



Tracking a Petrogenic Source: Forensic Characterization, Identification, and Quantification of Spilled Crude Oil



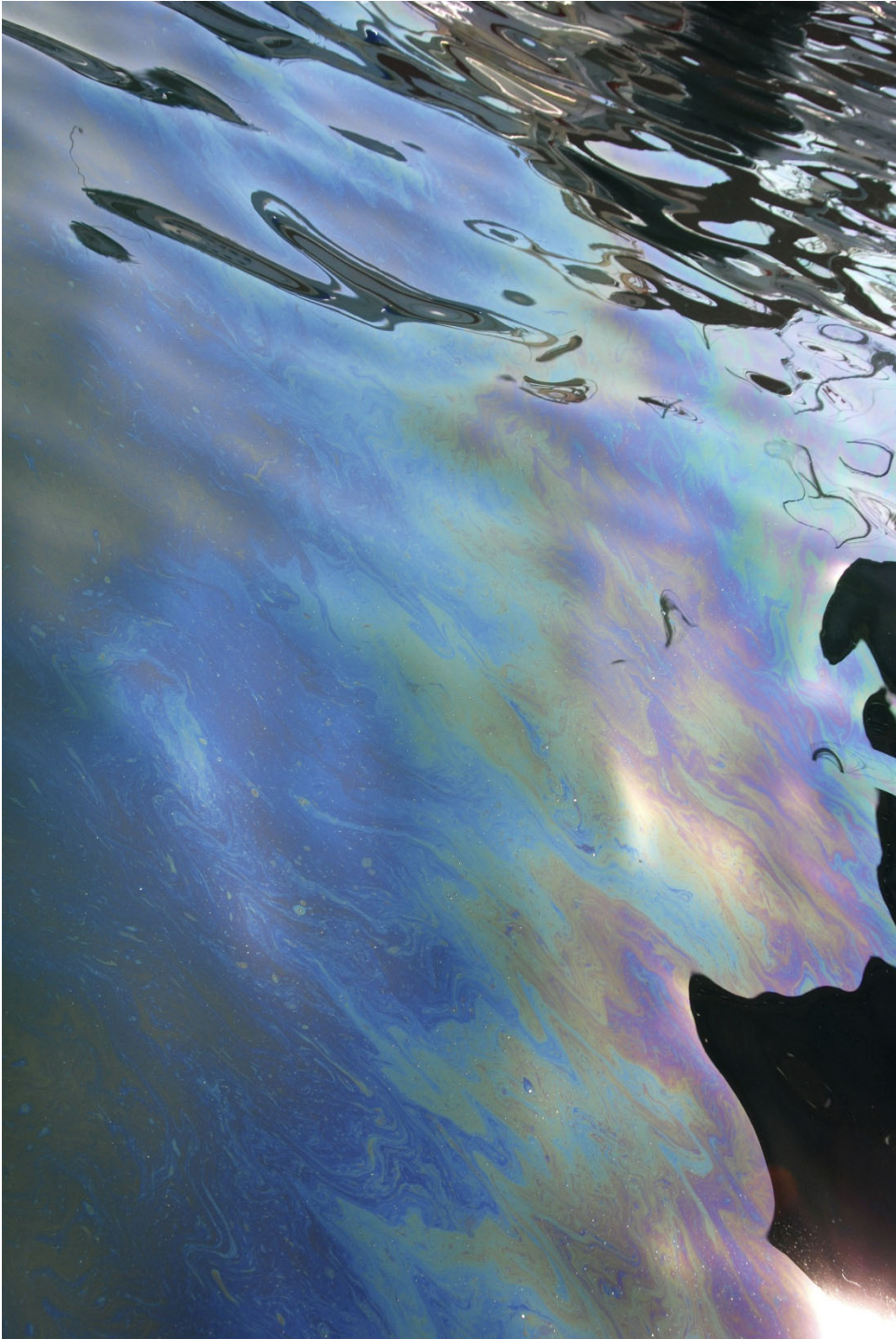
Deborah Chiavelli
February 13, 2019



Peter M. Simon
Philip B. Simon



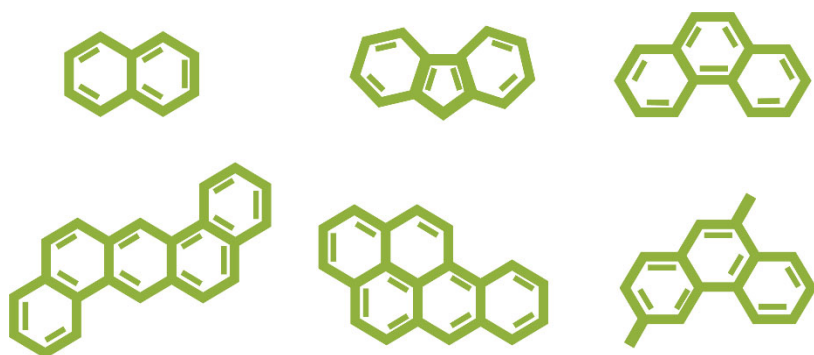
Michael Rury



Crude Oil Residuals Assessment

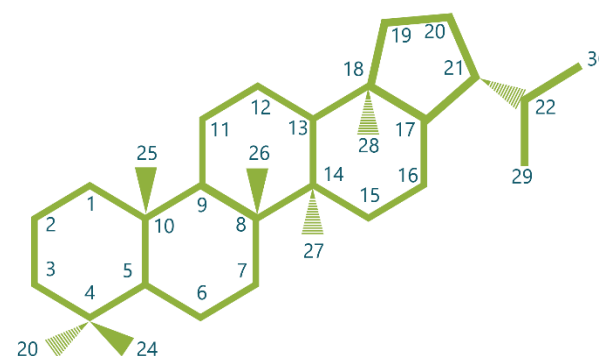
Forensic quantification
of crude oil residuals
in an urban waterway
several years after
sediment and
floodplain emergency
cleanup

Oil Fingerprinting Toolbox



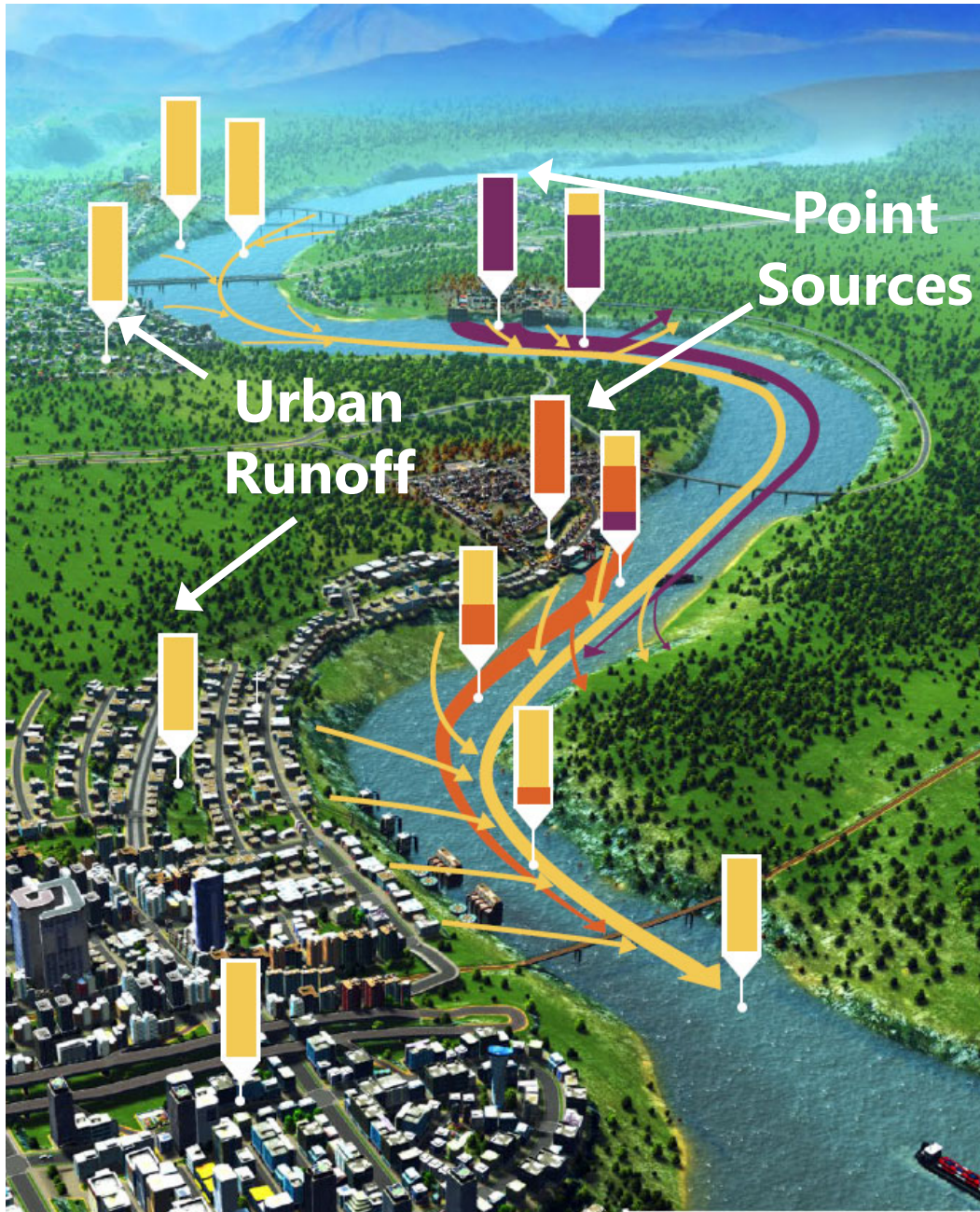
PAHs

- Sixteen priority pollutant PAHs
- More than 50 individual parent and alkylated PAHs are used to “fingerprint” PAH sources



Petroleum biomarkers

- Derived from bacteria and plant precursors in fossil fuels
- Source-specific and weathering-resistant



Urban PAH Sources

- Point sources
 - Manufactured gas plants (MGPs)
 - Oil refining and storage
 - Shipping traffic
 - Industrial facilities
- Urban runoff

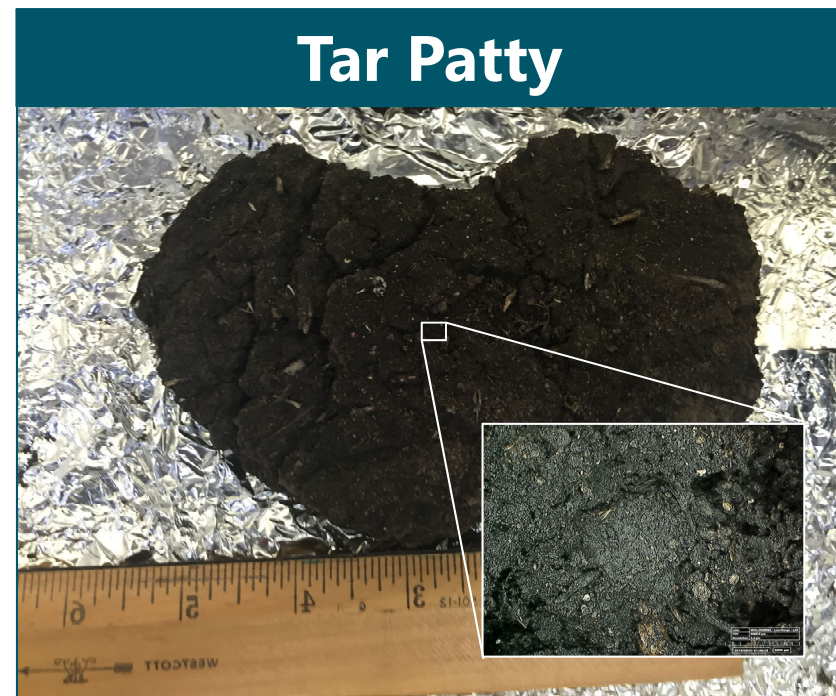
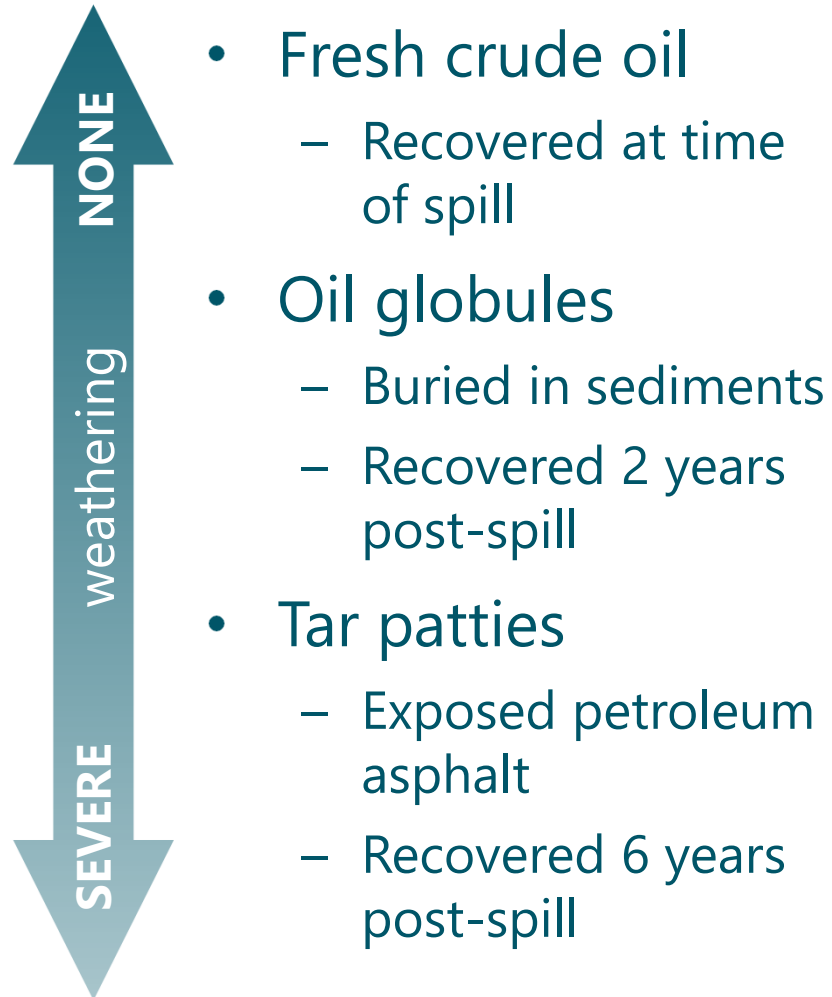


Background Characterization

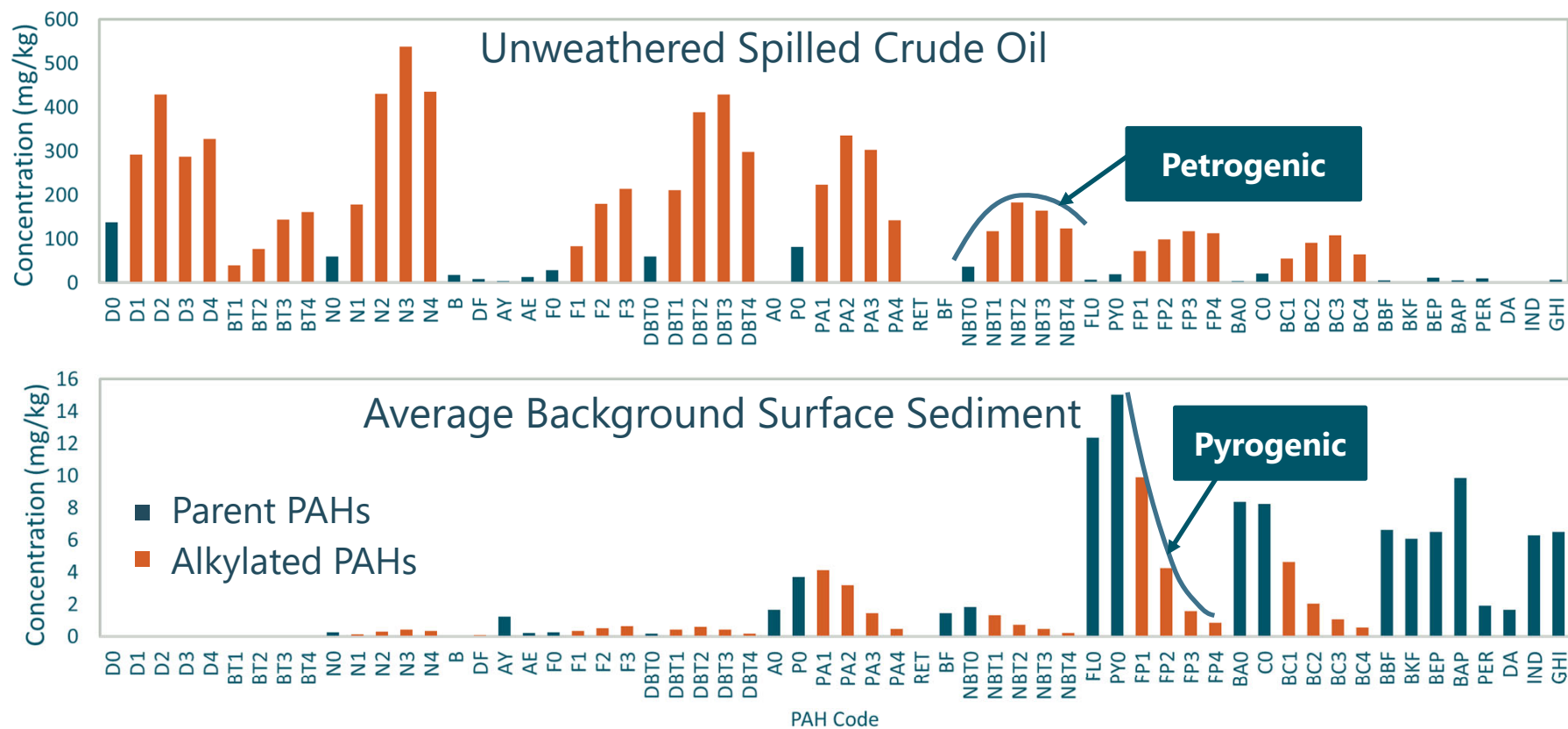
- Samples collected
 - Upstream sediment (18)
 - Upstream floodplain (29)
 - Tributary sediment (21)
- Indicated background hydrocarbon sources
 - Total PAH up to 127 mg/kg
 - Sheens, UV fluorescence
 - Non-spill hydrocarbon source fingerprints:
 - urban background, MGP, petrogenic

Fresh and Weathered Site Oil Samples

Weathering: Change in composition due to physical and biological processes



Site PAH Fingerprints

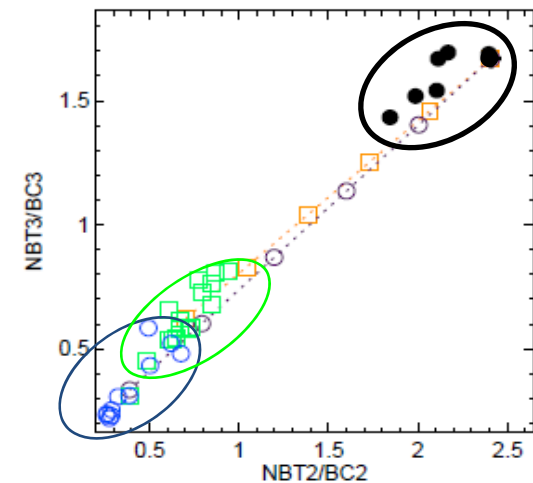
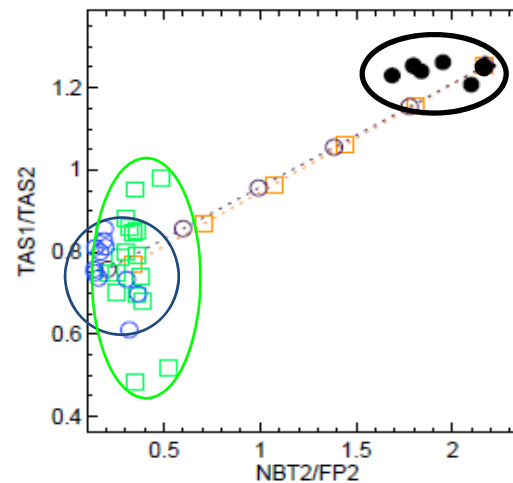
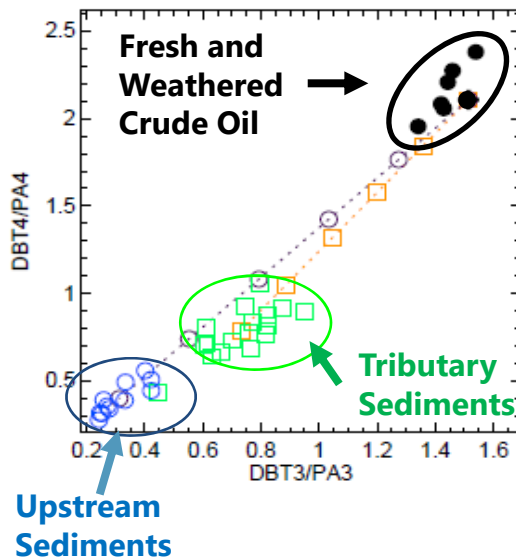


Sediment Oil Quantification - Approach

- Regulatory agency's estimate of residual oil appeared excessive
- Overestimated partially due to false positives
 - Non-specific indicators attributed background hydrocarbons to the spill
 - Sheens, UV fluorescence, non-specific diagnostic ratios
 - These indicators "found" spilled crude oil in upstream and tributary background samples
- **Our approach:** Multiple independent indicators improved precision in spill oil identification
 - PAH and biomarker profiles, GC/FID chromatograms, multiple site-specific diagnostic ratios

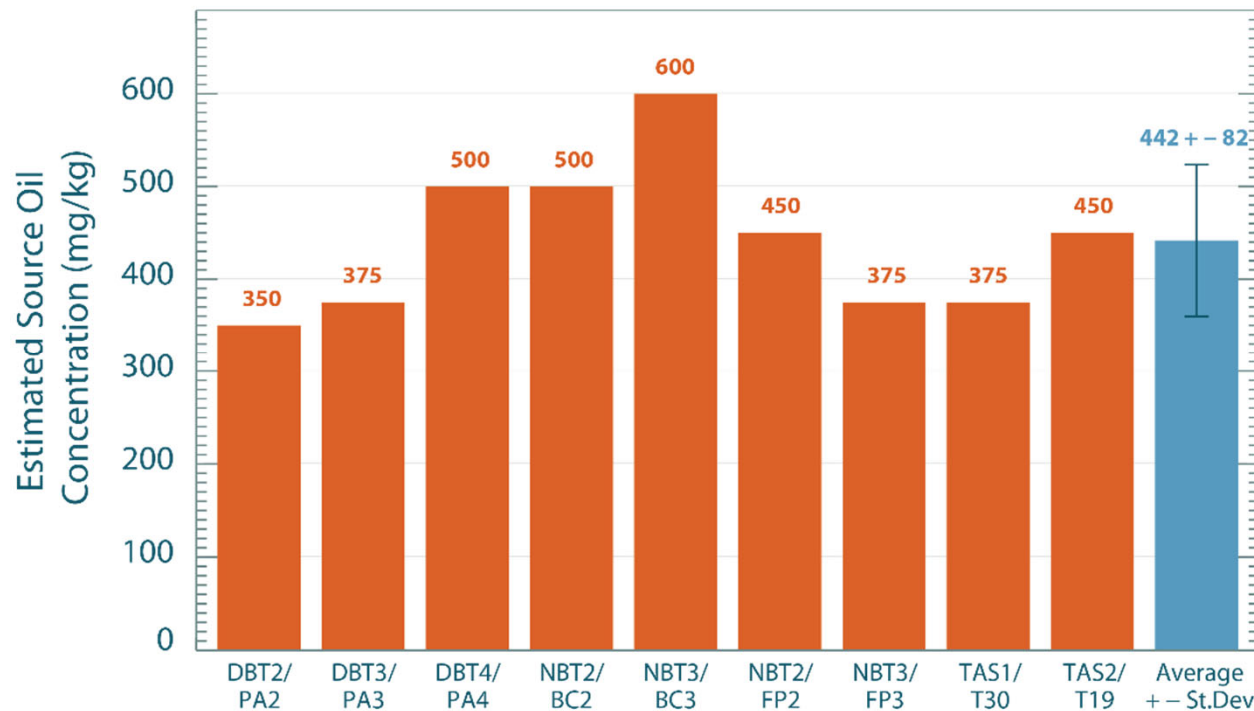
Sediment Oil Quantification - Diagnostic Ratios

- PAH and biomarker ratios evaluated
- Nine diagnostic ratios met selection criteria



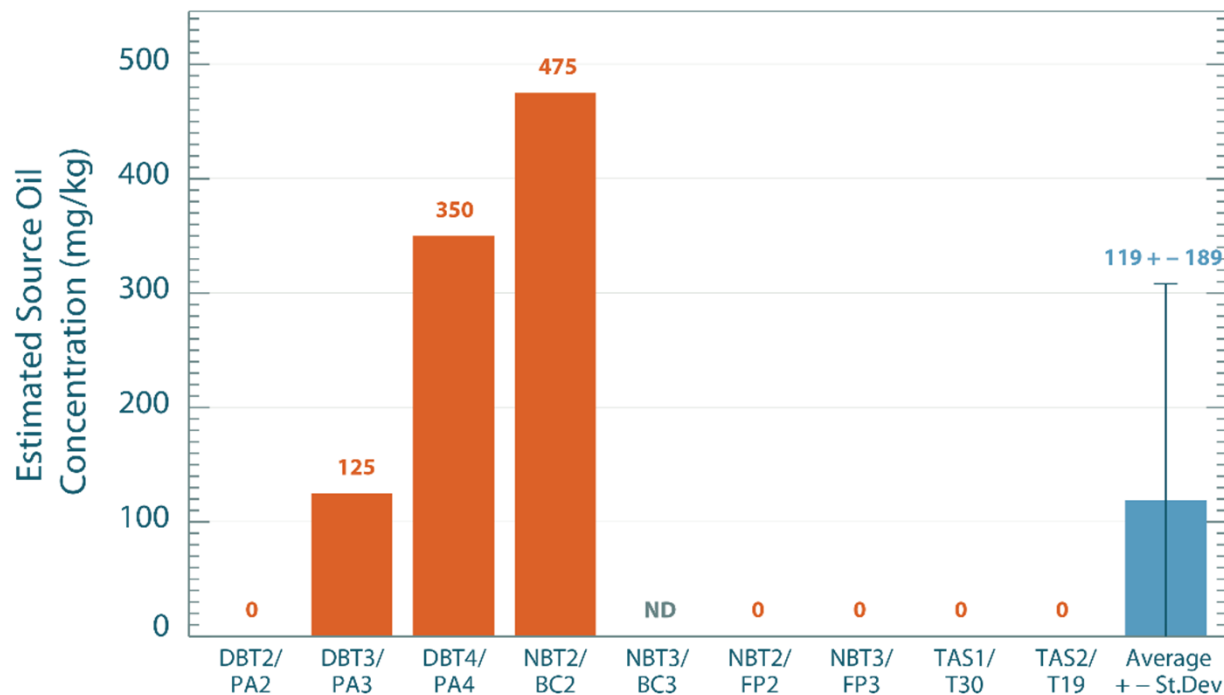
Sediment Oil Quantification - Mixing Model

- Multi-ratio, concentration-based
 - “Reverse oil titration” to get to background levels
 - Consistent results for all ratios -> average = oil concentration estimate



Sediment Oil Quantification - Mixing Model

- Inconsistent results among ratios -> other sources
 - Avoided false positives
- Validated model using “oily” background samples and site sediment samples spiked with crude oil

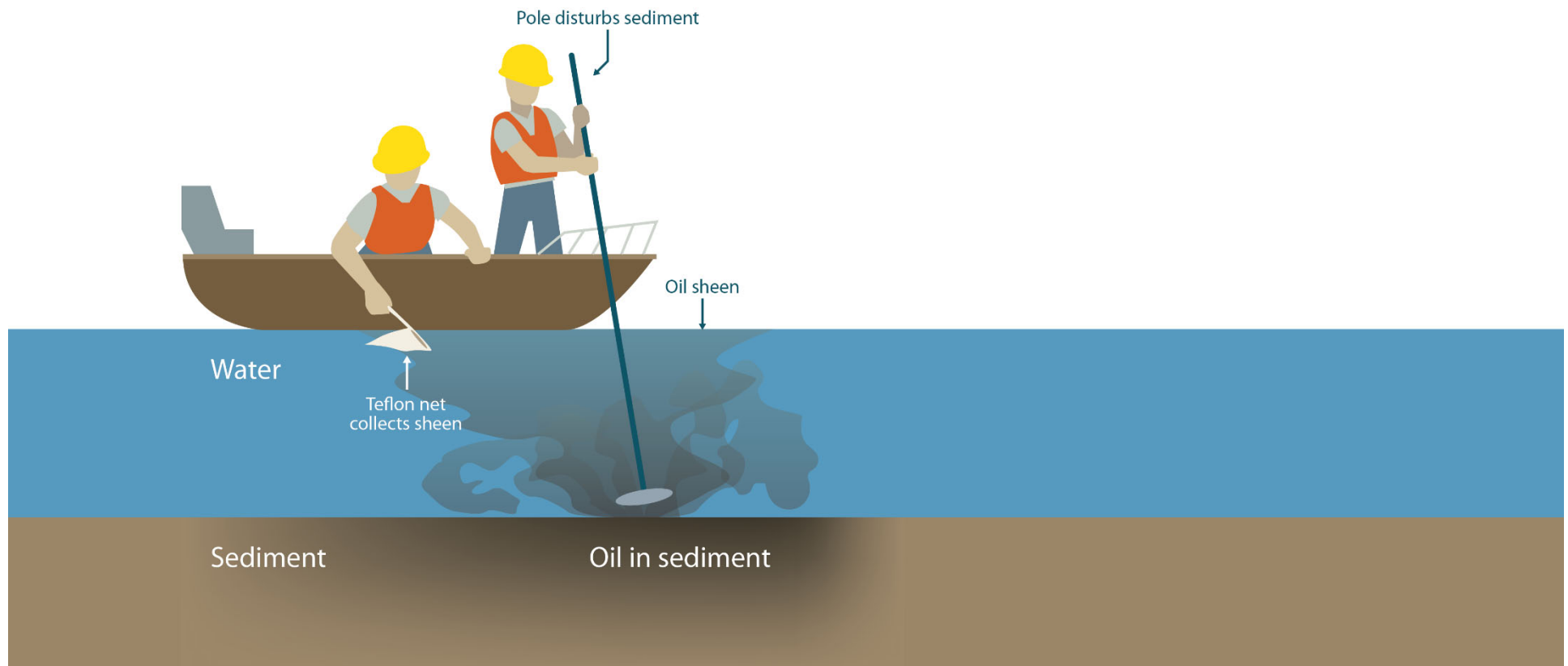


Sediment Oil Quantification - Results

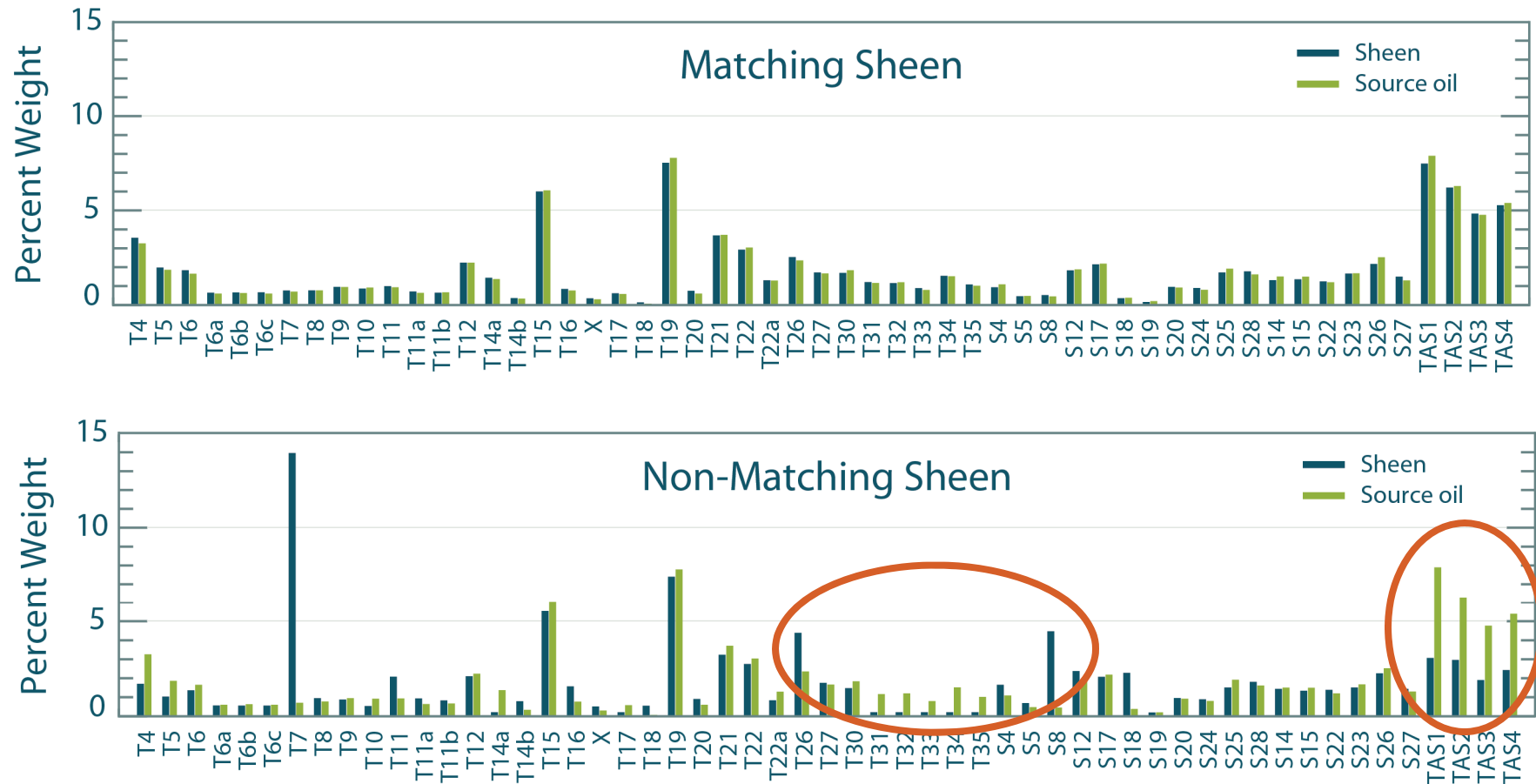
- Multiple ratio model
 - Accounted for presence of non-spill sources
 - Estimated 70% less residual crude oil than regulatory agency's estimate
- The agency subsequently released an estimate that was 50% reduced from their original estimate

Sheen Evaluation - Approach

- Sediments were agitated to produce sheens to delineate residual oil
- We used forensic chemistry to evaluate sheen source

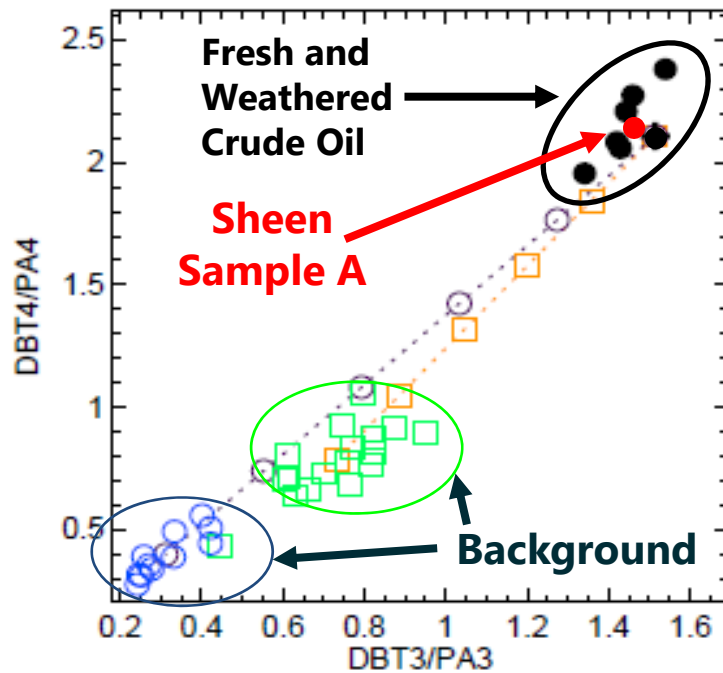


Sheen Evaluation – Biomarker Comparison

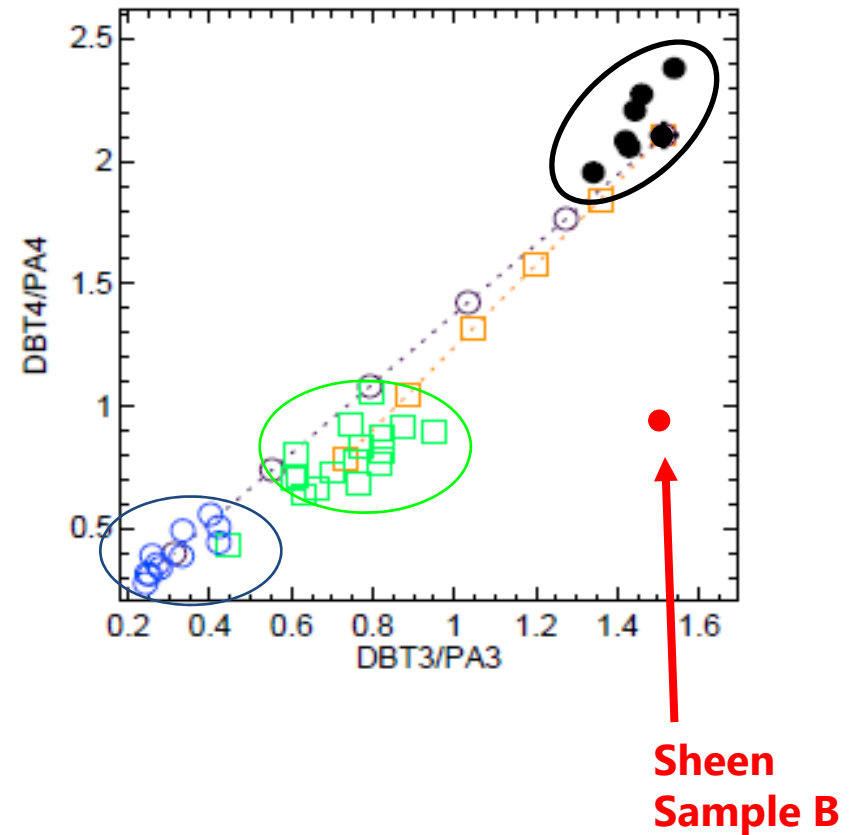


Sheen Evaluation – Diagnostic Ratios

Matching Sheen



Non-Matching Sheen

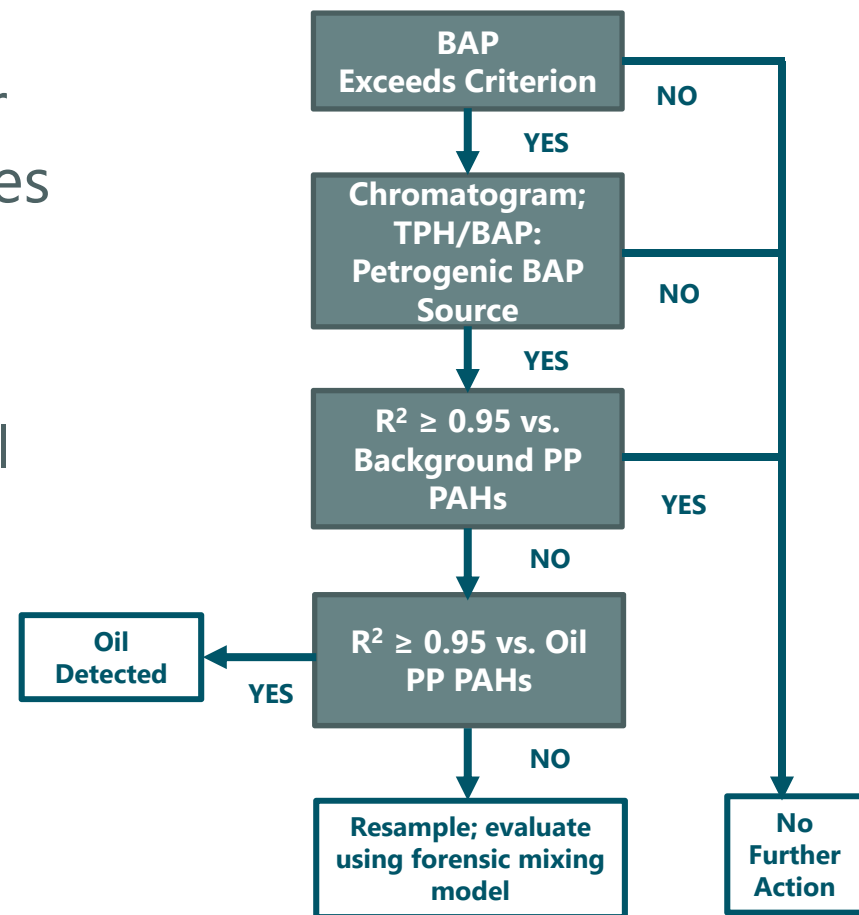


Sheen Evaluation - Results

- Approximately 50% of sheens matched spill oil
 - Lack of match and other lines of evidence indicated other sheen sources
- Avoided false positive identification of spill oil by providing evidence that not all sheens originated from spill oil
- Increased confidence in using sheens for delineation of residual oil

Floodplain Oil Quantification - Decision Tree

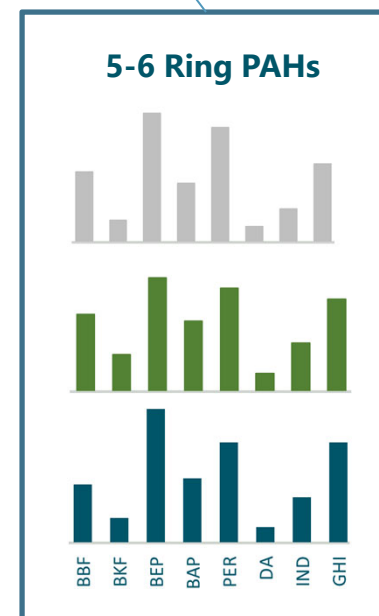
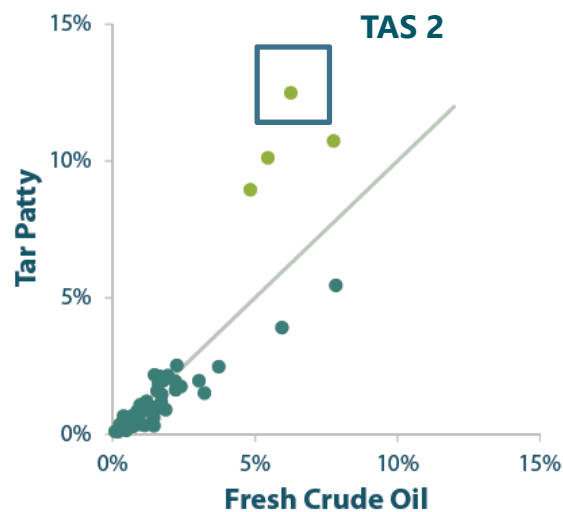
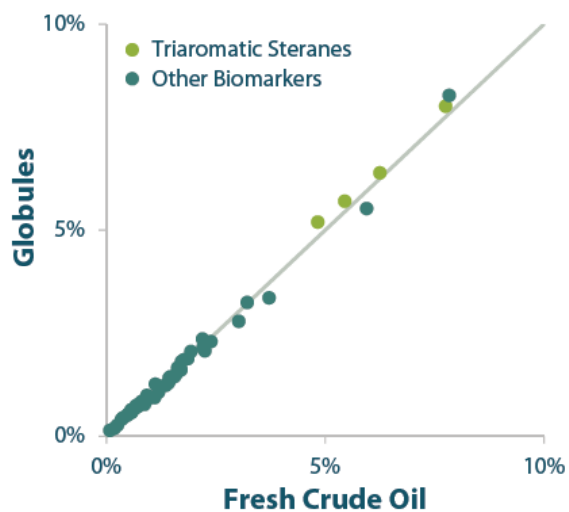
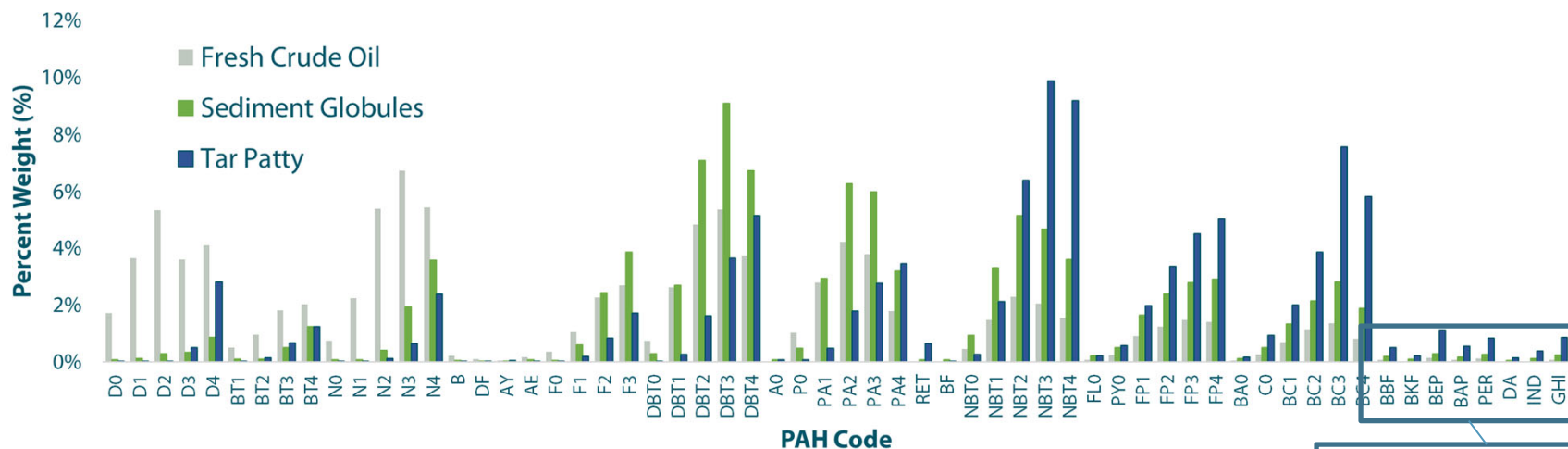
- Only priority pollutant (PP) PAHs and TPH available for most floodplain soil samples
- Decision tree leveraged all available data
 - No further action protocol
- Only uncertain results subjected to resampling and forensic analysis
- Resolved over 95% of locations



Floodplain Oil Quantification – Forensic Approach

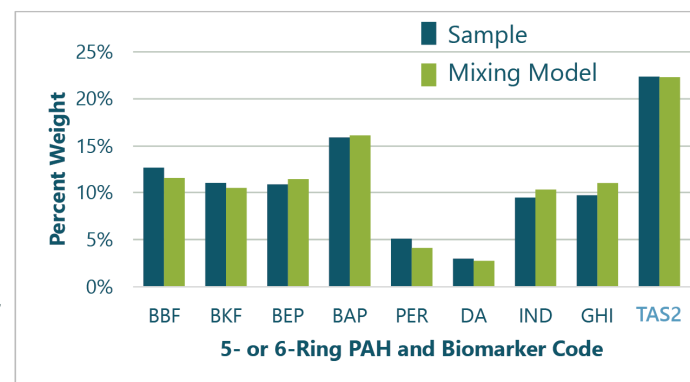
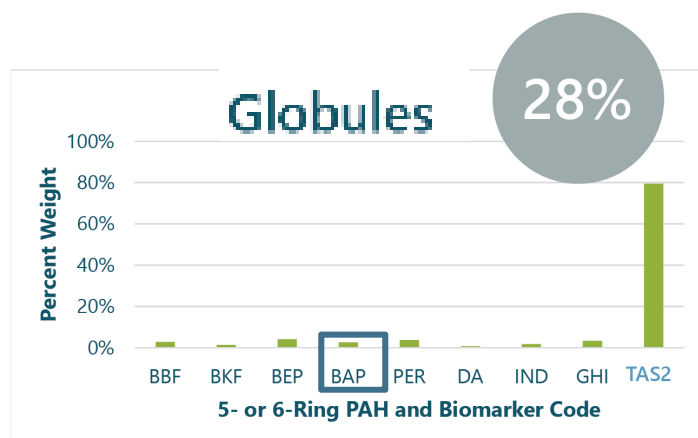
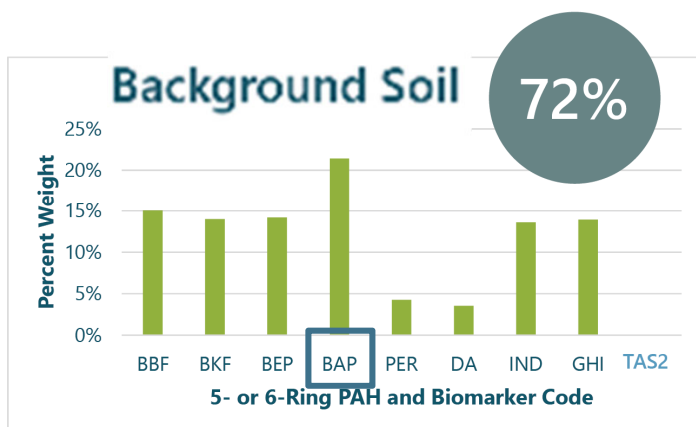
- Forensic hydrocarbon analysis of subset of upstream and spill area floodplain soil samples
 - Targeted impacted areas
- Diagnostic ratios from sediment analyses were unreliable for floodplain soil samples
 - Extreme weathering in floodplain
- New weathering reference was incorporated
 - Spill oil tar patty samples were collected for forensic chemical analysis
 - New oil quantification method using weathering-resistant chemicals

Floodplain Oil Quantification – Weathering



Floodplain Oil Quantification - Mixing Model

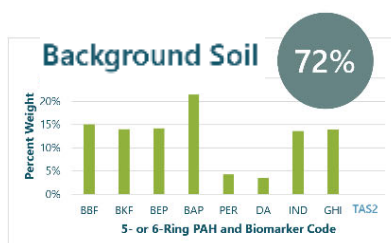
Sample BAP = 2.0 mg/kg



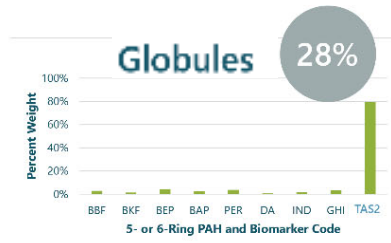
BAP from oil = 0.1 mg/kg

Floodplain Oil Quantification - Mixing Model

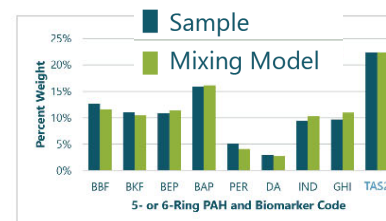
Low Oil



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BAP (mg/kg)

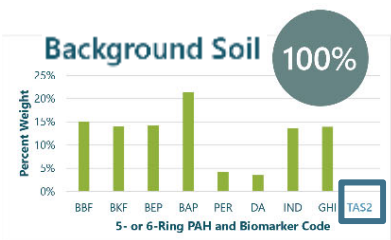
In Soil Sample

From Oil

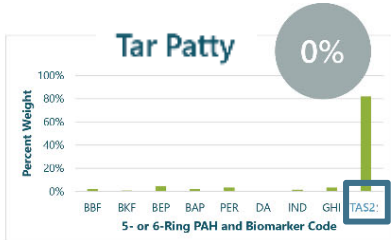
2.0

0.1

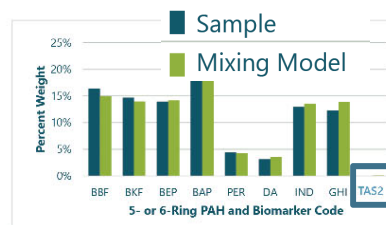
No Oil



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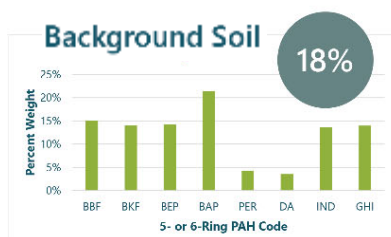
In Soil Sample

From Oil

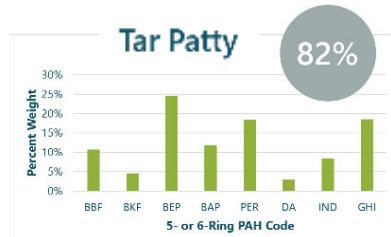
48.0

0.0

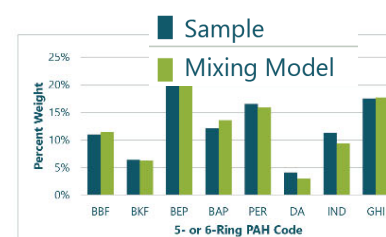
High Oil



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In Soil Sample

From Oil

1.8

1.3

Floodplain Oil Quantification - Results

- Addressed advanced oil weathering and sensitive to trace oil amounts
- Excellent model fit for most spill area soil samples
 - Reliable tool for PAH source apportionment
- Most BAP in the spill area was from background
- Poor model fit indicated other PAH sources
 - Other lines of evidence consistent with other sources

Summary and Conclusions

- At a site with background hydrocarbon sources, we successfully distinguished and quantified residual spilled crude oil
 - Utilized multiple, site-specific diagnostic tools
 - Applied tools in a flexible manner based on available data and degree of weathering
- Multiple lines of evidence approach avoided attributing background sources to the spill
- Positive regulatory agency responses included
 - Reduced sediment residual oil estimate and dredge area
 - Collaborative no further action protocol for floodplain

Questions/Discussion

