Why Current GC/MS Methods Produce Inaccurate Concentrations of Alkylated Polycyclic Aromatic Hydrocarbons (PAH) and Sulfur Heterocycles (PASH)

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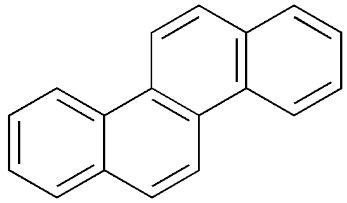
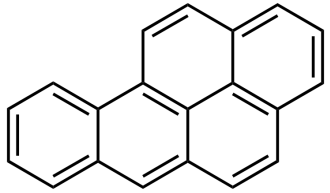
Importance of Polycyclic Aromatic Compounds

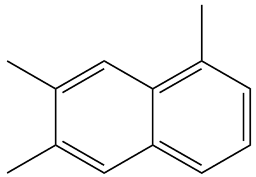
- Forensics
  - Weathering
  - Source Allocation
  - Liability
- Toxicology
  - Food chain
  - Aquatic/Terrestrial/Benthic
  - Flora/Fauna
  - PAH_{34} = 18 Parent PAH + 16 Alkyl PAH
- Remedial investigations
  - Soil, sediment, water
  - Background comparison studies

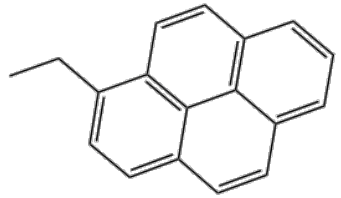
Parent PAH



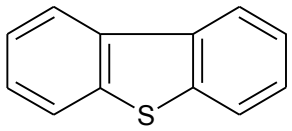


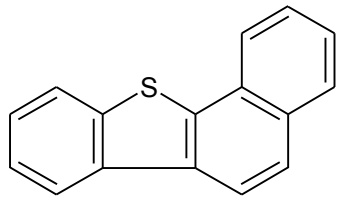
Alkylated PAH Homologues





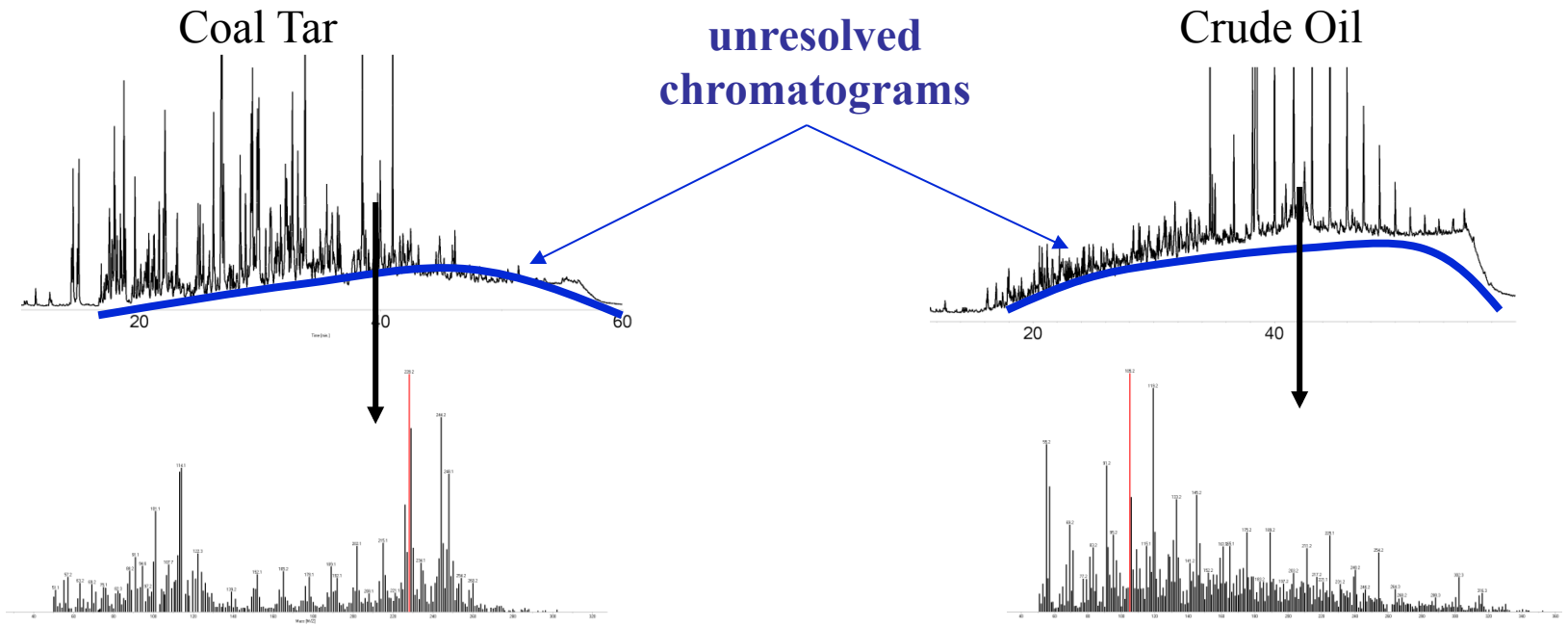
Parent PASH





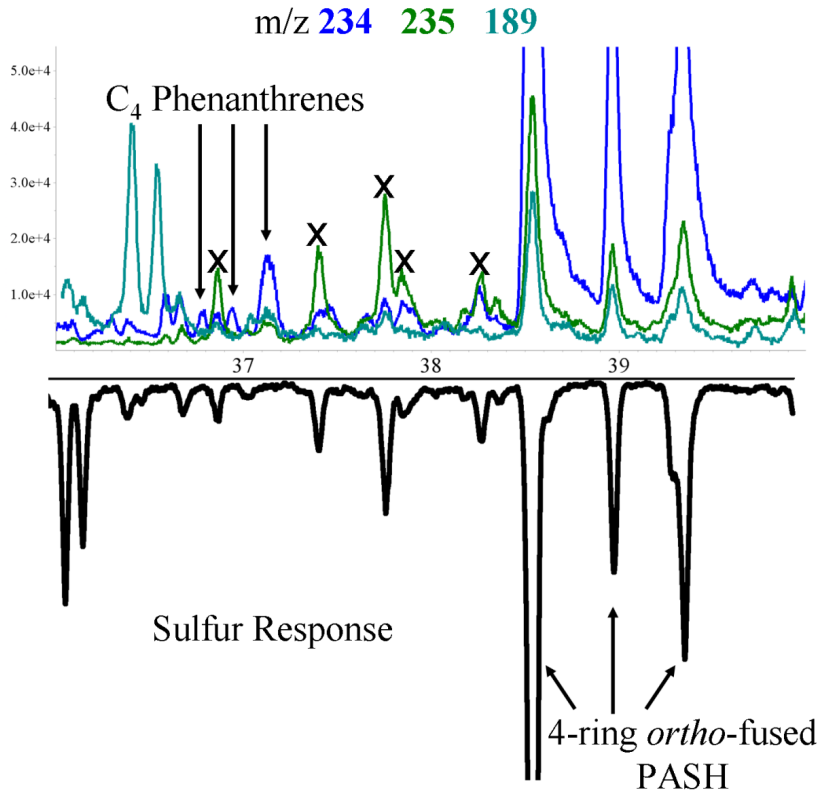
Sample Complexity

- Coal tar and crude oil contain thousands of unresolved organic compounds that interfere with forensic analyses of PAH and PASH homologues
- GC/MS alone cannot produce clean mass spectra nor differentiate one target compound from another if compounds coelute and/or have same mass spectra

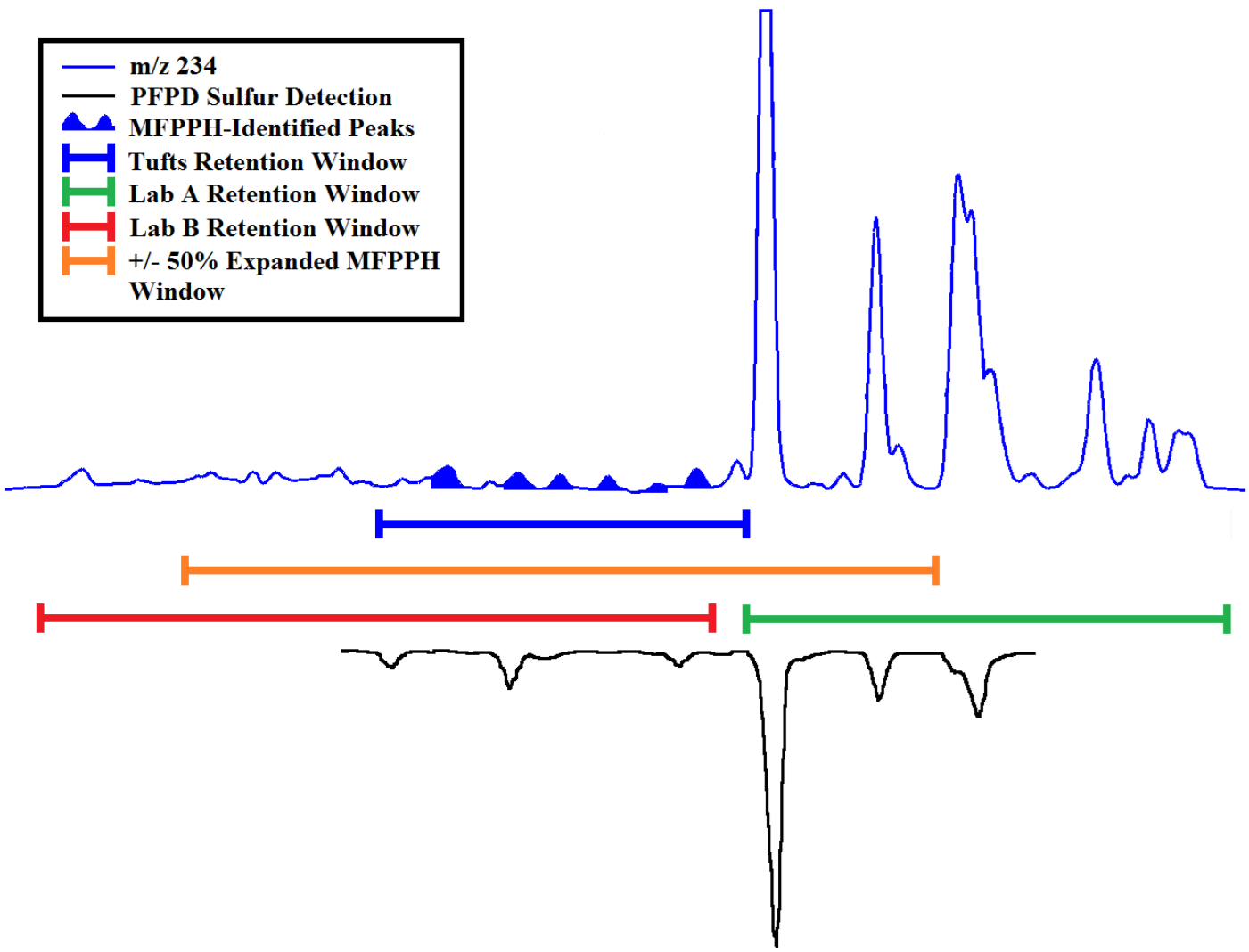


The Problem with Current Methods of Analysis

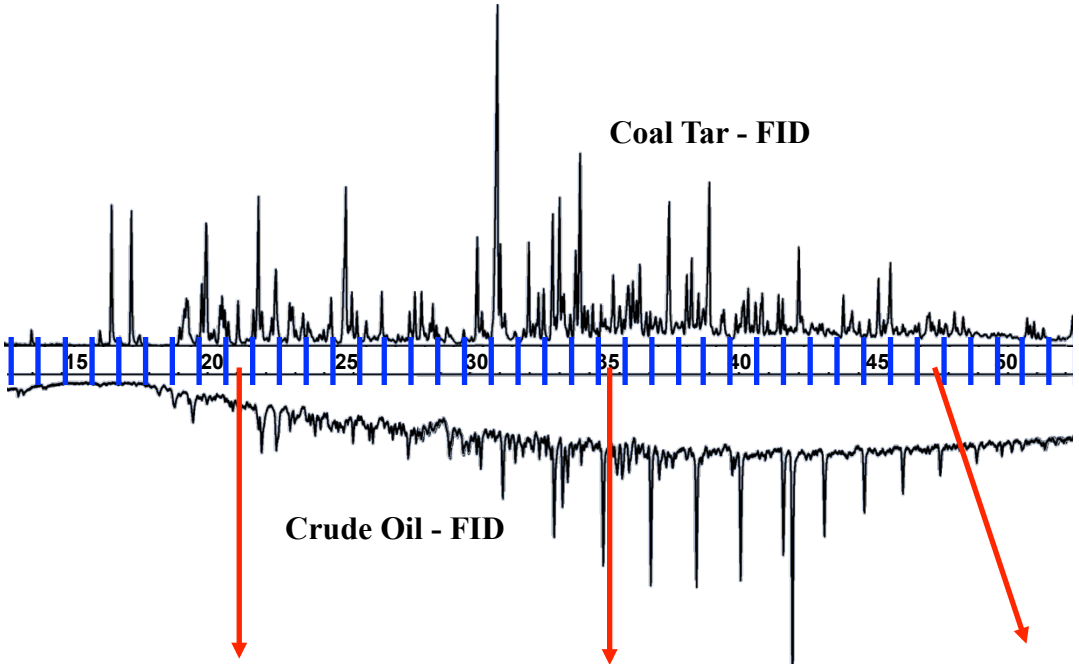
- A 15-year review of the literature shows 65% of PAH studies rely on selected ion monitoring (SIM) to obtain data
- Of these, the majority use only the molecular ion (1-ion) to detect PAH, the remainder use a second ion (2-ion) to confirm identity
- Commercial labs rely exclusively on retention windows and pattern recognition of SIM/1-ion peaks to quantify alkylated PAH, see ASTM and NOAA methods
- Matrix compounds, PAH and PASH interfere with one another, leading to false positives and inaccurate concentration estimates

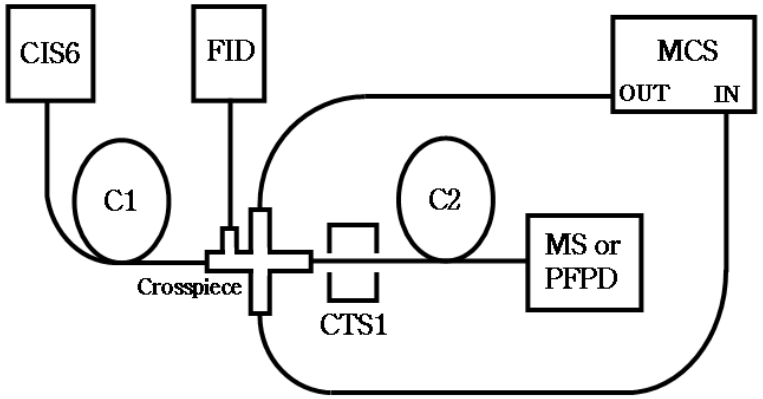


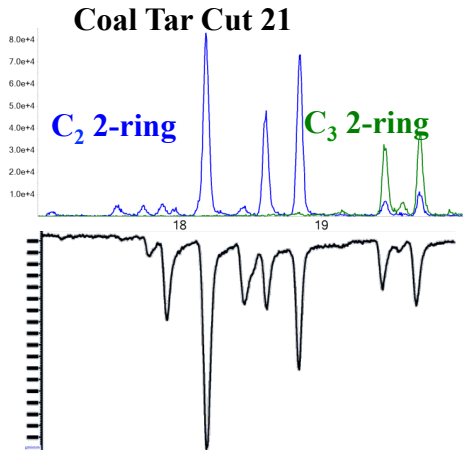
NELAC-Certified Analytical Lab Comparison: C_4 Phenanthrenes

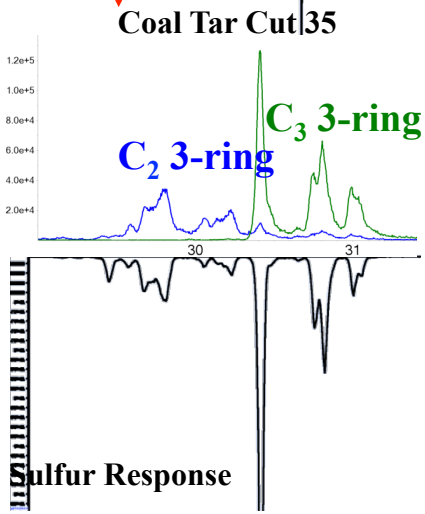


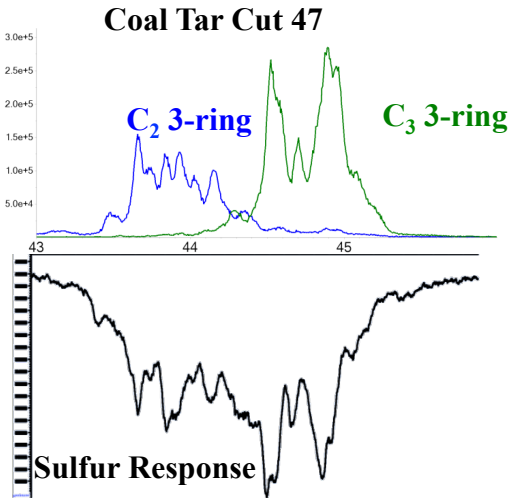
Combinatorial Library Building of PAH and PASH Retention Windows and Spectra by GC-GC/MS/PFPD



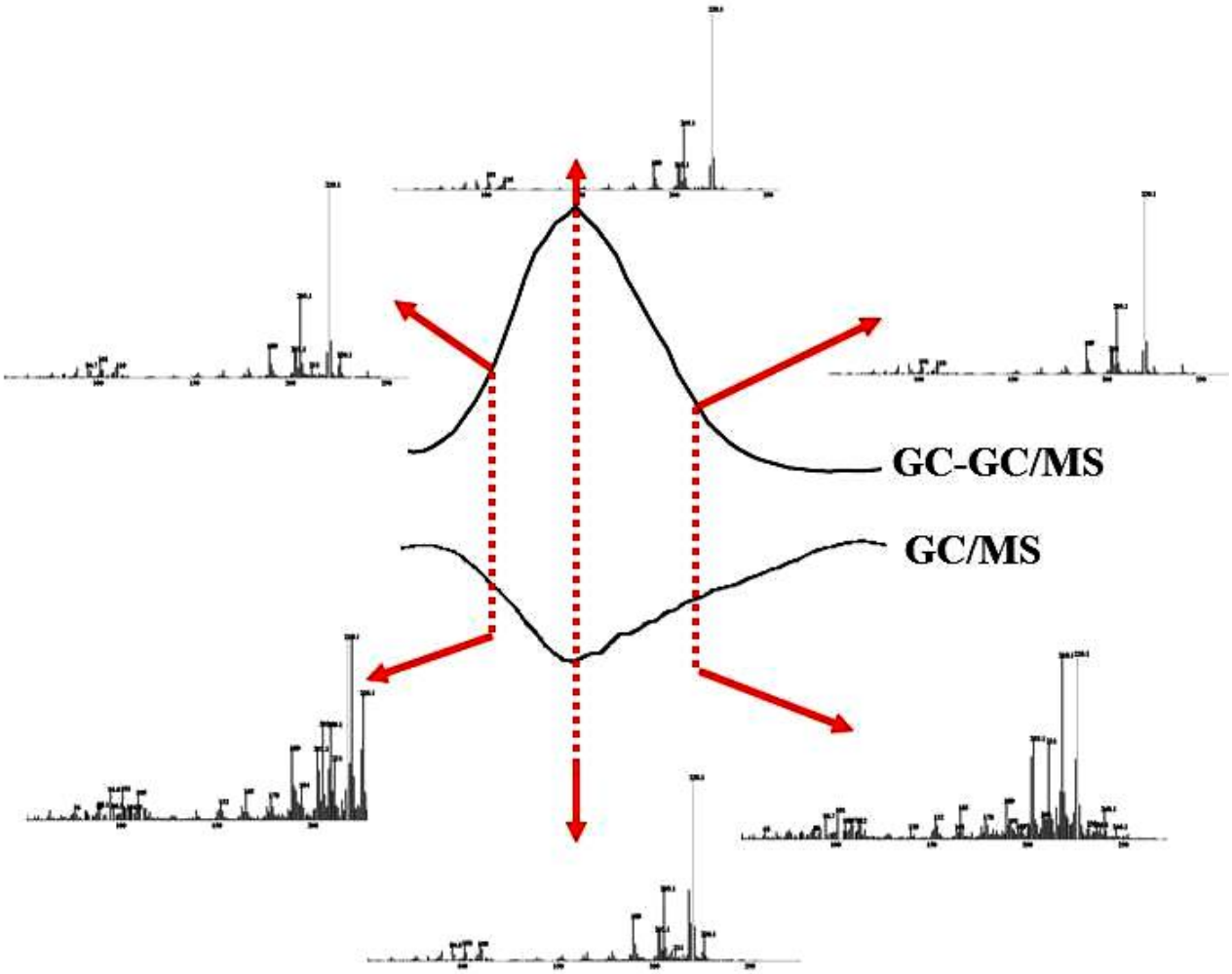






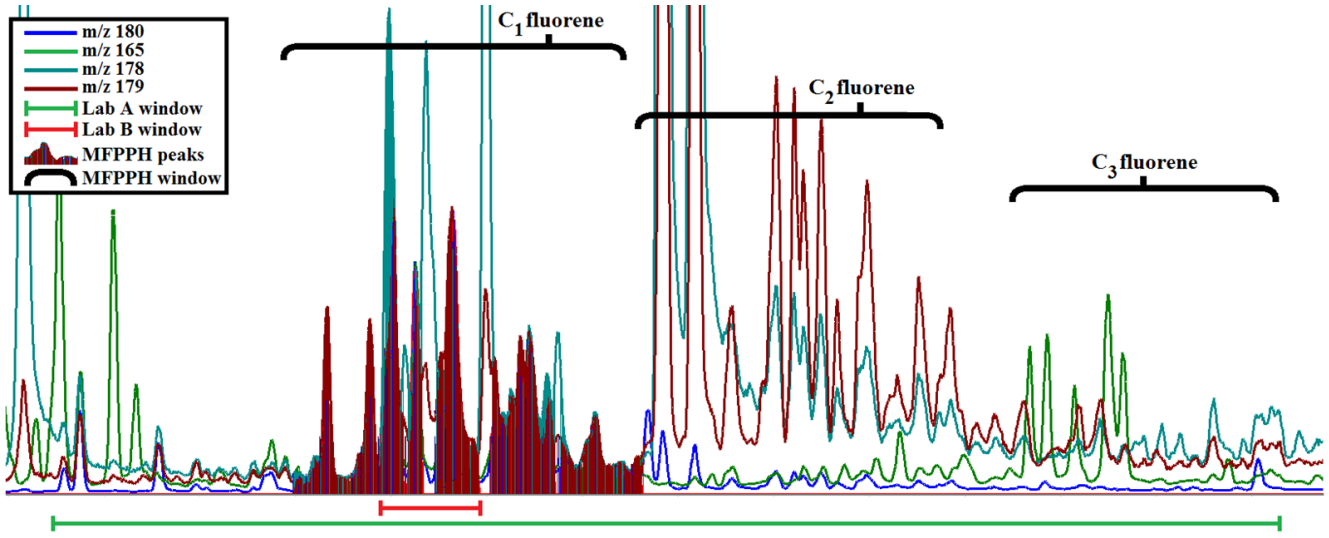


1D vs. 2D Spectra

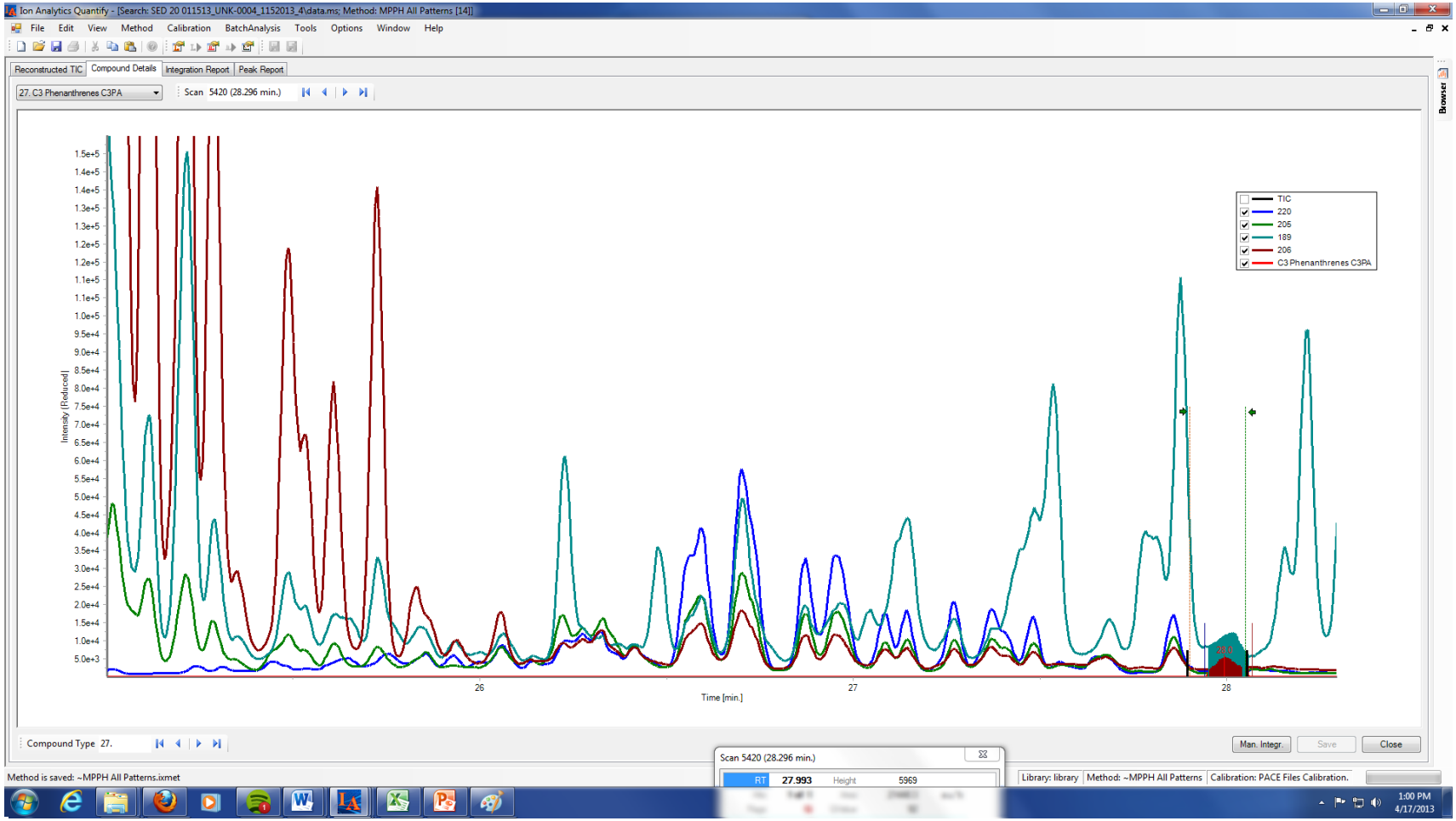


SIM/MFPPH: An Improvement Over SIM/1-ion

- Using literature fragmentation patterns for parent PAH and PASH and GC-GC/MS library patterns for alkylated PAH/PASH, a SIM method was crafted
- SIM/MFPPH:
  - 27 ions/group
  - 1-11 patterns of 3-5 ions per pattern for each homologue
- SIM/1-ion:
  - 9 ions/group
  - One ion for each homologue



SIM/MFPPH Example: C_3 Phenanthrenes



PAH Concentration Misestimation by SIM/1-ion

Compounds	Sample 1 (%)				Sample 2 (%)				Sample 3 (%)			
	Tufts	Literature	Lab A	Lab B	Tufts	Literature	Lab A	Lab B	Tufts	Literature	Lab A	Lab B
C1 Naphthalenes	1	2	0	0	0	1	-3	-3	2	2	1	1
C2 Naphthalenes	0	2	0	0	5	24	4	5	3	20	5	7
C3 Naphthalenes	8	12	11	8	9	19	12	9	5	17	11	6
C4 Naphthalenes	79	845	89	89	42	246	82	82	5	76	21	21
C1 Fluorenes	0	38	52	-21	6	35	48	-30	2	21	41	-41
C2 Fluorenes	0	48	121	6	9	41	87	14	6	30	71	8
C3 Fluorenes	288	442	1920	397	0	51	280	49	3	51	239	47
C1 Phenanthrenes	4	8	17	5	4	15	24	4	3	22	28	3
C2 Phenanthrenes	9	20	4	8	7	17	6	8	2	11	2	1
C3 Phenanthrenes	91	158	131	129	46	100	80	75	29	49	45	44
C4 Phenanthrenes	176	1360	2180	371	ND	ND	FP	ND	136	601	571	355
C1 Pyrenes	3	5	5	3	5	9	10	5	4	7	7	4
C2 Pyrenes	29	78	83	n/a[b]	11	33	46	n/a	8	35	42	n/a
C3 Pyrenes	452	542	466	n/a	FP	FP	FP	n/a	FP	FP	FP	n/a
C1 Chrysenes	4	24	18	11	21	54	51	24	6	19	21	8
C2 Chrysenes	1	43	107	90	32	63	105	86	11	81	86	59
C3 Chrysenes	210	363	1270	1130	ND	ND	ND	ND	FP	FP	FP	FP
C4 Chrysenes	441	2090	1340	1470	ND	ND	ND	ND	ND	FP	FP	FP

SIM/MFPPH vs. SIM/1-ion and Full-Scan Detection Limits

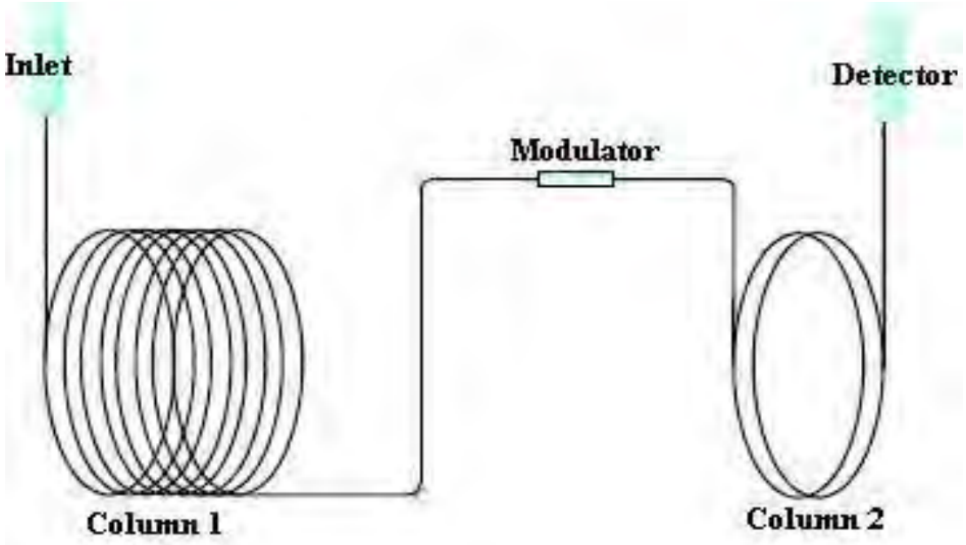
	SIM/1-ion			SIM/MFPPH			Full Scan		
Compound	**R^2**	**RF (%RSD)**	**IDL (ng/mL)**	**R^2**	**RF (%RSD)**	**IDL (ng/mL)**	**R^2**	**RF (%RSD)**	**IDL (ng/mL)**
Naphthalene	0.9998	1.12 (2.50)	0.79 ± 0.26	0.9991	1.21 (8.49)	1.34 ± 0.45	0.9980	1.16 (4.78)	22.5 ± 7.51
Acenaphthylene	0.9973	1.72 (10.4)	1.00 ± 0.34	0.9997	2.24 (5.03)	1.55 ± 0.52	0.9993	2.12 (6.33)	11.7 ± 3.72
Acenaphthene	0.9969	1.01 (10.8)	0.80 ± 0.27	0.9994	1.31 (10.3)	1.38 ± 0.46	0.9980	1.32 (4.48)	7.97 ± 2.66
Fluorene	0.9965	1.13 (10.1)	0.77 ± 0.26	0.9993	1.41 (9.64)	1.88 ± 0.63	0.9989	1.39 (2.20)	23.98 ± 8.00
Phenanthrene	0.9968	1.09 (4.65)	1.01 ± 0.34	0.9988	1.08 (16.2)	1.37 ± 0.46	0.9989	1.12 (4.14)	10.2 ± 3.42
Anthracene	0.9962	0.92 (12.6)	0.86 ± 0.29	0.9990	1.07 (3.00)	1.07 ± 0.36	0.9993	1.09 (2.58)	10.5 ± 3.33
Fluoranthene	0.9940	1.02 (14.0)	0.88 ± 0.29	0.9982	1.28 (7.93)	0.83 ± 0.28	0.9994	1.13 (1.76)	53.2 ± 17.7
Pyrene	0.9955	1.07 (14.8)	0.88 ± 0.29	0.9984	1.30 (8.54)	0.96 ± 0.32	0.9991	1.19 (2.59)	20.0 ± 6.37
Benz[a]anthracene	0.9973	0.99 (12.1)	1.62 ± 0.54	0.9993	1.25 (14.5)	1.29 ± 0.43	0.9987	1.12 (7.79)	52.1 ± 17.4
Chrysene	0.9966	1.10 (12.0)	1.64 ± 0.55	0.9992	1.16 (18.8)	1.13 ± 0.38	0.9998	1.19 (5.57)	17.4 ± 5.79
Benzo[b]fluoranthene	0.9984	1.25 (13.0)	1.85 ± 0.62	0.9996	1.30 (14.1)	1.11 ± 0.37	0.9986	1.25 (2.63)	63.8 ± 21.3
Benzo[k]fluoranthene	0.9980	1.08 (11.9)	1.70 ± 0.57	0.9994	1.39 (4.18)	1.31 ± 0.44	0.9987	1.32 (3.60)	48.6 ± 16.2
Benzo[a]pyrene	0.9988	0.86 (3.65)	2.15 ± 0.72	0.9997	1.24 (3.56)	1.21 ± 0.41	0.9974	1.24 (2.78)	73.1 ± 24.4
Indeno[1,2,3-cd]pyrene	0.9993	0.60 (17.7)	1.42 ± 0.45	0.9998	1.22 (5.75)	1.64 ± 0.55	0.9930	1.25 (7.51)	75.1 ± 25.0
Dibenz[ah]anthracene	0.9989	0.53 (18.8)	1.03 ± 0.33	0.9995	1.18 (6.72)	1.11 ± 0.37	0.9926	1.25 (4.22)	85.0 ± 28.4
Benzo[ghi]perylene	0.9995	0.81 (10.1)	1.23 ± 0.39	0.9998	1.24 (13.3)	2.70 ± 0.90	0.9974	1.41 (3.58)	63.8 ± 21.3

Misestimation of Toxicity According to PAH_{34}

	Sediment Concentration (mg/kg)			Toxic Units		
	All Methods			All Methods		
Parent PAH	15.414			0.5632		
	SIM/MFPPH (%RSD)	**Lab A**	**Lab B**	**SIM/MFPPH**	**Lab A**	**Lab B**
C1 Naphthalene	0.944 ± 9.7	0.92	0.92	0.0513	0.05	0.05
C2 Naphthalene	1.360 ± 2.7	1.41	1.42	0.0643	0.0667	0.0673
C3 Naphthalene	0.696 ± 6.1	0.782	0.762	0.0289	0.0325	0.0317
C4 Naphthalene	0.110 ± 3.8	0.2	0.2	0.004	0.0074	0.0736
C1 Fluorene	1.000 ± 1.4	1.49	0.701	0.0397	0.0588	0.0277
C2 Fluorene	0.407 ± 2.8	0.762	0.47	0.0143	0.0268	0.0164
C3 Fluorene	0.197 ± 7.6	0.748	0.294	0.0062	0.0235	0.0092
C1 Phenanthrene	2.200 ± 3.3	2.74	2.29	0.0794	0.988	0.0826
C2 Phenanthrene	0.896 ± 6.3	0.948	0.965	0.029	0.0307	0.0312
C3 Phenanthrene	0.244 ± 2.1	0.439	0.428	0.0071	0.0128	0.0125
C4 Phenanthrene	ND	0.38	ND	ND	0.01	ND
C1 Pyrene	2.250 ± 3.5	2.47	2.36	0.0706	0.0774	0.0741
C1 Chrysene	0.693 ± 3.2	1.05	0.857	0.018	0.0273	0.0223
C2 Chrysene	0.193 ± 3.9	0.395	0.358	0.0046	0.0095	0.0086
C3 Chrysene	ND	ND	ND	ND	ND	ND
C4 Chrysene	ND	ND	ND	ND	ND	ND
			ΣESBTU	0.981	1.09	1
			% Diff	--	11	2

Analysis by GCxGC/MS

- Comprehensive two-dimensional gas chromatography) (GCxGC/MS) mass spectrometry offers increased resolution of target compounds from matrix components
- Improved sensitivity due to compression of 2nd dimension peaks
- Improves forensic fingerprinting of oil and tar via weathering maps



Improved Accuracy of Alkylated PAH by GCxGC/MS

Compound/Homologue	GC×GC/MS (µg/g)	GC/MS (µg/g)	% RPD	2.5×AL (µg/g) and [1](RPD)
Naphthalene	0.7	0.7	0	5 (100)
C_1 Naphthalenes	8.0	10	-20	
C_2 Naphthalenes	15	19	-21	
C_3 Naphthalenes	11	11	0	
C_4 Naphthalenes	4.4	2.1	110	
Fluorene	25	23	9	35 (100)
C_1 Fluorenes	24	21	14	
C_2 Fluorenes	13	9.7	34	
C_3 Fluorenes	2.9	0.8	263	
C_4 Fluorenes	1.6	ND	N/A	
Phenanthrene/Anthracene	93	84	11	355 (100)
C_1 Phenanthrenes	78	87	-10	
C_2 Phenanthrenes	20	24	-17	
C_3 Phenanthrenes	5.5	6.8	-19	
C_4 Phenanthrenes	1.3	0.5	160	
Benzo(a)anthracene/Chrysene	29	34	-15	0.25 (60)
C_1 Chrysenes	27	37	-27	
C_2 Chrysenes	3.0	3.3	-9	
C_3 Chrysenes	0.8	ND	N/A	
C_4 Chrysenes	ND	ND	N/A	

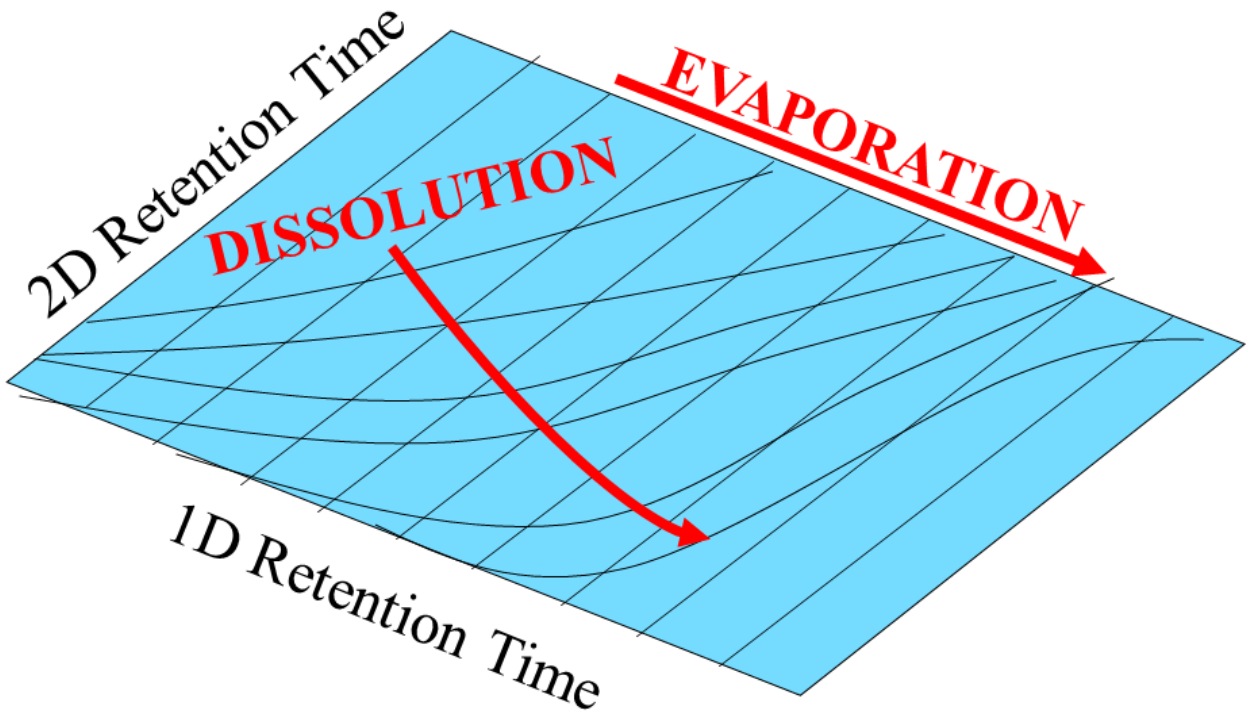
Compound/Homologue	GC×GC/MS (µg/g)	GC/MS (µg/g)	% RPD	2.5×AL (µg/g) and [1](RPD)
Pyrene/Fluoranthene	73	72	1	262.5 (100)
C_1 Pyrenes	61	76	-20	
C_2 Pyrenes	17	22	-23	
C_3 Pyrenes	4.2	1.9	121	
C_4 Pyrenes	1.1	ND	N/A	
C_1 2-Ring PASH	2.0	2.3	-13	
C_2 2-Ring PASH	3.6	4.3	-16	
C_3 2-Ring PASH	4.3	4.7	-9	
C_4 2-Ring PASH	1.4	1.3	8	
Dibenzothiophene	22	20	10	
C_1 3-Ring PASH	30	29	3	
C_2 3-Ring PASH	22	19	16	
C_3 3-Ring PASH	9.7	7.3	33	
C_4 3-Ring PASH	1.9	0.6	217	
C_1 4-Ring Fused PASH	17	14	21	
C_2 4-Ring Fused PASH	7.3	6.6	11	
C_3 4-Ring Fused PASH	0.7	ND	N/A	
C_4 4-Ring Fused PASH	0.6	0.8	-25	
C_1 4-Ring Condensed PASH	7.3	6.1	20	
C_2 4-Ring Condensed PASH	3.5	3.2	9	
C_3 4-Ring Condensed PASH	6.7	6.0	12	

Weathering Maps and Property Estimation

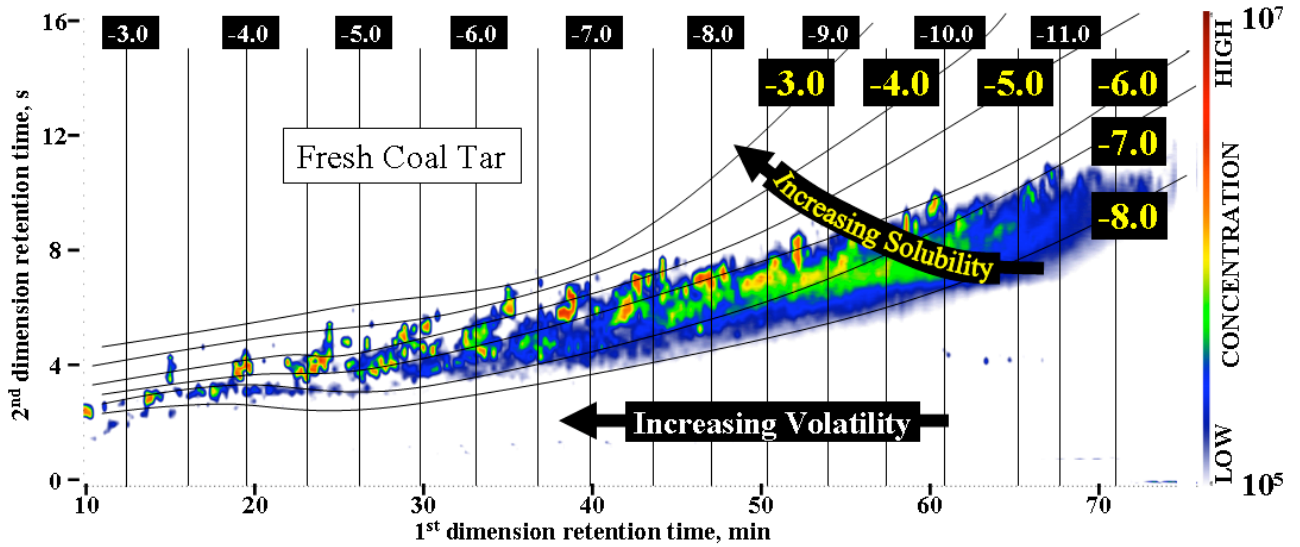
Conceptual Coal Tar Model

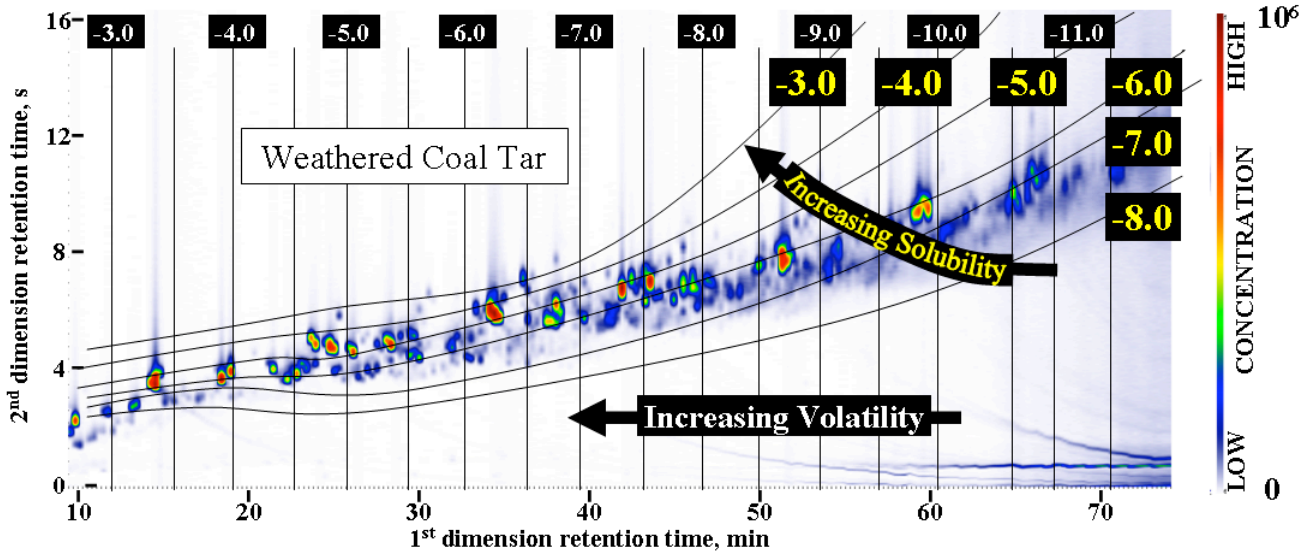
- **are components volatizing?**
- **has dissolution stopped?**
- **what is bioaccessible/available?**
- **is remediation necessary?**

- Dissolution: aqueous solubility (S_W)
- Evaporation: vapor pressure (V_P)
- Organic phase partition:
  octanol-water coefficient (K_{OW})



Weathering Maps and Property Estimation





Conclusions

- Methods that rely on SIM/1-ion overestimate alkyl PAH and PASH concentrations, while a single pattern underestimates
- Using automated sequential GC-GC/MS/PFPD, a library of fragmentation patterns for alkyl PAH/PASH was constructed
- Literature and library patterns were assembled into a standardized method for GC/MS: SIM/MFPPH
- GCxGC/qMS (full-scan) was used to quantify PAH and PASH in a sample for the first time and produce weathering maps
- Future work will see the development of GCxGC/MS: SIM/MFPPH