

Source Apportionment, Identification and Control: Improved Remedial Outcomes Through Forensic Evaluation

RemTech 2023
October 12, 2023



Heather Lord, Ph.D.

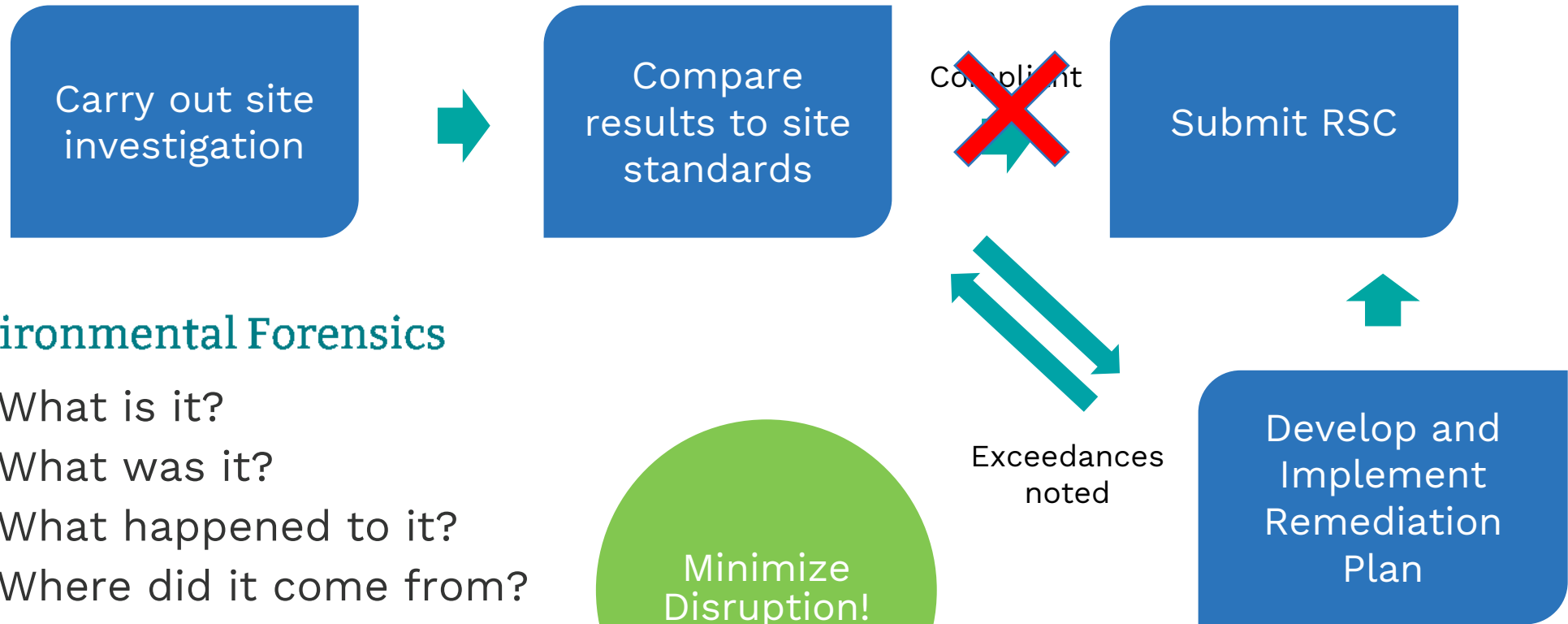
Senior Associate Forensic Chemist

David Thal, CQA, CEAC, CFS

Principal Chemist



Example Phase II ESA Process



Environmental Forensics

- What is it?
- What was it?
- What happened to it?
- Where did it come from?
- How did it get there?
- When was it released?
- Whose is/was it?
- How much of it is from each source?

Forensic Investigations

Strategy

- Define the question, identify risk, specify quality objectives

Tier 1 Evaluation

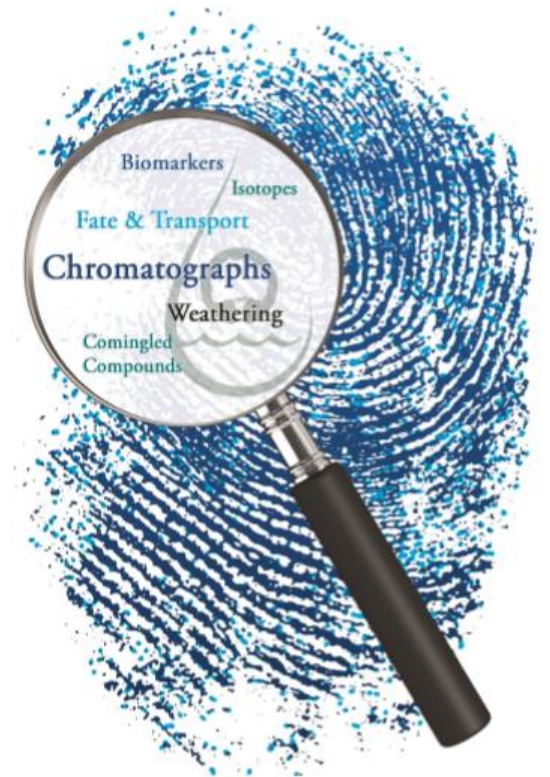
- Identify available data
- Initial forensic data review

Tier 2 Evaluation

- Identify gaps, risk reduction opportunities
- Targeted forensic investigation

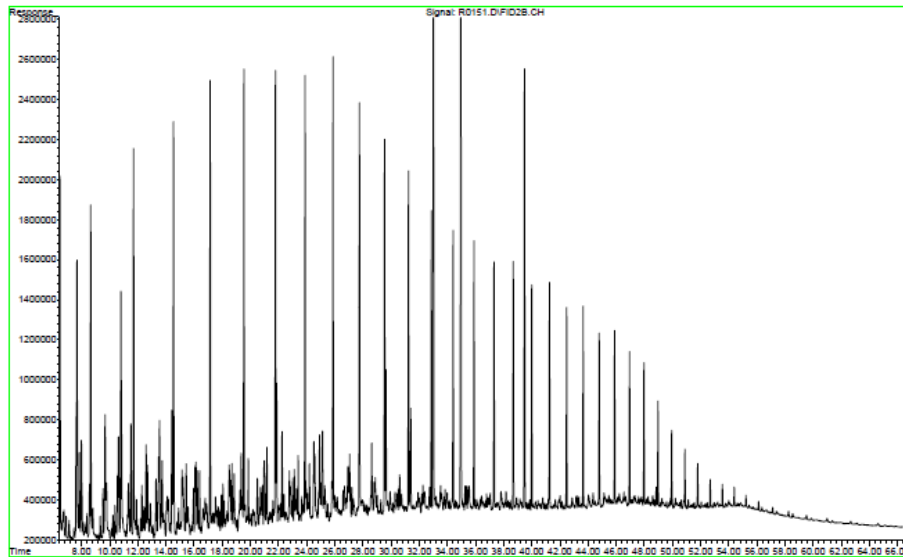
Communication

- Make the case: data presentation, justification, clarification, simplification



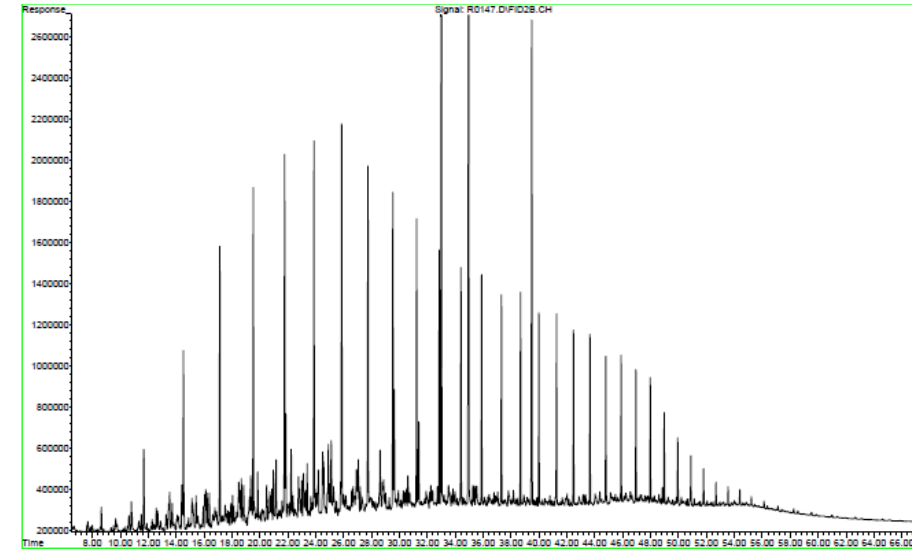
General Fingerprint – Crude Oil Tarballs

Source Sample



Left side – water soluble components

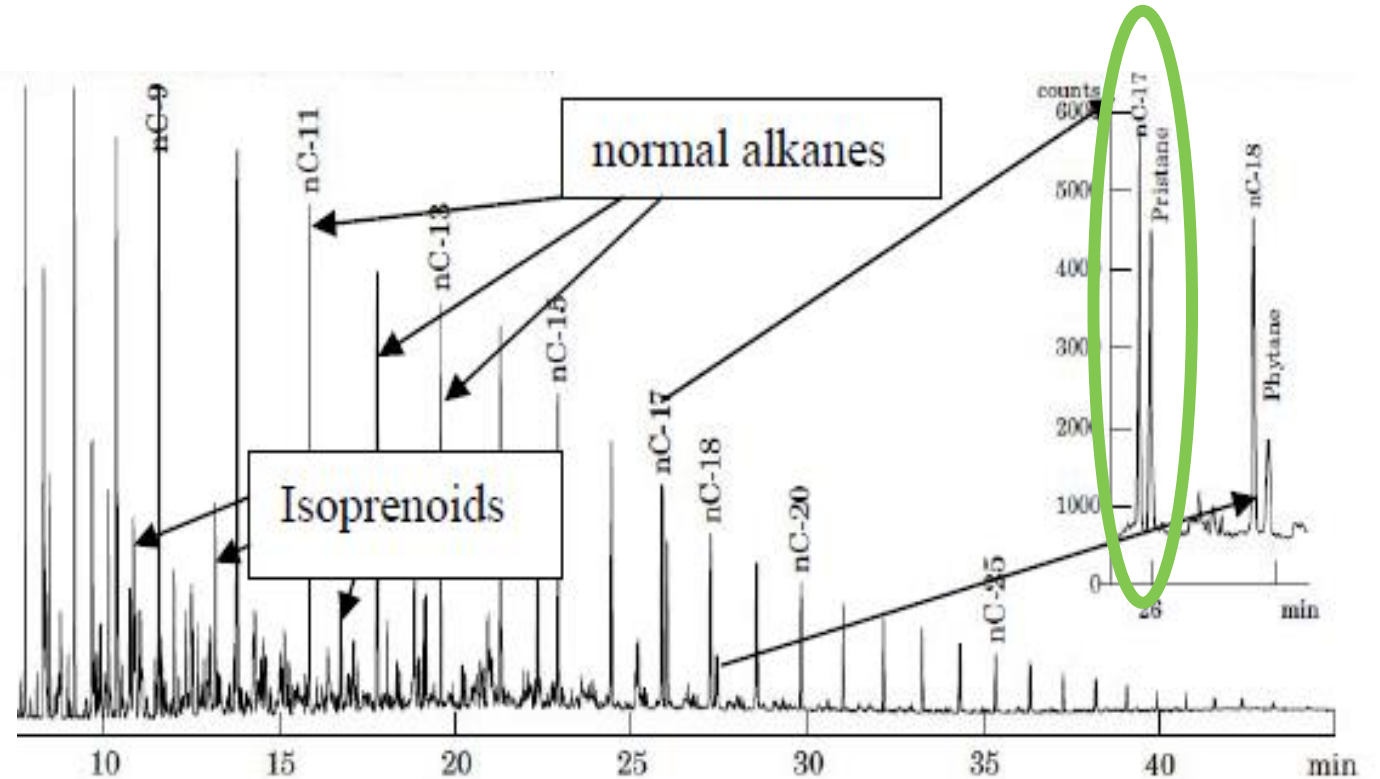
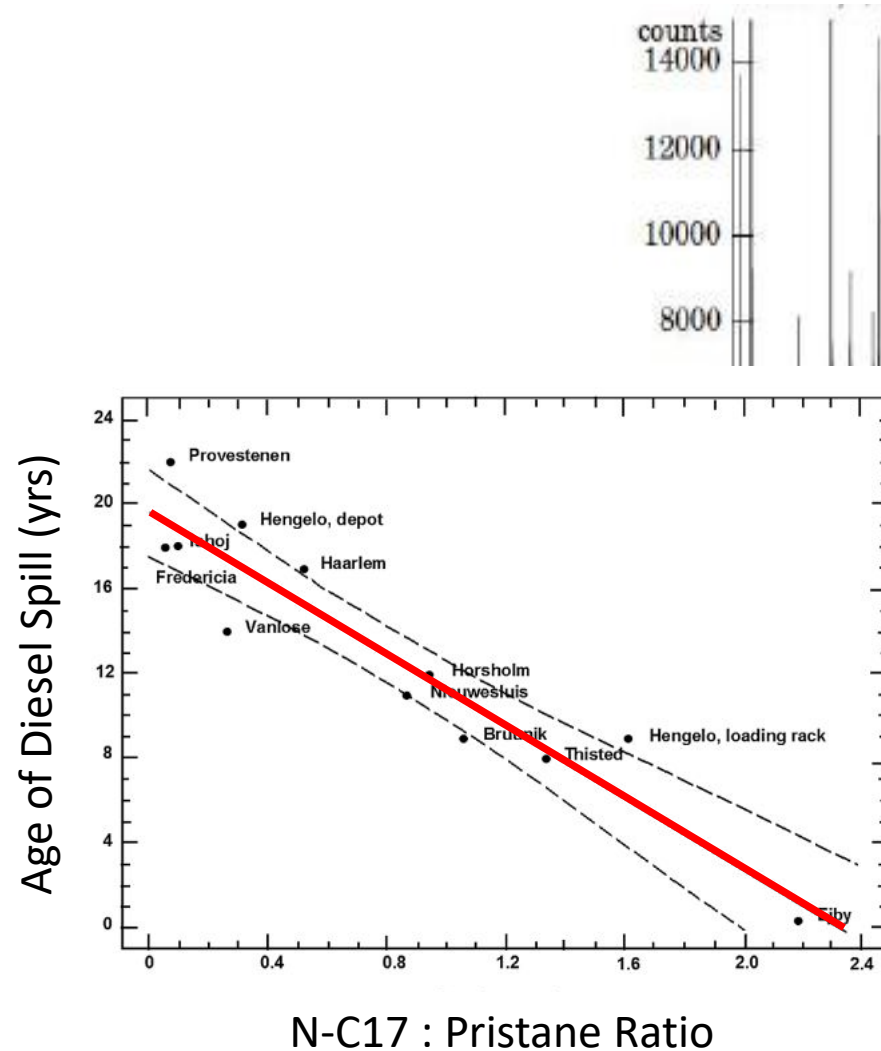
Cross-River Sample



Right side – unaffected by water



Weathering – Is it a New Release?



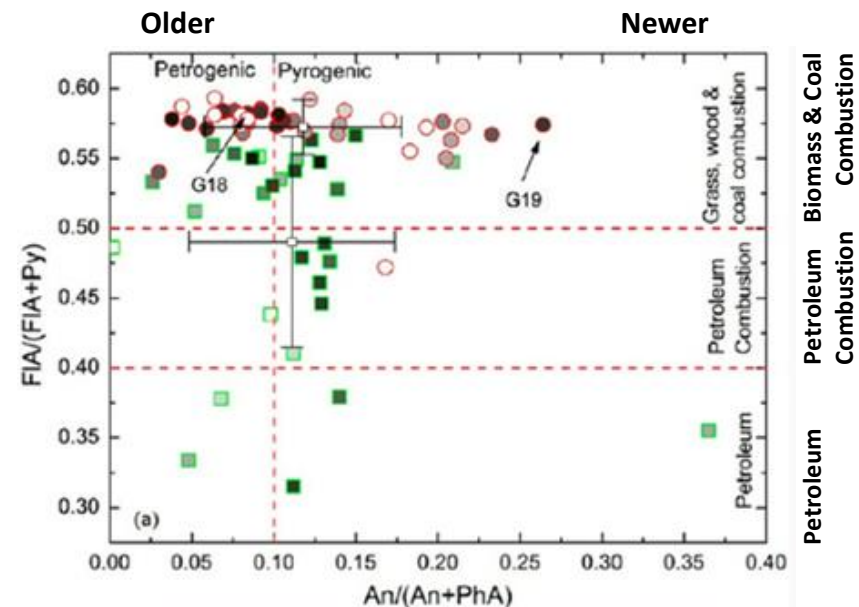
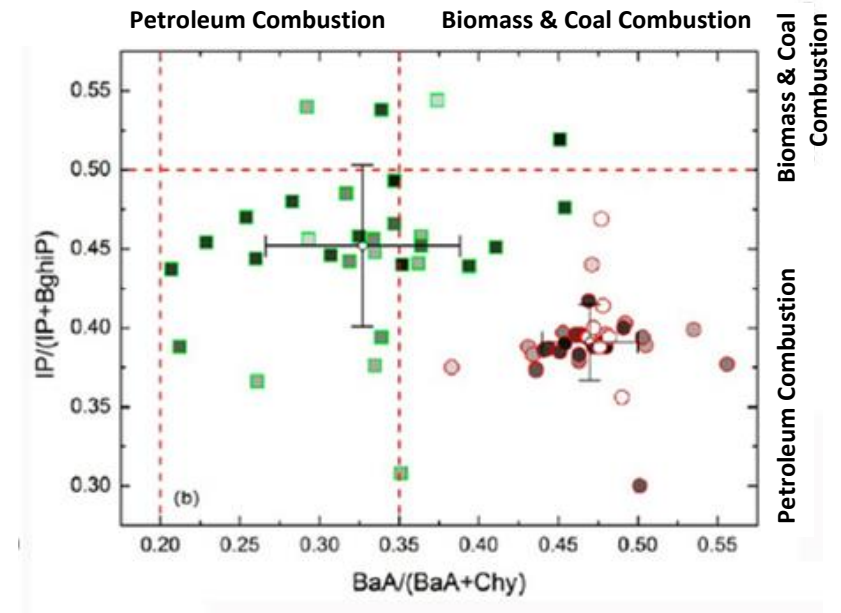
Christensen and Larsen, 1993

$$T(\text{year}) = -8.4(n\text{-C}17/\text{pr}) + 19.8$$

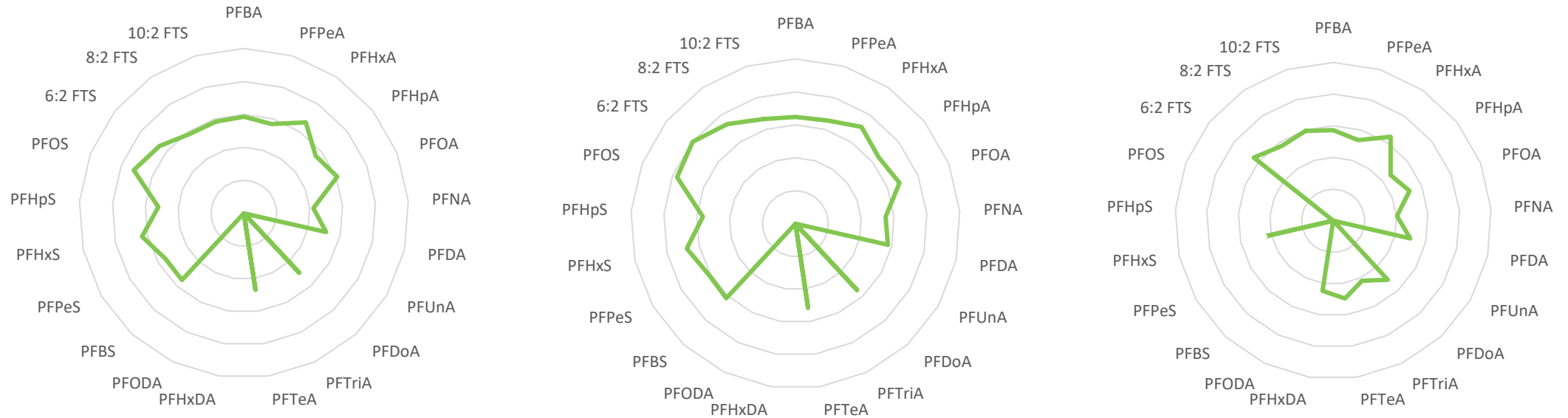
Numerous caveats to the use of this ratio have been identified.

Alkane, Isoprenoid and PAH/alkyl PAH Ratio Analyses

- Numerous other approaches proposed over the years.
- Some are specific to individual petroleum products.
- Some have proven more robust than others.
- Care is needed in selecting and justifying the most beneficial ratio analysis for your site.



PFAS Fingerprinting



- Radar Plots (Excel) offer an approach to easily visualize differences/similarities in PFAS distributions among potentially related samples
 - PFAS detected plotted clockwise: carboxylates – sulfonates - FTS
 - Rings indicate analyte concentrations (log scale)
 - When plotted on the same scale, enclosed areas roughly correlate to Σ PFAS

Tier II Evaluation

- What Risks Remain?
- What Information is Needed to Reduce Risk/Uncertainty?

Options:

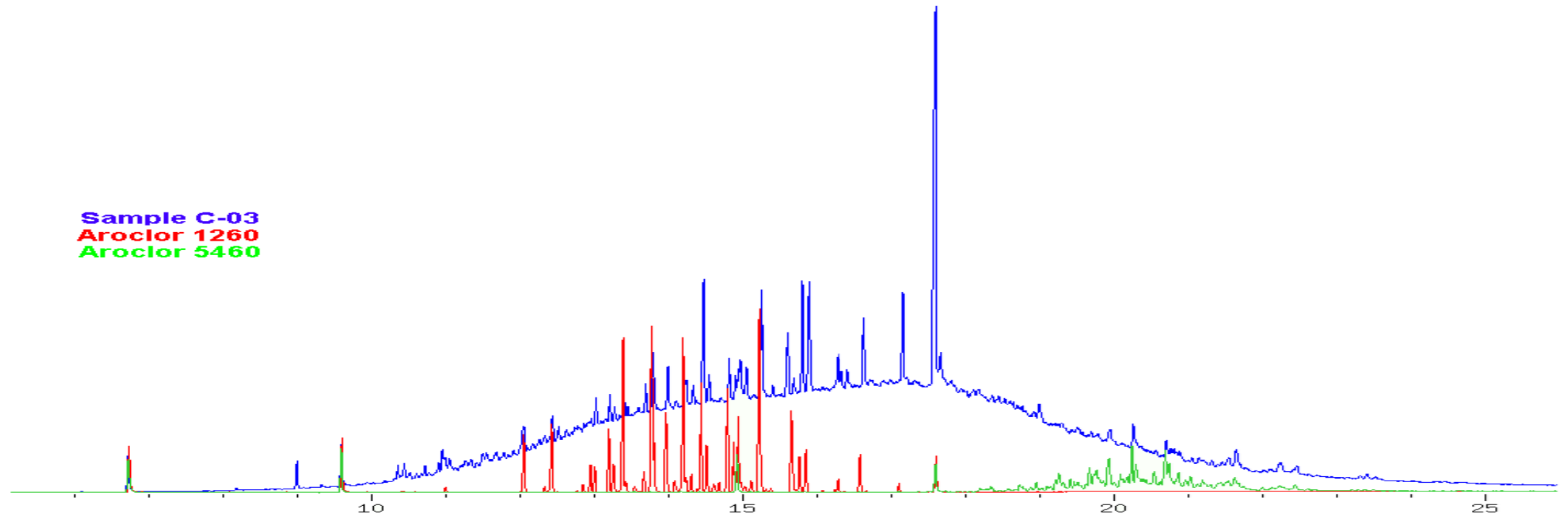
- Petroleum Biomarkers, alkylated PAHs, PIANO (light distillates), PCB congener, non-targeted analysis, CSIA (Compound-Specific Isotope Analysis).
- GC/FID (extended run), GC/HRMS, GC/MS, GC/MS/MS, LC/HRMS.
- Other parameters ... metals, sulphur, organic Pb, Mn, etc.



PCB Sample Assessment – Aroclors Contribution

Sample C-03 demonstrates compositions typical of samples containing PCBs, PCTs and PCNs

- PCTs/PCNs were successfully argued as a basis for cost allocation



Linear Mixing Models Using up to 209 Congeners

		Sample Conc.	Sample	Sum of Squares	Aroclor Calibration Standards												
		ng/mL		5.0826E-06	Aroclor 1016		Aroclor 1221		Aroclor 1232		Aroclor 1242		Aroclor 1248		Aroclor 1254		
Results					ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	
Aroclor 1016	24%	PCB 1	47		33,400	0.4023	18,800	0.2053	582	0.0059	141	0.0014	6	0.0001			
Aroclor 1221	0%	PCB 2	1		3,050	0.0367	1,740	0.0190	28	0.0003	8	0.0001	0				
Aroclor 1232	0%	PCB 3	1		14,200	0.1710	8,050	0.0879	143	0.0015	43	0.0004	4	0.0000			
Aroclor 1242	52%	PCB 4	2,400		5,320	0.0641	4,820	0.0526	3,000	0.0307	538	0.0055	0				
Aroclor 1248	0%	PCB 5	12		724	0.0087	547	0.0060	151	0.0015	37	0.0004	0				
Aroclor 1254	24%	PCB 6	1,080		3,140	0.0378	2,630	0.0287	1,340	0.0137	216	0.0022	0				
Aroclor 1260	0%	PCB 7	22		1,490	0.0179	1,070	0.0117	279	0.0029	60	0.0006	0				
Aroclor 1262	0%	PCB 8	5,000		10,100	0.1217	9,370	0.1023	6,210	0.0635	1,200	0.0123	16	0.0002			
Aroclor 1268	0%	PCB 9	42		1,530	0.0184	1,190	0.0130	539	0.0055	102	0.0010	0				
		PCB 10	1		524	0.0063	396	0.0043	146	0.0015	44	0.0004	0				
Total	100%	PCB 11			99	0.0012	78	0.0009	0		0		0				
		PCB 12	22		1,590	0.0192	1,100	0.0120	276	0.0028	66	0.0007	0				
		PCB 13			0		0		0		0		0				
		PCB 14			8	0.0001	15	0.0002	0		0		0				
		PCB 15	1,260		2,900	0.0349	2,470	0.0270	1,560	0.0159	335	0.0034	7	0.0001			
		PCB 16	2,630		261	0.0031	1,600	0.0175	3,250	0.0332	1,350	0.0138	49	0.0005			
		PCB 17	2,520		273	0.0033	1,530	0.0167	3,120	0.0319	1,250	0.0128	34	0.0003			
		PCB 18	5,200		400	0.0048	3,230	0.0353	6,430	0.0657	3,760	0.0384	127	0.0013			
		PCB 19	63		70	0.0008	393	0.0043	775	0.0079	264	0.0027	0				
		PCB 20	5,500		501	0.0060	3,310	0.0362	6,760	0.0691	3,760	0.0384	122	0.0012			
		PCB 21	3,763	0.0392	0.0393	5,690	0.0614	372	0.0045	2,310	0.0252	4,640	0.0474	2,340	0.0239	69	0.0007
		PCB 22	2,116	0.0220	0.0221	3,270	0.0353	202	0.0024	1,350	0.0147	2,580	0.0264	1,450	0.0148	44	0.0004
		PCB 23	12	0.0001	0.0001	16	0.0002	0		6	0.0001	16	0.0002	0			
		PCB 24	87	0.0009	0.0009	141	0.0015	22	0.0003	62	0.0007	105	0.0011	20	0.0002	0	
		PCB 25	428	0.0045	0.0045	660	0.0071	86	0.0010	300	0.0033	523	0.0053	163	0.0017	7	0.0001
		PCB 26	1,027	0.0107	0.0107	1,550	0.0167	139	0.0017	663	0.0072	1,270	0.0130	490	0.0050	12	0.0001
		PCB 27	356	0.0037	0.0037	515	0.0056	43	0.0005	233	0.0025	451	0.0046	160	0.0016	0	
		PCB 28	0	0.0000	0.0000	0		0		0		0		0		0	
		PCB 29	0	0.0000	0.0000	0		0		0		0		0		0	
		PCB 30	0	0.0000	0.0000	0		0		0		0		0		0	
		PCB 31	5,421	0.0565	0.0566	8,170	0.0881	391	0.0047	3,240	0.0354	6,650	0.0680	4,850	0.0495	207	0.0021
		PCB 32	1,439	0.0150	0.0150	2,160	0.0233	127	0.0015	901	0.0098	1,780	0.0182	936	0.0096	28	0.0003

Results	
Aroclor 1016	24%
Aroclor 1221	0%
Aroclor 1232	0%
Aroclor 1242	52%
Aroclor 1248	0%
Aroclor 1254	24%
Aroclor 1260	0%
Aroclor 1262	0%
Aroclor 1268	0%
Total	100%

Results	
Aroclor 1016	24%
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Aroclor 1262	0%
Aroclor 1268	0%
Total	100%

Linear Mixing Models Using up to 209 Congeners

			Sample Conc.	Sample	Sum of Squares	Aroclor Calibration Standards												
Results			ng/mL	mass fraction	sum of fractions	Aroclor 1016		Aroclor 1221		Aroclor 1232		Aroclor 1242		Aroclor 1248		Aroclor 1254		
						ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	
Aroclor 1016	24%	PCB 1	473	0.0049	5.0826E-06	760	0.0072	22,400	0.4023	18,800	0.2053	582	0.0059	141	0.0014	6	0.0001	
Aroclor 1221	0%	PCB 2	23	0.0002					0.0367	1,740	0.0190	28	0.0003	8	0.0001	0		
Aroclor 1232	0%	PCB 3	118	0.0012					0.1710	8,050	0.0879	143	0.0015	43	0.0004	4	0.0000	
Aroclor 1242	52%	PCB 4	2,417	0.0252					0.0641	4,820	0.0526	3,000	0.0307	538	0.0055	0		
Aroclor 1248	0%	PCB 5	123	0.0013					0.0087	547	0.0060	151	0.0015	37	0.0004	0		
Aroclor 1254	24%	PCB 6	1,086	0.0113					0.0378	2,630	0.0287	1,340	0.0137	216	0.0022	0		
Aroclor 1260	0%	PCB 7	224	0.0023					0.0179	1,070	0.0117	279	0.0029	60	0.0006	0		
Aroclor 1262	0%	PCB 8	5,053	0.0526					0.1217	9,370	0.1023	6,210	0.0635	1,200	0.0123	16	0.0002	
Aroclor 1268	0%	PCB 9	425	0.0044					0.0184	1,190	0.0130	539	0.0055	102	0.0010	0		
		PCB 10	118	0.0012					0.0063	396	0.0043	146	0.0015	44	0.0004	0		
Total	100%	PCB 11	6	0.0001					0.0012	78	0.0009	0		0		0		
		PCB 12	227	0.0024					0.0192	1,100	0.0120	276	0.0028	66	0.0007	0		
		PCB 13	0	0.0000						0		0		0		0		
		PCB 14	1	0.0000					0.0001	15	0.0002	0		0		0		
		PCB 15	1,263	0.0132					0.0349	2,470	0.0270	1,560	0.0159	335	0.0034	7	0.0001	
		PCB 16	2,635	0.0274					0.0031	1,600	0.0175	3,250	0.0332	1,350	0.0138	49	0.0005	
		PCB 17	2,524	0.0263					0.0033	1,530	0.0167	3,120	0.0319	1,250	0.0128	34	0.0003	
		PCB 18	5,216	0.0543					0.0048	3,230	0.0353	6,430	0.0657	3,760	0.0384	127	0.0013	
		PCB 19	630	0.0066					0.0008	393	0.0043	775	0.0079	264	0.0027	0		
		PCB 20	5,508	0.0574					0.0060	3,310	0.0362	6,760	0.0691	3,760	0.0384	122	0.0012	
		PCB 21	3,763	0.0392					0.0045	2,310	0.0252	4,640	0.0474	2,340	0.0239	69	0.0007	
		PCB 22	2,116	0.0220					0.0024	1,350	0.0147	2,580	0.0264	1,450	0.0148	44	0.0004	
		PCB 23	12	0.0001						6	0.0001	16	0.0002	0		0		
		PCB 24	87	0.0009					0.0003	62	0.0007	105	0.0011	20	0.0002	0		
		PCB 25	428	0.0045		0.0045	660	0.0071	86	0.0010	300	0.0033	523	0.0053	163	0.0017	7	0.0001
		PCB 26	1,027	0.0107		0.0107	1,550	0.0167	139	0.0017	663	0.0072	1,270	0.0130	490	0.0050	12	0.0001
		PCB 27	356	0.0037		0.0037	515	0.0056	43	0.0005	233	0.0025	451	0.0046	160	0.0016	0	
		PCB 28	0	0.0000		0.0000	0		0		0		0		0		0	
		PCB 29	0	0.0000		0.0000	0		0		0		0		0		0	
		PCB 30	0	0.0000		0.0000	0		0		0		0		0		0	
		PCB 31	5,421	0.0565		0.0566	8,170	0.0881	391	0.0047	3,240	0.0354	6,650	0.0680	4,850	0.0495	207	0.0021
		PCB 32	1,439	0.0150		0.0150	2,160	0.0233	127	0.0015	901	0.0098	1,780	0.0182	936	0.0096	28	0.0003

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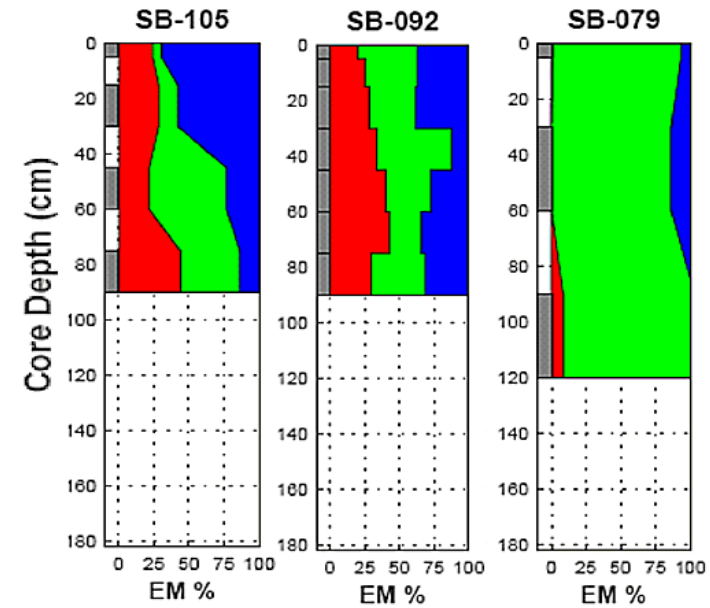
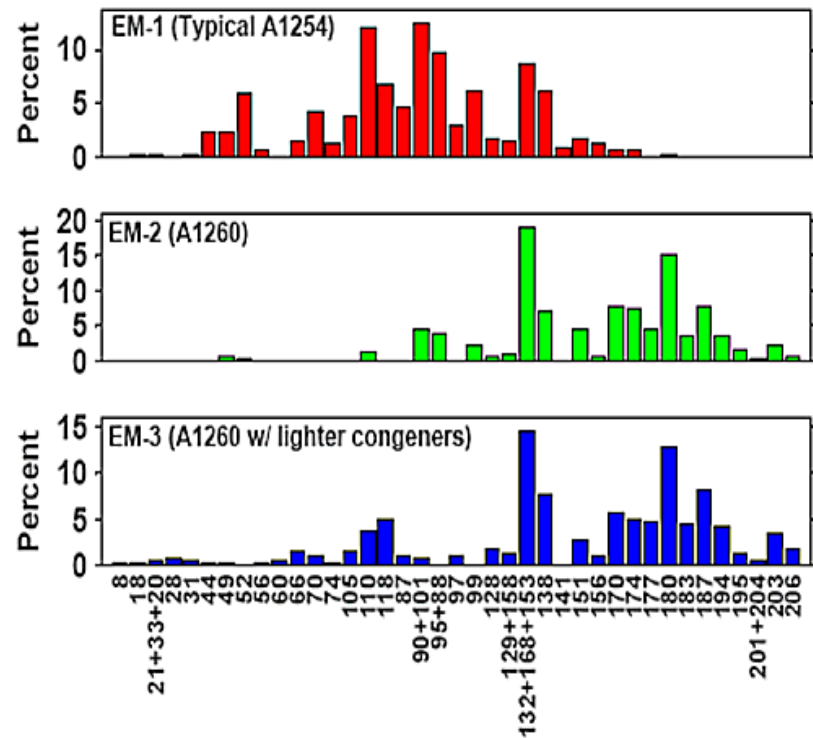
Aroclor 1016				Aroclor 1221				Sum of Squares	Aroclor Calibration Standards											
ng/mL	mass frac	ng/mL	mass frac					5.0826E-06	Aroclor 1016		Aroclor 1221		Aroclor 1232		Aroclor 1242		Aroclor 1248		Aroclor 1254	
ng/mL	mass frac	ng/mL	mass frac					sum of fractions	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac
							0.0030	720	0.0078	33,400	0.4023	18,800	0.2053	582	0.0059	141	0.0014	6	0.0001	
720	0.0078	33,400	0.4023				0.0003	37	0.0004	3,050	0.0367	1,740	0.0190	28	0.0003	8	0.0001	0		
37	0.0004	3,050	0.0367				0.0013	184	0.0020	14,200	0.1710	8,050	0.0879	143	0.0015	43	0.0004	4	0.0000	
184	0.0020	14,200	0.1710				0.0252	3,650	0.0394	5,320	0.0641	4,820	0.0526	3,000	0.0307	538	0.0055	0		
3,650	0.0394	5,320	0.0641				0.0013	192	0.0021	724	0.0087	547	0.0060	151	0.0015	37	0.0004	0		
192	0.0021	724	0.0087				0.0113	1,660	0.0179	3,140	0.0378	2,630	0.0287	1,340	0.0137	216	0.0022	0		
1,660	0.0179	3,140	0.0378				0.0023	335	0.0036	1,490	0.0179	1,070	0.0117	279	0.0029	60	0.0006	0		
335	0.0036	1,490	0.0179				0.0528	7,780	0.0839	10,100	0.1217	9,370	0.1023	6,210	0.0635	1,200	0.0123	16	0.0002	
7,780	0.0839	10,100	0.1217				0.0044	614	0.0066	1,530	0.0184	1,190	0.0130	539	0.0055	102	0.0010	0		
614	0.0066	1,530	0.0184				0.0012	179	0.0019	524	0.0063	396	0.0043	146	0.0015	44	0.0004	0		
179	0.0019	524	0.0063				0.0001	28	0.0003	99	0.0012	78	0.0009	0		0		0		
357	0.0039	1,590	0.0192				0.0024	357	0.0039	1,590	0.0192	1,100	0.0120	276	0.0028	66	0.0007	0		
							0.0000	0		0		0		0		0		0		
							0.0000	7	0.0001	8	0.0001	15	0.0002	0		0		0		
							0.0132	1,920	0.0207	2,900	0.0349	2,470	0.0270	1,560	0.0159	335	0.0034	7	0.0001	
							0.0275	3,980	0.0429	261	0.0031	1,600	0.0175	3,250	0.0332	1,350	0.0138	49	0.0005	
							0.0264	3,810	0.0411	273	0.0033	1,530	0.0167	3,120	0.0319	1,250	0.0128	34	0.0003	
							0.0545	7,860	0.0848	400	0.0048	3,230	0.0353	6,430	0.0657	3,760	0.0384	127	0.0013	
							0.0066	970	0.0105	70	0.0008	393	0.0043	775	0.0079	264	0.0027	0		
							0.0576	8,390	0.0905	501	0.0060	3,310	0.0362	6,760	0.0691	3,760	0.0384	122	0.0012	
							0.0393	5,690	0.0614	372	0.0045	2,310	0.0252	4,640	0.0474	2,340	0.0239	69	0.0007	
							0.0221	3,270	0.0353	202	0.0024	1,350	0.0147	2,580	0.0264	1,450	0.0148	44	0.0004	
							0.0001	16	0.0002	0		6	0.0001	16	0.0002	0		0		
							0.0009	141	0.0015	22	0.0003	62	0.0007	105	0.0011	20	0.0002	0		
							0.0045	660	0.0071	86	0.0010	300	0.0033	523	0.0053	163	0.0017	7	0.0001	
							0.0107	1,550	0.0167	139	0.0017	663	0.0072	1,270	0.0130	490	0.0050	12	0.0001	
							0.0037	515	0.0056	43	0.0005	233	0.0025	451	0.0046	160	0.0016	0		
							0.0000	0		0		0		0		0		0		
							0.0000	0		0		0		0		0		0		
							0.0000	0		0		0		0		0		0		
							0.0566	8,170	0.0881	391	0.0047	3,240	0.0354	6,650	0.0680	4,850	0.0495	207	0.0021	
							0.0150	2,160	0.0233	127	0.0015	901	0.0098	1,780	0.0182	936	0.0096	28	0.0003	

Linear Mixing Models Using up to 209 Congeners

Results			Sample Conc.	Sample	Sum of Squares	Aroclor Calibration Standards											
Results			ng/mL	mass fraction	sum of fractions	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac	ng/mL	mass frac		
Aroclor 1016	24%	PCB 1	473	0.0049	0.0050	720	0.2053	582	0.0059	141	0.0014	6	0.0001				
Aroclor 1221	0%		23	0.0002	0.0003	37	0.0190	28	0.0003	8	0.0001	0					
Aroclor 1232	0%		118	0.0012	0.0013	134	0.0879	143	0.0015	43	0.0004	4	0.0000				
Aroclor 1242	52%		2,417	0.0252	0.0252	3,650	0.0526	3,000	0.0307	538	0.0055	0					
Aroclor 1248	0%		123	0.0013	0.0013	192	0.0060	151	0.0015	37	0.0004	0					
Aroclor 1254	24%		1,088	0.0113	0.0113	1,660	0.0287	1,340	0.0137	216	0.0022	0					
Aroclor 1260	0%		224	0.0023	0.0023	335	0.0117	279	0.0029	60	0.0006	0					
Aroclor 1262	0%		5,053	0.0526	0.0528	7,780	0.1023	6,210	0.0635	1,200	0.0123	16	0.0002				
Aroclor 1268	0%		423	0.0044	0.0044	614	0.0130	539	0.0055	102	0.0010	0					
Total	100%		118	0.0012	0.0012	179	0.0043	146	0.0015	44	0.0004	0					
			6	0.0001	0.0001	28	0.0009	0	0	0	0	0					
			227	0.0024	0.0024	357	0.0120	276	0.0028	66	0.0007	0					
			0	0.0000	0.0000	0	0	0	0	0	0	0					
			1	0.0000	0.0000	7	0.0002	0	0	0	0	0					
			1,263	0.0132	0.0132	1,920	0.0270	1,560	0.0159	335	0.0034	7	0.0001				
			2,635	0.0274	0.0275	3,980	0.0175	3,250	0.0332	1,350	0.0138	49	0.0005				
			2,524	0.0263	0.0264	3,810	0.0167	3,120	0.0319	1,250	0.0128	34	0.0003				
			5,216	0.0543	0.0545	7,860	0.0353	6,430	0.0657	3,760	0.0384	127	0.0013				
			630	0.0066	0.0066	970	0.0043	775	0.0079	264	0.0027	0					
			5,508	0.0574	0.0576	8,390	0.0362	6,760	0.0691	3,760	0.0384	122	0.0012				
			3,763	0.0392	0.0393	5,690	0.0252	4,640	0.0474	2,340	0.0239	69	0.0007				
			2,116	0.0220	0.0221	3,270	0.0147	2,580	0.0264	1,450	0.0148	44	0.0004				
			12	0.0001	0.0001	16	0.0001	16	0.0002	0	0	0					
			87	0.0009	0.0009	141	0.0007	105	0.0011	20	0.0002	0					
			428	0.0045	0.0045	660	0.0033	523	0.0053	163	0.0017	7	0.0001				
			1,027	0.0107	0.0107	1,550	0.0072	1,270	0.0130	490	0.0050	12	0.0001				
			356	0.0037	0.0037	515	0.0025	451	0.0046	160	0.0016	0					
			0	0.0000	0.0000	0	0.0056	0	0.0005	233	0.0025	0					
			0	0.0000	0.0000	0	0	0	0	0	0	0					
			0	0.0000	0.0000	0	0	0	0	0	0	0					
			0	0.0000	0.0000	0	0	0	0	0	0	0					
			5,421	0.0565	0.0566	8,170	0.0881	391	0.0047	3,240	0.0354	6,650	0.0680	4,850	0.0495	207	0.0021
			1,439	0.0150	0.0150	2,160	0.0233	127	0.0015	901	0.0098	1,780	0.0182	936	0.0096	28	0.0003

Forensic Evaluations and Fingerprinting

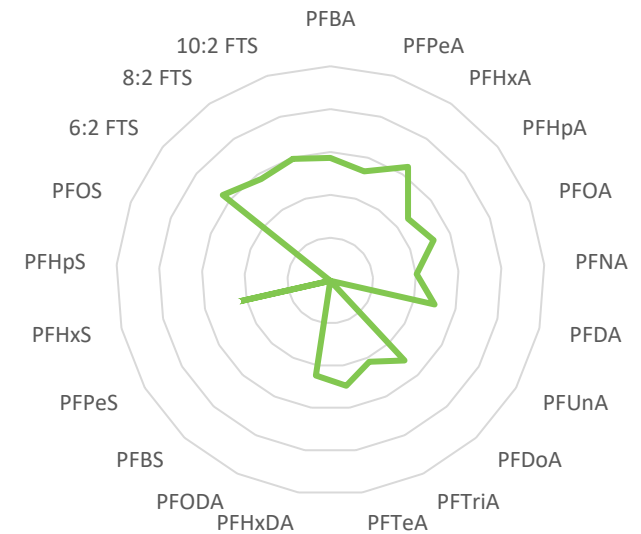
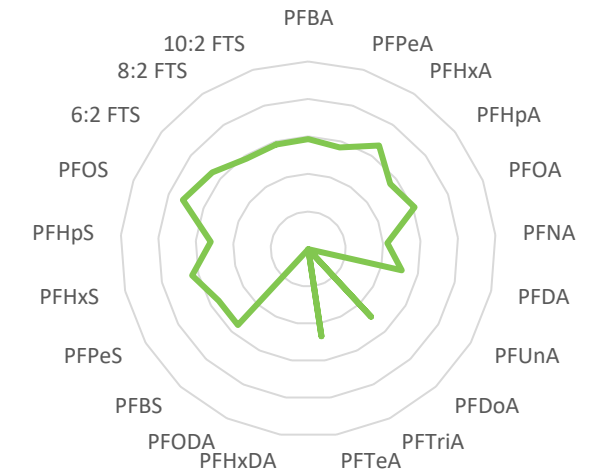
Identify and run likely sample constituents.
Condition the data set.
Solve model for constituent proportions.



Tier II PFAS Investigation Part A

- Total Oxidizable Precursors Assay (TOP)
 - Green: Pre-Oxidation
 - Blue: Post Oxidation
- Summation of Total Detected Fluorine

Sample	Total F Pre (mmol/L)	Total F Post (mmol/L)	Fold Increase
Top	1.0	104	100x
Bottom	0.3	100	380x



Tier II PFAS Investigation Part B

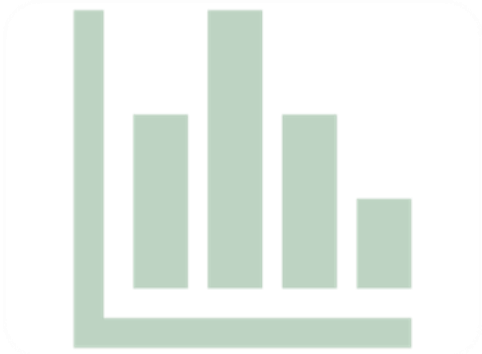
Non-Targeted Analysis

- 38 Compounds either positively identified or determined not detected
- 71% (27 compounds) had similarity between Samples 1 and 2, and differences in Sample 3

Sample 1	Sample 2	Sample 3	CAS#
N	N	Y	171184-02-4
N	N	Y	1287702-47-9
N	N	Y	1980039-46-0
N	N	Y	129498-18-6
N	N	Y	86803-38-5
N	N	Y	67939-36-0
N	N	Y	68227-97-4
N	N	Y	1376331-61-1
N	N	Y	82137-36-8
N	N	Y	159414-98-9
Y	Y	Y	86060-96-0
Y	Y	Y	1207756-42-0
Y	Y	Y	1383438-88-7
Y	Y	Y	1513863-95-0
Y	Y	Y	862134-26-7
N	N	Y	677324-20-8
Y	Y	N	70900-38-8
Y	Y	N	106790-26-5
Y	Y	N	1513864-12-4
N	N	Y	NOCAS_1009316
N	N	Y	68298-76-0
N	N	Y	80242-51-9
N	N	Y	61660-12-6
Y	Y	Y	677324-21-9
N	N	Y	68298-74-8
Y	Y	Y	677324-22-0
Y	Y	Y	15953-40-9
Y	Y	Y	462996-01-6
N	N	Y	68298-72-6
N	N	Y	1075687-38-5
N	N	Y	192326-53-7
N	N	Y	27619-97-2
Y	Y	N	123708-11-2
Y	Y	Y	62880-95-9
Y	Y	N	102040-62-0
Y	Y	N	54207-61-3
Y	Y	N	93345-48-3



Tier I and Tier II Evaluations - Summary



Type and Quantity of Data

- Available Data: historic, hydrologic, geologic, chemical, isotopic, etc.
- Identify Tier I Analytical Approach
 - Identify gaps, risk reduction opportunities
- Specify Tier II Data Requirements – benefits and tradeoffs



Data Analysis

- Completeness check, data validation, data conditioning and framing.
- Develop Multiple Lines of Evidence:
 - Does site hydrogeology fit with analytical data?
 - Do multiple chemical measurements converge or not?

Information = Reduction of Data Uncertainty



Communication

Solid Communication of Investigation Outcome is Critical for Decision-Making

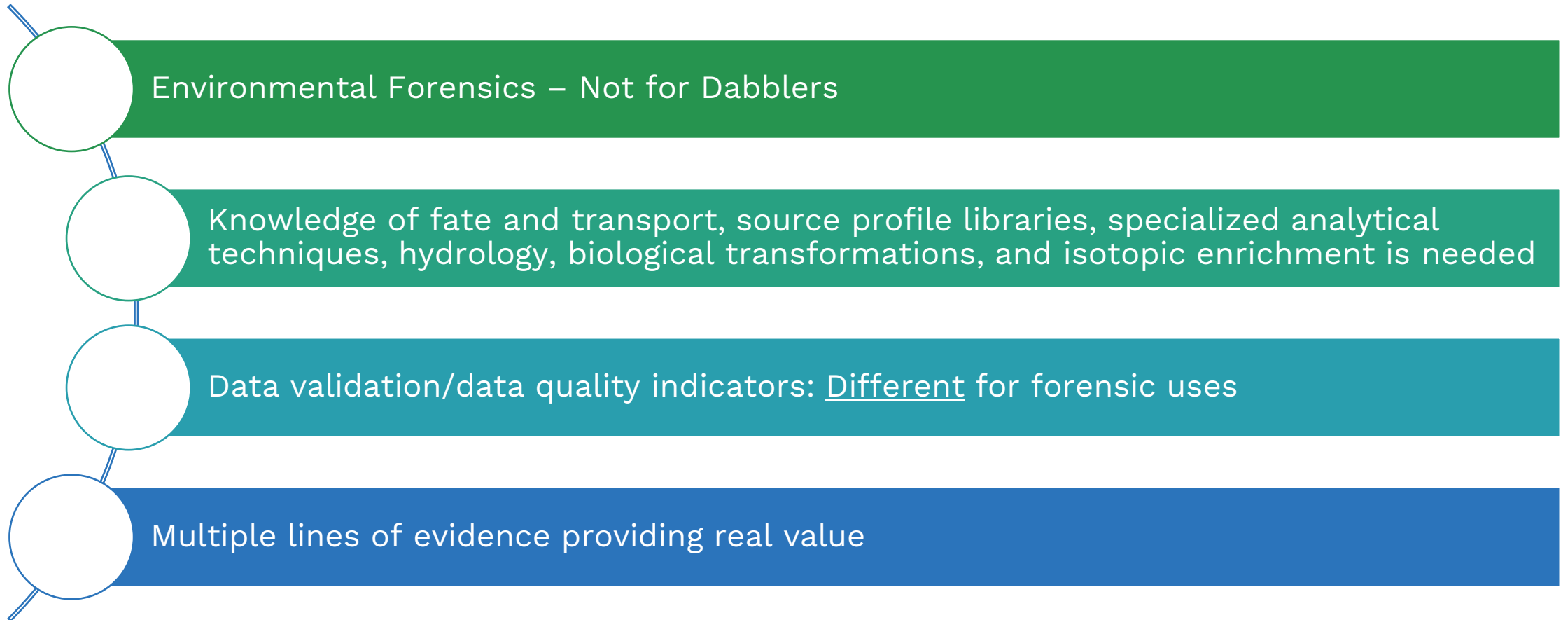
- Make the case: data presentation and justification
- Communicated in a clear and concise manner
- Accessible to:
 - Scientific and lay communities
 - Corporate and management staff
 - Legal, Financial and Business analysts

Work Product should include:

- Fully documented report
- Executive summary



Parting Thoughts



Strategy is Critical – Communication is Key



The Future of Environmental Solutions





Thank you – Questions?



Heather L. Lord, Ph.D.

Senior Associate Forensic Chemist

519.240.9228

hlord@envstd.com