

A tiered approach to fingerprinting dioxins: Distinguishing between an HCP manufacturing source and a barrel reconditioning facility

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Exponent

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Background

- Sediment and soil contaminated with a variety of chemicals, including 2,3,7,8-TCDD, PCBs, other dioxins and furans.
- Risk driven by 2,3,7,8-TCDD
- Two adjacent candidate sources of 2,3,7,8-TCDD

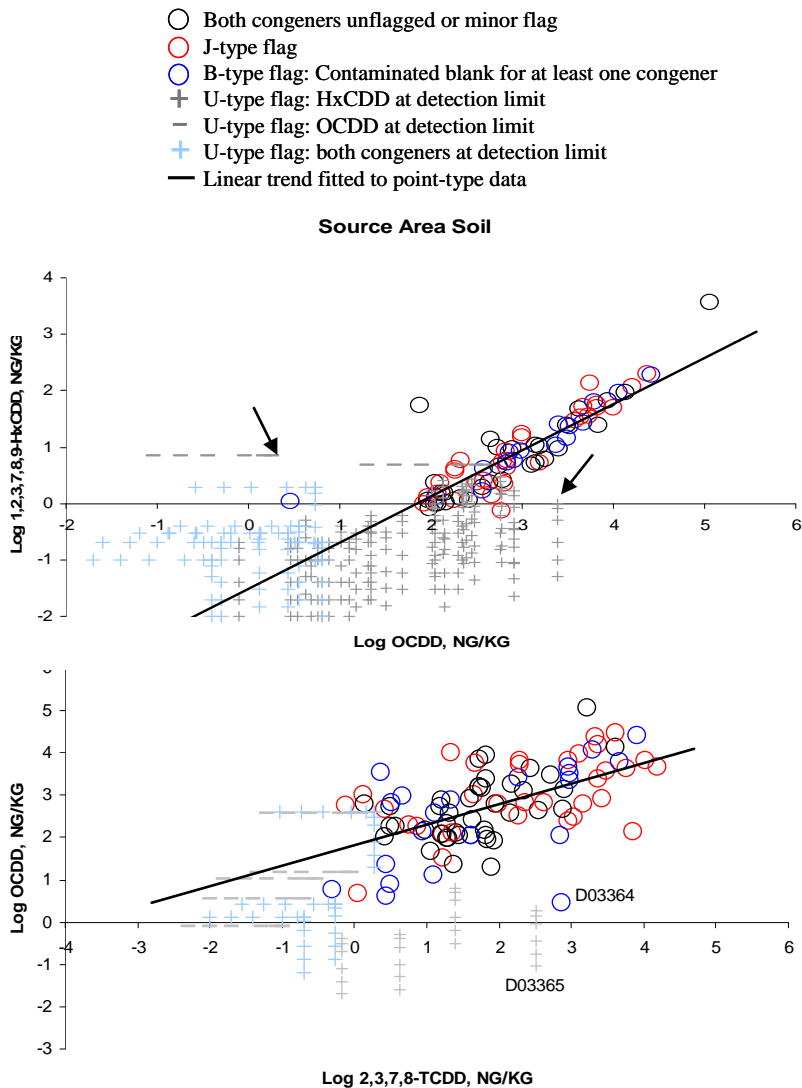
Objective

Determine whether neither, both or only one of two sources contributed to 2,3,7,8-TCDD releases and how much.

Tiered Approach

- Data analysis methods:
 - Qualify usability of flagged data
 - Sample dioxin and furan distribution comparisons
 - Correlation analysis among congeners
 - Statistical decomposition
- Compare results to other lines of evidence

Flagged Data

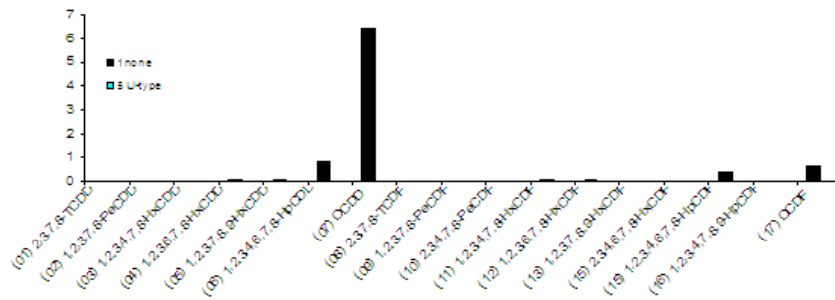


- Point data:
 - Unflagged, minor flag, J (estimated), B (contaminated blanks)
- Range data:
 - U: detection limits and estimated maximum possible concentrations (U-type flag). Multiple dots for possibility that concentration could be any lower value.
- Flags with unknown meaning omitted from analysis.
- Arrows point to two detection limit values that fall somewhat outside the range of values determining the trend.
- Overall, flagged data align with unflagged data and reinforce the same relationship: included in all analyses.

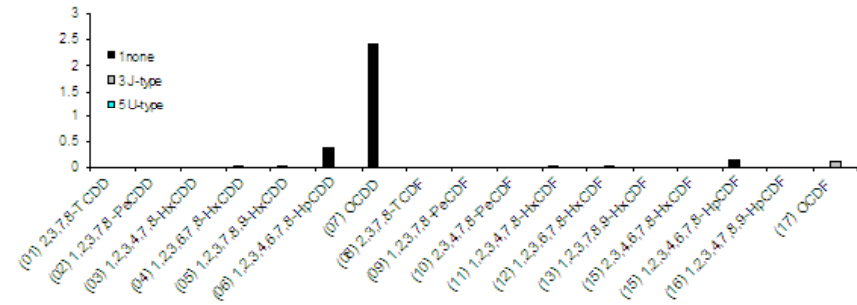
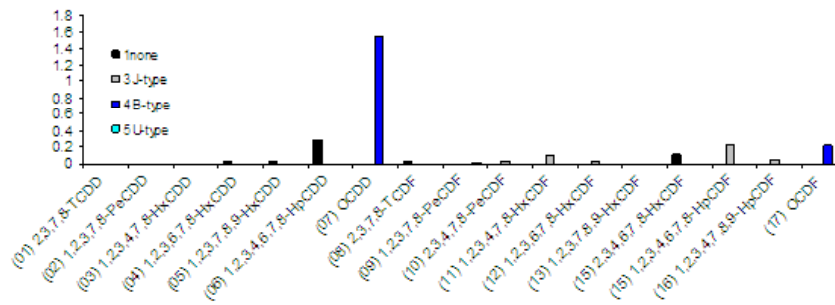
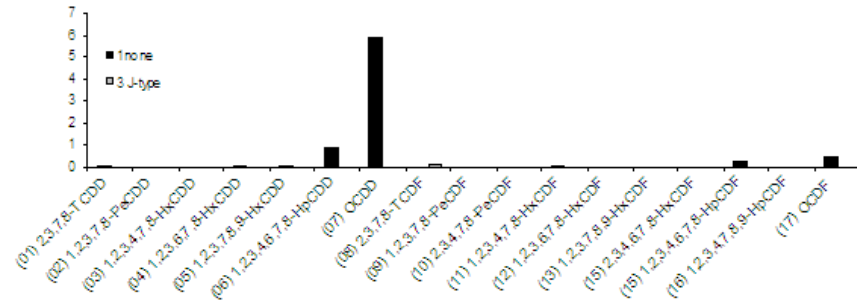
Profile Comparison

Background – Individual Samples

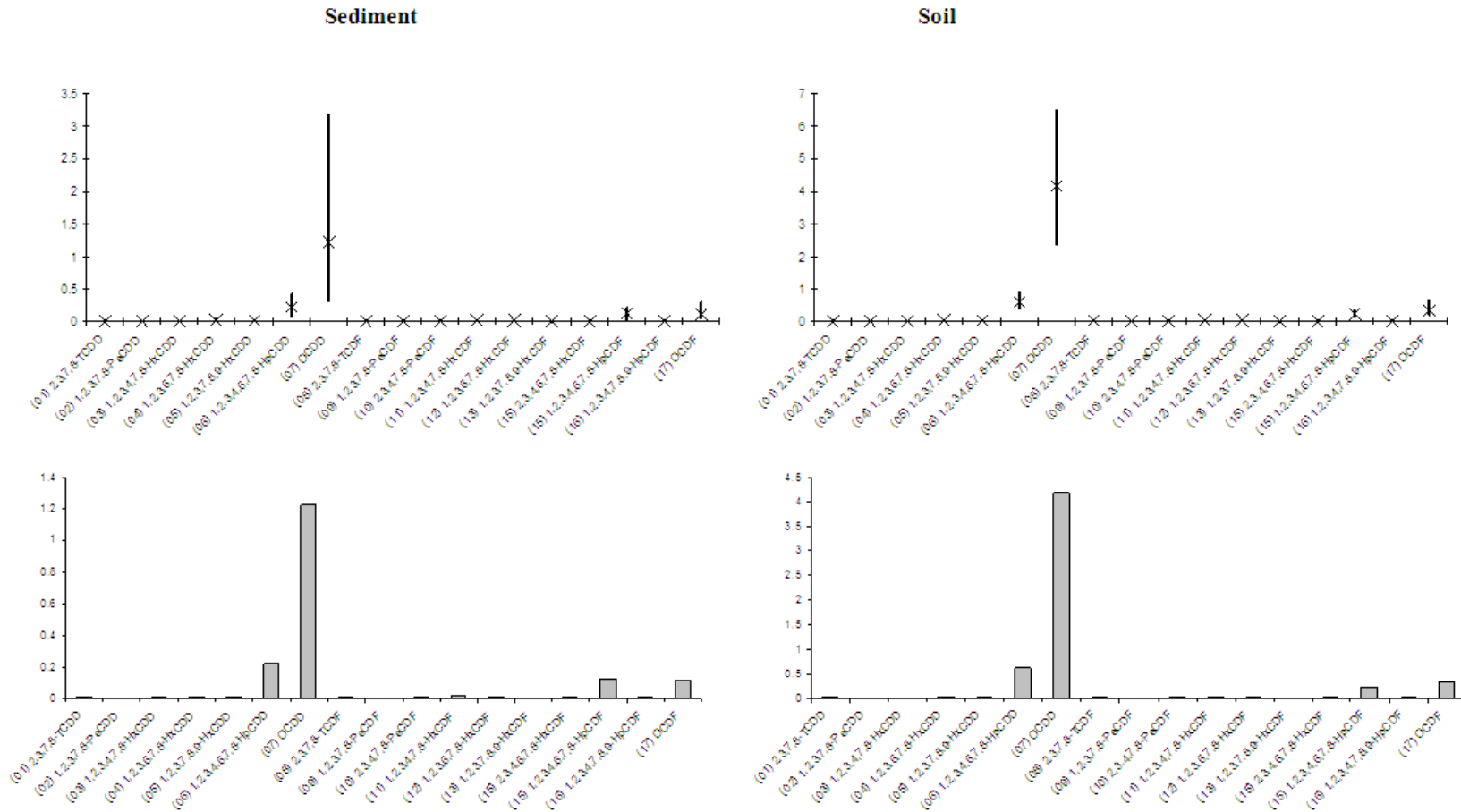
Sediment



Soil

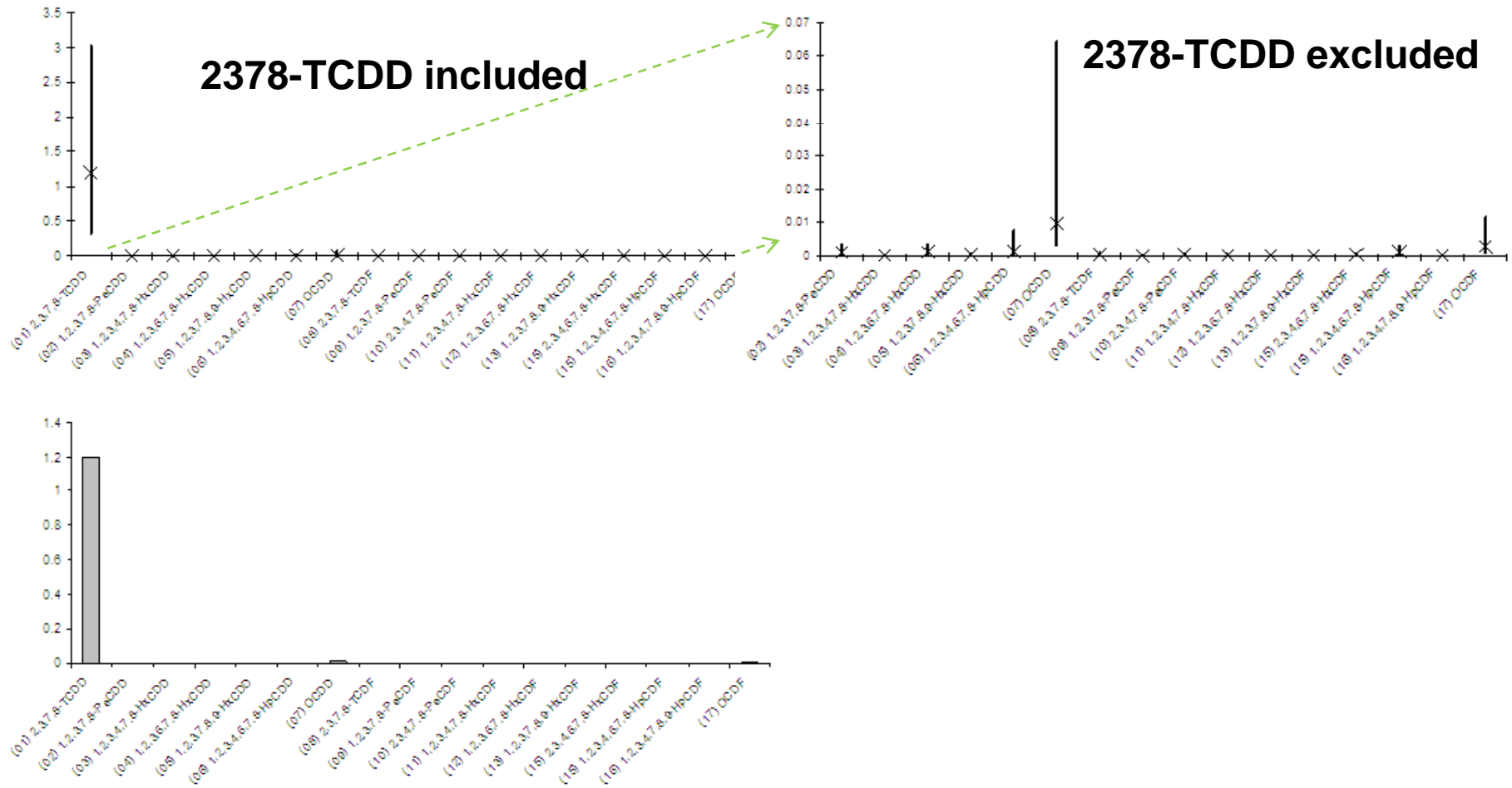


Background – All Samples

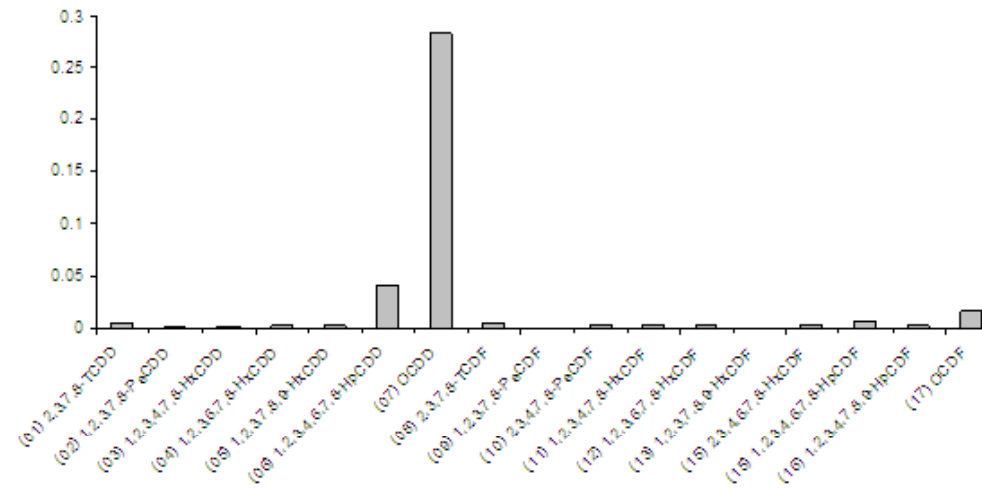
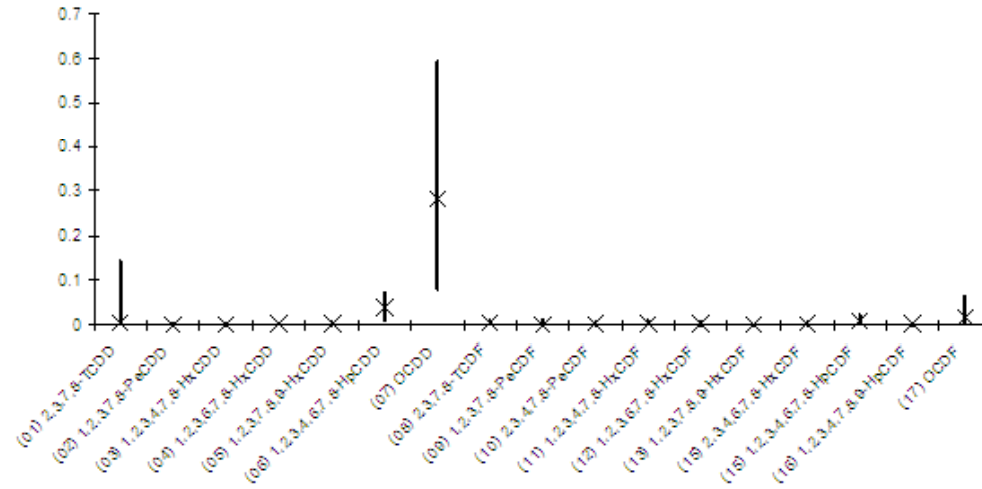


Background sediment and soil sample composition. The top graph shows the median and the range of variation between the lower and upper quartiles. The bottom graph shows the median only. The vertical axis shows concentration in µg/kg.

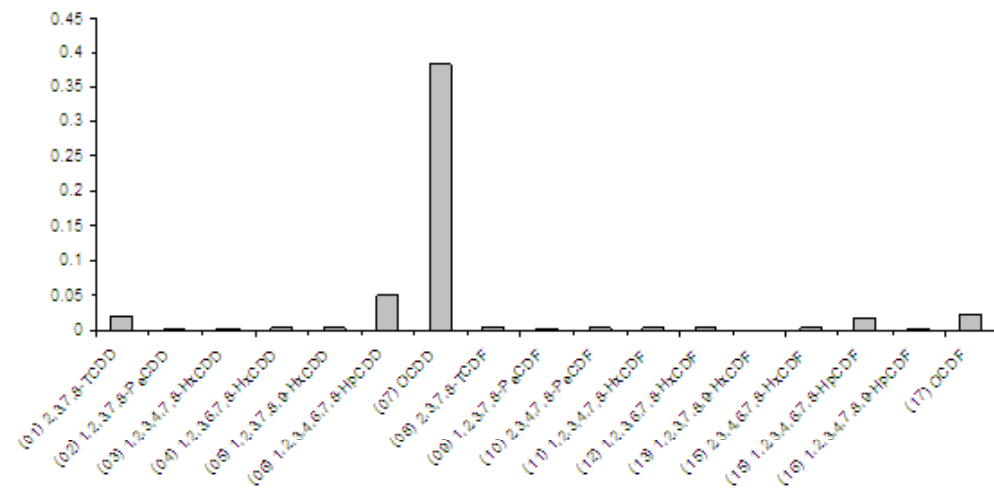
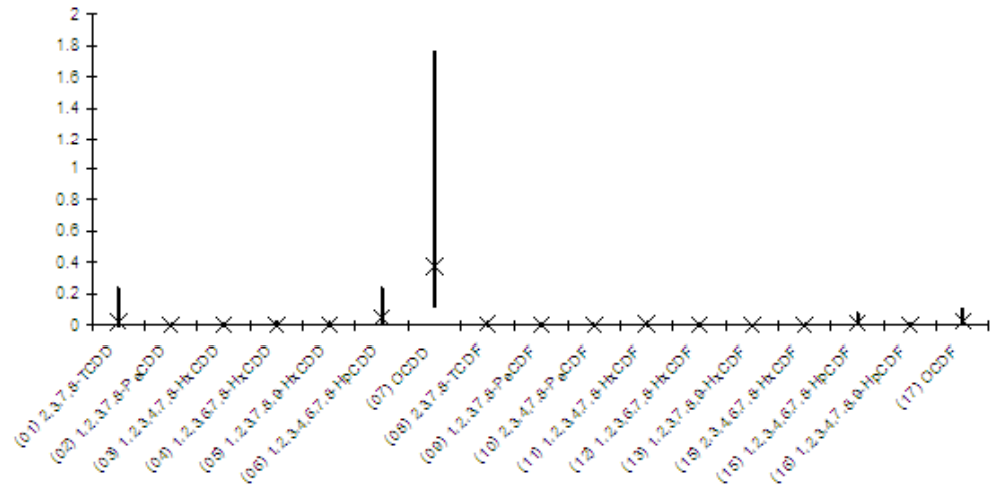
Hexachlorophene Area Soil



Barrel Reconditioning Area Soil

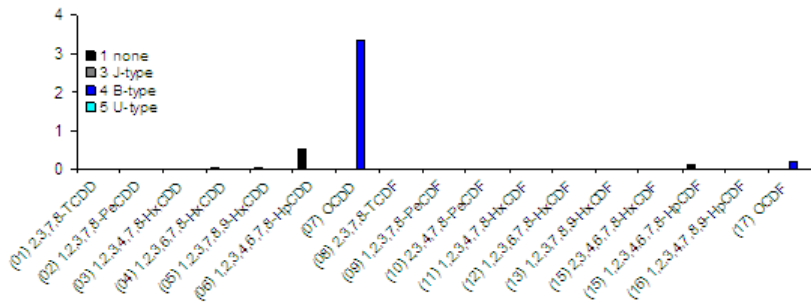


Other On-Site Soil

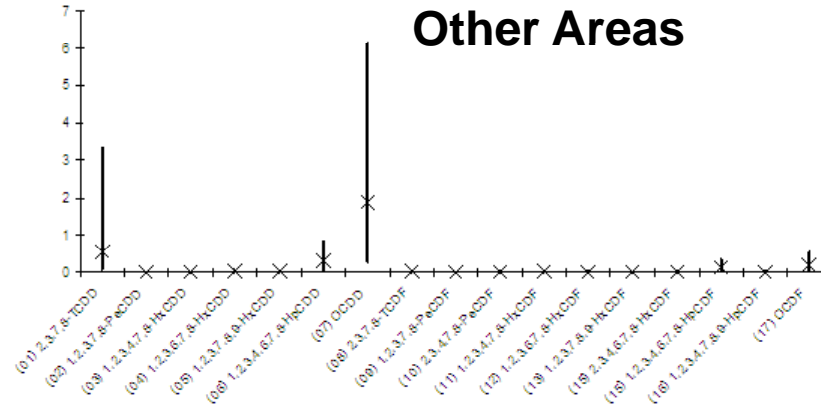


Sediment (Fewer Samples)

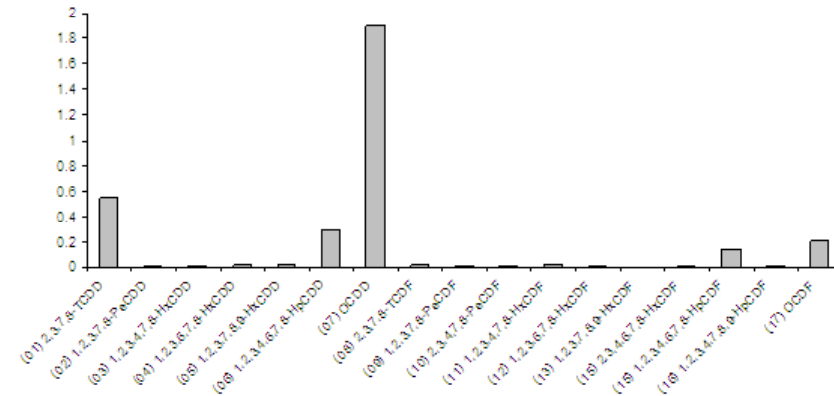
Near Barrel Reconditioning



Other Areas

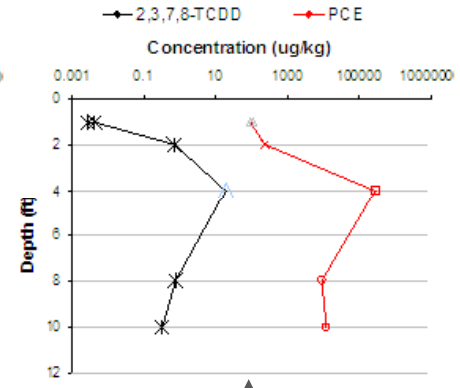
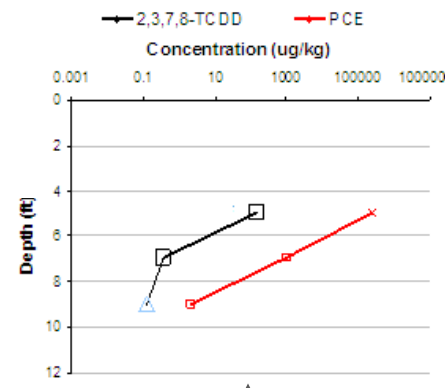
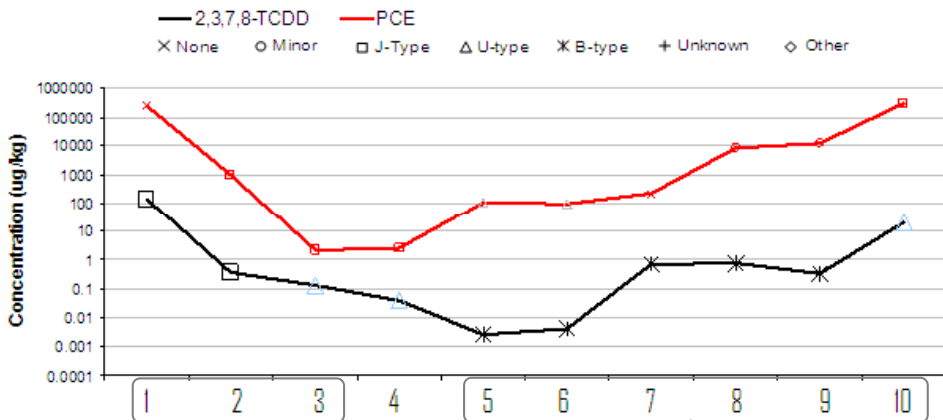
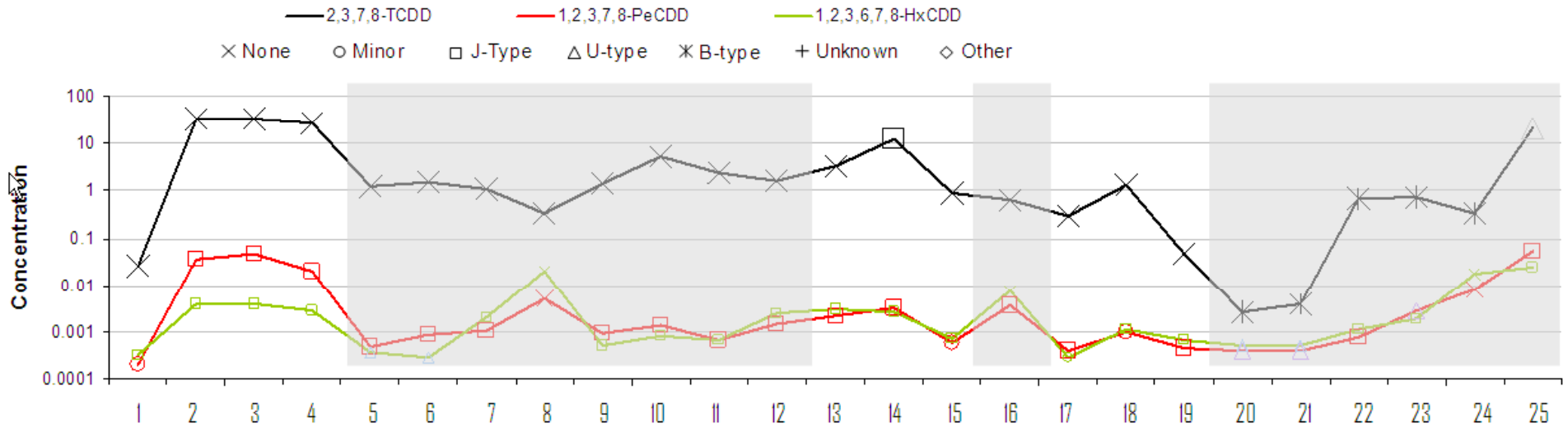


No sediment samples near HCP facility

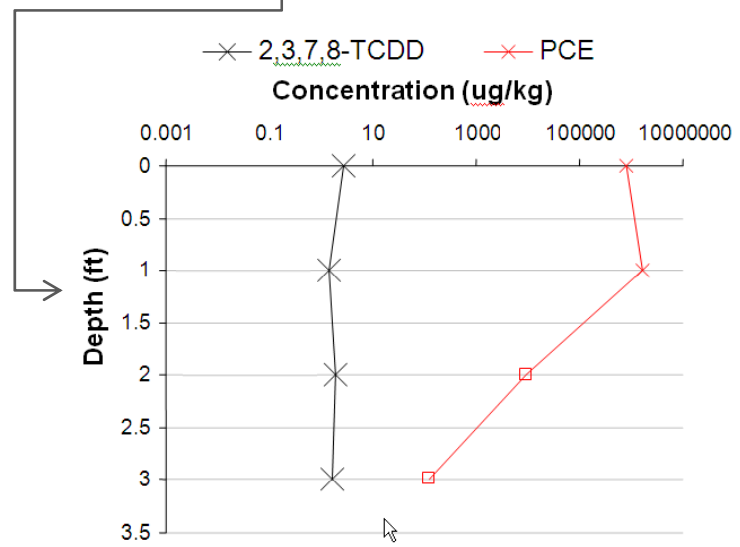
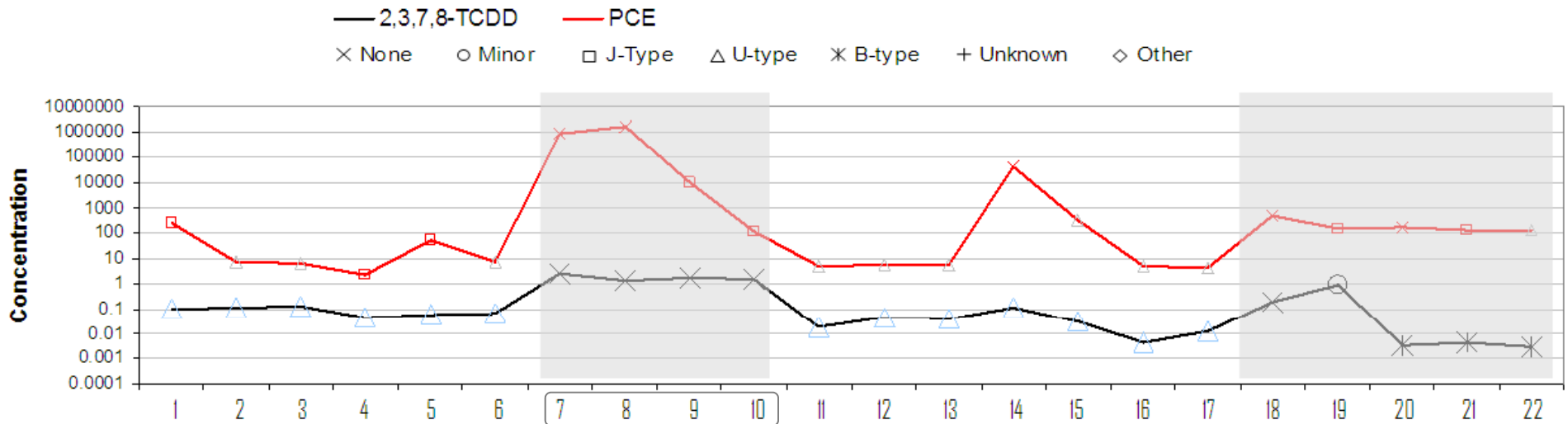


Contaminant Correlation

HCP Area Soil Samples

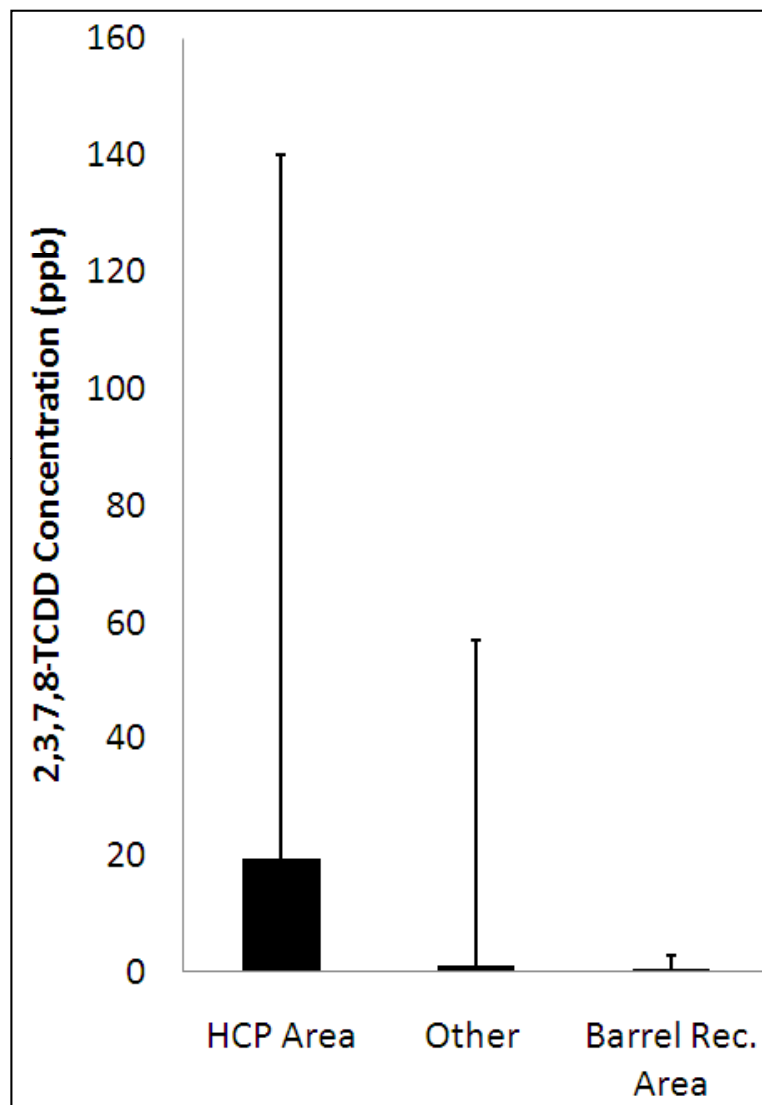


Barrel Reconditioning Area Soil



Concentrations By Area

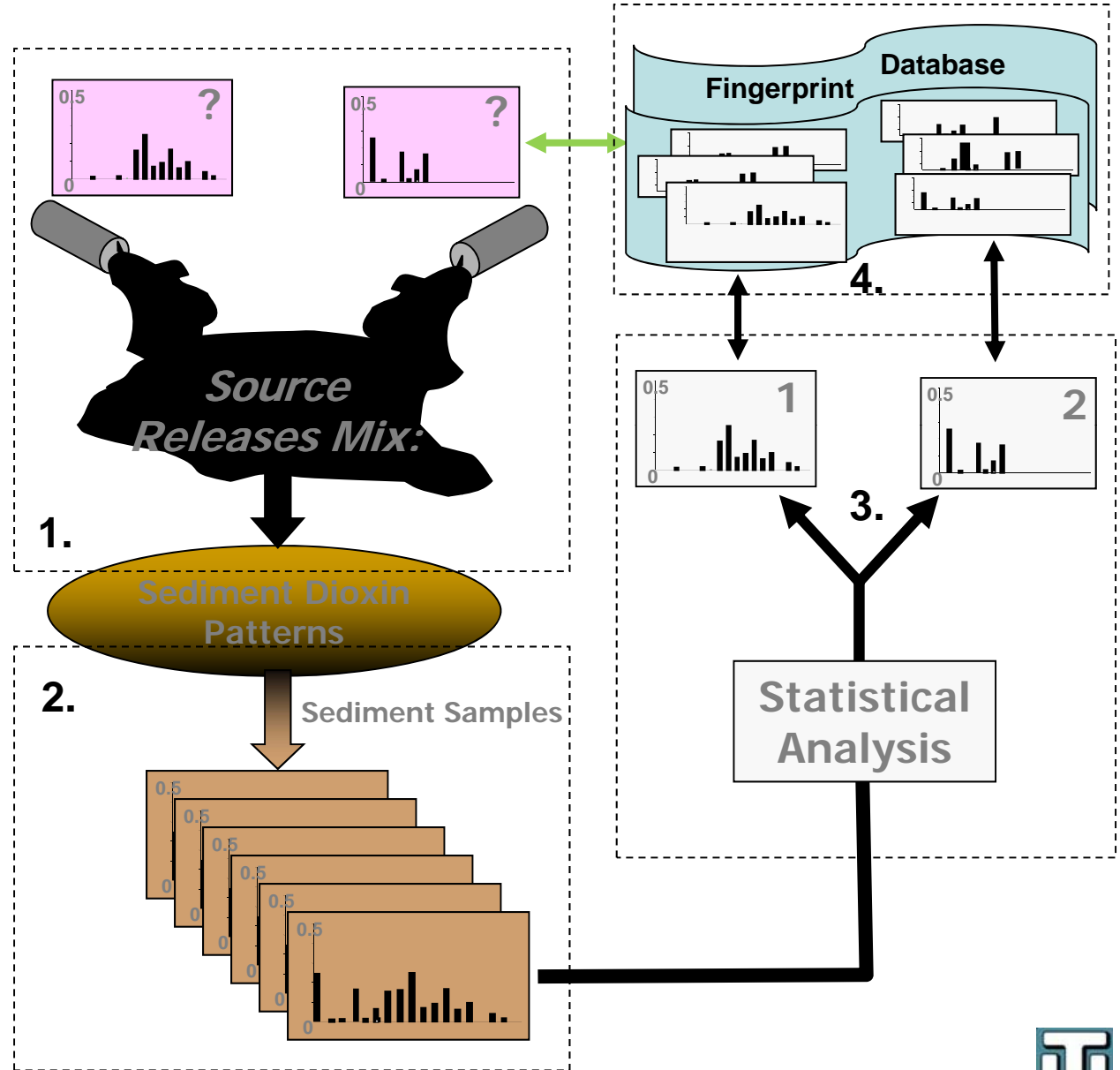
■ Average
┆ Maximum



Statistical Fingerprinting (Polytopic Vector Analysis or PVA)

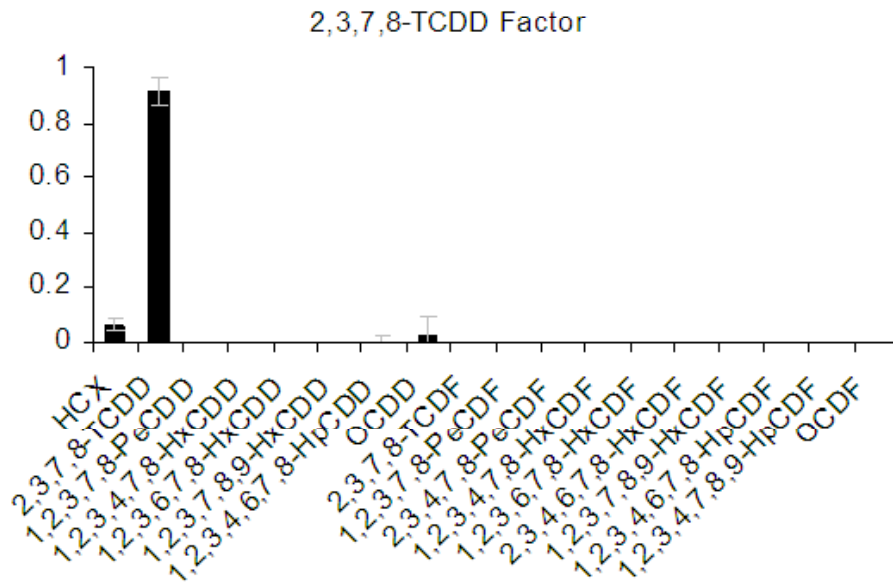
The Concept of Statistical Fingerprinting

1. Each source emits a unique composition of chemicals (dioxin congeners here) = Fingerprint
2. Once emitted into environment, individual source compositions mix, leading to different patterns measured in sediment samples.
3. Correlations among the dioxin congeners help establish which congeners occur together in stable compositions, and each sample is decomposed into these stable patterns.
4. Comparison with a database of source fingerprints leads to identification of sources that have contributed to the mix in each sample.

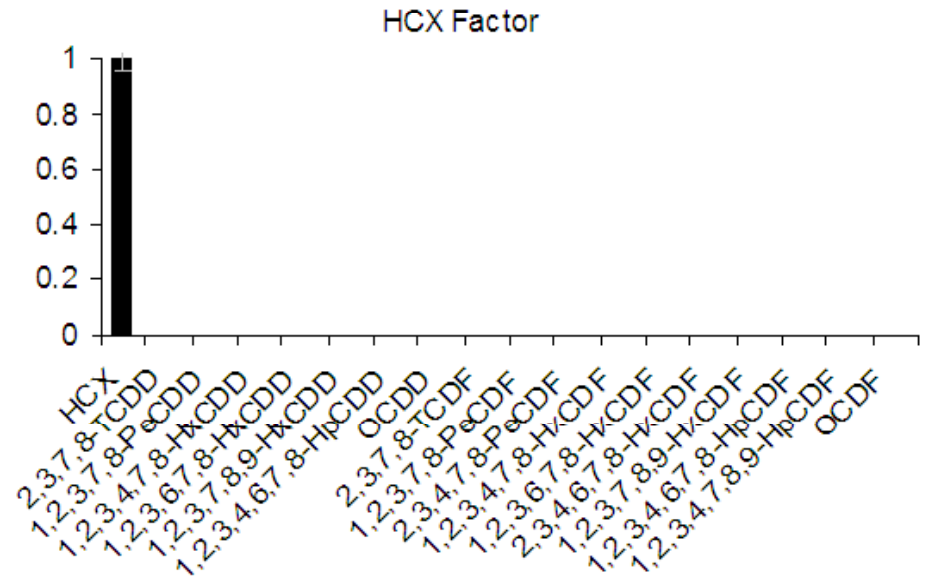


PVA Results 1

Both of these compositions are known to be typical of the HCP manufacturing process

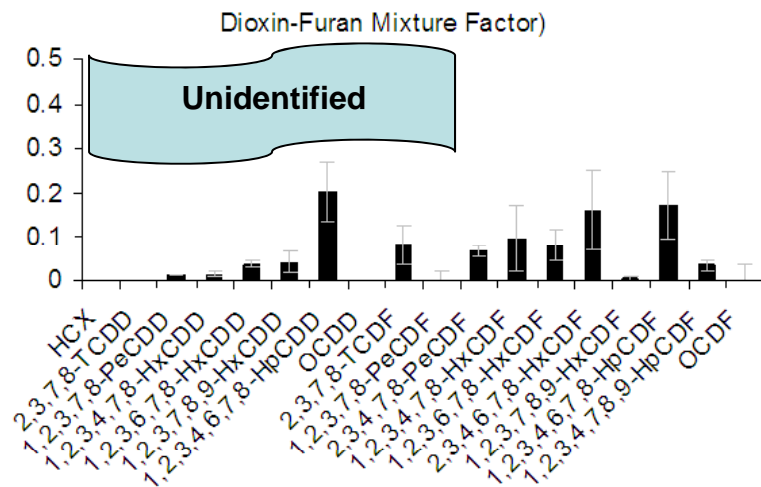
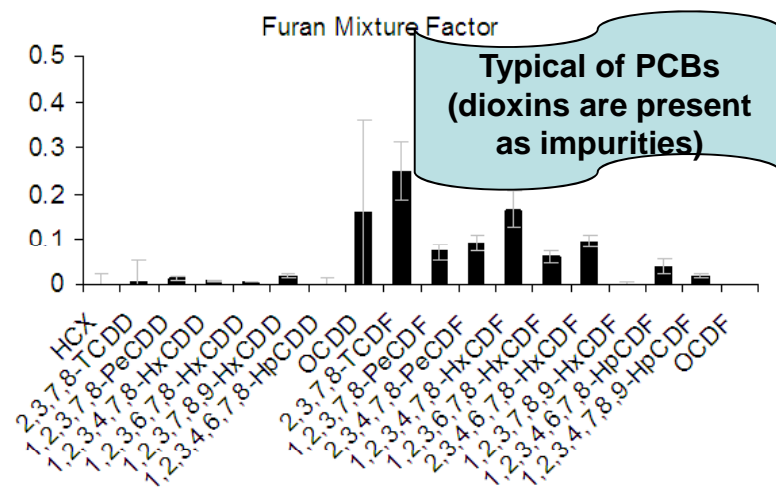
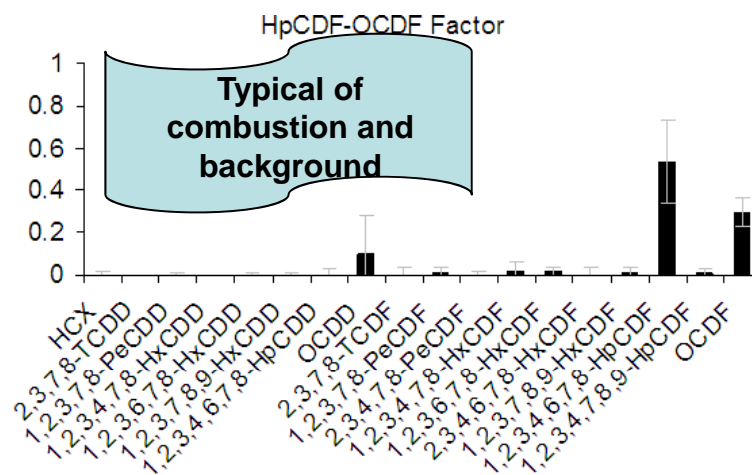
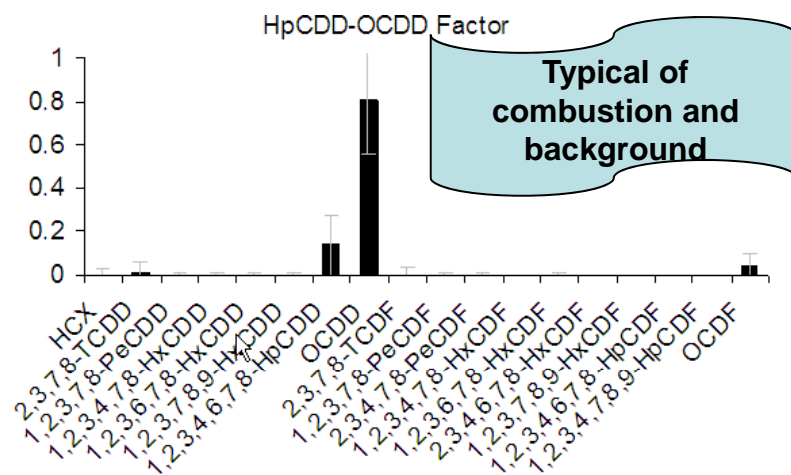


Present in the feed,
was removed in
initial steps, prior to
reactor.

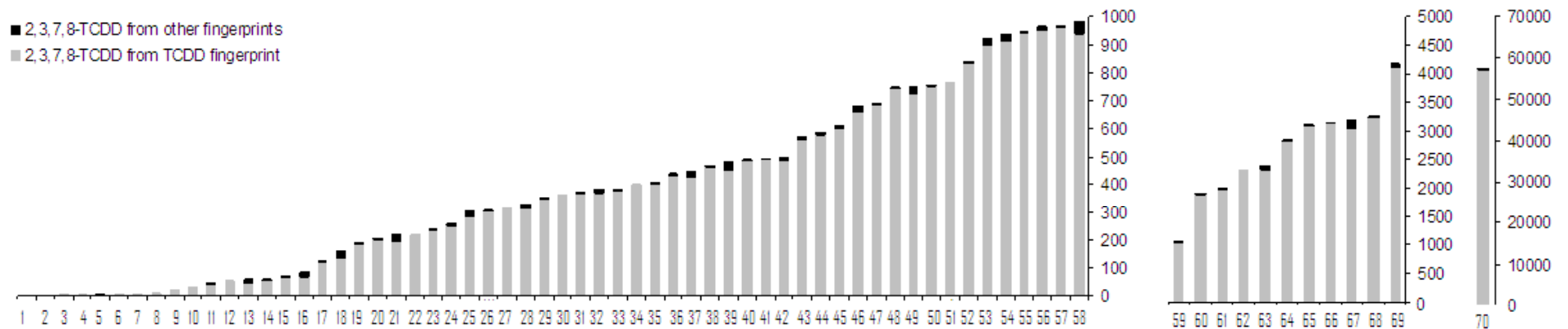


Byproduct of HCP
reaction, removed in
steps after reactor.

PVA Results 2



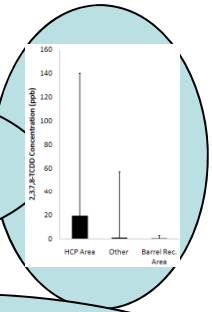
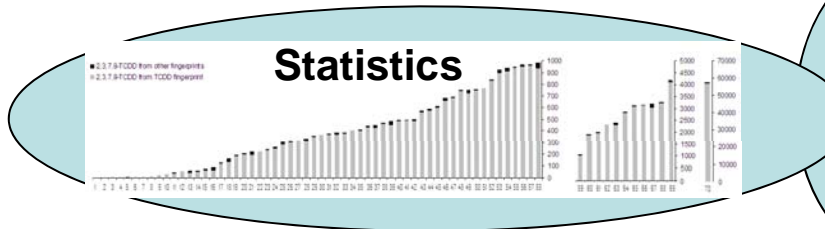
How Much TCDD From Each Source?



Overall, the 2,3,7,8-TCDD factor identified as HCP manufacturing contributes 99.04% of concentration.

Other Evidence

When all is considered together ...



Documented purification stage losses.

Diamond Alkali (TCP supplier) documentation of 2,3,7,8-TCDD content

Date	2,3,7,8-TCDD in TCP Solution (ppm)	% TCP in Solution	2,3,7,8-TCDD Concentration in TCP (ppm)
May-65	16	40	40
May-65	10	40	25
Jun-65	28	31	90
Jun-65	38	44	86
Jun-65	35	44	80
...

Presence of HCX at HCP building and elsewhere

...

Spatial distributions: TCP, 2,3,7,8-TCDD, PCE all peak in the vicinity of HCP building and decrease away from building