Environmental Forensics

ANCHOR QEA

Presented by
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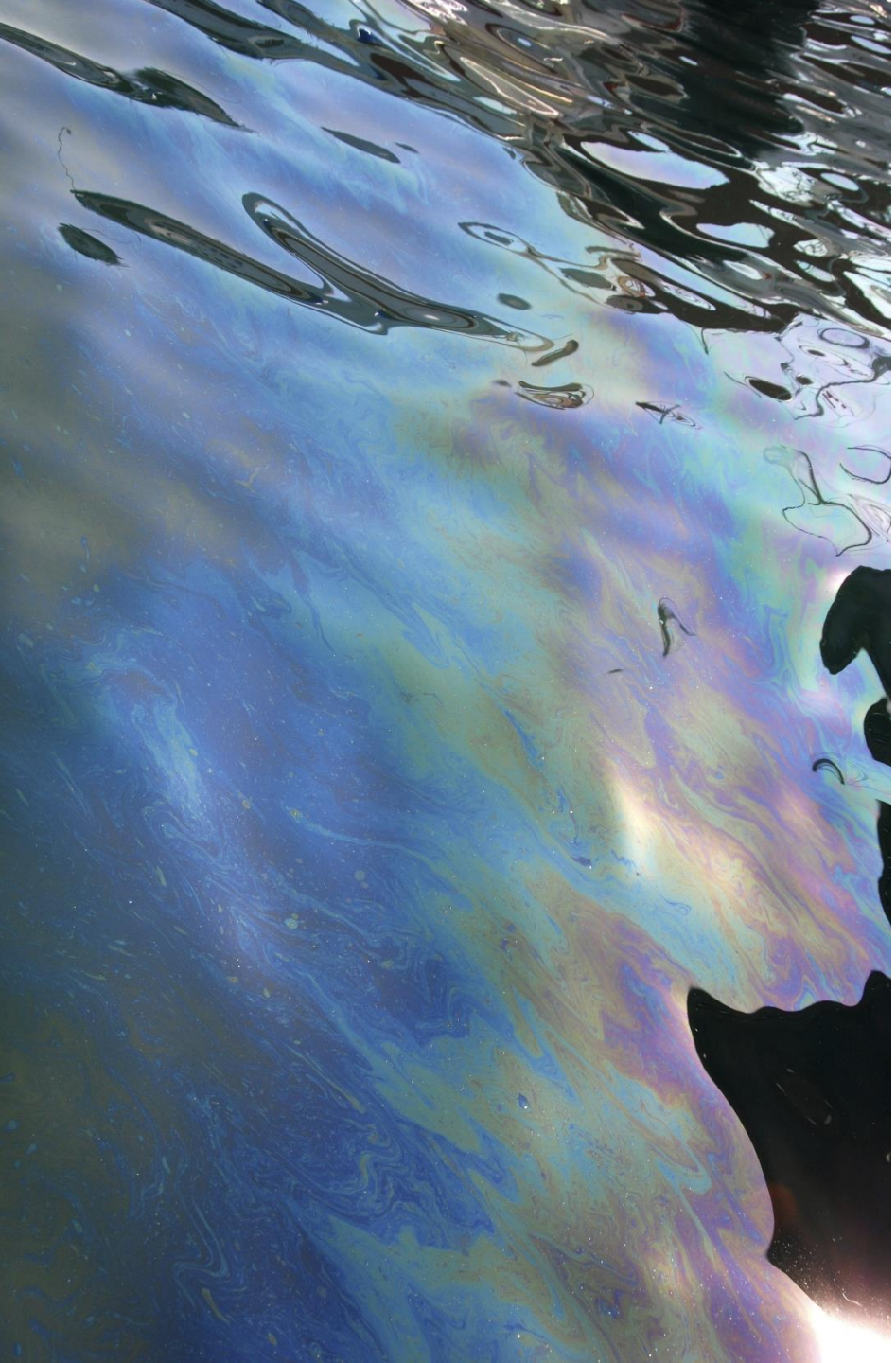

Agenda

- Environmental Forensics Introduction
- Sampling and Chemical Analysis Considerations
- Example Investigation
- Case Studies

Environmental Forensics

Environmental Forensics Introduction

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Environmental Forensics

- Evaluation of chemical, physical, and historical information to identify and differentiate sources of contamination in the environment
- Uses chemical fingerprinting as a line of evidence

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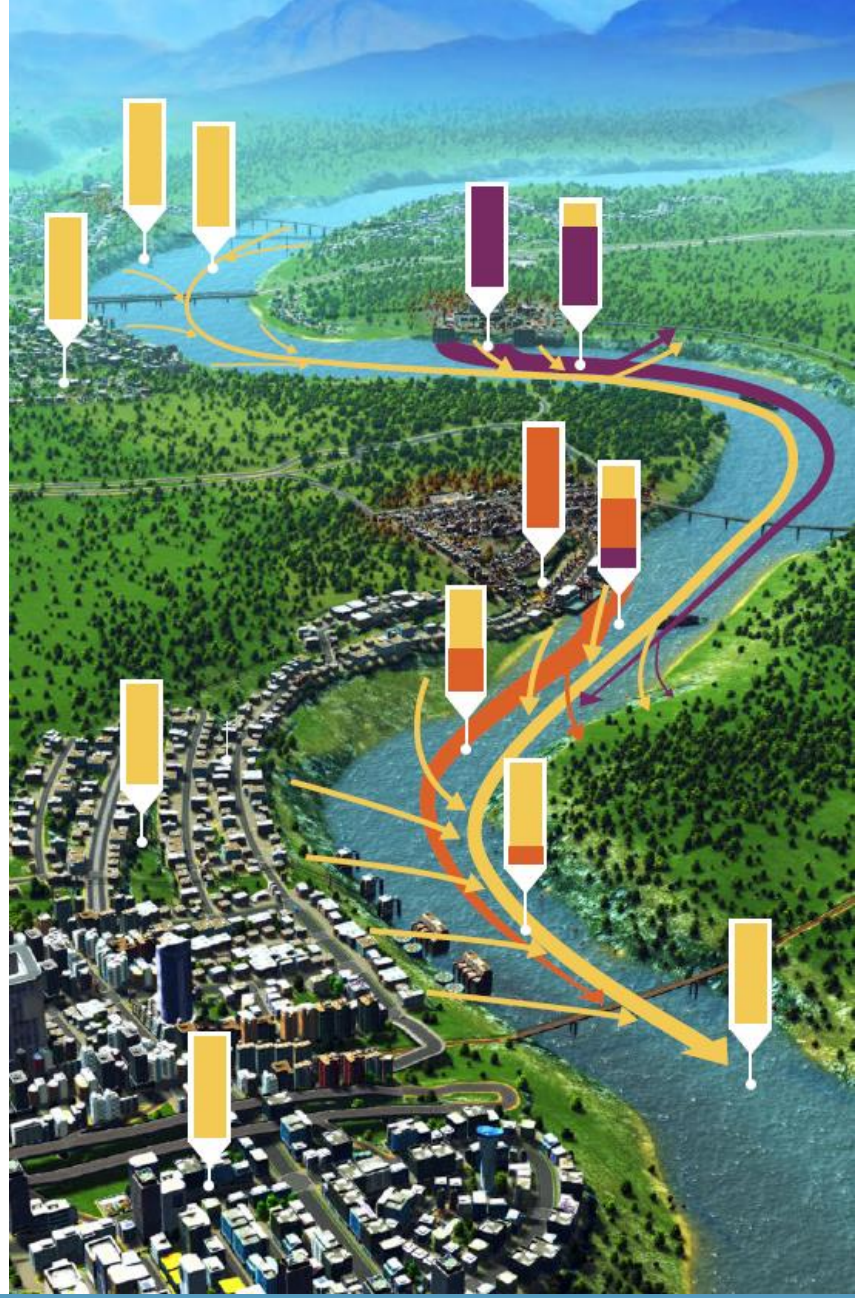
Scope of Forensic Investigations

- Single building lot to dozens of facilities
- One sample to large, multi-party data sets
- Soils, surfaces, oil/tar, groundwater, vapor, sediments, sheens
- Qualitative fingerprint evaluation to quantitative mass estimates



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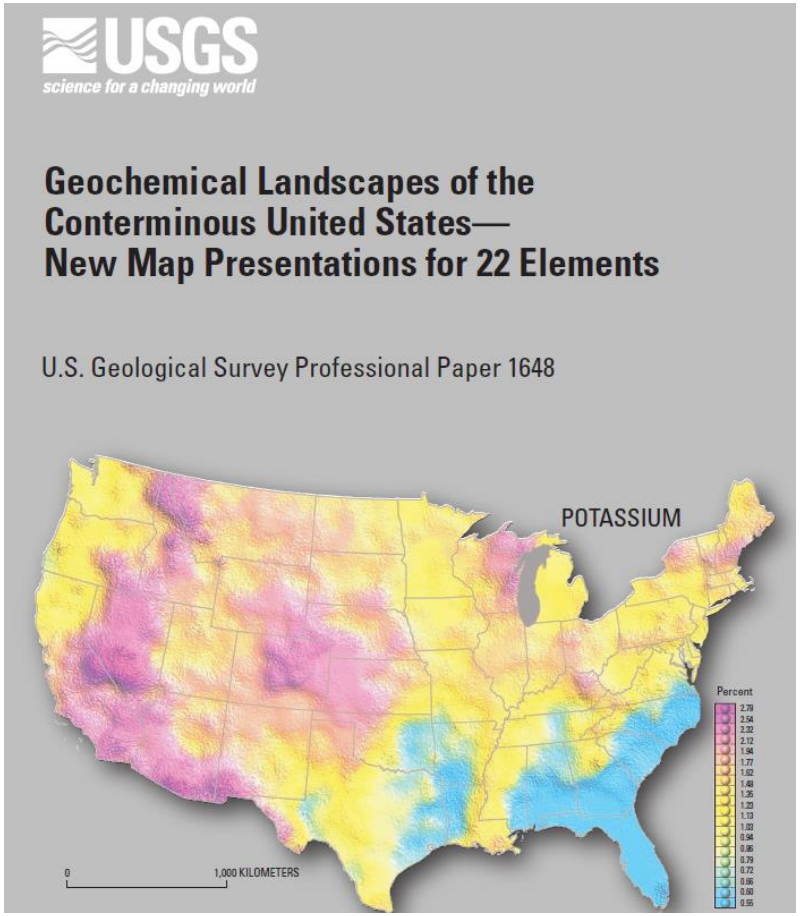
Multiple Lines of Evidence Approach

- Contaminant source evaluation uses a multiple lines of evidence (MLOE) approach
- Fingerprinting should include multiple, independent diagnostics
- And be supported by
  - Background analysis
  - Site operations research
  - Concentration trends
  - Transport pathway analysis
  - Weathering analysis



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Sampling and Chemical Analysis Considerations

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Contaminant Source Sampling

- Site engineer: “We don’t need to analyze that! We know it’s our stuff!”
- Forensic analyst: “Make sure you analyze that! We need to know what our stuff looks like!”

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Background and Off-Site Sampling

- Collect upgradient/off-site samples to assess background contamination
- Collect from likely point source impact locations from other facilities (if accessible)

Conventional vs. Forensic Laboratory Methods

- Conventional analytical methods may lack resolution to distinguish sources
- First: assess what you can answer with the data at hand
- If needed: conduct additional sampling
- If needed: consider next tier analytical methods
  - PCB congeners instead of Aroclors
  - Expanded PAH list – including alkylated PAHs
  - Expanded VOC list – PIANO VOCs
  - Compound specific isotope analysis

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Example Multiple Lines of Evidence Forensic Investigation

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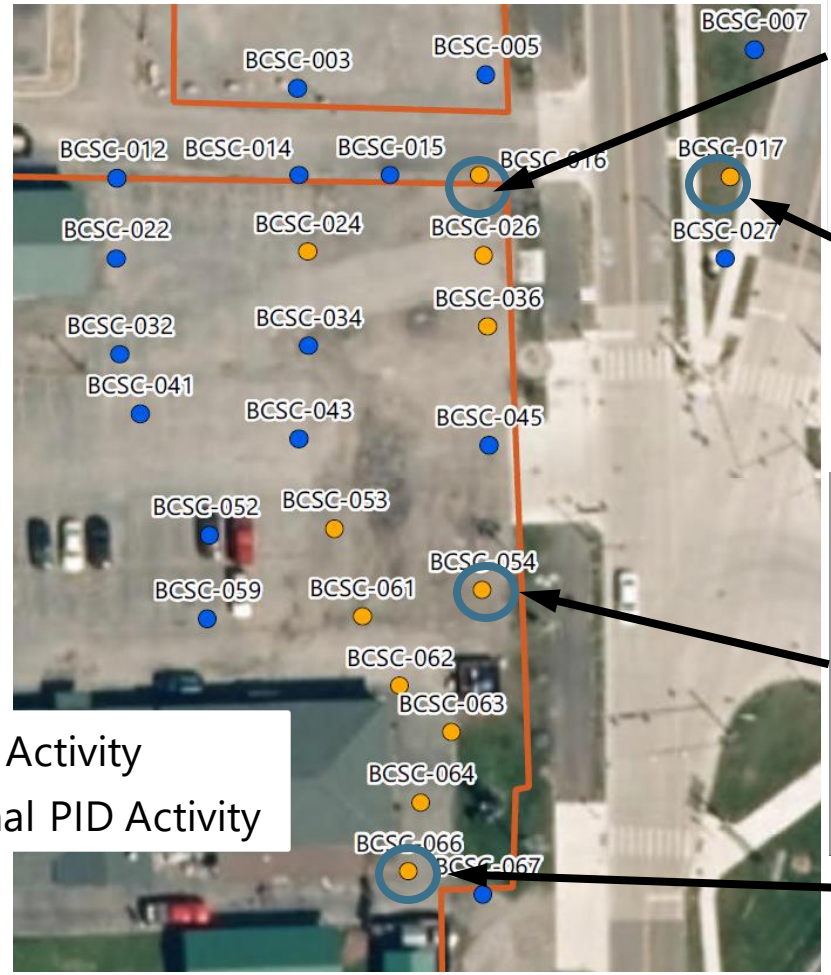
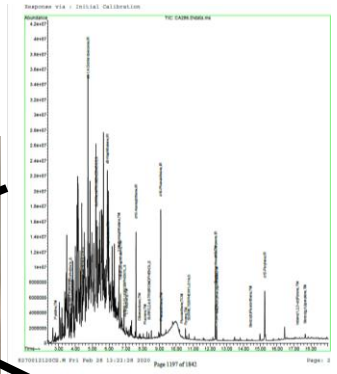
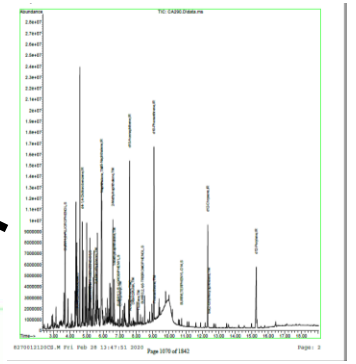
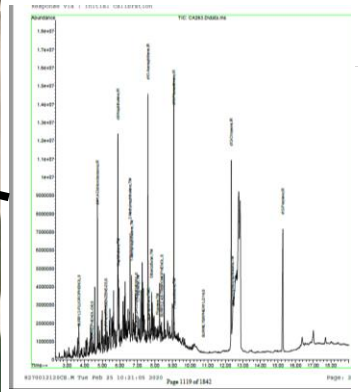
PID pattern indicates unexpected north activity – what's going on?

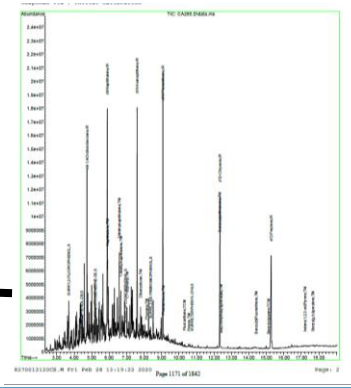
GC/FID chromatogram patterns indicate potential for multiple fuel sources











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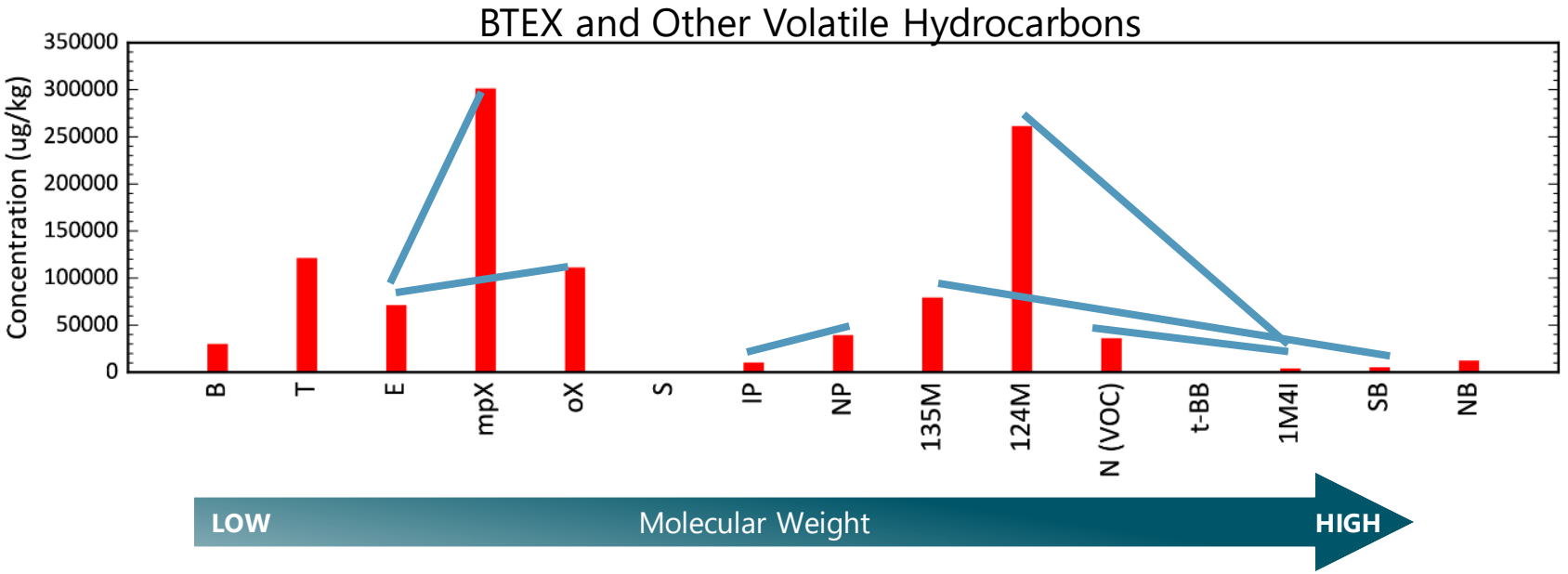
Diagnostic Ratios to Distinguish Fuel Sources

- A good diagnostic ratio is
  - Consistent within each source – must have
  - Distinct between sources – must have
  - Resistant to weathering effects – nice to have
  - Consistently detected – nice to have



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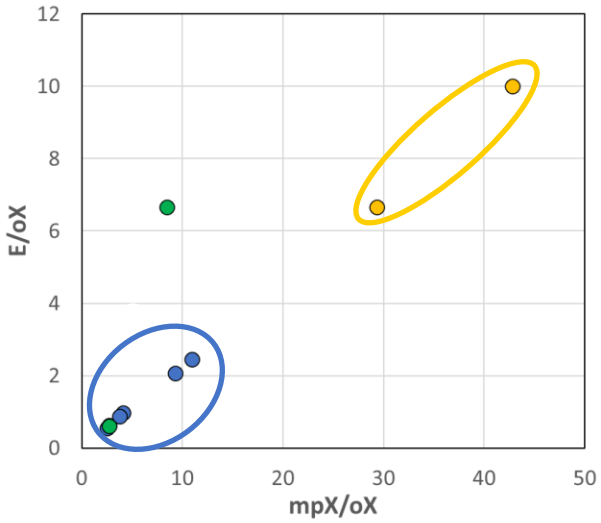
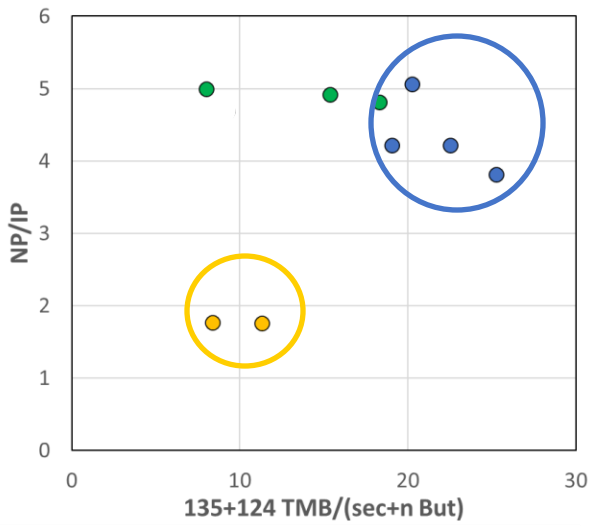
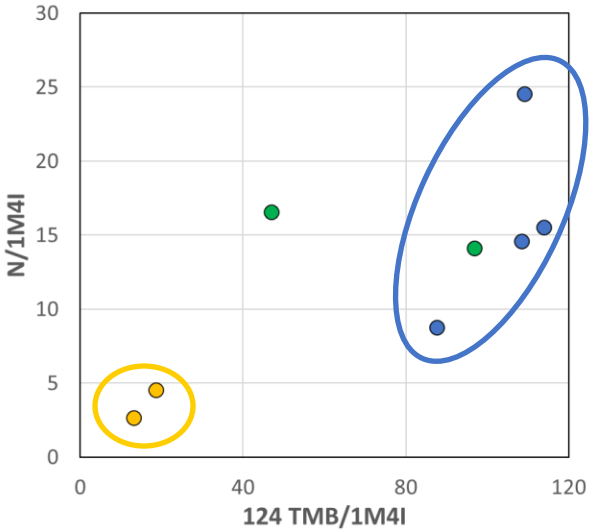
Double Ratio Plot Diagnostic Ratio Results

- Six VOC diagnostic ratios consistently separate north and south sources
- Provides a reference for evaluation of other samples







Northern Cluster

Southern Cluster

Intermediate Locations

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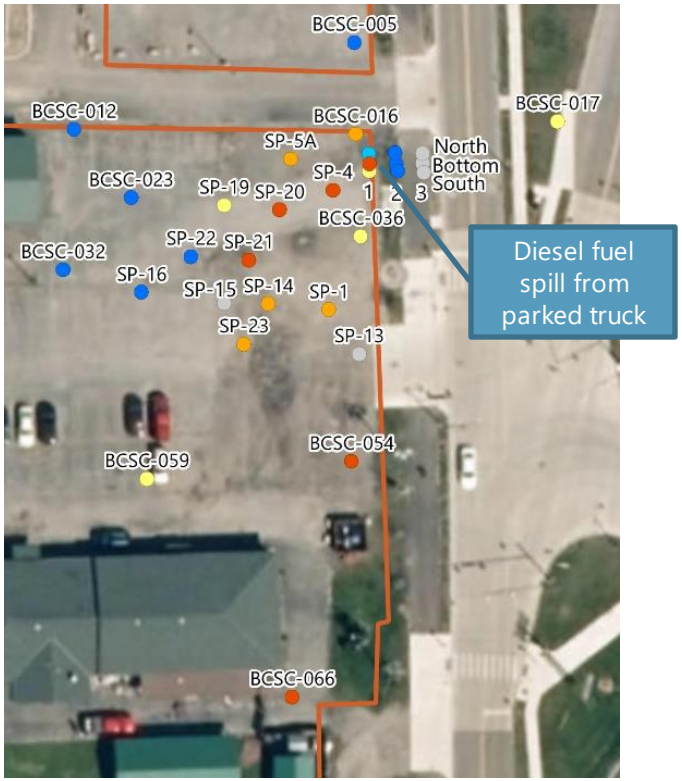
Groundwater Flow

Volatile Hydrocarbon Concentrations



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Summary of MLOE Investigation

- Distinguished two main petroleum hydrocarbon sources on site: north and south
- Lines of evidence
  - Field screening spatial PID pattern
  - Gas chromatograms
  - Chemical fingerprinting diagnostic ratios
  - Groundwater flow direction
  - Volatile hydrocarbon concentration spatial pattern
  - Site data consistent with
    - Site fuel tank records for south source
    - Parking lot diesel spill record for north source

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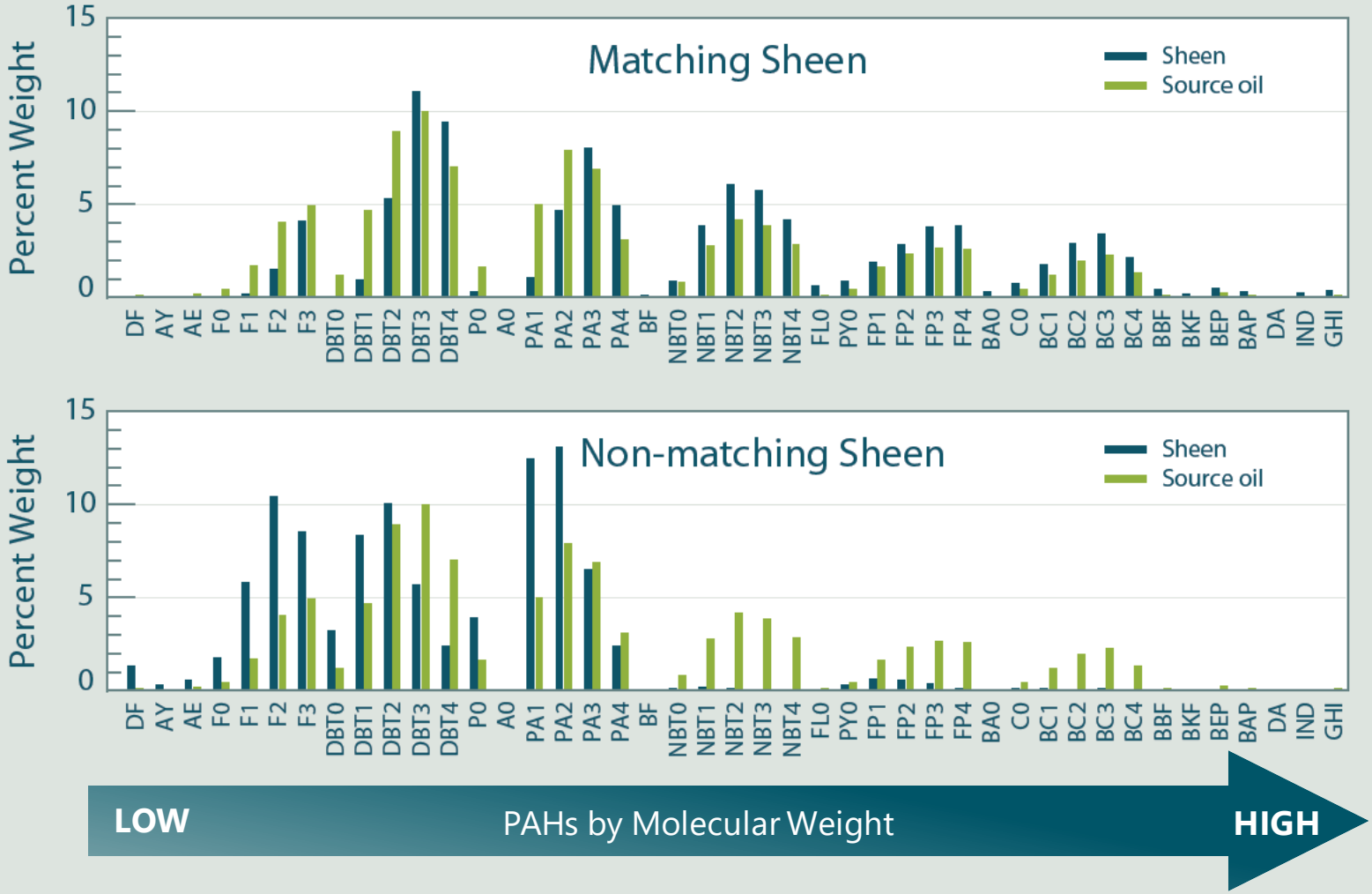
Case Studies

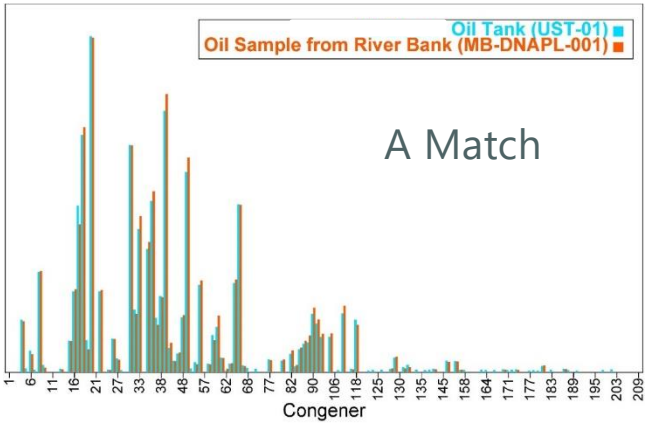
Qualitative Comparison to Released Material

- Surface water oil sheens collected during cleanup were compared to source crude oil from a pipeline spill
- Not all sheens matched the released oil, indicating other sources



Case Study – PCB Cleanup Liability Litigation

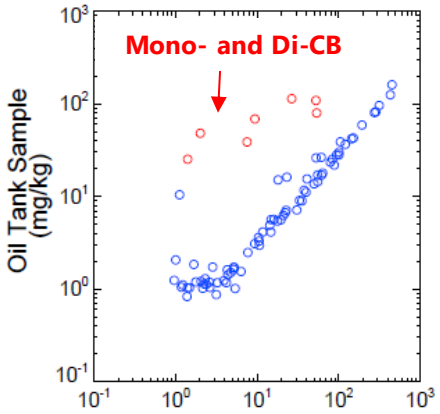
Congener Profile Comparisons



Congener Concentration Cross Plots Helped Evaluate Matches to Site PCB Oil

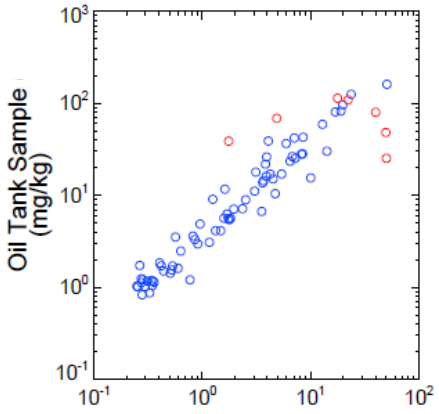
Weathering Analysis Identified Weathered Site Signatures in the Study Area

PCB Volatilization



Shallow Soil Sample (0-4 ft.)

PCB Dechlorination



Deep Soil Sample (16-20 ft.)

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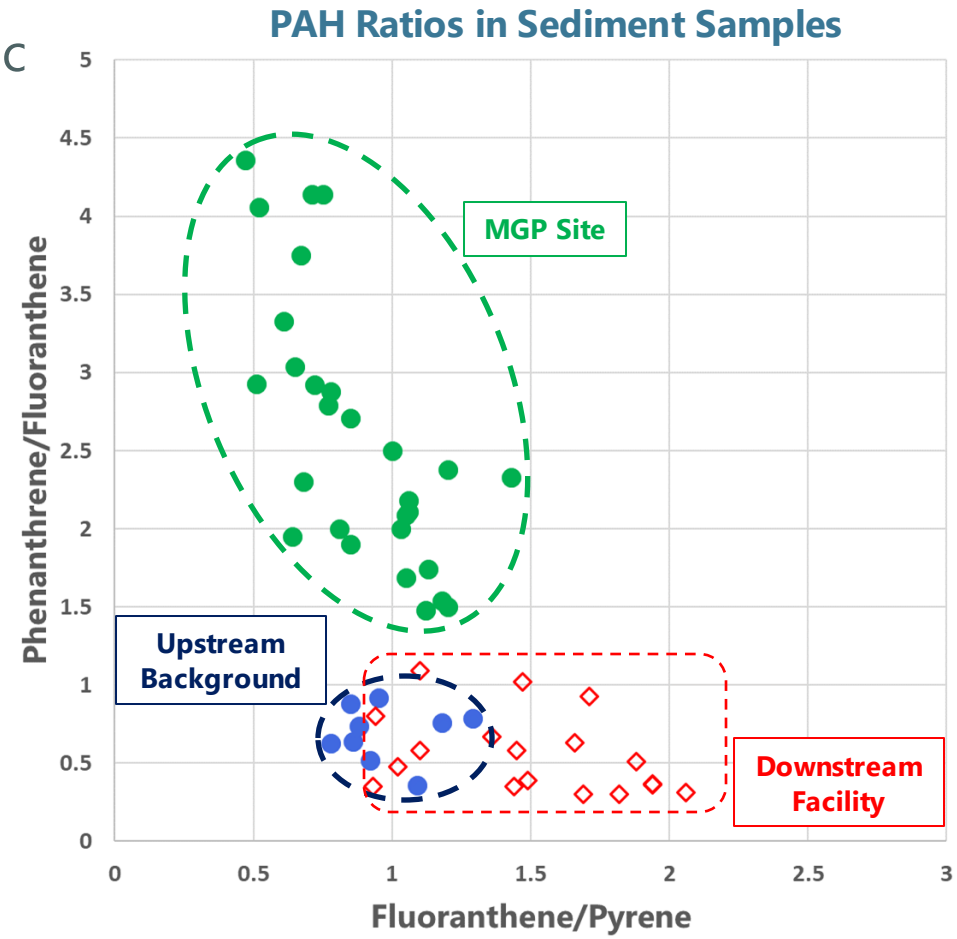
Double-Ratio Plots Distinguish PAH Sources

- A ratio selection model identified effective, site-specific PAH diagnostic ratios
  - Consistent within source
  - Distinct between sources
  - Resistant to weathering
- Demonstrated that the MGP site was not the source of contamination near a downstream facility
- Reduced client's remedial footprint by about 30%



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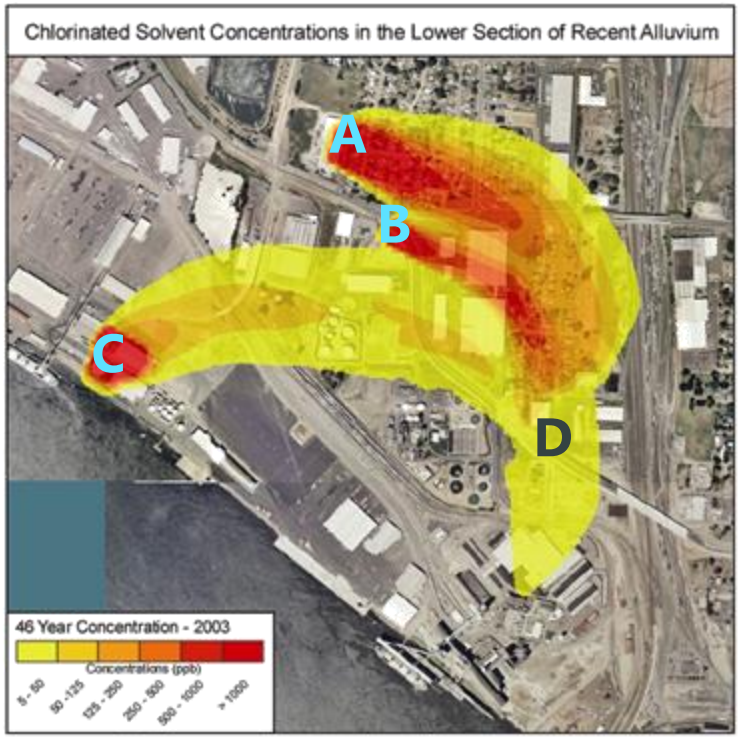
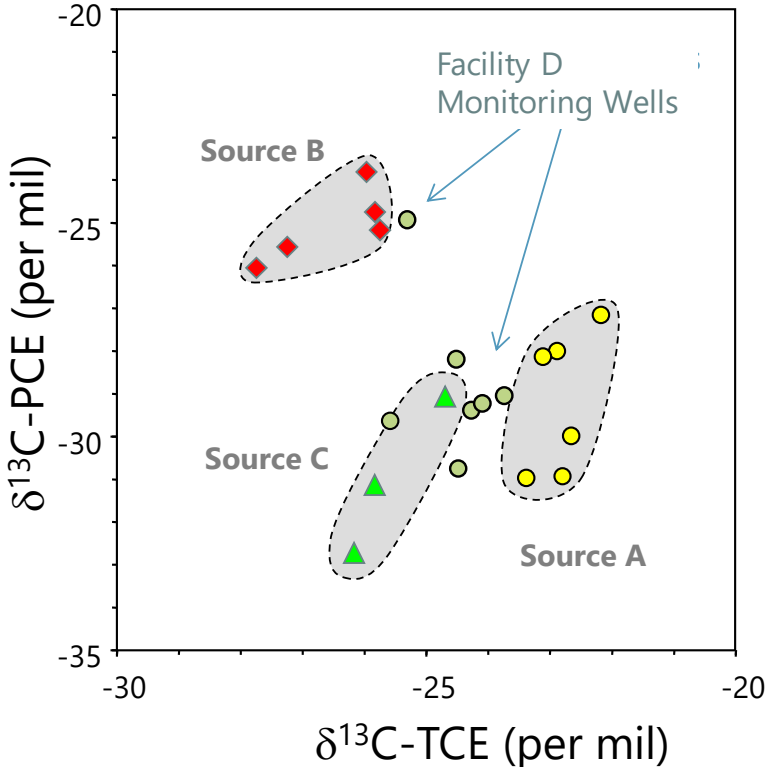
Chlorinated Solvents Fingerprinted With Isotopes

- Compound-specific isotope analysis (CSIA) of chlorinated solvents discriminated comingled groundwater plumes





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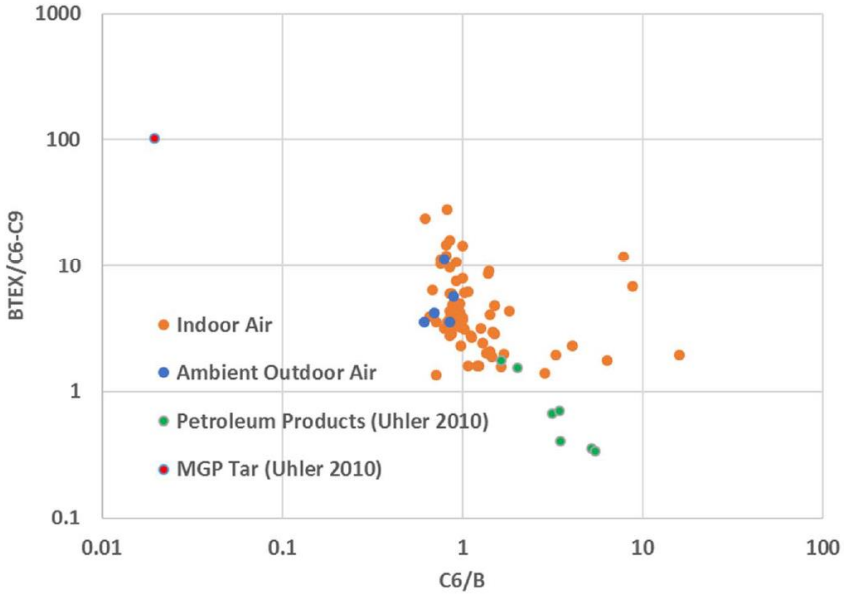
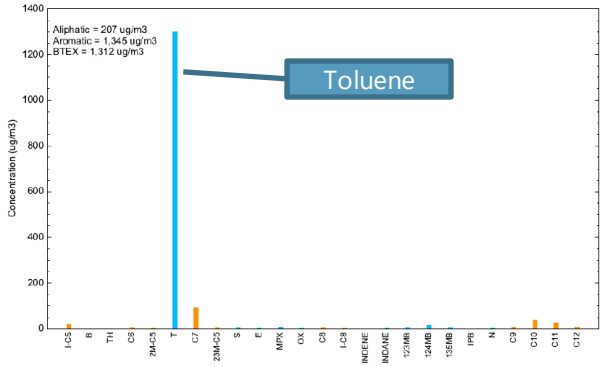
Aromatic vs. Aliphatic Hydrocarbon Ratios Rule Out MGP Source for Indoor Air Contamination

- Indoor air monitoring in apartment complex over a former MGP site
- Pyrogenic hydrocarbon sources (e.g., MGP, creosote)
  - Aromatic >> Aliphatic
- Petrogenic hydrocarbon sources (e.g., diesel, fuel oil)
  - Aliphatic >> Aromatic
- Most indoor air matched outdoor air or trended toward petrogenic (aliphatic) source signatures
- Except two samples with high toluene (aromatic) found in a room with stored paint and paint thinner





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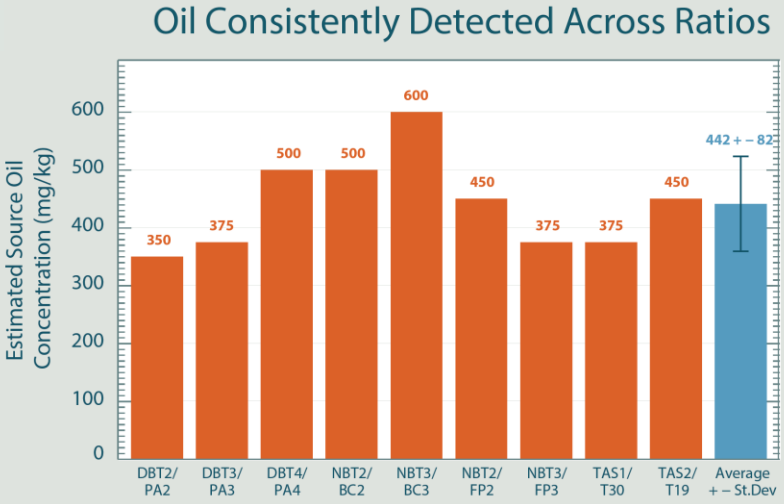
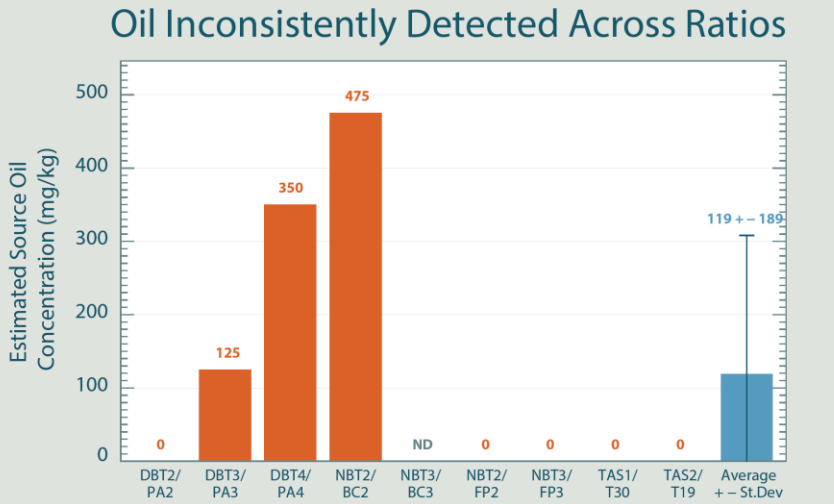
Apportionment Tool Example – Mixing Model Estimation of Residual Oil Spill Mass

- Avoided false positives using combined results from nine diagnostic ratio mixing models
- Concentration-based results: $mg_{crude\ oil}$ /$kg_{sediment}$
- 100s of samples evaluated, whole river mass estimated



Result from ratio average: 442 mg crude/kg sediment



Result from ratio average: 0 mg crude/kg sediment

PFAS Source Fingerprinting is Challenging

- Source fingerprints can change with environmental degradation and vary across manufacturers and time periods
- > 10,000 chemicals; most compounds are not standardly measured
- Using standardly measured compounds – even if most compounds are missed – may distinguish sources at a site
  - There is an element of luck involved. Avoid identifying different weathering stages as different sources
- More advanced methods are being researched – the science is rapidly developing

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PFAS Case Study 1 – PFAS in Purchased Products – Herzke et al. 2012

- Simple profile fingerprint using standard analyte list
- Variable composition within the same product class
- Shift in composition to shorter chain compounds following ban of PFOS in Europe

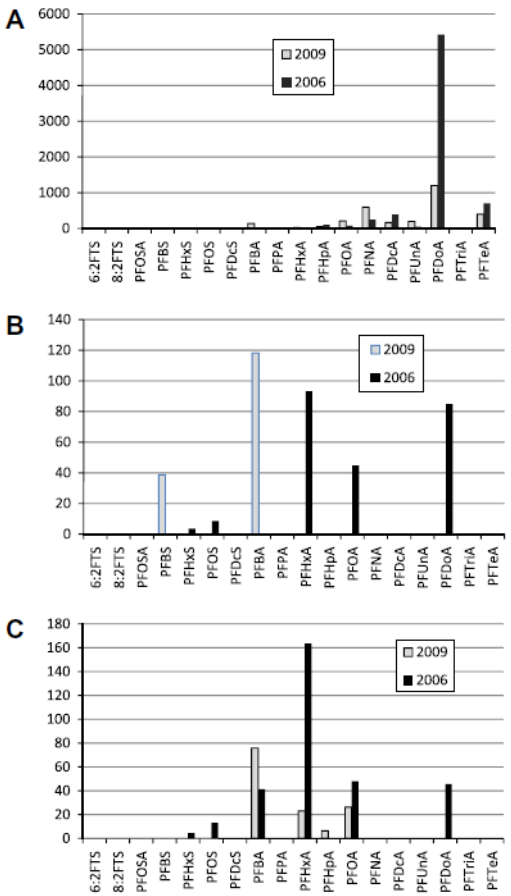

Fig. 2. PFAS concentrations in three waterproofing products A, B and C purchased and analyzed in both 2006 and 2009 (μg L^{-1}).

Herkze et al. 2012. "Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study." *Chemosphere* 88 (2012) 980–987

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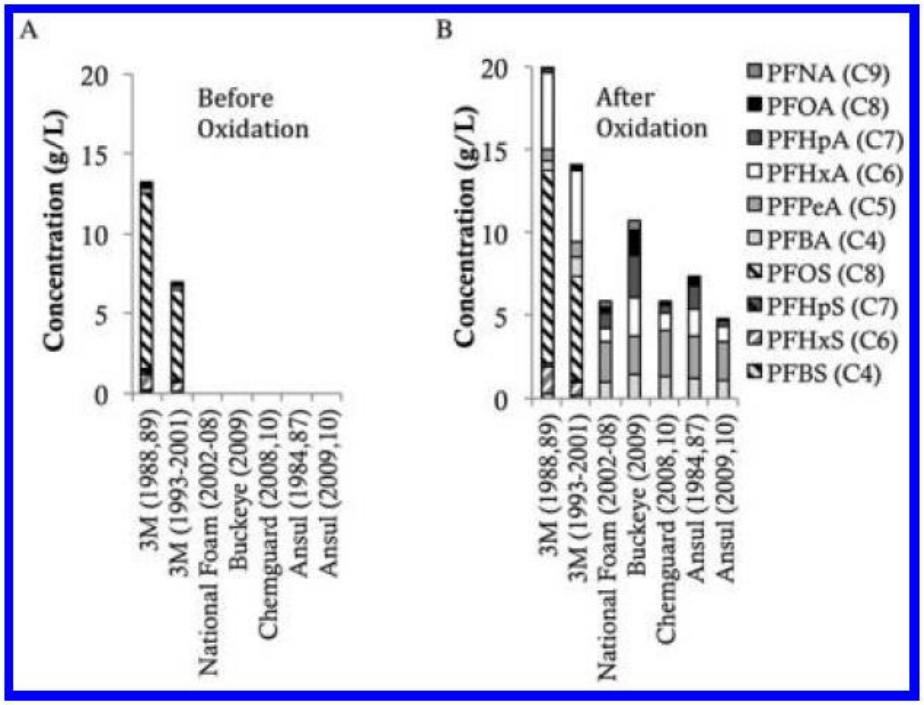
PFAS Case Study 2 – AFFF Source Characterization – Houtz et al. 2013



- Aqueous film-forming foams (AFFFs) are one of the primary environmental PFAS sources
- Application of TOP oxidation assay to 7 AFFFs improved resolution of source fingerprints
- Provided identification of potential environmental degradation products in each source

Houtz et al. 2013. "Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil." *Environ. Sci. Technol.* 2013, 47, 8187–8195

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Summary

- Environmental forensic investigation can help understand what is causing those numbers in your results tables
- Investigations can address any type of chemical and any size project
- An MLOE approach is critical for defensible source assessment

???

SD-C801 SD-C801_0-0.5 10/3/2018 17:33 0 - 0.5 ft N SE	SD-C801 SDC-C801_1.4-1.9 10/3/2018 17:40 1.4 - 1.9 ft N SE	SD-C802 SD-C802_0-0.5 10/4/2018 8:05 0 - 0.5 ft N SE	SD-C802 SDC-C802_0.9-1.4 10/4/2018 8:11 0.9 - 1.4 ft N SE
--	1060	--	1680
0.117	0.096 J	0.156	0.463
230	8.1	8	29000
110	2	47	14000
460	9.9	28	47000
540	7.1	96	43000
600	6	130	100000
--	--	--	--
560	4.4	140	30000
290	2.5	71	16000
210 J	2	61	14000
220	1.9	50	12000
430	5.1	79	31000
57	0.76 U	15	3500 J
1300	14	120	80000
210	5.9	9.3	21000
240	1.9	69	16000 J
8.1	0.62 J	1.7	960
110	1.7	29	5800
1400	32	62	260000
1800	27	200	290000
200	3.9	60	25000
520	8.4	74	52000
250	5.6	13	29000
74	5.9	4.5	7800
1100	22	67	300000
50	1.3	17	6600
230	4.3	15	27000
520	15	22	63000
540	8.2	50	54000
30	0.76 U	7.1	1600
110	0.76 U	0.79 U	10000
750	14	23	68000
130	1.5	18	13000
25	0.76 U	0.79 U	86 U
320	4.4	15	27000
26	0.76 U	0.79 U	2400

Questions/Discussion