Analytical Considerations for the Determination of Petroleum Biomarkers

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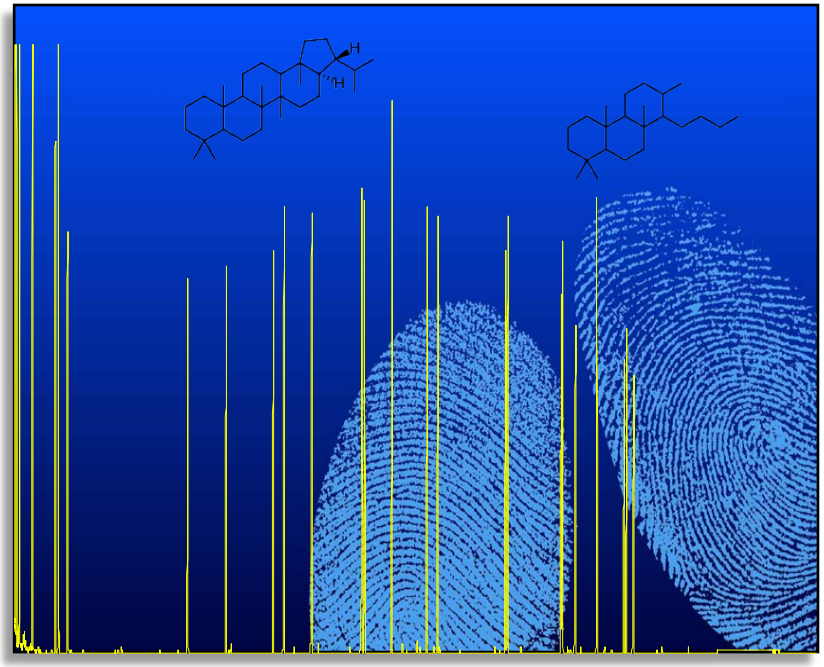
Battelle

Petroleum Biomarkers

- Molecular fossils of lipids
- Provide information on…
  - Organic matter in source rock
  - Environmental conditions during deposition and burial (diagenesis)
  - Thermal maturity (catagenesis)
  - Age



- Helps “fingerprint” oil and are therefore used in environmental forensic applications

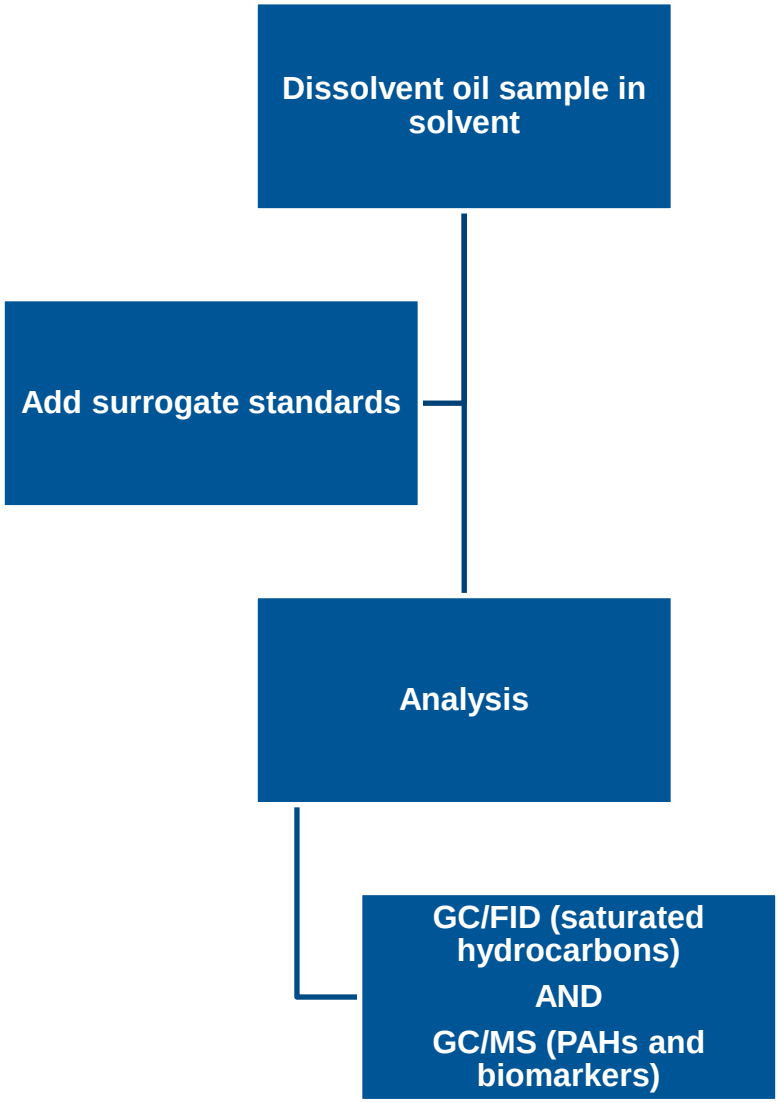
Applications of Biomarkers

- First discussed in Eglinton et al. (1964)
- Used extensively in applications of petroleum geochemistry and oil exploration (Peters et al. (1993)
- Also used in environmental forensics, see Wang et al. (2006)
- *This presentation will discuss different analytical approaches highlighting how improvements in sensitivity and selectivity improve interpretation*

Battelle Biomarker Database

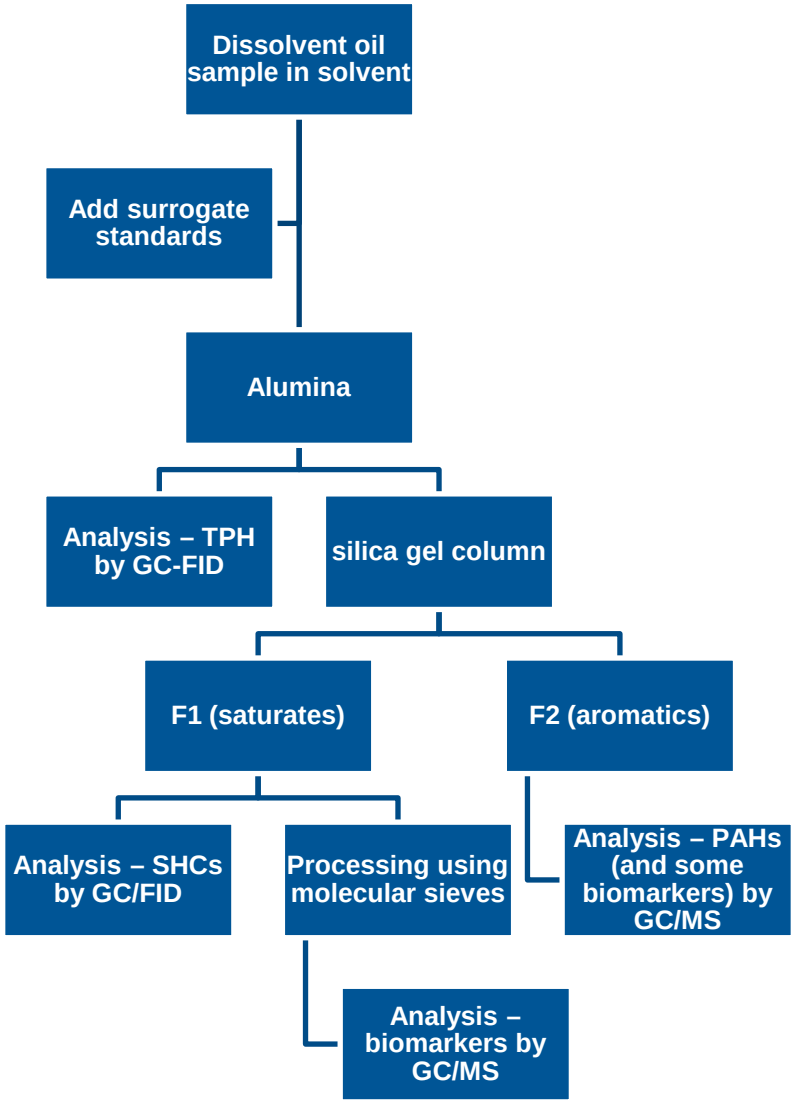
- Numerous crude oils, refined products, weathered materials, etc.
  - For this talk will discuss 40 crude oil samples, 26 of which were analyzed using two sample preparation methods
- Each sample is analyzed for
  - Saturated hydrocarbons by GC-FID (36 compounds)
  - PAHs by GC-MS (74 compounds)
  - ***Petroleum Biomarkers by GC-MS (87 compounds)***

Measuring Biomarkers, sample preparation and GC/MS



- 50 mg of oil dissolved into 10 mL of solvent
- 1 mL of solvent is removed and analyzed
- The following ions are monitored for biomarkers
  - 191 (hopanes)
  - 217 & 218 (steranes & diasteranes)

Measuring Biomarkers, sample preparation and GC/MS

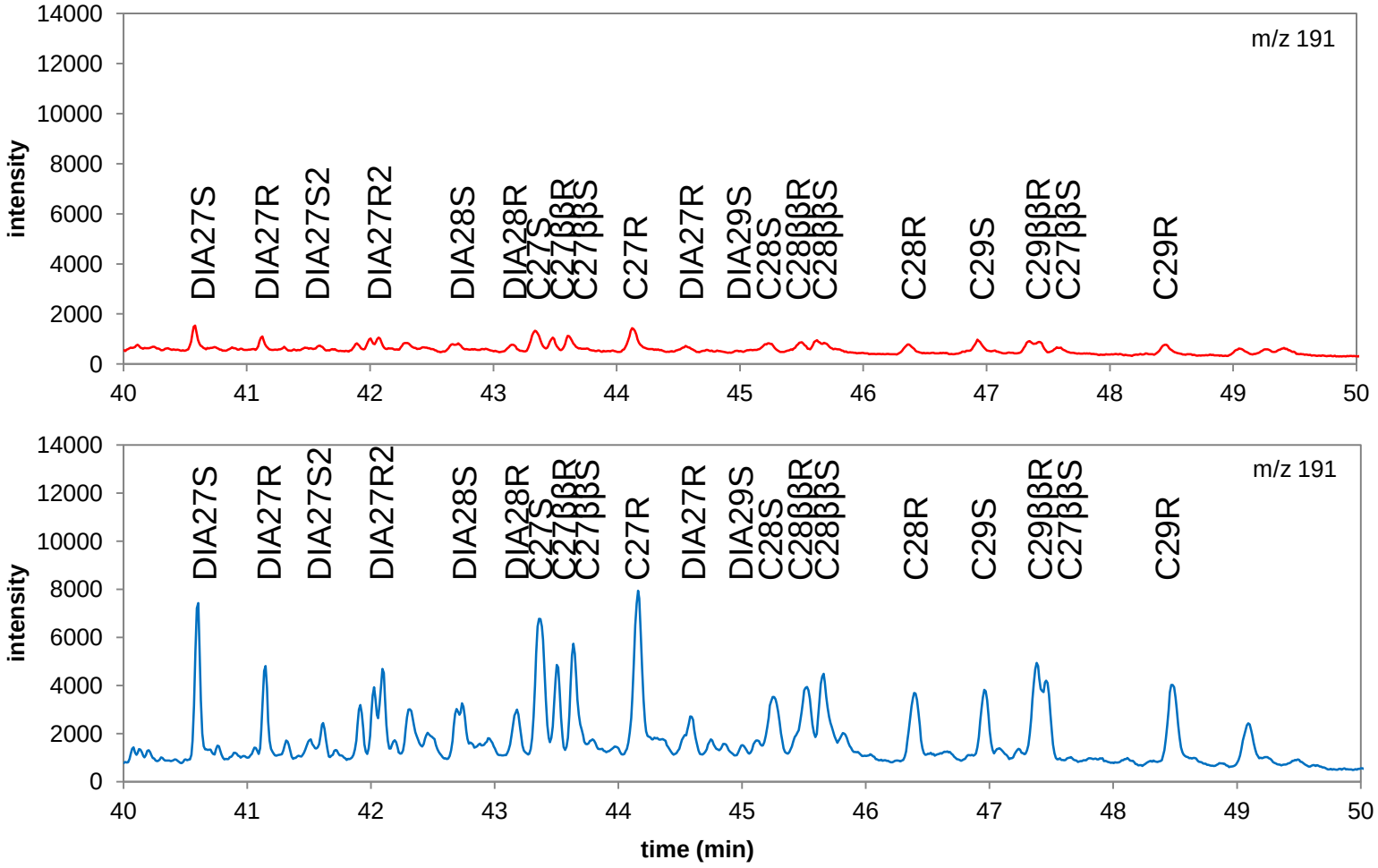


- 50 mg of oil is dissolved into 10 mL of organic solvent.
- Entire extract processed through alumina
  - 5 mg/mL fraction removed for TPH analysis by GC/FID
- Remaining extract is fractionated using silica
  - F1 fraction (saturates)
    - Split analyzed for SHCs by GC/FID
    - Split processed using molecular sieves and analyzed for biomarkers by GC/MS
  - F2 fraction
    - Analyzed for PAHs by GC/MS

Cleanup Increases Sensitivity and Selectivity

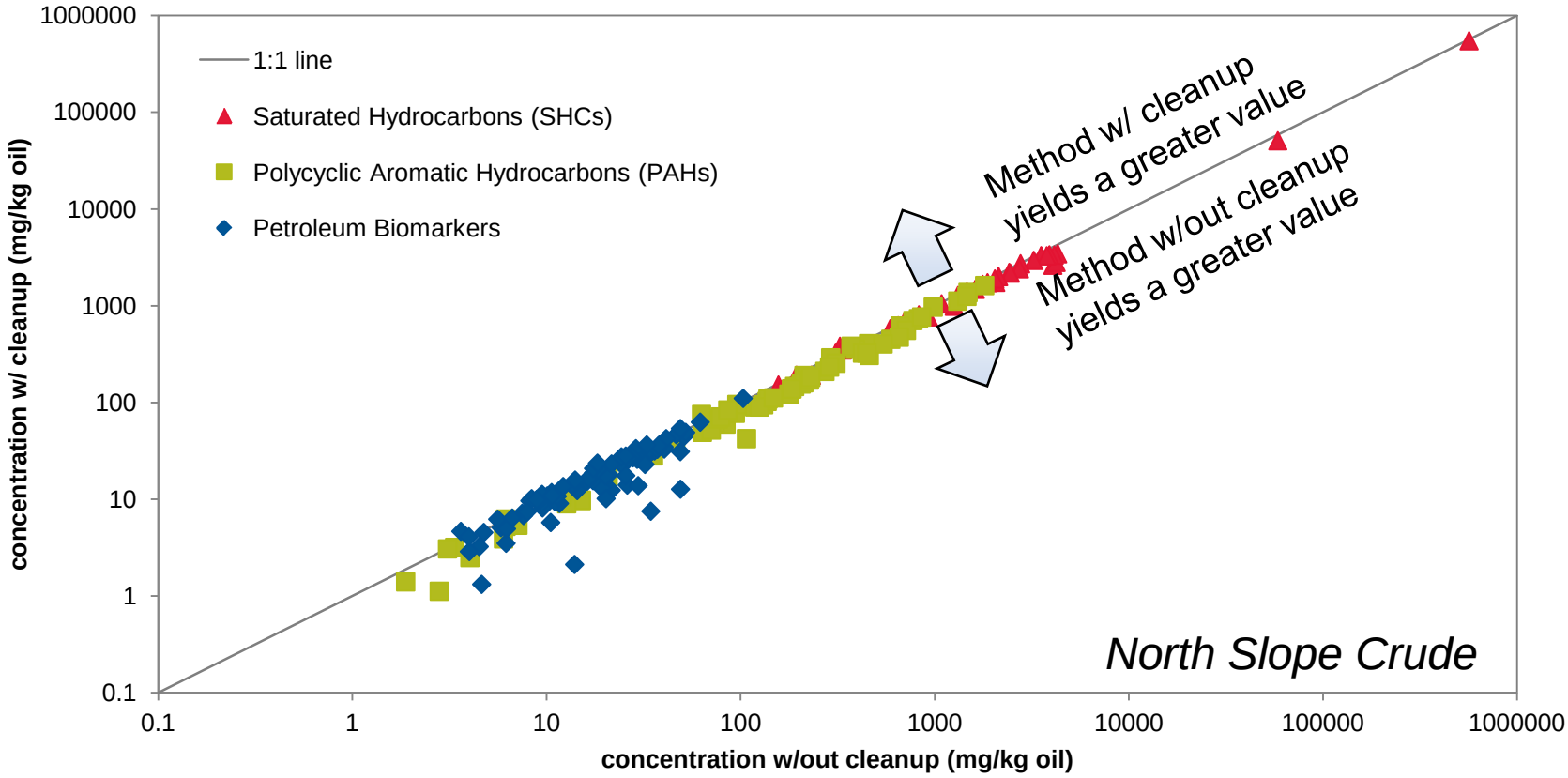
without cleanup

with cleanup



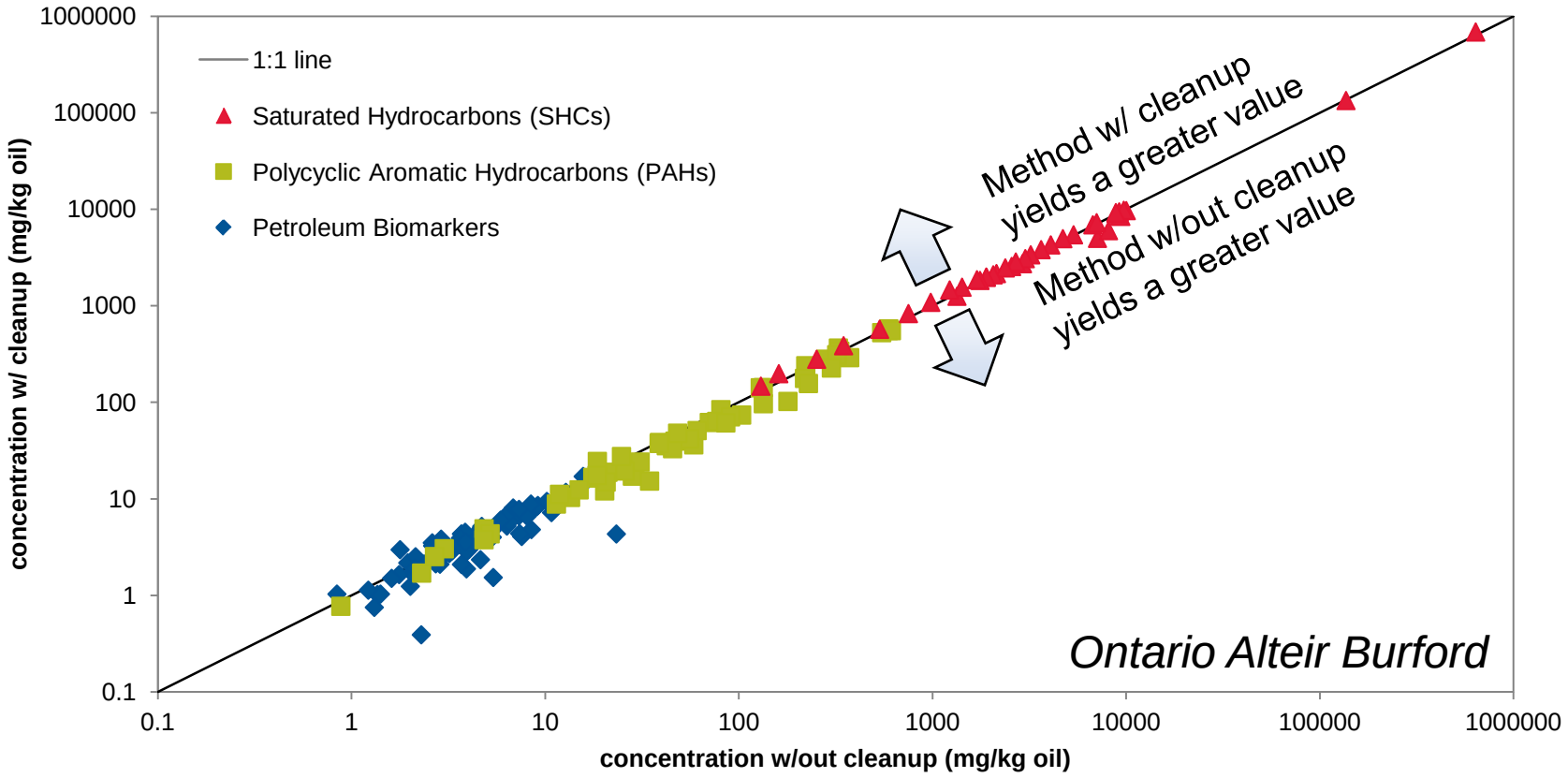
Cleanup Increases Sensitivity and Selectivity

This animation illustrates the differences in the three different analyses of the same oil sample with and without cleanup



Cleanup Increases Sensitivity and Selectivity

This is particularly important for samples with relatively low concentrations of petroleum biomarkers



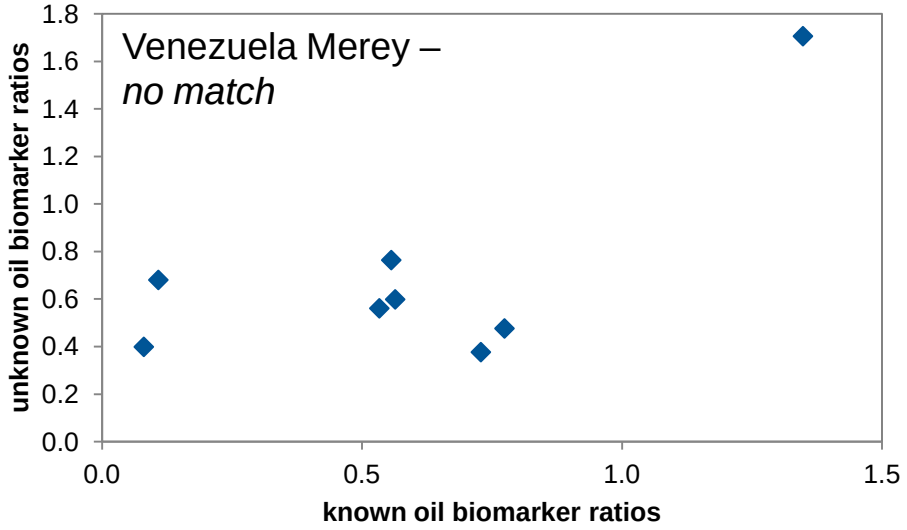
Database of Biomarker Concentrations

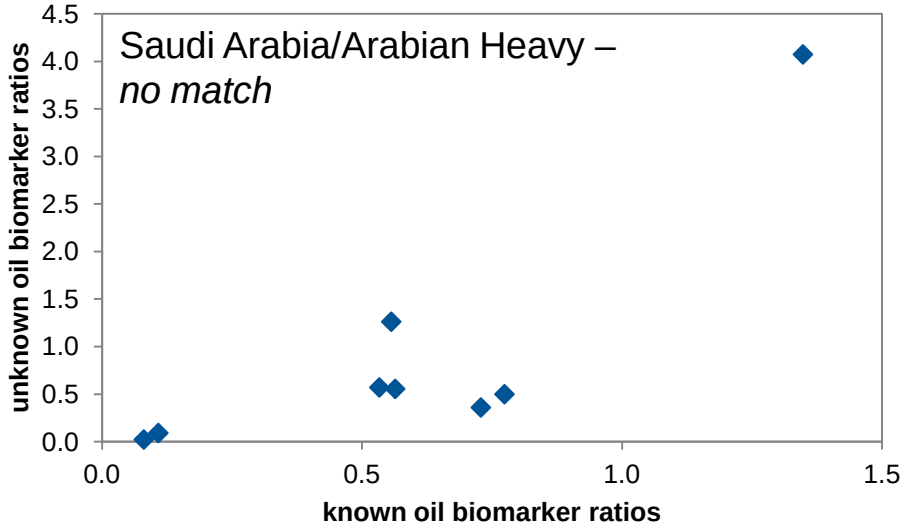
Biomarker (Battelle ID)	North Slope Crude	Louisiana USA	Venezuela Merey	Venezuela Leona	Columbia Vasonia	Equador Oriente	Hoops Blend	Iraq/Basrah Light	Nigeria	Ontario/Sydney Earl Can Enerco #10 Dev #2 Enniskillen 1-17-	Ontario/Aleir Burfurd	Ontario/McMaster #3	Saudi Arabia/Arabian Heavy	Saudi Arabia/Zuluf/Marjan
C_{21}-Diterpane (T2)	17.55	4.35	27.63	27.46	16.67	16.62	6.32	3.22	8.4	17.86	17.65	7.2	7.14	3.28	3.16
C_{22}-Diterpane (T3)	2.12	1.08	1.50	1.50	2.29	2.21	2.08	1.90	4.35	1.86	7.30	1.53	1.55	2.73	2.76
C_{23}-Diterpane (T4)	42.32	5.93	73.38	71.48	32.82	43.32	12.36	12.82	10.69	42.29	29.98	8.83	9.19	13.48	12.66
C_{24}-Diterpane (T5)	27.56	4.40	43.02	43.73	22.80	27.14	7.27	3.62	9.28	25.68	23.92	6.63	6.54	3.31	3.17
Norhopane (T15)	62.67	30.45	82.39	79.07	50.68	115.32	68.33	169.69	250.31	66.65	162.03	9.39	12.93	186.38	149.63
Hopane (T19)	110.28	54.75	107.86	112.43	90.01	203.88	103.57	127.13	414.68	96.49	387.94	17.05	22.36	147.76	119.12
Homohopane-S (T21)	53.82	17.48	63.76	64.76	37.31	87.91	43.73	66.65	99.53	49.84	186.31	7.77	10.49	90.17	72.61
Homohopane-R (T22)	35.83	13.53	42.76	43.47	23.88	54.66	33.86	55.14	71.83	32.31	126.92	4.00	6.88	72.28	56.10
Bishomohopane-S (T26)	360.5	9.63	37.6	38.25	24.14	48.63	24.78	34.67	60.12	34.33	178.07	4.92	7.55	54.16	43.30
Bishomohopane-R (T27)	27.45	8.43	29.43	28.80	18.76	35.54	20.90	27.20	48.79	25.01	134.44	3.58	5.53	40.82	32.97
Trishomohopane-S (T30)	27.98	7.16	27.6	27.42	19.7	35.22	17.97	26.77	39.54	26.46	111.69	3.00	4.76	37.25	30.01
Trishomohopane-R (T31)	20.45	5.88	18.94	20.51	16.24	27.34	12.50	16.59	29.74	18.17	74.12	3.26	3.42	23.07	18.00
Tetrakishomohopane-S (T32)	20.83	4.61	17.69	17.41	12.26	20.63	10.43	18.26	21.07	19.85	187.23	3.82	3.30	26.45	21.45
Tetrakishomohopane-R (T33)	13.54	2.97	11.42	11.26	8.00	13.32	6.84	12.88	14.61	12.85	129.18	1.50	2.32	18.40	14.65
Pentakishomohopane-S (T34)	23.60	3.33	22.25	21.29	10.60	16.53	7.79	21.70	9.97	24.72	142.86	1.13	1.69	28.90	23.85
Pentakishomohopane-R (T35)	15.78	2.14	14.92	14.67	7.94	11.34	5.29	13.64	6.65	16.14	95.07	nd	1.27	19.23	15.15
Trisnorhopane-Ts (T11)	18.75	9.48	16.26	15.39	16.11	24.73	21.19	13.13	60.37	15.49	64.13	6.01	7.01	24.77	23.36
Trisnorhopane-Tm (T12)	23.16	12.25	34.14	33.91	19.31	35.83	25.57	52.04	71.66	23.29	79.18	4.33	5.53	49.62	39.78

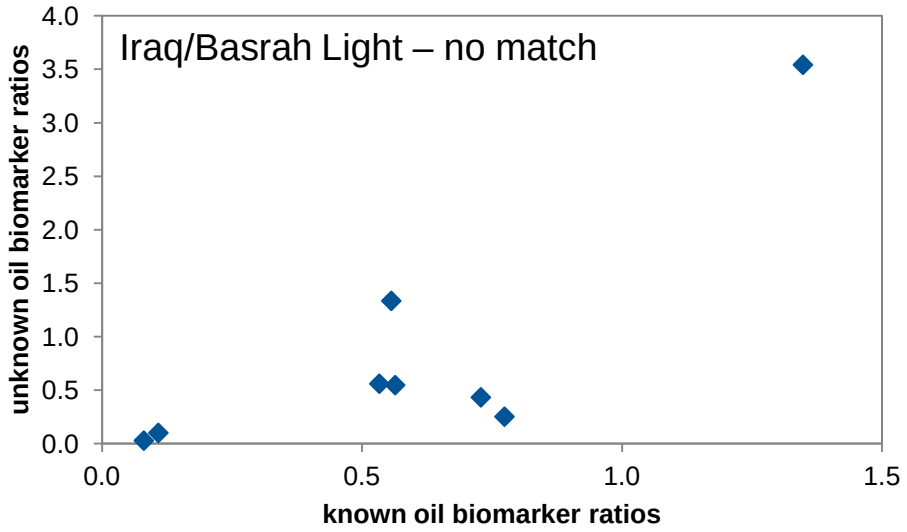
Database of Biomarker Diagnostic Ratios

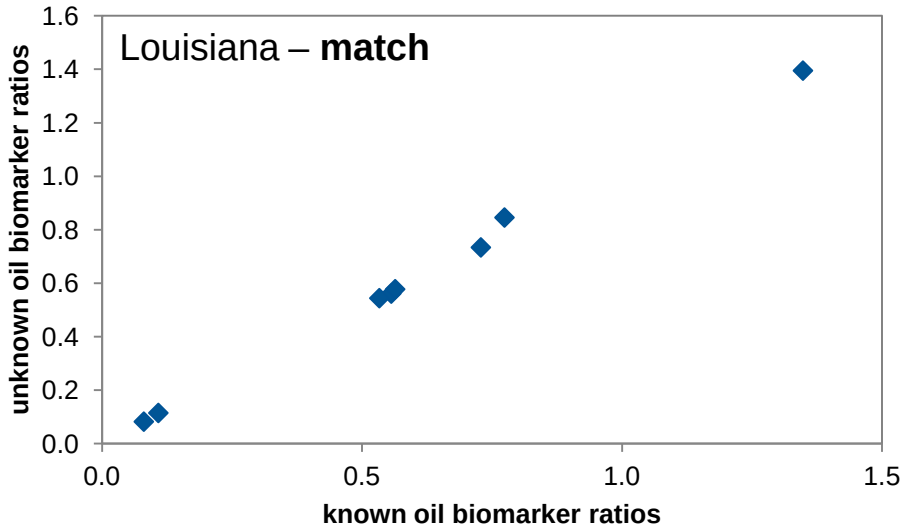
Ratio	North Slope Crude	Louisiana USA	Venezuela Merey	Venezuela Leona	Columbia Vasonia	Equador Oriente	Hoops Blend	Iraq/Basrah Light	Nigeria	Ontario/Sydney Earl	Can Enerco #10 Dev #2 Enniskillen 1-17-X	Ontario/Aleir Burfurd	Ontario/McMaster #3	Saudi Arabia/Arabian Heavy	Saudi Arabia/Zuluf/Marjan
C_{23}-Diterpane C_{24}-Diterpane	1.54	1.35	1.71	1.63	1.44	1.60	1.70	3.54	1.15	1.65	1.25	1.33	1.41	4.07	3.99
C_{23}-Diterpane/Hopane	0.38	0.11	0.68	0.64	0.36	0.21	0.12	0.10	0.03	0.44	0.08	0.52	0.41	0.09	0.11
C_{24}-Diterpane/ Hopane	0.25	0.08	0.40	0.39	0.25	0.13	0.07	0.03	0.02	0.27	0.06	0.39	0.29	0.02	0.03
Norhopane/ Hopane	0.57	0.56	0.76	0.70	0.56	0.57	0.66	1.33	0.60	0.69	0.42	0.55	0.58	1.26	1.26
Homohopane-S/ Homohopane-S+R	0.60	0.56	0.60	0.60	0.61	0.62	0.56	0.55	0.58	0.61	0.59	0.66	0.60	0.56	0.56
Bishomohopane-S/ Bishomohopane-S+R	0.57	0.53	0.56	0.57	0.56	0.58	0.54	0.56	0.55	0.58	0.57	0.58	0.58	0.57	0.57
Trisnorhopane-Ts/ Trisnorhopane-Tm	0.81	0.77	0.48	0.45	0.83	0.69	0.83	0.25	0.84	0.67	0.81	1.39	1.27	0.50	0.59
Hopane/(Homohopanes+ Bishomohopanes+Trisnorhopanes+ Tetrakishopane+Pentakishopane)	0.40	0.73	0.38	0.39	0.50	0.58	0.56	0.43	1.03	0.37	0.28	0.52	0.47	0.36	0.36

Example – Identifying Oil/Tarball with Biomarker Ratios



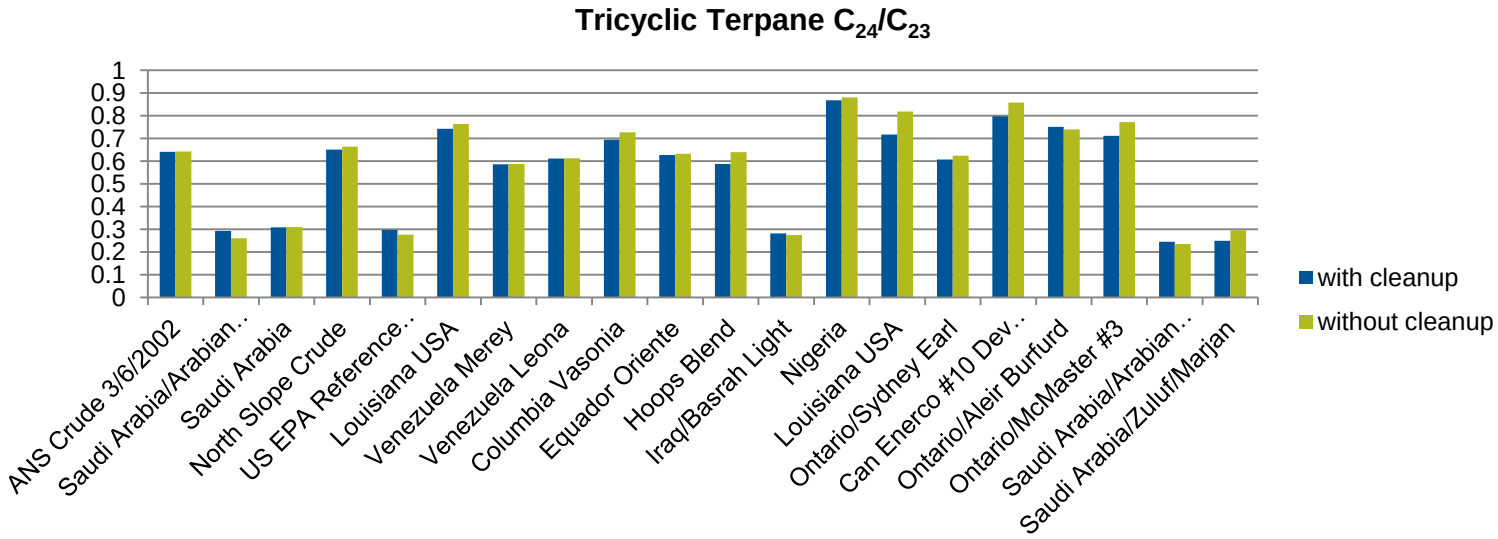




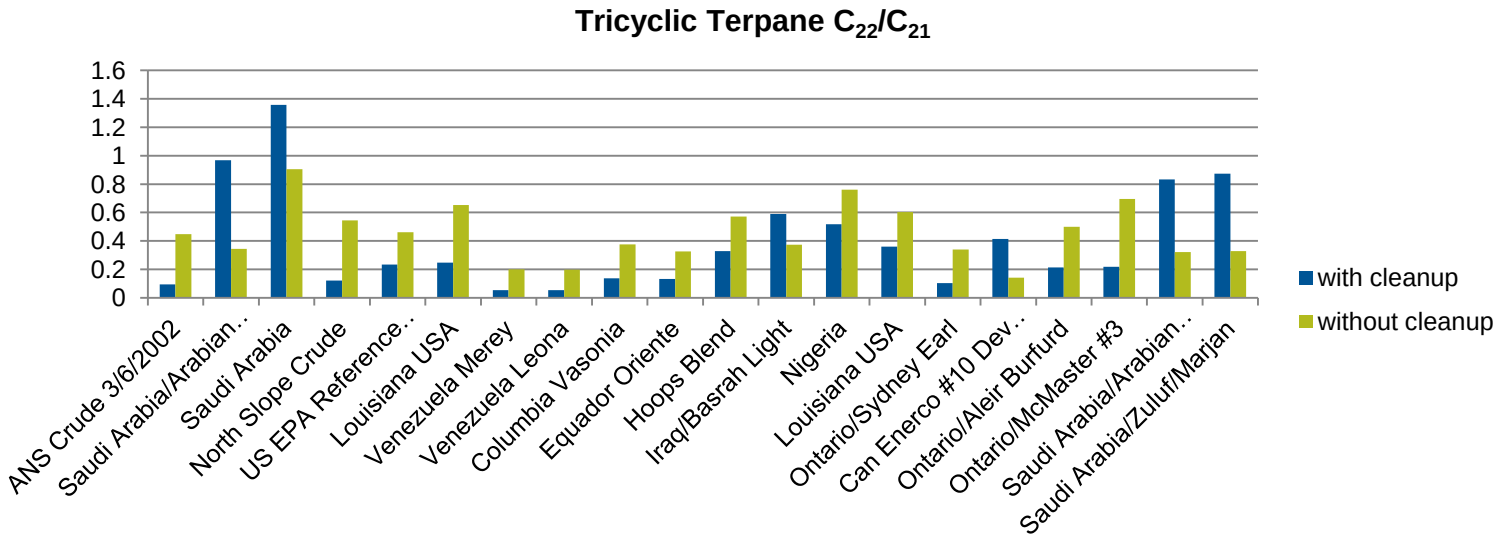


Cleanup Improves Petroleum Biomarker Data

The effects of cleanup are not apparent for ratios of biomarkers in relatively high concentrations…

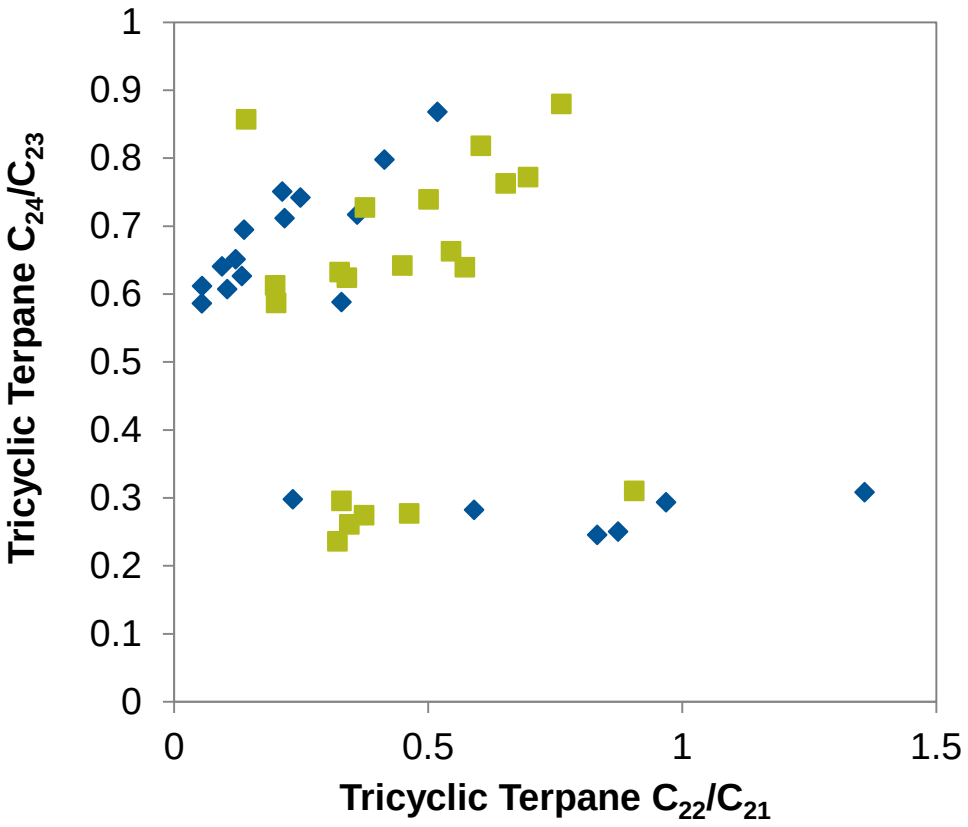


… but are very noticeable for ratios of biomarkers in relatively low concentrations



Cleanup Improves Petroleum Biomarker Data, continued

High C_{22}/C_{21} and low C_{24}/C_{23} tricyclic terpanes distinguish oils from carbonate source rocks



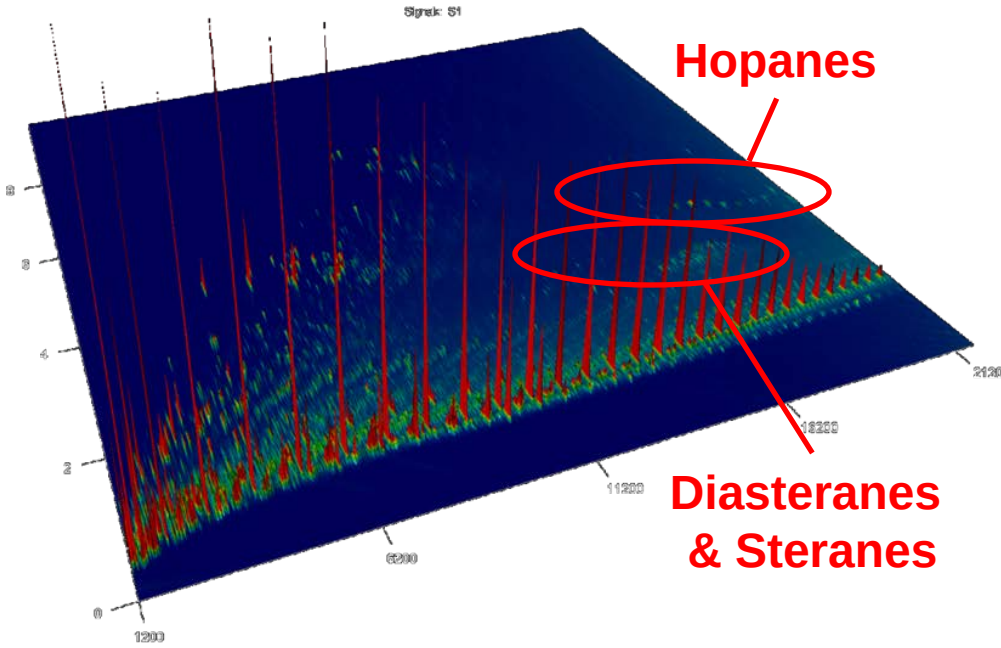
Better sensitivity of biomarker analysis may help interpretation by providing more accurate data, particularly for those compounds at relatively low concentrations

GC-MS/MS for Petroleum Biomarker Analysis

- Measures presence of pairs of ions (“parent” > “daughter”) often unique to a single compound
- Much greater selectivity and sensitivity compared to GC-MS operated in SIM mode
  - Do not need long runs (~2 hours) common for GC-MS biomarker analysis to separate compounds
- GC-MS/MS is best suited as a tool to use in specific cases where biomarker concentrations may be too low to measure with GC/MS
  - Very light oils
  - Extremely weathered samples

GC×GC-ToF-MS for Petroleum Biomarker Analysis

- Comprehensive GC (GC×GC) with time-of-flight MS (ToF)-MS
  - Separates compounds in two dimensions: boiling point and polarity
  - Generates mass spectra for each peak
- GC×GC-ToF-MS will include
  - Automated data processing
  - Chemometric data interpretation



Conclusions/Future Work

- Adding a cleanup step affords greater sensitivity
  - More oil may be loaded into a sample
  - Biomarker signal is not affected by co-elution by aromatic or C15+ alkanes
  - This is particularly helpful for interpretation of relatively low concentrations of biomarker data as one may have in very mature oils and/or weathered samples
- *Expand this approach to other types of samples (sediments/soils and waters)*
- *Include other types of analyses/data processing*
  - *GC-MS/MS*
  - *GC-ToF-MS*

Questions?

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