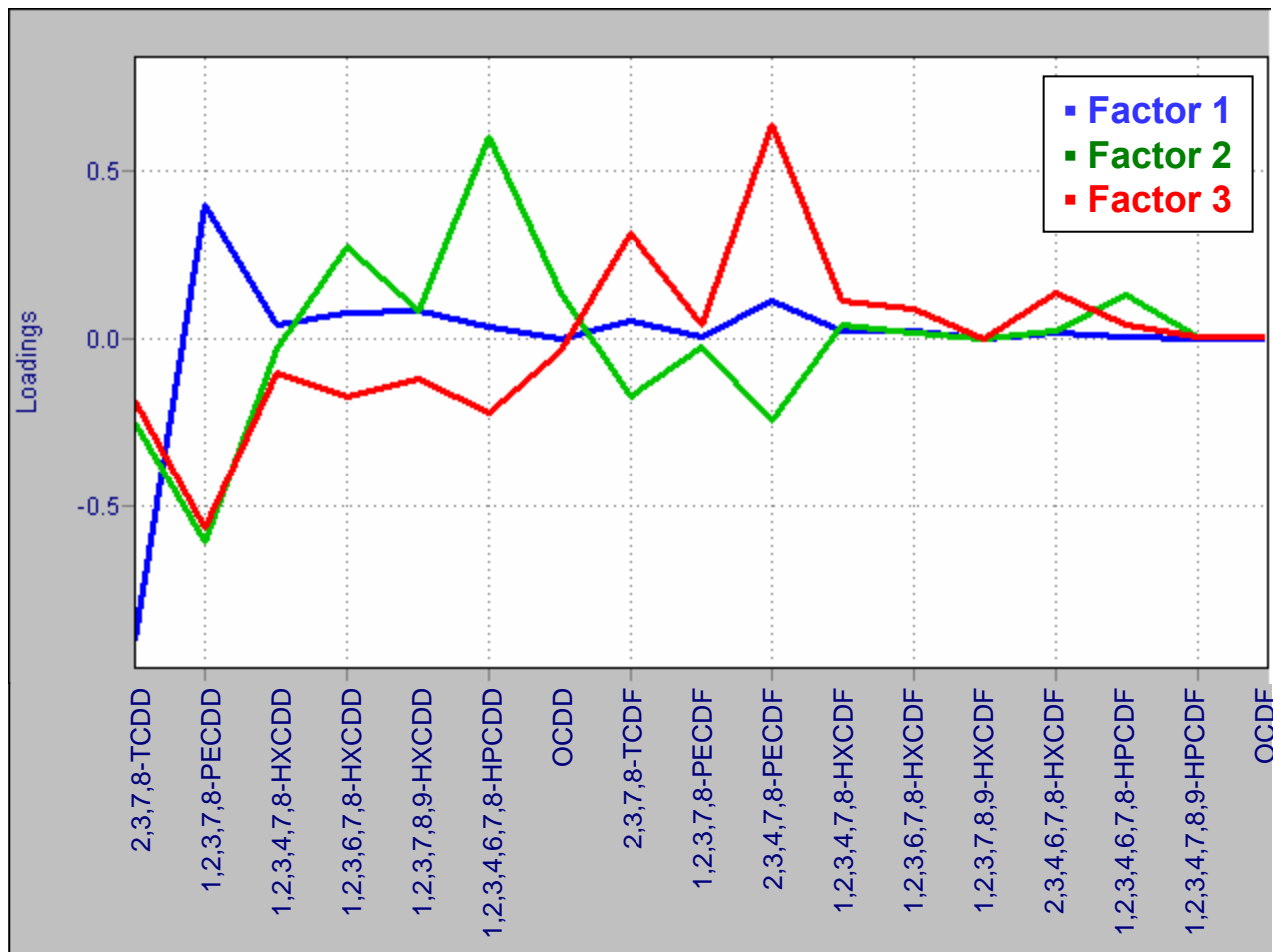
Congener Data, TEF-scaled and Normalized



PCA - Method

- Given a data matrix X composed of n samples on which m measurements were made, decompose into two matrices
 - Eigenvectors are linear combinations of original measurements, where the magnitude expresses how much a variable loads into the eigenvector (thus, the term loadings)
 - Scores are coefficients of samples on the eigenvectors, represent relative spatial positions, allow comparison of samples
- Eigenvectors are described by amount of variance they explain; each successive eigenvector describes progressively less variance
- Eigenvectors are abstract, may not be obviously related to underlying components

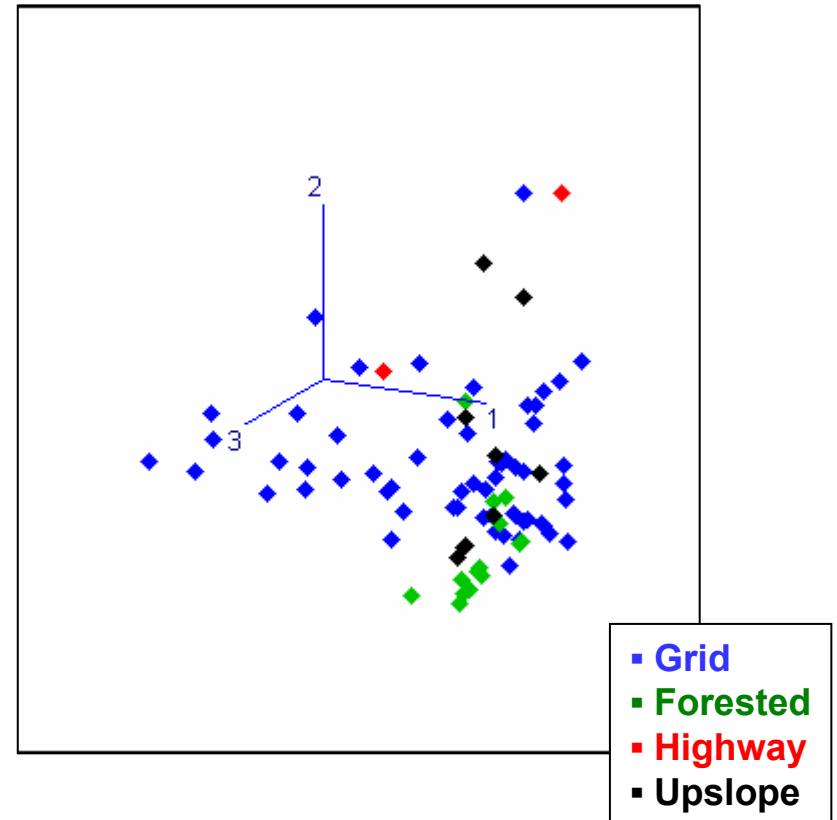
PCA Loadings



PCA Scores

- Cross-validation indicates 3 important factors

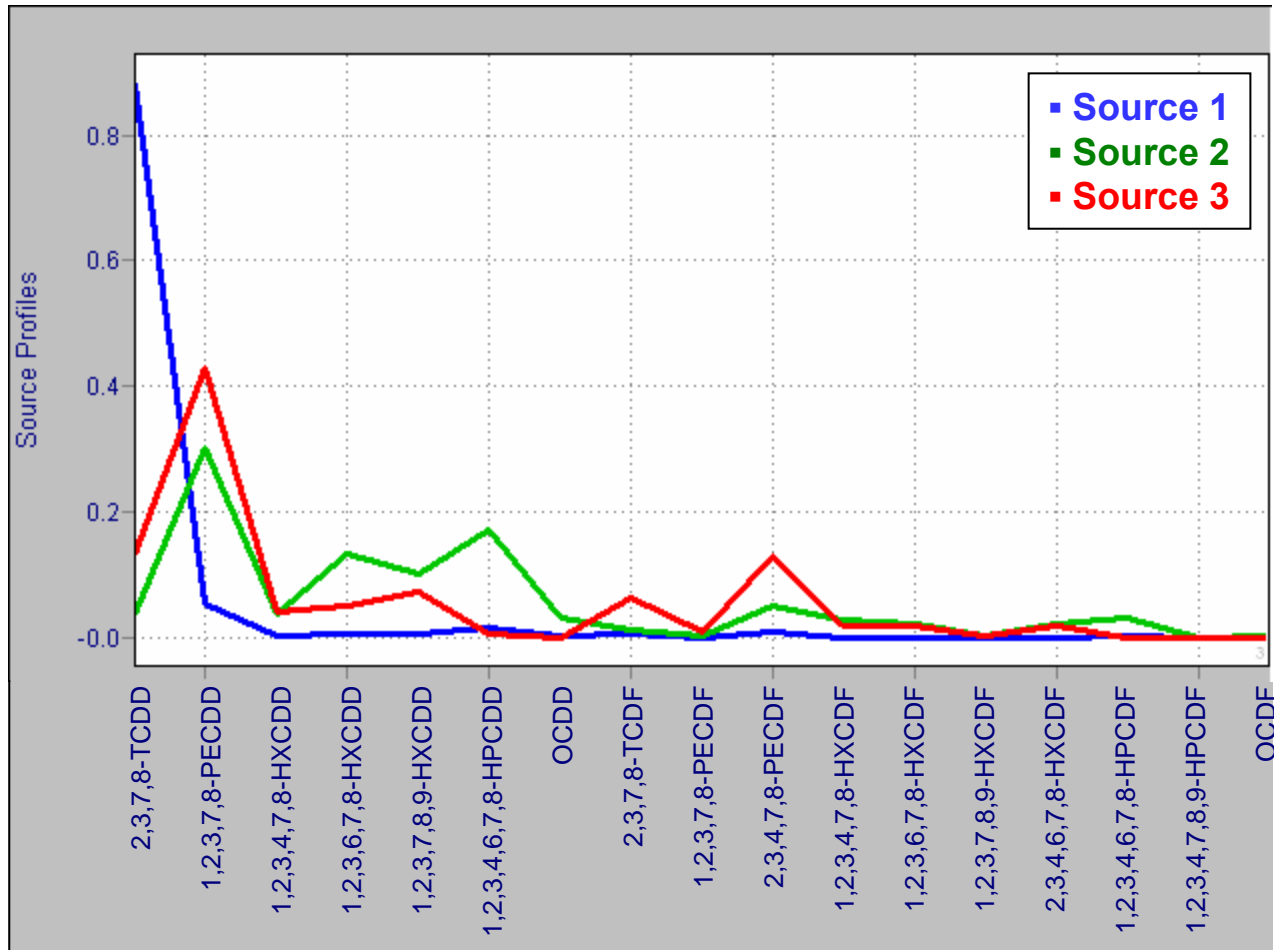
- Factor 1 93.04%
- Factor 2 5.16%
- Factor 3 1.26%



MCR-ALS Method

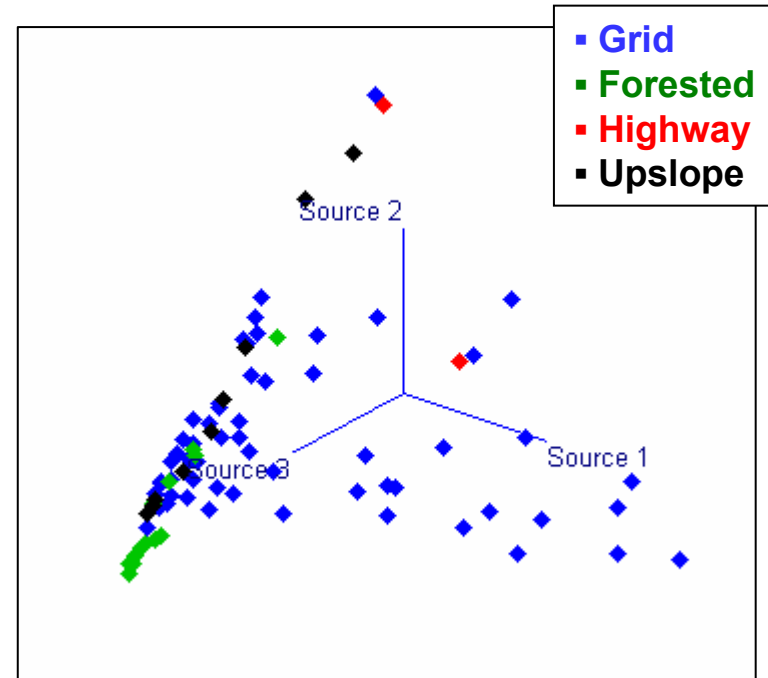
- Given a data matrix X composed of n samples on which m measurements were made, decompose into two matrices, one containing one or more unique patterns (sources, or end-members) and another containing the magnitude of the contributions of each source pattern to the samples.
- Algorithm relies on alternating least squares to estimate first the source profiles, then the source contributions.
- Constraints are applied during each step of ALS, and convergence is achieved when no further improvement is found.
 - A common constraint includes non-negativity—in source profile intensities and in the contributions

MCR-ALS Source Profiles



MCR-ALS Source Contributions

- Majority of samples dominated by Source 3 pattern
- Four samples related to pattern of Source 2
- Several samples show contribution from a Source 1 pattern



Comparison Patterns

- Patterns from other studies were collected to allow comparisons to study samples
 - Dioxin/Furan studies in scientific literature
 - EPA inventory*
 - Communication with other jurisdictions that have coastal hog fuel boilers
 - Previous studies in region

- Each comparison data set was also modified by TEF-scaling

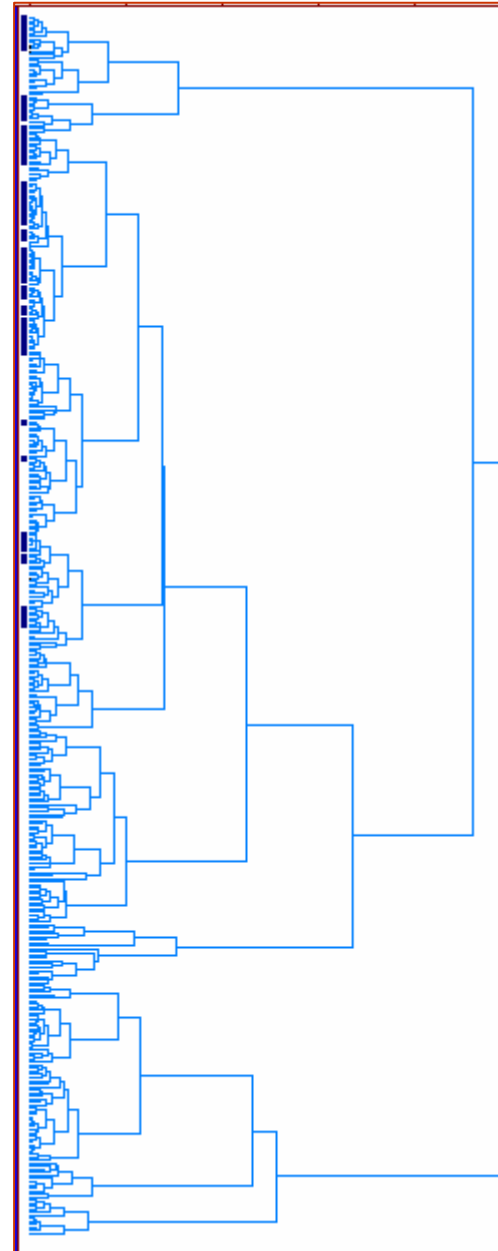
*U.S. Environmental Protection Agency (EPA), November, 2006. National Center for Environmental Assessment, Office of Research and Development. An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000. EPA/600/P-03/002F.

Comparison Methods

- Many Comparison patterns obviously unrelated; need objective methods to remove from consideration
- Cluster analysis
 - Run HCA on combined set of Study and Comparison patterns
 - Filter out those Comparison patterns that do not cluster with any Study sample
- Correlation coefficients
 - Filter out those Comparison patterns below 0.9
- Target testing
 - Assign candidate patterns as potential sources and run ALS on combined data sets, removing targets that do not contribute

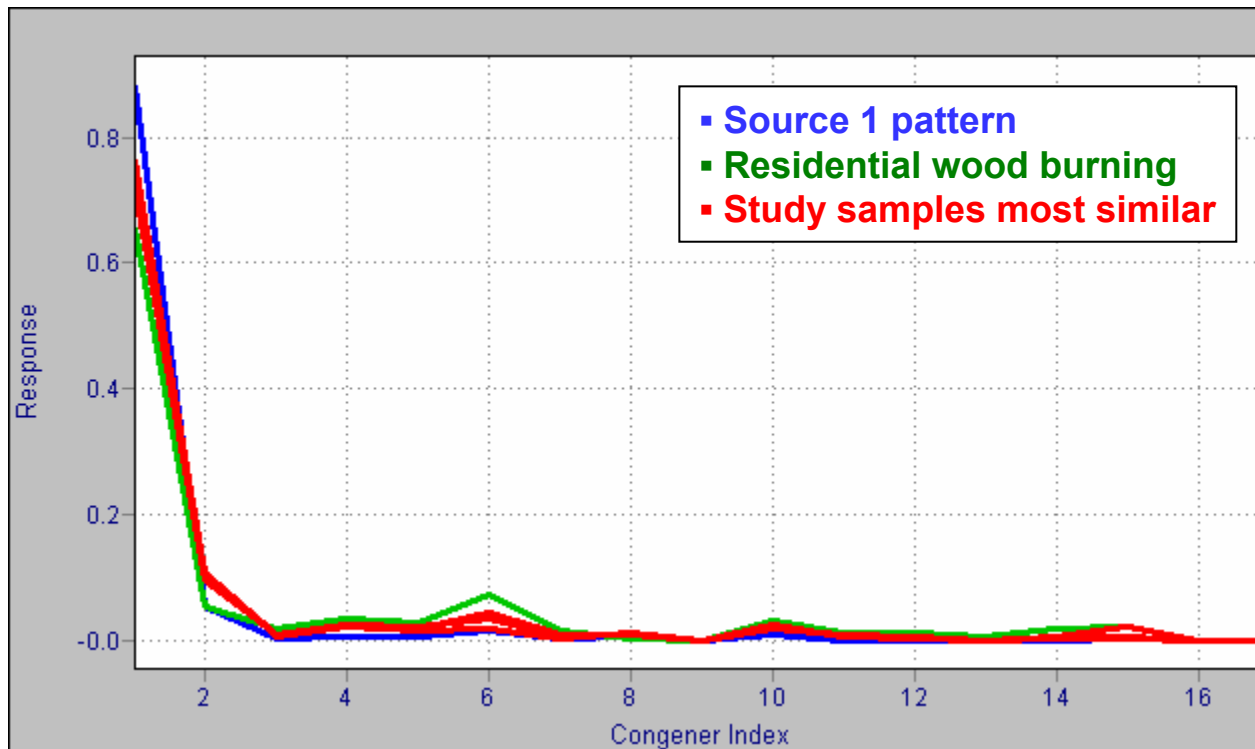
Cluster Analysis of Study and Comparison Patterns

- Plot symbols at leaf node are Study samples
- Branches that contain no Study samples include unrelated comparison patterns; these can be removed from further consideration



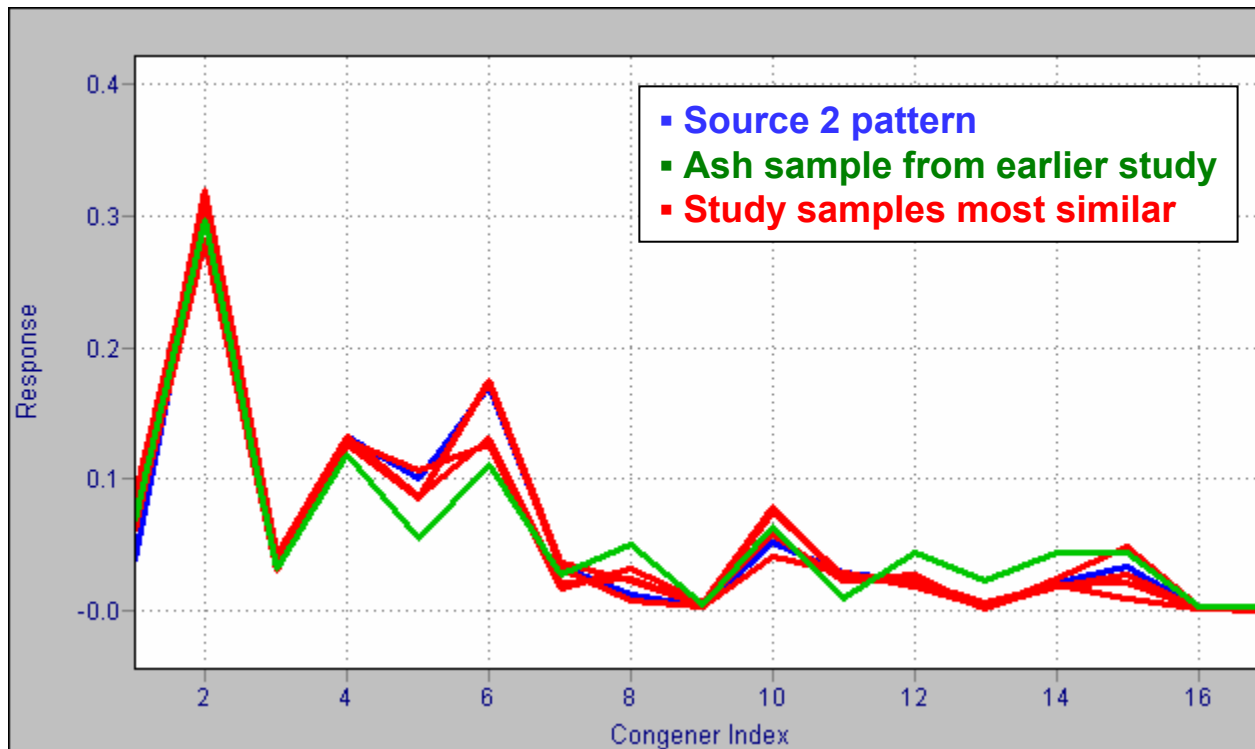
Source 1 Discussion

- Several samples show correlation to a Source 1 pattern
- Pattern from residential wood burning is comparable



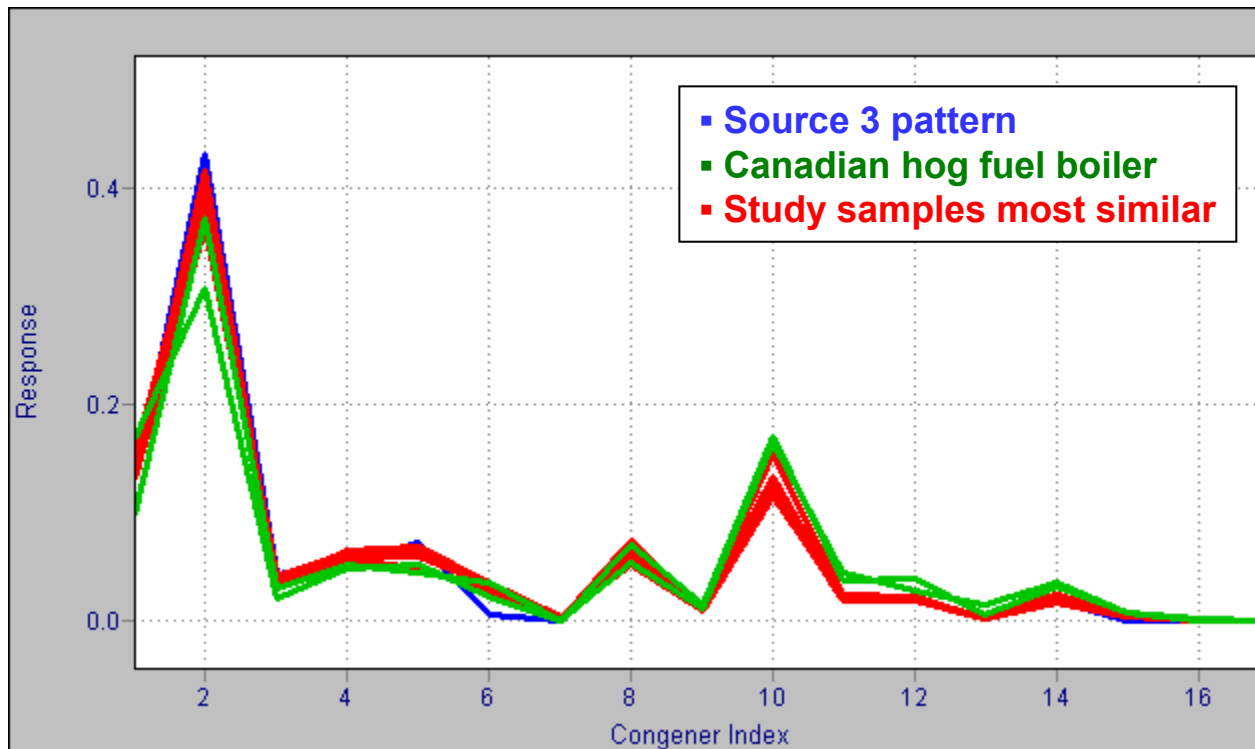
Source 2 Discussion

- Four samples related to pattern of Source 2
- Only comparable pattern found in ash from earlier study



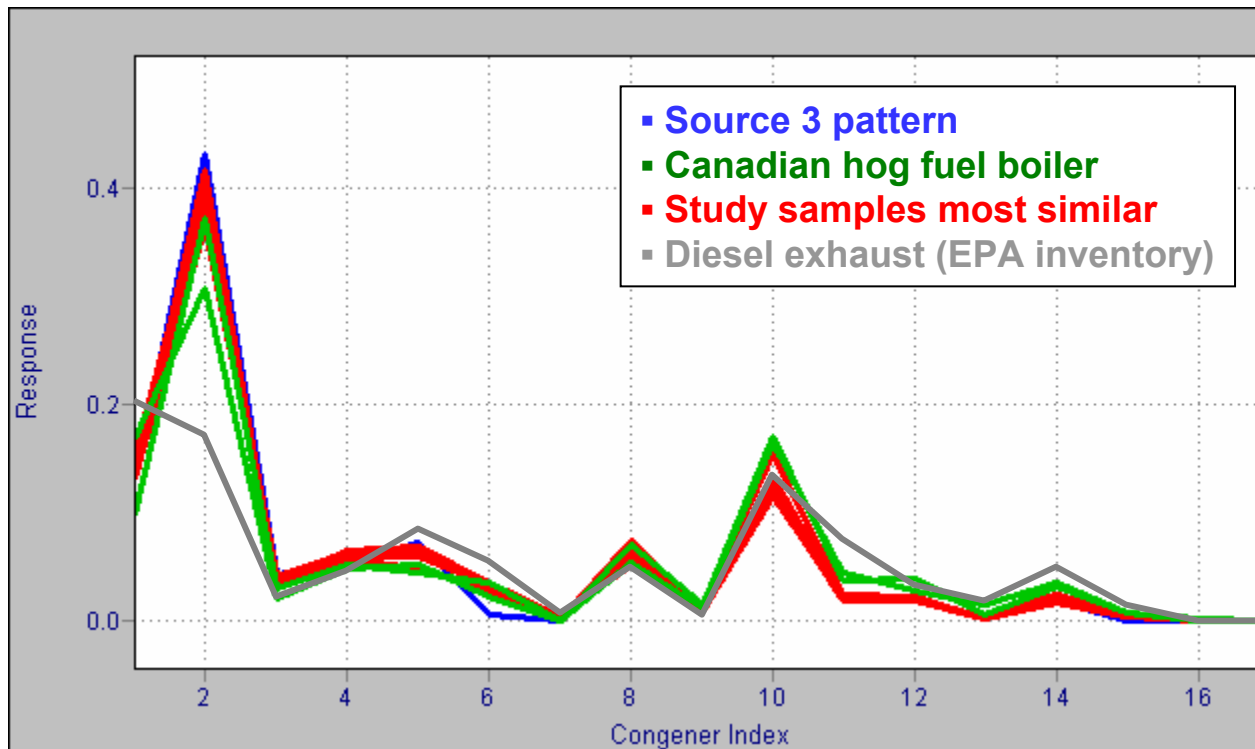
Source 3 Discussion

- Majority of samples dominated by Source 3 pattern
- Only comparables, outside of study region, found near Canadian hog fuel boiler sites



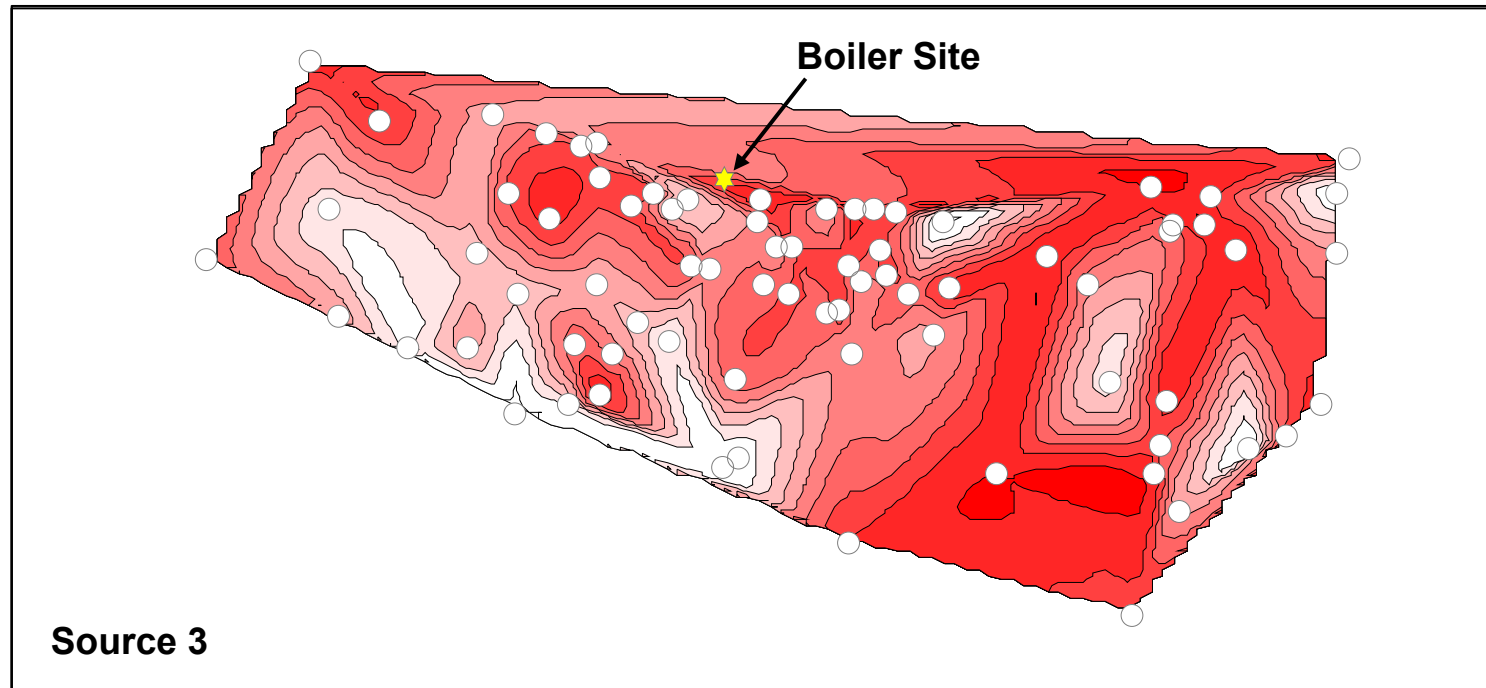
Source 3 Discussion (cont'd)

- ...
- Less comparable, but interesting, is the pattern from diesel exhaust



Spatial Distribution of Source Contributions

- Contributions of each proposed source pattern to study locations
- Magnitude of source contribution proportional to color intensity
- Upslope samples not shown



Summary

- Mixture analysis suggests that the study samples can be apportioned into three sources, two of which show interesting contributions from the tetra-, penta- and hexa-chloro dioxin and furan congeners
- Source 1 pattern is dominated by 2,3,7,8-TCDD and is the major contributor in about 10 of the study samples. Based on similar patterns found from other studies, it is likely that these sites had a major contribution from residential wood combustion
- Source 3 pattern is characteristic of the majority of samples in the Study. Similar profiles were found in samples analyzed in other studies of the basin as well as in studies of hog fuel boilers in western Canada. Samples that exhibit this pattern are found in all regions studied within the basin, at low and high TEQ levels
- Contribution of Source 3 pattern to areas further from the city is diminished, giving way to a more typical rural congener pattern reflecting residential wood burning
- Using multivariate tools has helped characterize the nature of the issues in this community in ways not possible with univariate tools.

Acknowledgments

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