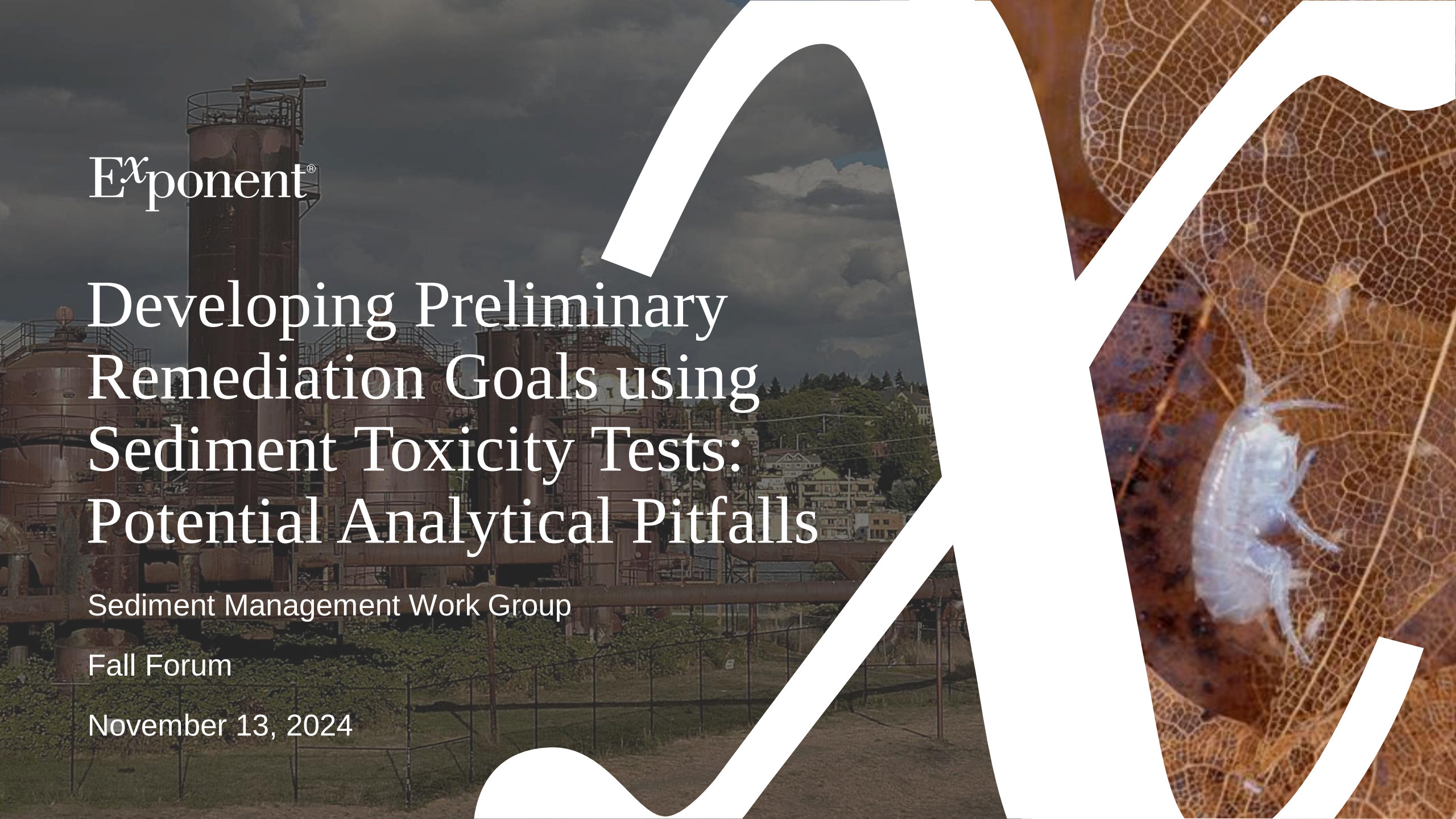


Exponent®

Developing Preliminary Remediation Goals using Sediment Toxicity Tests: Potential Analytical Pitfalls

Sediment Management Work Group

Fall Forum

November 13, 2024

The Team

- **Exponent Inc.**

  Susan Kane Driscoll, Sean Ryan, and Linda Cook*

- **Ramboll**

  Abigail Small

- **WEC Energy Group**

  Frank Dombrowski

* Currently with Weston & Sampson

Agenda

Introduction to the Site

Site-specific Sediment Assessment

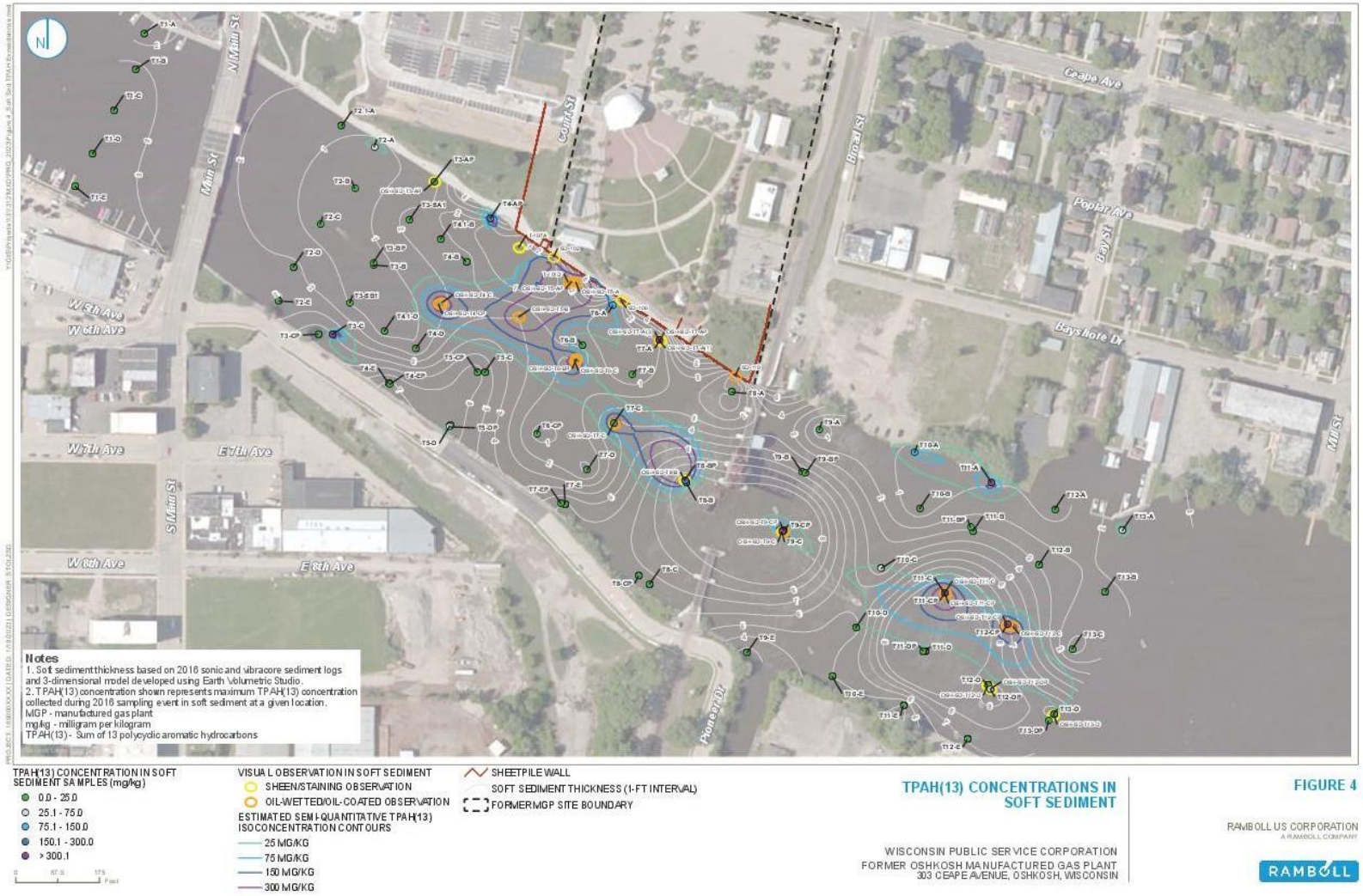
Analytical Issues

Recommendations

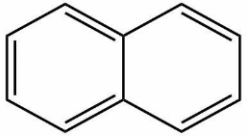
Oshkosh Manufactured Gas Plant Site

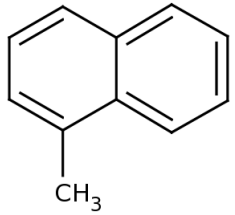
Photo courtesy of the City of Oshkosh

2016 – Areas of Elevated PAHs



PAHs at MGP Sites





Comparison of Pyrogenic and Petrogenic PAHs		
Attribute	**Pyrogenic**	**Petrogenic**
Source	Combustion of organic matter	Petroleum-related activities
Formation Process	High temperature processes (e.g., MGP)	Low temperature processes (e.g., oil or gas spills)
Molecular Characteristics	Dominance of un-alklylated PAHs	Dominance of alky-substituted PAHs

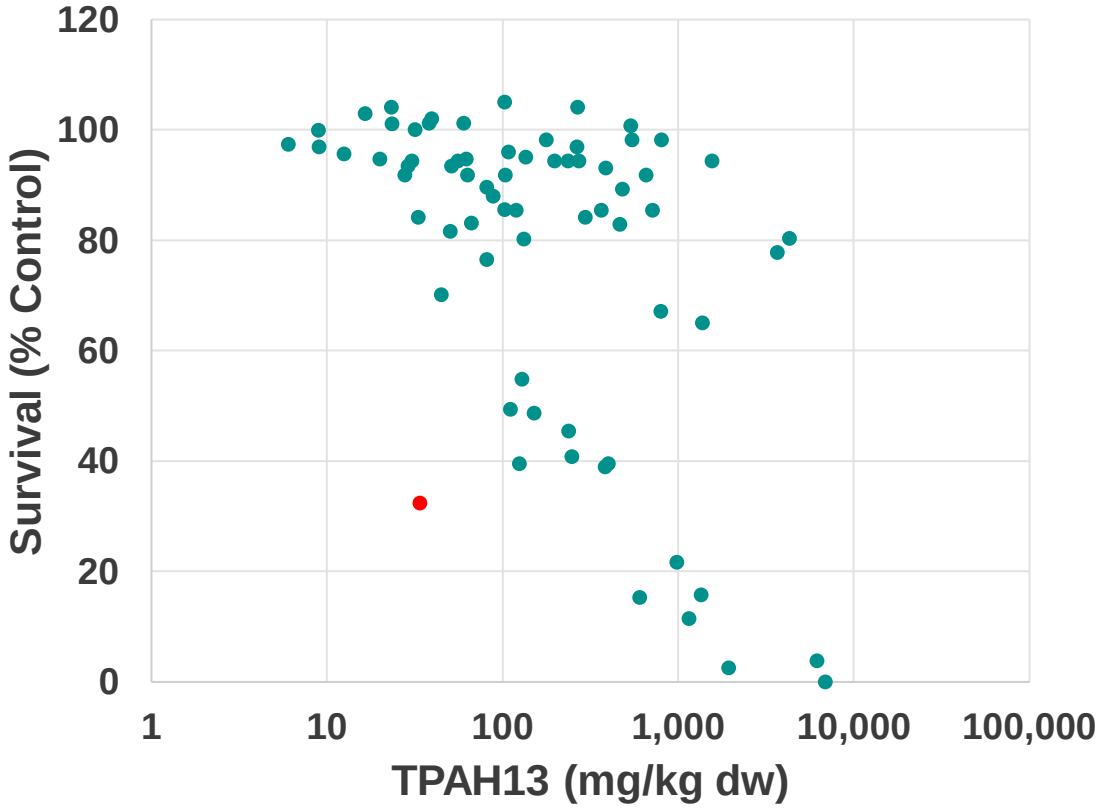
Analysis of both 13 un-alkylated “parent” PAHs and 21 alkylated PAHs (TPAH34) potentially useful for:

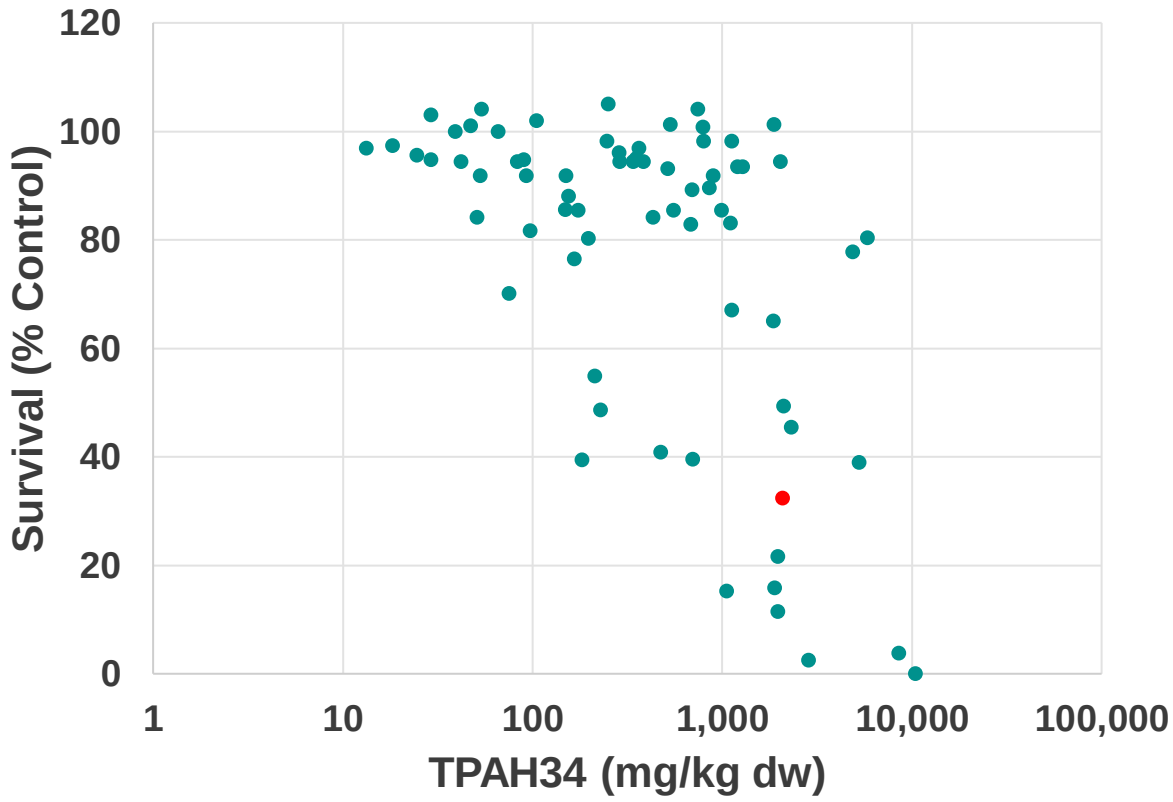
- Forensic identification of sources
- Predicting or explaining observed toxicity

Oshkosh Baseline Risk Assessment (10/2022)

Risk-based toxicity thresholds based on data from 5 MGP sites (not including Oshkosh)

Thresholds developed based on multiple exposure metrics, including TPAH13 and TPAH34





Site-specific Sediment Assessment

Site-specific Sediment Assessment (SSA)

10/4/2023 – 10/12/2023

Collected 55 sediment samples. Homogenized. Subsamples sent for **Preliminary Analysis** (rapid TAT) for 13 PAHs

10/24/2023

Combined certain samples to produce 14 composite samples with specific concentrations. **Preliminary Re-Analysis** (rapid TAT) of 14 samples for 13 PAHs

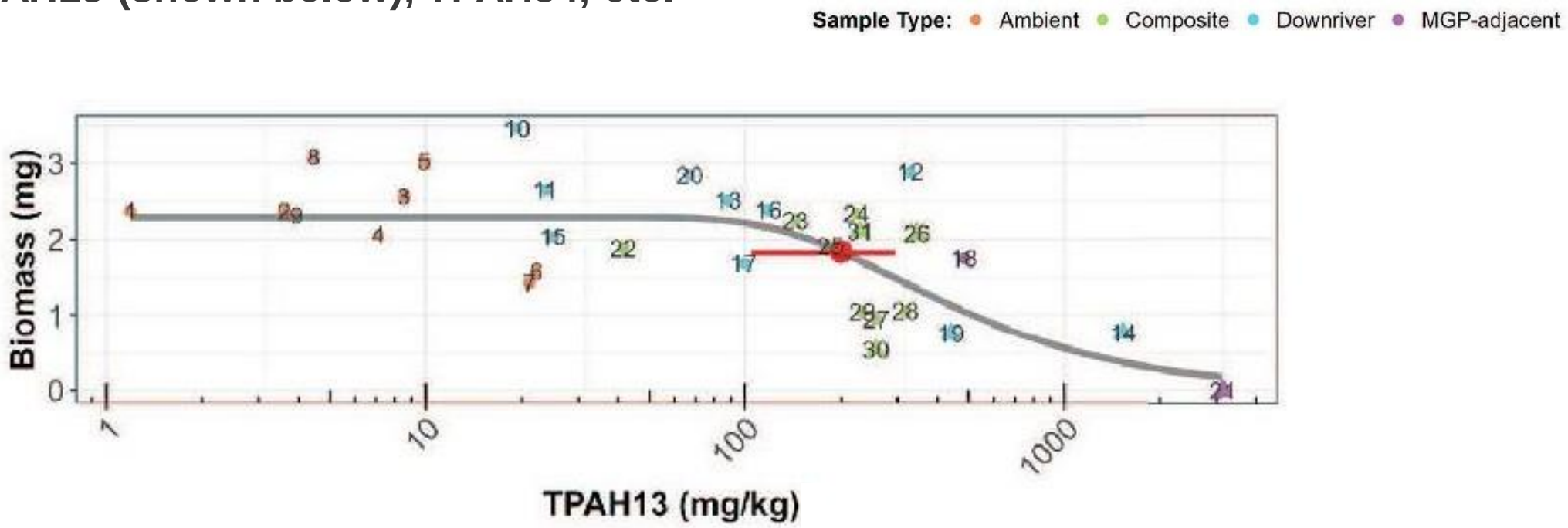
11/14/2023 – 11/15/2023

Selected final subset of 36 samples for toxicity testing. Remixed each sample and subsampled for toxicity testing and **Full Investigative Analysis** of 34 PAHs (including 13 PAHs), VOCs, metals, TOC, grain size, etc.

Target No. Samples for Full Analytical Suite	TPAH-13 Concentration (mg/kg)
2-4	0-25
6-8	25-75
4-6	75-150
3-5	150-300
1-3	>300

Site-specific Sediment Assessment (SSA)

Investigative data used to developed risk-based thresholds using multiple exposure metrics, including TPAH13 (shown below), TPAH34, etc.

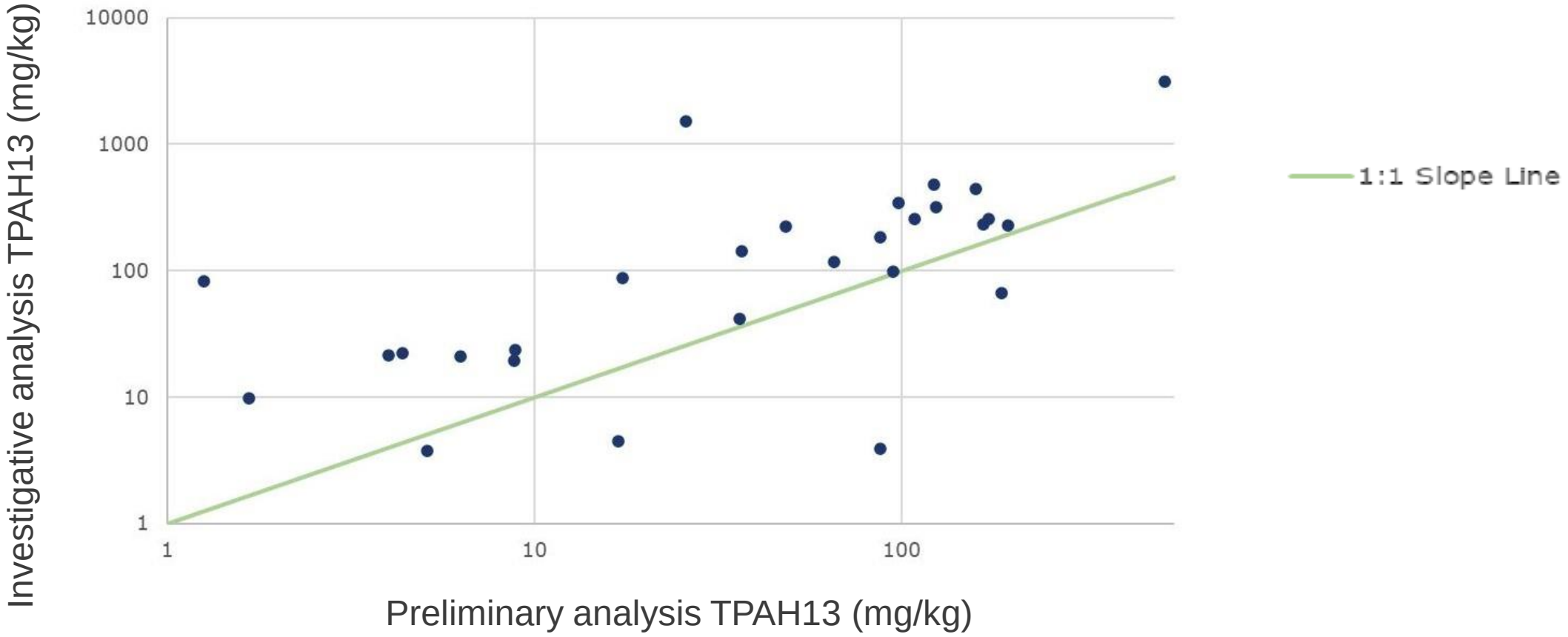


EC20* = 199 mg/kg (95% Confidence intervals = 105-294 mg/kg)

*EC20 = Concentration corresponding to 20% reduction in response

Analytical Issues

Results of the Preliminary Analyses are biased low in comparison to Results of the Investigative Analyses



Primary difference between the two results appears to be the extraction method

Preliminary 2023 Analyses	Investigative 2023 Analyses
• Used to select subset of samples for toxicity testing	• Used for exposure-response modelling
• Microwave extraction method	• Shaker table solvent extraction method
• Analysis method: 8270-SIM for 13 PAHs	• Analysis method: 8270-SIM for 34 PAHs (including 13 parent PAHs)
• Chromatographic run: 13 min	• Chromatographic run: 75 min

Extraction Methods and Dilutions Likely Contributed to Differences Between Analyses

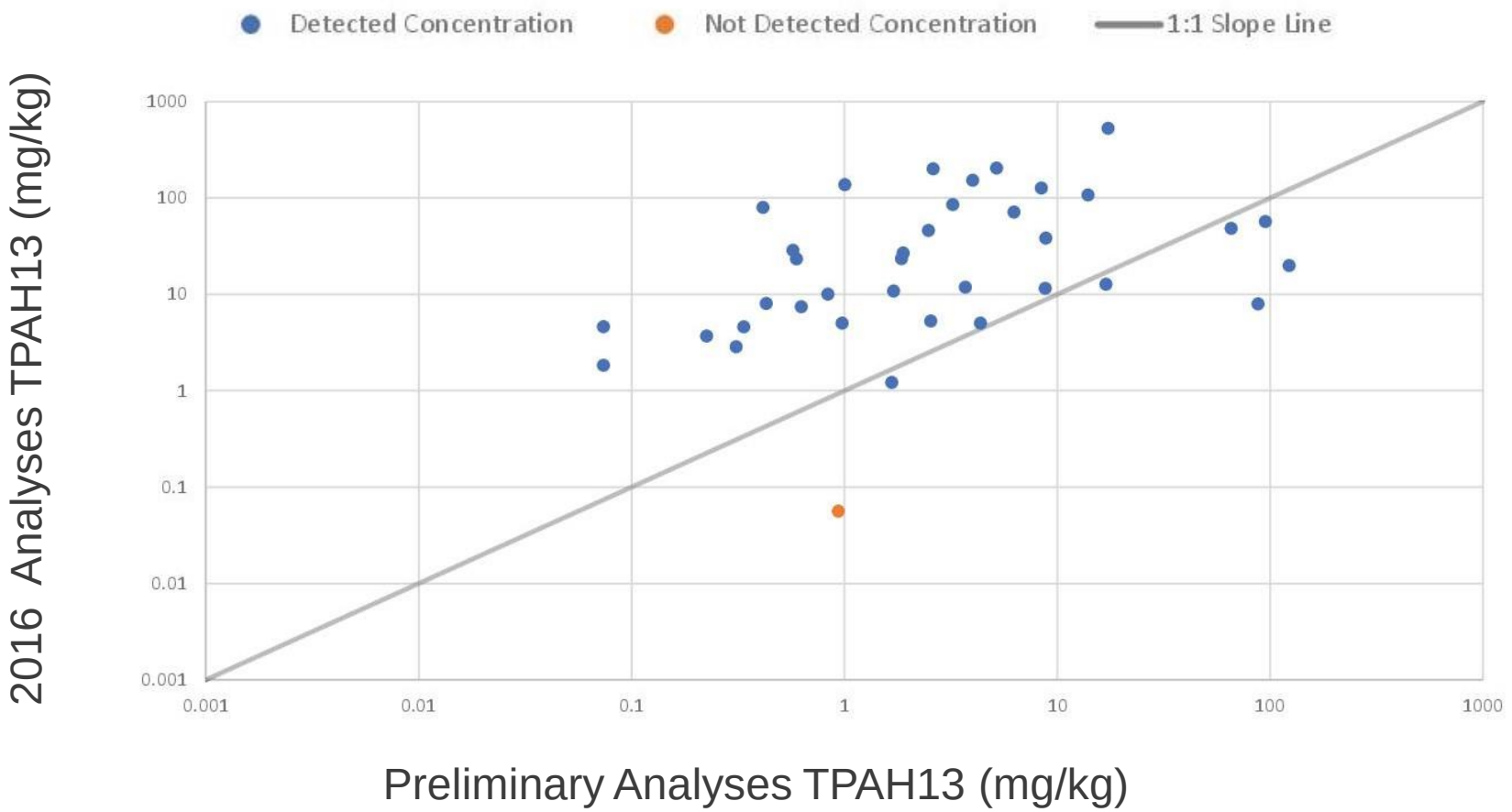
	Preliminary 2023 Analyses	**Investigative 2023 Analyses**
Extraction Method	Reduced extraction efficiency for high moisture sediment samples	No decrease in extraction efficiency with high moisture samples
Surrogate Recovery	Used biphenyl and terphenyls Many surrogate recoveries < 50% Average surrogate recovery 45%	Used carbon-13 labeled PAHs All surrogate recoveries 50-130% Average surrogate recovery 82%
Dilution	Extracted 30 g of sample regardless of concentration. Most samples diluted for analysis, which can reduce accuracy/precision of final sample result	Reduced mass of high concentrations sample extracted to limit need for dilution
Detection Limits (DL)	Consistently higher DL due to sample dilution	

Both datasets considered usable per the data validation review

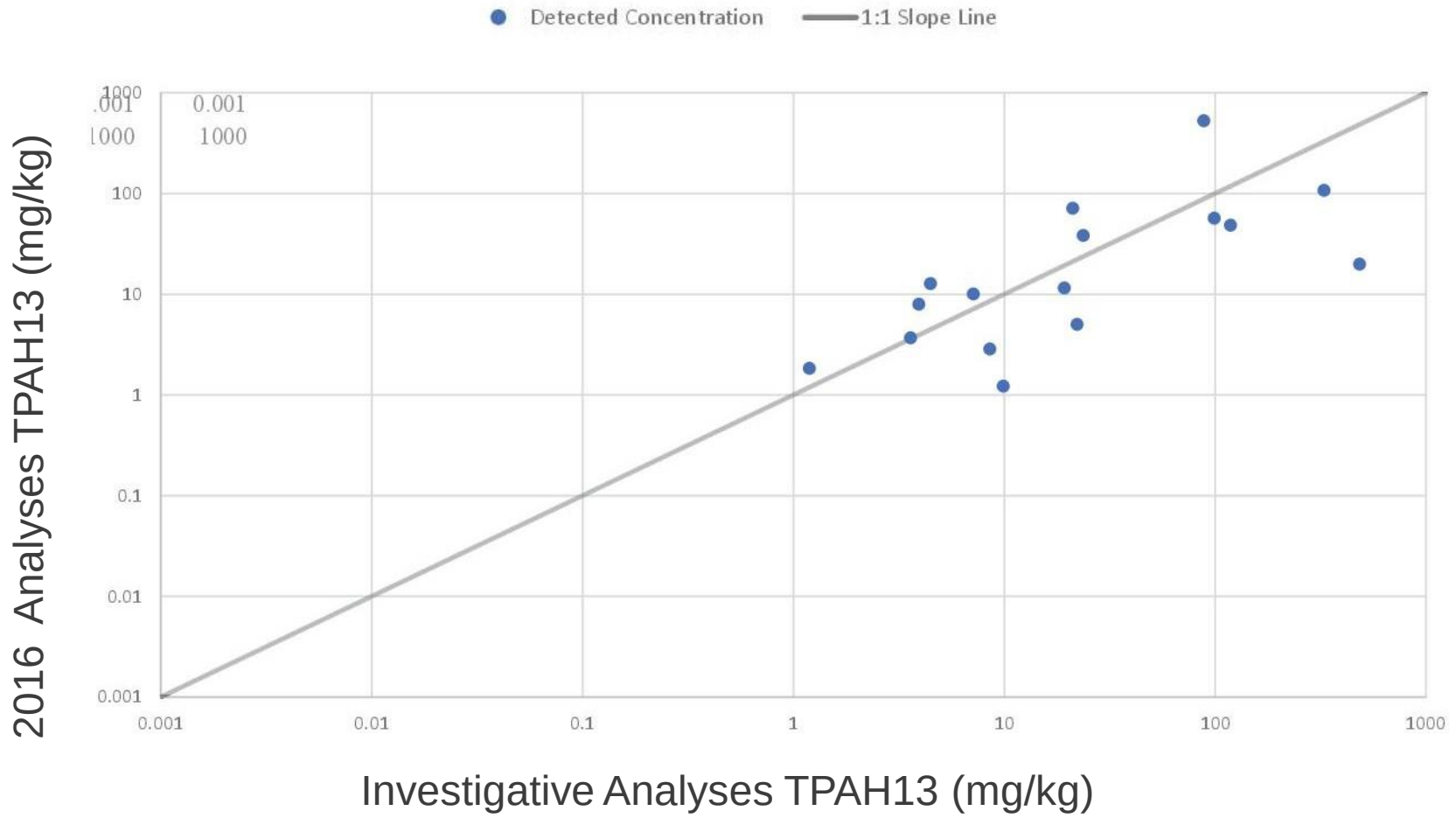
Methods used for Investigative Analyses Similar to 2016 Methods

	Preliminary 2023 Analyses	Investigative 2023 Analyses	2016 Analyses
Extraction Method	Microwave extraction. Reduced extraction efficiency with high moisture samples	Shaker table solvent extraction. No decrease in extraction efficiency with high moisture samples	Microscale solvent extraction
Run Time	13 min	75 min	27 min
Surrogate Recovery	Average surrogate recovery 45%	Average surrogate recovery 82%	Average surrogate recovery 106%
Dilutions	Extracted 30 g of sample regardless of concentration. Most samples diluted for analysis, which can reduce accuracy/precision	Reduced mass of high concentrations sample extracted to limit need for dilution	Extracted 5 g. Most samples analyzed at 1:1 dilution

Comparison of Co-located Samples Indicates that Results from 2023 Preliminary Analyses are Biased Low in Comparison to Results from 2016 Analyses

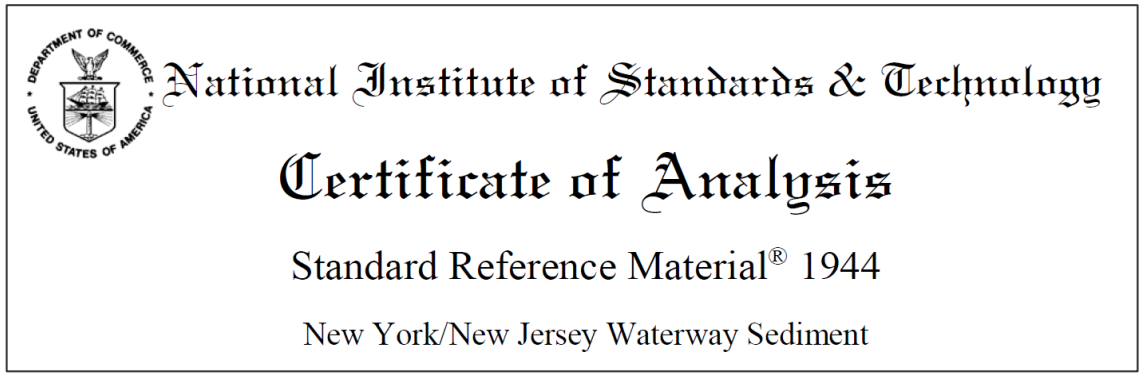


Comparison of Co-located Samples Indicates that Results from 2023 Investigative Analyses are Not Biased in Comparison to Results from 2016 Analyses



Recommendations

Recommendations


National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1944

New York/New Jersey Waterway Sediment

- Include Standard Reference Material in all analysis programs
- Have a chemist examine analytical results early in the program
- Consider possible analytical issues related to the use of multiple lab/methods over time
- Use consistent analytical methods throughout the Remedial Investigation

Thank You!