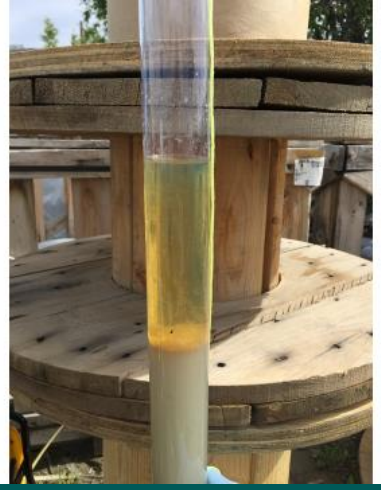


Light Petroleum Biomarker Mixtures: Challenges in Forensic Investigations

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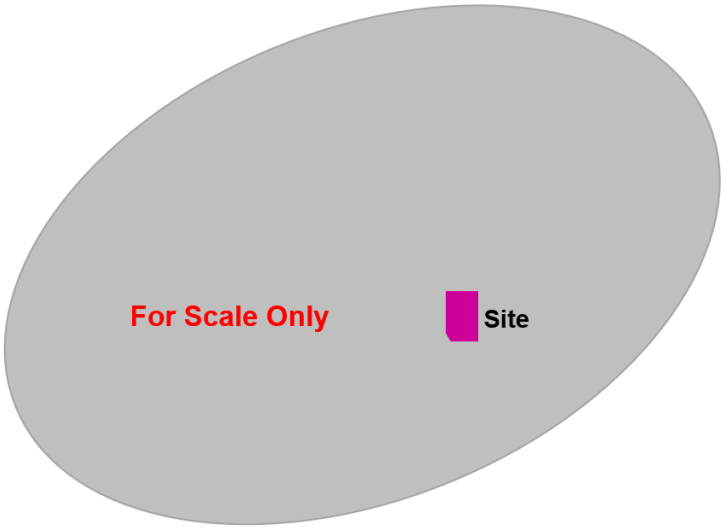
Birkholz, Consulting

PARACEL LABORATORIES LTD.

Hemmera
An Ausenco Company

Site Setting

- Site is located in Whitehorse, Yukon Territory, Canada
- North of 60° with typically cold winters
- Current site is part of a much larger historical industrial site with multiple potential sources of fuels



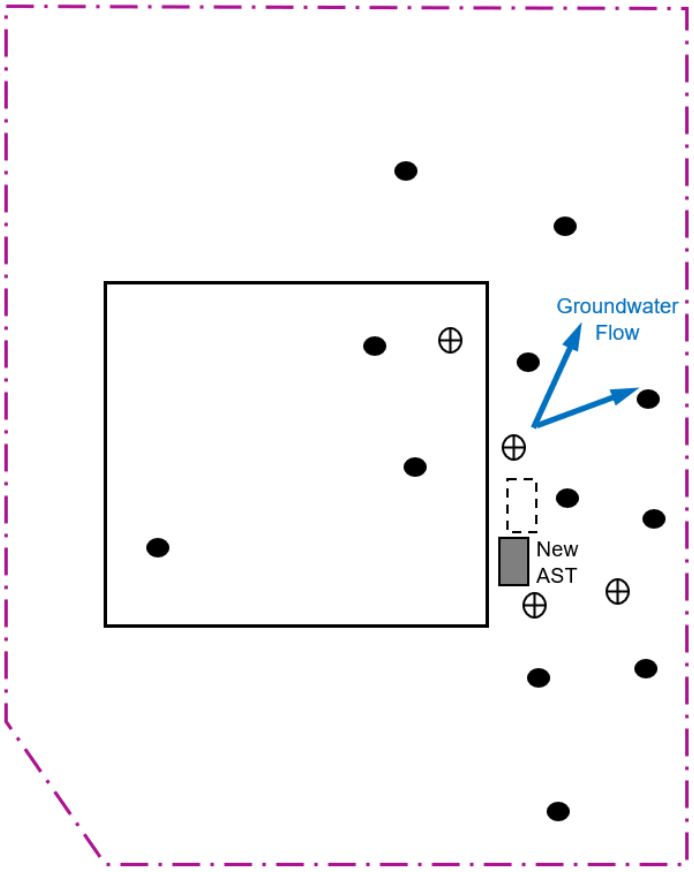
Map Image Source:
https://en.wikipedia.org/wiki/Yukon#/media/File:Yukon_in_Canada.svg

Phase II ESA

Completed two rounds of investigation in 2016

- 4 BHs and 12 MWs
- 4 interior holes, but locations were limited by available access
- Depth to groundwater

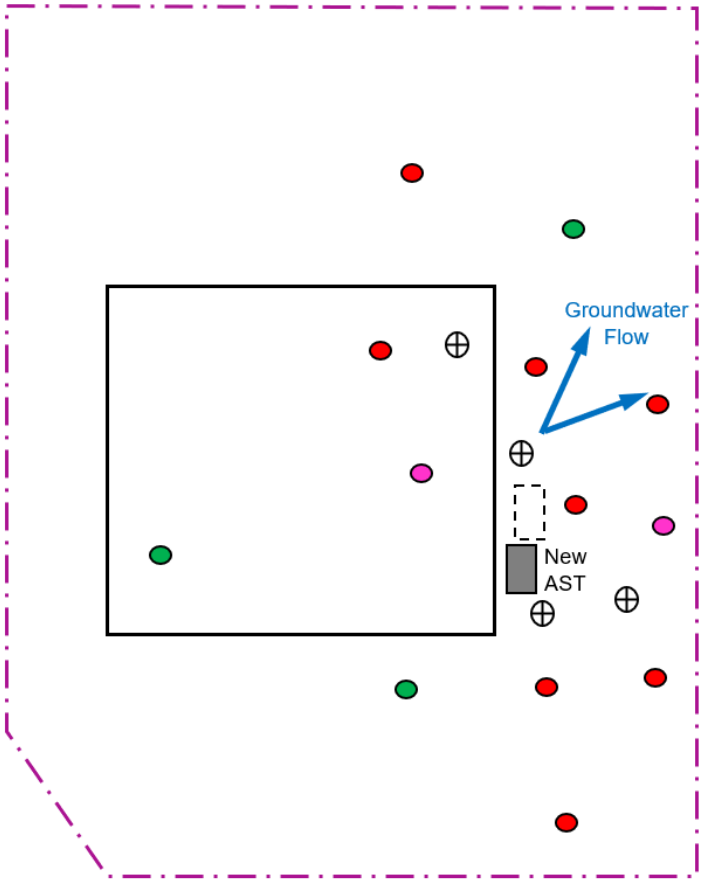
  4.5 to 5.0 m below grade
- Groundwater flow is to NE
- Silts with sand lenses found
- Some limitations noted with commercial analyses



Assessing Liability

Other sources of contamination possible?

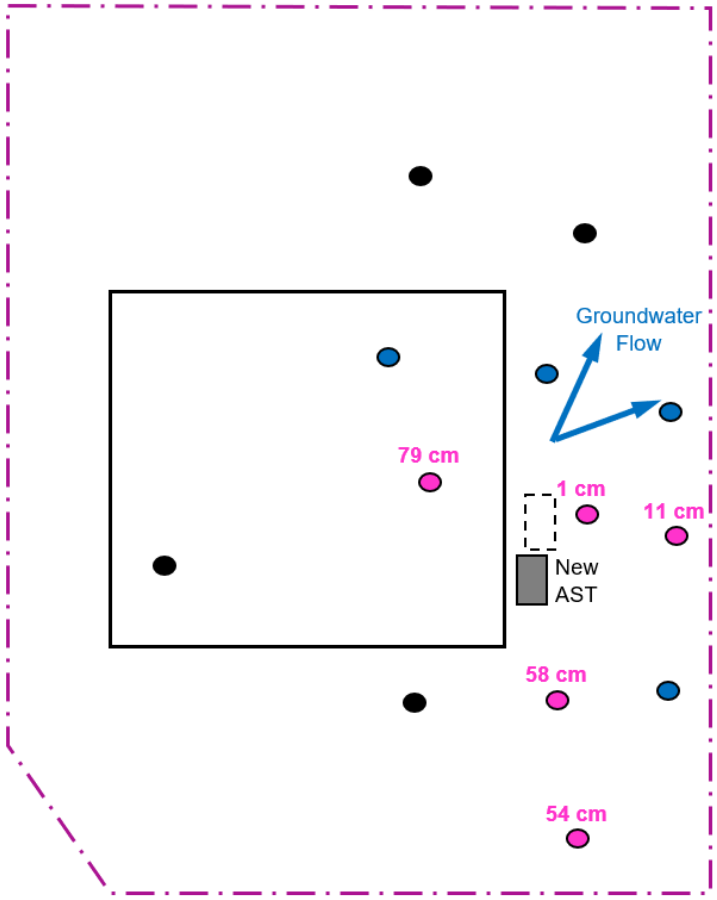
- Gasoline and heating oil identified
- Other sources were possibly located up to 15 m away from the former tank in silty soils?
- Age of spill and related contaminants unknown
- Tenant to cover their liability
- Free product - secondary source
- No utility information from City



Forensic analyses proposed

Based on Results of 2018 Monitoring Round

- June 2018, 2 years after Phase II ESA
- Significant product found
- LNAPL and water samples collected w/ legal protocols (prepared by Birkholz)
- Lab analyses performed by Paracel Labs in Calgary, Alberta, c/o Dr. Ralitsch



Forensic Analytical Methods

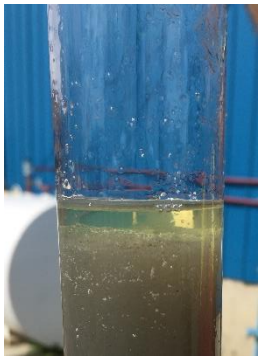
- Gas chromatograph / mass spectrometer
- Use of a high-resolution capillary column (PONA column)
- PIANO Analysis looks at paraffins, isoparaffins, aromatics, naphthenes, and olefins (GC/MS-SCAN)
- In addition, analytical procedure advocated by the Center for European Norms (EN 20xx) for light to heavy petroleum spills. Data collected for 44 compounds. (GC/MS-SIM).
- All samples were analyzed in duplicate.
- Legal sampling protocols complete with duplicates, field blanks, rinse blanks and trip blanks

LIST OF SAMPLES

Client I.D.	Matrix	Test(s) Required
MW 16-10	LNAPL	Forensics
MW 16-7	LNAPL	Forensics
MW 16-7 (Field Duplicate)	LNAPL	Forensics
MW 16-2 (source)	LNAPL	Forensics
MW 16-6	Water	Forensics
MW 16-4	Water	Forensics
MW 16-5	Water	Forensics
MW 16-14	LNAPL	Forensics

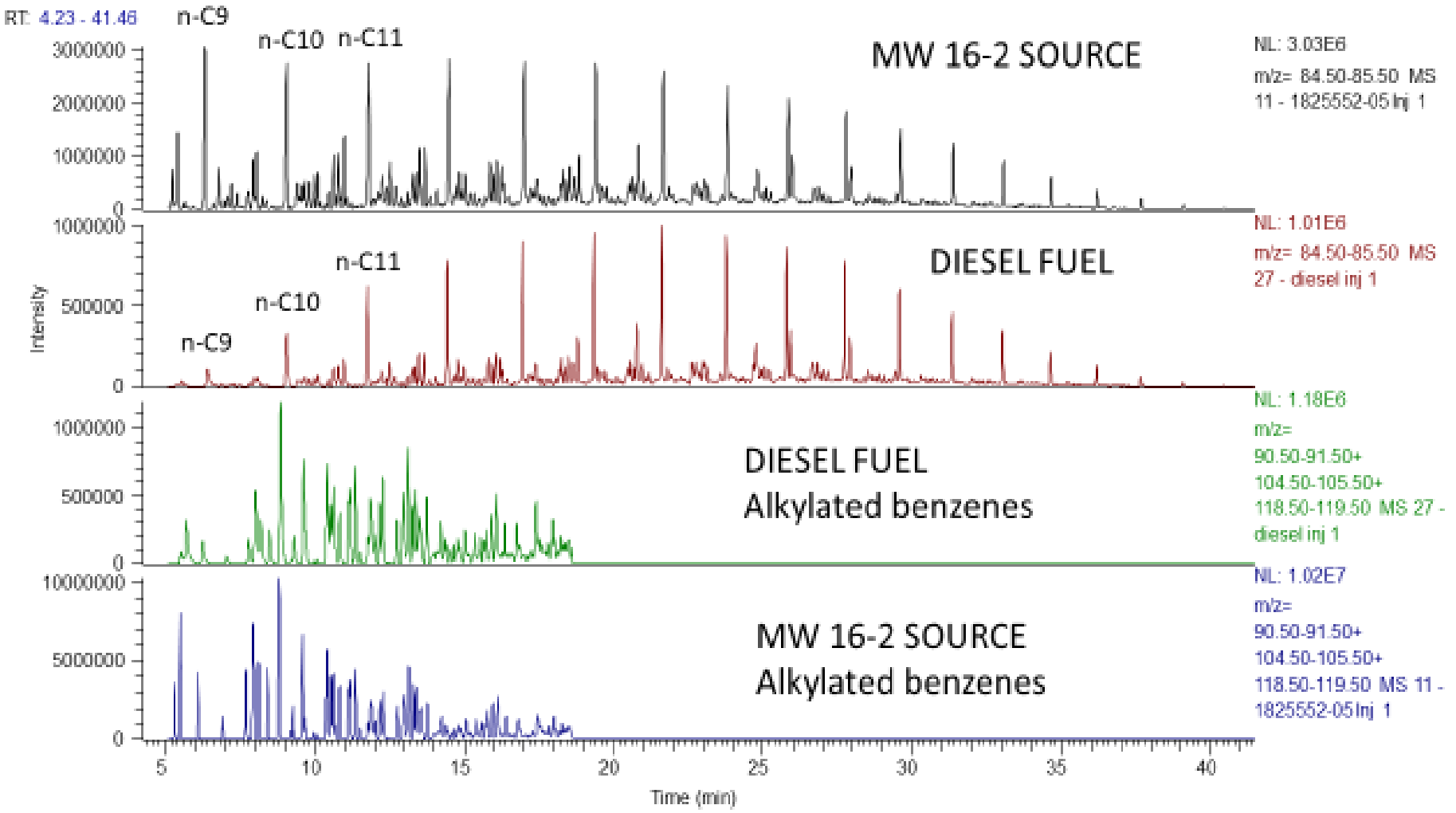
LNAPL Observations

MW1	MW2	MW3	MW4	MW5
1 cm	79 cm	11 cm	58 cm	54 cm

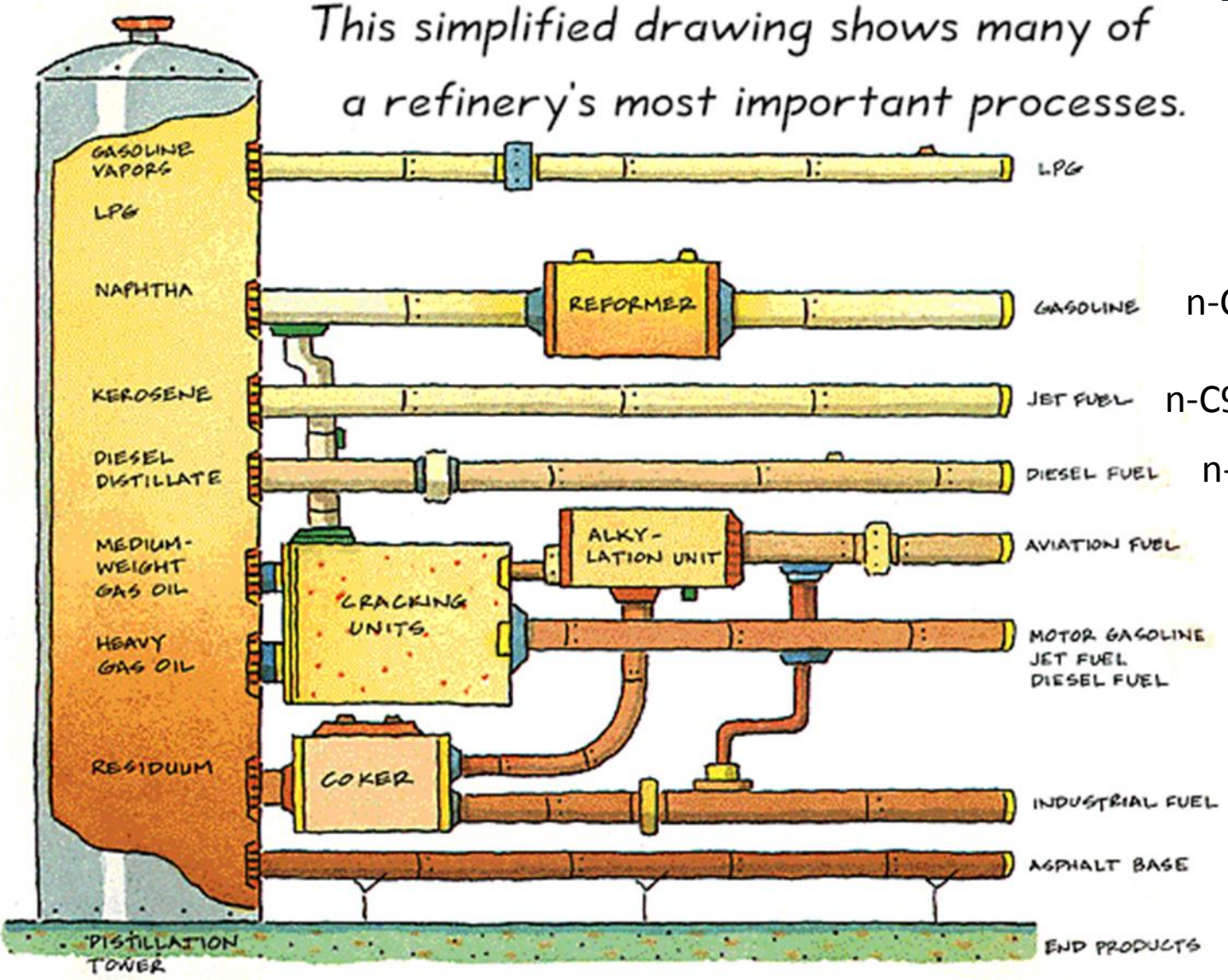


Water sample only

Alkanes and Alkylated Benzenes



Refining



n-C3 – n-C12

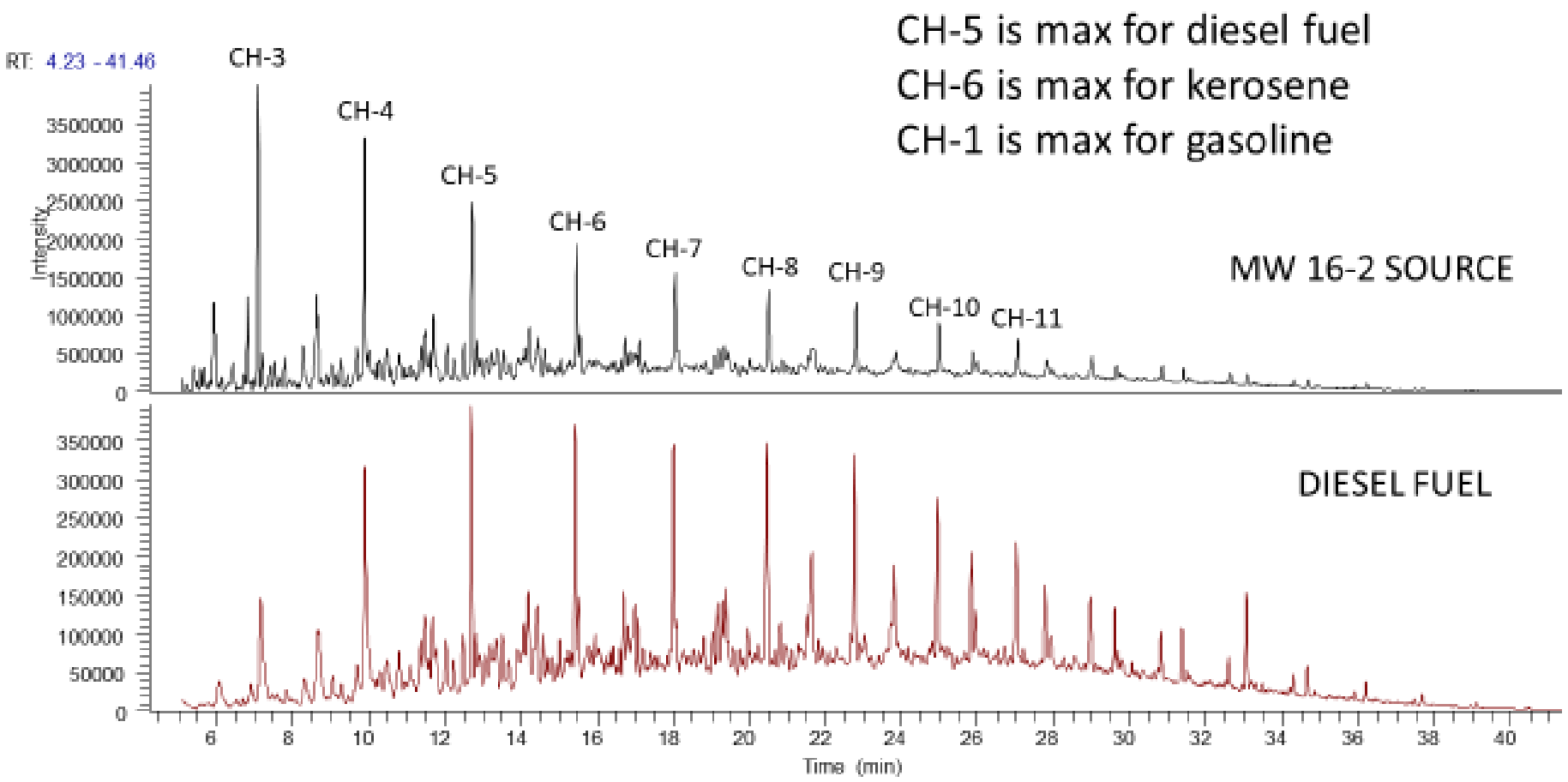
n-C9 – n-C15

n-C9 – n-C22

WINTER DIESEL

- Under winter conditions summer diesel (Diesel No. 2) can gel-up and turn into a gelatinous mess.
- To stop this from happening Winter diesel (Diesel No. 1) is prepared by adding kerosene which helps lower the pour-point & cloud point of the diesel to prevent it from gelling up and keep it flowing easily.
- Ratio of diesel to kerosene is: 80:20; 70:30; 60:40 and 50:50 depending upon temperature in the winter.
- Winter Diesel usually a mixture between Diesel No.1 and No.2. Ratios of 80:20 and 50:50 have been used No.1 : No.2

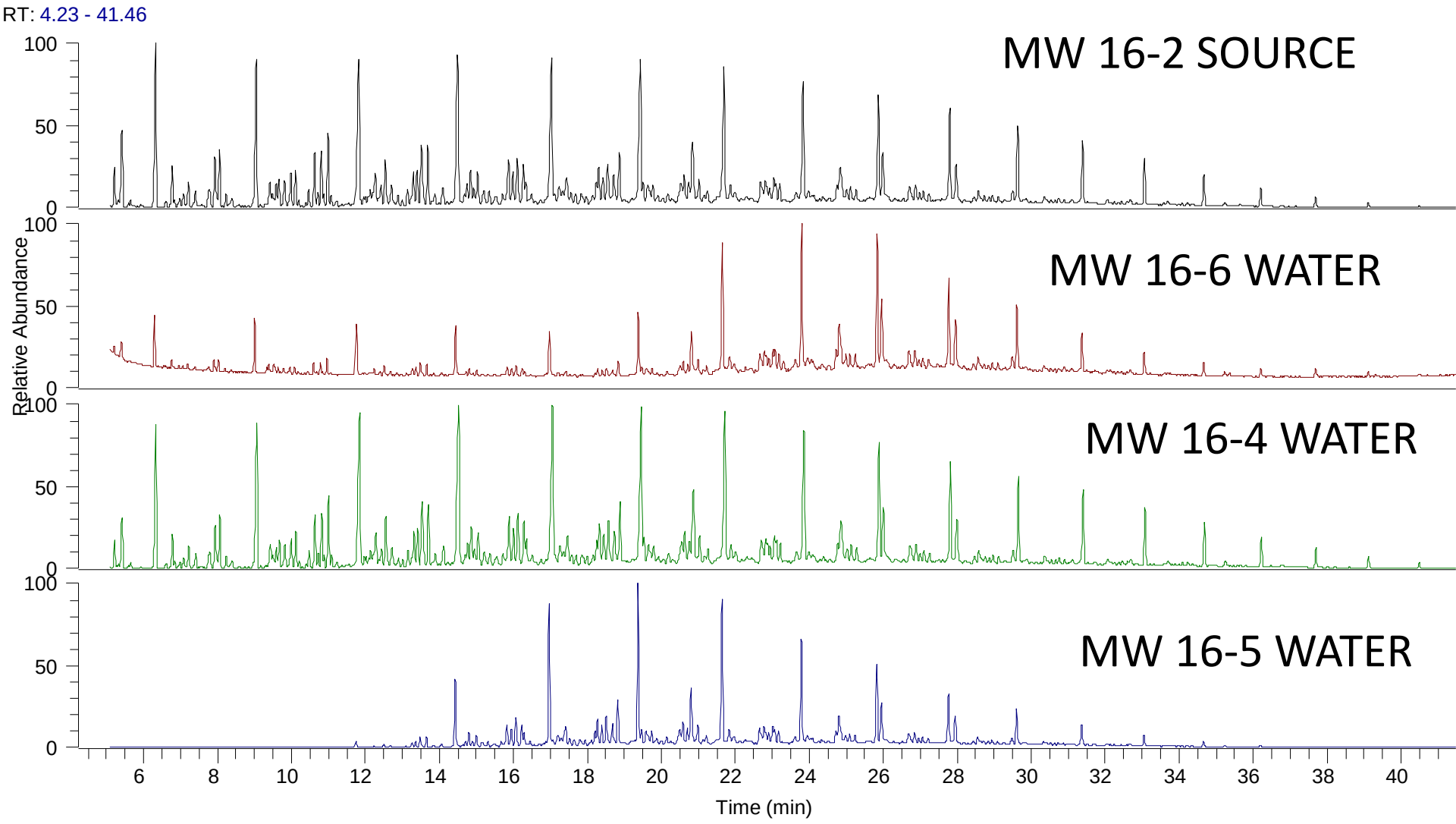
ALKYLCYCLOHEXANES



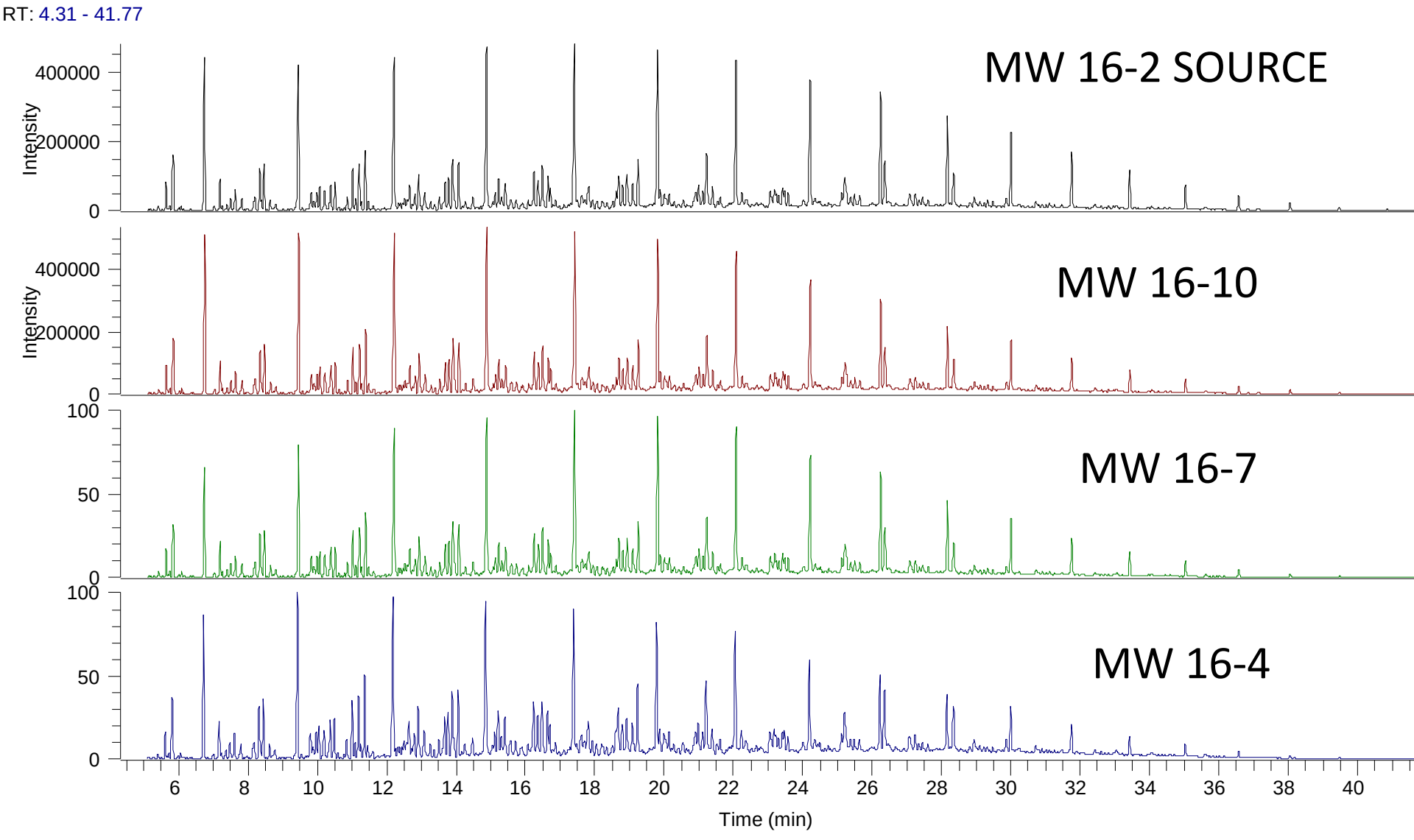
MW 16-2 SOURCE

- Is clearly a mixture containing gasoline and diesel fuel
- No evidence of kerosene
- Why they mixed gasoline with diesel is unknown, perhaps to make a winter diesel, ie. keep diesel fuel from gelling up
- This mixture represented the source of the spill material.

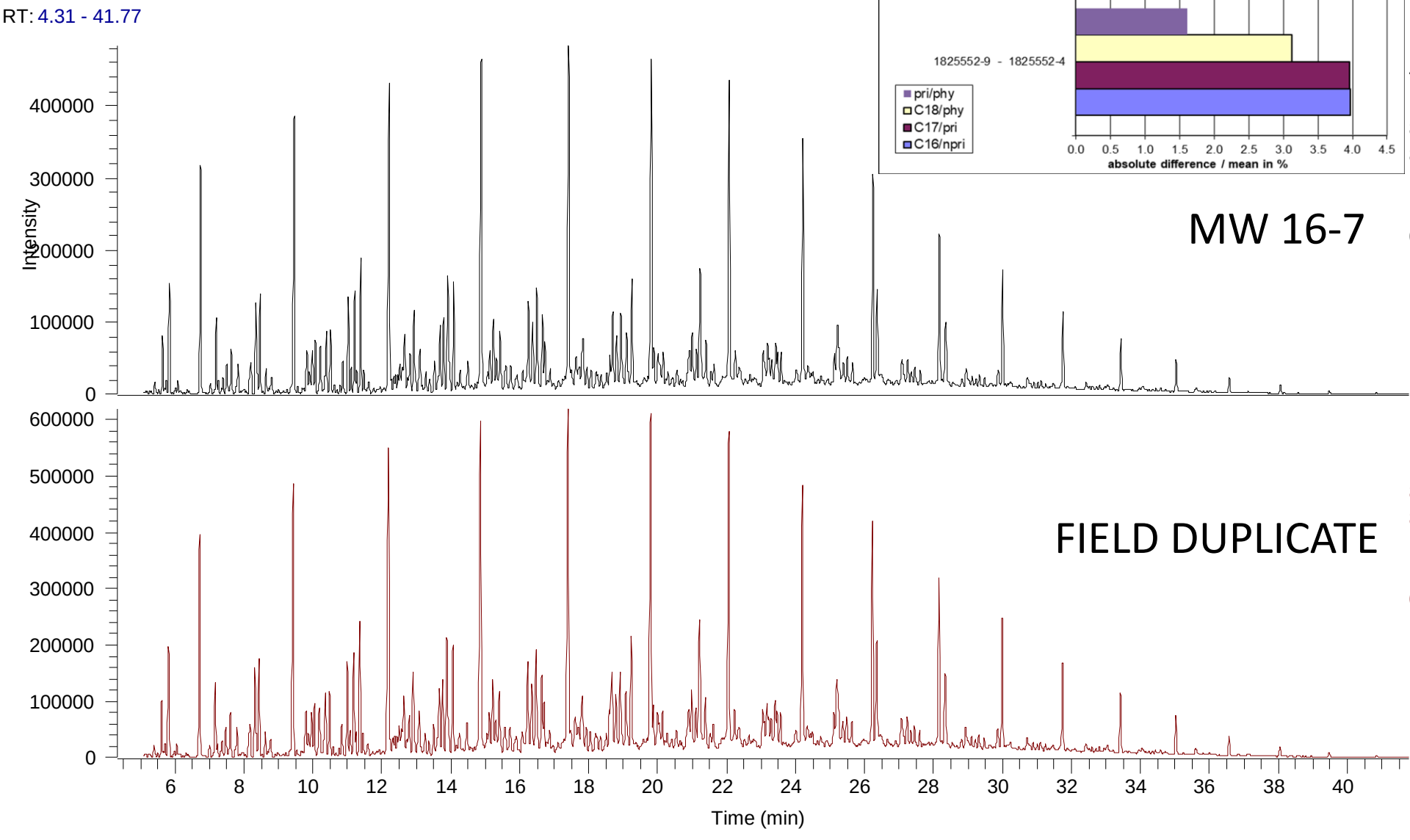
Comparison Source and Water Samples



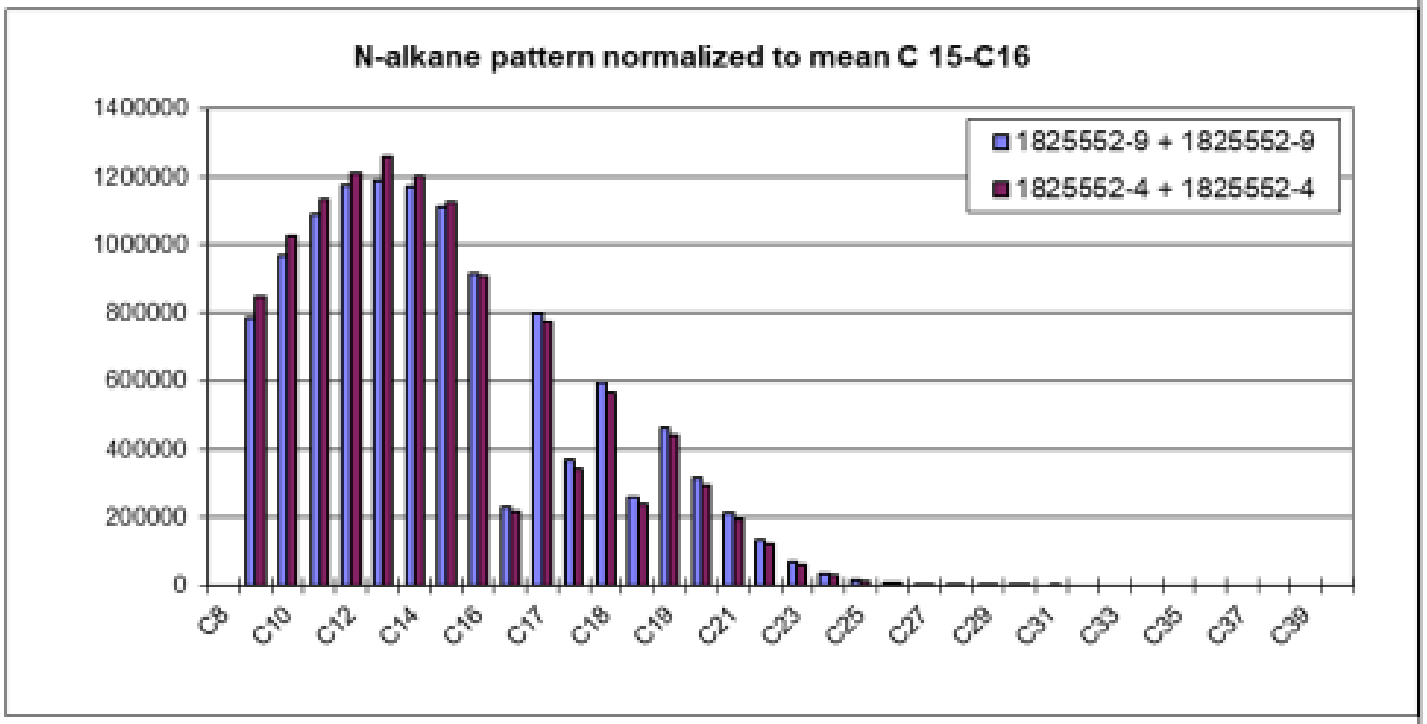
COMPARISON SOURCE AND LNAPL

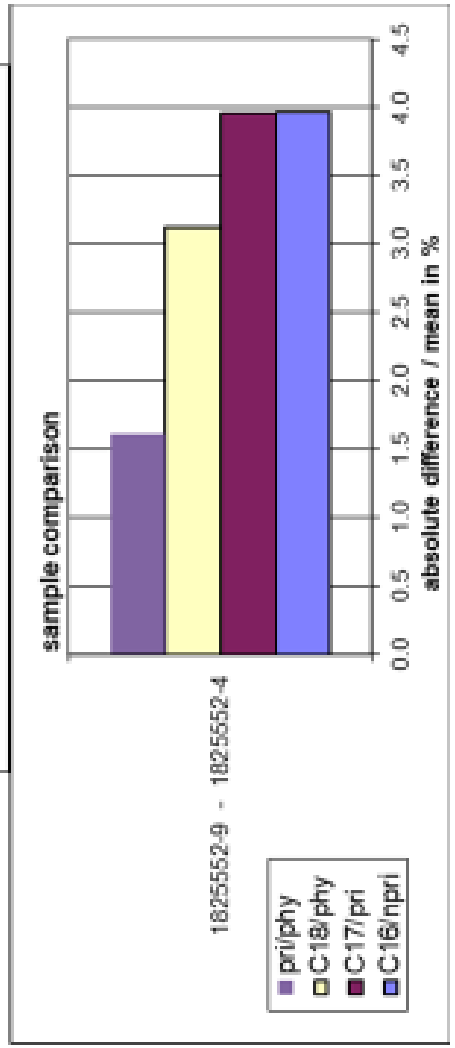


COMPARISON FIELD DUPLICATE



Comparison of MW 16-7 with Field Duplicate





COMPARISON OF MW-16-7 (-4) WITH FIELD DUPLICATE (-9)

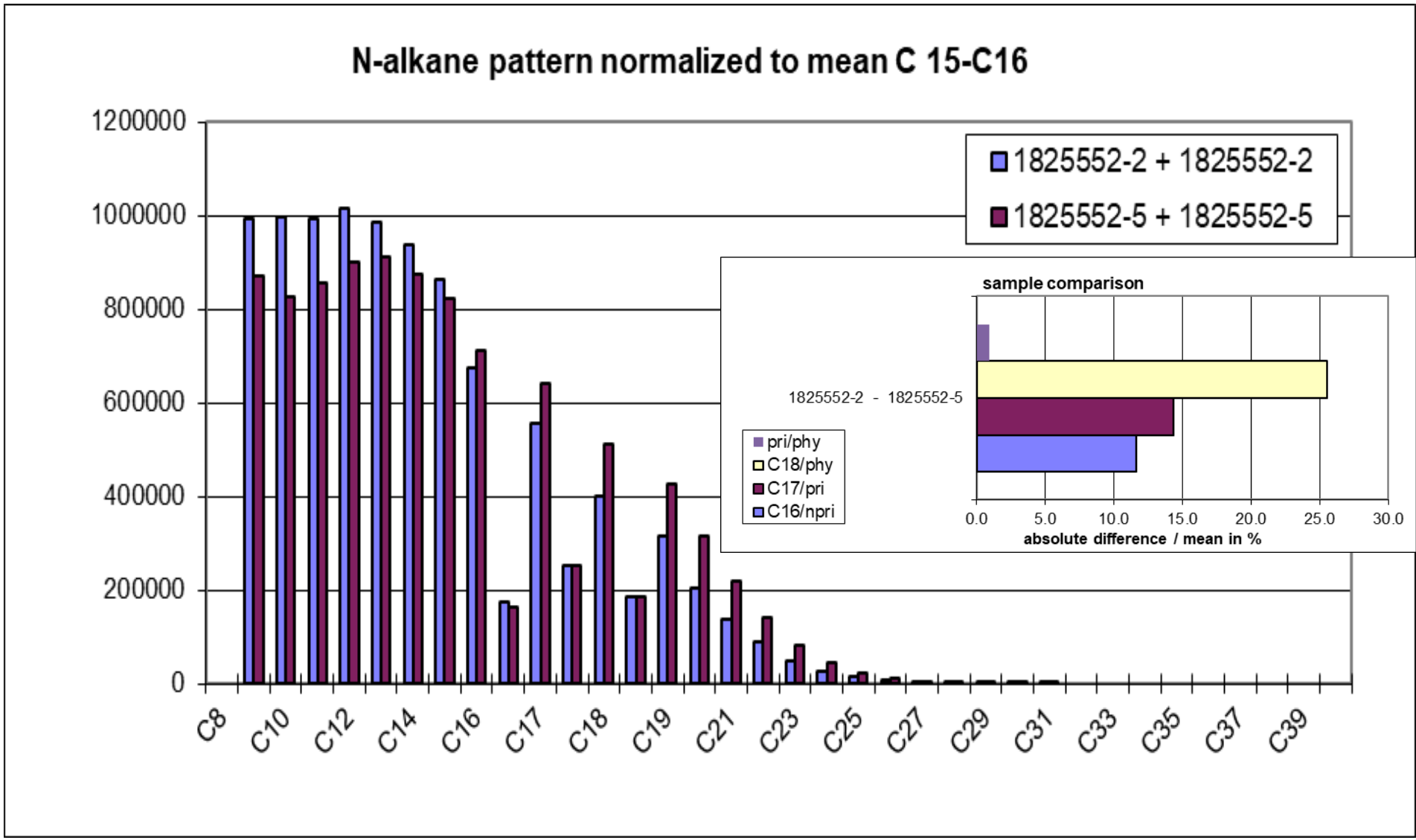
ALKANE/ISOPRENOID RATIOS

Sample	MW 16-2	MW 16-6	MW 16-10	MW 16-4	MW 16-7	MW 16-7D	MW 16-5	MW 16-14
Matrix	LNAPL	WATER	LNAPL	WATER	LNAPL	LNAPL	WATER	LNAPL
Alk/Isp Ratio	USING EN 20XX i.e. m/z 113							
n-C17/Pri	0.72	**0.59**	0.64	0.69	0.65	0.66	**0.61**	**0.40**
n-C18/Phy	1.35	**0.99**	**1.13**	1.30	1.20	1.24	**1.03**	**0.67**
Pri/Phy	2.09	2.30	2.11	2.05	2.19	2.21	**2.43**	2.06
	SOURCE			**MATCH**	**MATCH**	**MATCH**		

RATIOS IN RED EXCEED 14% RELATIVE DIFFERENCE

CONCLUDE A NON-MATCH ***UNLESS CAN BE EXPLAINED***

Comparison Source (-05) with MW 16-10 LNAPL (02)



EN 20xx Method

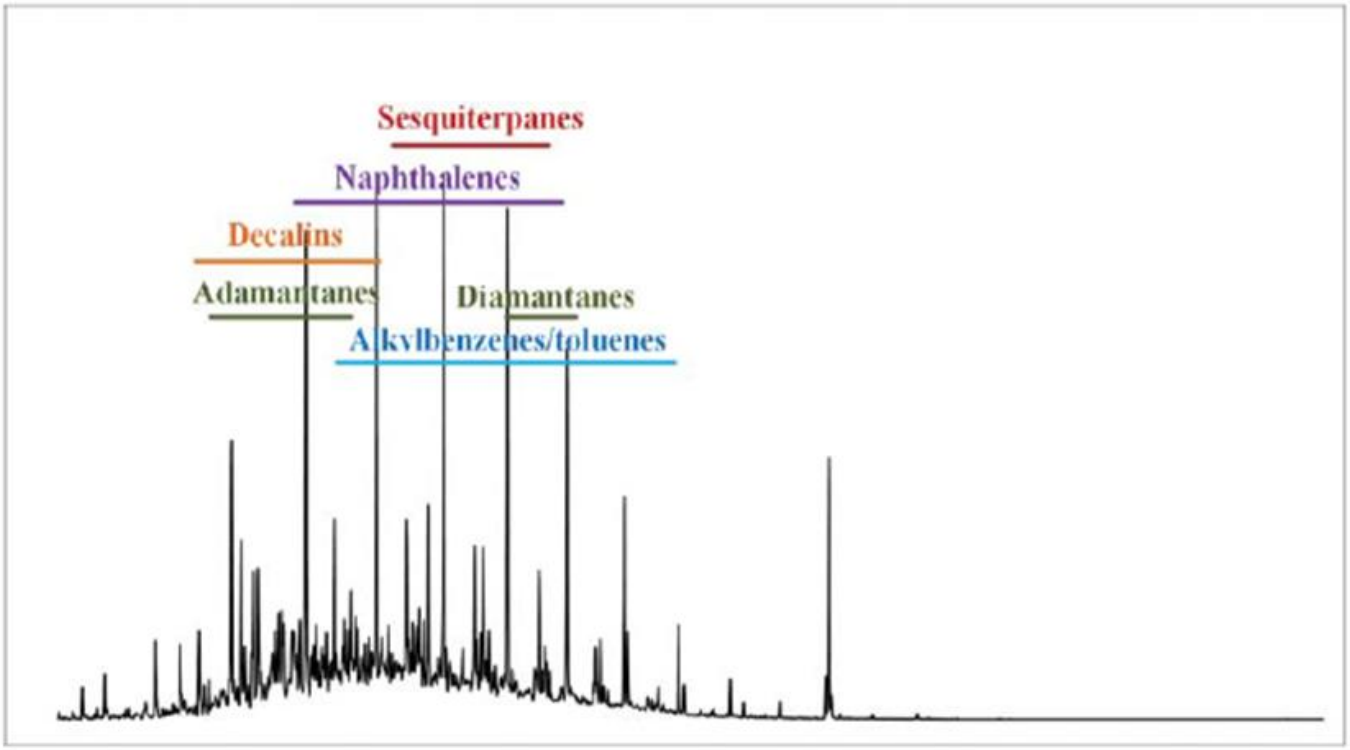
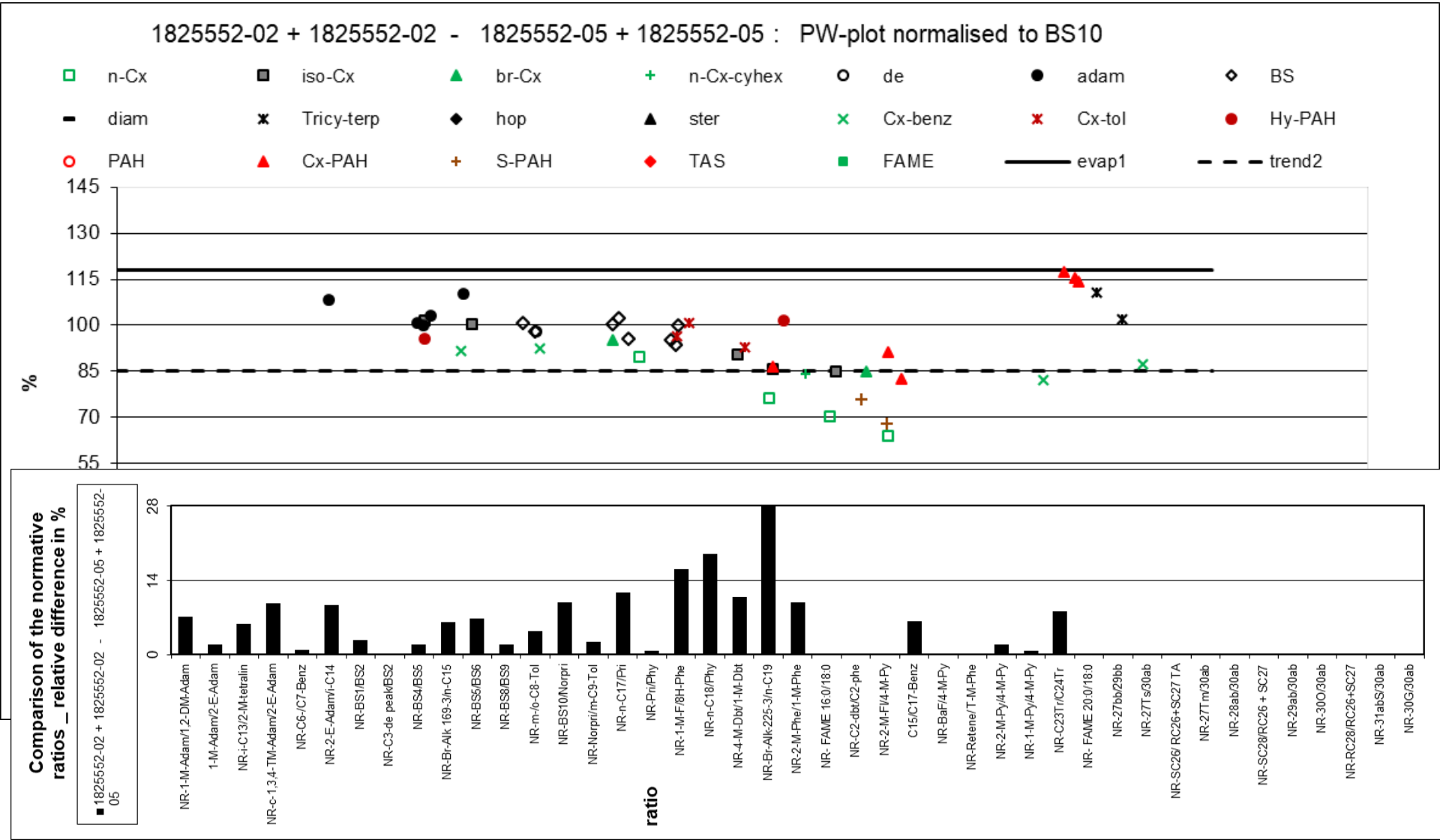
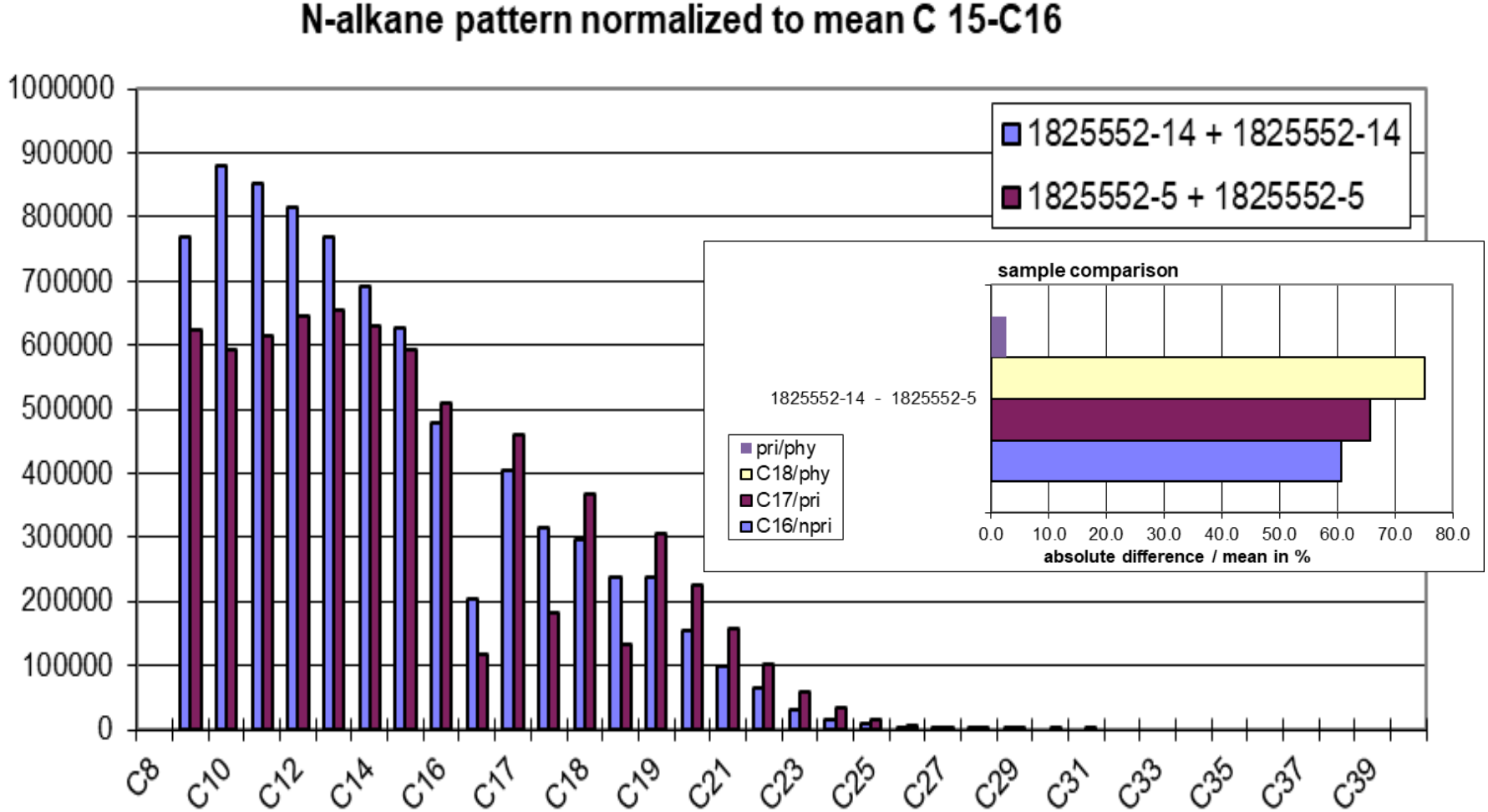


Figure 1. Chromatographic intervals, compared against a MK1 diesel oil chromatogram, for (a) the 70 compounds in the CEN (2012) guidelines and (b) the compounds in the present study.

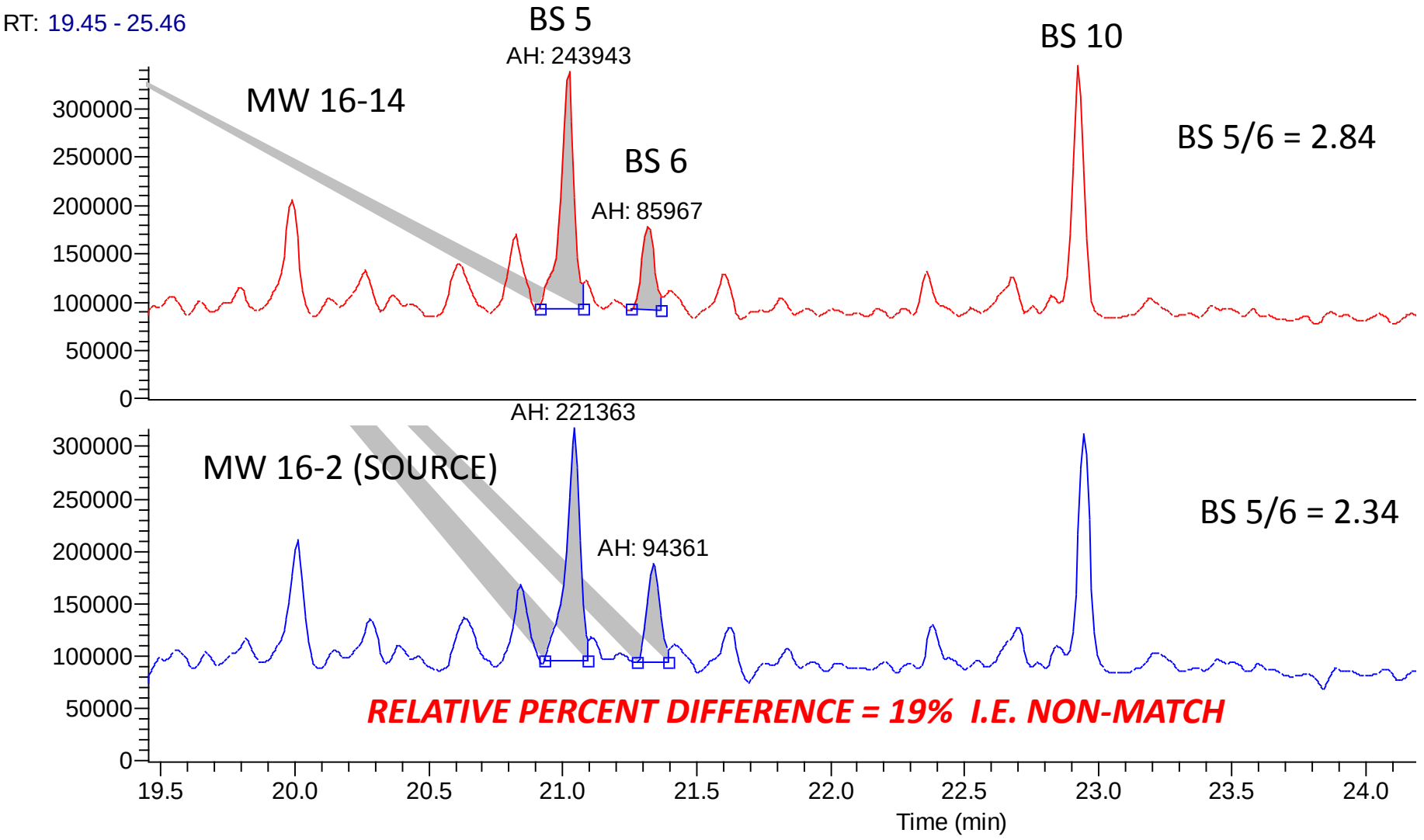
COMPARISON SOURCE & MW 16-10 (LNAPL)



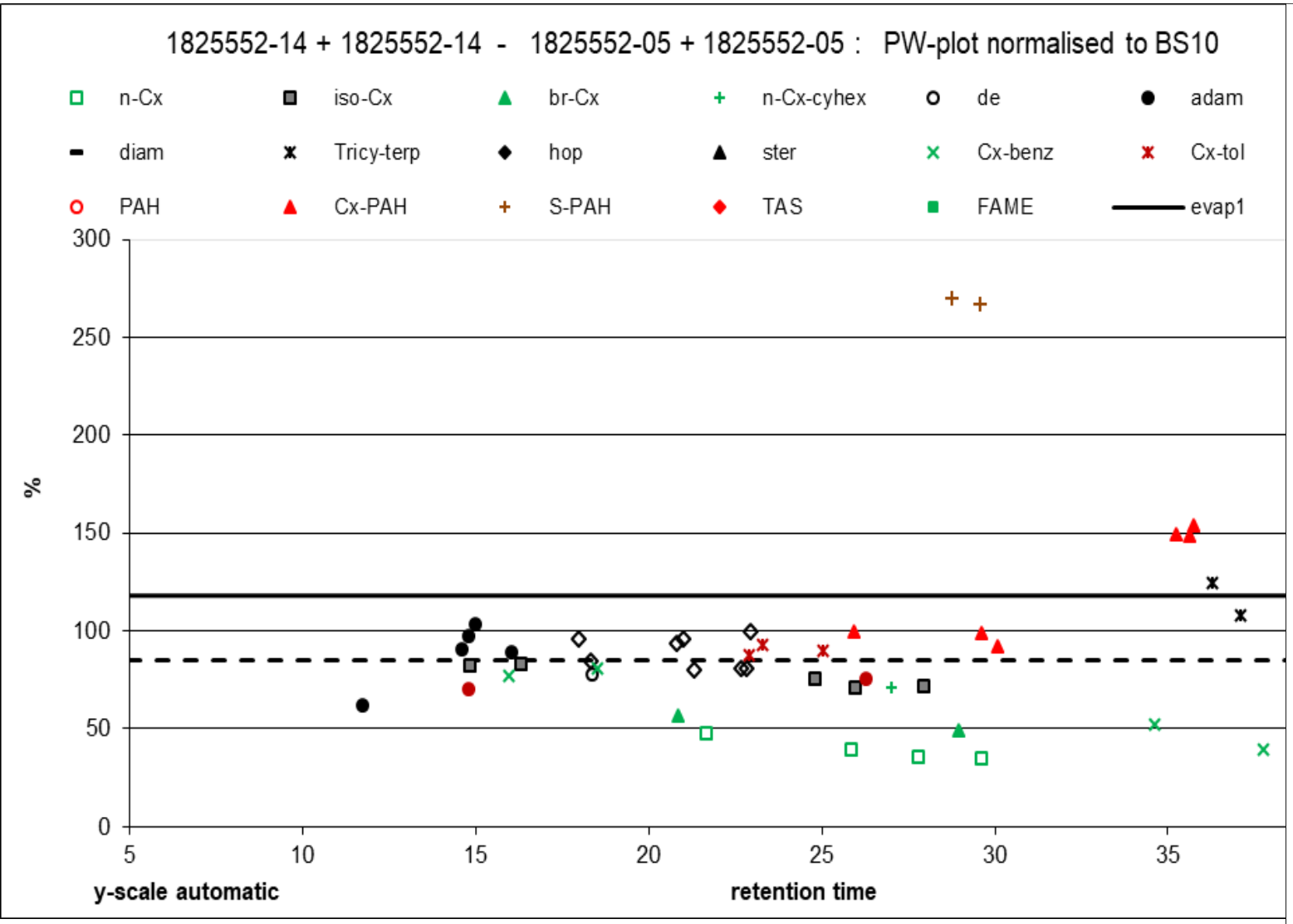
Comparison of MW-14 (-14) LNAPL with Source (-05)

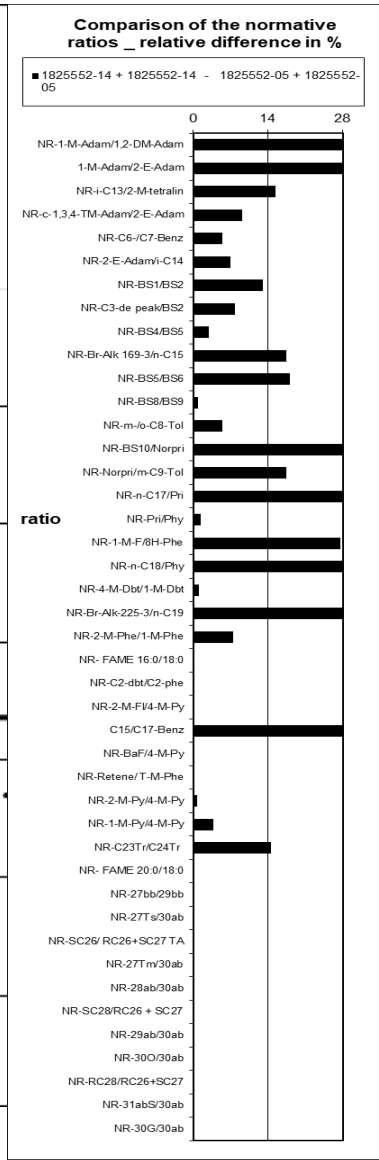


COMPARING MW 16-14 and SOURCE BICYCLIC SESQUITERPANE RATIOS

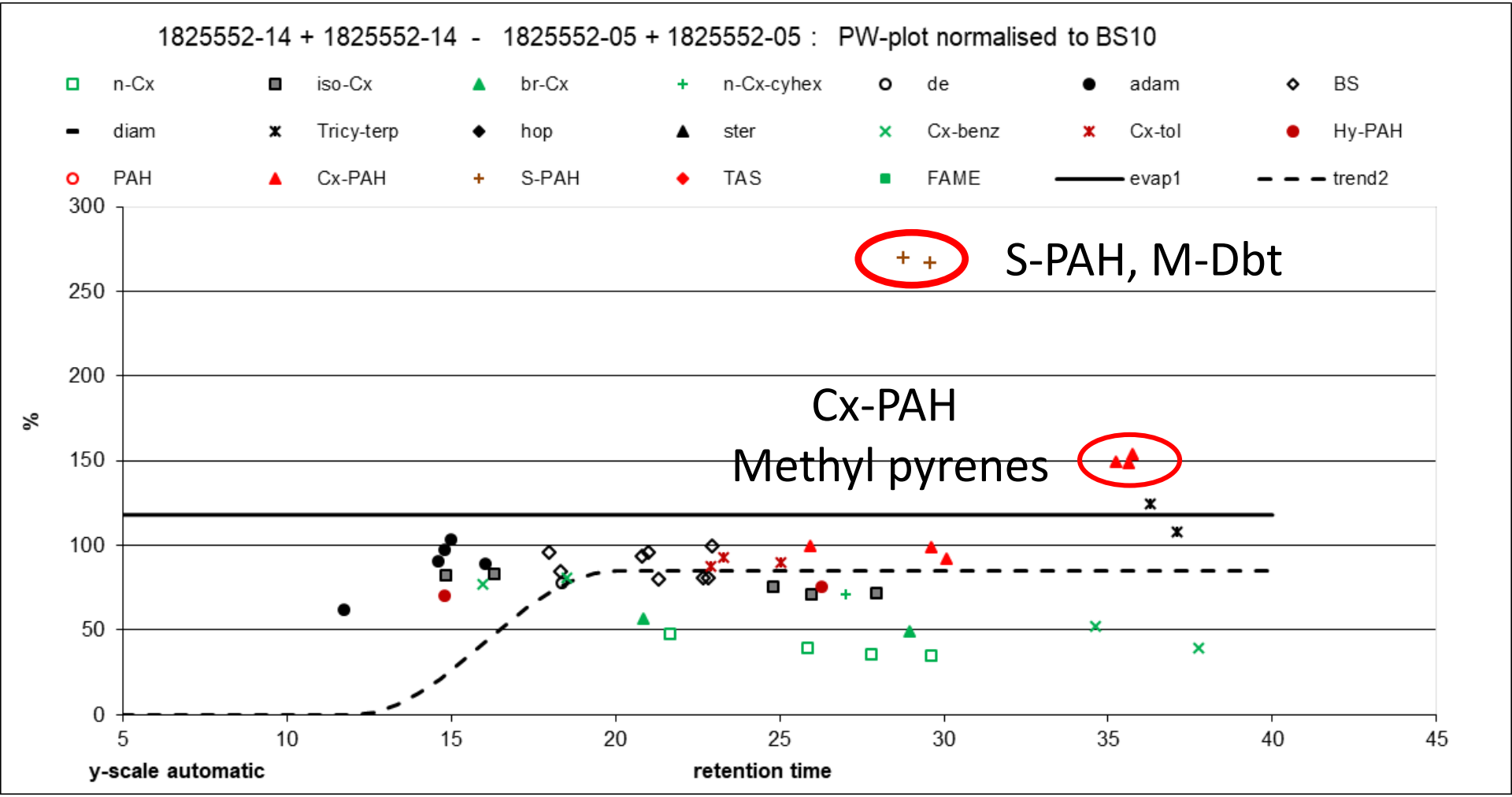


Comparison MW -14 (-14) LNAPL with SOURCE (-05)

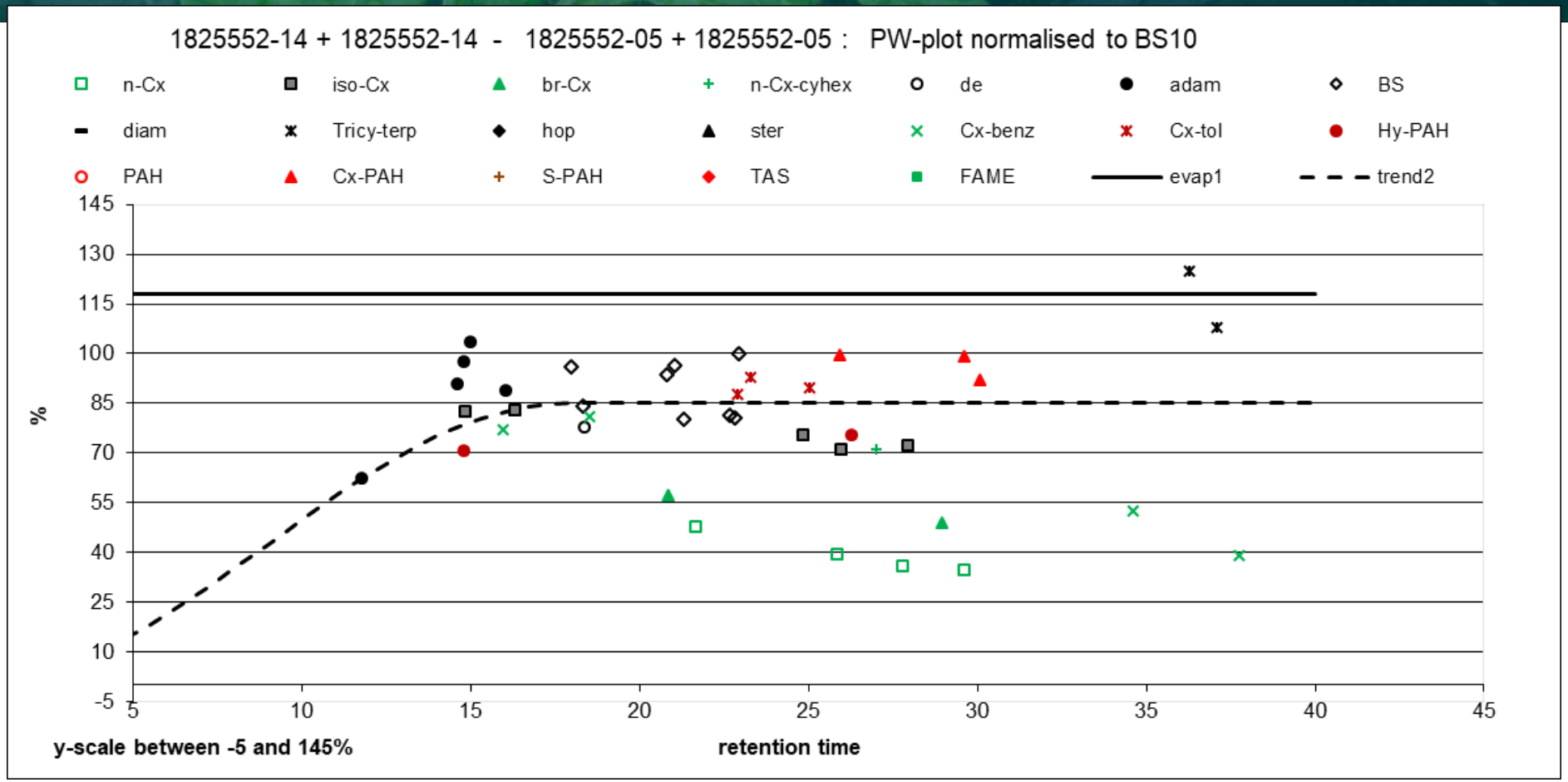




Comparison of MW 16-14 and source

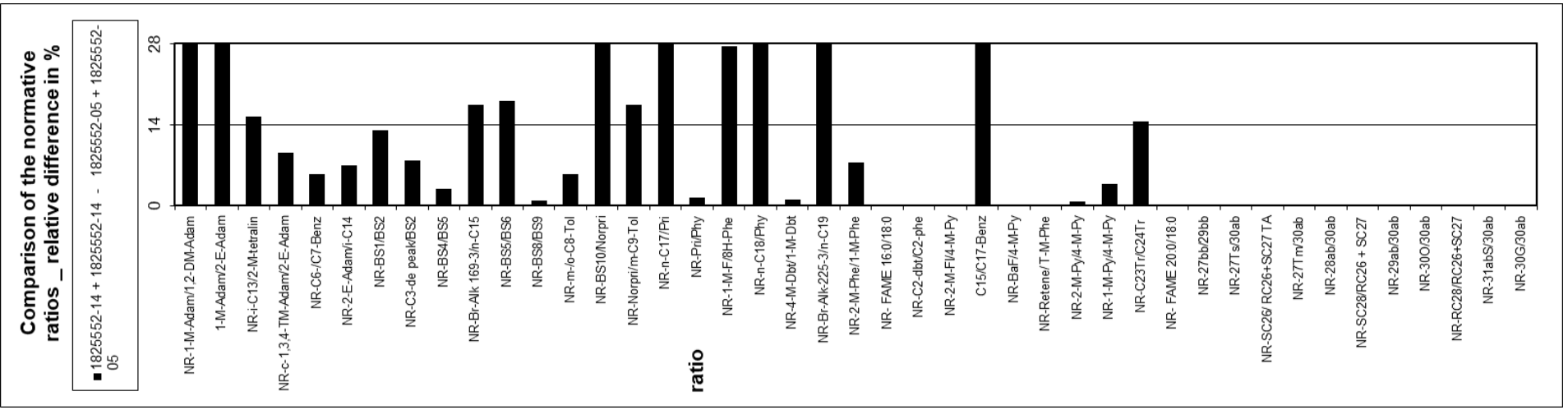


Comparison of MW 16-14 and source



Lower levels of 1-M-Adam, n-alkanes, branched alkanes, sesquiterpanes, isoprenoids, alkylated benzenes, indicative of evaporation and biodegradation

Comparison of MW 16-14 and source



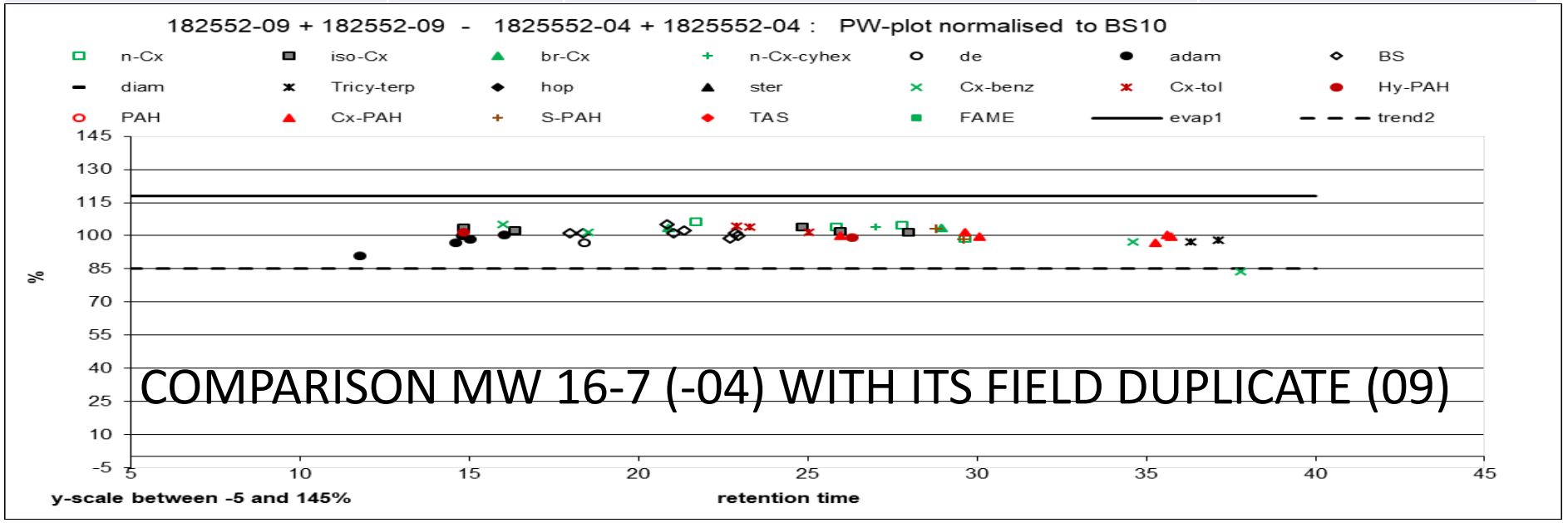
13 normative ratios exceed 14% relative difference

Based on the GC/MS PW plots all can be explained by weathering (evaporation and biodegradation)

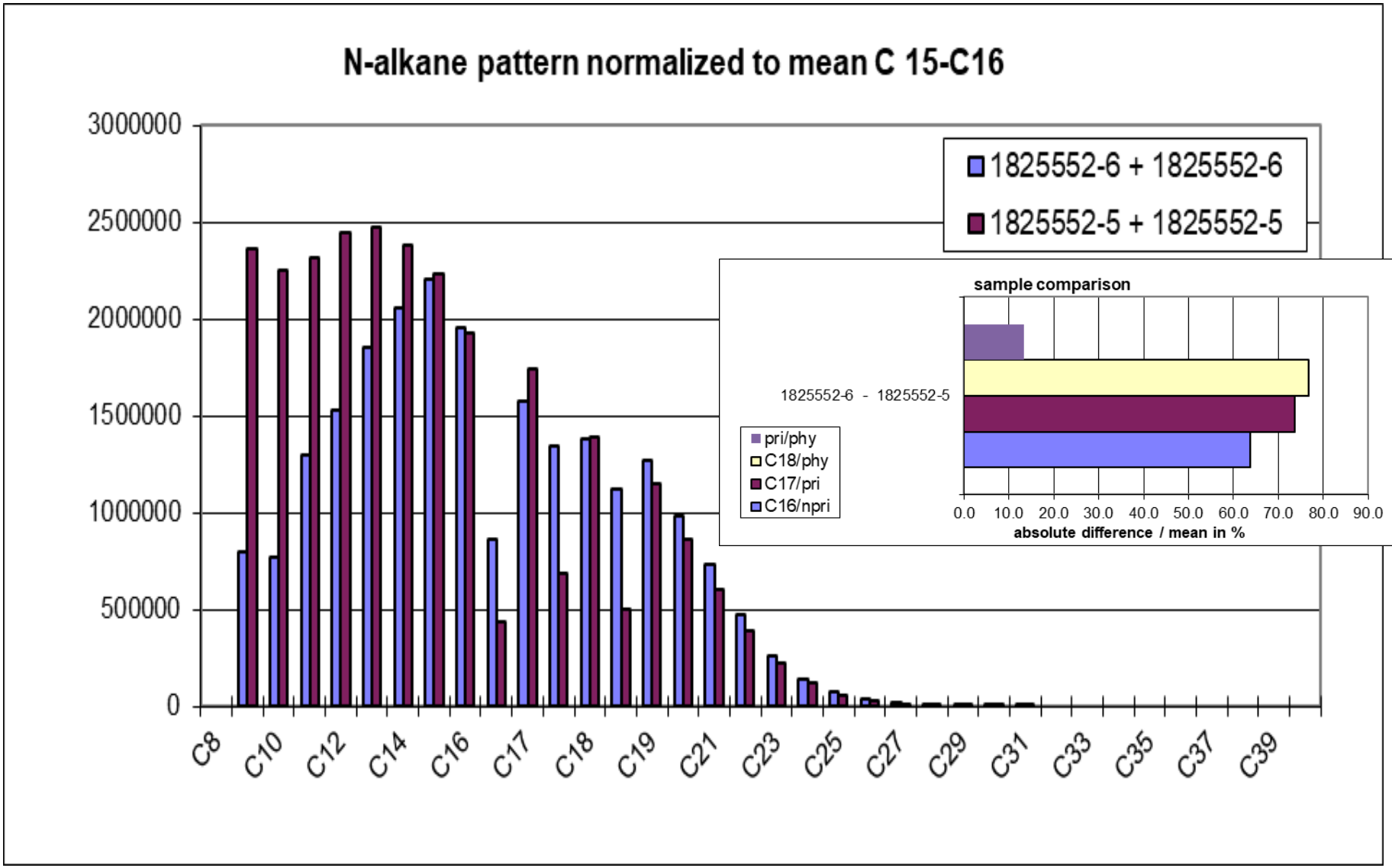
We conclude that MW 16-14 is a positive match with source MW 16-2

LNAPL COMPARISONS WITH SOURCE

Sample ID	#-Flags	Explained by weathering	Conclusion
MW16-10	3	yes	Positive match
MW16-7	1	Yes	Positive match
Duplicate MW16-7	2	Yes	Positive match
MW16-14	13	Yes	Positive match

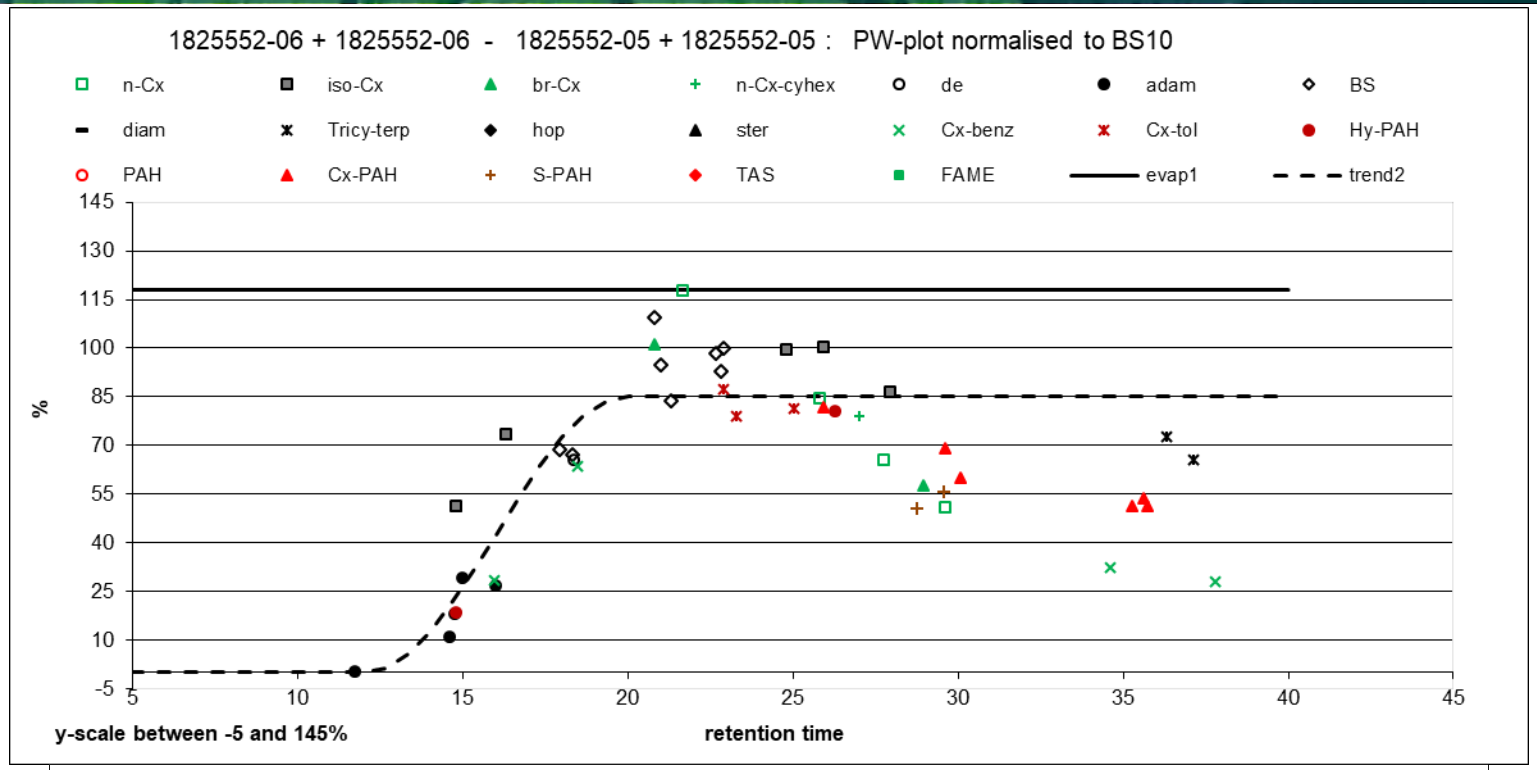


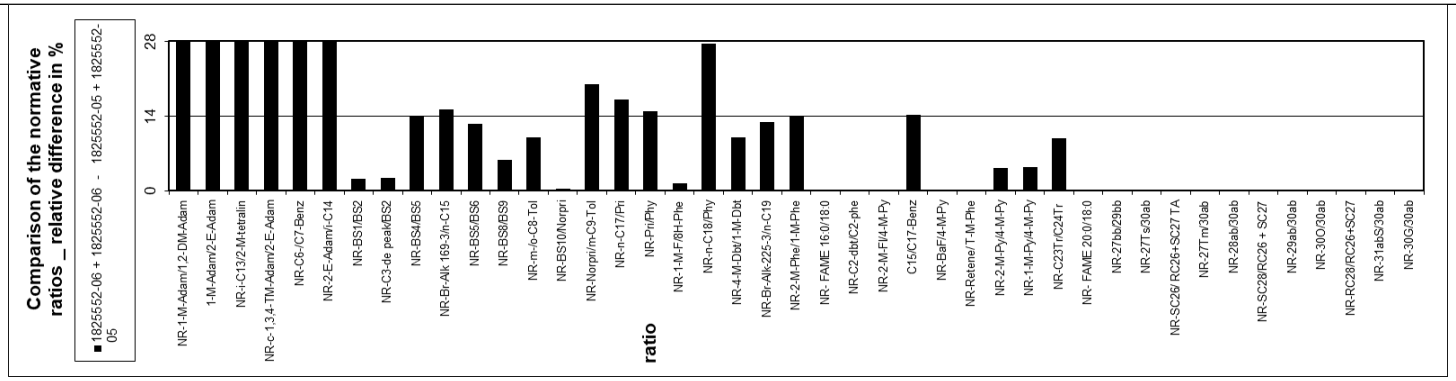
Comparison of MW 16-5 water (-06) with Source (-05)



Comparison of MW 16-5 (water) with Source

CONCENTRATION DIFFERENCE 40-FOLD





Comparison of Water Samples with Source

Sample ID	# of Flags	Explained	Conclusion
MW16-6	15	Yes	Positive match
MW16-4	12	Yes	Positive match
MW16-5	13	Yes	Positive match

Conclusions

- LNAPL samples MW 16-10 MW16-7, its Duplicate and MW16-14 deemed a positive match with MW16-2 (source)
- Water samples MW16-4, MW 16-5 and MW 16-6 deemed a positive match with MW16-2
- Chromatograms can be misleading and reliance upon them for source sample comparisons can be erroneous.
- The same applies for chemical ratios
- GC/MS PW plots are essential in understanding the behaviour of petroleum biomarkers.
- They allow us to explain differences.
- For mixtures, concentration differences between source and spill can be a challenge for interpretation

Thank You. Questions?

Contact Us

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