APPENDIX M

Dioxin Technical Workgroup Findings

Appendix M

Dioxin Technical Workgroup Presentations

November 17, 2009

Introduction

Report by Infometrix

Presentation by Respondents

Presentation by EPA

Note, the information on MIS variance in the introduction and EPA presentation are superseded by Appendix L.

T117 Dioxin/Furan Findings, PCB UCLs and Path Forward

Purpose of meeting

- Overview of technical work completed regarding dioxin/furans
- Overview of variability in Multiple Increment Sampling (MIS) PCB results and calculation of Upper Confidence Limits (UCLs) for PCBs in yards and streets
- Discussion of conclusions, areas of consensus and communication messages

T117 – Technical Findings

Regarding dioxin/furans in uplands, yards and streets

- We don’t have enough technical information to definitively state that T117 is the major source of dioxin/furans in yards
- T117 is likely a source of dioxin/furans in some streets
- Dioxin/furans in the former Malarkey area are likely from T117
- More investigations and data are needed to put the dioxin/furan levels in the streets and yards in context with other areas

T117 Agency Direction

Current direction regarding cleanup of dioxin in yards above 11 ppt

- PCB cleanup will be the driver for streets and yards
- Wherever PCB cleanup occurs, that will also address dioxins
- Where PCB level is below cleanup, but dioxins are above 11 ppt; no cleanup will occur as part of this removal action. Further investigation is needed.

T117 Areas of Policy Consensus

High dioxin levels in the neighborhood

- Agencies recognize there are areas where dioxin levels are higher than other urban areas
- With available data, we don't think T117 is the major source in this neighborhood
- We don't have enough data to know where the dioxin came from
- T117 cleanup cannot be delayed any further
- Dioxin levels don't require immediate action
- Agencies will try to offer some options for those concerned about dioxins

T117 – Direction Provided by EPA Regarding PCB Data

Multiple Increment Sampling (MIS) – evaluation of variability and calculation of Upper Confidence Limits (UCL)

- Decision Units (DU) with 3 replicate MIS results – those 3 values used to calculate UCL for DU
- DUs with only 1 MIS result – that sample result combined with estimates of variability from other DUs to calculate UCL for DU

T117 – Direction Provided by EPA Regarding PCB Data

Multiple Increment Sampling (MIS) – evaluation of variability and calculation of Upper Confidence Limits (UCLs) (continued)

- DUs in yards and streets with only 1 MIS result – 95% or better confidence that DU is below PCB cleanup level of 1 ppm when single MIS result is at or below 0.5 ppm

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T117 EAA SOILS INVESTIGATION

Multivariate Analysis of Chlorinated Dioxins and Furans

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INTRODUCTION

Infometrix was asked to evaluate a data set from the T117 EAA Soils Investigation using a multivariate perspective. Data were supplied in a CSV-formatted file and contained concentration estimates for 17 dioxin/furan congeners measured on 77 samples collected in the T117 study area. No further background information was supplied to facilitate interpretation.

Per request, analyses were performed on both the bulk congener concentrations as well as on TEF-scaled components. Because results from these two approaches may differ, any interpretations made from these analyses should take into account the nature of the differences, particularly in regard to interconversion of the source information resulting from the multivariate computations.

Finally, an additional request was made to analyze two samples from catch basins on the Uplands property.

The data as supplied contained, in addition to the congener concentrations, a categorical column indicating the sample type. In order to use this information for visualization of sample type in data plots, these categories were converted to numerical values according to the following table.

Table 1. Sample type code and coloring

Sample type	Category	Color
Streets	1	■
Yards	2	■
Uplands	3	■

The order of presentation of the congeners does not impact the data analysis, however, the order customarily used in studies of this type—increasing chlorination and increasing substitution position—was imposed and is shown in the following table.

Table 2. Congener names and ordering

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

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DATA ANALYSIS

Preliminary analysis was done by visual examination of various data plots and by Principal Components Analysis (PCA) to evaluate the suitability of the data for more extensive processing. Subsequently, mixture analyses were performed with the objective of finding possible end-members, or sources, of contributing profiles.

Visualization

It is common to present graphical views of environmental profiles as column plots, however, line plots are easier to appreciate trends and similarities among profiles when shown simultaneously and was chosen as the primary method of presentation in this study.

A line plot of an overlay of all of samples shows that there is a range of relative concentration, both among the different samples as well as across the different variables (the congeners). In particular, it is clear that congener 7, OCDD, is dominant for almost all samples, and that OCDF (congener 17) is the second most intense compound, with the exception of two samples.

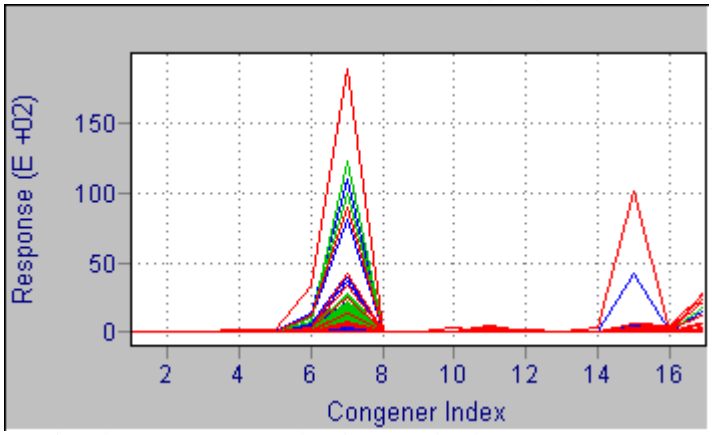


Figure 1. Line plot of all samples, color coded by sample type

If the samples' concentrations are normalized to minimize the variations due to different sample amounts, extraction efficiency, chromatographic injection, etc., the profiles that result can be useful to see differences among the patterns, not just the differences in abundance. A plot of the normalized profiles is shown in Figure 2.

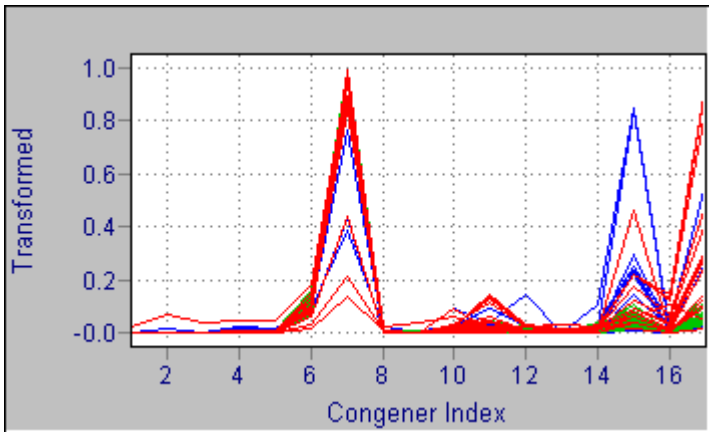


Figure 2. Sample line plots of normalized profiles, color coded by sample type

In this view, it is clear that the majority of the sample profiles are still dominated by the OCDD peak, but that there are also several samples for which OCDD is not the predominant compound and that one or two of the furans are major contributors in many samples.

A scatter plot showing pairs of variables simultaneously can show possible correlation between the variables while at the same time showing relative differences in abundance for these variables among the samples.

For example, in Figure 3, two of the upland samples are relatively higher in the PCDD than in the TCDD, while there is a range in concentration among the yard samples (green).

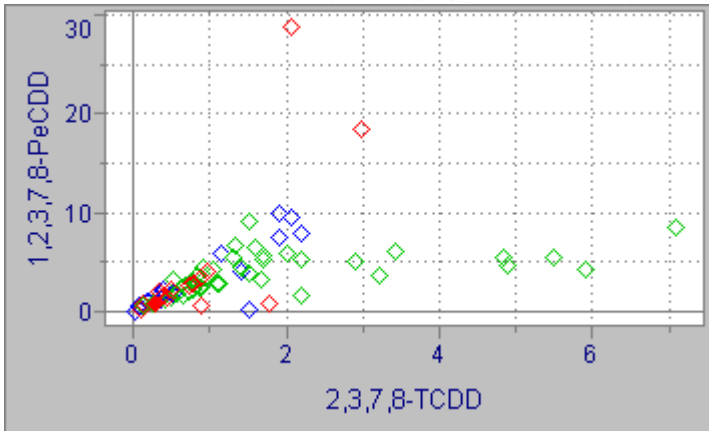


Figure 3. Scatter plot of the first 2 congeners, color coded by sample type

A multiplot can show several of these 2D scatter plots simultaneously. The following multiplot shows all seven of the dioxin congeners.

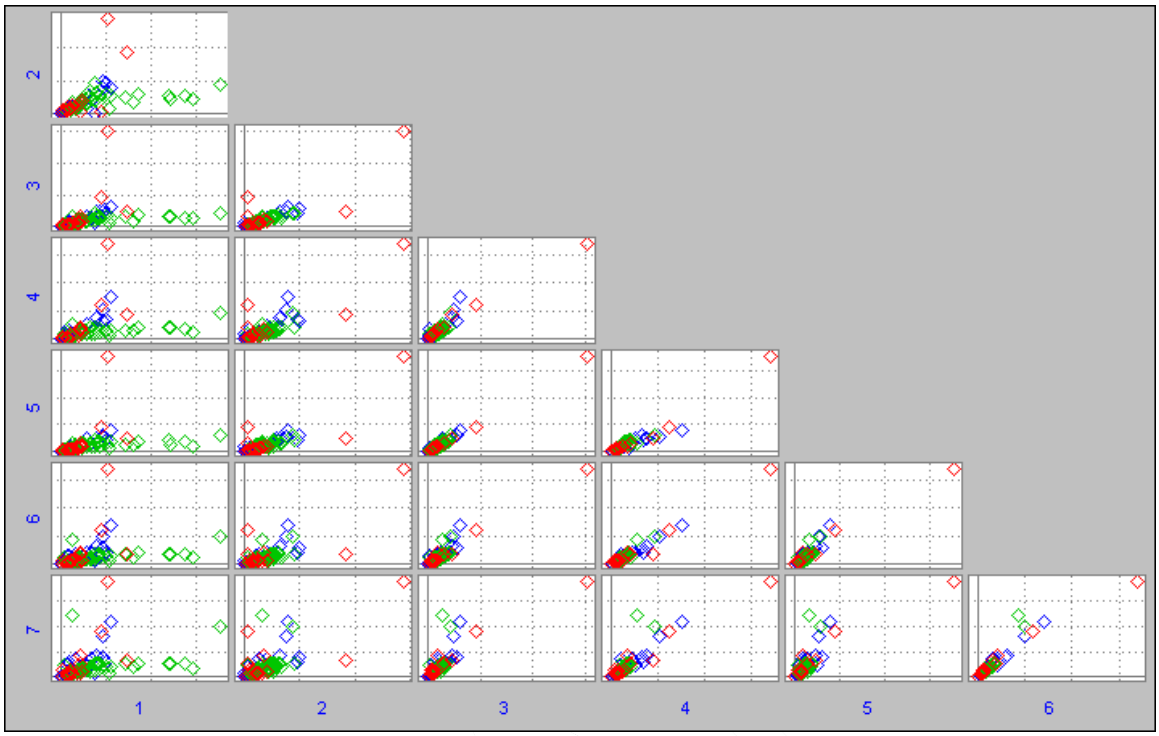


Figure 4. Multiplot of dioxin congeners, color coded by sample type; plot labels are congener indices

While TCDD response varies in relation to that of other congeners, there appears to be a direct correlation in response among the higher chlorinated dioxins.

The next plot shows a multiplot of the furan congeners, in which the yard samples have significant amounts of the TCDF and PCDF congeners but the other furan congeners are relatively minor contributors for these samples.

Many of the upland samples (in red) have relatively higher concentrations in many of the furans. This phenomenon will be revisited when discussing the multivariate analyses.

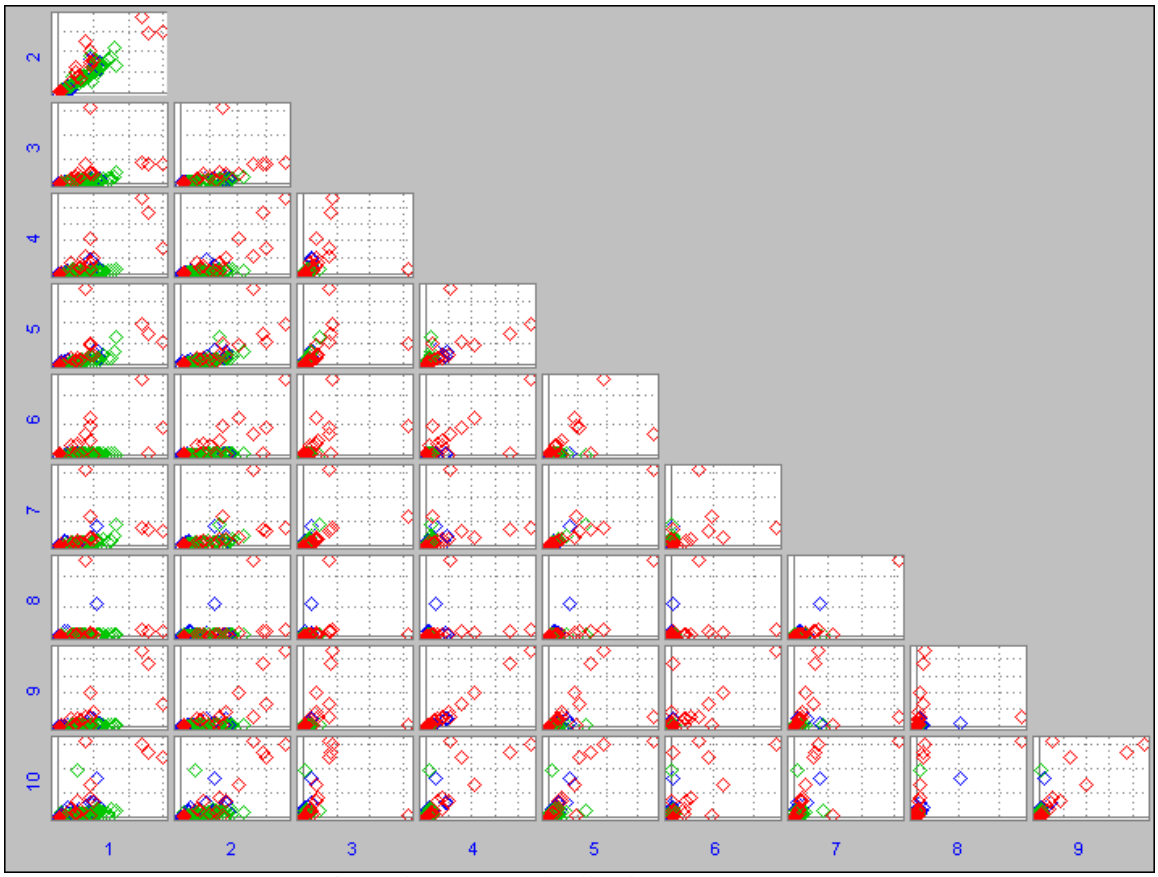


Figure 5. Multiplot of furan congeners, color coded by sample type; plot labels are congener indices

In only a small number of cases are there direct correlations among the furans (e.g., congener 4 vs. congener 9). A handful of Uplands samples (in red) appear dominant in almost all congeners.

Exploratory Analysis

Two exploratory algorithms—Principal Components Analysis (PCA) and Hierarchical Cluster Analysis (HCA)—were run on the data set to facilitate characterization of trends and groups in the data. The first analyses were run on the raw data, with no normalization, but with mean-centering as a preprocessing step.

In the following plot, the PCA scores from factor 1 are plotted as a function of sample index and show that samples occur at three differing levels: less than 2.5, 5 – 10, and near 20.

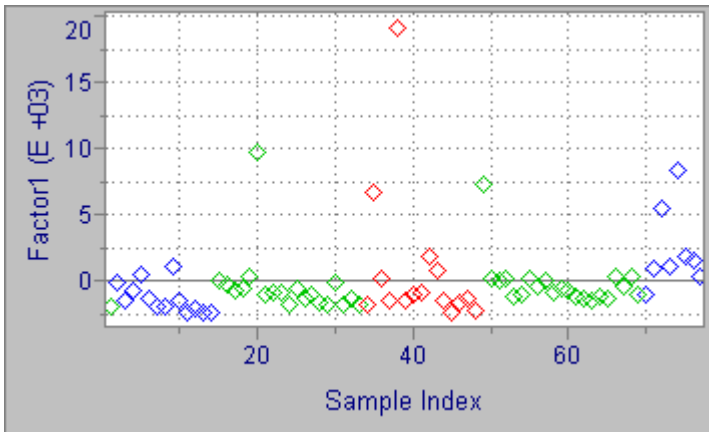


Figure 6. PCA scores of raw data, color coded by sample type

The factor 1 scores show that relative intensity is the major relationship among the samples. The corresponding line plots (below) are for the samples of lowest intensity on score 1, the 5 samples of moderate intensity, and one sample of high intensity.

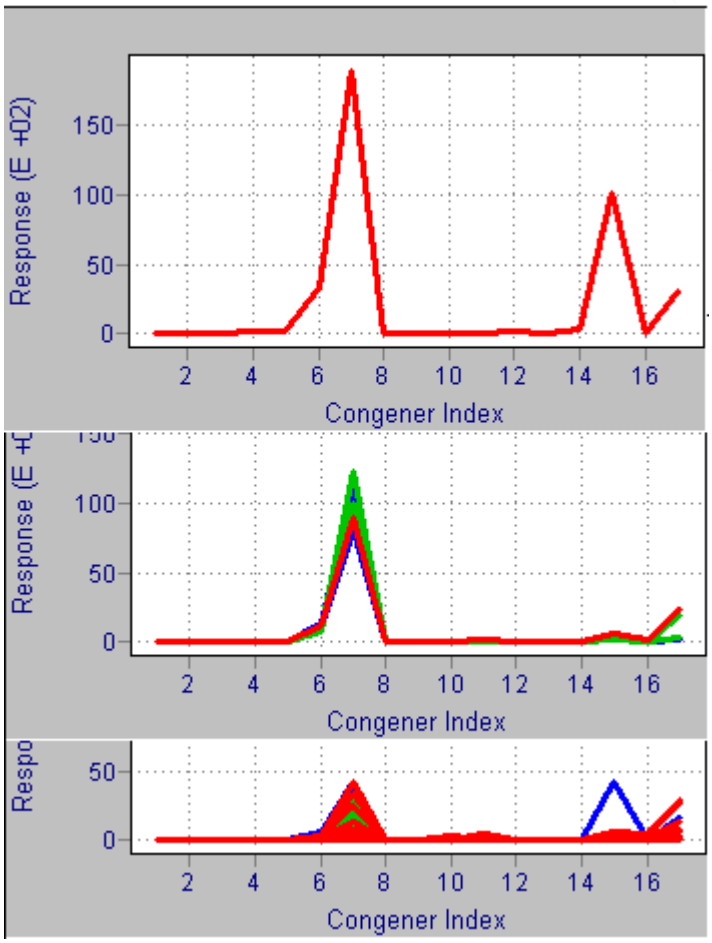


Figure 7. Line plots of samples corresponding to score 1 intensity, color coded by sample type

It is not surprising, then, that the first PCA eigenvector (Figure 8) shows congener 7 to be the heaviest loaded variable, expressing the largest variation in the data.

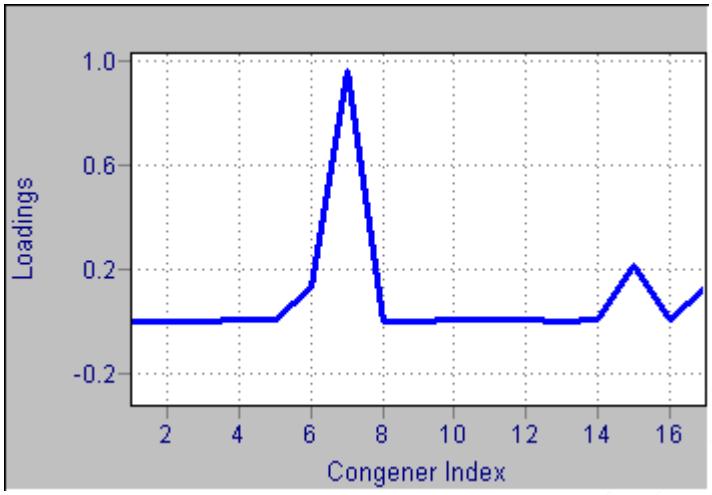


Figure 8. First eigenvector from PCA on bulk congener data

Similarly, the second factor is also dominated by features present in samples of relatively high intensity, shown as the filled points of Figure 9 which correspond to the profiles in the two upper plots of Figure 7.

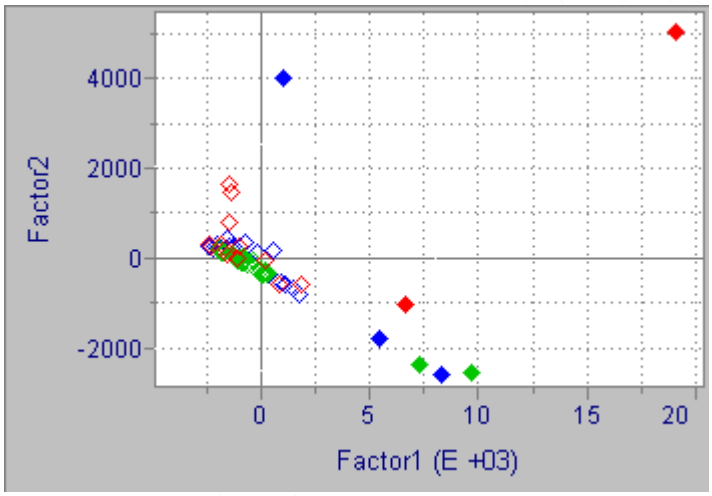


Figure 9. PCA scores from first two factors, color coded by sample type

To minimize the effects of widely varying intensities, the analysis was repeated with the data normalized prior to running the PCA. The corresponding PCA scores plot of the first two factors shows a number of samples that appear as extremes, however, these are not the same samples as in Figure 9 where the extremes were those of highest intensity. Instead, these extremes are those samples whose congener pattern differs the most from the majority. To make this more clear, a plot of the first 3 factors is shown next.

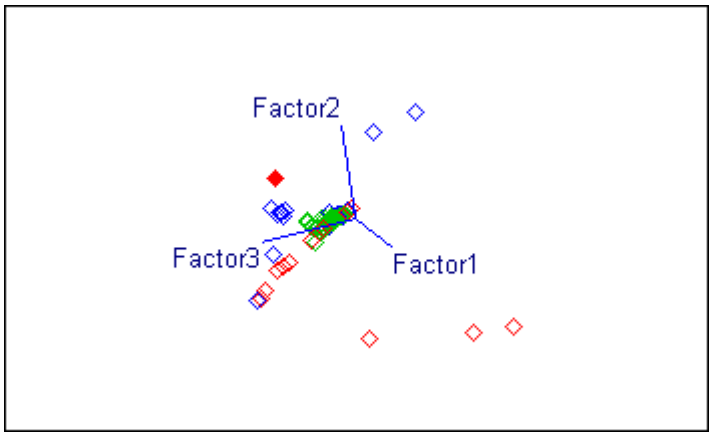


Figure 10. PCA scores of normalized data, color coded by sample type

In this view, there appear to be at least 5 groups of samples that appear as groups, indicating similarity in their patterns. This can also be observed in the HCA dendrogram where samples of similar composition should appear in distinct clusters.

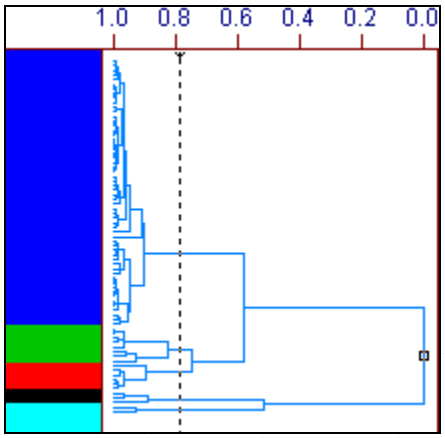


Figure 11. HCA dendrogram of normalized data, color coded by cluster

The large cluster of samples in the dendrogram (adjacent the blue band) correspond to the group of samples near the center of the scores plot. All of the yards samples fall in this group as well as a portion of the streets and uplands samples. The congener patterns for this group of samples are quite similar and are dominated by a single peak, that of OCDD, with only small contributions from other congeners, as seen in the following figure.

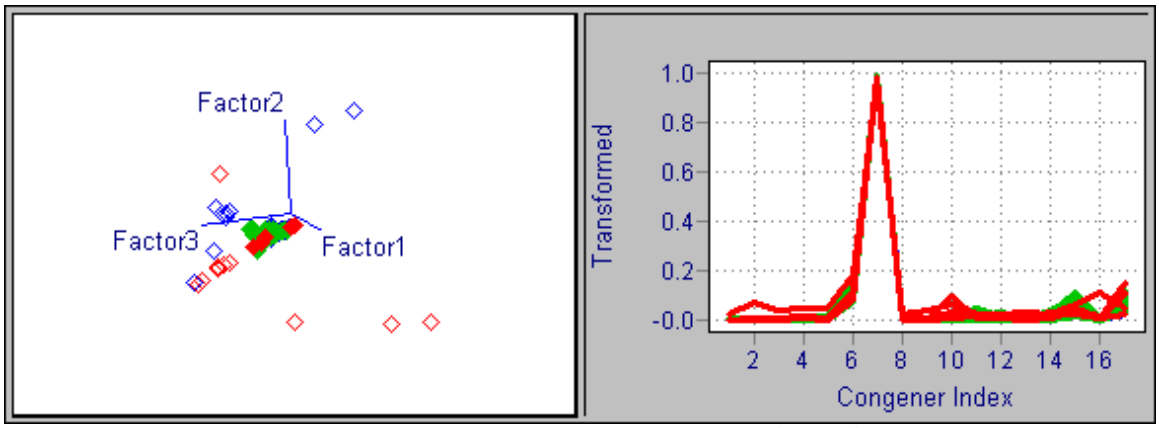


Figure 12. Congener patterns of cluster 1 samples, highlighted in the scores plot, color coded by sample type

The other 4 clusters exhibit different congener patterns. The following figures show the patterns that correspond to the samples highlighted in the companion scores plot.

The OCDD peak is dominant in the samples of cluster 2 (see Figure 13), followed by the OCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,7,8-HxCDF. Eight samples are in this group: 2 of the yards type and 6 of the uplands type.

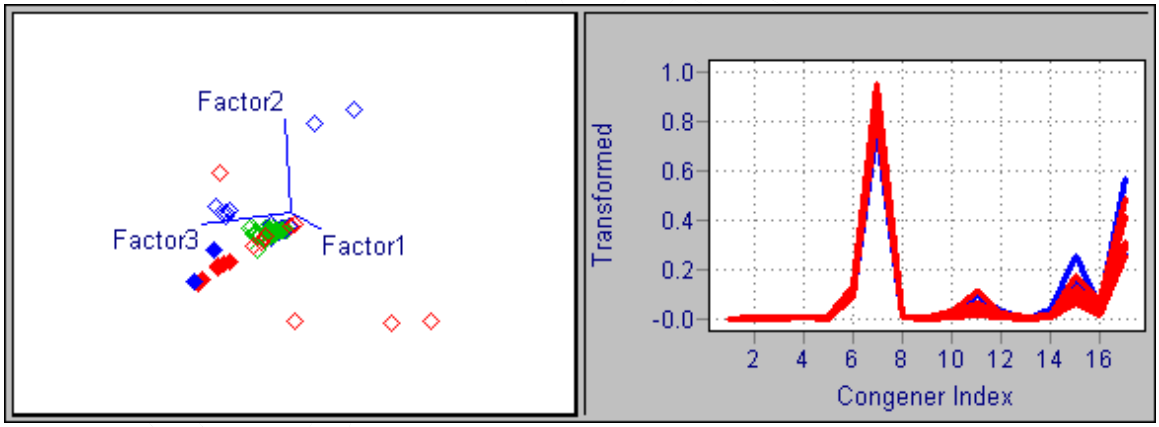


Figure 13. Congener patterns of samples in cluster 2, highlighted in the scores plot, color coded by sample type

The samples in cluster 3 (Figure 14) are dominated by OCDD, followed by lower intensities of 1,2,3,4,6,7,8-HpCDF, OCDF and 1,2,3,4,6,7,8-HpCDD. Of the six samples in this group, 5 are from yards and 1 from the uplands type.

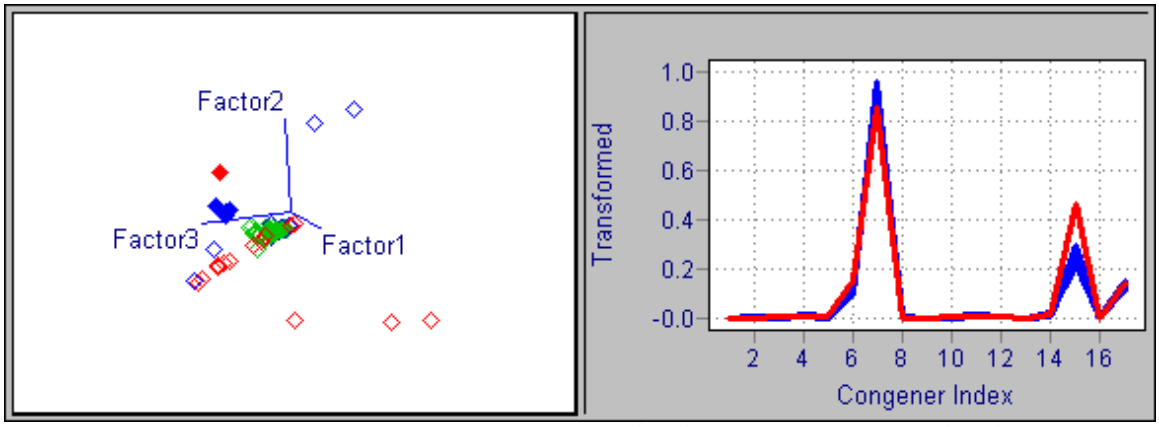


Figure 14. Congener patterns of samples in cluster 3, highlighted in the scores plot, color coded by sample type

The 3 samples in cluster 4 (see Figure 15), all of the uplands type, are dominated by OCDF, with lower intensities of OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDD. Finally, the last two samples are of the yards type; 1,2,3,4,6,7,8-HpCDF is the major peak in these samples, with lower intensities of OCDD and OCDF.

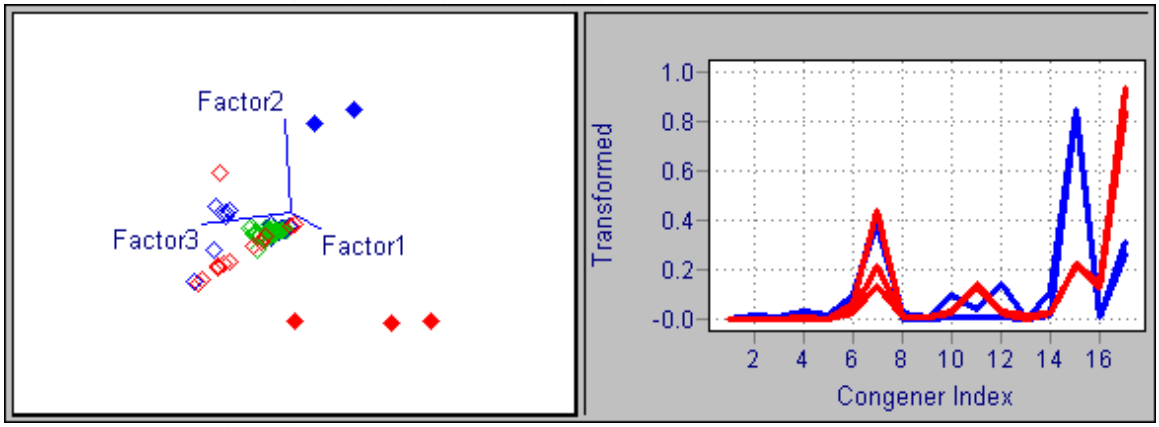


Figure 15. Congener patterns of samples in clusters 4 and 5, highlighted in the scores plot, color coded by sample type

Mixture Analysis – Bulk Congener Data

Because the loadings (or eigenvectors) that result from PCA are abstract, they may bear only some resemblance to patterns that represent the sources that make up the sample mixtures. Instead, a mixture analysis algorithm can prepare estimates of the patterns of proposed sources as well as the fractional compositions of the sources in each sample. For this study, the method known as Multivariate Curve Resolution by Alternating Least Squares (ALS) was applied.

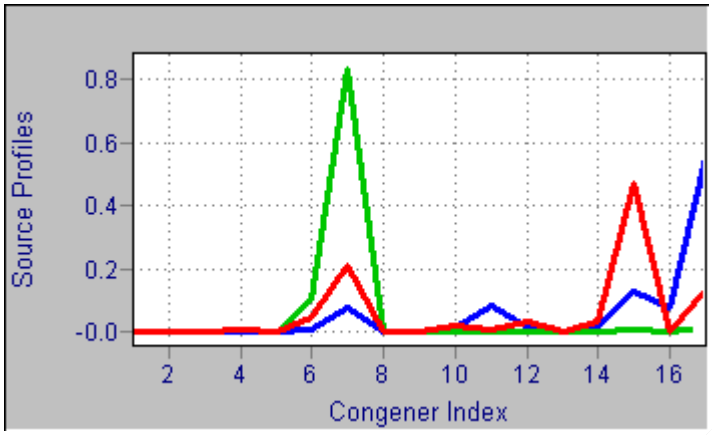
The ALS algorithm converges to a result after applying constraints to the estimates made during the alternating least squares steps. The constraints are natural: neither the congener intensities nor the source contributions are allowed to have negative values. In addition, mass balance can be imposed by a closure constraint: the contributions to a sample sum to a constant value.

It is possible mathematically to allow the ALS algorithm to compute solutions for any number of sources, therefore, it is necessary to guide it to a rational choice of the number of sources. One method for doing this is the Akaike Information Criterion (AIC). This method computes a goodness of fit for a statistical model—by comparing the AIC value for the computation of different numbers of sources, that computation which produces the lowest AIC should be the best. For the ALS processing of bulk congener data, without normalization, this metric indicated 3 sources as appropriate.

Many other methods exist for estimating the optimal number of factors or sources in a multivariate analysis. One of these, cross validation, was also applied in this study. For the raw data, 3 sources were found to be appropriate; with normalized data, 4 sources were indicated.

In any situation, however, it is important to consider not only the indication from the chosen metric, but to also evaluate the source patterns found for reasonableness and to look at the residuals from the calculations for unexplained information. Discussions that follow will consider these implications.

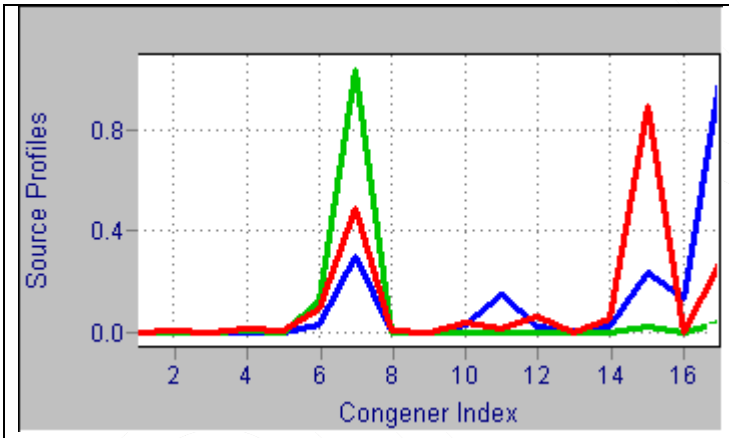
A 3-source ALS solution, with no closure, produces the source patterns below.



Source ID	Color
1	■
2	■
3	■

Figure 16. Source profiles from ALS with no closure, color coded by source ID

The result with closure produces the following source profiles.



Source ID	Color
1	■
2	■
3	■

Figure 17. Source profiles from ALS with closure, color coded by source ID

Source 2 (green) in these two solutions (without and with closure) are almost identical, as are the patterns for source 3 (red). Only source 1 (blue) differs between the two treatments, in the relative proportion of the OCDD congener.

Two other solutions were considered for this data set, with 2 and with 4 sources. With 2 sources, the residuals retain structure, indicating more sources are required to adequately describe the data, while with 4 sources, two of the source profiles obtained were almost identical. Thus, a 3-source solution was determined to be appropriate for the bulk congener data. A table of the source profiles can be found in the Appendix (Table 3).

The source contributions to the samples corresponding to the 3-source ALS result, with no closure, are shown in the following figure. The graphical representation of the closed ALS solution is similar and is not shown.

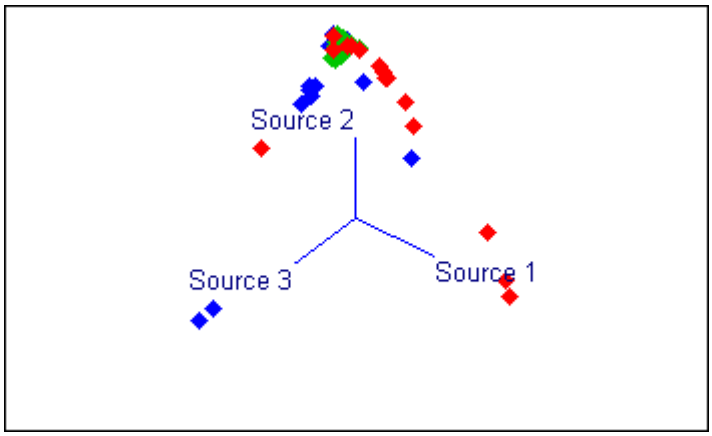


Figure 18. Source amounts from ALS, without closure, color coded by sample type

In this ternary diagram, the samples near the extremes of a source axis are those samples which most resemble the corresponding source patterns. Samples in the interior portion of the diagram would have compositions that are mixtures of the 3 sources.

In this result, several samples lie along edges between sources 2 and 3 and between sources 1 and 2. These samples would show patterns that would indicate their intermediate composition. No samples lie along the line between sources 1 and 3.

Thus, the 3 uplands samples to the lower right show, below, a pattern (upper figure) very similar to that of source 1 (lower figure) which shows the OCDF as dominant.

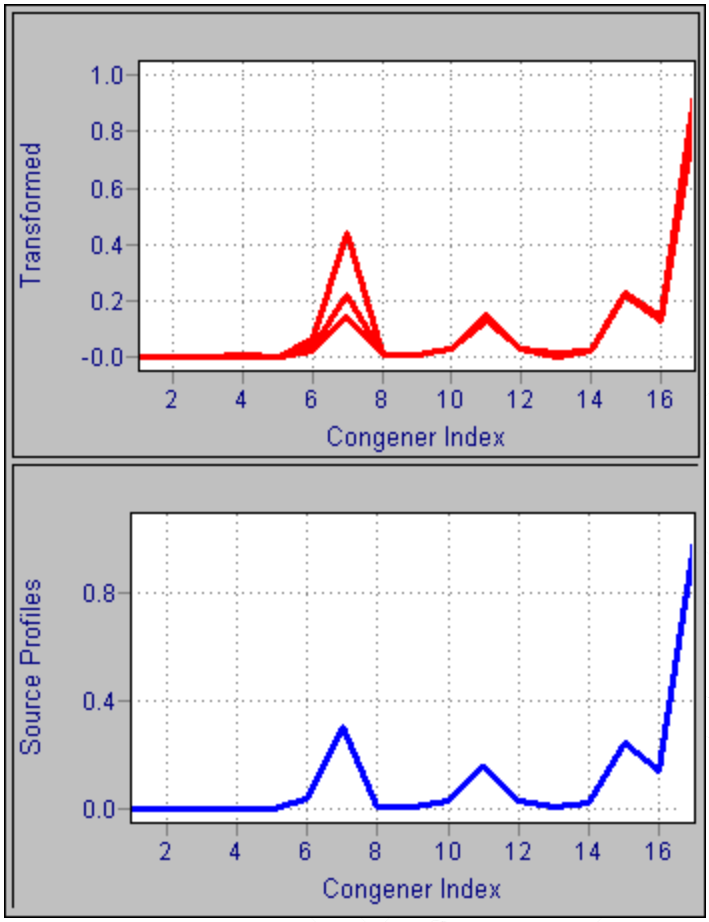


Figure 19. Selected sample profiles (upper) similar to those of source 1 (lower)

Similarly, the two samples in the lower left of Figure 18 have a pattern (shown in the upper figure, below) that resembles the pattern of source 3 (lower figure), with the dominant HpCDF peak.

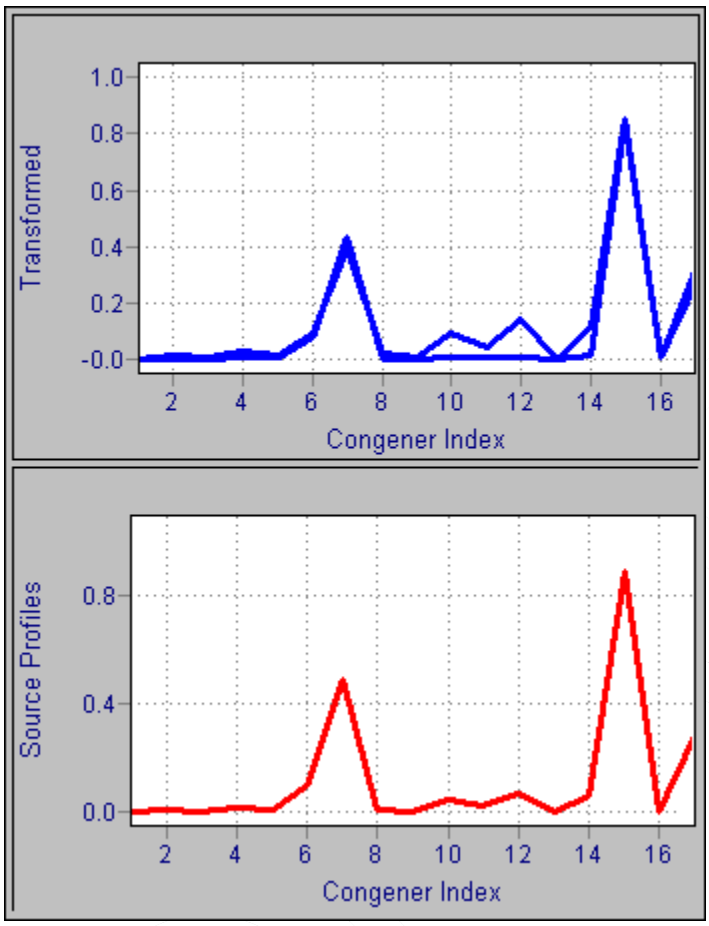


Figure 20. Selected sample profiles (upper) similar to those of source 3 (lower)

The majority of the remaining samples, which include all of the yard samples, show a pattern (a few examples are shown in upper figure) that resembles closely that of source 2 (lower figure) whose composition is over 80% OCDD.

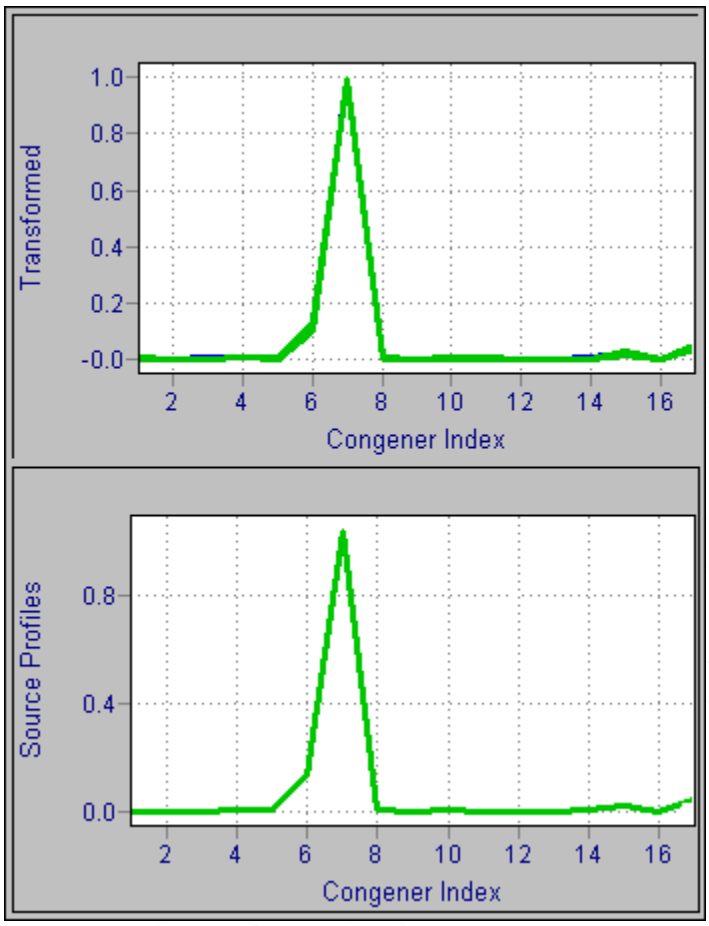


Figure 21. Selected sample profiles (upper) similar to those of source 2 (lower)

In the following figure, a number of uplands samples, plus two streets samples, fall on the mixing line between sources 1 and 2 (lower figure) and exhibit patterns (upper figure) intermediate between these two source patterns.

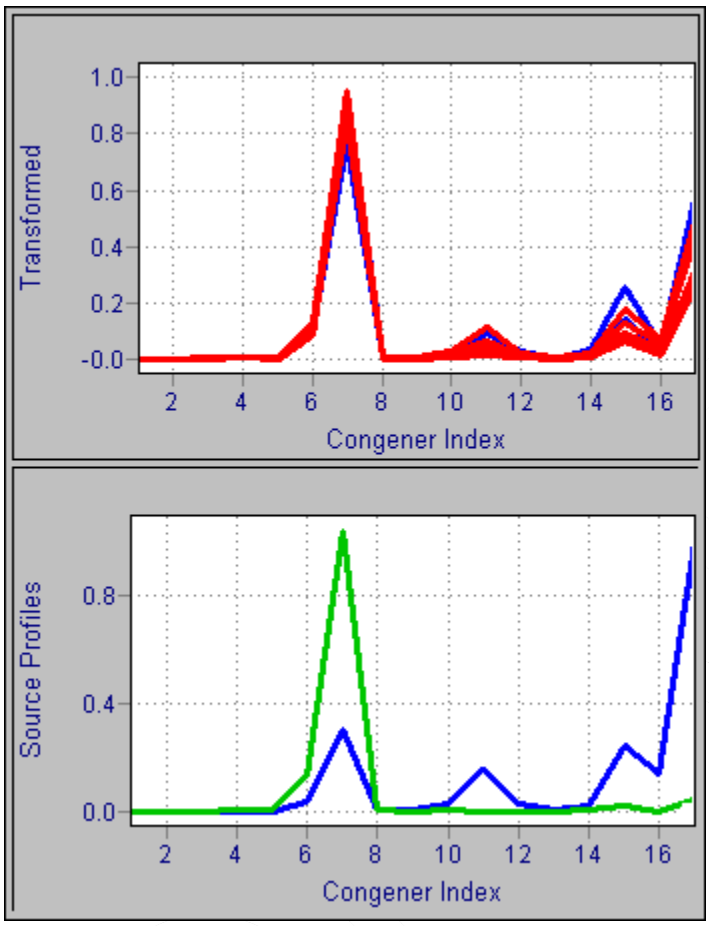


Figure 22. Selected sample profiles (upper) intermediate between those of sources 1 and 2 (lower)

And several streets samples, plus one uplands sample, show patterns (upper figure) intermediate between sources 2 and 3 (lower figure).

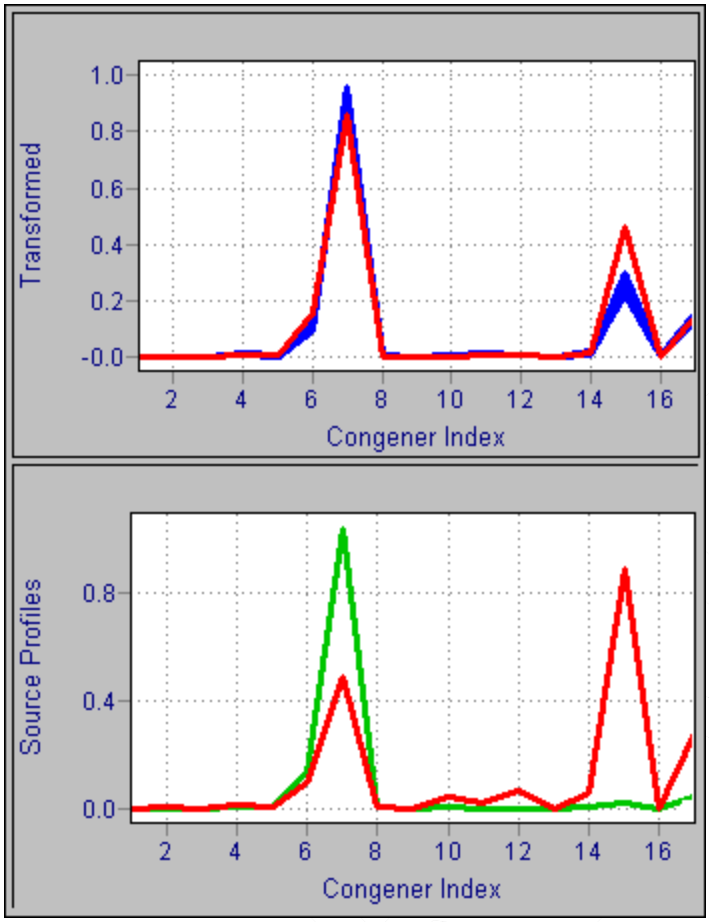


Figure 23. Selected sample profiles (upper) intermediate between those of sources 2 and 3 (lower)

The contributions from the 3 sources to each sample are shown in the Appendix (Table 4).

The additional samples—those from the catch basins—were evaluated by comparing their patterns to the mixture analysis model created from the original 77 samples in the T117 data set. If these test samples are similar to those in the training set, then their residual patterns (information left over after fitting to the model) should resemble those from samples in the model.

In the next figure, the residuals from samples in the model and those of the two new samples are shown. One of the catch basin samples shows a poor fit for the hepta-chloro dioxin, but, otherwise, these samples fit the model reasonably well.

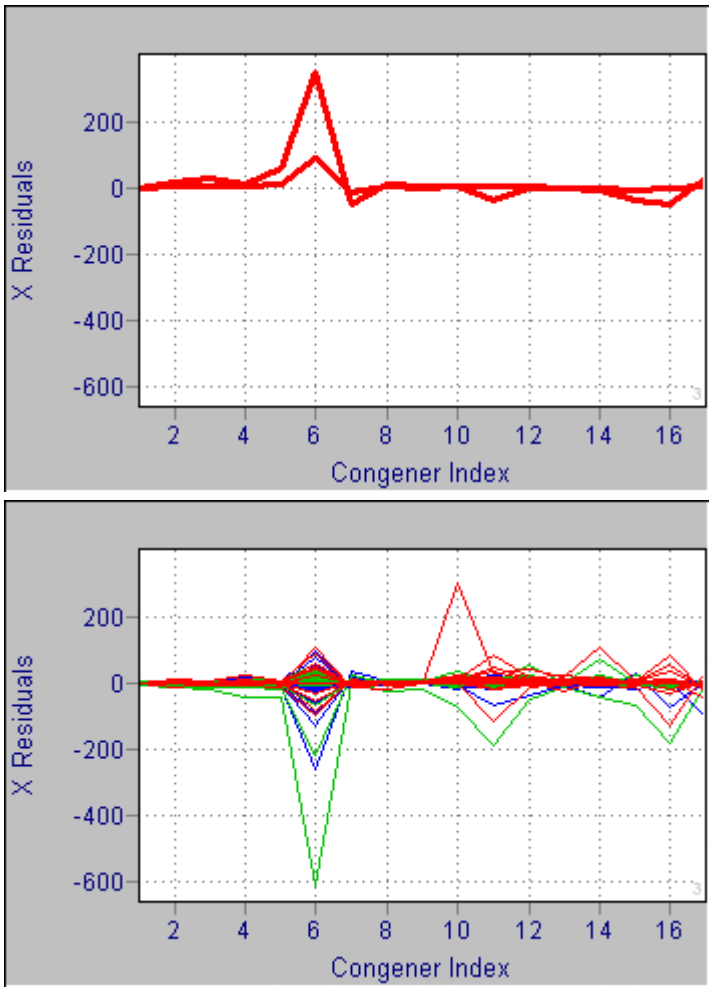


Figure 24. Pattern residuals from fitting the catch basin (upper) and training (lower) samples to the ALS model, color coded by sample type

A ternary plot (below) of the source contributions (normalized data) illustrates that the two catch basin samples are similar to most of the yard samples.

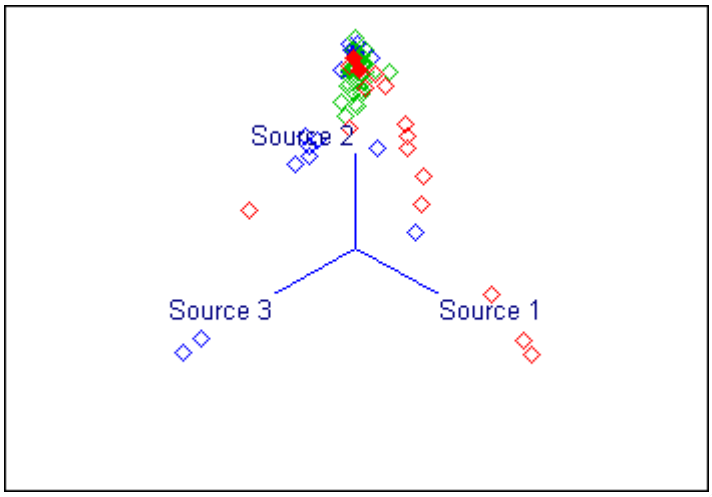


Figure 25. Source contributions, including the test samples (red, filled points) , color coded by sample type

Including the catch basin samples with the original T117 data has no effect on the extracted source profiles in a separate ALS analysis.

Mixture Analysis – TEF-scaled Data

Another strategy often used in the analysis of dioxins is to scale each congener independently, where the scaling is related to risk or toxicity. The most common method of scaling is by the toxic equivalency factor (TEF; for values, see Table 2) whose values have been suggested by the World Health Organization. Another effect of this scaling is that the range in scaled intensities across the dioxins can be as much as two orders of magnitude smaller than the range in raw congener concentrations. A ramification is that multivariate analyses of TEF scaled congeners will not be dominated by the ubiquity in the octa-chloro isomers. However, another effect of such scaling is that results of source apportionment may differ from those without scaling. The following analyses were performed on TEF-scaled data.

Viewing a line plot of the TEF-scaled T117 data shows that, although several congeners exhibit similar intensity, there remains considerable variation in sample intensity.

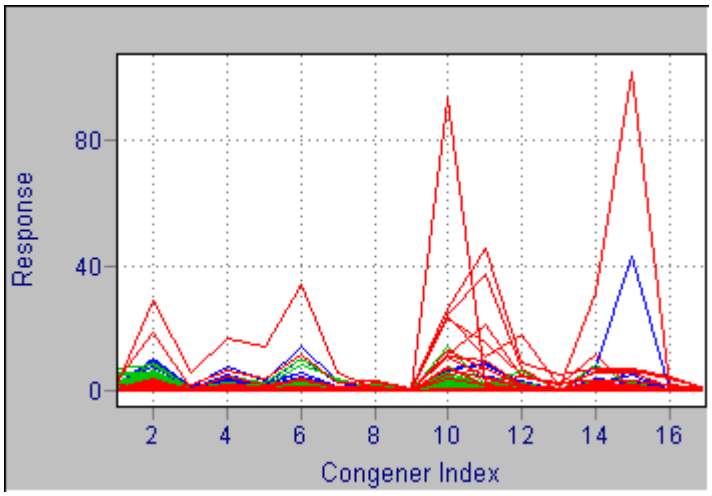


Figure 26. TEF-scaled data, color coded by sample type

If the TEF-scaled data are also normalized to minimize concentration effects, the variability in sample intensity is minimized and differences—and similarities—among patterns become more obvious.

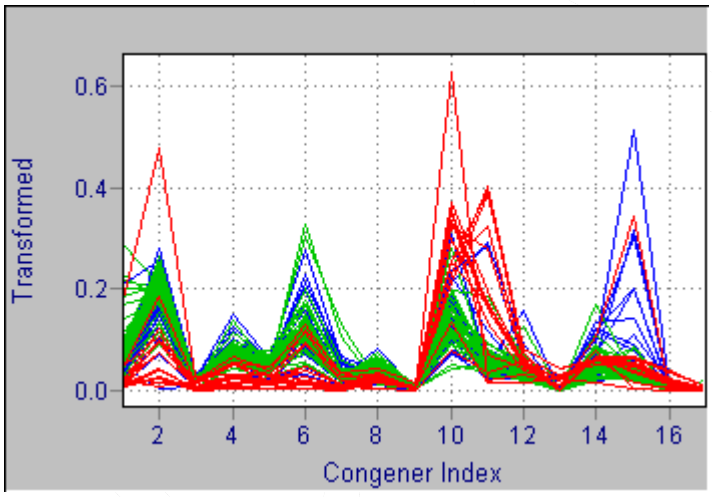


Figure 27. Normalized TEF-scaled data, color coded by sample type

In this view, as in the earlier discussions, the yards samples (in green) present a mostly uniform pattern, but in this scaling regime show intensities for many congeners within the same order of magnitude. A group of streets samples (in blue) show a dominance of a hepta-chloro furan isomer, while another group of uplands samples (in red) show greatest intensities in penta- and hexa-chloro furan isomers.

The AIC metric was not diagnostic for these data, but a cross-validation (leave-one-out) with PCA indicated 4 factors as optimal. However, rather than relying on a single diagnostic, the results with different numbers of sources were computed and evaluated for reasonableness, as discussed below. ALS was run with the TEF-scaled data and was also run with the same data normalized to area percent.

A 3-source solution from ALS produces the following source profiles.

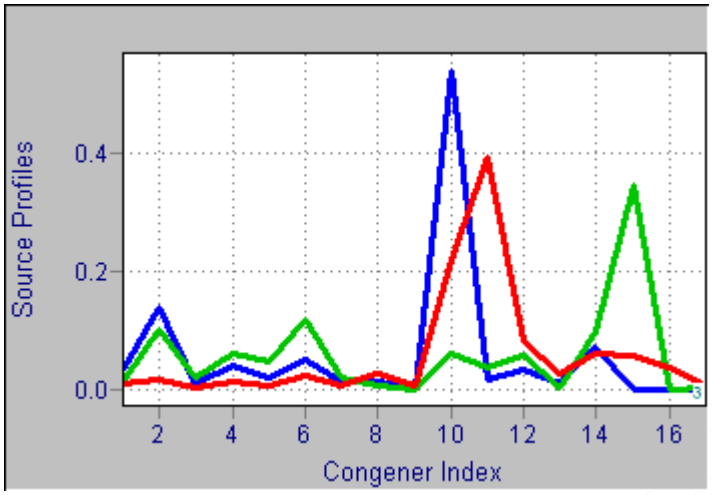


Figure 28. ALS 3-source solution, TEF-scaled data, color coded by source ID

However, the residuals, shown below, indicate important information has not been included in this model. For example, all of the yards samples (in green) show positive residuals in the dioxins; a residuals plot should ideally show distributions that look like noise, with no remaining structure.

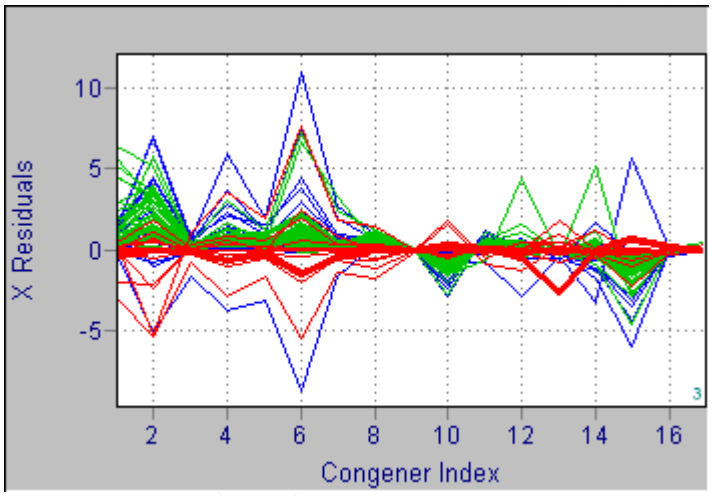


Figure 29. Residuals from 3-source solution, color coded by sample type

A 4-source solution incorporates information from the yards samples, producing the following set of source profiles.

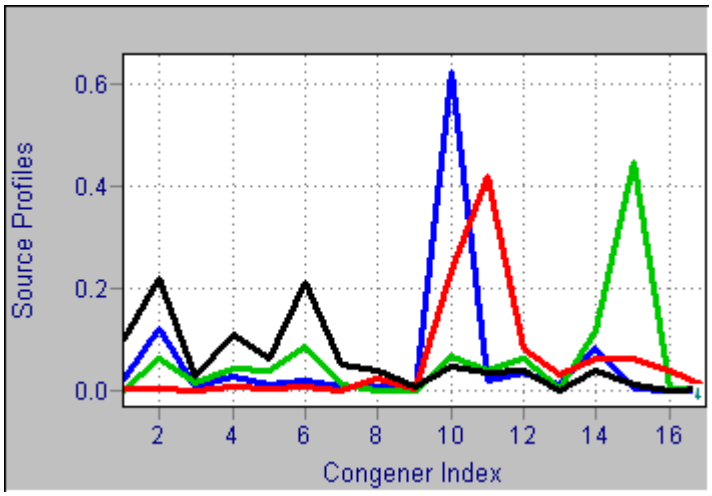


Figure 30. ALS 4-source solution, TEF-scaled data, color coded by source ID

Even in a 4-source model, the corresponding residuals exhibit some structural information in the dioxin congeners, implying that there may still be unmodeled information.

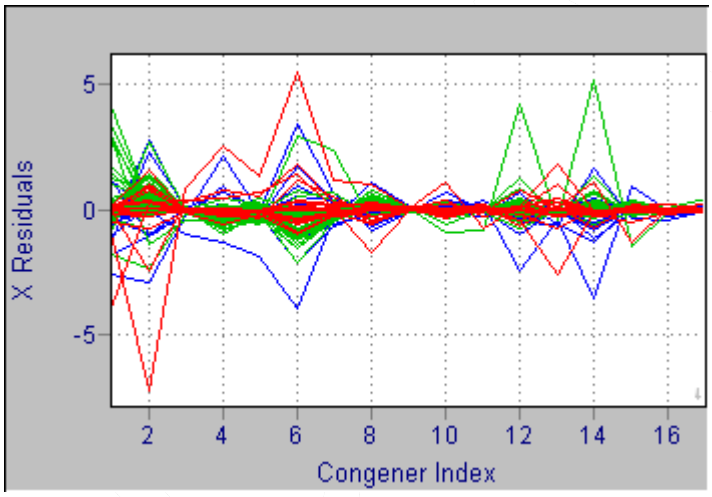


Figure 31. Residuals from 4-source solution, color coded by sample type

Computing 5 sources produces the profiles in the following plot, and the residuals retain only a minimal amount of structure.

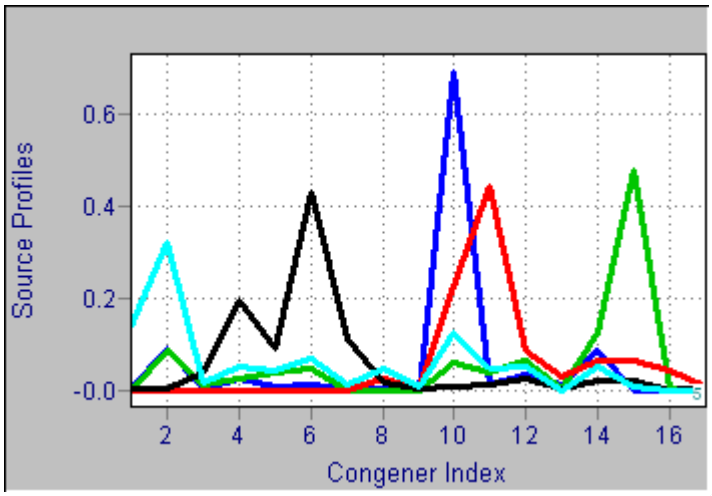


Figure 32. ALS 5-source solution, TEF-scaled data, color coded by source ID

The difference between these latter two solutions occurs only in the sources beyond 3: the pattern for source 4 in Figure 30 (in black) is divided into two patterns (black and cyan) in Figure 32, and the portion of the penta-chloro isomer that is part of source 1 (in blue) is reduced slightly. Sources 4 (and 5) relate almost exclusively to the yards samples. The following figure shows the TEF-scaled congener profiles for a selected subset of the yards samples.

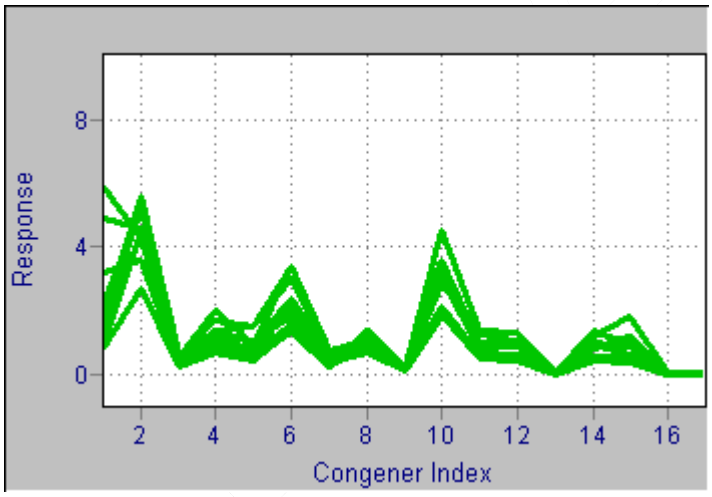


Figure 33. Patterns of TEF-scaled congeners in some yards samples, color coded by sample type

In this plot, the similarity between these patterns and those of sources 4 and 5 imply that these source patterns are the major contributors to the yards patterns. A table of the source profiles from a 5-source solution can be found in the Appendix (Table 5).

A similar story is told by an ALS analysis using normalized, TEF-scaled congener data. The following figure shows the source profiles from a 5-source solution in which

the similarity with the patterns in Figure 32 is obvious (the colors for the sources are different because they are computed in a different order during ALS calculations).

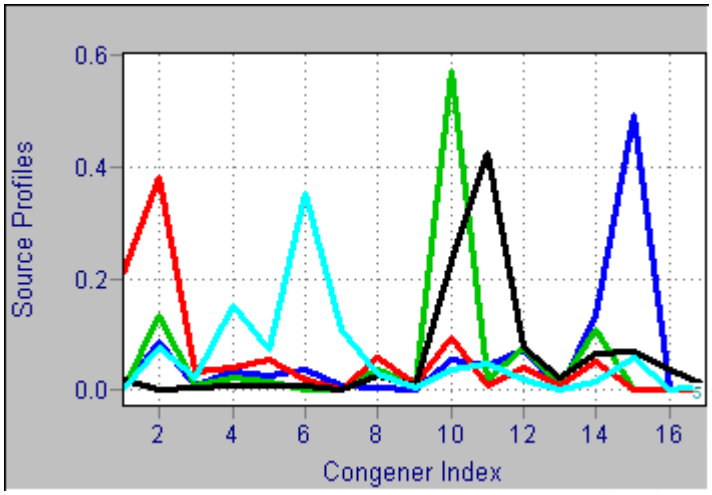


Figure 34. ALS 5-source solution, normalized TEF-scaled data, color coded by source ID

The yards samples subset shown in Figure 33 are shown again in the following figure of normalized TEF-scaled congener profiles.

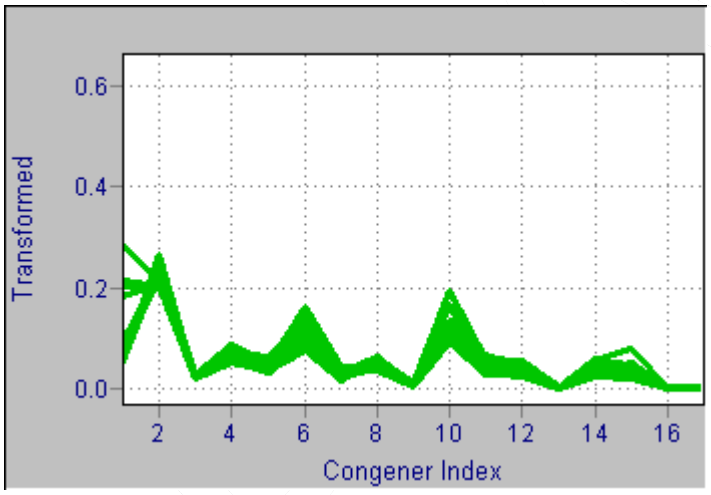


Figure 35. Patterns of normalized TEF-scaled congeners in some yards samples, color coded by sample type

Because the normalization has minimized variation in sample magnitude, the similarity in their patterns produces a more consistent plot when overlaid. By comparing patterns visually, these samples appear to be mixtures of primarily source 3 (red in Figure 34) and to a slightly lesser extent, sources 5 and 2. The numerical contributions of the 5 sources to the sample compositions are listed in the Appendix (Table 6).

Similar to what was done with the bulk congener data, the catch basin samples were compared to the mixture analysis model based on TEF-scaled data. And, as before,

there is evidence of poor fit to the model for one of the samples, as shown in the pattern residuals below.

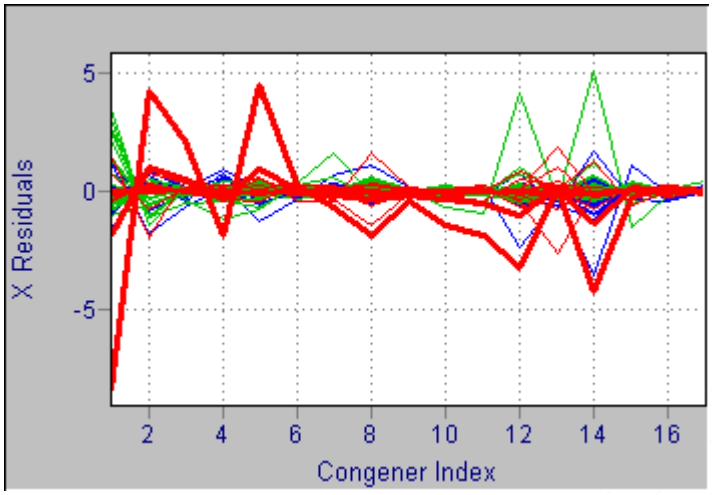


Figure 36. Pattern residuals from fitting the catch basin (thick lines) and training (thin lines) samples to the ALS model built from TEF-scaled data, color coded by sample type

If these test data are incorporated into a superset containing also the 77 T117 samples, a mixture analysis model with 5 sources produces a set of source patterns that are largely the same as before (compare with Figure 32).

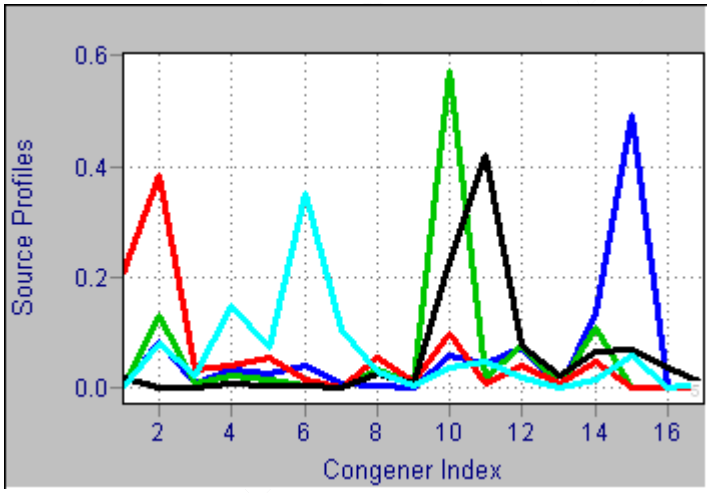


Figure 37. Source profiles from normalized TEF-scaled data, including catch basin samples, color coded by source ID

As mentioned previously, the Yards samples have predominant contributions from the two sources with higher proportions of chlorinated dioxins. Plotting the sample points as a function of the two sources (red and cyan in Figure 37) shows that the catch basin samples are similar to the Yards samples.

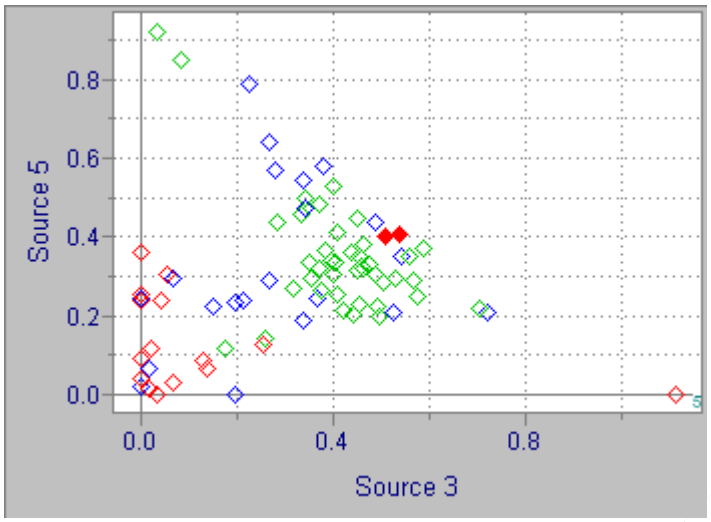


Figure 38. T117 plus catch basin samples (filled points), plotted against contributions from Sources 3 and 5, color coded by sample type

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APPENDIX – TABLES OF SOURCE PROFILES AND CONTRIBUTIONS

Table 3. Source profiles, bulk congener data

	Source 1	Source 2	Source 3
2,3,7,8-TCDD	0.000	0.000	0.000
1,2,3,7,8-PeCDD	0.001	0.001	0.000
1,2,3,4,7,8-HxCDD	0.002	0.001	0.000
1,2,3,6,7,8-HxCDD	0.004	0.005	0.000
1,2,3,7,8,9-HxCDD	0.004	0.003	0.000
1,2,3,4,6,7,8-HpCDD	0.082	0.097	0.000
OCDD	0.249	0.863	0.077
2,3,7,8-TCDF	0.000	0.001	0.005
1,2,3,7,8-PeCDF	0.000	0.001	0.003
2,3,4,7,8-PeCDF	0.002	0.002	0.015
1,2,3,4,7,8-HxCDF	0.006	0.000	0.077
1,2,3,6,7,8-HxCDF	0.007	0.001	0.015
1,2,3,7,8,9-HxCDF	0.001	0.000	0.005
2,3,4,6,7,8-HxCDF	0.013	0.002	0.011
1,2,3,4,6,7,8-HpCDF	0.492	0.000	0.118
1,2,3,4,7,8,9-HpCDF	0.005	0.000	0.075
OCDF	0.131	0.022	0.600

Table 4. Source contributions, bulk congener data

	Source 1	Source 2	Source 3
HA1	96.91	501.97	51.72
P100	477.69	2324.41	828.01
P88	438.96	916.95	85.02
P89	943.74	1490.37	157.31
P90	1290.36	2874.21	190.29
P91	464.42	1092.42	118.89
P92	49.67	438.15	6.84
P93	196.10	377.10	45.12
P94	8448.78	23.82	778.75
P95	307.11	724.11	855.19

	Source 1	Source 2	Source 3
P96	63.90	0.00	3.52
P97	20.85	275.01	4.76
P98	0.19	5.33	0.07
P99	0.99	19.59	2.01
YC02	167.48	2776.83	206.91
YC03	283.17	2259.67	272.78
YC04	228.52	1891.23	174.00
YC05	100.28	2016.28	94.77
YC06	127.65	3108.40	226.29
YC07	0.00	14028.98	2656.91
YC08	101.78	1621.04	58.86
YC09	73.69	1726.54	53.16
YC10	101.42	1764.94	178.89
YC11	29.59	742.31	42.86
YC12	99.54	2025.83	116.23
YC13	64.37	1263.53	61.97
YC14	79.88	1552.52	153.70
YC15	42.75	864.92	69.53
YC16	22.93	724.23	81.95
YC17	63.75	2591.34	151.89
YC18	40.82	690.08	35.66
YC19	111.15	1134.66	54.29
YC20	37.46	736.23	30.74
SB53-0.5	101.89	516.36	461.19
SB54-2	396.23	9939.53	3522.57
SB54-3.5	164.41	2837.13	1155.39
SB55-2	167.45	555.81	2151.60
SB55-3.5	20736.77	16044.06	0.00
SB56-1	53.90	955.35	99.80
SB57b-2	49.88	1537.16	198.26
SB57b-3.5	141.08	1442.95	993.14
SB58-0.5	128.61	4811.41	878.88
SB58-2	140.35	3790.59	0.00
SB59-1.5	239.43	0.00	4902.66
SB59-3	1.46	12.39	0.49

	Source 1	Source 2	Source 3
SB60-0.5	59.03	822.90	377.34
SB60-2	236.00	261.73	4371.99
SB60-3.5	5.95	84.54	38.35
DU01-surface	267.93	11482.25	90.30
DU01-subsurface	221.34	2940.65	112.15
DU02-surface	178.75	2836.55	123.00
DU02-subsurface	129.75	2967.80	125.30
DU03-surface	52.90	1484.94	68.64
DU03-subsurface	78.72	1652.75	69.26
DU05-surface	158.26	2943.91	314.43
DU05-subsurface	206.27	2130.87	234.08
DU07-surface	115.08	2867.57	28.86
DU07-subsurface	83.51	1831.29	33.86
DU09-surface	93.12	2059.16	41.56
DU10-surface	334.35	1746.14	143.18
DU10-subsurface	167.14	1337.70	73.27
DU11-surface	168.71	1220.20	132.78
DU11-subsurface	106.19	1050.31	119.49
DU12-surface	57.76	1365.75	91.94
DU12-subsurface	76.31	1131.60	105.29
DU13-surface	274.09	3047.55	92.44
DU13-subsurface	233.90	2132.88	103.96
DU14-surface	249.41	3086.76	172.88
DU14-subsurface	108.32	1584.16	99.16
DU16-surface	63.50	1596.75	91.64
DU16-subsurface	68.71	3880.90	336.32
DU17-surface	430.78	9280.50	0.00
DU17-subsurface	211.05	4105.83	51.91
DU18-surface	305.88	12663.22	134.70
DU18-subsurface	175.22	4938.84	87.83
DU19-surface	211.71	4574.41	176.37
DU19-subsurface	176.69	3185.32	206.39

Table 5. Source profiles, TEF-scaled data

	Source 1	Source 2	Source 3	Source 4	Source 5
2,3,7,8-TCDD	0.004	0.000	0.002	0.004	0.137
1,2,3,7,8-PeCDD	0.093	0.086	0.000	0.003	0.322
1,2,3,4,7,8-HxCDD	0.005	0.015	0.001	0.041	0.019
1,2,3,6,7,8-HxCDD	0.026	0.028	0.002	0.194	0.052
1,2,3,7,8,9-HxCDD	0.009	0.037	0.001	0.092	0.044
1,2,3,4,6,7,8-HpCDD	0.013	0.050	0.000	0.431	0.068
OCDD	0.005	0.000	0.000	0.112	0.014
2,3,7,8-TCDF	0.004	0.000	0.026	0.016	0.049
1,2,3,7,8-PeCDF	0.001	0.000	0.005	0.003	0.009
2,3,4,7,8-PeCDF	0.690	0.062	0.224	0.008	0.124
1,2,3,4,7,8-HxCDF	0.014	0.041	0.443	0.012	0.046
1,2,3,6,7,8-HxCDF	0.034	0.066	0.085	0.026	0.051
1,2,3,7,8,9-HxCDF	0.014	0.004	0.031	0.007	0.000
2,3,4,6,7,8-HxCDF	0.086	0.126	0.063	0.020	0.054
1,2,3,4,6,7,8-HpCDF	0.002	0.479	0.064	0.022	0.009
1,2,3,4,7,8,9-HpCDF	0.000	0.003	0.043	0.000	0.001
OCDF	0.000	0.003	0.009	0.009	0.000

Table 6. Source contributions, TEF-scaled data

	Source 1	Source 2	Source 3	Source 4	Source 5
HA1	1.18	0.65	4.55	0.91	4.72
P100	3.68	3.60	18.16	5.69	0.34
P88	0.96	4.48	1.06	1.54	3.54
P89	0.06	10.10	0.14	2.20	3.62
P90	0.19	13.30	1.34	4.25	2.76
P91	0.48	5.10	0.84	1.74	4.00
P92	0.62	0.42	0.36	0.48	2.51
P93	0.30	2.21	0.46	0.62	3.52
P94	0.79	87.39	1.31	0.00	0.00
P95	2.64	3.12	20.61	2.10	1.63
P96	1.23	0.77	0.27	0.00	1.21
P97	0.53	0.11	0.18	0.32	3.69
P98	0.00	0.00	0.00	0.00	0.05

	Source 1	Source 2	Source 3	Source 4	Source 5
P99	0.04	0.01	0.04	0.03	0.09
YC02	0.90	1.18	1.06	4.57	19.33
YC03	16.39	5.70	4.22	2.97	16.71
YC04	3.27	2.50	1.76	3.40	11.23
YC05	0.35	0.72	1.49	3.99	6.92
YC06	0.00	1.04	1.47	5.92	10.27
YC07	0.00	3.51	0.47	17.34	7.37
YC08	1.02	0.57	1.50	4.08	6.40
YC09	0.48	0.43	0.86	3.48	8.33
YC10	1.13	0.96	1.48	3.21	9.91
YC11	0.53	0.29	0.72	1.31	3.47
YC12	1.21	1.02	1.23	3.68	10.17
YC13	1.73	0.42	1.52	2.23	7.46
YC14	0.92	0.73	2.19	2.79	8.44
YC15	0.00	0.08	0.39	1.31	6.99
YC16	0.17	0.23	0.29	1.48	2.48
YC17	0.00	0.79	0.36	4.37	1.31
YC18	0.23	0.27	0.43	1.32	4.43
YC19	0.91	0.89	0.87	1.95	6.83
YC20	0.41	0.19	0.45	1.16	5.44
SB53-0.5	2.26	0.01	14.75	0.47	4.72
SB54-2	21.61	6.50	33.75	26.89	0.00
SB54-3.5	14.06	1.87	14.76	8.23	0.00
SB55-2	0.43	0.62	46.96	1.03	5.71
SB55-3.5	9.40	212.17	0.24	48.90	27.43
SB56-1	8.94	0.23	2.22	0.89	9.37
SB57b-2	3.97	0.44	3.82	1.93	1.29
SB57b-3.5	8.64	0.97	20.76	2.26	2.05
SB58-0.5	10.94	1.71	9.26	7.54	6.49
SB58-2	132.94	0.07	0.00	0.18	17.77
SB59-1.5	3.24	0.89	102.75	0.00	6.73
SB59-3	0.00	0.00	0.00	0.00	2.35
SB60-0.5	6.90	0.34	7.54	1.35	2.23
SB60-2	7.14	2.00	82.17	0.87	5.24
SB60-3.5	0.77	0.03	0.76	0.08	0.54

	Source 1	Source 2	Source 3	Source 4	Source 5
DU01-surface	0.78	0.98	0.63	17.72	29.58
DU01-subsurface	5.88	2.59	2.06	3.14	24.30
DU02-surface	4.86	1.85	1.85	4.03	17.76
DU02-subsurface	0.62	0.27	0.33	4.28	20.41
DU03-surface	0.35	0.43	0.00	2.41	6.09
DU03-subsurface	0.67	0.41	1.00	2.73	8.54
DU05-surface	0.59	1.44	1.05	5.04	16.11
DU05-subsurface	0.92	1.62	0.94	4.07	15.57
DU07-surface	0.00	0.00	0.00	5.05	17.51
DU07-subsurface	0.00	0.00	0.00	2.02	18.00
DU09-surface	0.00	0.11	0.16	3.51	12.97
DU10-surface	2.15	3.21	0.35	2.00	14.40
DU10-subsurface	1.82	1.47	0.35	1.48	12.53
DU11-surface	3.27	1.50	1.40	1.64	14.86
DU11-subsurface	2.28	0.99	0.72	0.90	12.20
DU12-surface	1.22	0.45	0.20	1.82	7.60
DU12-subsurface	1.30	0.64	0.10	1.90	8.28
DU13-surface	1.94	1.98	1.70	5.18	15.71
DU13-subsurface	2.13	1.83	3.88	3.58	16.75
DU14-surface	1.12	1.65	2.69	5.31	19.27
DU14-subsurface	0.62	0.83	0.51	2.11	11.54
DU16-surface	0.68	0.48	0.59	2.86	5.22
DU16-subsurface	0.79	1.07	0.71	5.71	7.21
DU17-surface	1.46	2.06	2.80	19.25	20.57
DU17-subsurface	0.53	1.39	1.00	7.70	11.37
DU18-surface	0.91	0.82	0.76	28.83	22.24
DU18-subsurface	0.67	0.61	0.54	11.45	18.31
DU19-surface	1.49	0.97	0.91	9.05	27.33
DU19-subsurface	0.94	0.75	1.94	5.72	26.45

Dioxins at T-117

Source evaluation summary

November 13, 2009

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Discussion Topics

- Site background
- Statement of the problem
- Criteria and lines of evidence
- Use of concentrations and TEQs
- Evaluation of the lines of evidence
- Answering the question
- Updating the CSM

T-117 Dioxin Investigations - Streets and Yards

Review of historical data in 2008 identified 2005 samples with high concentrations of dioxins.

- 2005 street dust and catch basin samples (SD52 and CB41)

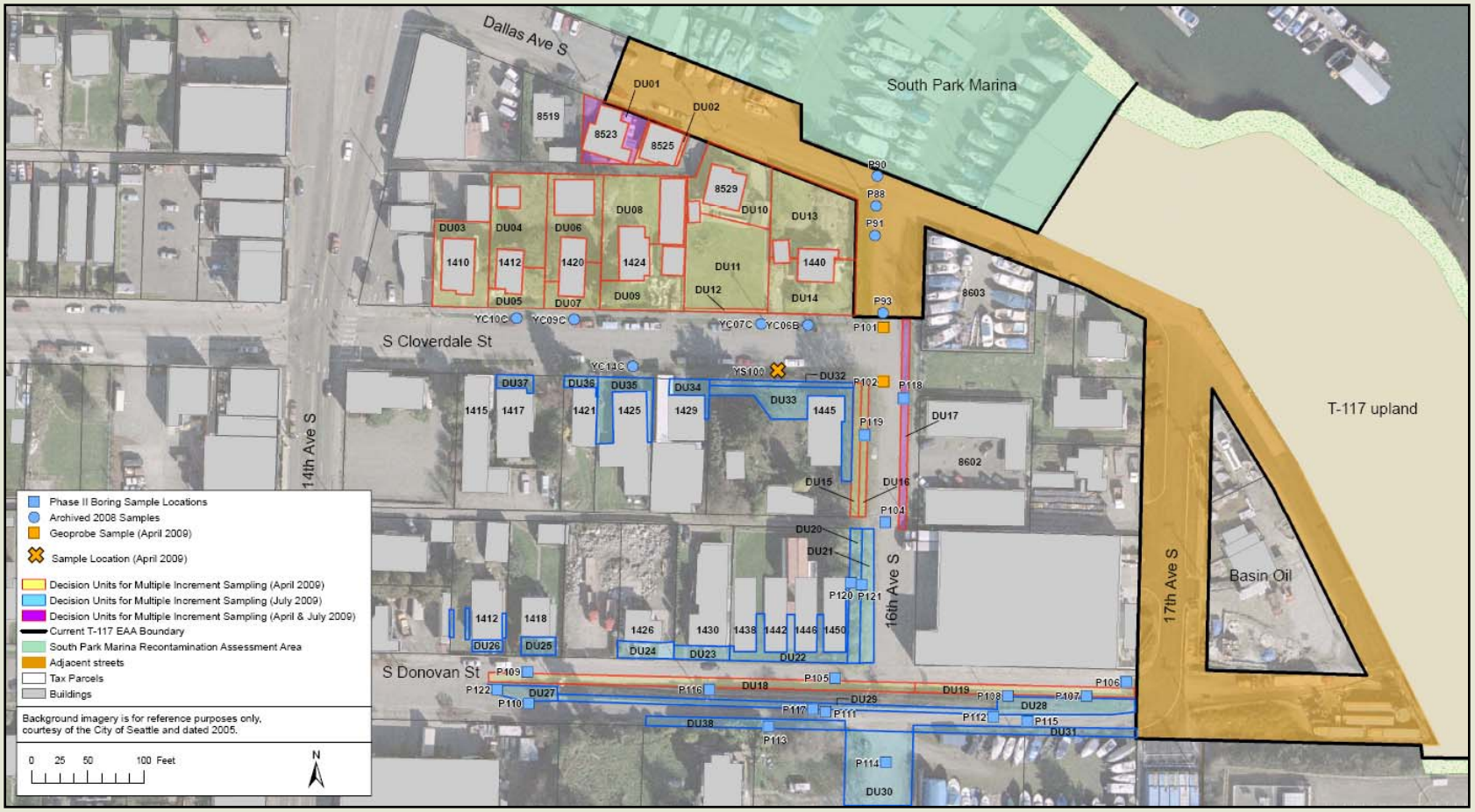
2008 investigation

- Three-point composite sampling in yards and borings in streets (also sampling in uplands and sediments)
- Dioxin and PCBs above CULs at some locations in yards on Cloverdale and in street borings

2009 investigations

- MI sampling protocols
- April investigation
  - Residences north of Cloverdale and ROW areas on 16th and Donovan.
  - PCB detections near the CUL at some yard locations
  - PCB detection greater than CUL at some ROW locations
  - Selected samples analyzed by Ecology for dioxins resulted in detections between ~9 and ~50 ng/kg
- August investigation
  - Residences south of Cloverdale Ave. S and additional ROWs on 16th and Donovan
  - PCB detections near the CUL at some yard locations on Cloverdale
  - PCB detections greater than CUL at some ROW locations
  - Dioxins not analyzed

Site Map


Dallas Ave S
South Park Marina
S Cloverdale St
14th Ave S
16th Ave S
17th Ave S
S Donovan St
T-117 upland
Basin Oil
Phase II Boring Sample Locations
Archived 2008 Samples
Geoprobe Sample (April 2009)
Sample Location (April 2009)
Decision Units for Multiple Increment Sampling (April 2009)
Decision Units for Multiple Increment Sampling (July 2009)
Decision Units for Multiple Increment Sampling (April & July 2009)
Current T-117 EAA Boundary
South Park Marina Recontamination Assessment Area
Adjacent streets
Tax Parcels
Buildings
Background imagery is for reference purposes only, courtesy of the City of Seattle and dated 2005.
0 25 50 100 Feet
N

Statement of the Problem (As a Question)

Is the T-117 site a source of dioxins and furans to adjacent streets and residential yards, and if so, what is the contribution?

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Conclusion

Based on the results of unmixing and other lines of evidence, the fraction of dioxins/furans in yards that can be attributed to T-117 sources is small — in the range of zero to a few percent.

Several street samples adjacent to the upland portion of the site have a dioxin/furan pattern consistent with a PCB source at T-117.

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Criteria and Lines of Evidence

A. Pattern
   1. Similarity Analysis
   2. Discriminant Function Analysis
   3. Unmixing Analysis
B. Pathway
   1. Correlation of PCBs and dioxins/furans in yards
   2. Wind patterns
C. Gradient
   1. Spatial patterns of concentration
   2. Regression of concentration with distance

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Concentrations vs. TEQs for Data Analysis

- Concentrations represent the material released and dispersed
- TEQs represent the risk
- There should be 1:1 correspondence and equivalent conclusions
  - But detection frequencies are lower for congeners with high TEFs
- Most analyses were carried out using both approaches

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LOE A1: Similarity Analysis

- Dioxin and furan concentrations were log-transformed, centered, and scaled consistent with standard methods to emphasize pattern
- Similarity calculated between each pair of samples
- The strongest similarities for each sample were evaluated

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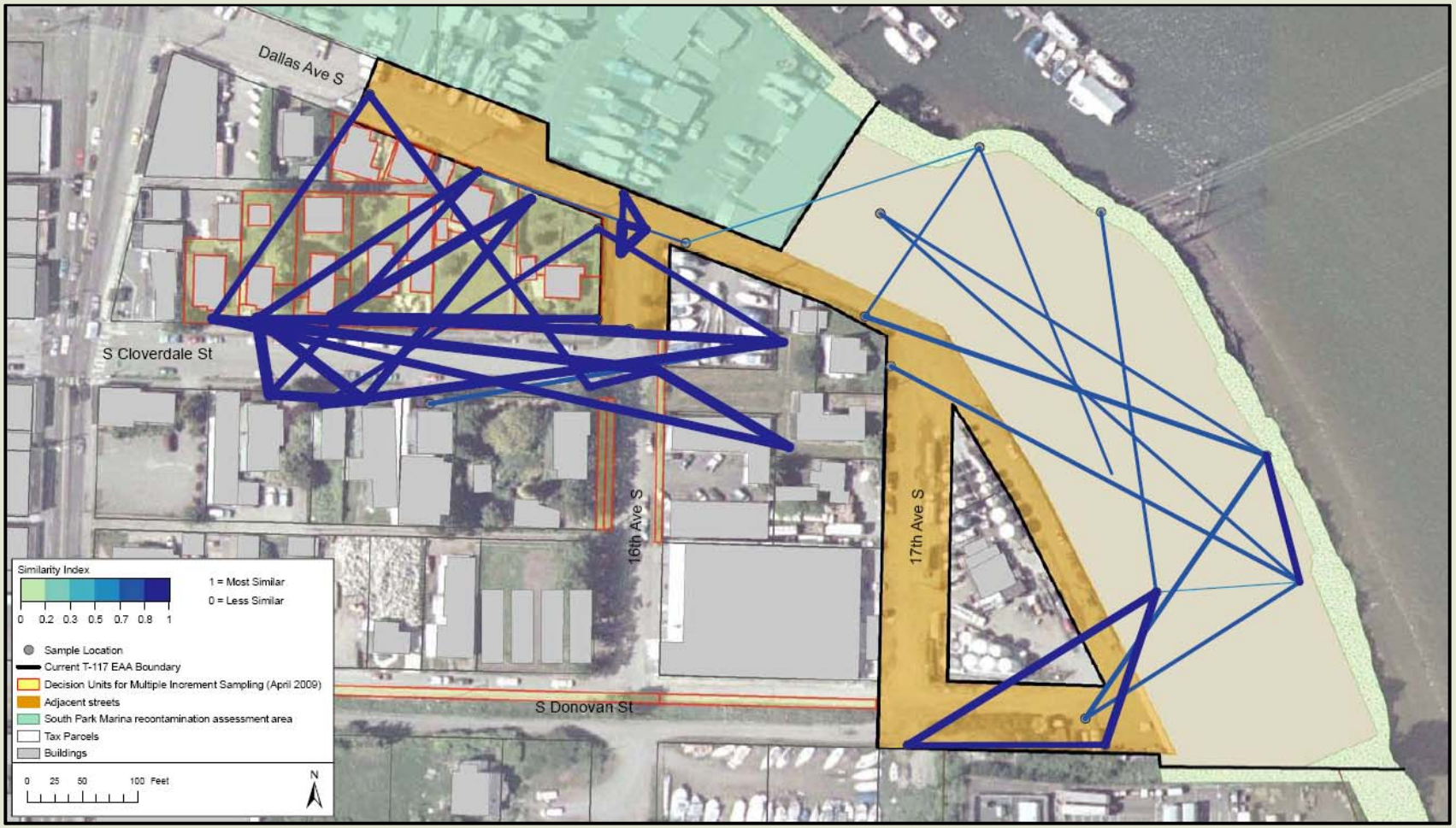
LOE A1: Similarity Analysis Results



LOE A2: Discriminant Function Analysis

- Multivariate method classifies target samples as having one of a set of possible patterns
- Potential signatures (patterns):
  - T-117 upland (from trackout and combustion)
  - LDW sediment
  - Seattle catch basin sediment
  - Auto exhaust
- Target samples: all yard and street samples
- All data log-transformed, centered, and scaled

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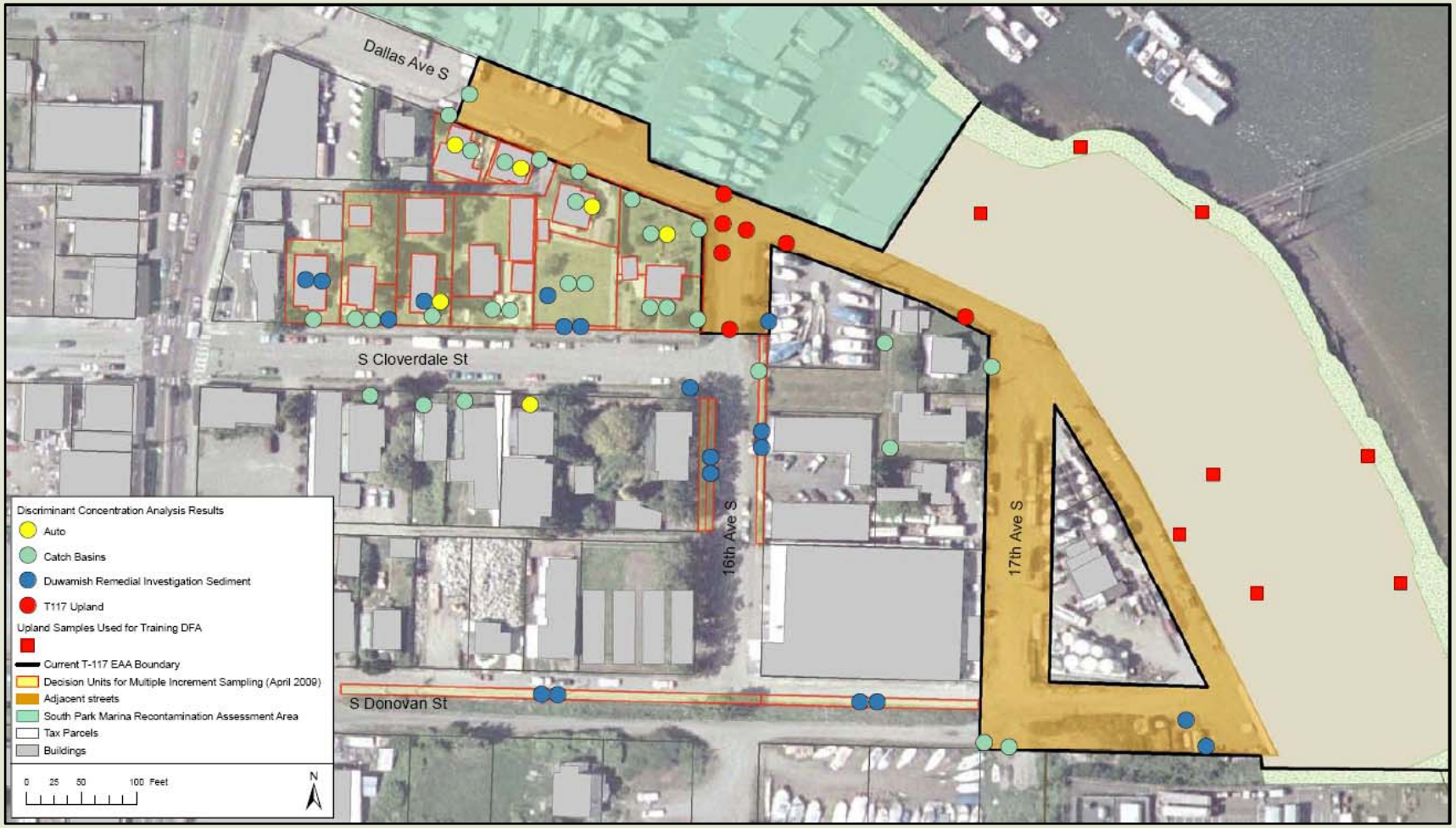
LOE A2: Discriminant Analysis Results—Concentrations



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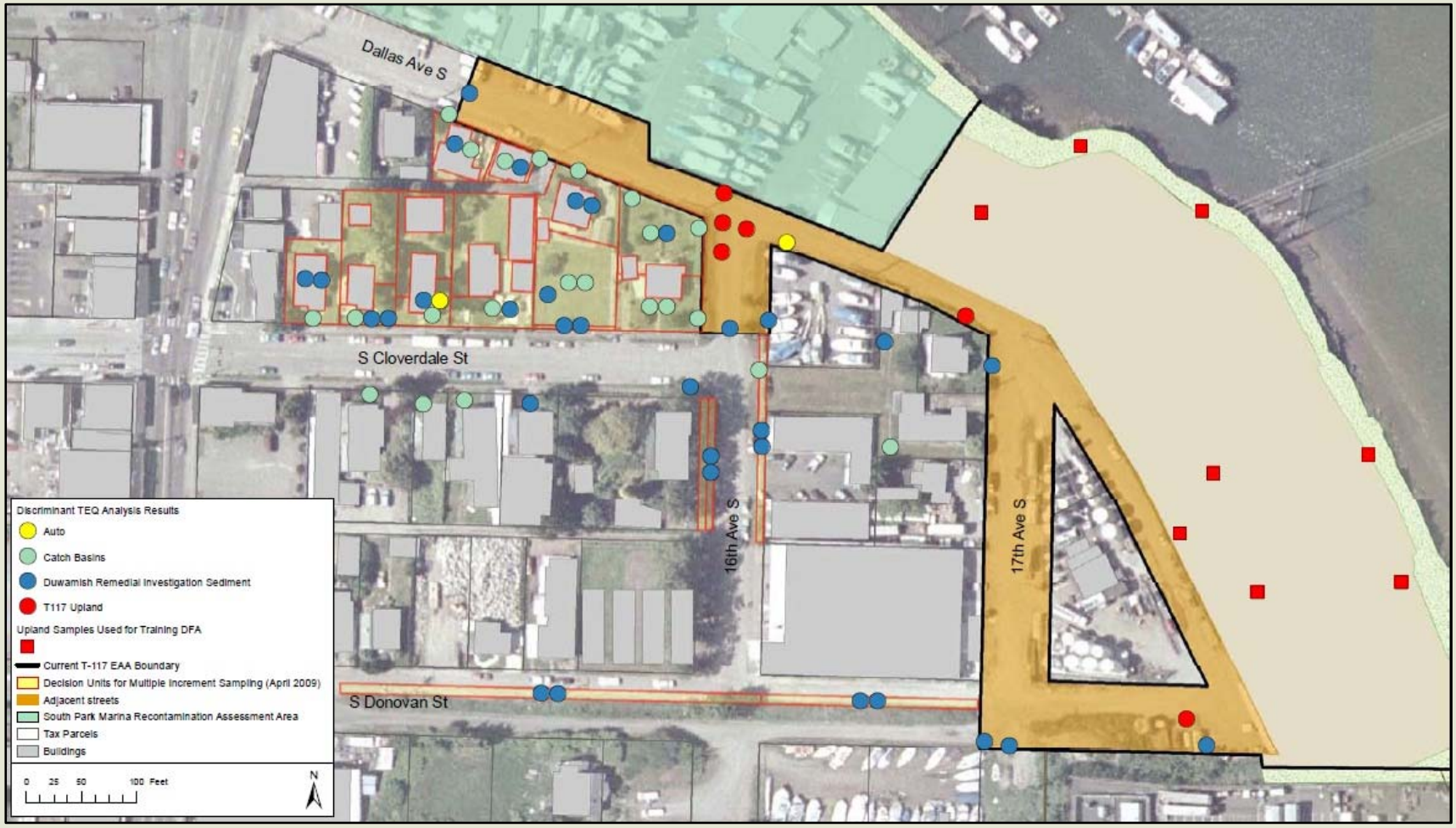
LOE A2: Discriminant Analysis Results—TEQs



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LOE A3: Unmixing Analysis

- A multivariate technique to estimate the composition of materials that could have been mixed to produce observed sample results
- Unmixing analysis performed by both Integral and Infometrix
- Data handling
  - No transformation, centering, or scaling—magnitude matters
  - Infometrix converts concentrations to percent of total
  - Analyses run on concentrations and TEQs

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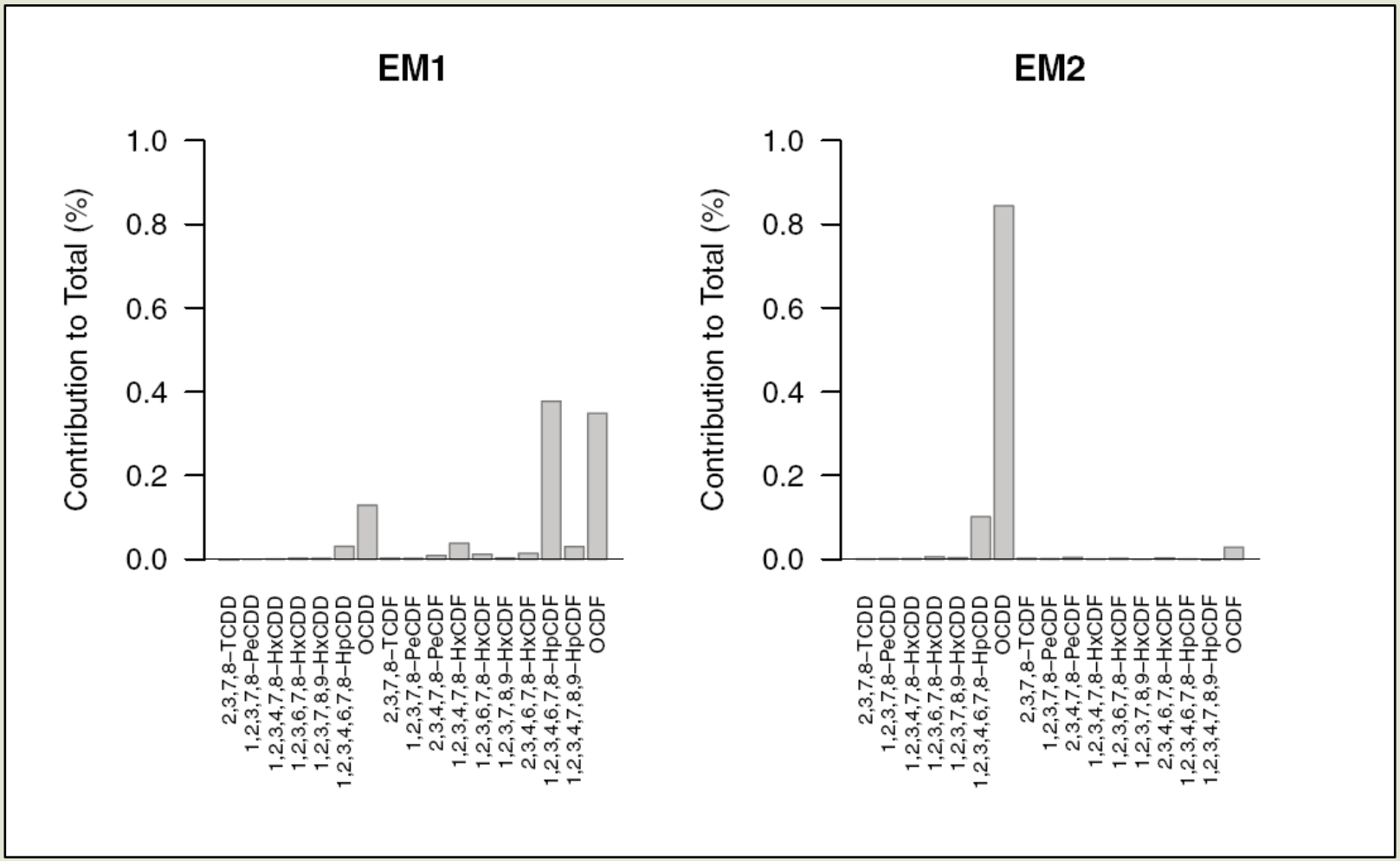
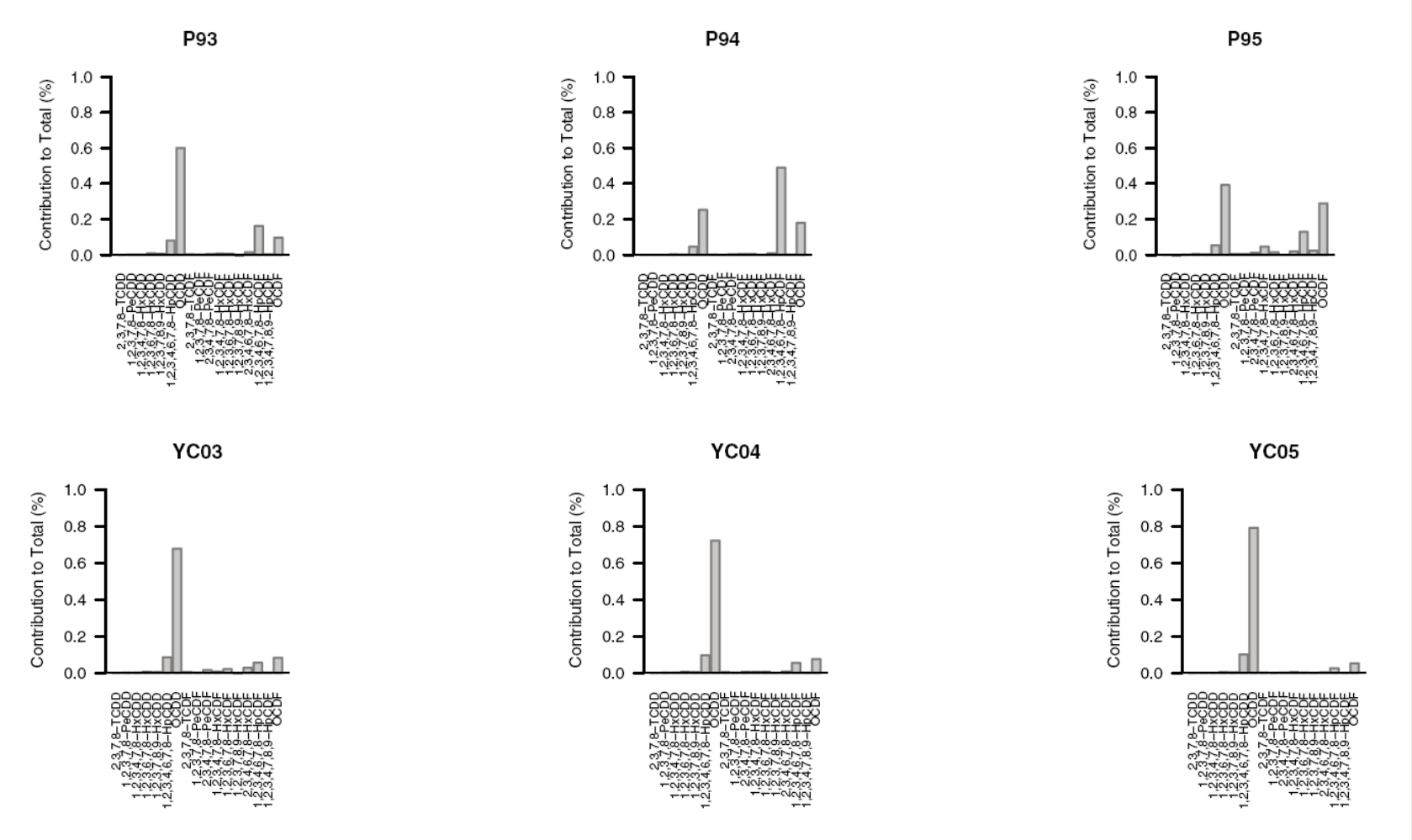
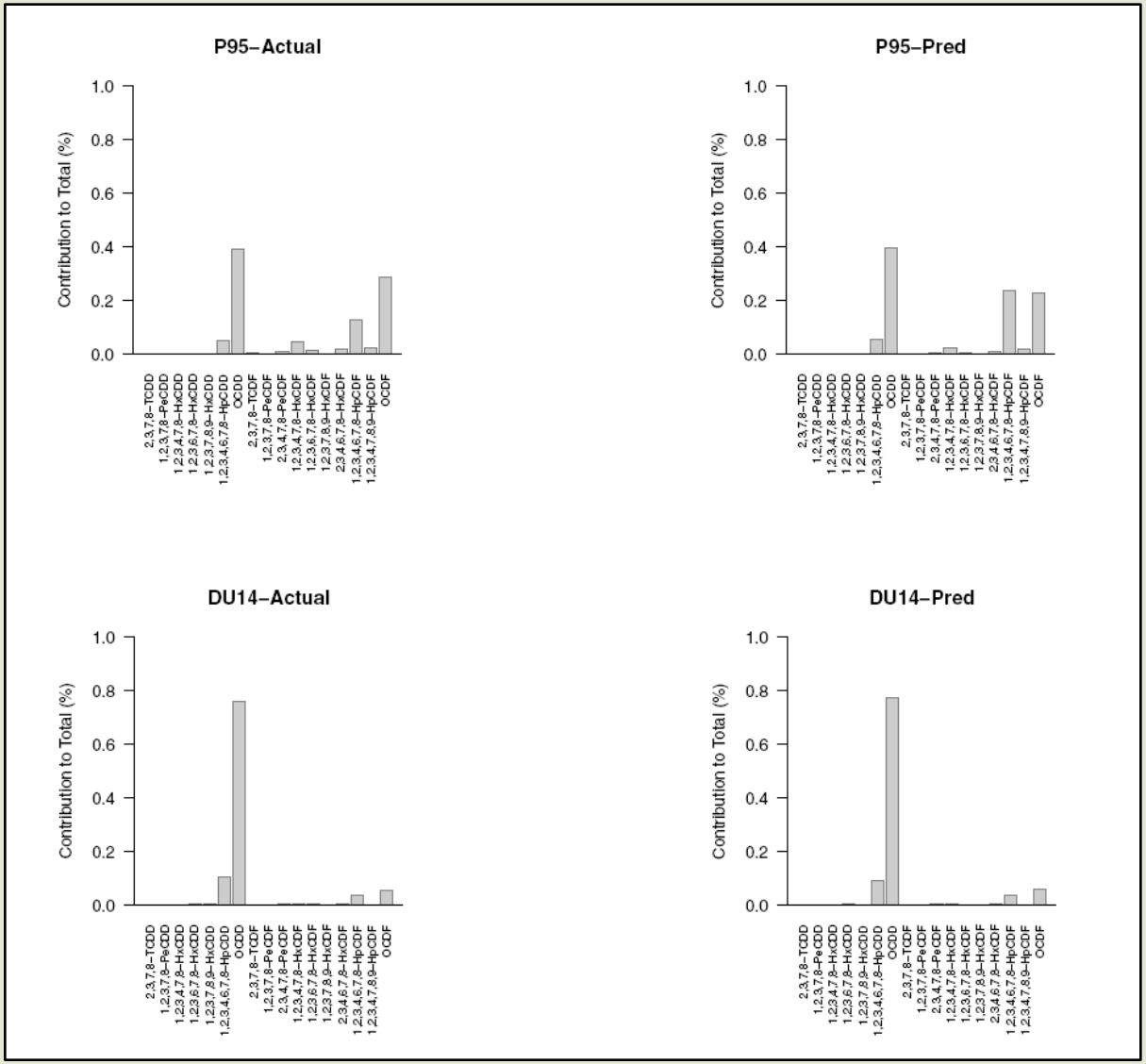
LOE A3: End Member Profiles



LOE A3: Example Site Profiles

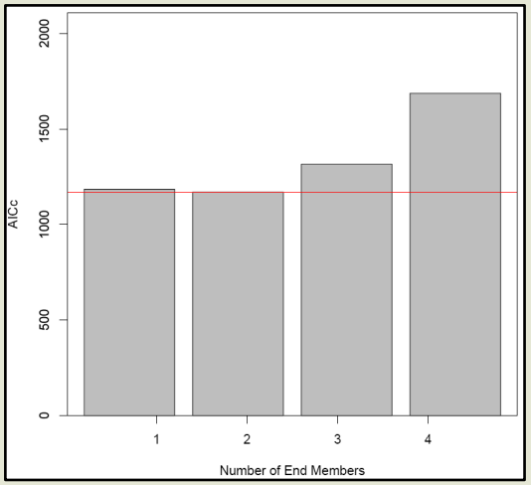


Example: Actual *vs.* Predicted



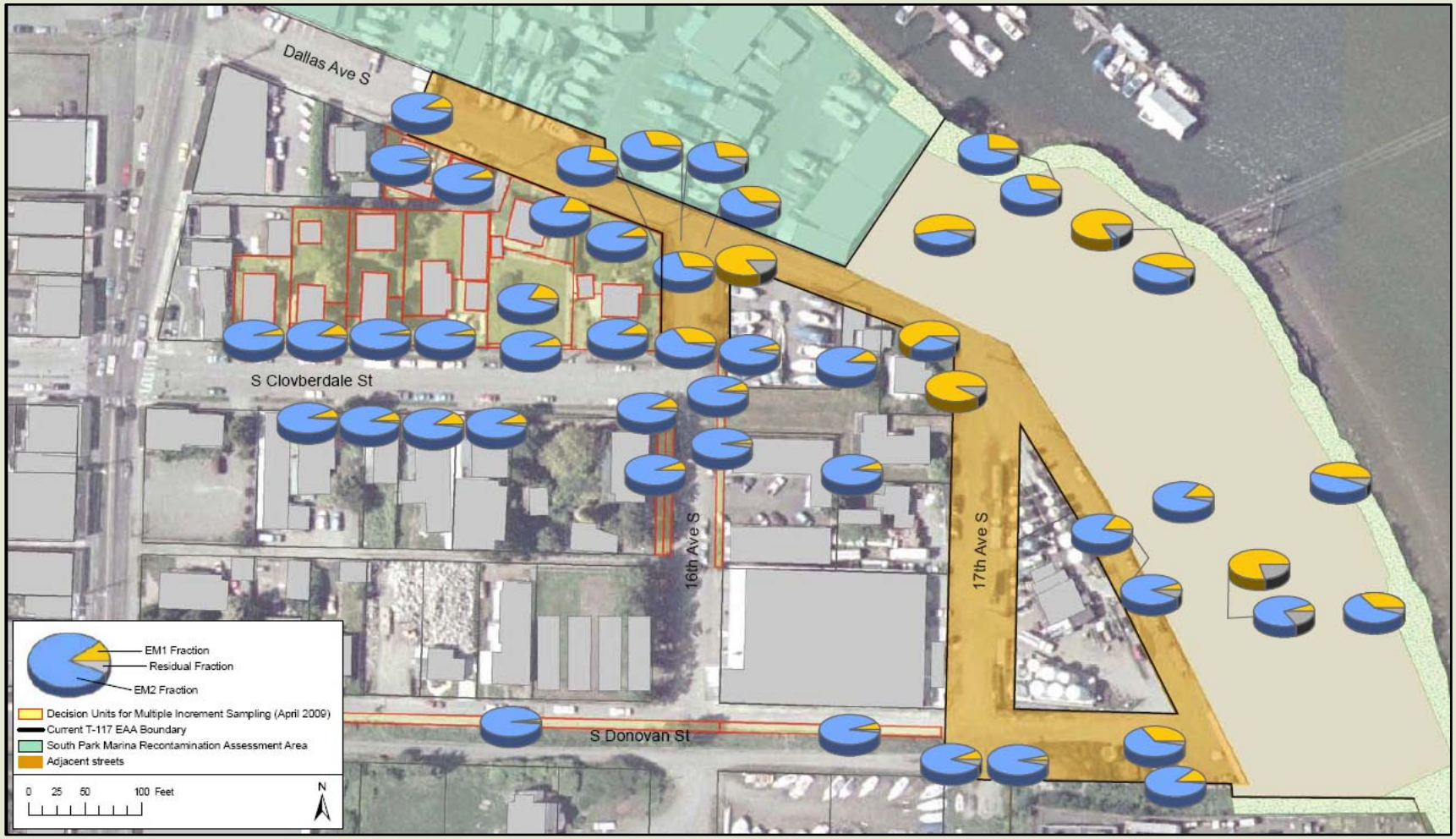
LOE A3: Comparison of Unmixing Results

- Differences
  - Concentration data—Integral: 2 EM; Infometrix: 3 EM
  - TEQ data—Integral: 1 EM; Infometrix: 5 EM

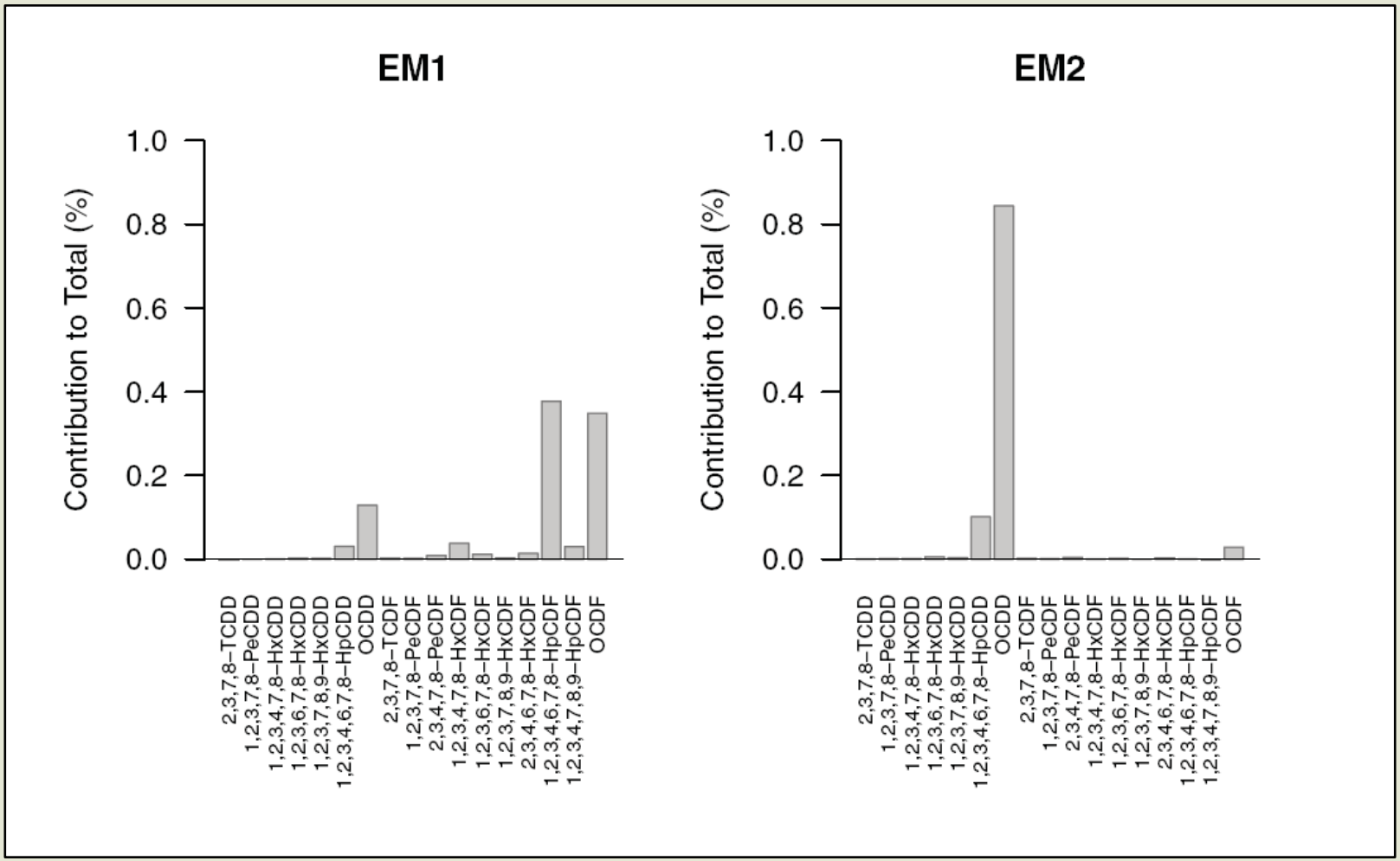


- Similarities
  - End members potentially associated with T-117 contribute only a small fraction, at most, to yards
- Concentrations *vs*. TEQ
  - Overall conclusions correspond

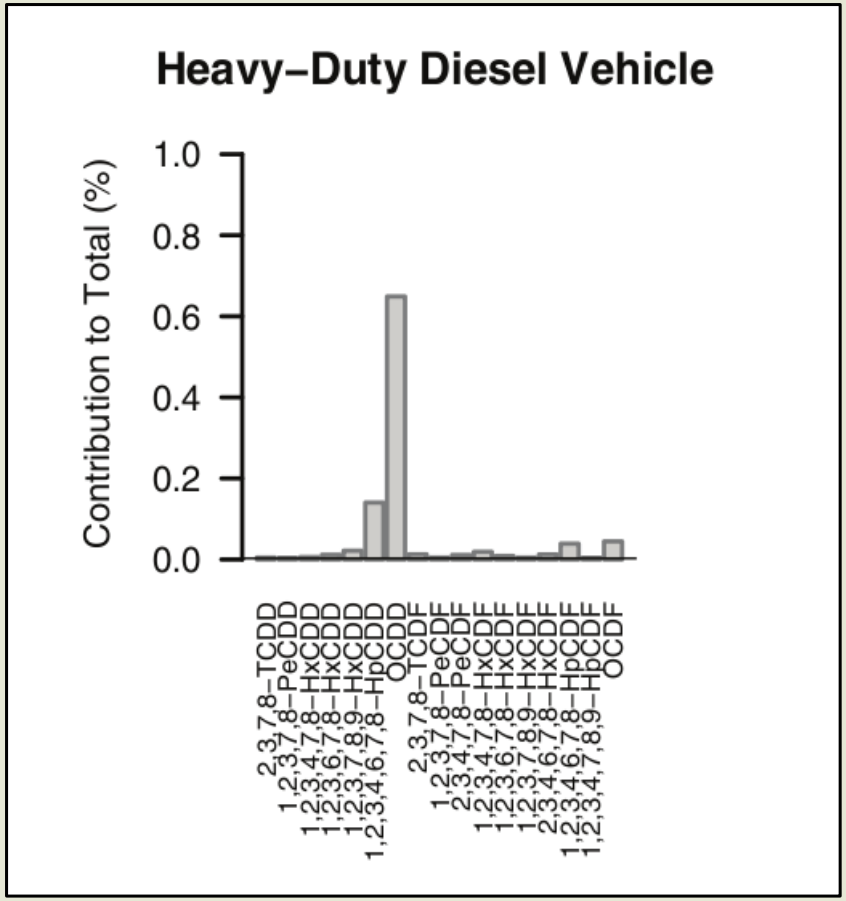
LOE A3: End Member Fractions (Integral)

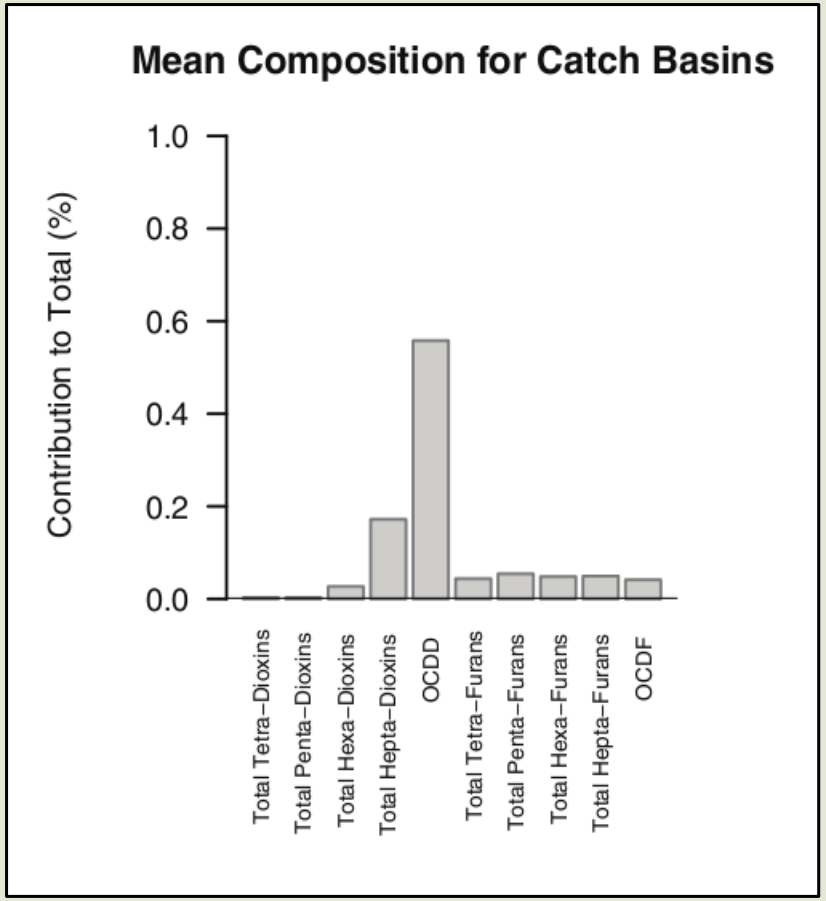


End Member Profiles



Other Urban Patterns





LOE A3: Uncertainties of Unmixing Analysis

- Uncertainties
  - End members may not be correctly identified
  - End members are not necessarily sources
  - Fractional contributions may not be accurate
- Uncertainty cannot be calculated, but can be illustrated

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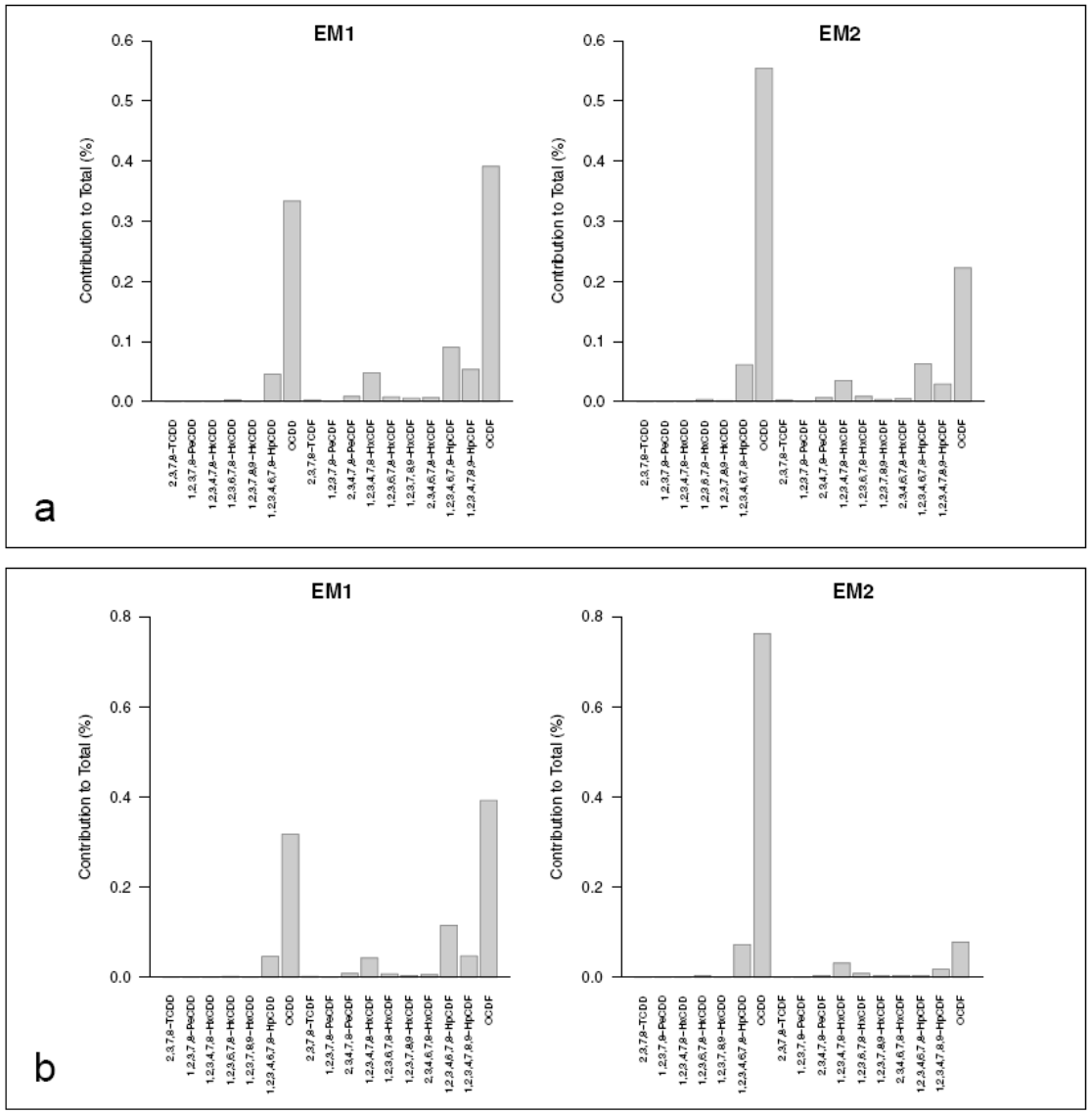
Unmixing Uncertainty in End Member Characterization

Different results for the same data set.



Unmixing Uncertainty in Fractional Contribution

		Contribution of apparent T-117 source (%)		
Data analyzed	Samples	Average	Min	Max
Concentration	Uplands	36	1.7	100
	Yards	5.1	0.3	12
	P.S. reference	7.1	0.6	40
TEQ	Uplands	40	0.3	89
	Yards	9.7	4.2	17
	P.S. reference	8.7	3.6	17

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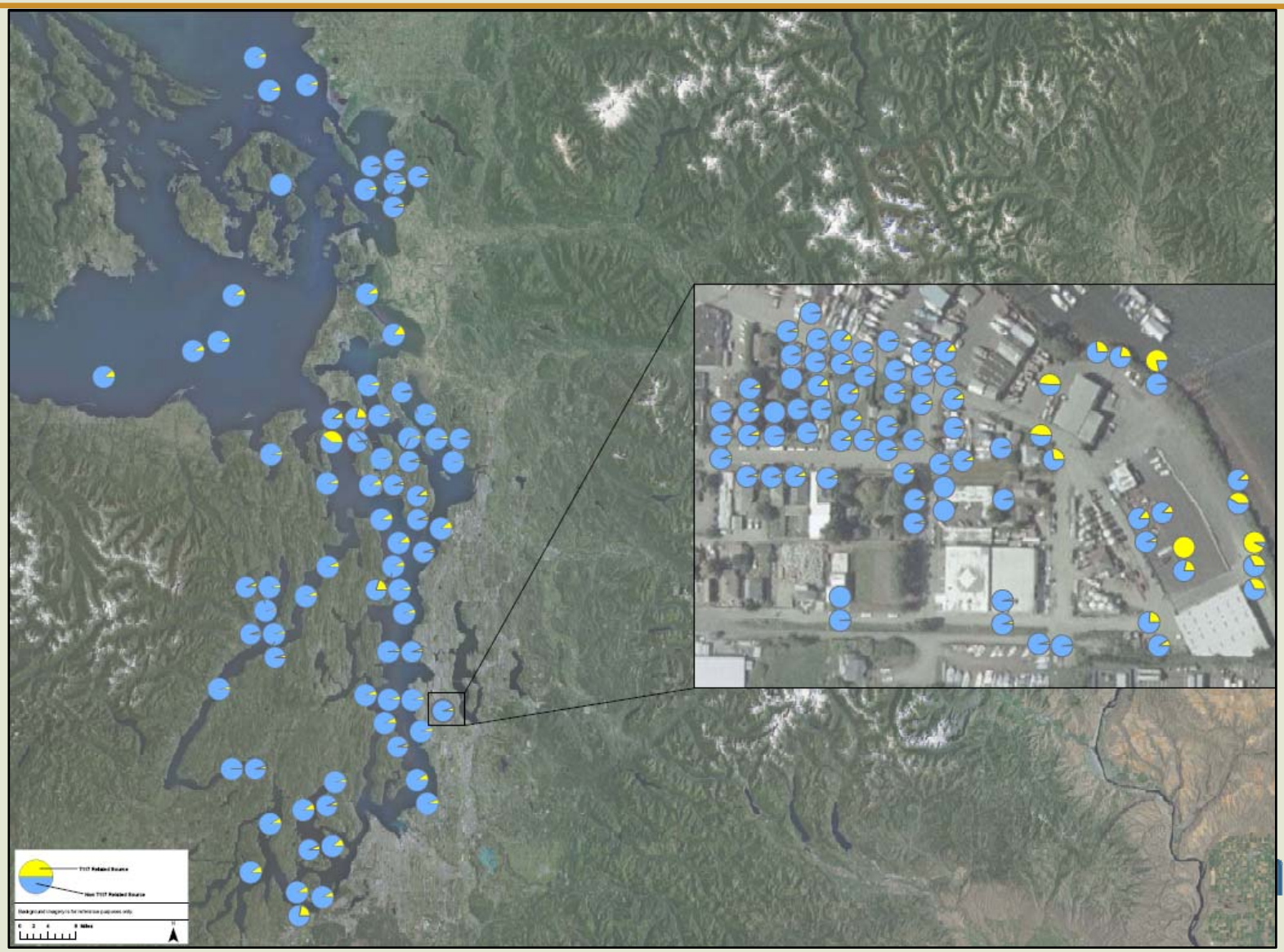
End Members of Site and Background Data



Criteria and Lines of Evidence

A. Pattern
   1. Similarity Analysis
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   3. Unmixing Analysis
B. Pathway
   1. Correlation of PCBs and dioxins/furans in yards
   2. Wind patterns
C. Gradient
   1. Spatial patterns of concentration
   2. Regression of concentration with distance

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LOE B1: Correlation of PCBs and Furans in Yards

- Data from MIS sampling were used
- PCB correlated to furans: furans may be present in commercial PCB mixtures and in PCB combustion products
- Concentrations were log-transformed to meet requirements for correlation analysis

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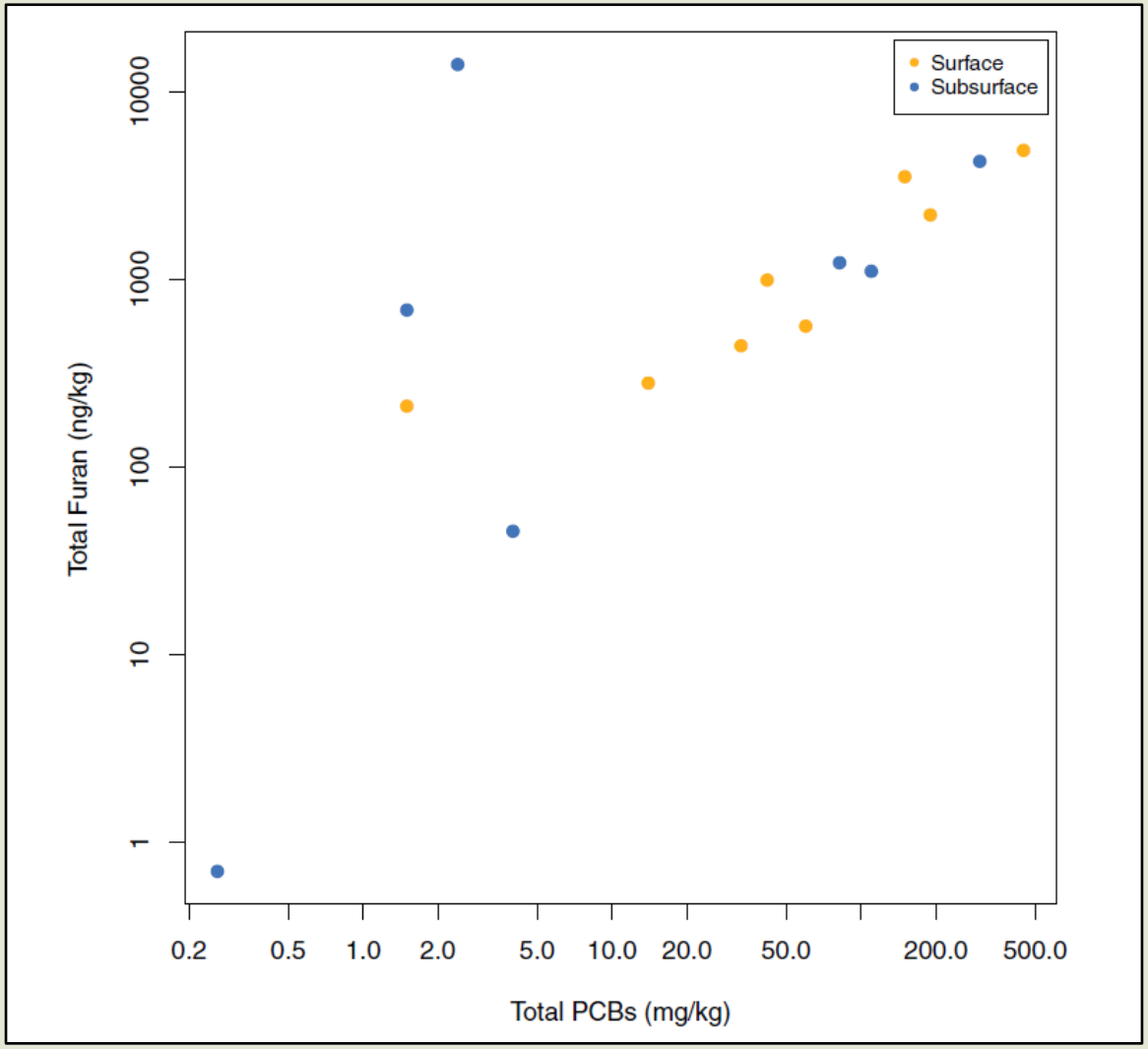
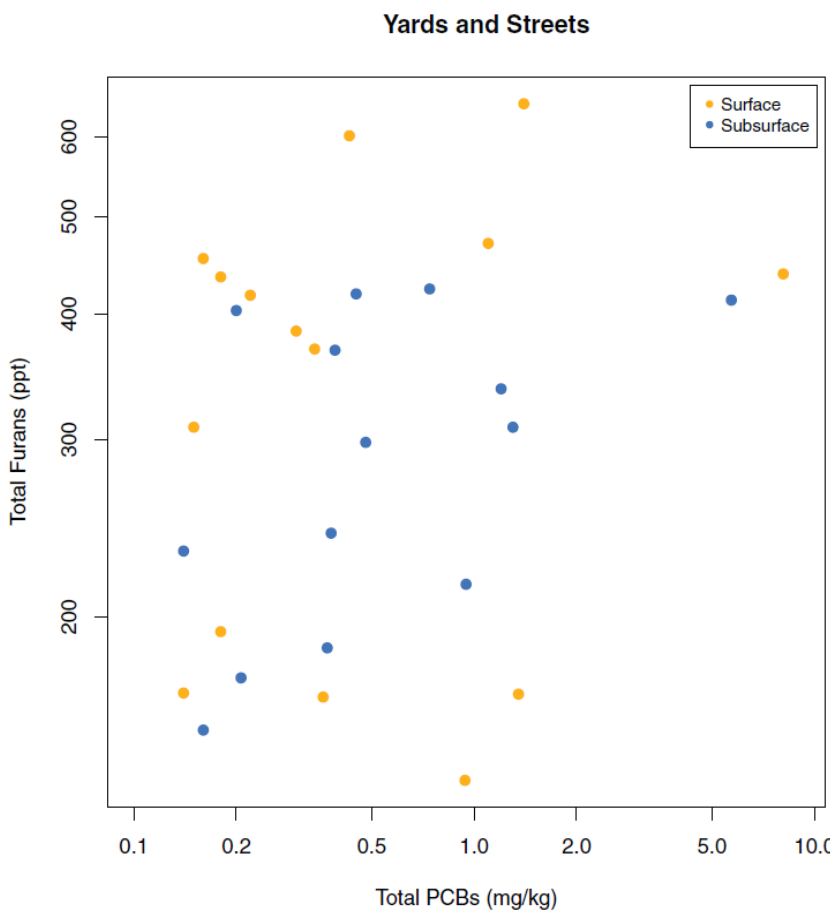
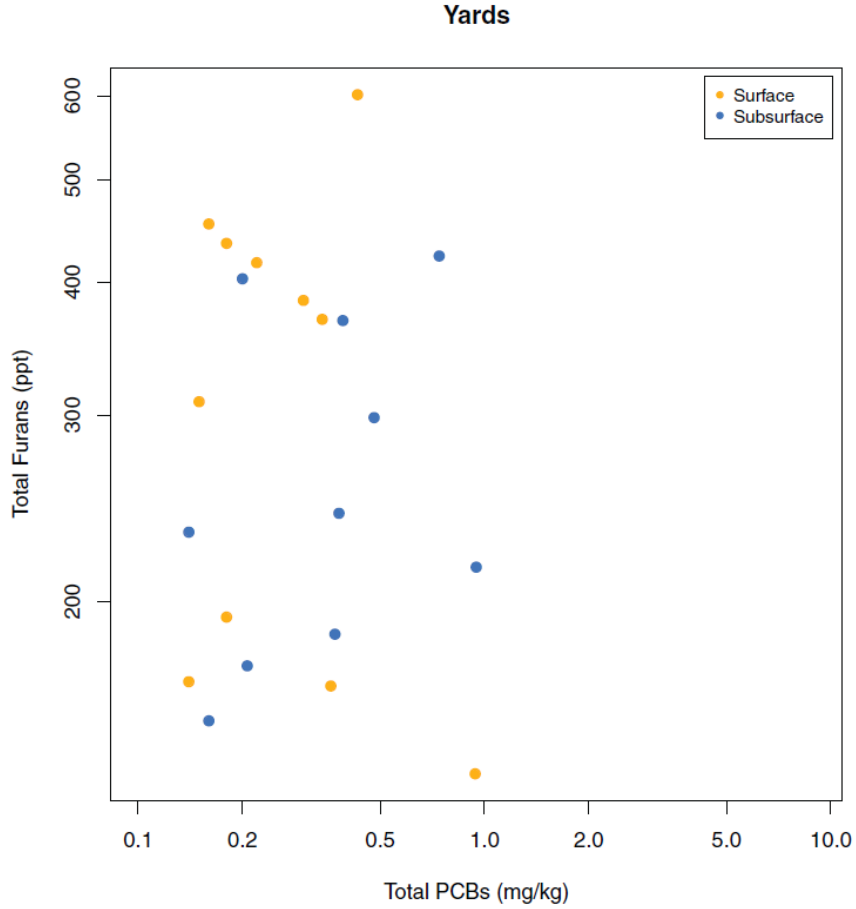
LOE B1: PCB Correlation Results—Uplands

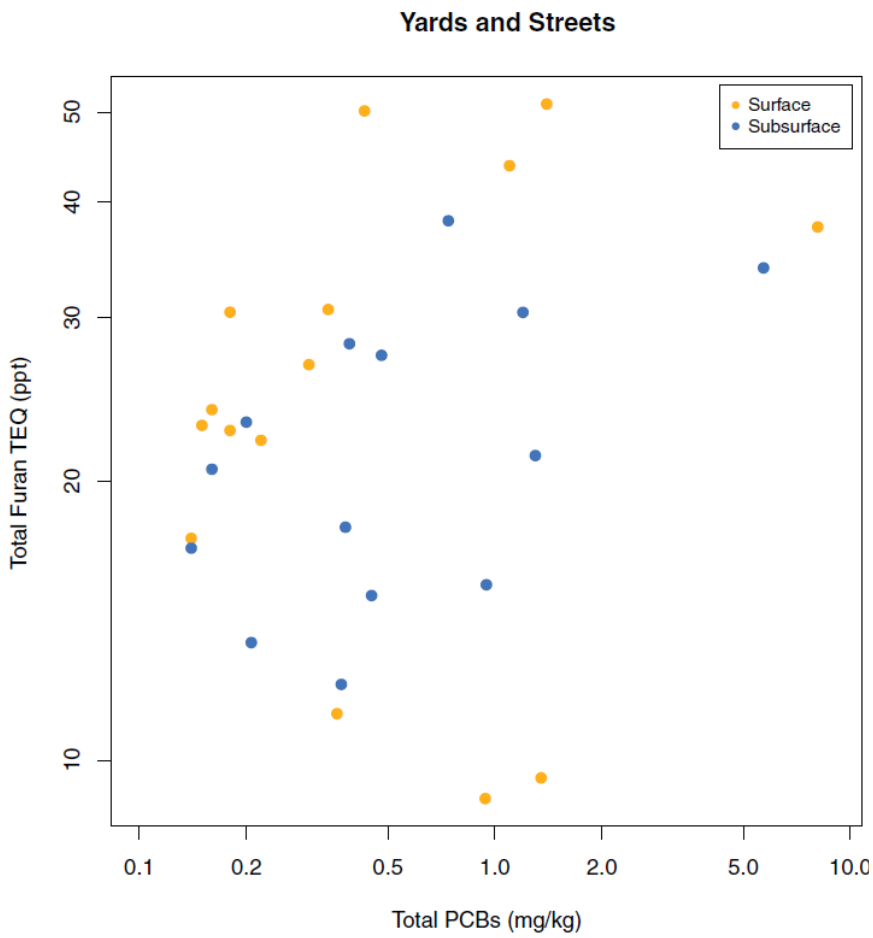


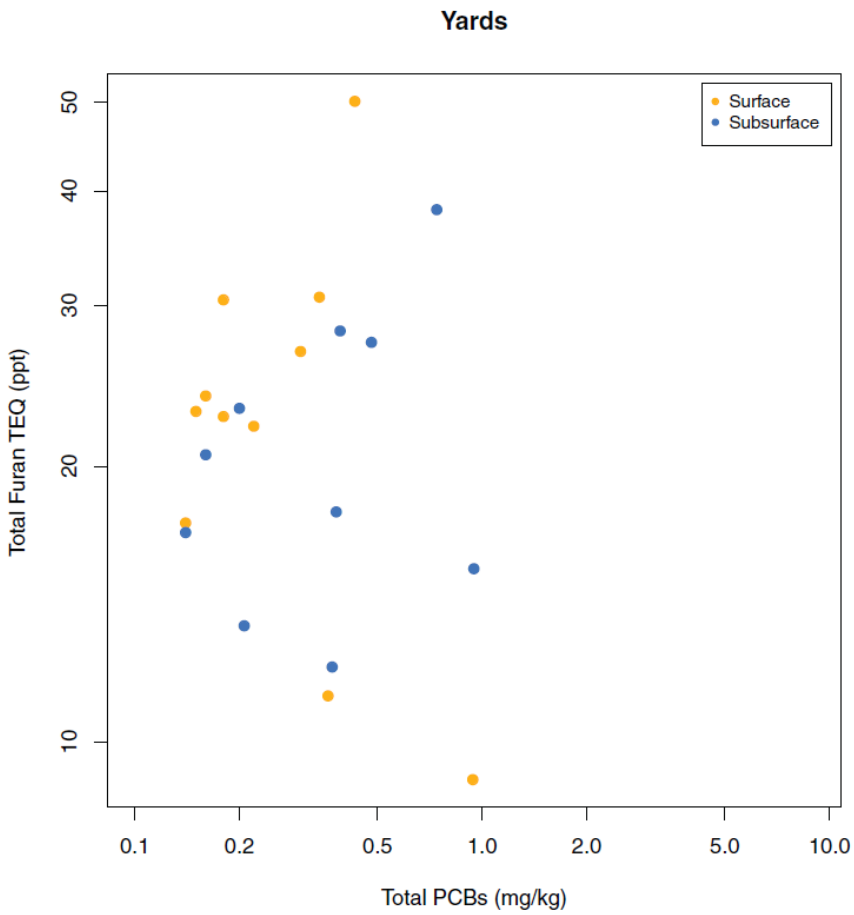
LOE B1: PCB Correlation Results—Concentrations in Yards and Streets





LOE B1: PCB Correlation Results—TEQs in Yards and Streets

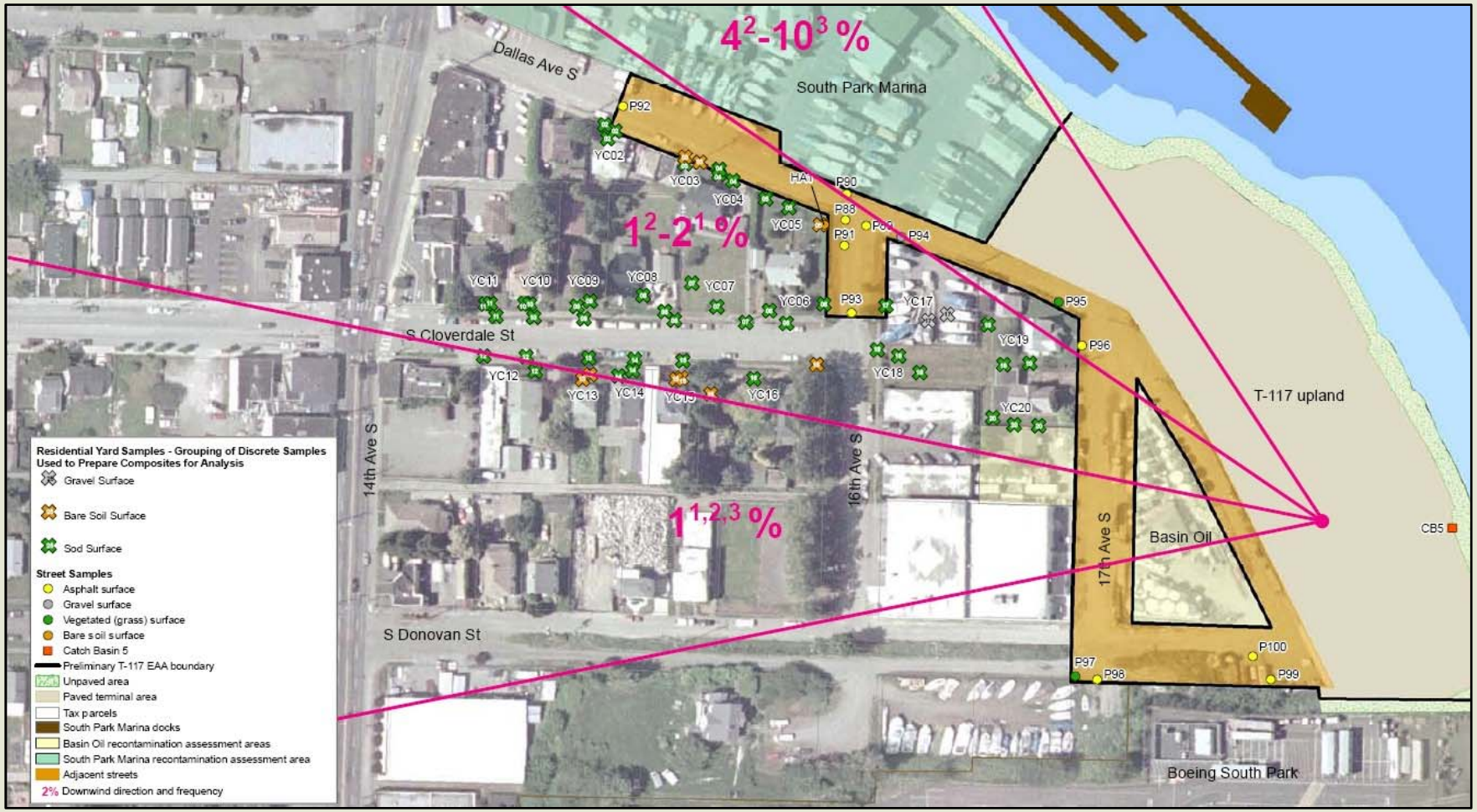




LOE B2: Wind Patterns

- Data from three meteorological stations were used
  - Duwamish Valley: 1/1/1990 to 11/14/2008
  - South Park Elmgrove: 5/18/2000 to 12/1/2002
  - On-site: 9/8/2006 to 10/31/2006.
- Wind frequency and direction were evaluated

LOE B2: Wind Pattern Results



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Criteria and Lines of Evidence

A. Pattern
   1. Similarity Analysis
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   3. Unmixing Analysis
B. Pathway
   1. Correlation of PCBs and dioxins/furans in yards
   2. Wind patterns
C. Gradient
   1. Spatial patterns of concentration
   2. Regression of concentration with distance

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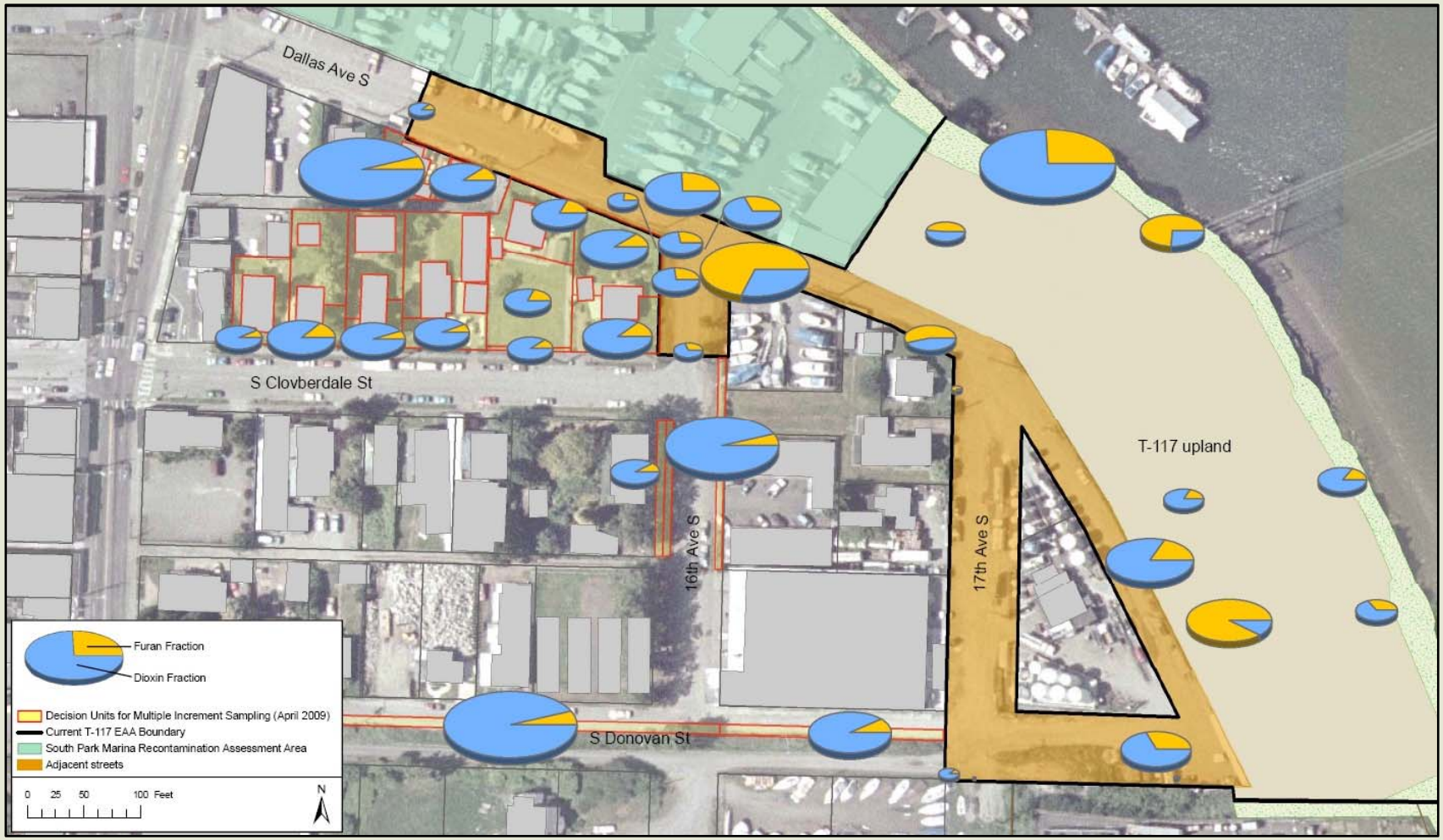
LOE C1: Spatial Gradient



LOE C2: Regression of Concentration Against Distance

- Spearman's rank correlation
  - No significant trend with distance from site:
    - » Bulk congener concentrations
      - All data
      - Surface
      - Subsurface
    - » TEQs
      - All data
      - Surface
      - Subsurface

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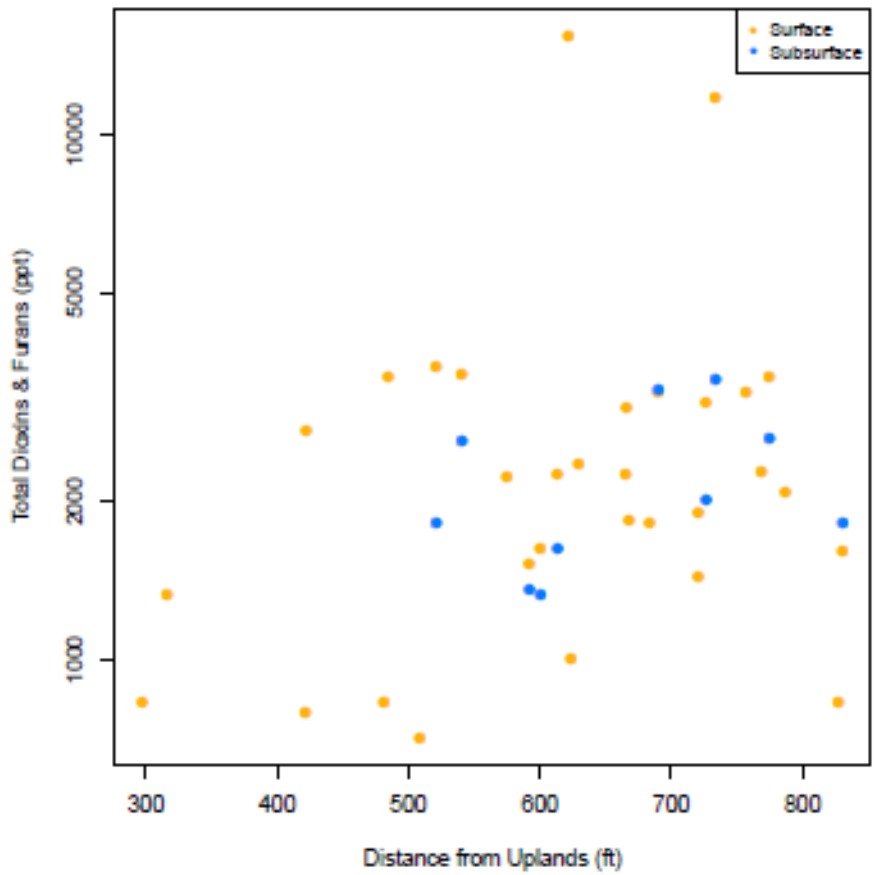
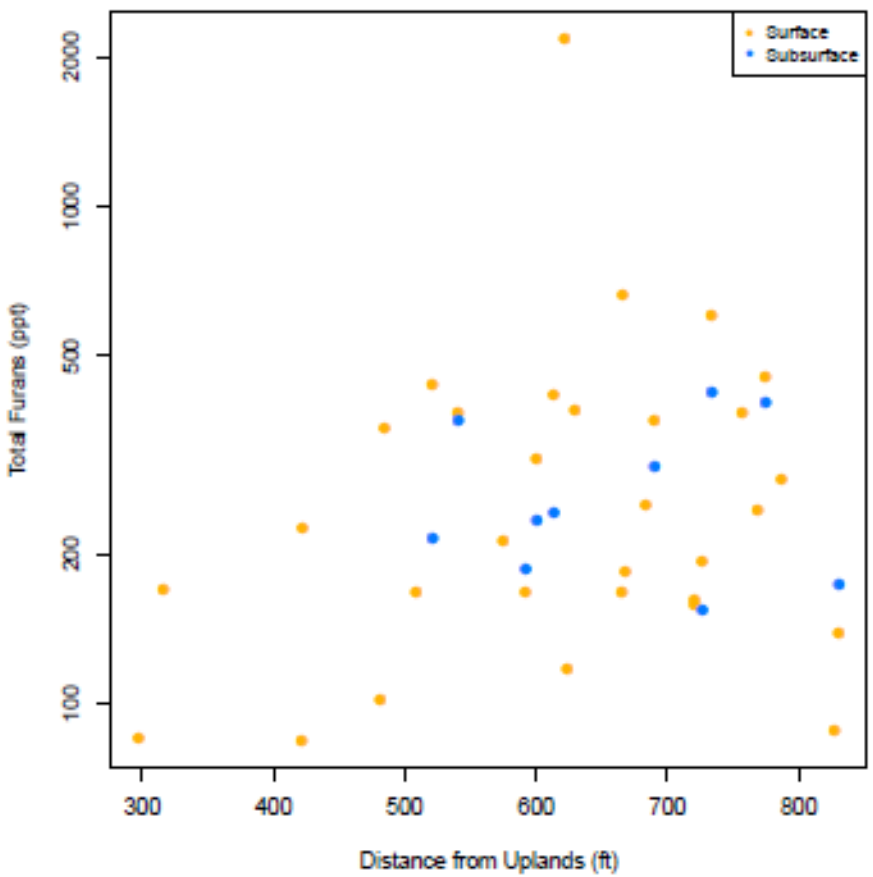
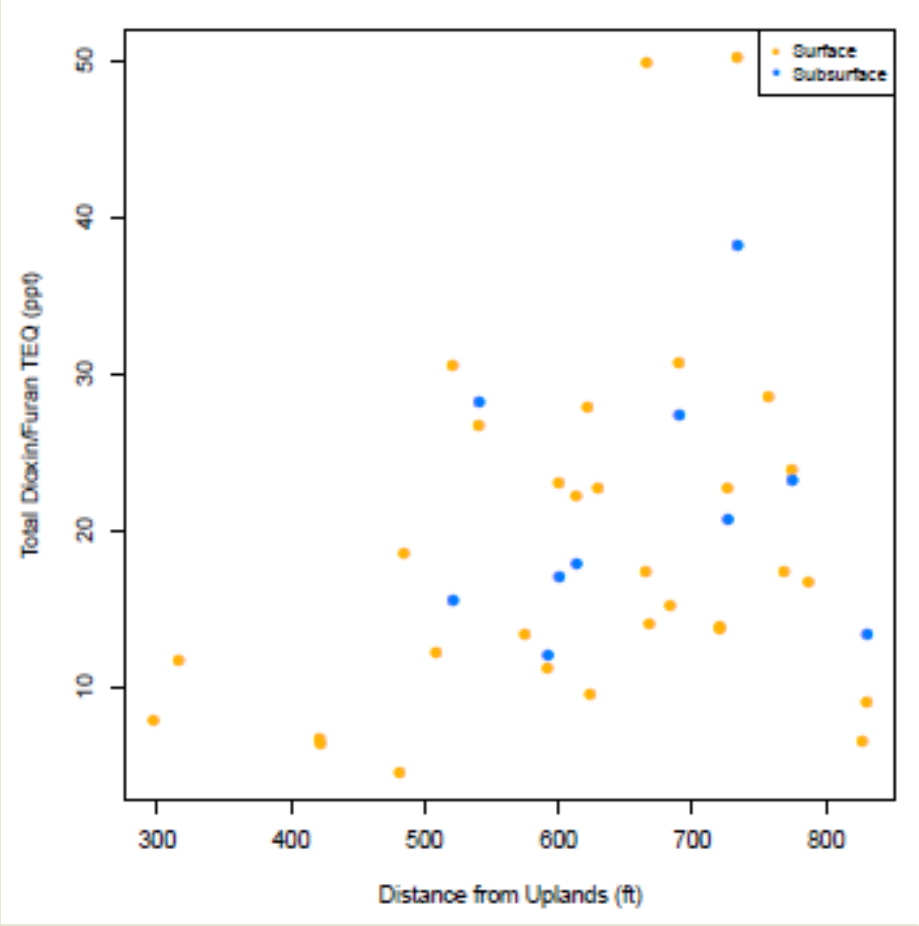
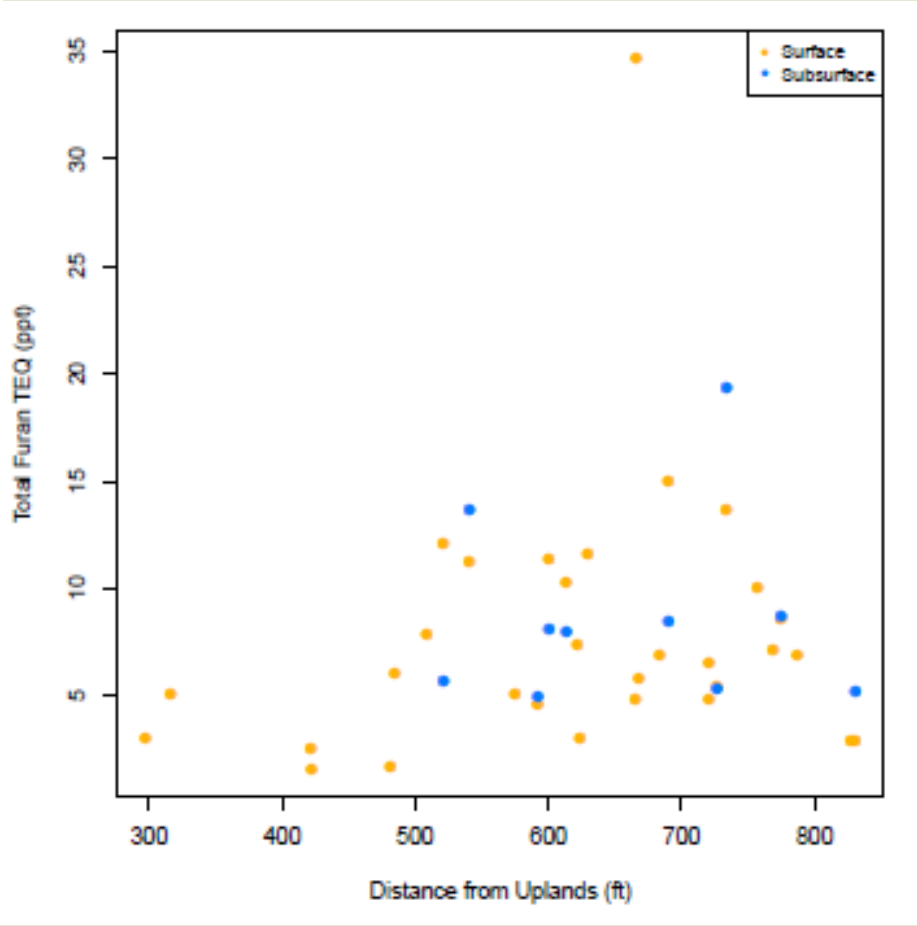
LOE C2: Regression Results for Concentrations





LOE C2: Regression Results for TEQs





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Patterns of Dioxin/Furans: Summary of LOE

- A1. Similarity Analysis: Dioxin/furan patterns are not similar between upland and yard samples. Some street samples are similar to upland.
- A2. Discriminant Function Analysis: Yard samples are classified with regional dioxin samples, not with upland samples.
- A3. Unmixing Analysis: Potential contribution of upland to yards is a few percent at most, and may be zero.

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Pathway: Summary of LOE

- B1. Correlation of PCB and furans: PCBs and furans are correlated in upland samples, but not in yard samples
- B2. Aerial transport pathway: For 98-99% of the time, wind over the yards is from directions other than the upland property

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Spatial Gradient: Summary of LOE

- C1. Visible spatial pattern: There is no clear trend of systematically decreasing dioxin/furan concentrations with distance in the yards
- C2. Regression analysis: There is no statistically significant trend of decreasing dioxin/furan concentrations with distance in the yards

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Evaluation of Criteria

- A. Are dioxin/furan patterns in yard and street samples similar to upland samples?
  - The patterns in yard and upland samples are distinct and spatially separated. Some street samples are similar to upland.
- B. Is there a demonstrated pathway to yards (trackout or aerial deposition)?
  - No. Data do not demonstrate that either pathway is significant.
- C. Is there a spatial gradient of concentration in yards away from the upland area?
  - No. Concentrations vary, but do not decrease systematically with distance.

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Answering the Question

Is the T-117 site a source of dioxins and furans to adjacent streets and yards, and if so, what is the contribution?

- All three criteria are answered in the negative for yards.
- Some street samples appear to be influenced by the T-117 site.
- The T-117 site cannot be identified as a major source of dioxins and furans to most street samples or any yard sample.

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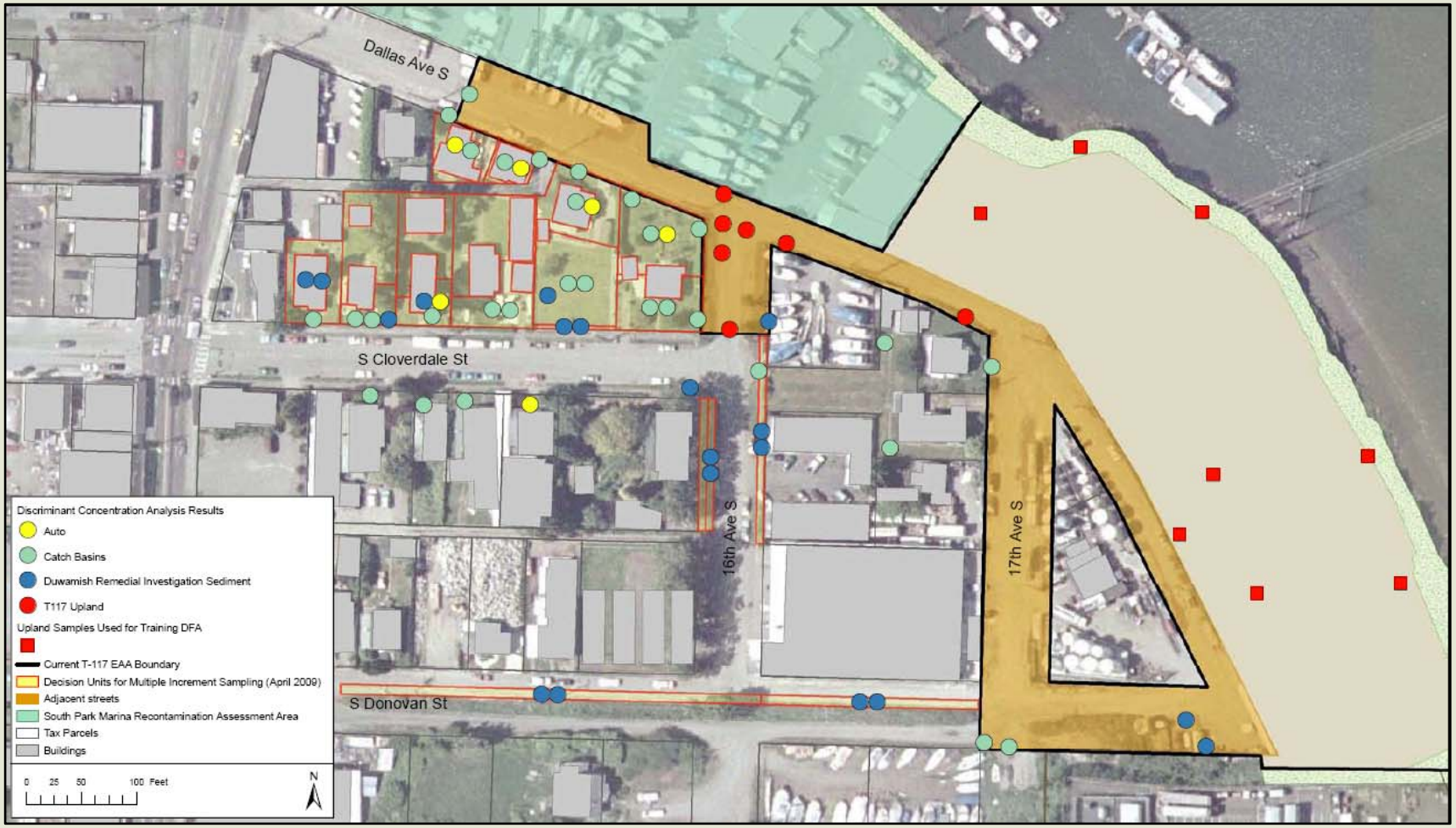
Conclusion

Based on the results of unmixing and other lines of evidence, the fraction of dioxins/furans in yards that can be attributed to T-117 sources is small — in the range of zero to a few percent.

Several street samples adjacent to the upland portion of the site have a dioxin/furan pattern consistent with a PCB source at T-117.

T-117 Influence (Discriminant Analysis)



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A Follow-up Question

- Is the absolute total TEQ magnitude of T-117 yard data consistent with other data from urban-industrial areas?
  - Representative dataset: Denver Front Range
  - Method of comparison: Reference envelope

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Reference Envelope Comparison

Denver urban background TEQs

Sample Stratum	N	Distribution	Min	Max	95th %ile	95%/90% UTL
Residential+Industrial +Commercial	100	lognormal	0.2	156.4	43.3	**51.6**
Residential	39	lognormal	0.2	156.4	37.7	**72.2**
Industrial	30	lognormal	0.2	54.8	43.7	**83.6**
Commercial	31	lognormal	0.4	143.5	38.8	**72.0**

T-117 TEQs

Sample Class	Mean	Median	Min	Max	95th %ile	N	Exceed Denver UTL
Yards	19.5	17.4	4.6	50.1	38.2	41	**0**
Streets	22.3	16.0	0.1	83.5	51.0	21	**1**
Uplands	65.8	35.3	1.6	297.0	193.9	15	**6**

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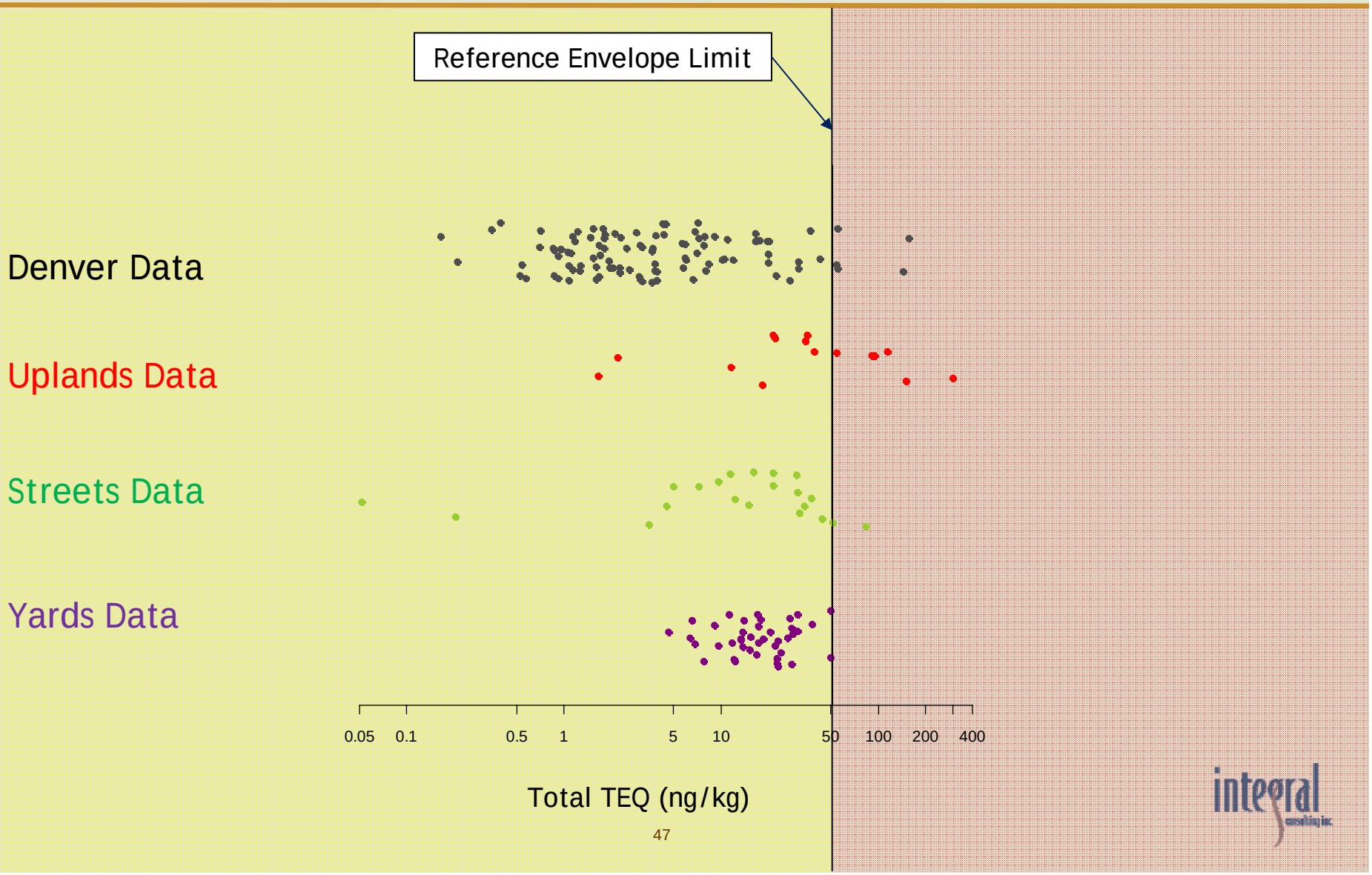
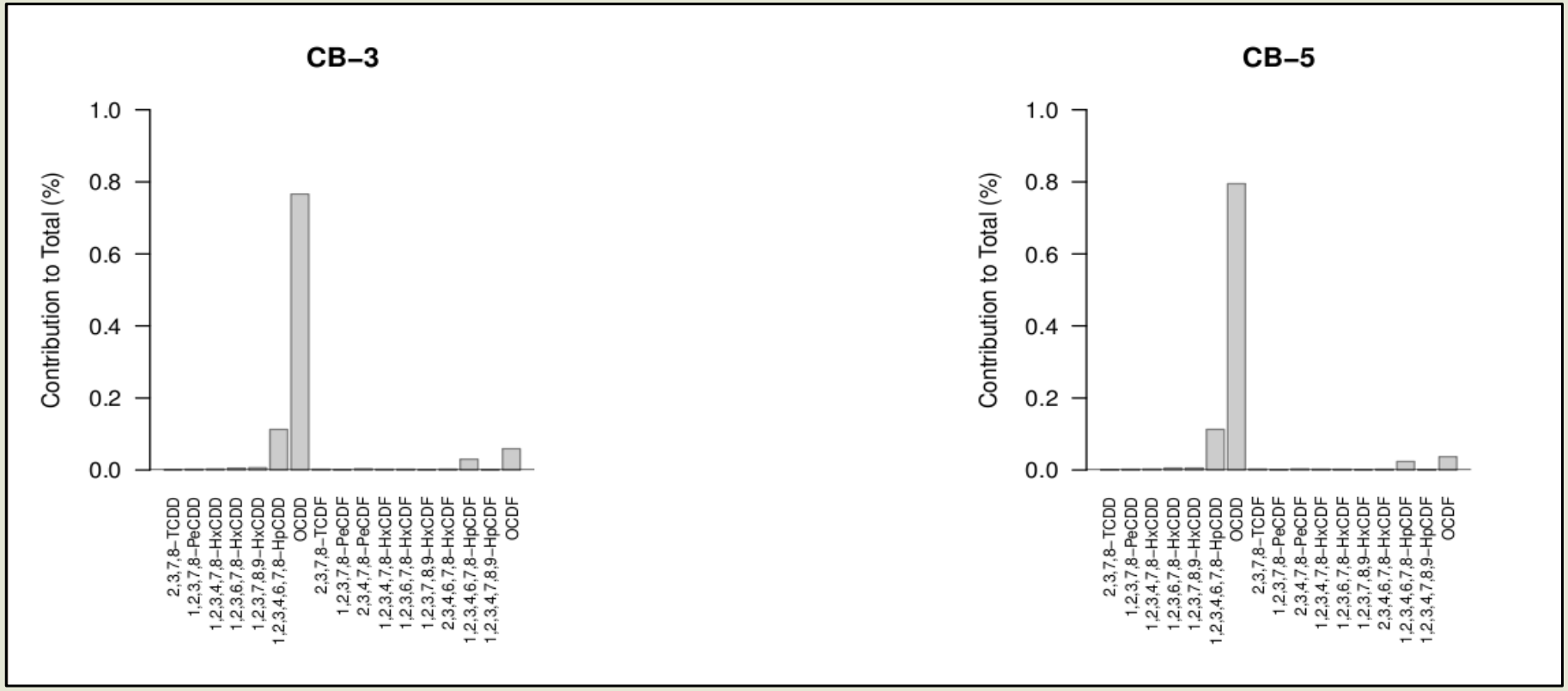
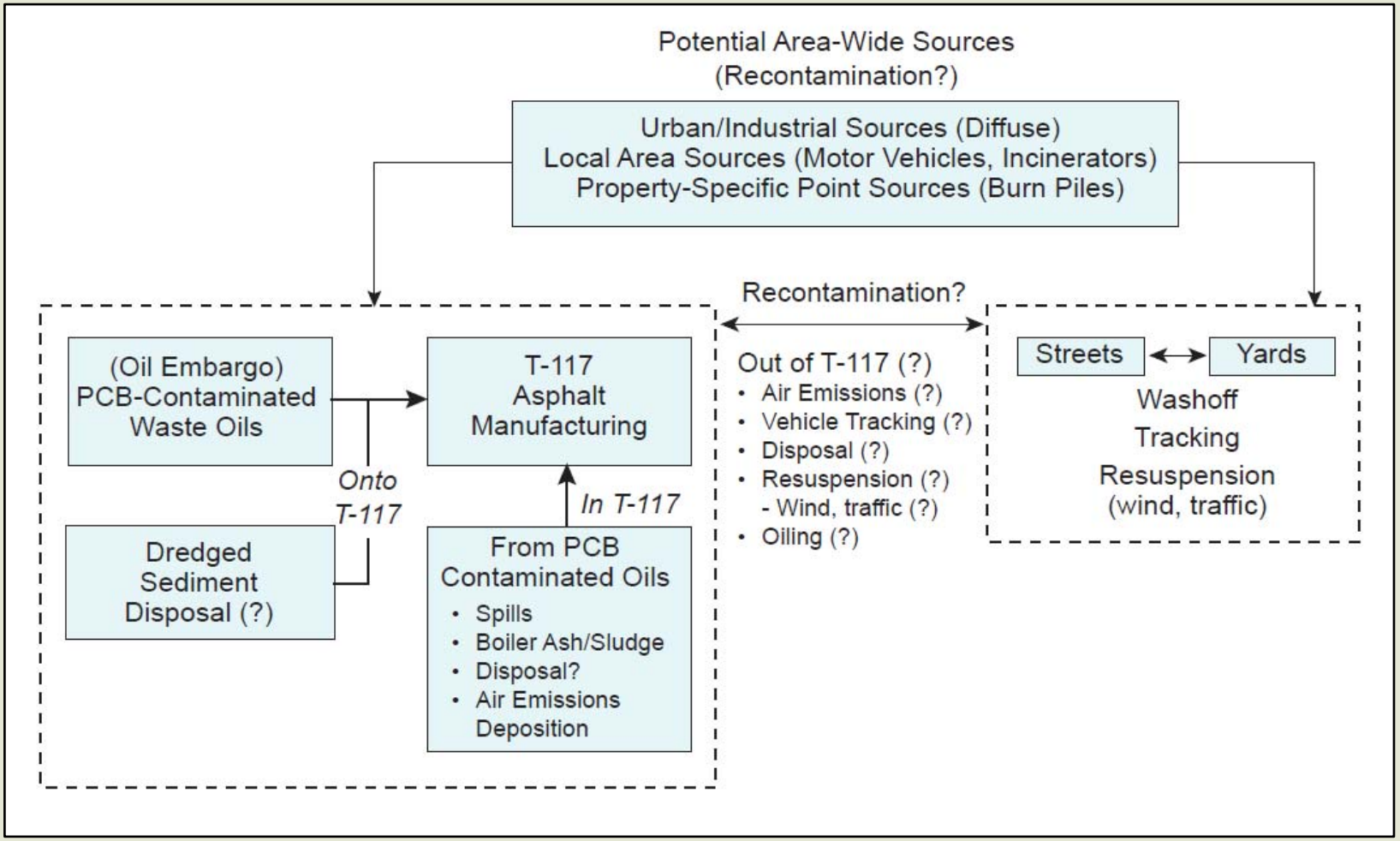
Reference Envelope Comparisons-Total TEQ



2009 Catch Basin Samples



Conceptual Site Model—Original

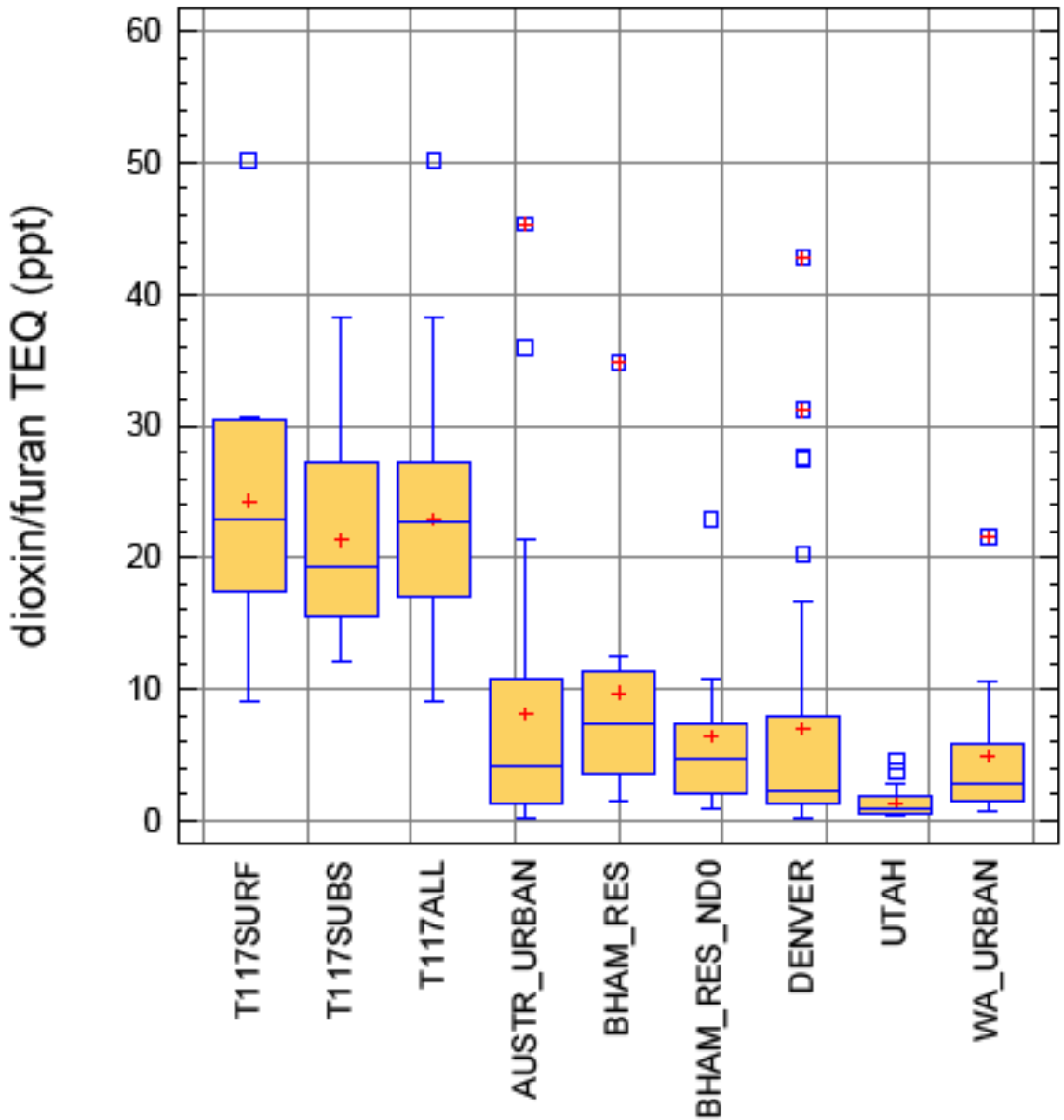


Questions?

T117 Dioxins/Furans: Source Evaluations

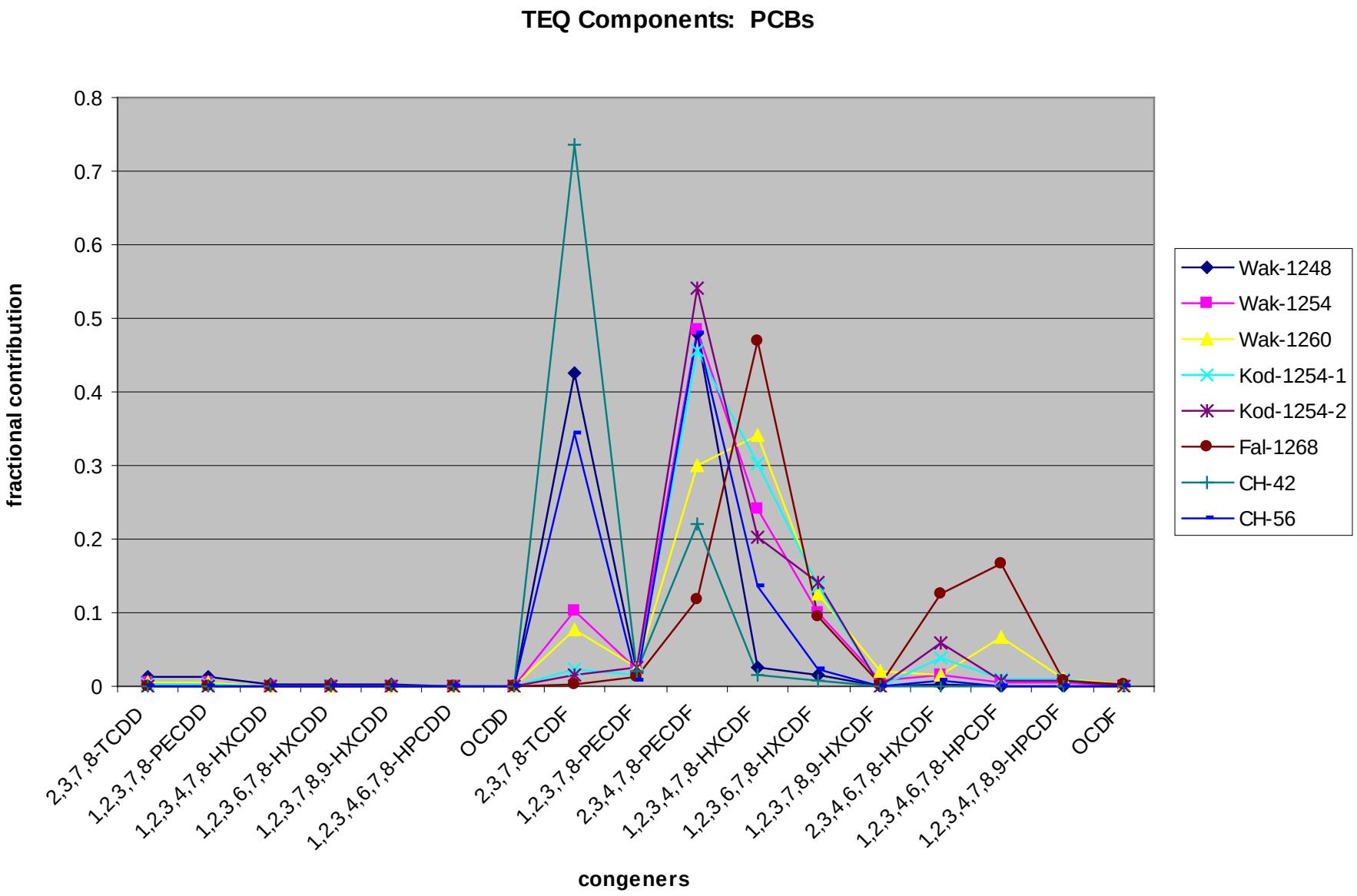
- TWG consultations, multiple evaluations
- T117 dioxin/furan data sets
- New information from unmixing analyses, MIS sampling
  - Source identification and contributions
  - Interpretations of unmixing results

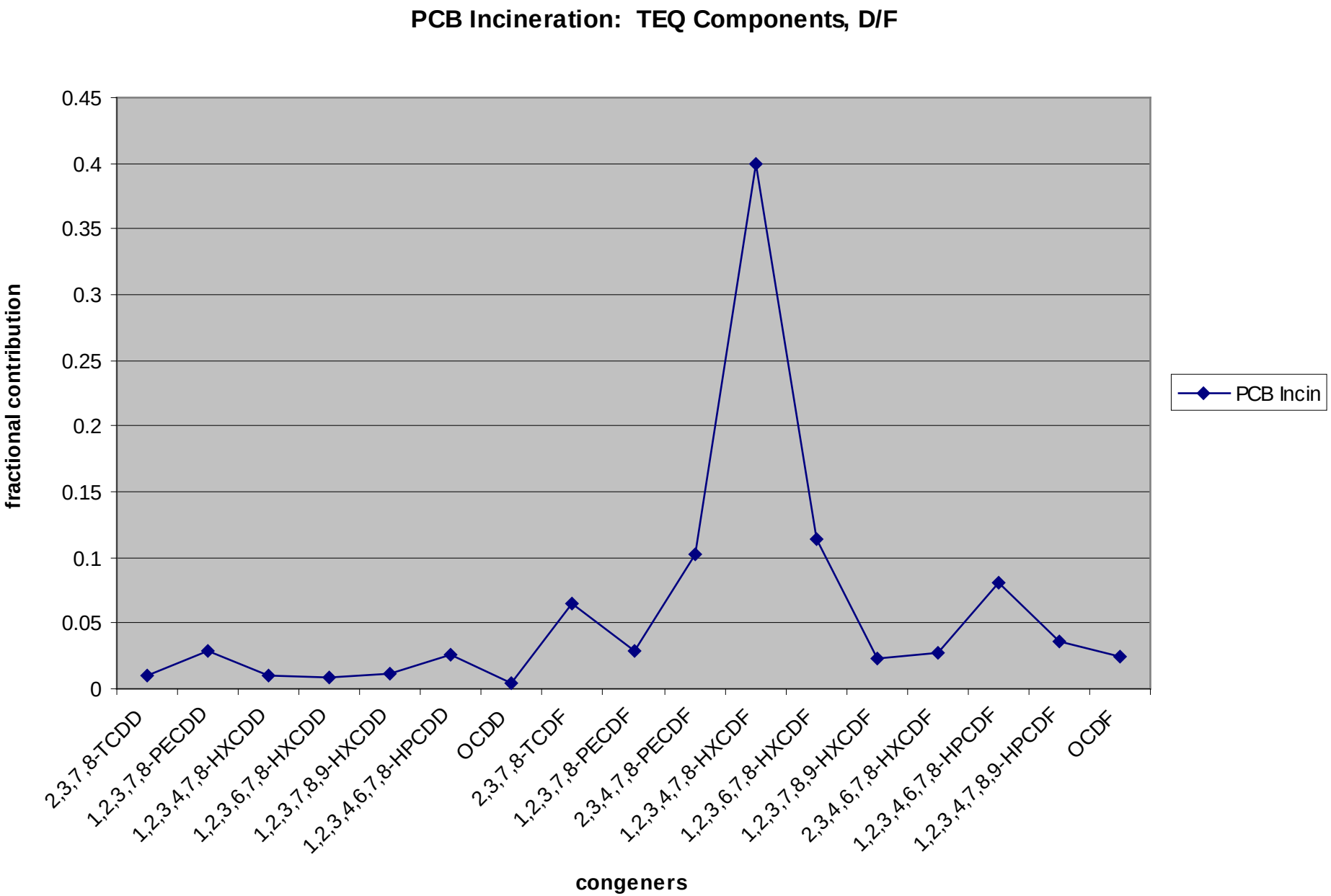
T117: Yard Dioxin TEQ Comparisons

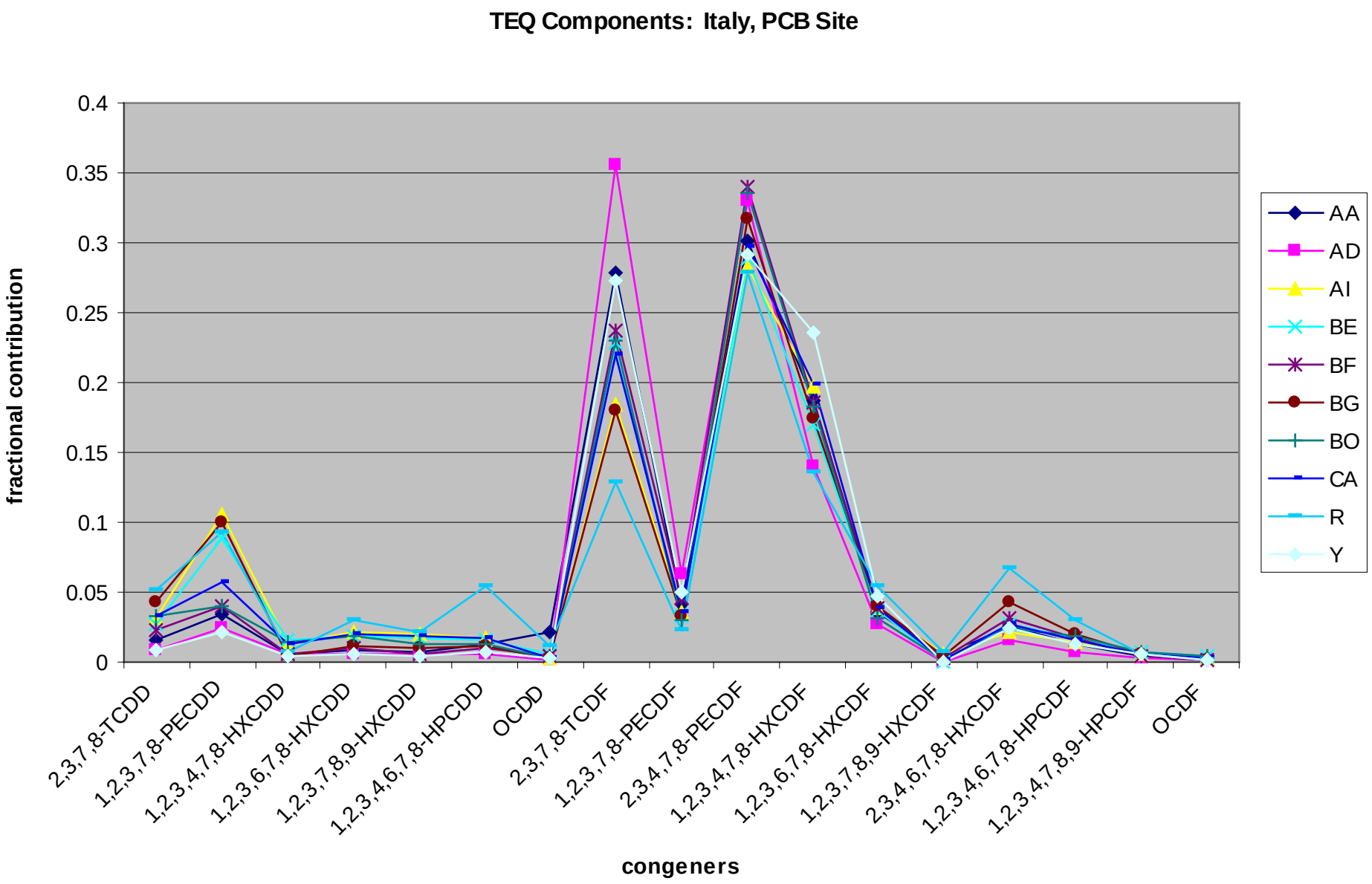


Conceptual Site Model

- Many sources of dioxins
  - Regional (background)
  - Local (sources)
  - Property-specific
- Potential T117 releases
  - PCB spills and trackout
  - PCB burning
  - Typical fuel burning (oil-fired boiler)


TEQ Components: PCBs
fractional contribution
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
Wak-1248
Wak-1254
Wak-1260
Kod-1254-1
Kod-1254-2
Fal-1268
CH-42
CH-56


PCB Incineration: TEQ Components, D/F
fractional contribution
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
PCB Incin

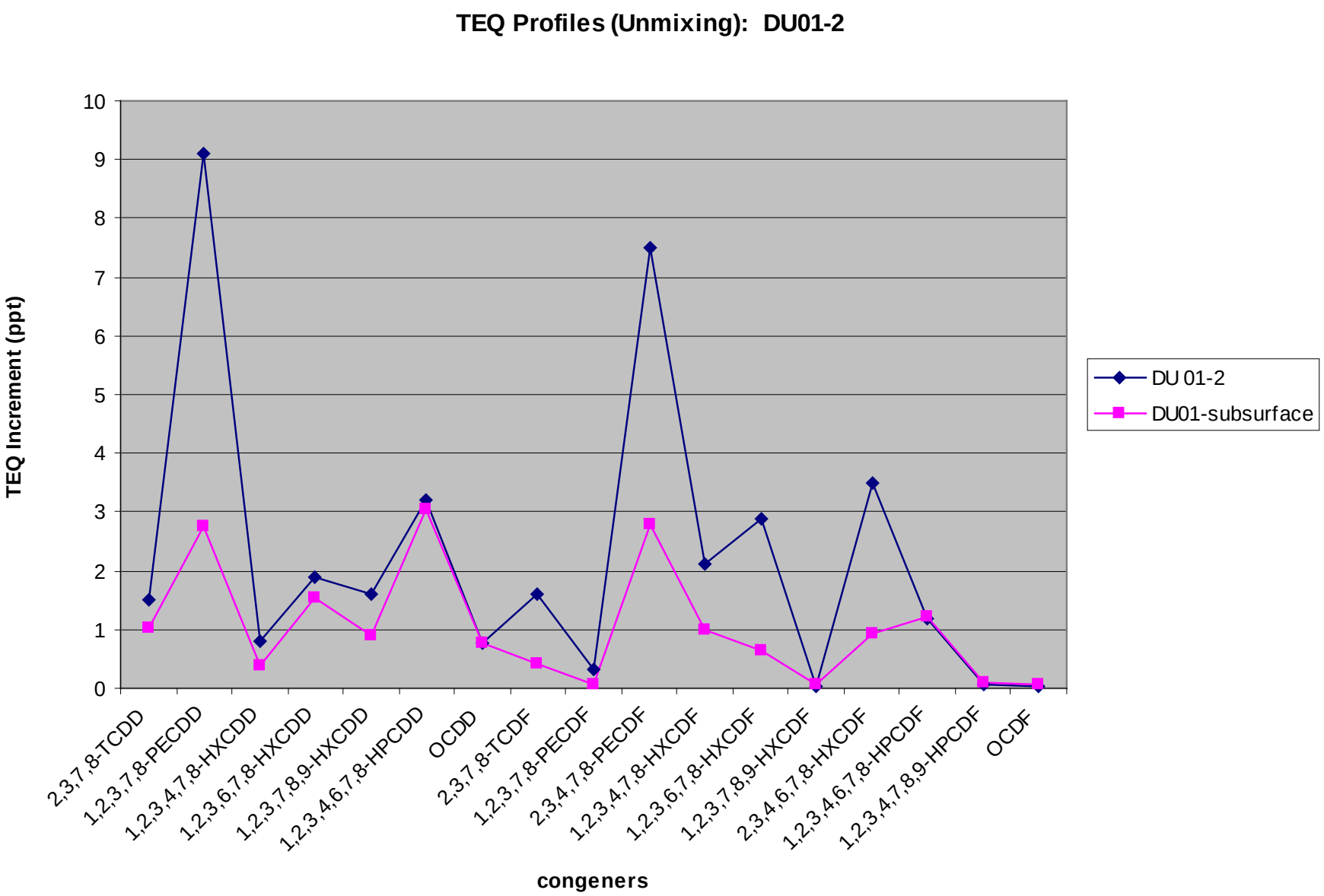

TEQ Components: Italy, PCB Site
fractional contribution
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
AA
AD
AI
BE
BF
BG
BO
CA
R
Y

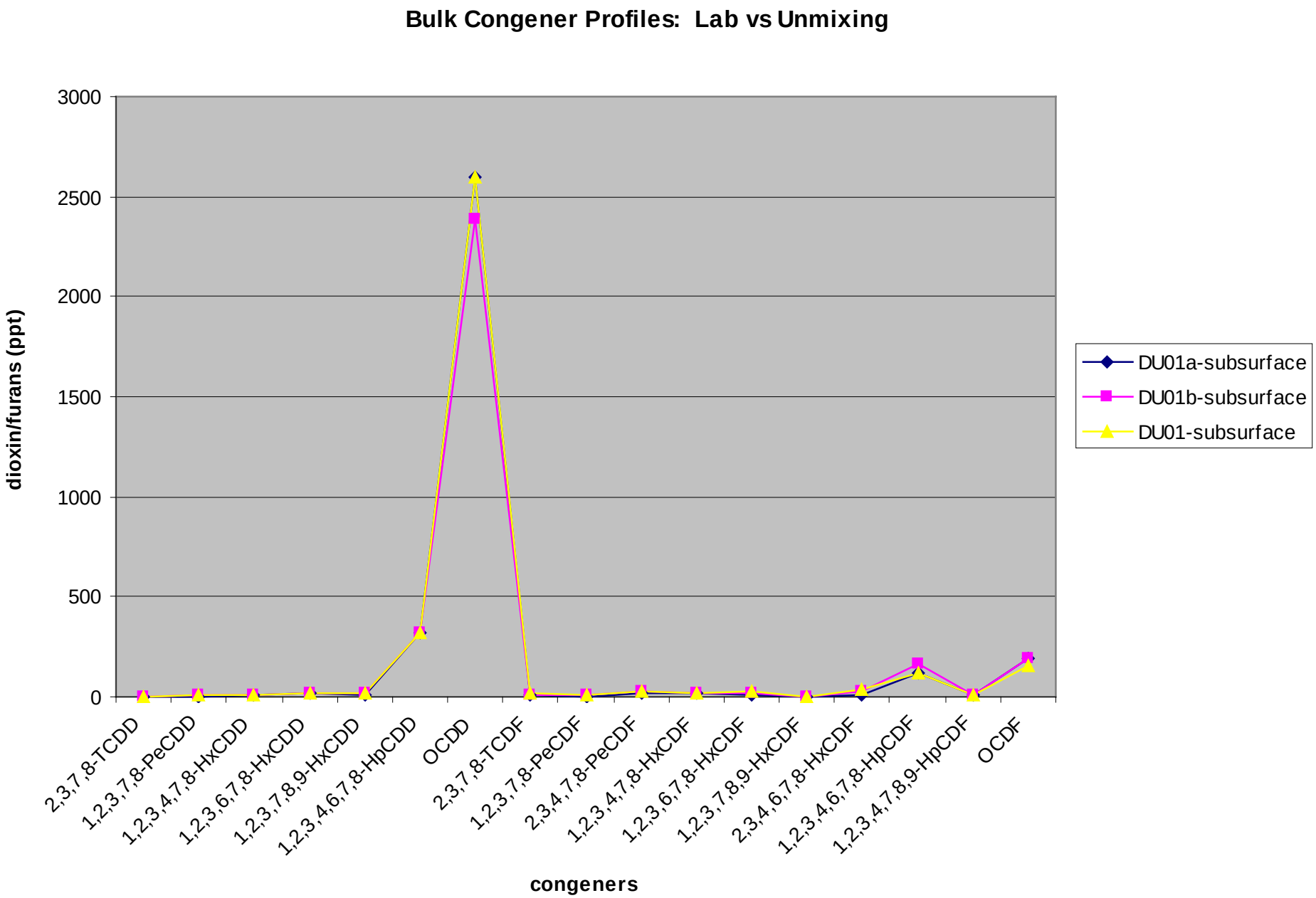
Dioxin/Furan Metrics

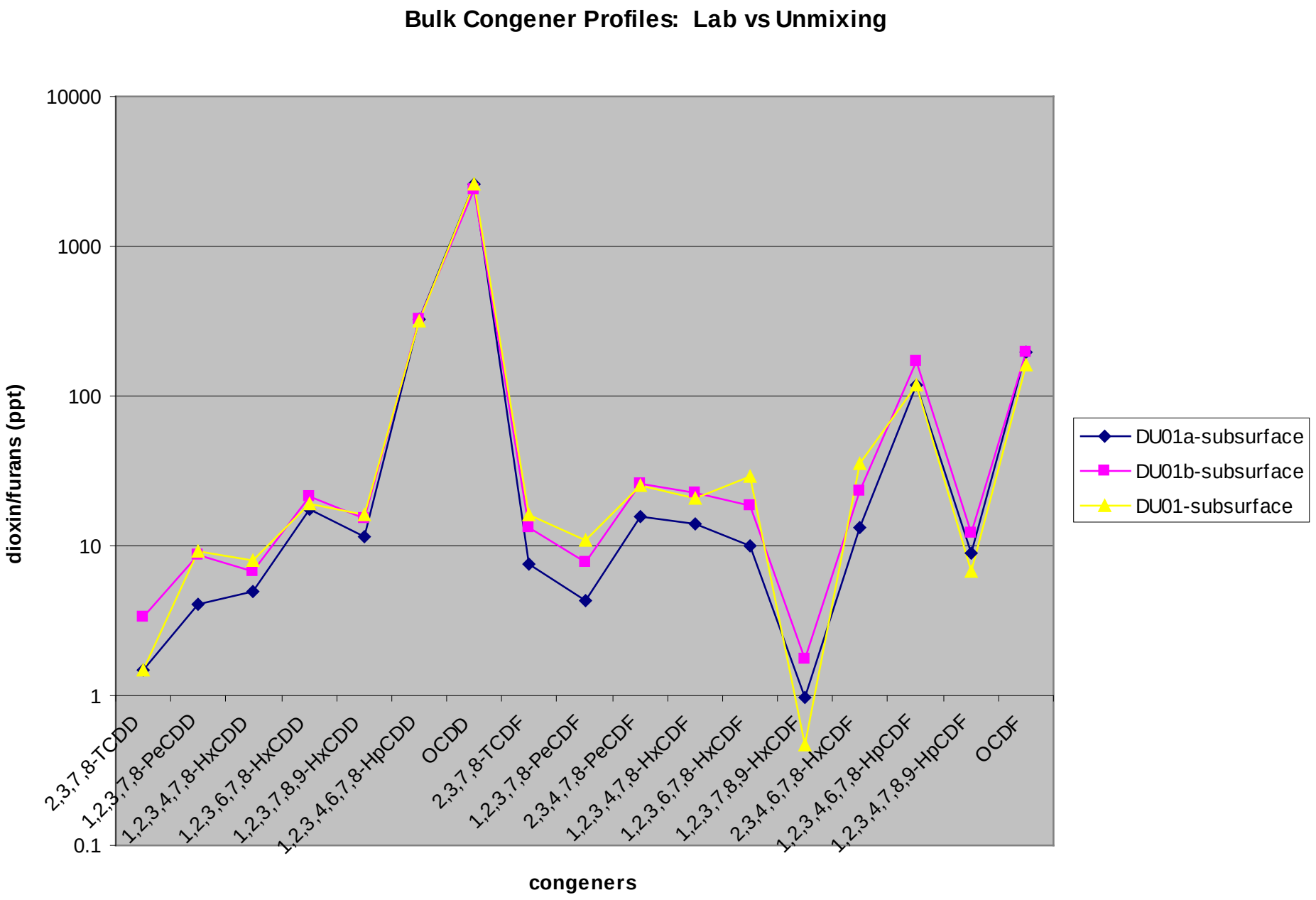
- Measured as bulk congeners or TEQs
  - One source profile or sample result defined in either manner can be converted using TEFs (one-to-one)
- Ranking of sources by contributions can be different
  - Result of compositional variability among sources and high TEF variability
- Bulk congeners
  - Physical reality of sources, actual chemical deposition
- TEQs
  - Calculated from validated analytical data
  - Used for decisions on exposure, risk, cleanup, compliance

Metrics

- Lessons learned during TWG evaluations
  - Different metric = different number of sources
  - Some source profiles equivalent under TEF-conversion, some not
  - Different metric = difference in residuals and whether bulk congener or TEQ profiles are better matched
  - Multiple TWG approaches allow for comparisons

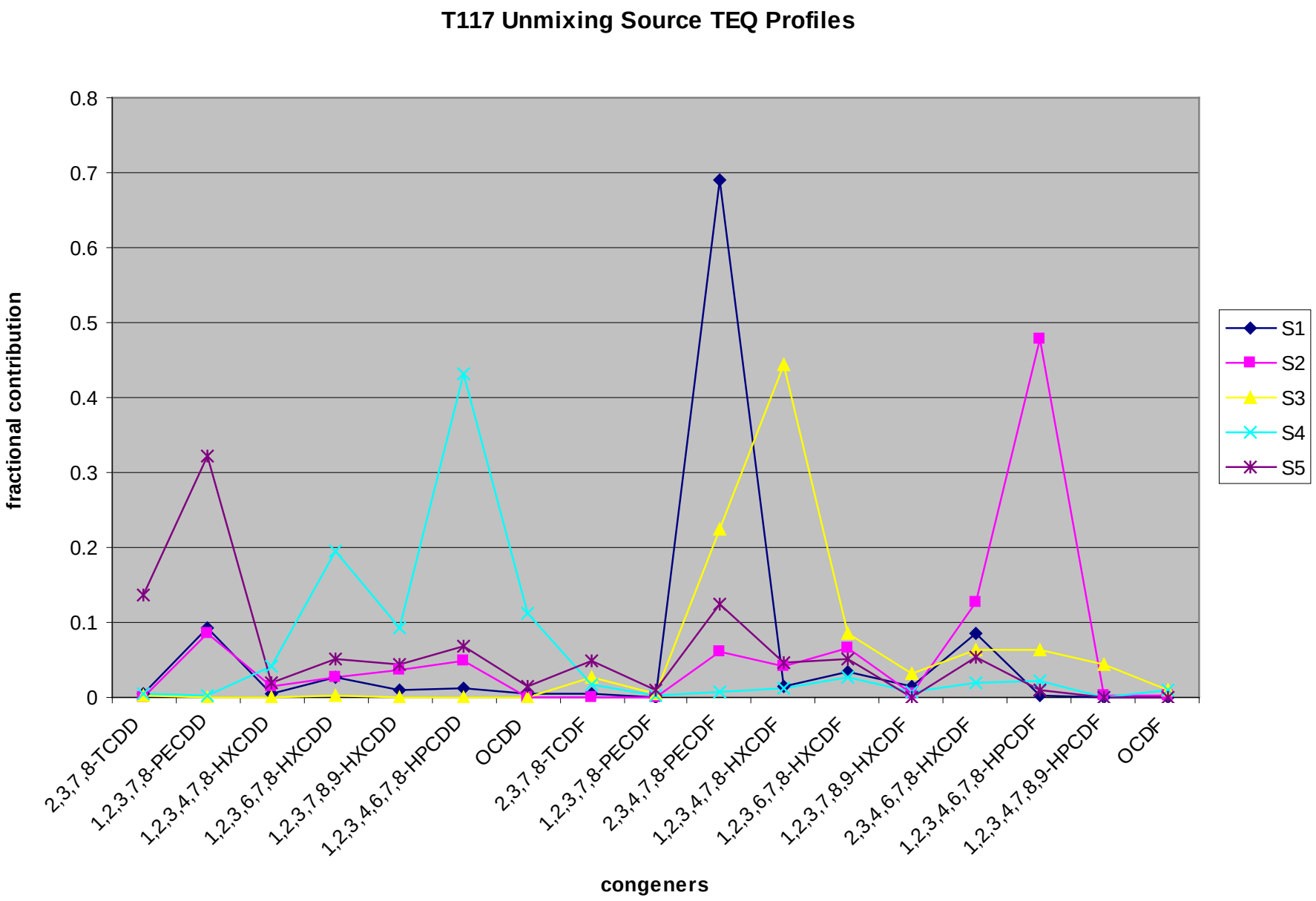

TEQ Profiles (Unmixing): DU01-2
TEQ Increment (ppt)
10
9
8
7
6
5
4
3
2
1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
DU 01-2
DU01-subsurface


Bulk Congener Profiles: Lab vs Unmixing
dioxin/furans (ppt)
3000
2500
2000
1500
1000
500
0
2,3,7,8-TCDD
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
OCDF
congeners
DU01a-subsurface
DU01b-subsurface
DU01-subsurface


Bulk Congener Profiles: Lab vs Unmixing
10000
1000
100
10
1
0.1
dioxin/furans (ppt)
2,3,7,8-TCDD
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
OCDF
congeners
DU01a-subsurface
DU01b-subsurface
DU01-subsurface

Unmixing Models

- Multiple mathematical approaches
  - For matched data sets and approaches, similar results
- Options for application, judgment in adopted model
- Multiple approaches used by TWG
- Focus here: TEF-scaled data (TEQ profiles) by ALS (Infometrix)
- Unmixing analysis provides:
  - Number of sources
  - Source profiles
  - Contributions of sources to samples
- Unmixing is mathematics – interpretation is required


T117 Unmixing Source TEQ Profiles
fractional contribution
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
S1
S2
S3
S4
S5

TEQ Increments

- Unmixing model provides
  - Source profiles
  - Contributions of sources to samples
- From this information, the contribution of one source to a sample TEQ can be calculated
  - TEQ increment
  - Sum of TEQ increments over sources for total TEQ (and residuals)
- More information than total TEQ available for interpretation

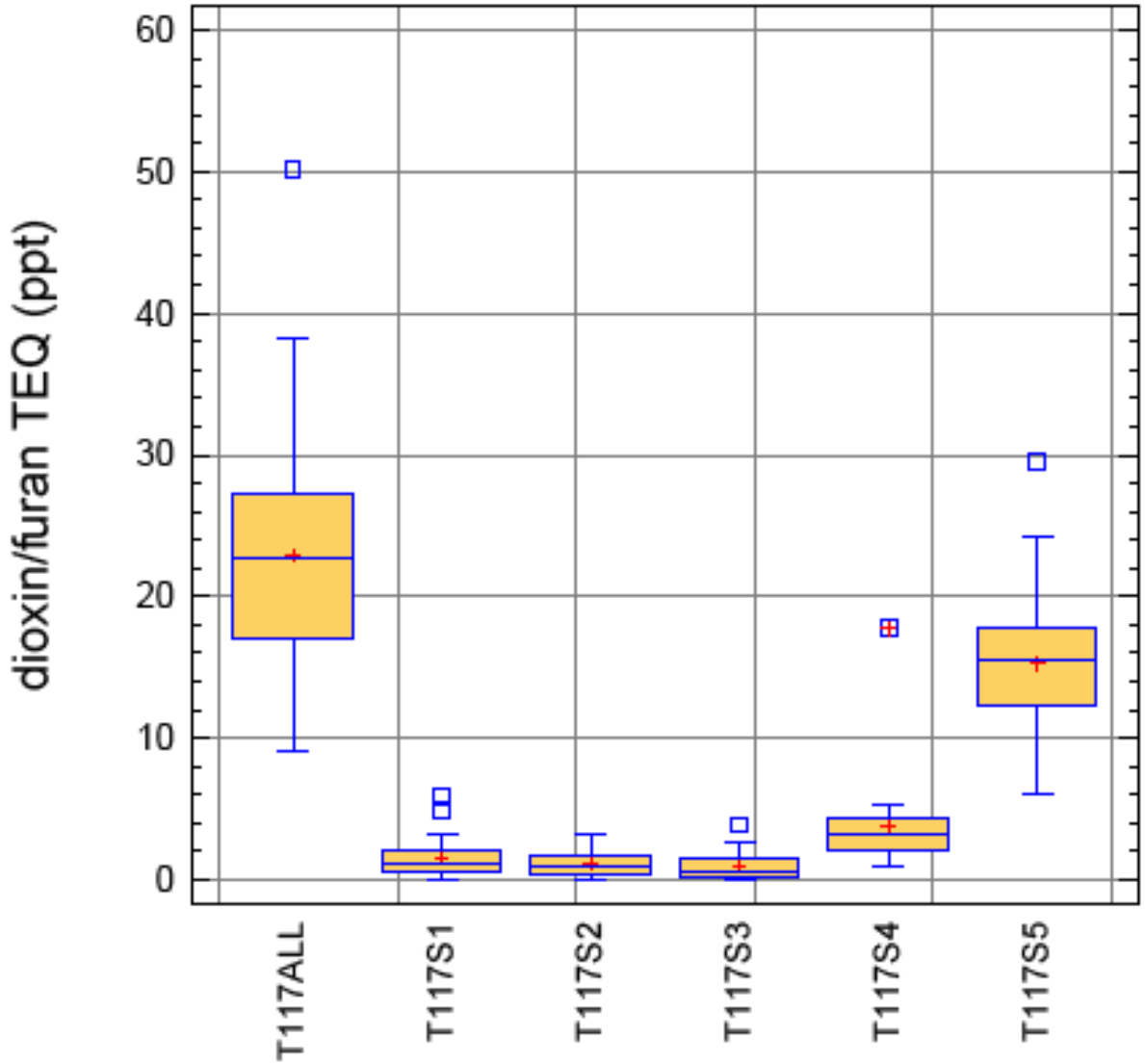
Unmixing Analysis Results: Interpretation

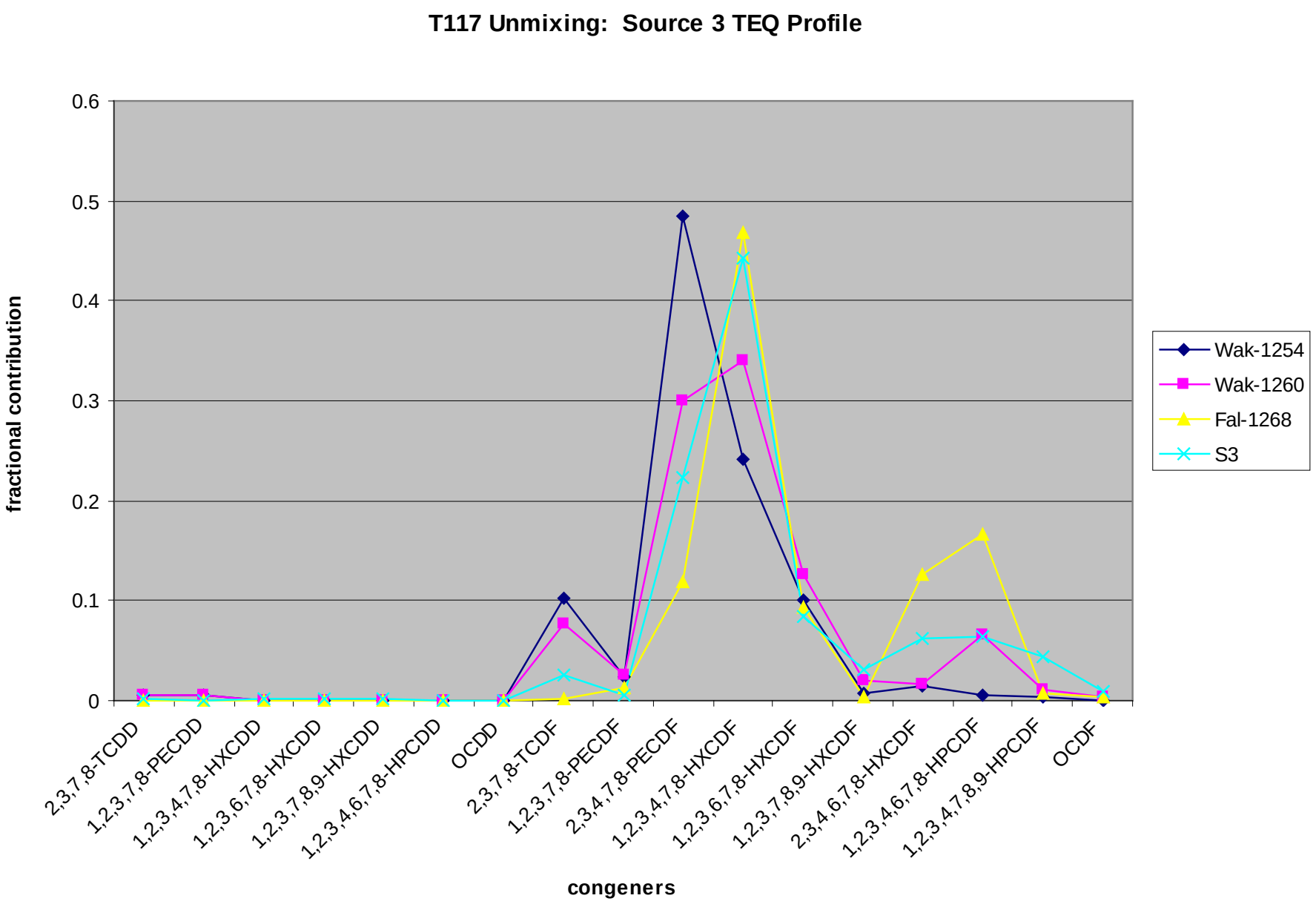
- Mathematical results alone don’t tell us what we want to know
- Getting from source profiles to source identification
- Using information not incorporated into unmixing analysis
  - Spatial locations
  - Sample types
- Confidence in interpretation
  - Reasonableness
  - Lines of evidence
  - Consistency

Source Evaluation Criteria

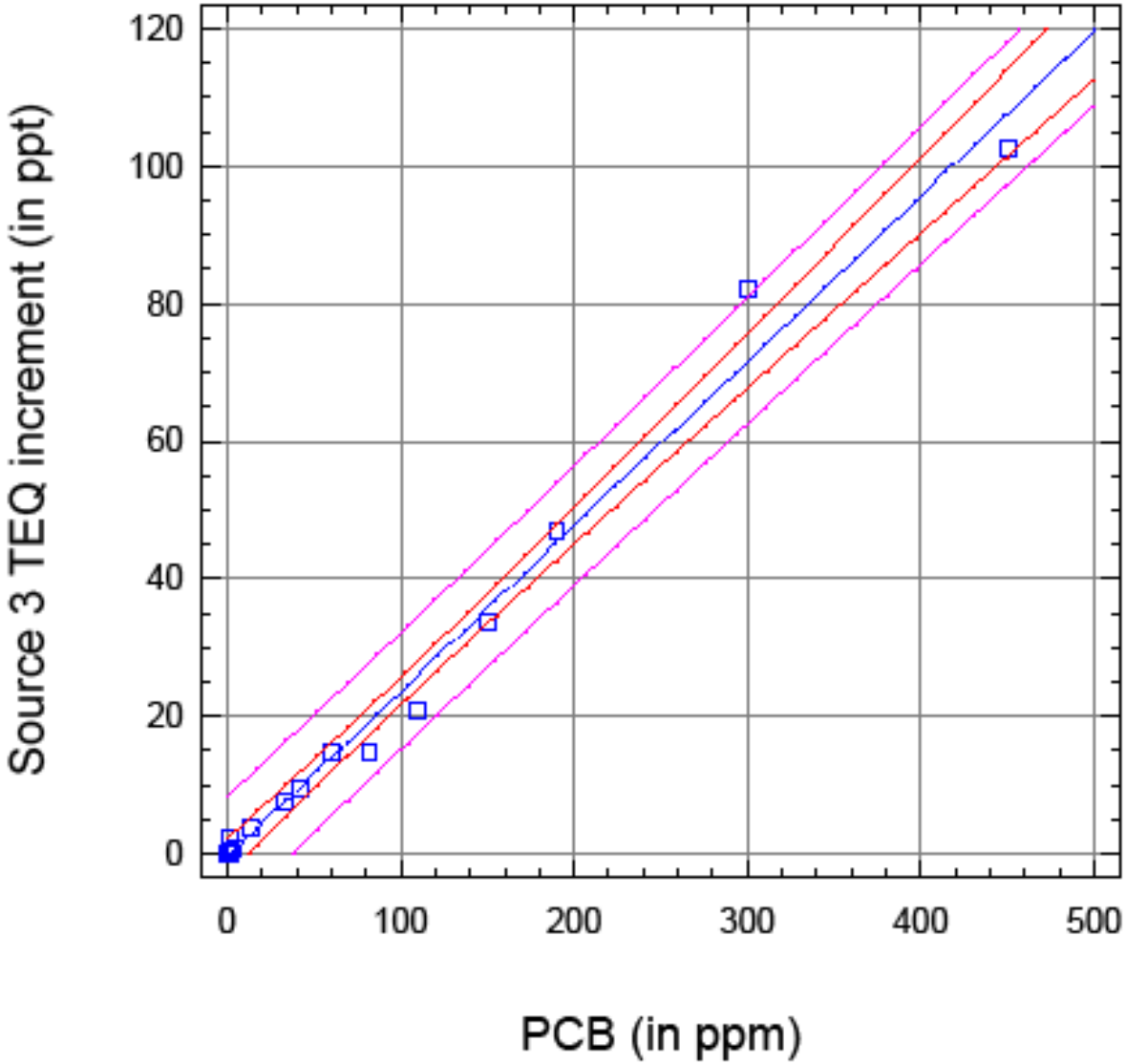
- Chemical pattern
- Spatial pattern
- Magnitude
- Mass balance
- Temporal pattern

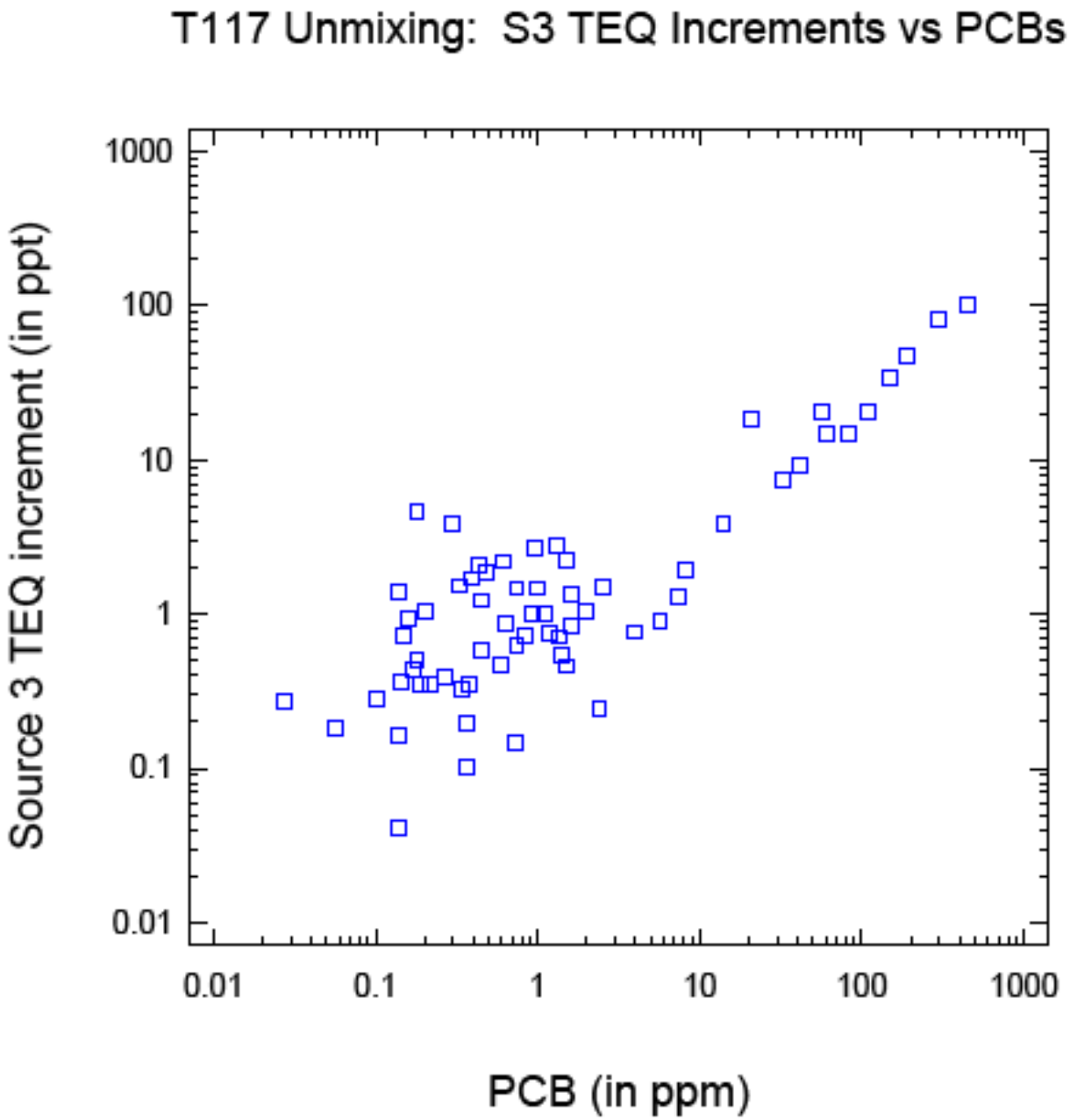
T117 Yards (MIS): TEQ Increments



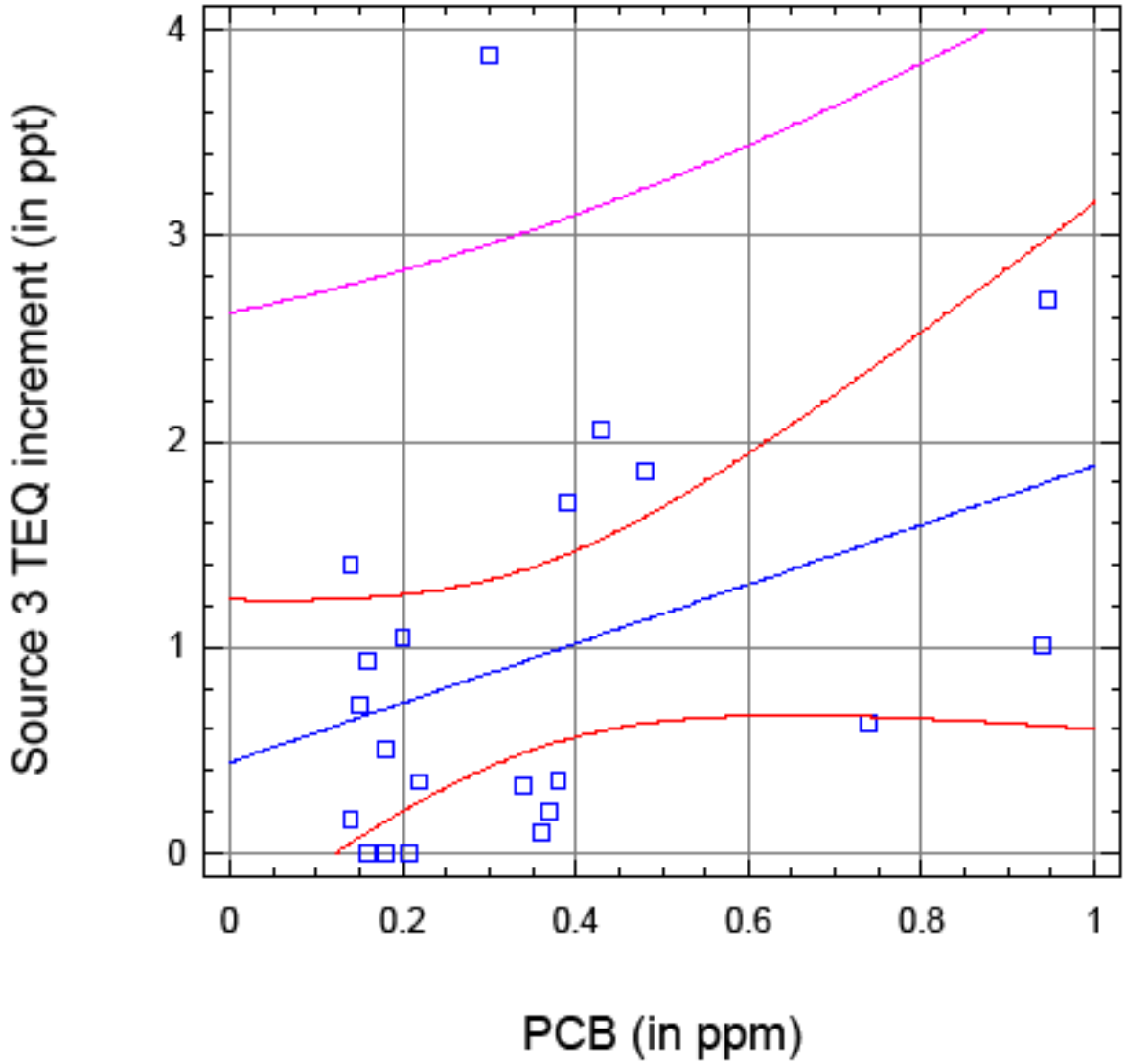

T117 Unmixing: Source 3 TEQ Profile
fractional contribution
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
Wak-1254
Wak-1260
Fal-1268
S3

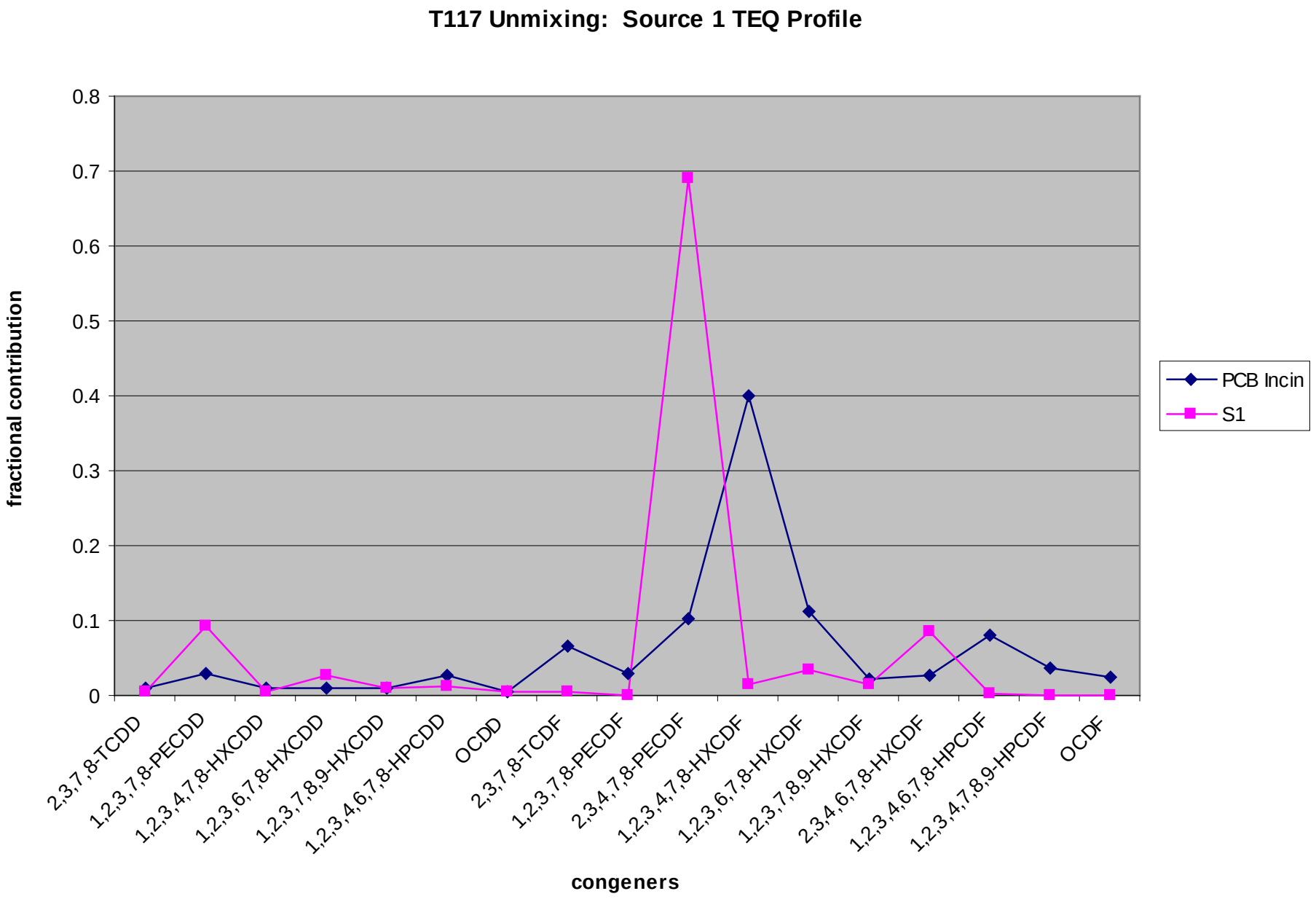
T117 Unmixing: S3 TEQ Increments vs PCBs - Uplands

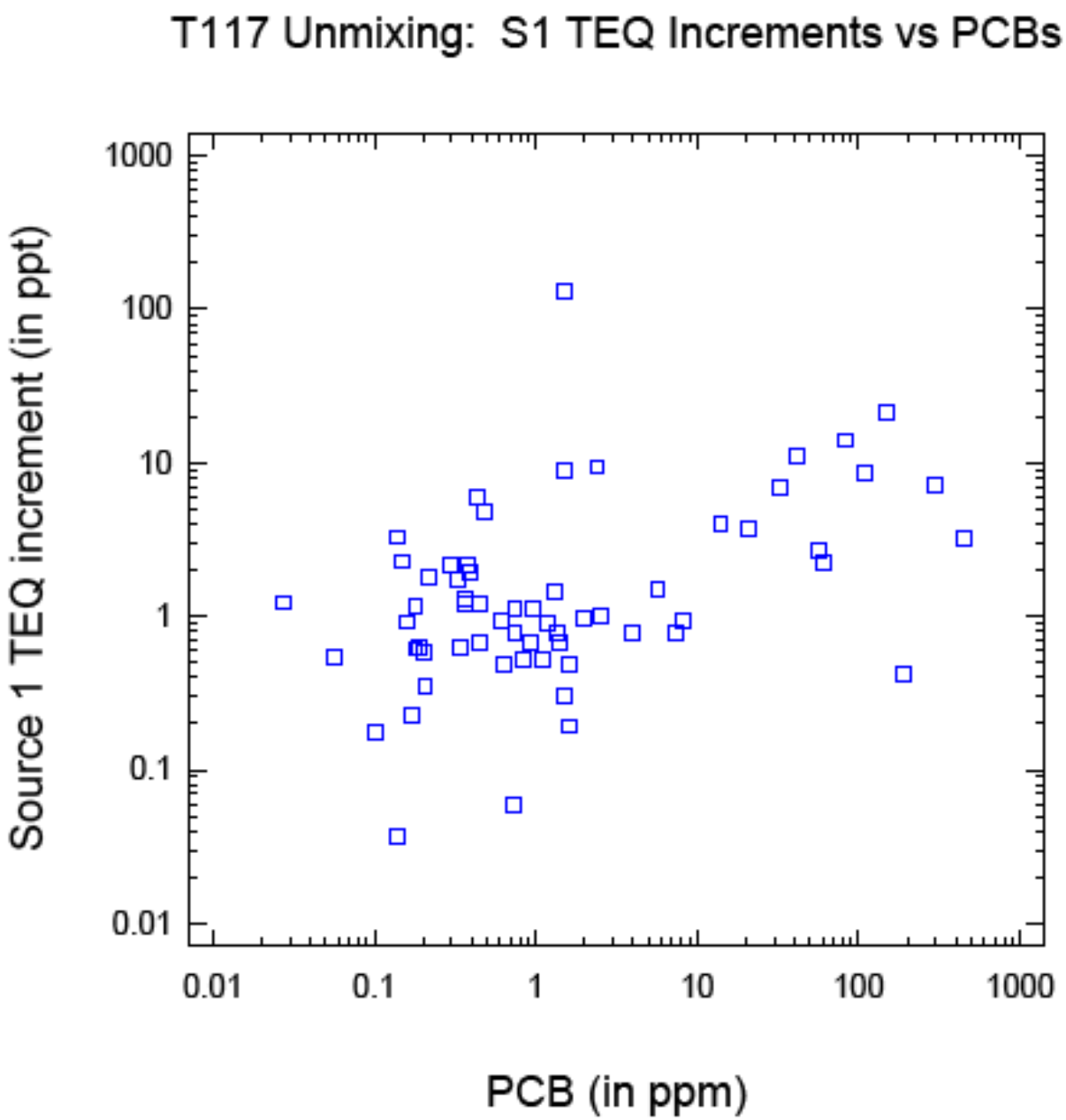


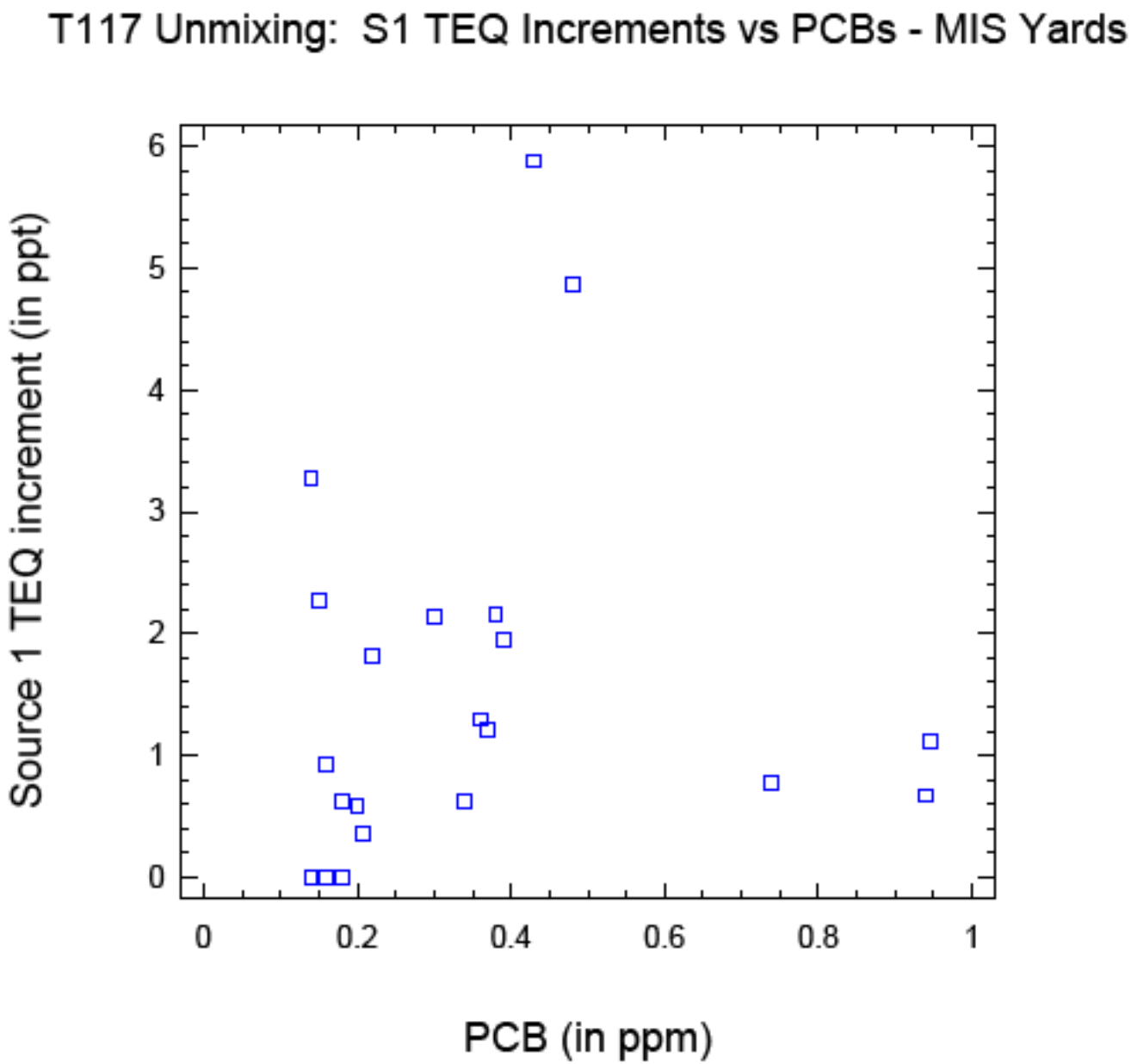

T117 Unmixing: S3 TEQ Increments vs PCBs
Source 3 TEQ increment (in ppt)
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
PCB (in ppm)

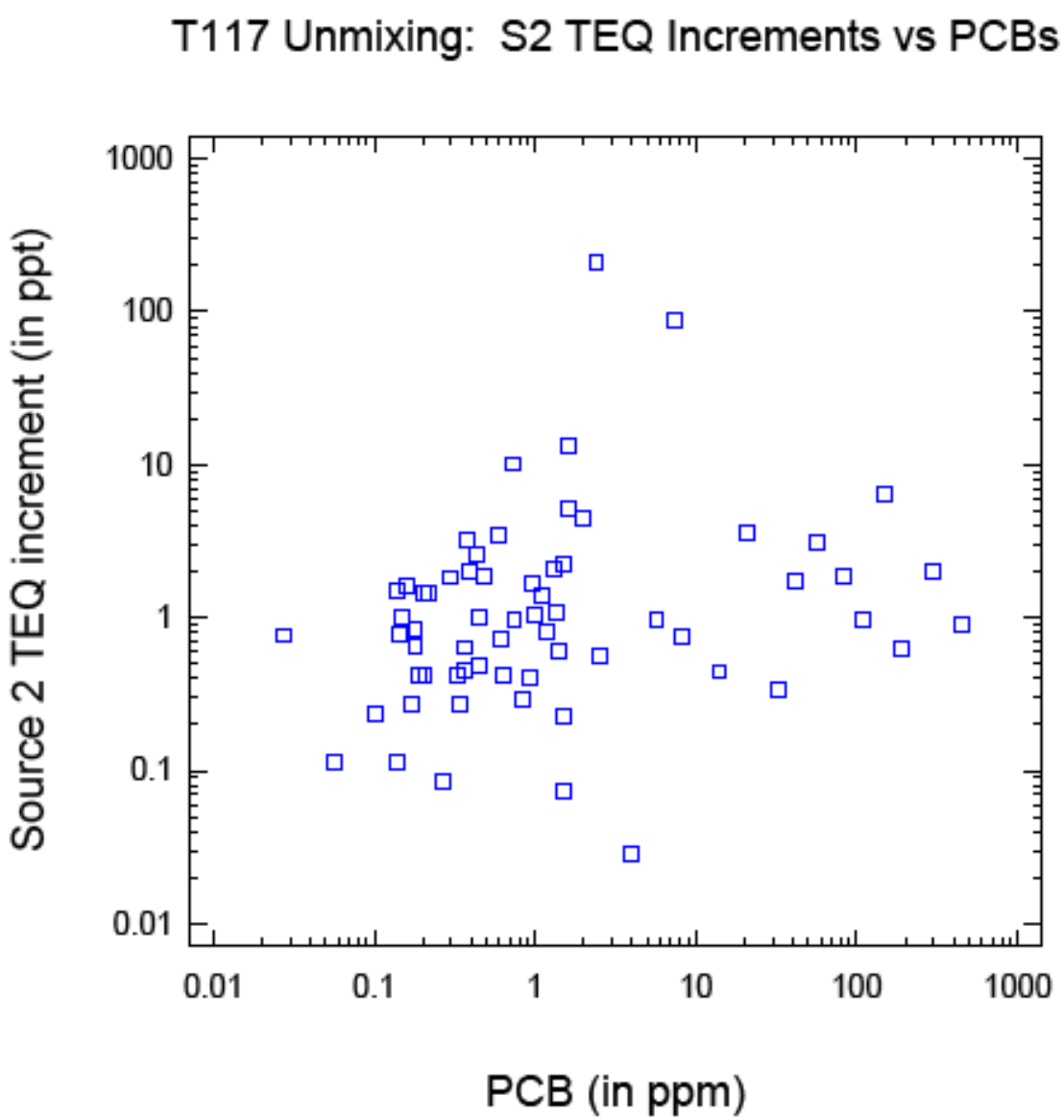
T117 Unmixing: S3 TEQ Increments vs PCBs - MIS Yards

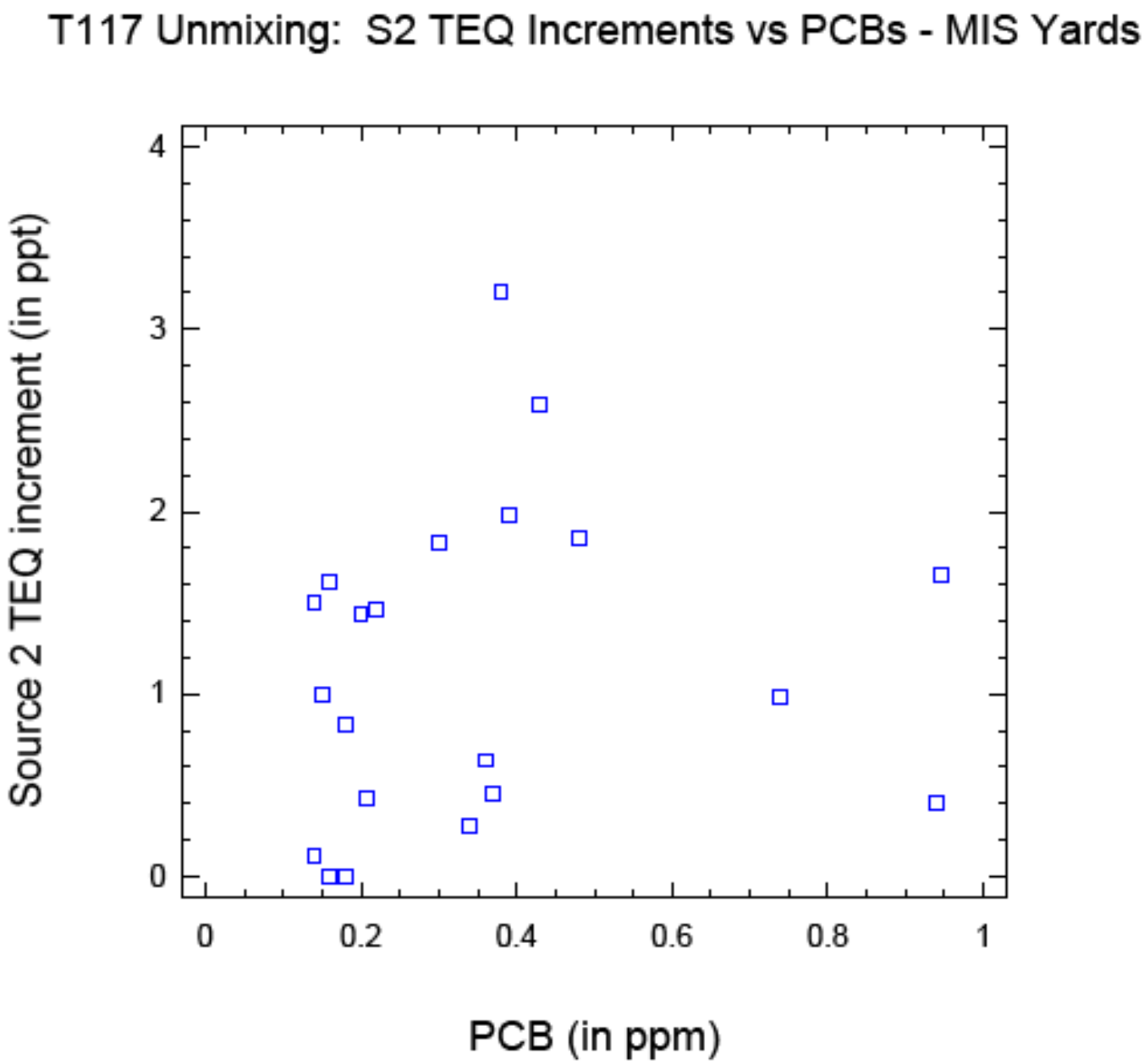


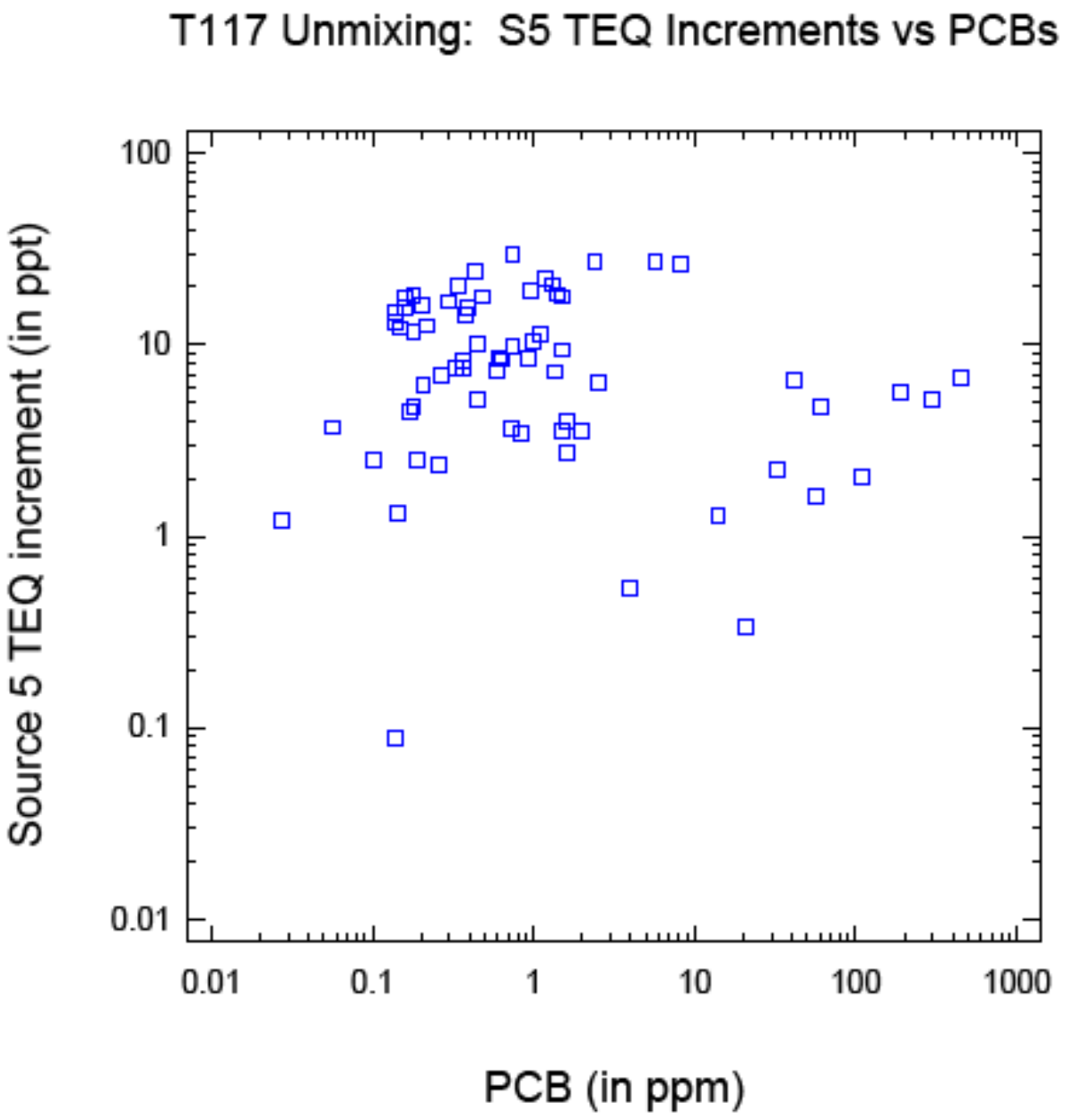

T117 Unmixing: Source 1 TEQ Profile
fractional contribution
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
PCB Incin
S1

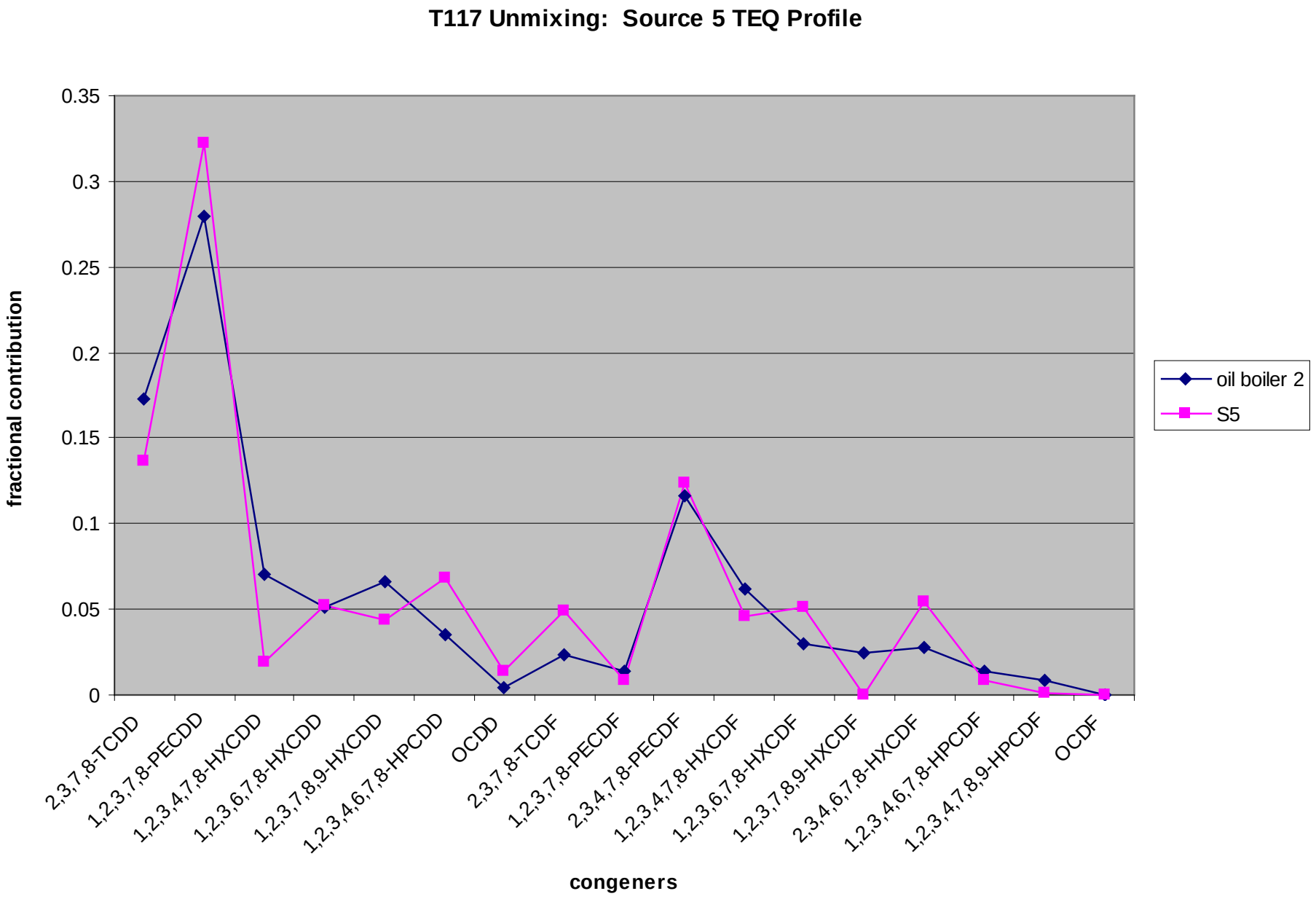

T117 Unmixing: S1 TEQ Increments vs PCBs
Source 1 TEQ increment (in ppt)
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
PCB (in ppm)

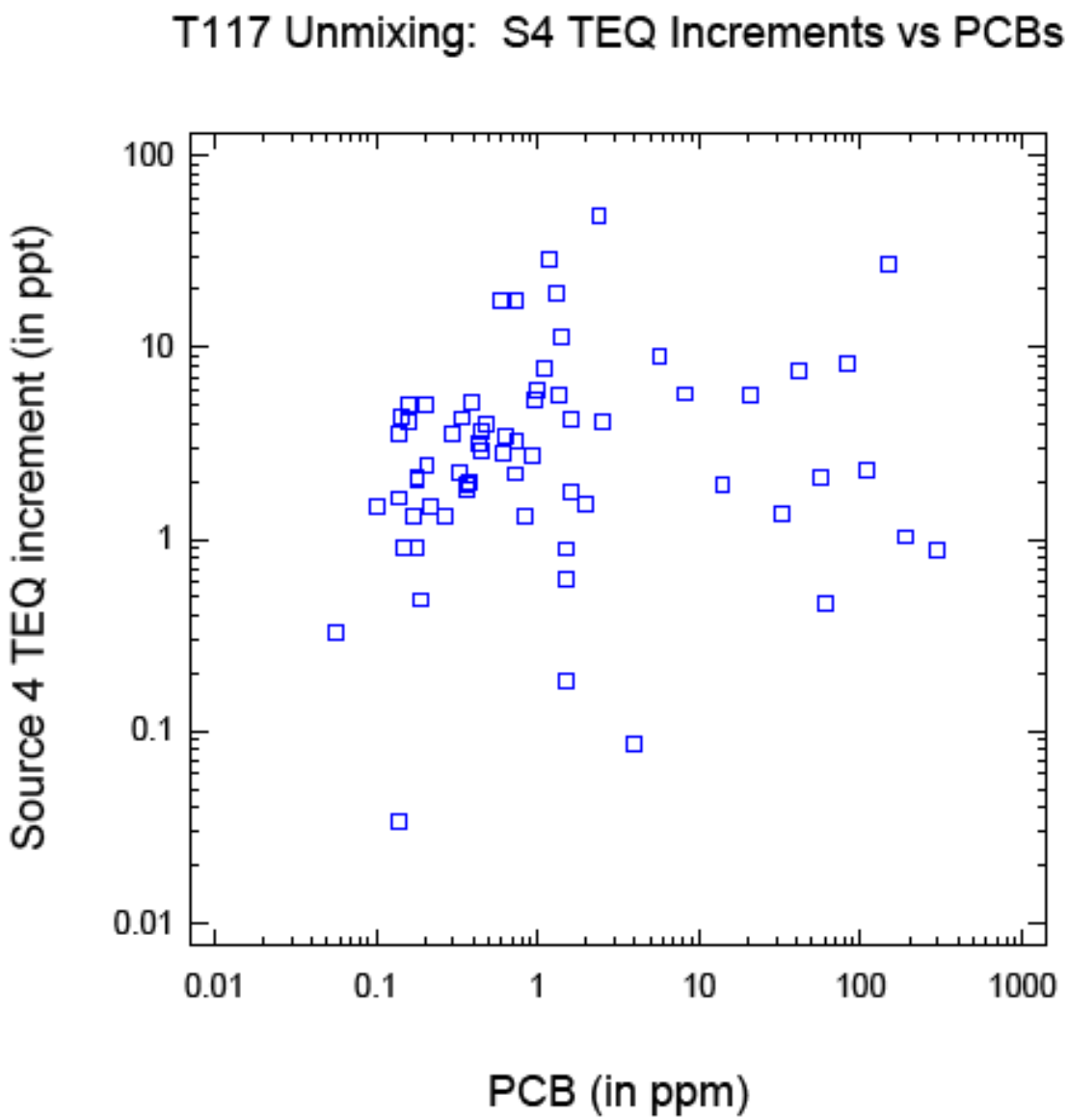

T117 Unmixing: S1 TEQ Increments vs PCBs - MIS Yards
Source 1 TEQ increment (in ppt)
0
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1
PCB (in ppm)

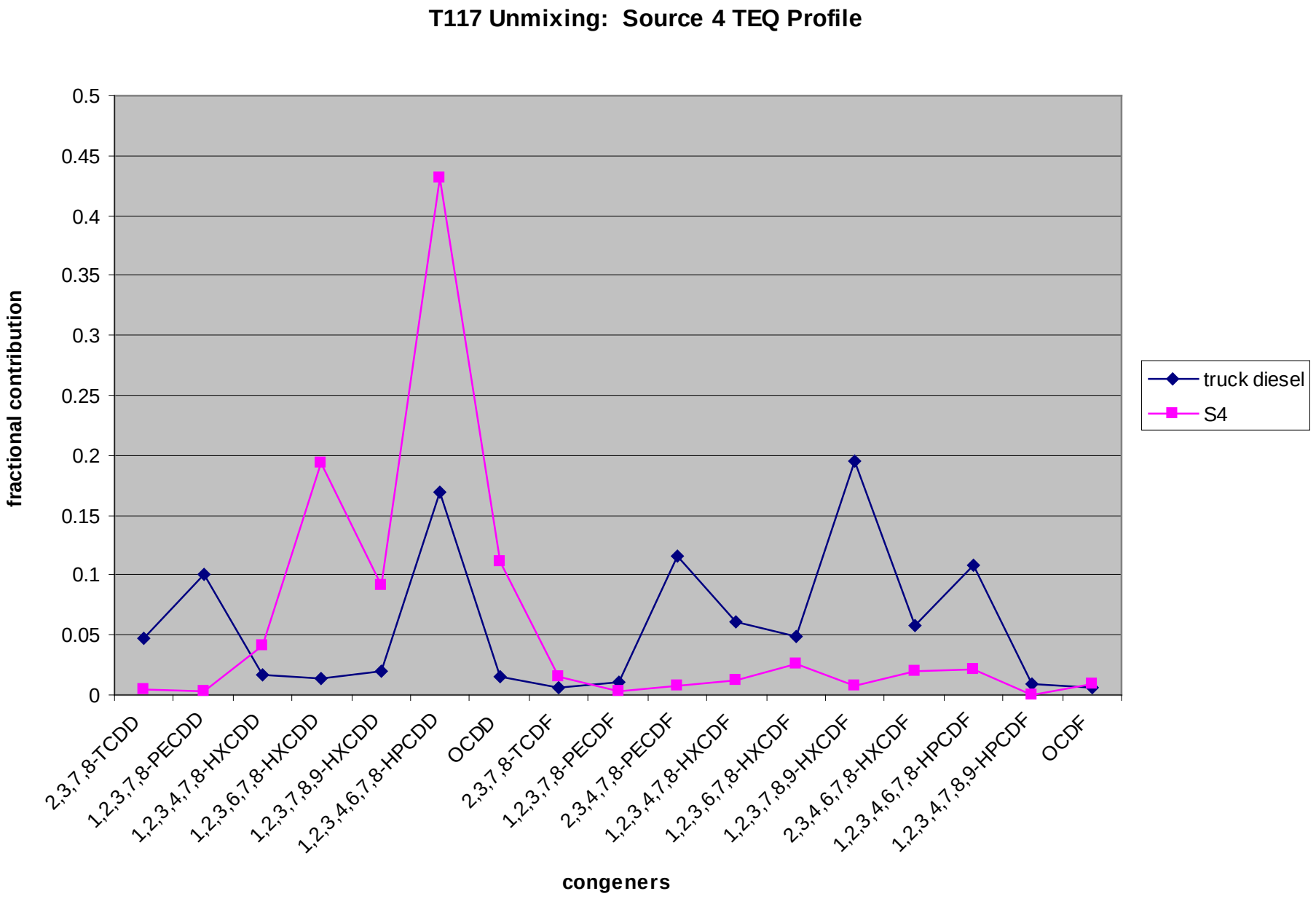

T117 Unmixing: S2 TEQ Increments vs PCBs
Source 2 TEQ increment (in ppt)
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
PCB (in ppm)

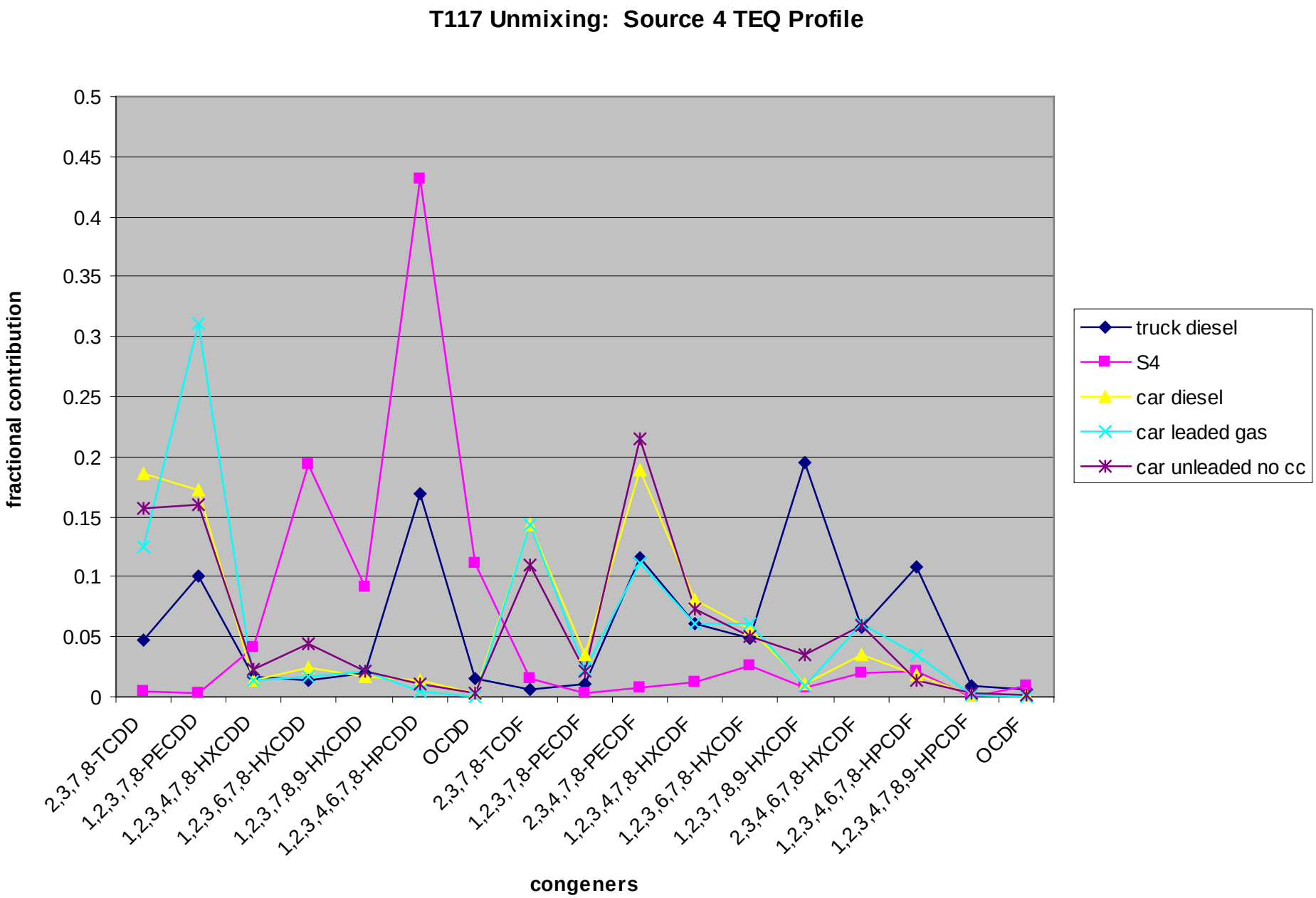

T117 Unmixing: S2 TEQ Increments vs PCBs - MIS Yards
Source 2 TEQ increment (in ppt)
PCB (in ppm)
0
1
2
3
4
0
0.2
0.4
0.6
0.8
1

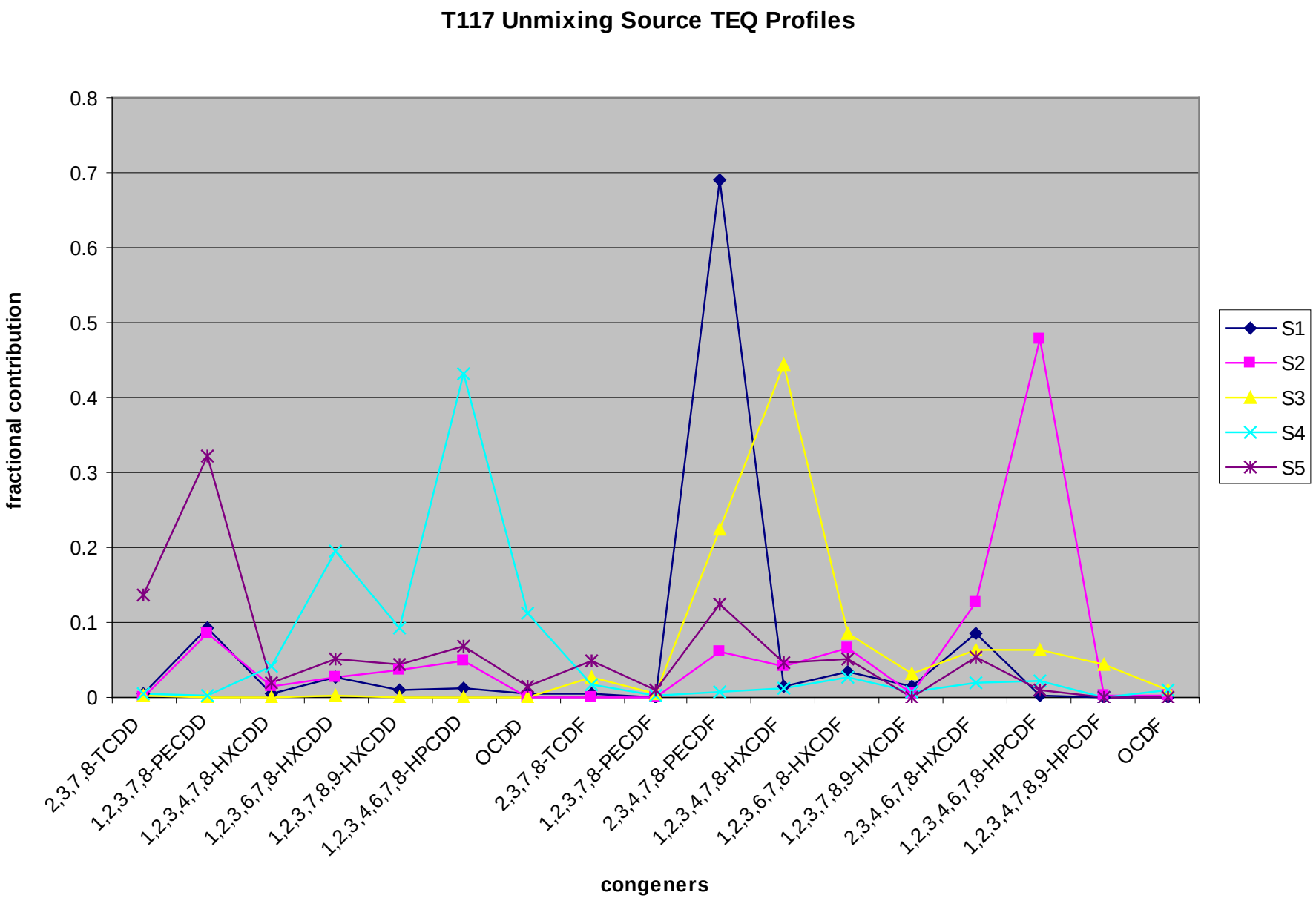

T117 Unmixing: S5 TEQ Increments vs PCBs
Source 5 TEQ increment (in ppt)
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
PCB (in ppm)


T117 Unmixing: Source 5 TEQ Profile
fractional contribution
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
oil boiler 2
S5


T117 Unmixing: S4 TEQ Increments vs PCBs
Source 4 TEQ increment (in ppt)
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
PCB (in ppm)

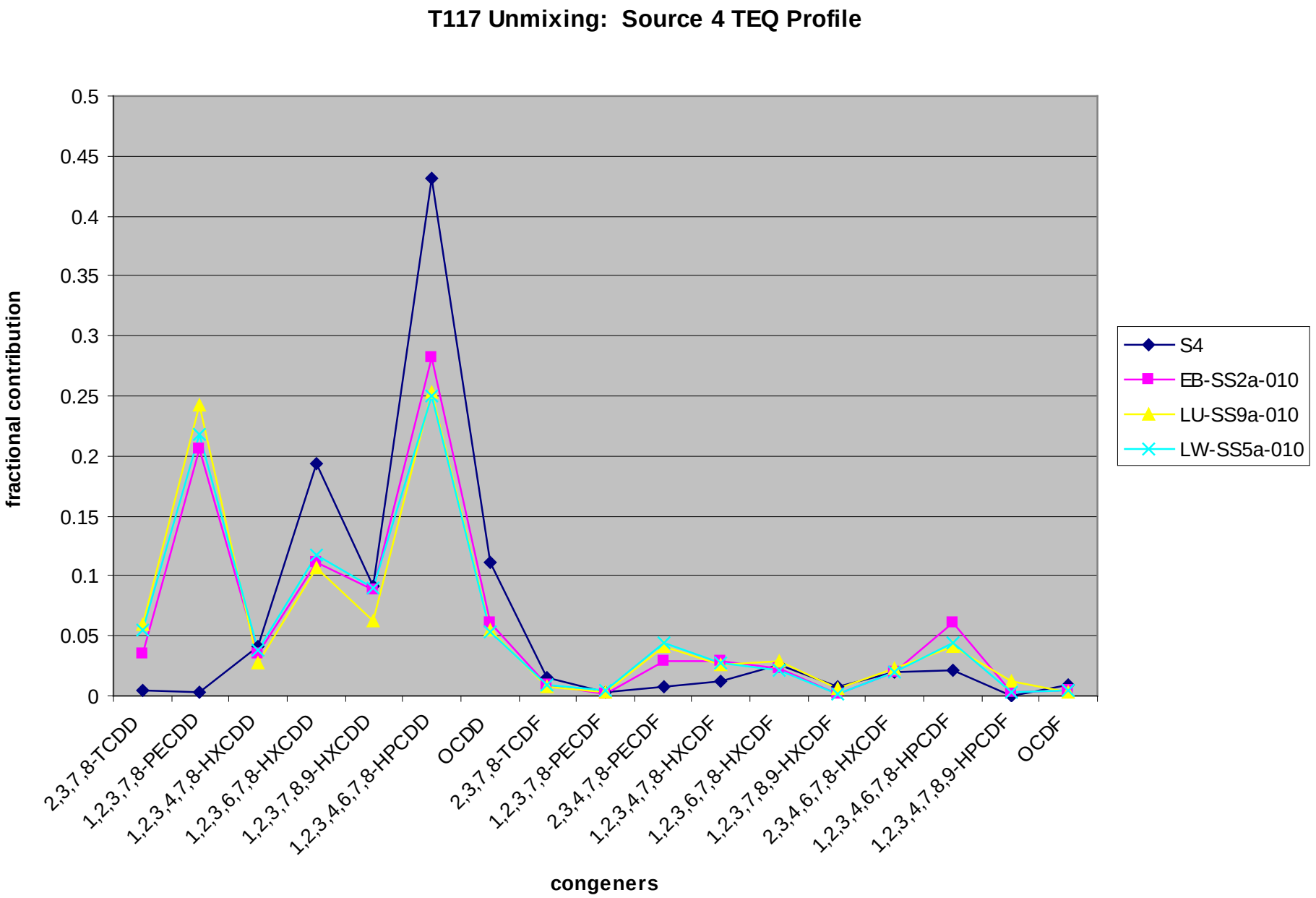

T117 Unmixing: Source 4 TEQ Profile
fractional contribution
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
truck diesel
S4

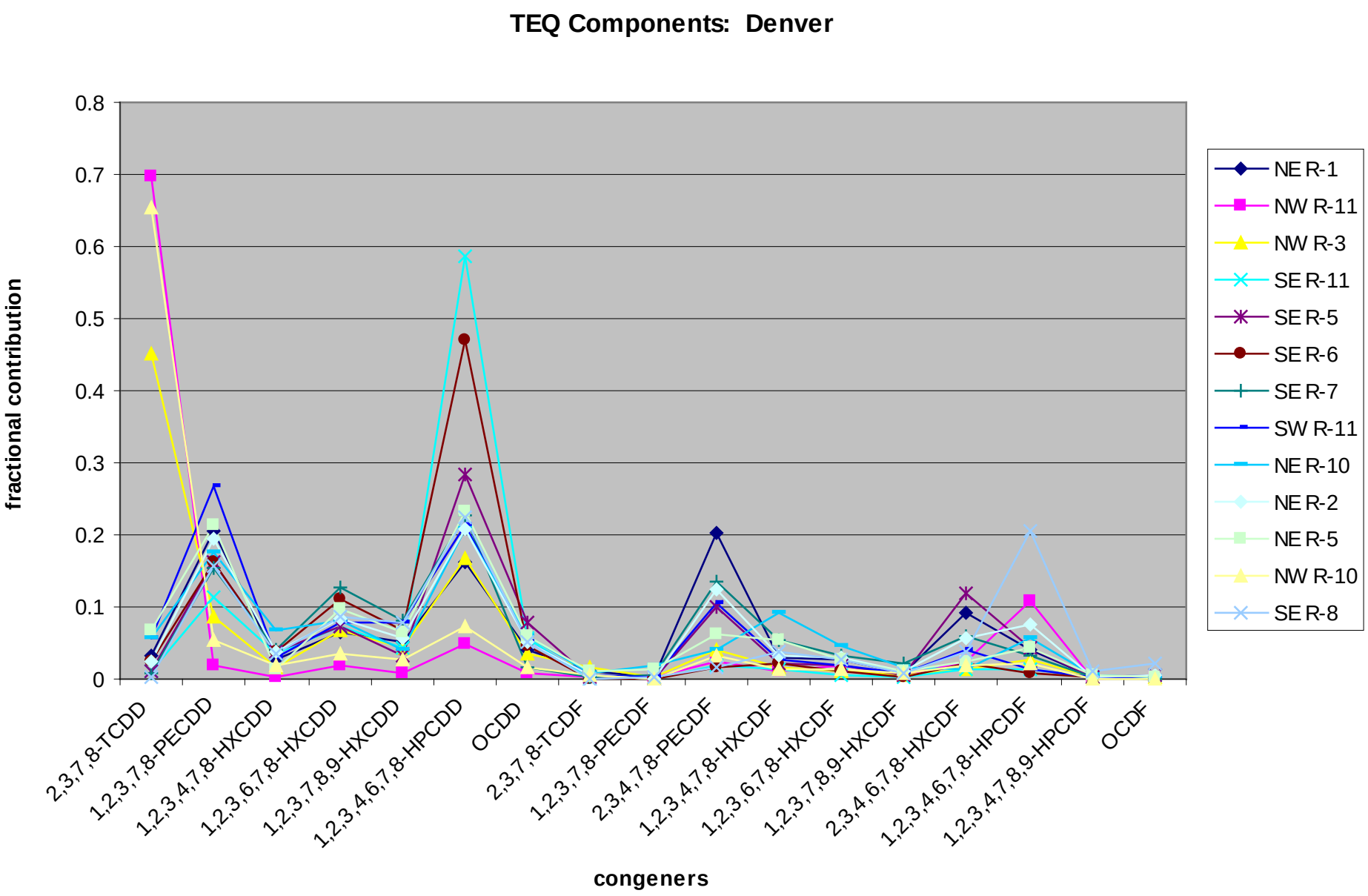

T117 Unmixing: Source 4 TEQ Profile
fractional contribution
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
truck diesel
S4
car diesel
car leaded gas
car unleaded no cc

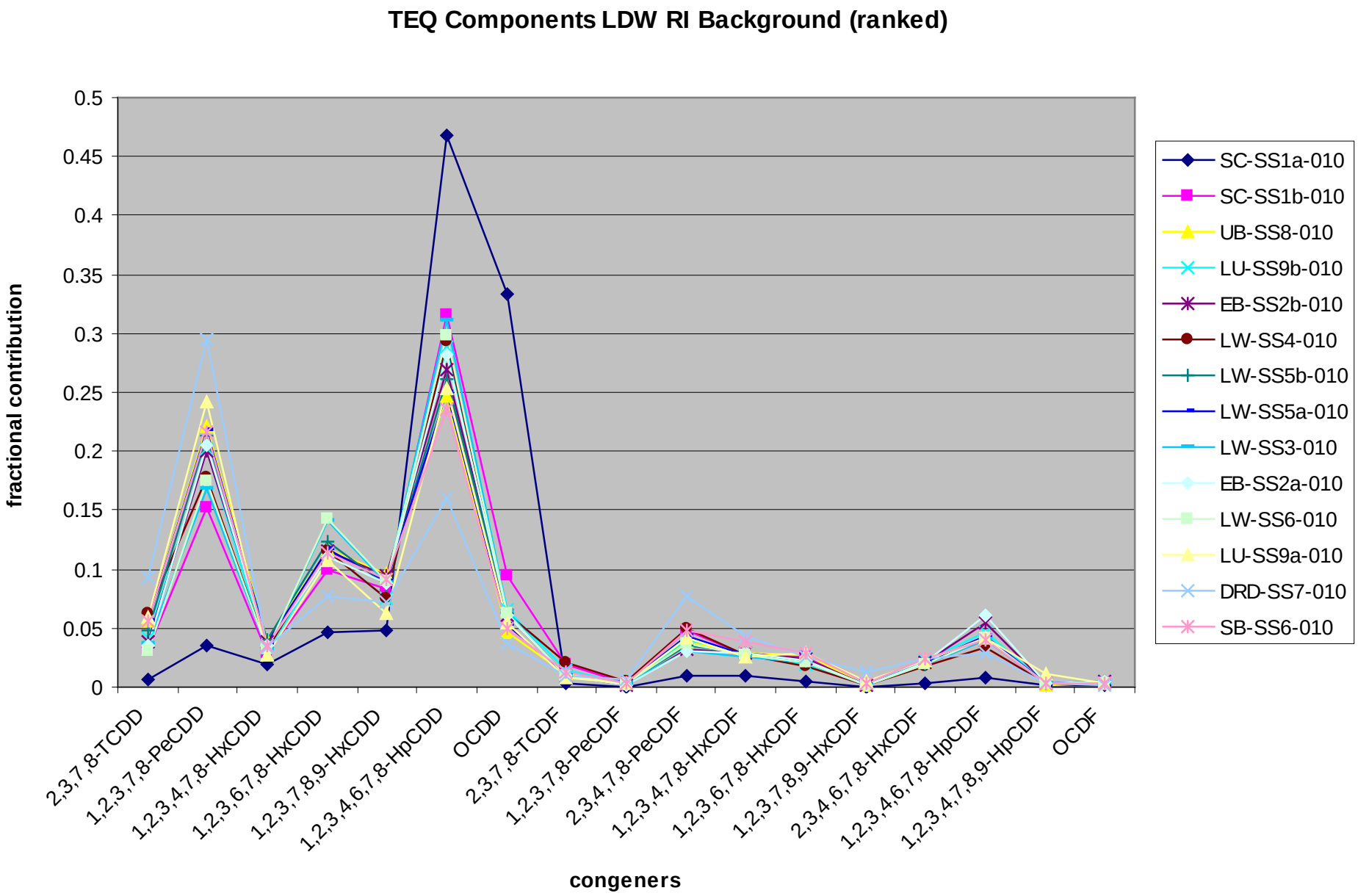

T117 Unmixing Source TEQ Profiles
fractional contribution
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
S1
S2
S3
S4
S5

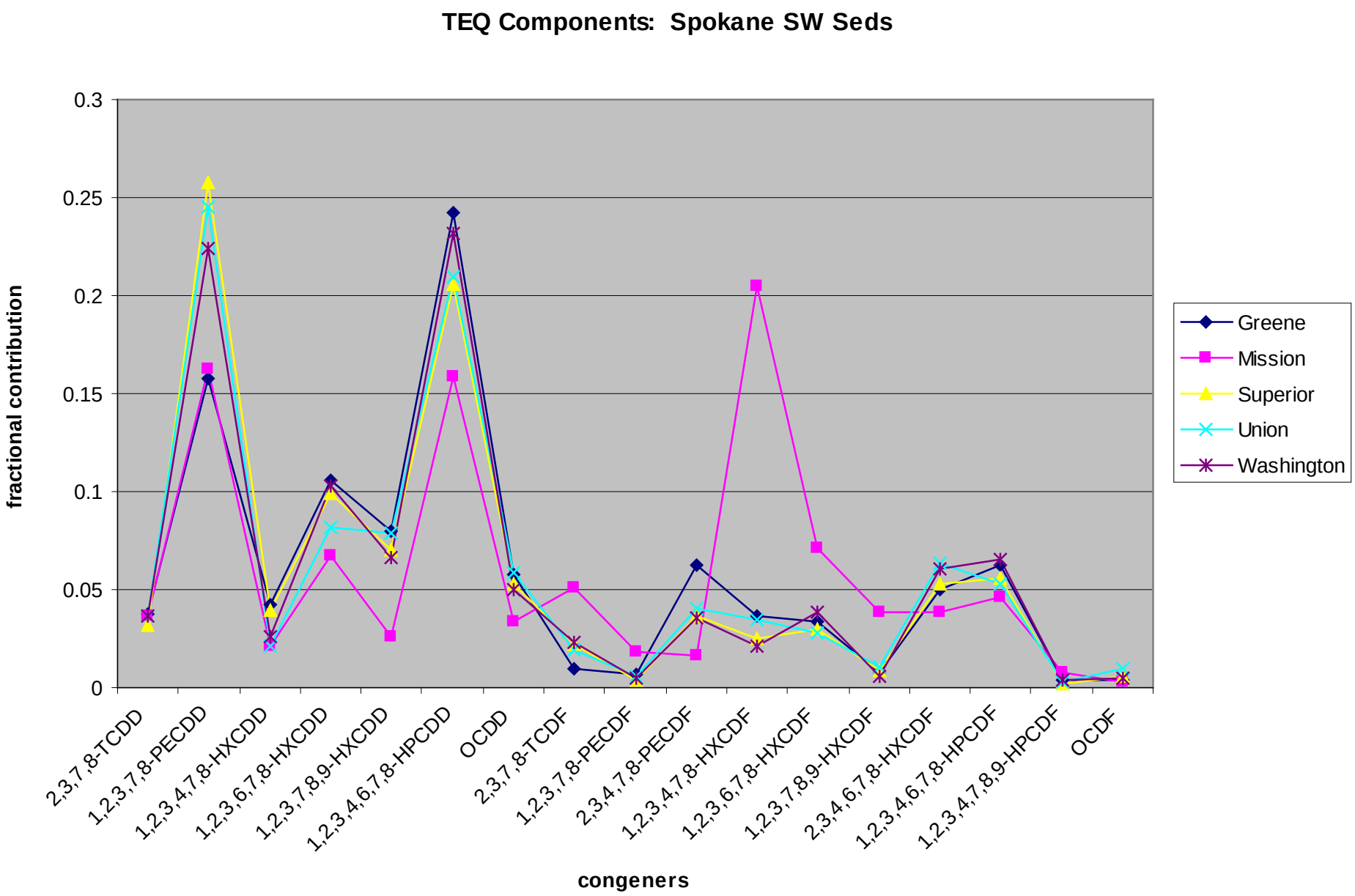
Source 4 and Source 5 Profiles

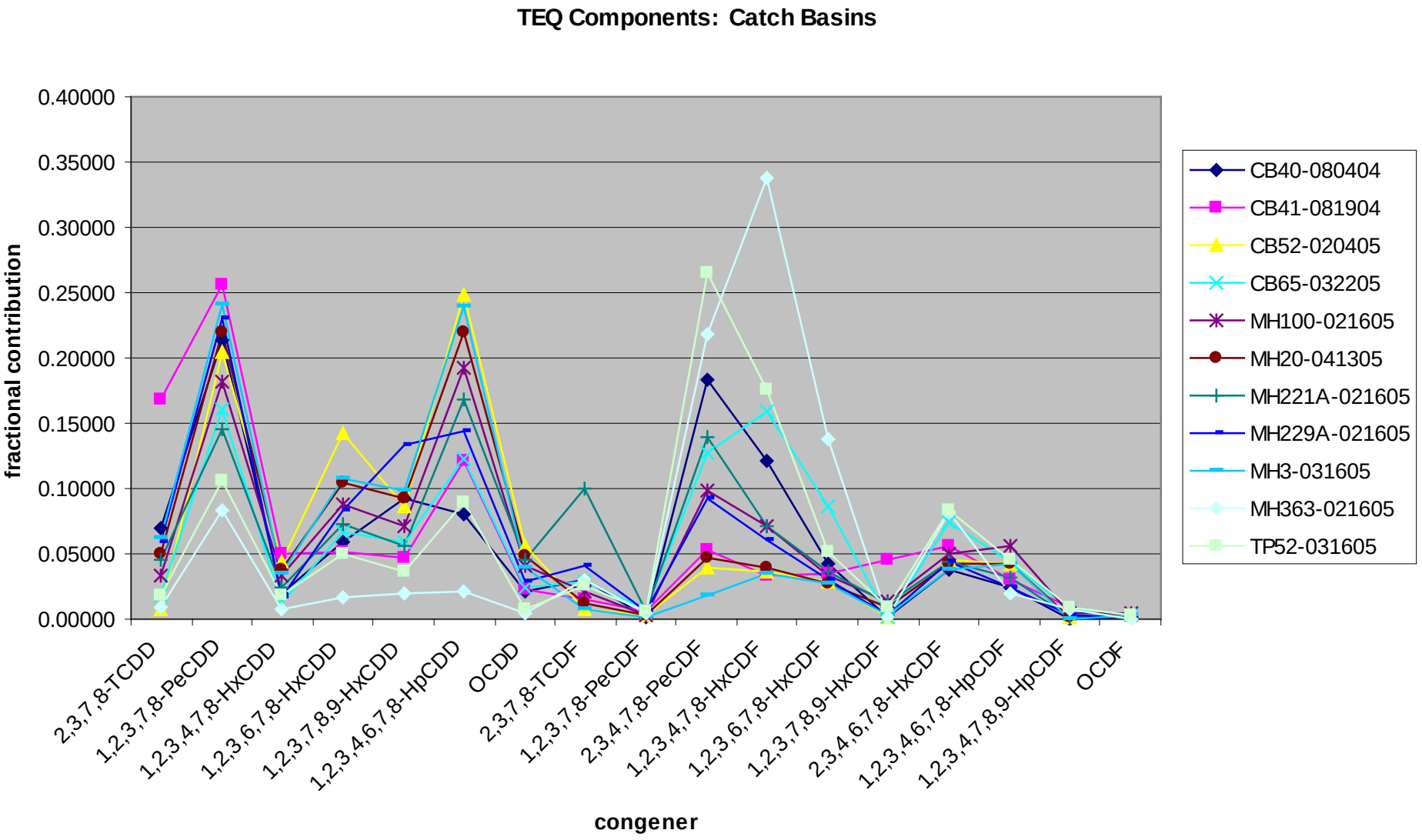
- Choice of combining or separating for unmixing model
- Three prominent dioxin congener peaks
- Comparison data sets
- Background, typical urban profiles
  - Background is composite of multiple sources
  - Interpretation of components(s) of background

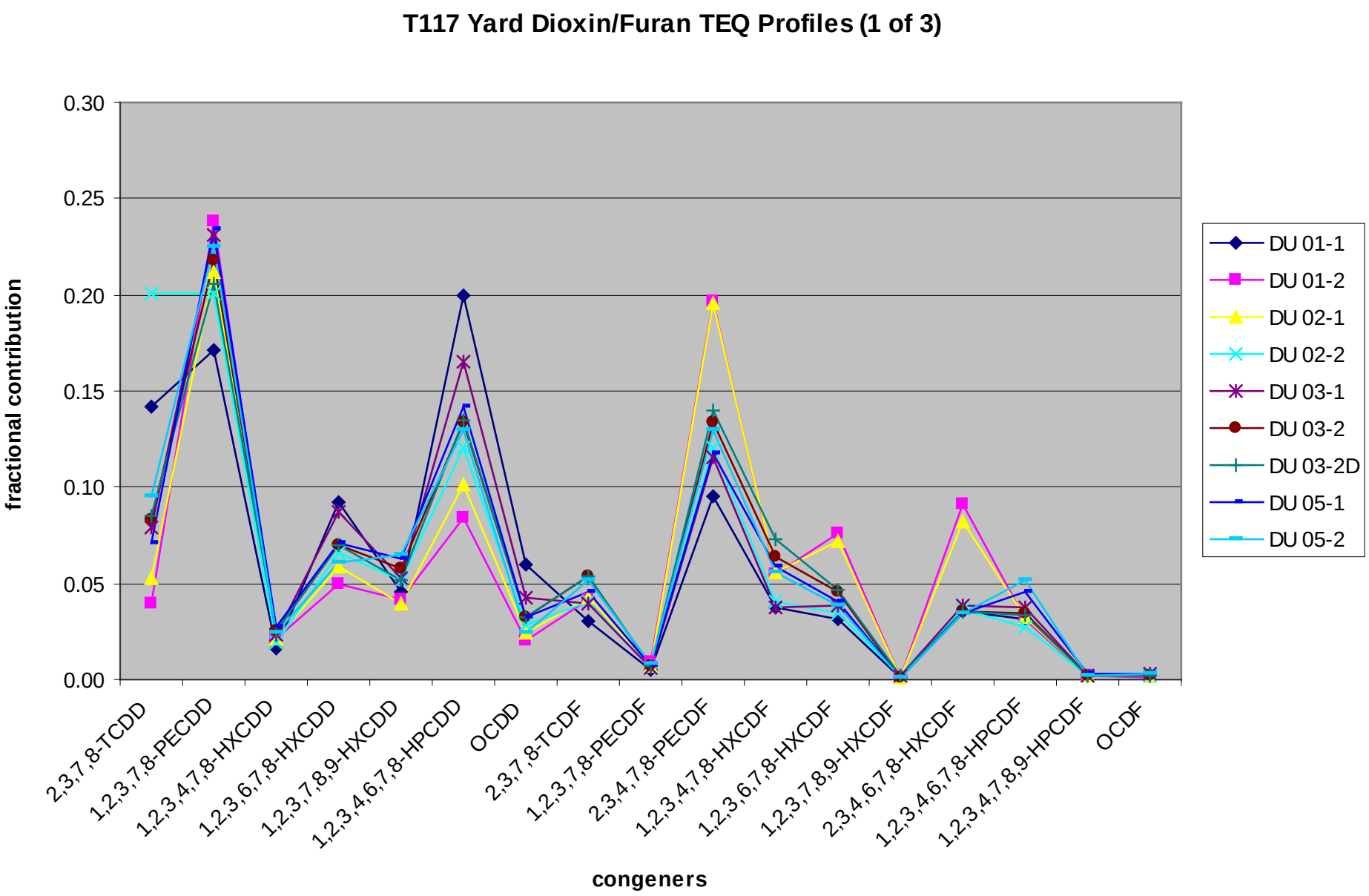

T117 Unmixing: Source 4 TEQ Profile
fractional contribution
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
S4
EB-SS2a-010
LU-SS9a-010
LW-SS5a-010

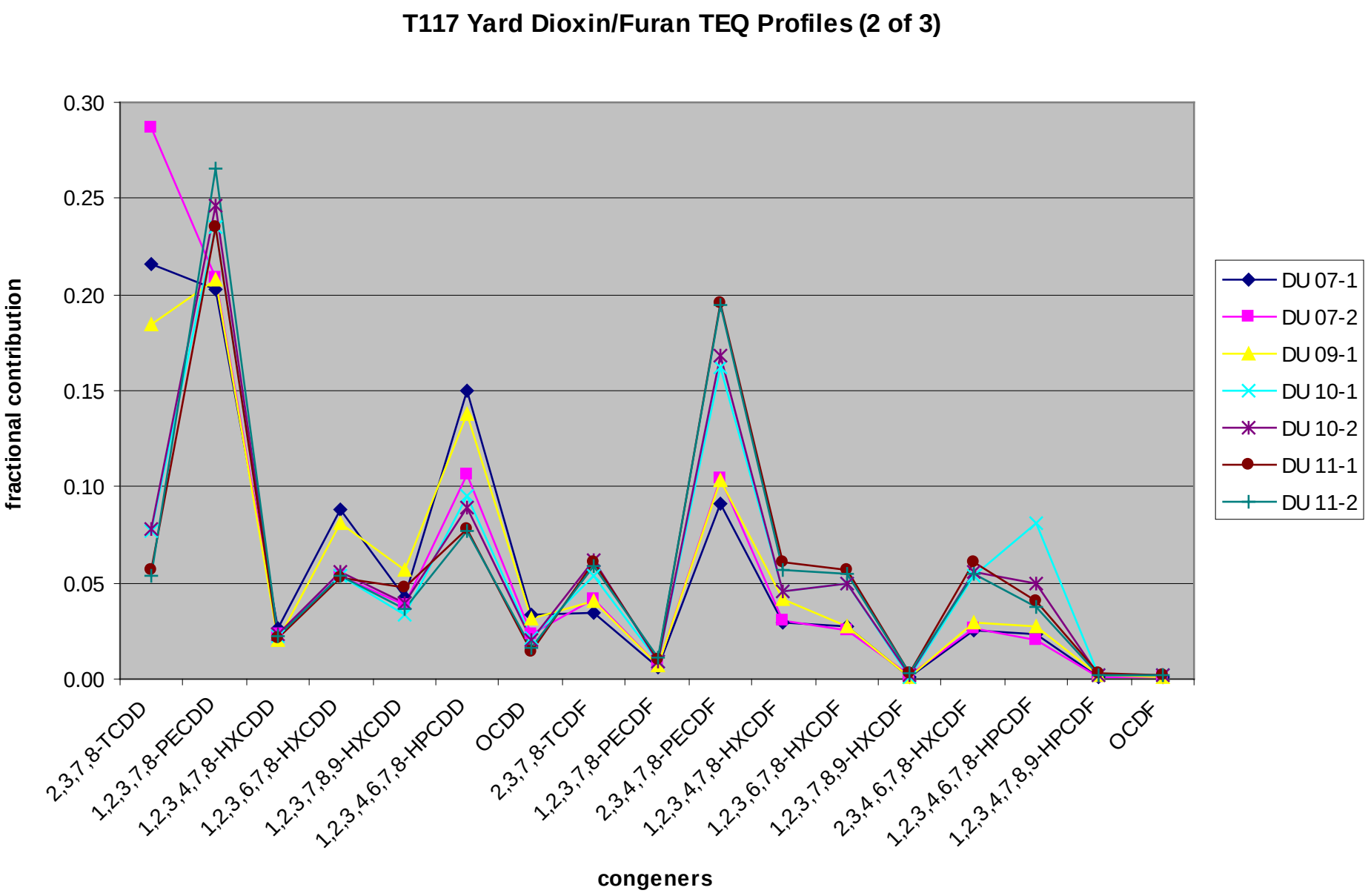

TEQ Components: Denver
fractional contribution
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
NE R-1
NW R-11
NW R-3
SE R-11
SE R-5
SE R-6
SE R-7
SW R-11
NE R-10
NE R-2
NE R-5
NW R-10
SE R-8

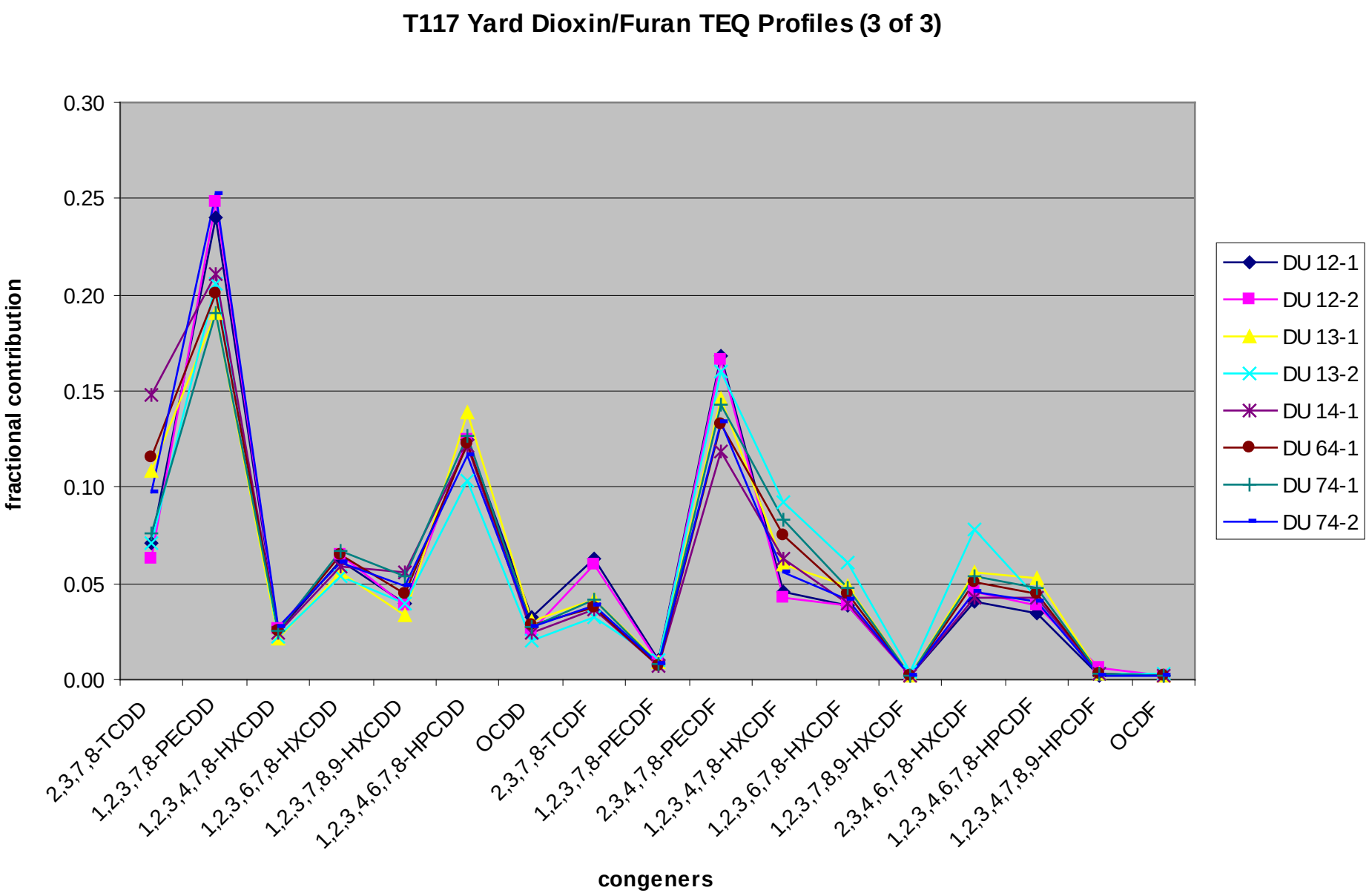

TEQ Components LDW RI Background (ranked)
fractional contribution
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
OCDF
congeners
SC-SS1a-010
SC-SS1b-010
UB-SS8-010
LU-SS9b-010
EB-SS2b-010
LW-SS4-010
LW-SS5b-010
LW-SS5a-010
LW-SS3-010
EB-SS2a-010
LW-SS6-010
LU-SS9a-010
DRD-SS7-010
SB-SS6-010


TEQ Components: Spokane SW Seds
fractional contribution
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
Greene
Mission
Superior
Union
Washington


TEQ Components: Catch Basins
fractional contribution
0.40000
0.35000
0.30000
0.25000
0.20000
0.15000
0.10000
0.05000
0.00000
2,3,7,8-TCDD
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
OCDF
congener
CB40-080404
CB41-081904
CB52-020405
CB65-032205
MH100-021605
MH20-041305
MH221A-021605
MH229A-021605
MH3-031605
MH363-021605
TP52-031605

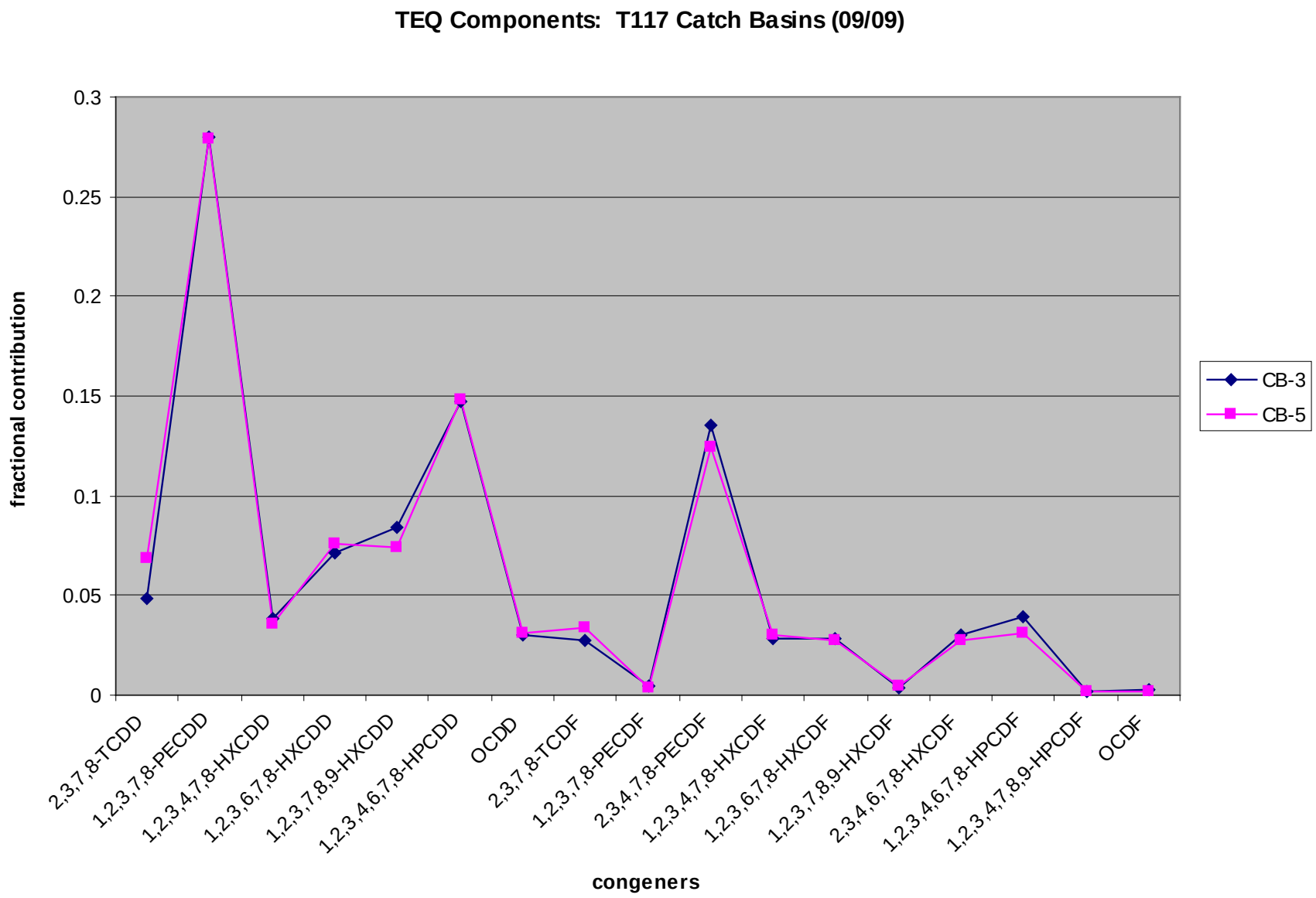

T117 Yard Dioxin/Furan TEQ Profiles (1 of 3)
fractional contribution
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
DU 01-1
DU 01-2
DU 02-1
DU 02-2
DU 03-1
DU 03-2
DU 03-2D
DU 05-1
DU 05-2


T117 Yard Dioxin/Furan TEQ Profiles (2 of 3)
fractional contribution
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
DU 07-1
DU 07-2
DU 09-1
DU 10-1
DU 10-2
DU 11-1
DU 11-2


T117 Yard Dioxin/Furan TEQ Profiles (3 of 3)
fractional contribution
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
DU 12-1
DU 12-2
DU 13-1
DU 13-2
DU 14-1
DU 64-1
DU 74-1
DU 74-2

T117 Catch Basin Samples (2009)

- TEQs in range of 50-150 ppt TEQ
- Source evaluation from unmixing model
  - Some remaining unexplained residual


TEQ Components: T117 Catch Basins (09/09)
fractional contribution
0.3
0.25
0.2
0.15
0.1
0.05
0
2,3,7,8-TCDD
1,2,3,7,8-PECDD
1,2,3,4,7,8-HXCDD
1,2,3,6,7,8-HXCDD
1,2,3,7,8,9-HXCDD
1,2,3,4,6,7,8-HPCDD
OCDD
2,3,7,8-TCDF
1,2,3,7,8-PECDF
2,3,4,7,8-PECDF
1,2,3,4,7,8-HXCDF
1,2,3,6,7,8-HXCDF
1,2,3,7,8,9-HXCDF
2,3,4,6,7,8-HXCDF
1,2,3,4,6,7,8-HPCDF
1,2,3,4,7,8,9-HPCDF
OCDF
congeners
CB-3
CB-5

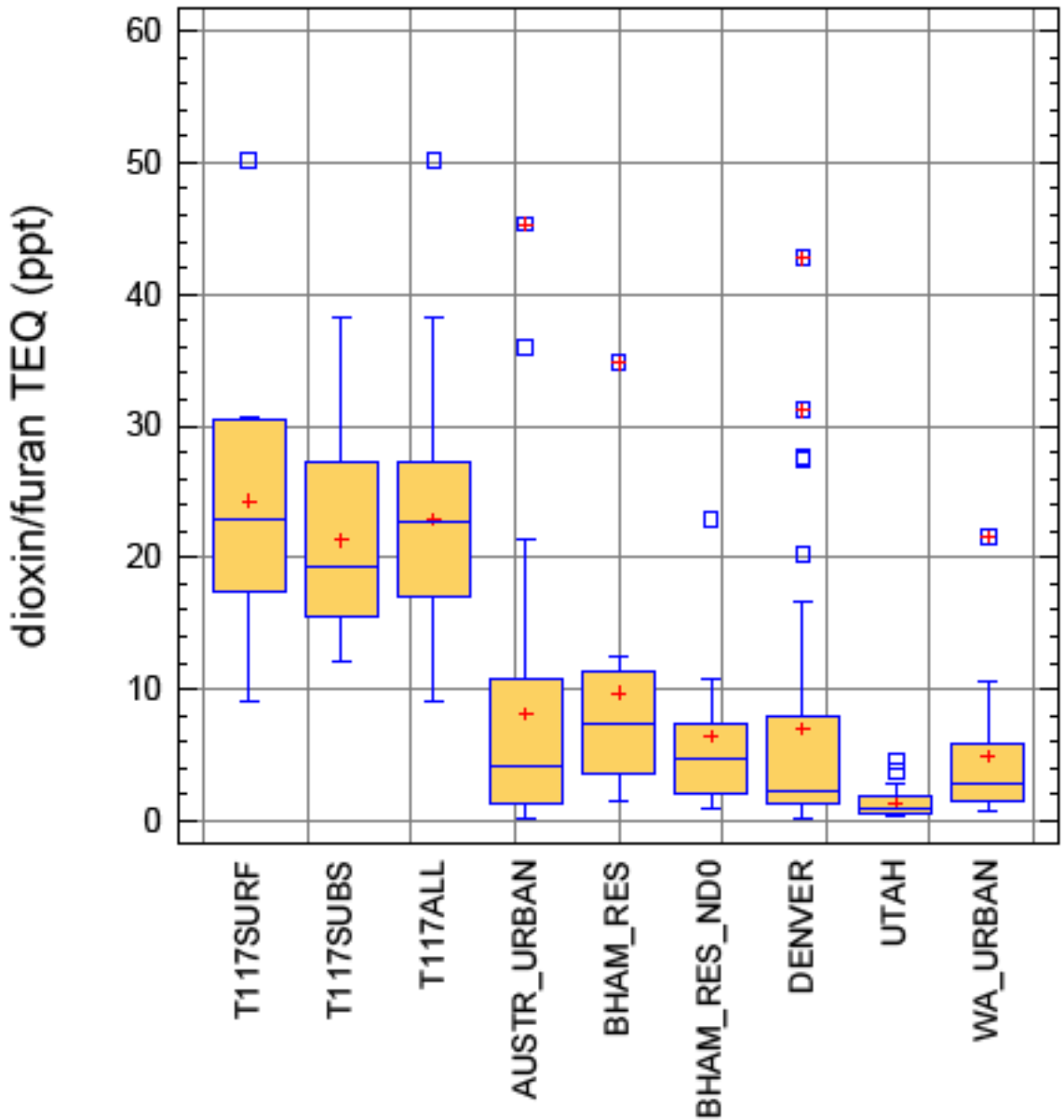
Urban Soil Background

- Chemical profiles
- Magnitude: TEQs
- Comparison data sets
  - Local LDW data limited
  - Seattle and Washington data limited
  - Representativeness issues
    - Land use
    - Protocols
- Multiple sources, variation by location
- T117 question: are yard TEQs elevated or consistent with background?

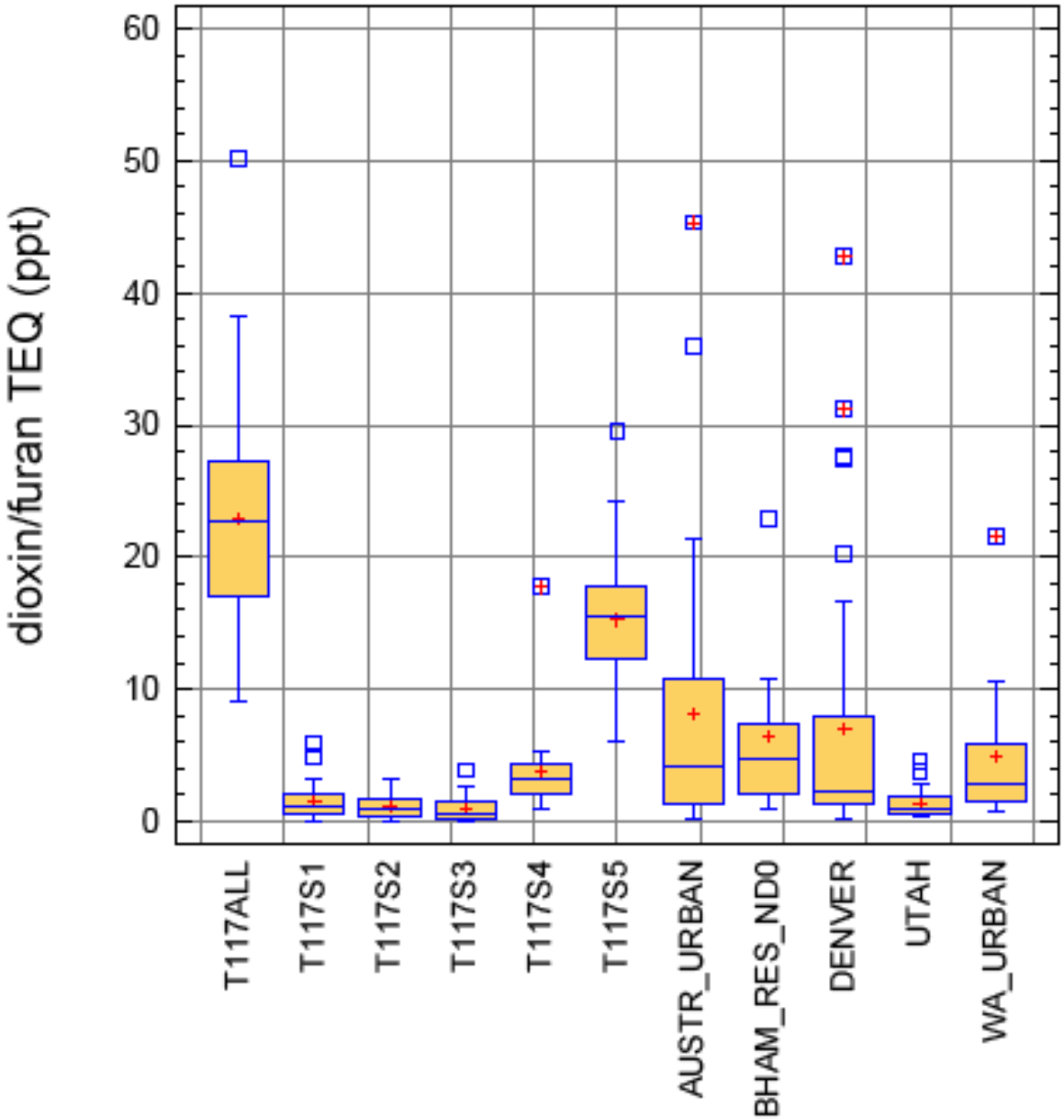
Annual Soil Increments from Atmospheric Deposition

- Screening approach to inform background evaluations
- Japan (Ogura et al. 2001)
  - Tokyo (highest) at annual loading of 17 ng TEQ/m2/yr
  - Calculate annual 0-2 inch soil increment of 0.26 ppt TEQ/yr
- 2009 T117 catch basin samples
  - AECOM data on volume collected, catchment area
  - Assume 100% atmospheric deposition
  - Calculate range of 0.0071 to 0.0625 ppt TEQ for annual 0-2 inch increment
- Results are low, not likely to account for tens of ppt TEQ in T117 yards

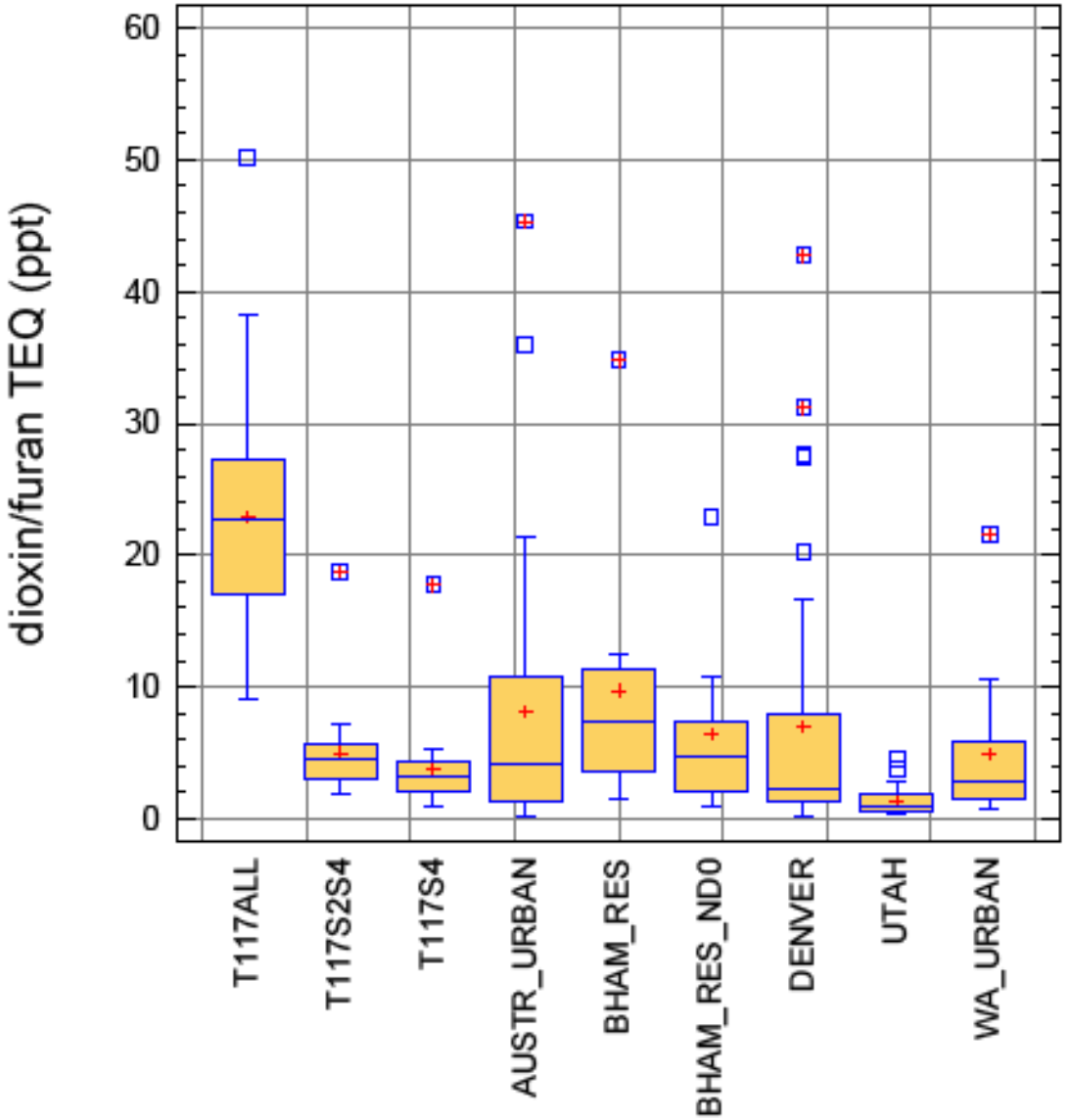
T117: Yard Dioxin TEQ Comparisons



T117 Yards (MIS): TEQ Comparisons



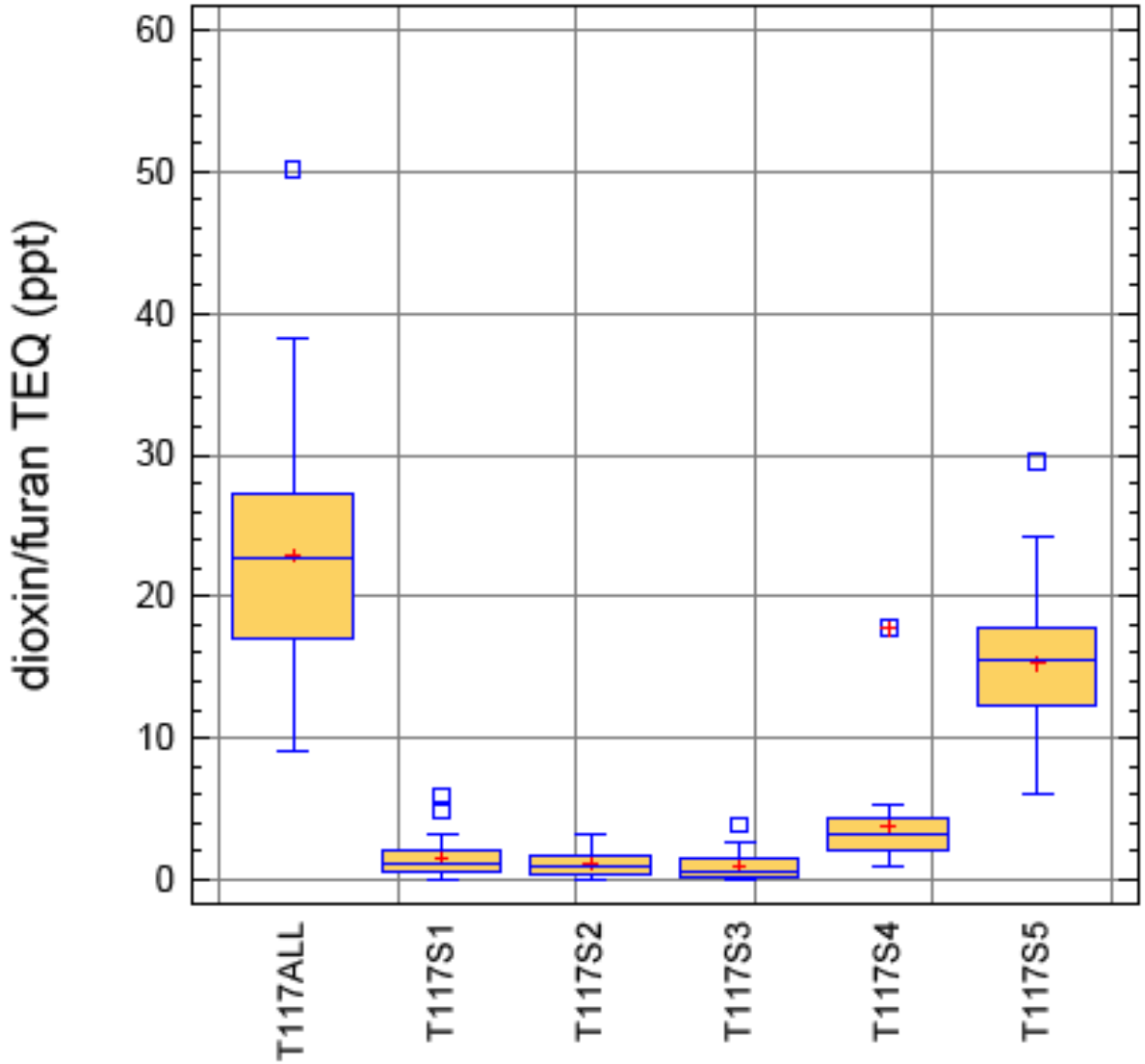
T117: Yard Dioxin TEQ Increments Comparisons



SUMMARY

- S1: (furans dominant) related to PCB burning?
- S2: (fgurans dominant) unknown
- S3: (furans dominant) PCB 1260
- S4: (dioxins dominant) typical urban background components
- S5: (dioxins dominant) oil-fired boiler emissions, also component of typical urban background profile
- TEQ increments – see Box & Whisker Plot

T117 Yards (MIS): TEQ Increments



CONCLUSIONS

- Unmixing model, based on TEF-scaled data (TEQ profiles), with 5 sources provides good fit to measured TEQs (low residuals)
- Interpretations are available for most unmixing source profiles (lines of evidence including chemical patterns, correlations, spatial patterns, consistency with site history and CSM)

CONCLUSIONS

- T117 PCB-related contributions to measured TEQs in yards and streets appear small, with only a few exceptions
  - Streets
    - 2 samples with elevated S3 TEQ increments
    - 3 samples (clustered) with elevated S2 TEQ increments
    - Remaining furan-dominated source TEQ increments are small

CONCLUSIONS

- T117 PCB-related contributions to measured TEQs in yards and streets appear small, with only a few exceptions
  - Yards
    - One location (DU01 and YC03) with elevated furan-dominated source TEQ increments
    - Remaining furan-dominated source TEQ increments are small

CONCLUSIONS

- One source –S5 (dioxins dominated) – closely matches the TEQ profile for oil-fired boilers
  - CSM: T117 had oil-fired boiler
  - Similar source profile common to T117 and other oil burners
  - Elevated S5 TEQ increments for majority of yard and street MIS samples (but not discrete street samples)
  - Lines of evidence suggest possible, but unquantified, T117 S5-related contributions to yards and streets
  - Unmixing model S5 TEQ increments likely reflect both T117-related and regional background-related contributions
- Additional information required to better understand any non-PCB related T117 contributions to yards and streets TEQs

MIS UCLs

- One MIS sample provides an estimate of DU average
- Repeated MIS samples not expected to provide exactly the same results
- UCLs used to provide high confidence for cleanup decisions, given measurement uncertainty
- T117 field replicate MIS sampling (x3)
  - 4 yard DUs, 4 street DUs
  - 2 depth intervals
  - Total of 16 data sets to examine variability of MIS

MIS UCLs

- UCL for field replicate DUs uses 3 results
- Method required for estimating UCL for single MIS samples
  - Equation
  - Estimate of SD

MIS UCLs

- Regression analyses
  - Yards + streets, yards, streets
  - Average PCB vs SD, CV
  - Depth intervals separate or combined
- Average SD, CV for interval below CUL = 1 ppm PCBs
- Calculation of critical value for MIS UCL = 1
  - Multiple cases, range of results

MIS UCLs

- Recommendation
  - Yards + streets combined
  - Based on average CV: critical value = 0.5 ppm PCBs
    - Based on average SD, 0.34 ppm PCBs
  - Streets alone, all cases have lower critical value
  - Yards alone give slightly higher values (all cases) up to 0.62 ppm PCBs
    - Minor difference in that range in DUs for cleanup