Electronic Supplementary Material (ESI) for Analytical Methods.
This journal is © The Royal Society of Chemistry 2020

Tiered approach to long-term weathered lubricating oil analysis: GC/FID, GC/MS diagnostic ratios, and multivariate statistics

Supplementary Information

SI Table 1 List of 78 biomarker ratios examined in diagnostic ratio analysis[1]

NR-1-M-Adam/1,2-DM-Adam	NR-29ab/30ab
NR-1-M-Adam/2-E-Adam	NR-30O/30ab
NR-i-C13/2-M-tetralin	NR-RC28/RC26+SC27 TA
NR-c-1,3,4-TM-Adam/2-E-Adam	NR-31abS/30ab
NR-C6-/C7-Benz	NR-30G/30ab
NR-2-E-Adam/i-C14	De/1-M-Adam
NR-BS1/BS2	1-M-Adam/2-M-Adam
NR-C3-de peak/BS2	1,3,5-TM-Adam/tr-1,4-DM-Adam
NR-B/2-E-N	1,3,5-TM-Adam/1,3,6-TM-Adam
NR-2-E-N/2,6+2,7 DM-N	C1-de_s/C2-de_s
NR-BS4/BS5	tetralin/2-M-tetralin
NR-Br-alk-169-3/n-C15	1,2,5,7-TeM-Adam/2-E-Adam
NR-BS5/BS6	1,2,5,7-TeM-Adam/BS10
NR-BS8/BS9	m-C6-Tol/BS10
NR-m-/o-C8-Tol	m-/o-C6-tol
NR-BS10/Norpri	C7-/C10-Benz
NR-Norpri/m-C9-Tol	BS3/BS5
NR-C10-Benz/n-C11-CyC6	1,6-DM-N/1,3+1,7-DM-N
NR-n-C_{17}/Pri	ANY/ 1,2-DM-N
NR-Pri/Phy	Diam/4-M-Diam
NR-n-C_{18}/Phy	FAME 12:0/16:0
NR-4-M-Dbt/1-M-Dbt	1,3,7 TM-N/1,3,6-TM-N
NR-Br-alk-225-3/n-C19	BS8/BS10
NR-2-M-Phe/1-M-Phe	8H-A/8H-Phe
NR-FAME 16:0/18:0	1-M-F/8H-Phe
NR-C2-dbt_s/C2-phe_s	FAME 14:0/16:0
NR-2-M-Fl/4-M-Py	FAME 16:1/16:0
NR-C15-Benz/C17-Benz	1-E-Phe/1,7-DM-Phe
NR-BaF/4-M-Py	C3-dbt_s/C3-phe_s
NR-Retene/ 29bb	FAME 18:2/18:0
NR-2-M-Py/4-M-Py	FAME 18:1 +18:3/18:0
NR-1-M-Py/4-M-Py	C21Tr/C23Tr
NR-C23Tr/C24Tr	C23Tr/phy-tol
NR-27bb/29bb	FAME 20:0/18:0
NR-27Ts/30ab	C20TA/C21TA
NR-SC26/ RC26+SC27 TA	C21TA/ RC26+SC27 TA
NR-27Tm/30ab	C28(22S)/30ab
NR-28ab/30ab	BaPy/BePy
NR-SC28/RC26 + SC27 TA	29aaS/29aaR

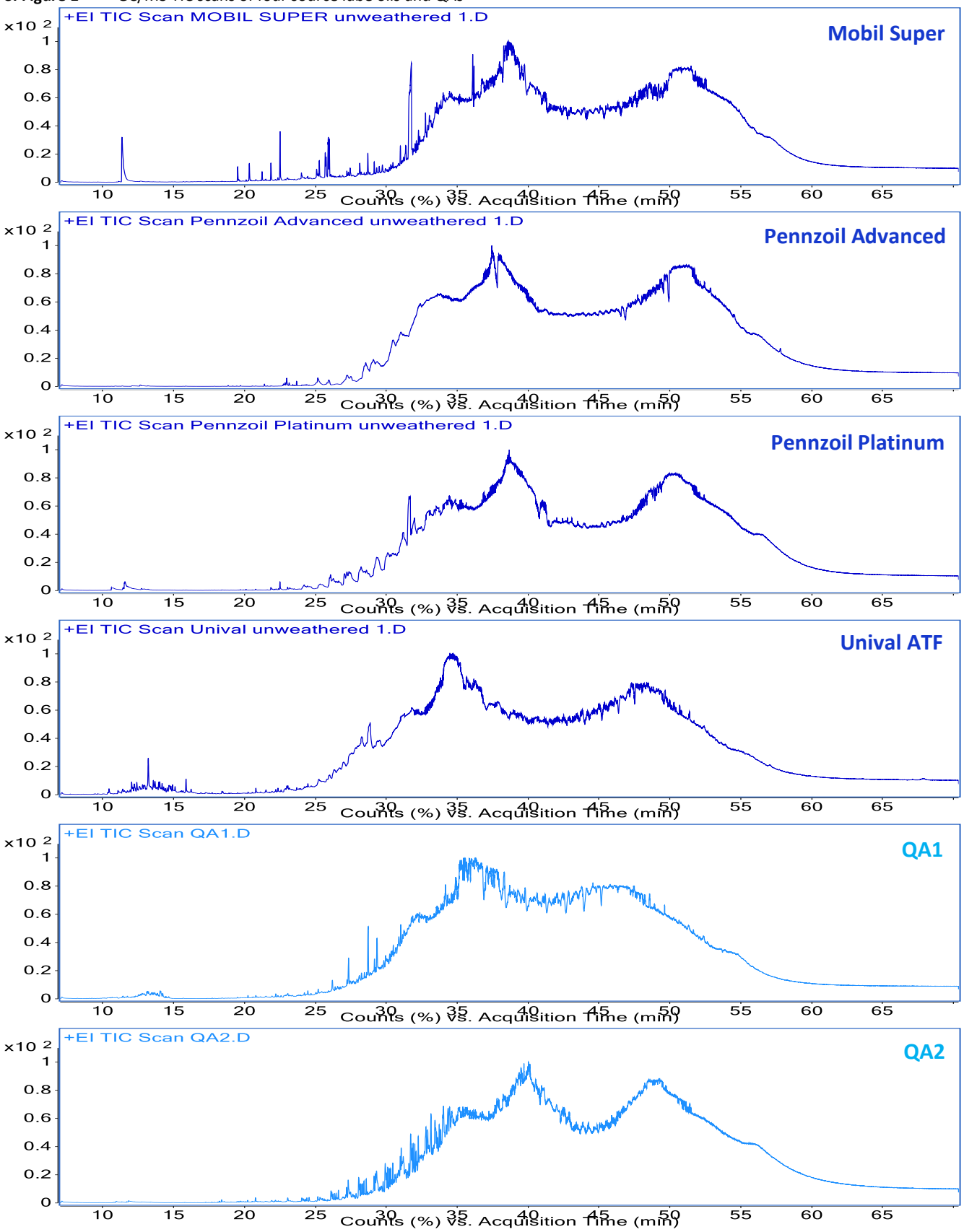
SI Table 2 PLSDA model confidence values

Identifier	Oil Name	Predicted Label	Confidence Measure
Mobil Super unweathered-1	Mobil Super	Mobil Super	0.807
Mobil Super unweathered-2	Mobil Super	Mobil Super	0.832
Mobil Super unweathered-4	Mobil Super	Mobil Super	0.989
Mobil Super unweathered-5	Mobil Super	Mobil Super	0.745
Mobil Super unweathered-6	Mobil Super	Mobil Super	0.848
Pennzoil Advanced unweathered-1	Pennzoil Advanced	Pennzoil Advanced	0.772
Pennzoil Advanced unweathered-2	Pennzoil Advanced	Pennzoil Advanced	0.870
Pennzoil Advanced unweathered-4	Pennzoil Advanced	Pennzoil Advanced	0.888
Pennzoil Advanced unweathered-5	Pennzoil Advanced	Pennzoil Advanced	0.883
Pennzoil Advanced unweathered-6	Pennzoil Advanced	Pennzoil Advanced	0.994
Pennzoil Platinum unweathered-1	Pennzoil Platinum	Pennzoil Platinum	0.922
Pennzoil Platinum unweathered-2	Pennzoil Platinum	Pennzoil Platinum	0.955
Pennzoil Platinum unweathered-4	Pennzoil Platinum	Pennzoil Platinum	0.803
Pennzoil Platinum unweathered-5	Pennzoil Platinum	Pennzoil Platinum	0.923
Pennzoil Platinum unweathered-6	Pennzoil Platinum	Pennzoil Platinum	0.847
Unival ATF unweathered-1	Unival ATF	Unival ATF	0.933
Unival ATF unweathered-2	Unival ATF	Unival ATF	0.940
Unival ATF unweathered-4	Unival ATF	Unival ATF	0.961
Unival ATF unweathered-5	Unival ATF	Unival ATF	0.950
Unival ATF unweathered-6	Unival ATF	Unival ATF	0.948

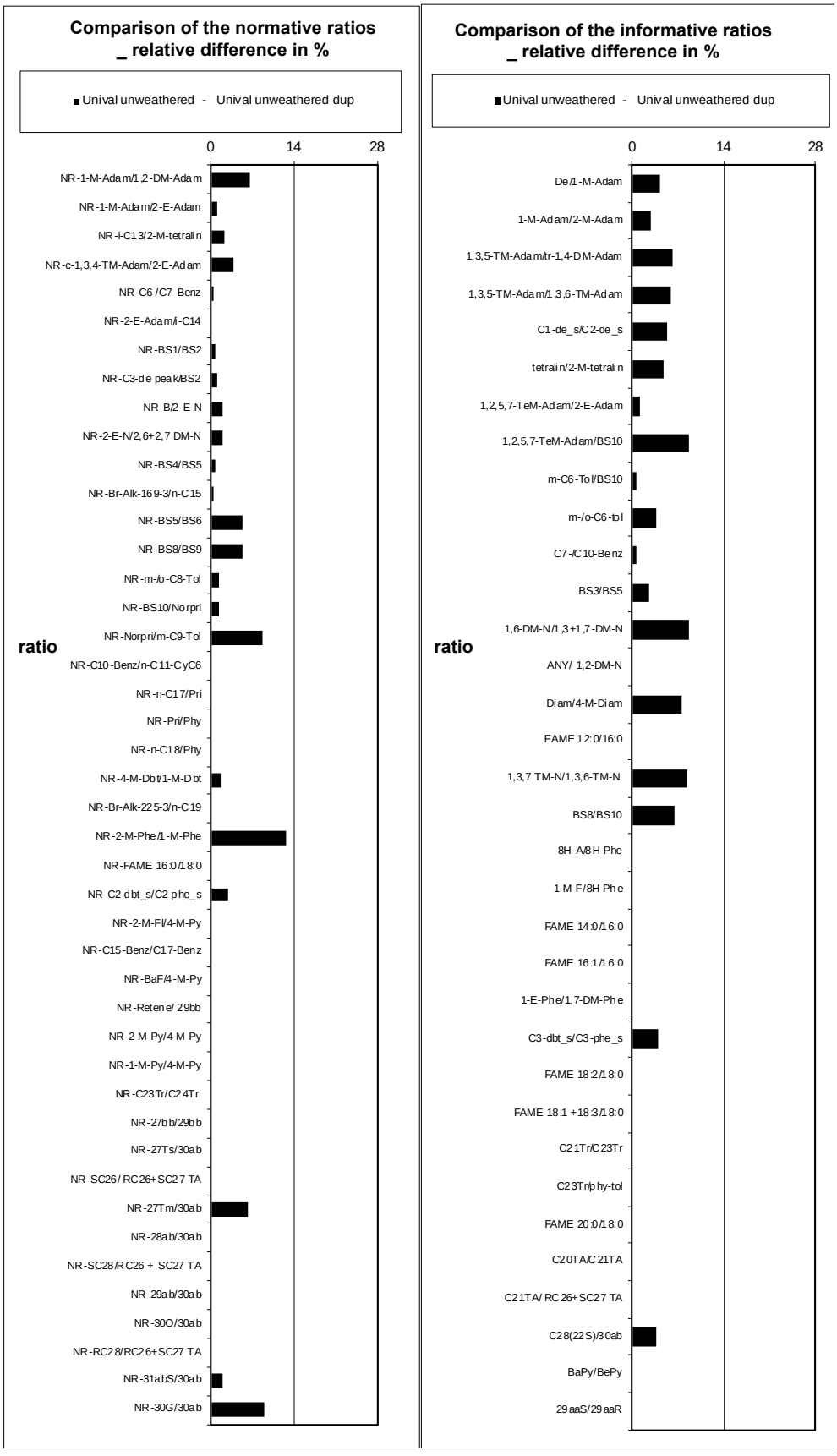
SI Table 3 QA prediction results

Sample	Predicted	Confidence Measure
QA1 weathered_1	Univall ATF	0.7719174
QA1 weathered_2	Univall ATF	0.9208309
QA1 weathered_3	Univall ATF	0.51569426
QA1 weathered_4	Univall ATF	0.5129282
QA1 weathered_5	Univall ATF	0.5327892
QA1 weathered_6	Univall ATF	0.8621741
QA2 weathered_1	Pennzoil Platinum	0.59242207
QA2 weathered_2	Pennzoil Platinum	0.5922304
QA2 weathered_3	Pennzoil Platinum	0.60734797
QA2 weathered_4	Pennzoil Platinum	0.63046694
QA2 weathered_5	Pennzoil Platinum	0.64511806
QA2 weathered_6	Pennzoil Platinum	0.54152304

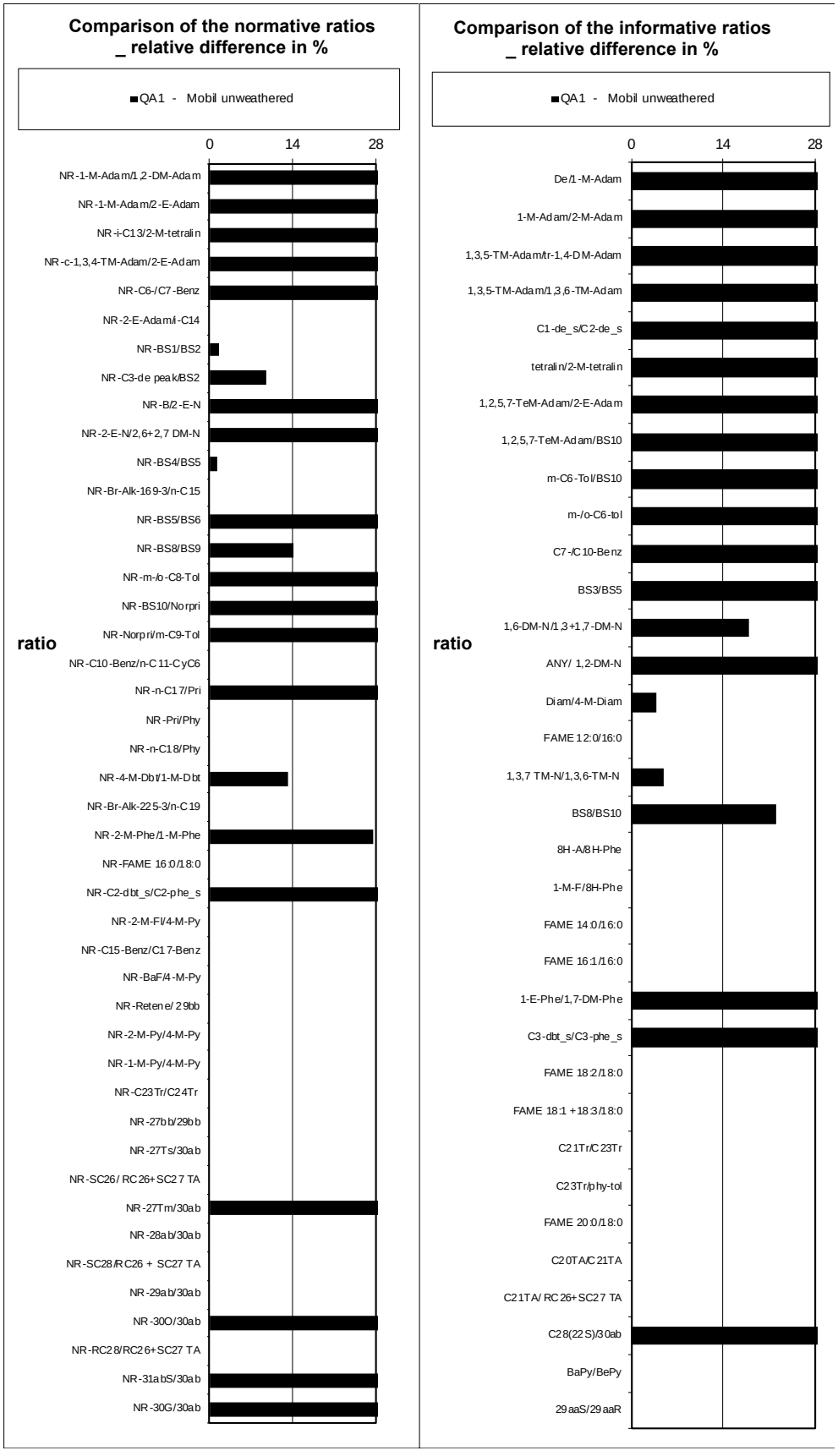
SI Figure 1 GC/MS TIC scans of four source lube oils and QAs



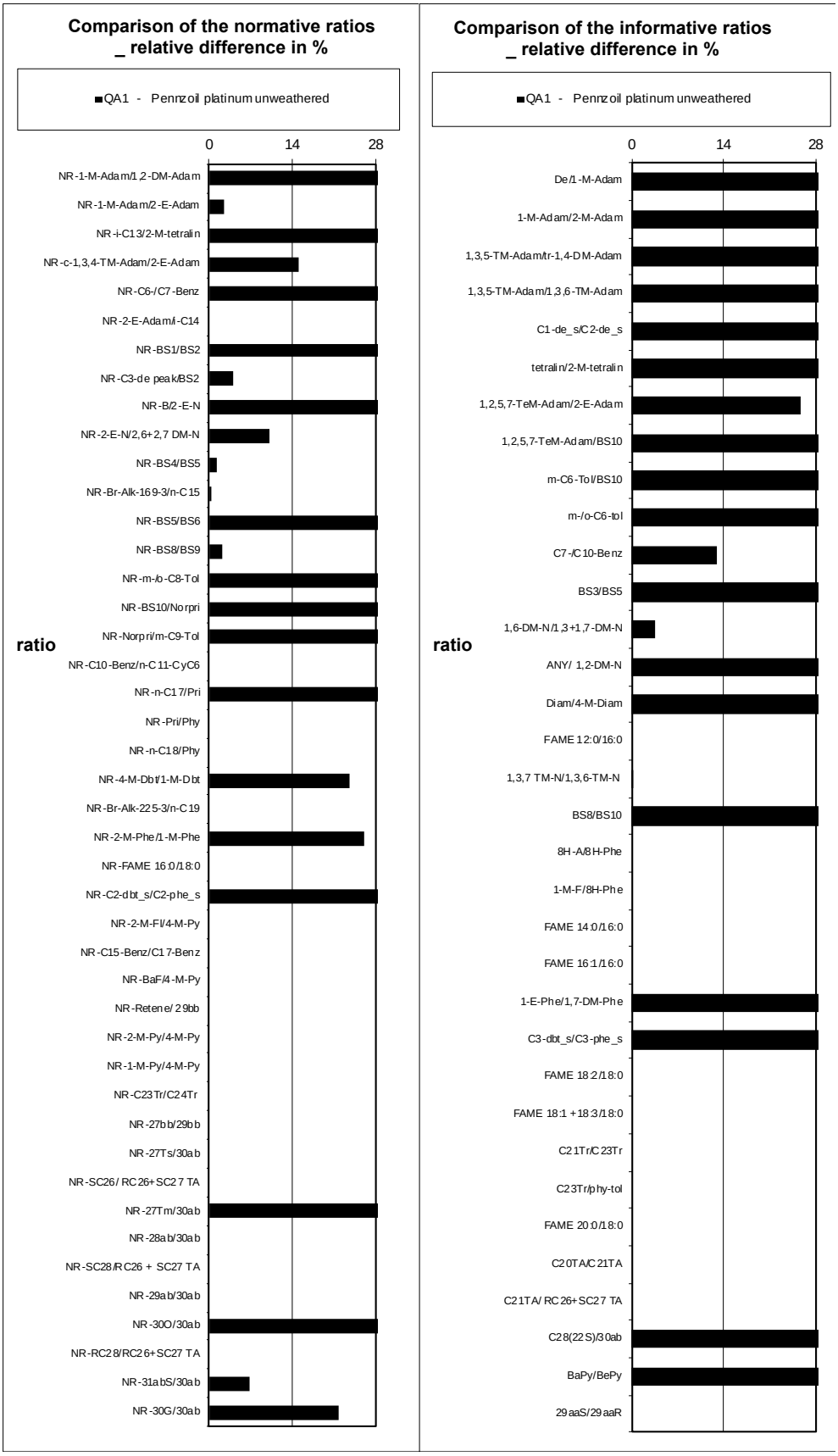
SI Figure 2 Diagnostic ratio comparison for duplicate analysis between two Unival ATF unweathered samples[1]



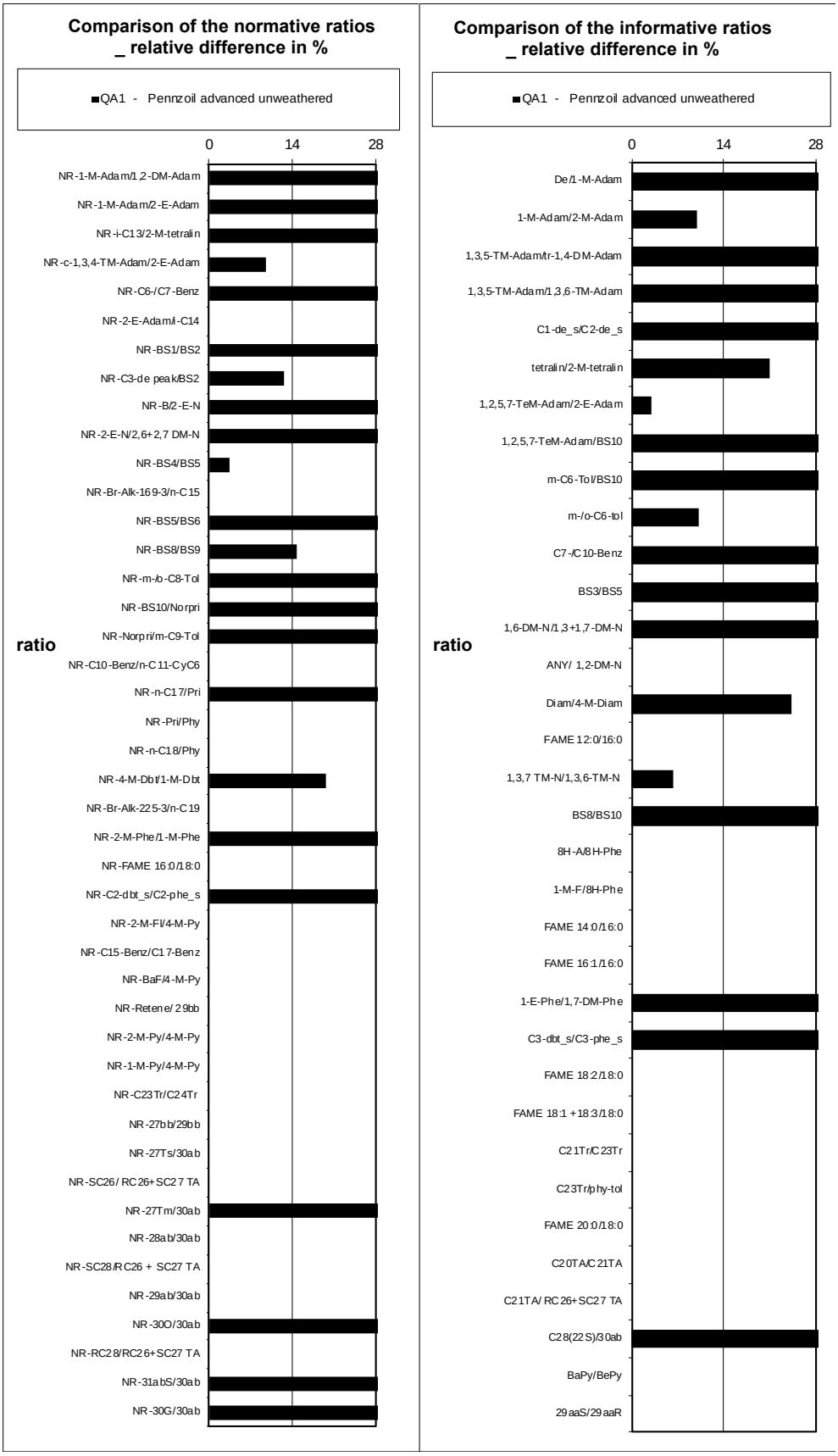
SI Figure 3 Diagnostic ratio comparison for QA1 versus Mobil Super



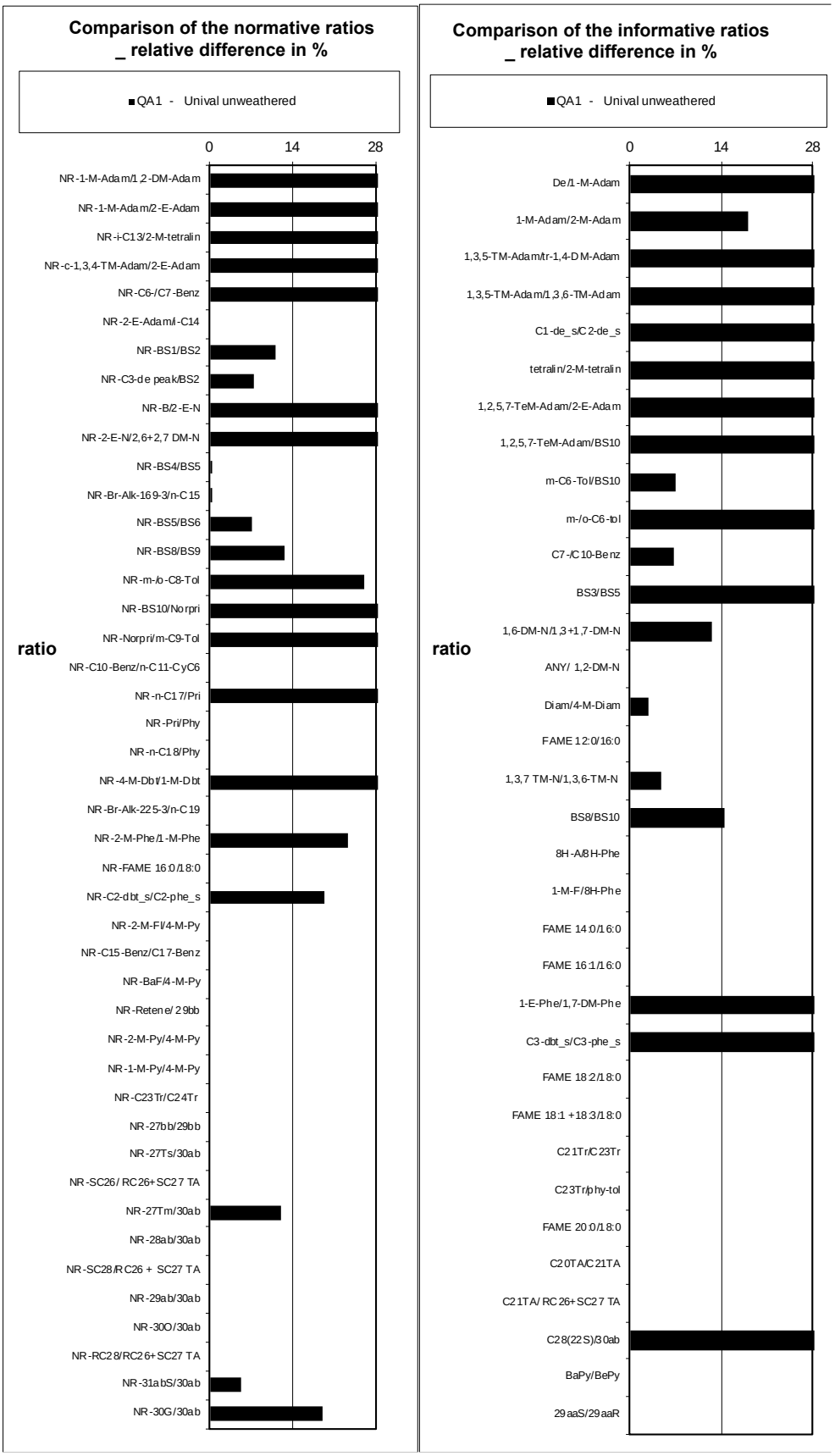
SI Figure 4 Diagnostic ratio comparison for QA1 versus Pennzoil Platinum



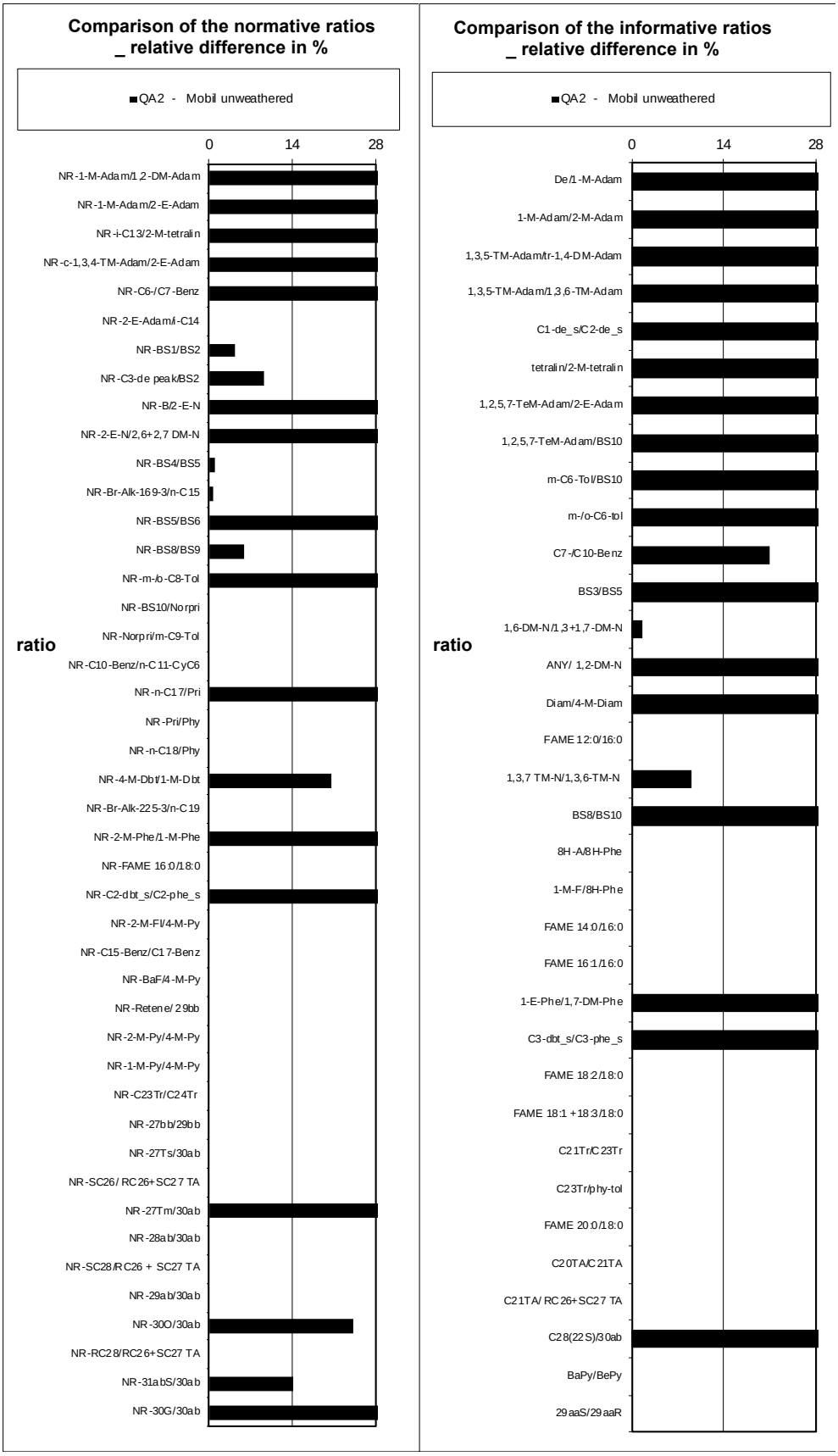
SI Figure 5 Diagnostic ratio comparison for QA1 versus Pennzoil Advanced



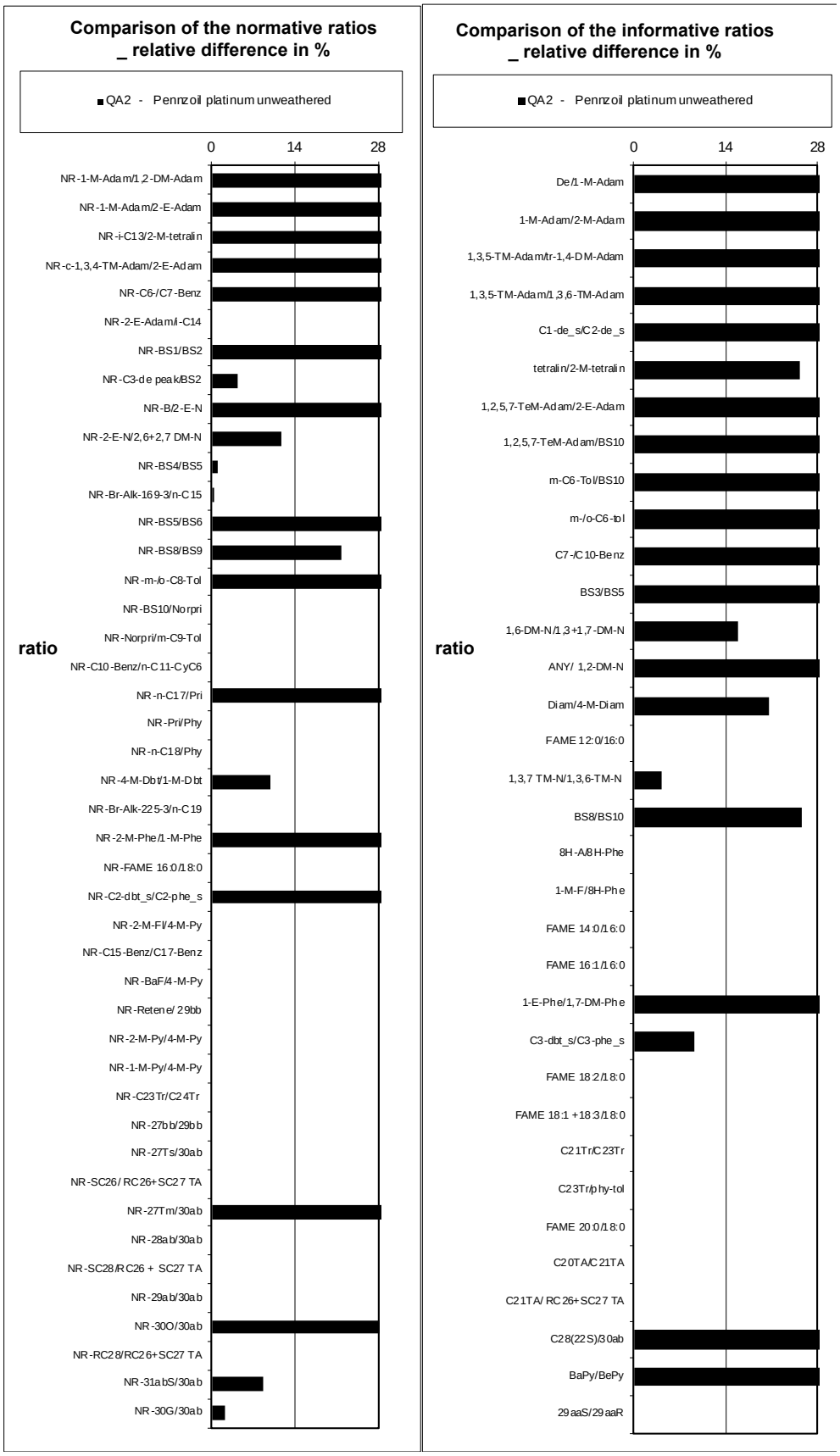
SI Figure 6 Diagnostic ratio comparison for QA1 versus Unival ATF



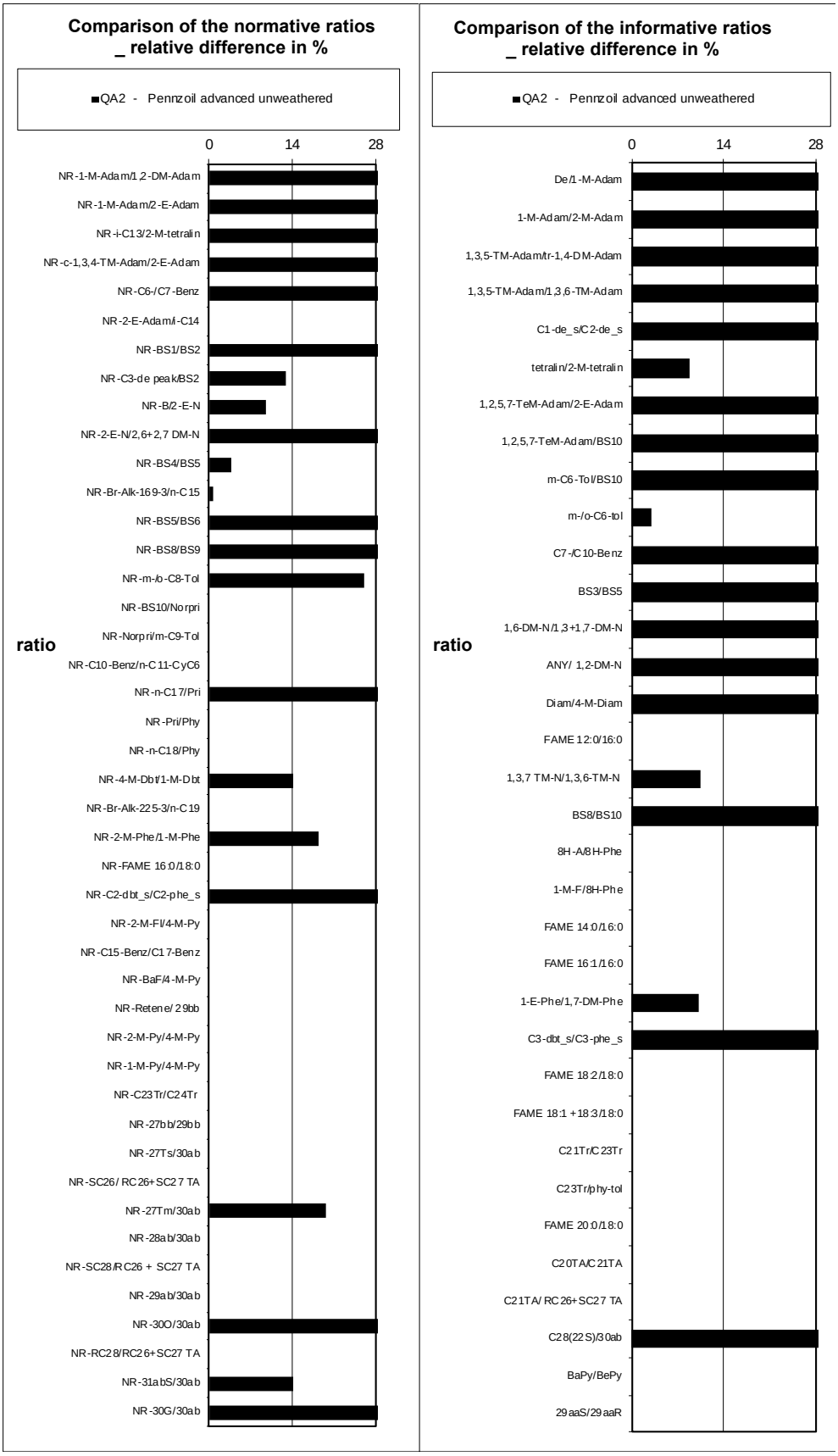
SI Figure 7 Diagnostic ratio comparison for QA2 versus Mobil Super



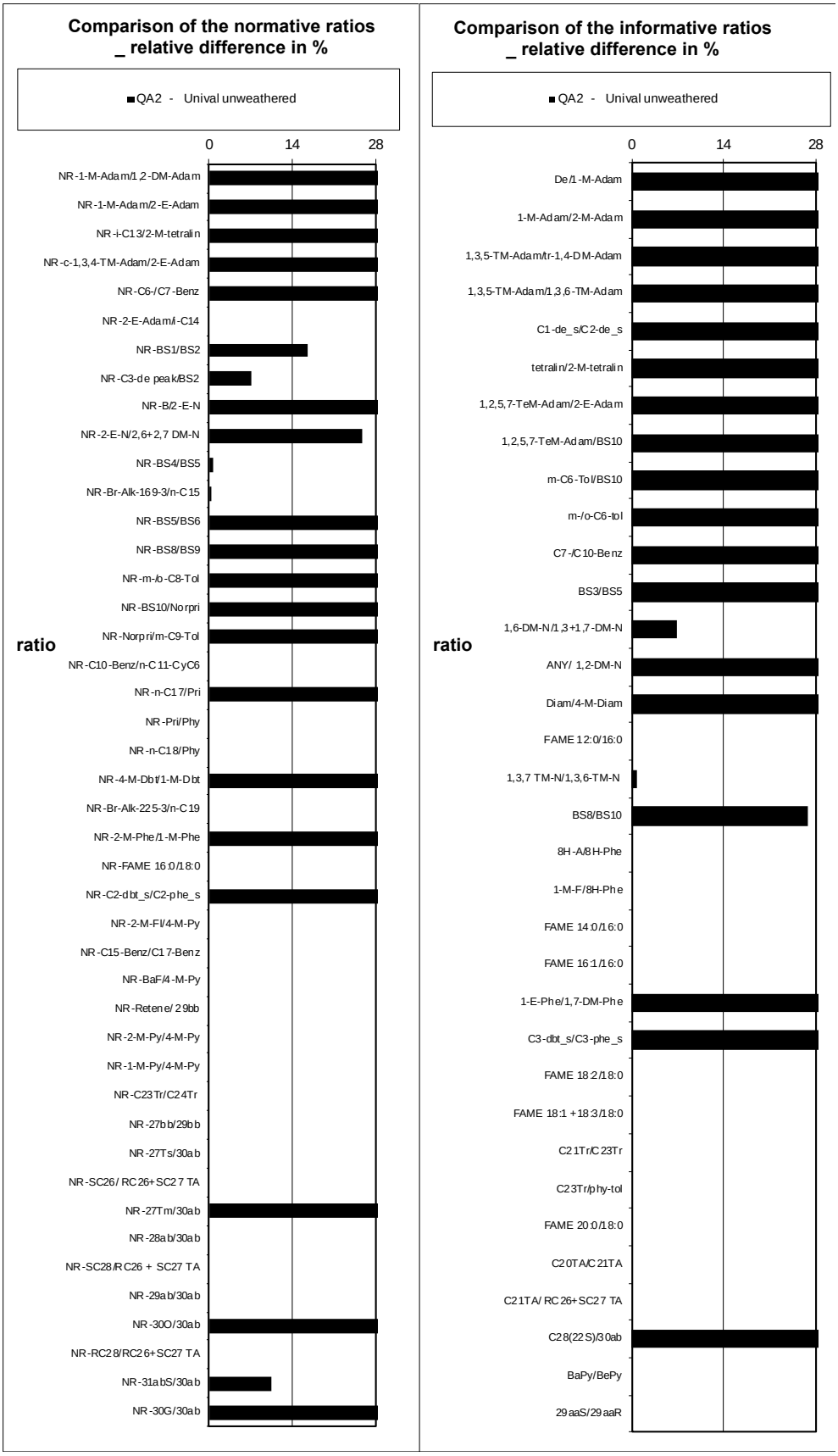
SI Figure 8 Diagnostic ratio comparison for QA2 versus Pennzoil Platinum



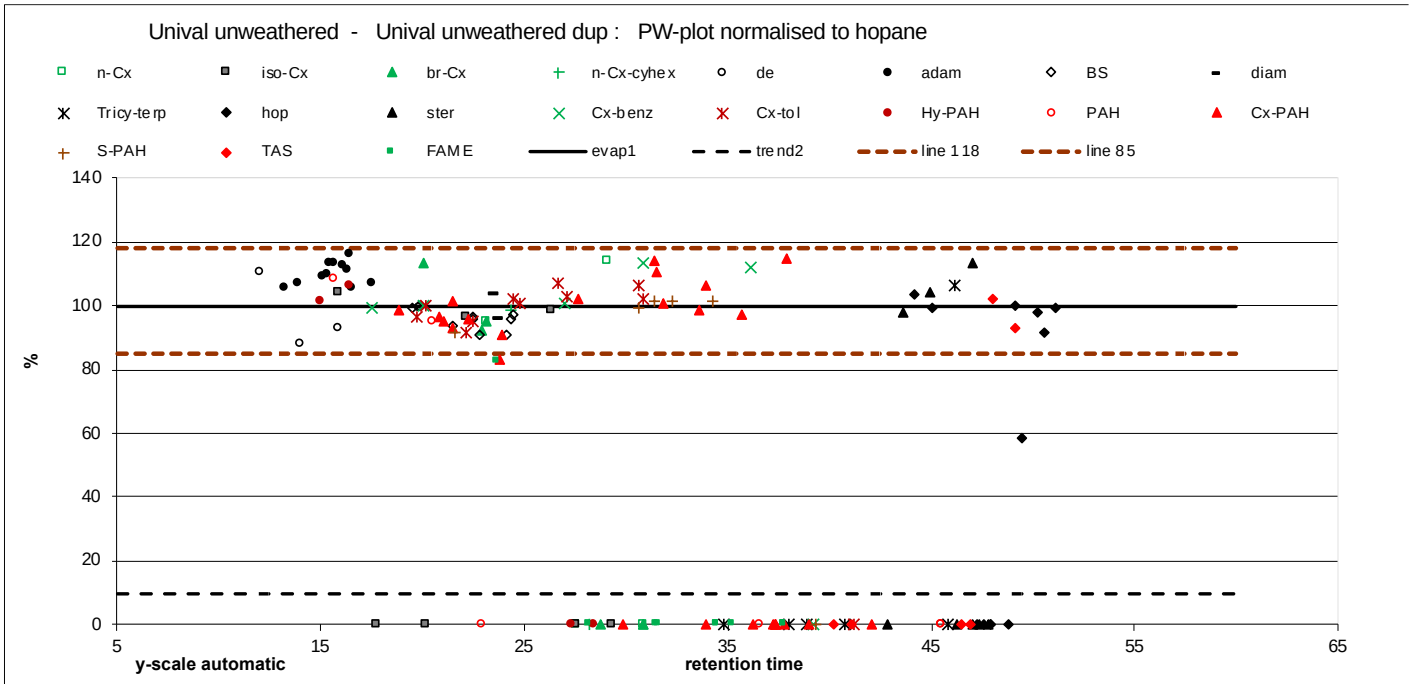
SI Figure 9 Diagnostic ratio comparison for QA2 versus Pennzoil Advanced



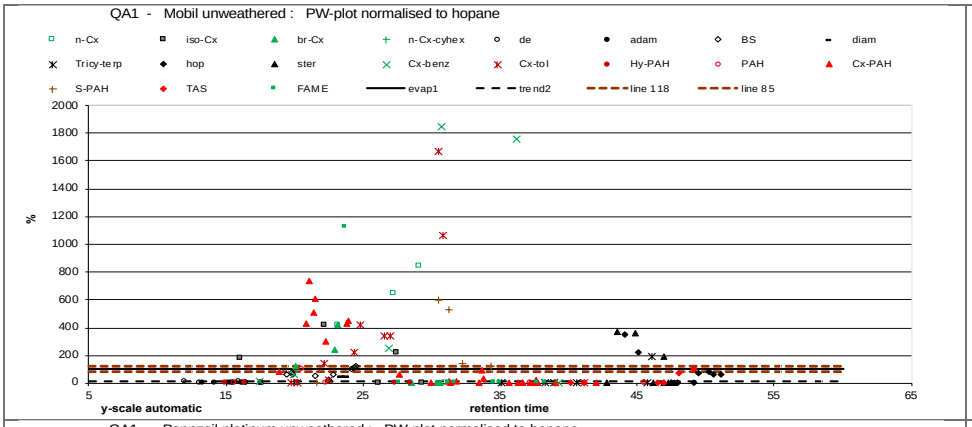
SI Figure 10 Diagnostic ratio comparison for QA2 versus Unival ATF



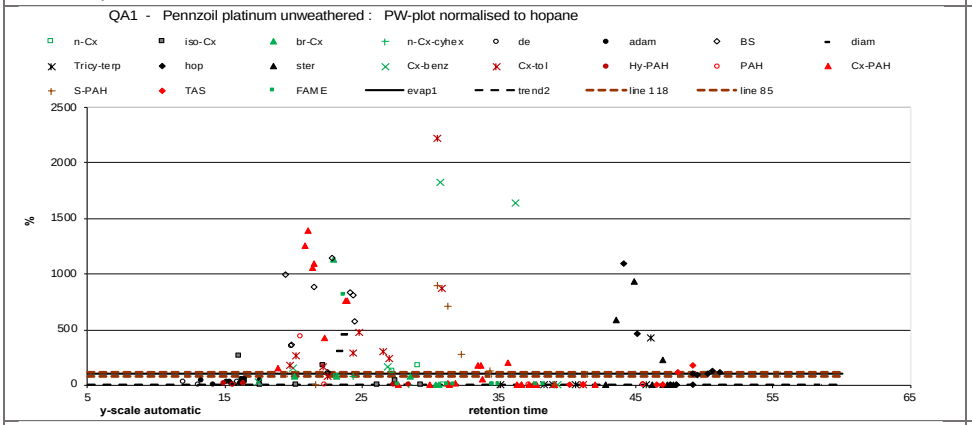
SI Figure 11 MS-PW plot comparing duplicate analyses of two Unival ATF unweathered samples normalised to hopane[1]



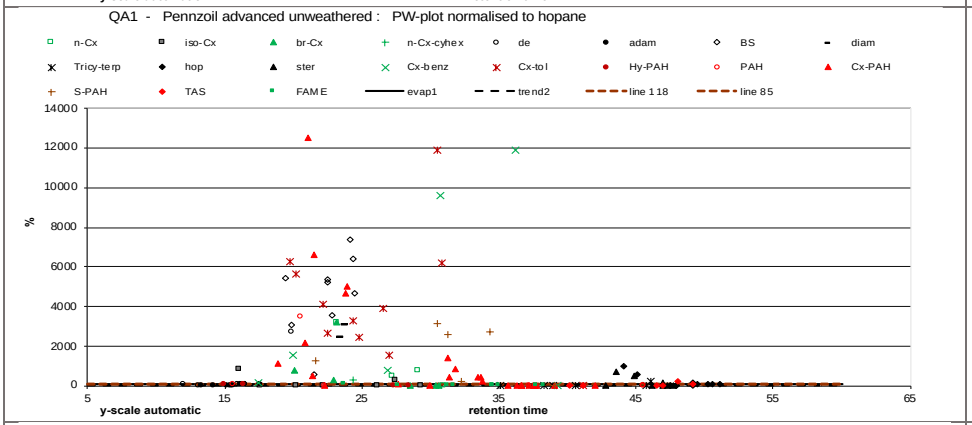
SI Figure 12 MS-PW plot comparing QA1 with source oils and normalised to hopane



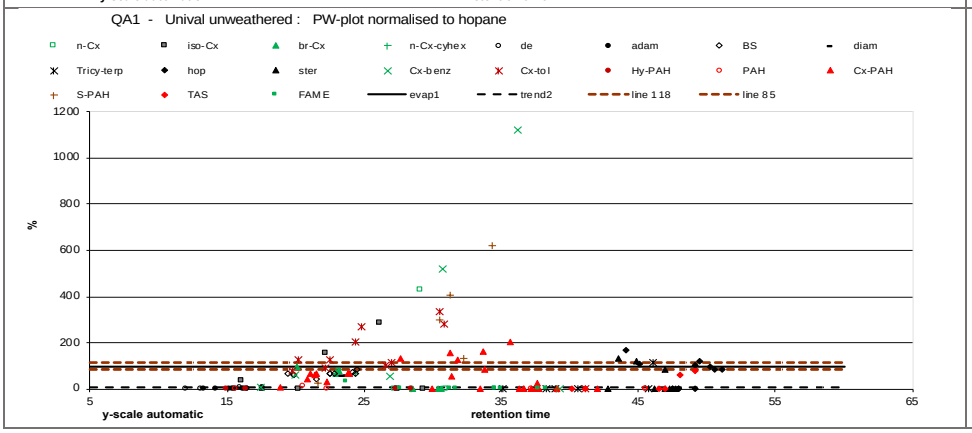
QA1 versus Mobil Super



QA1 versus Pennzoil Platinum

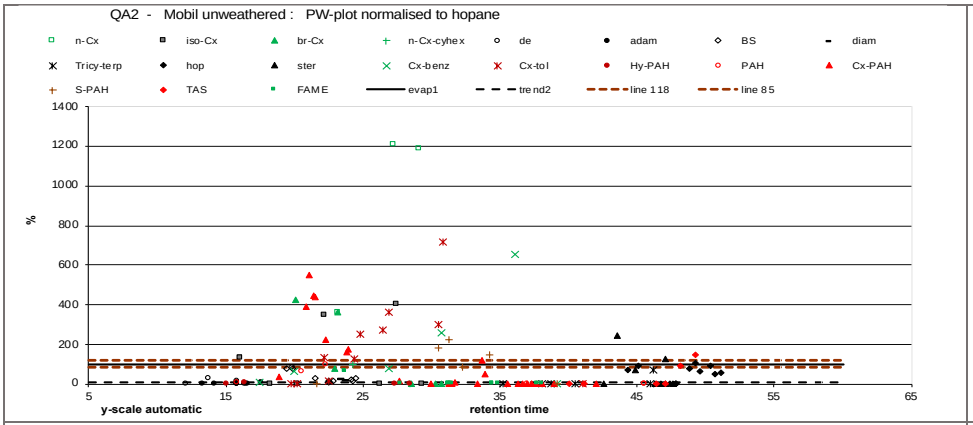


QA1 versus Pennzoil Advanced

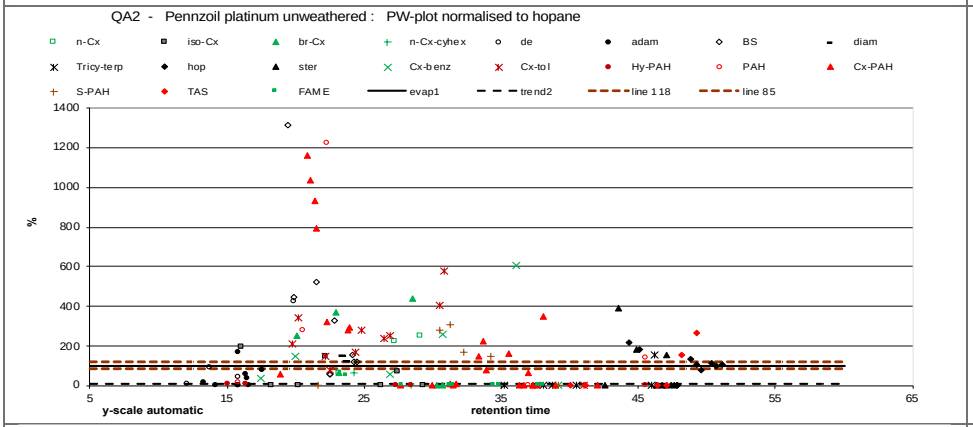


QA1 versus Unival ATF

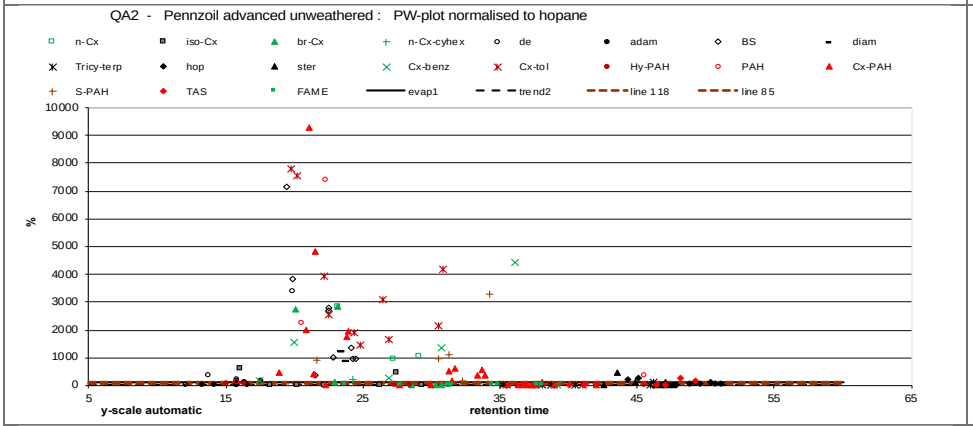
SI Figure 13 MS-PW plot comparing QA2 with source oils and normalised to hopane



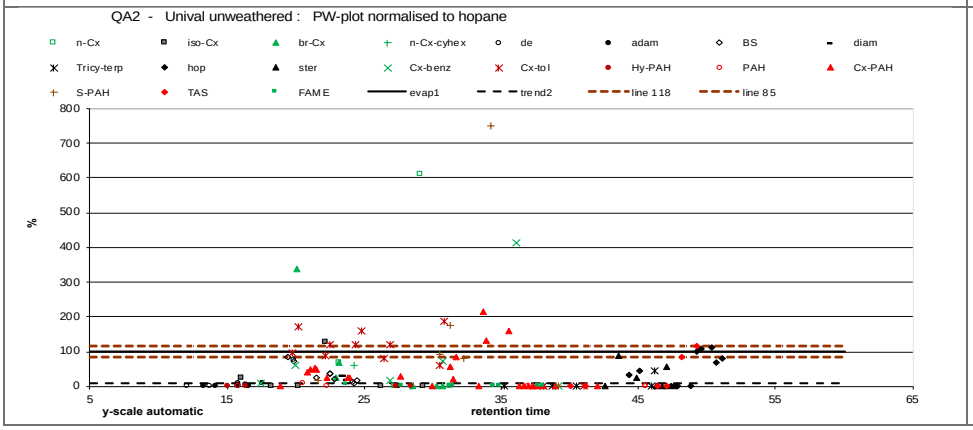
QA2 versus Mobil Super



QA2 versus Pennzoil Platinum

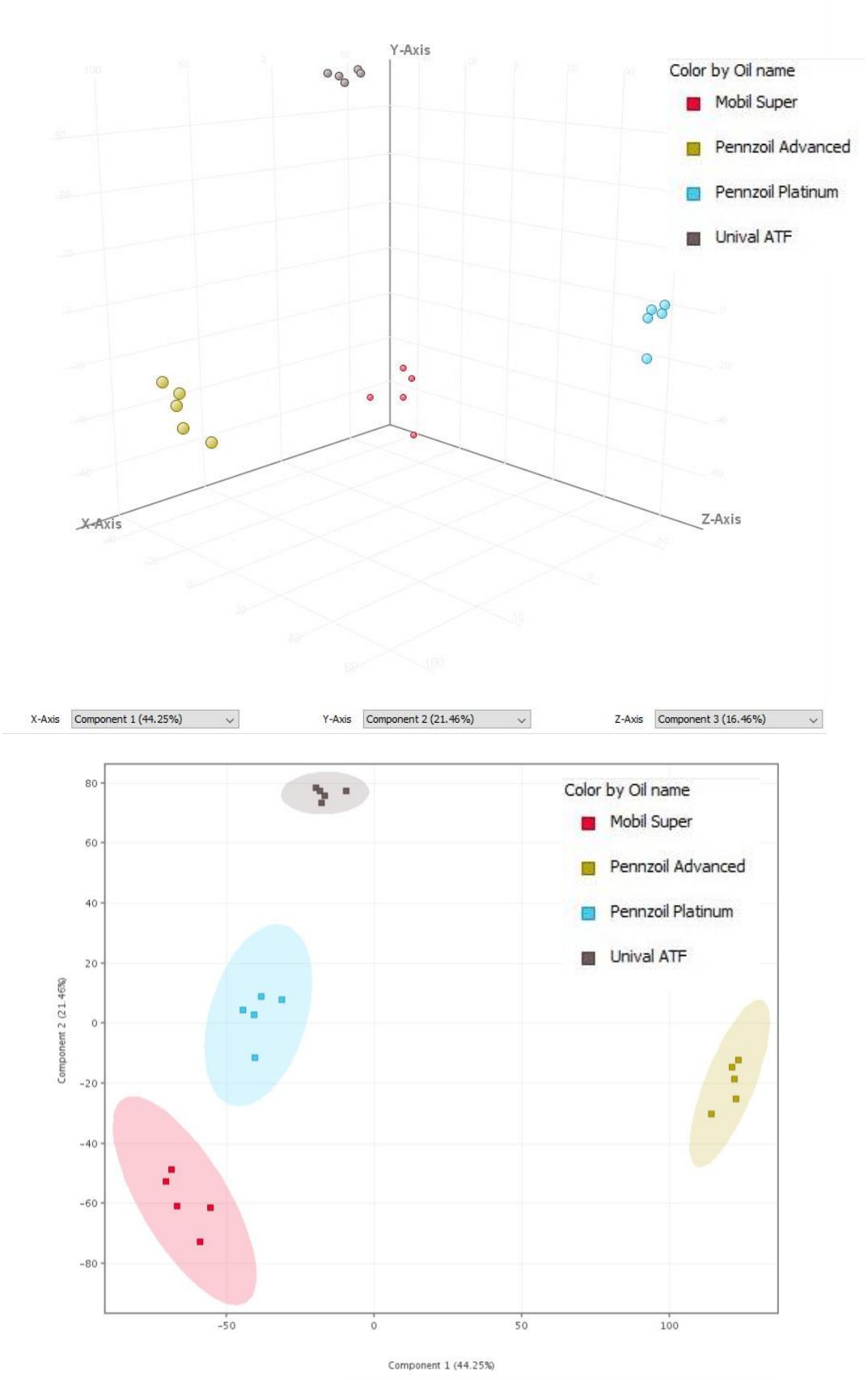


QA2 versus Pennzoil Advanced

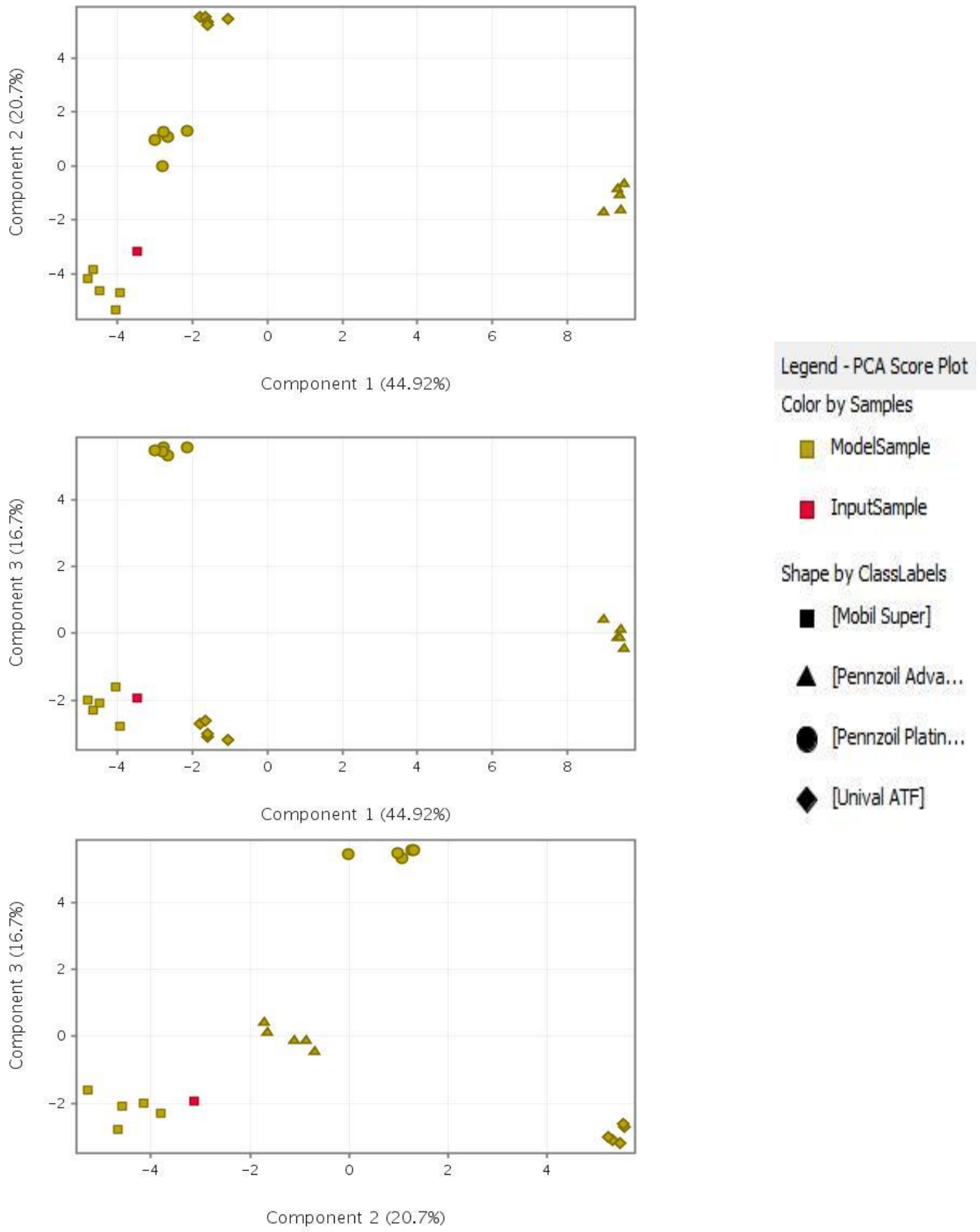


QA2 versus Unival ATF

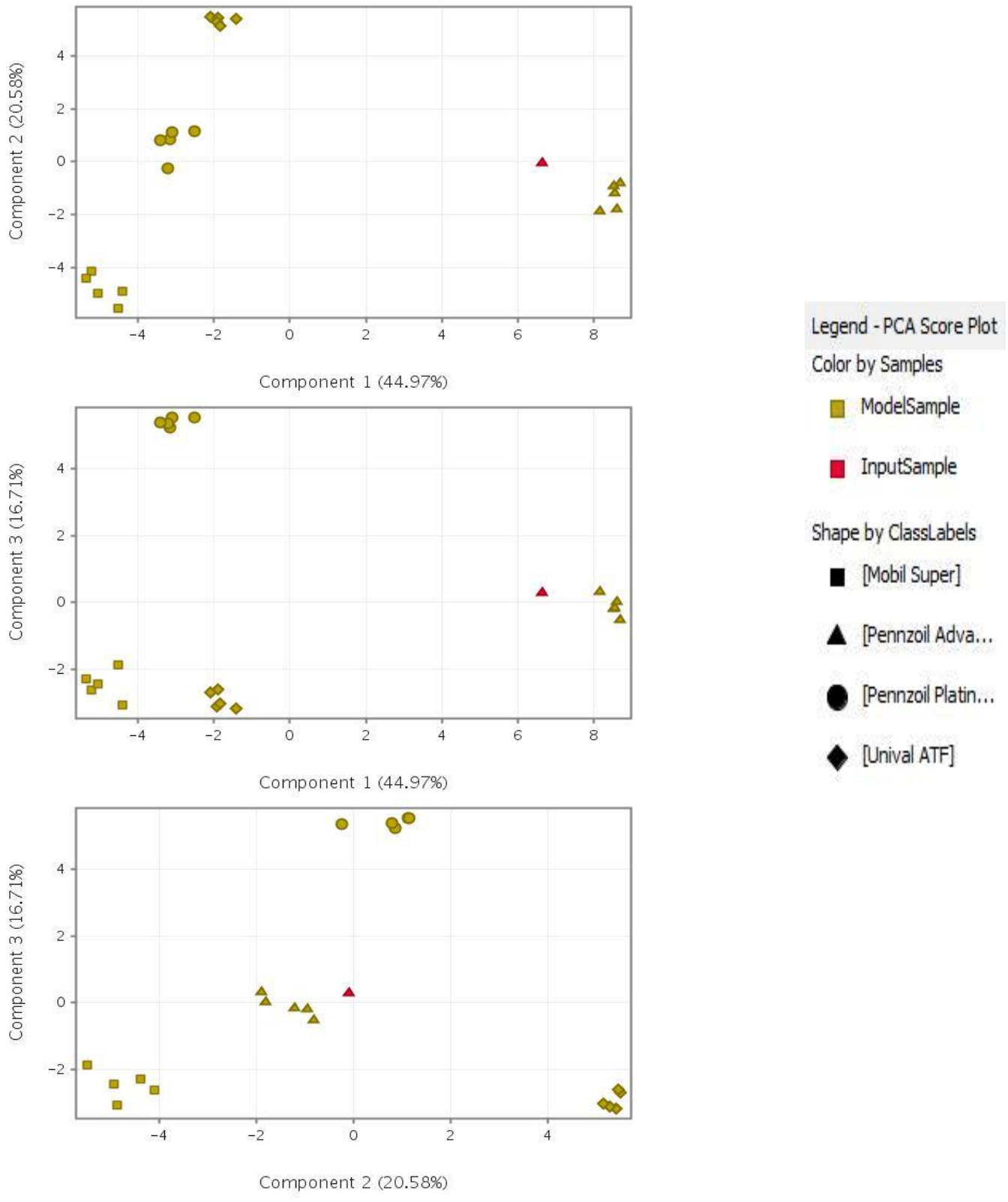
SI Figure 14 3D and 2D PCA scatterplot clustering of four source lube oils



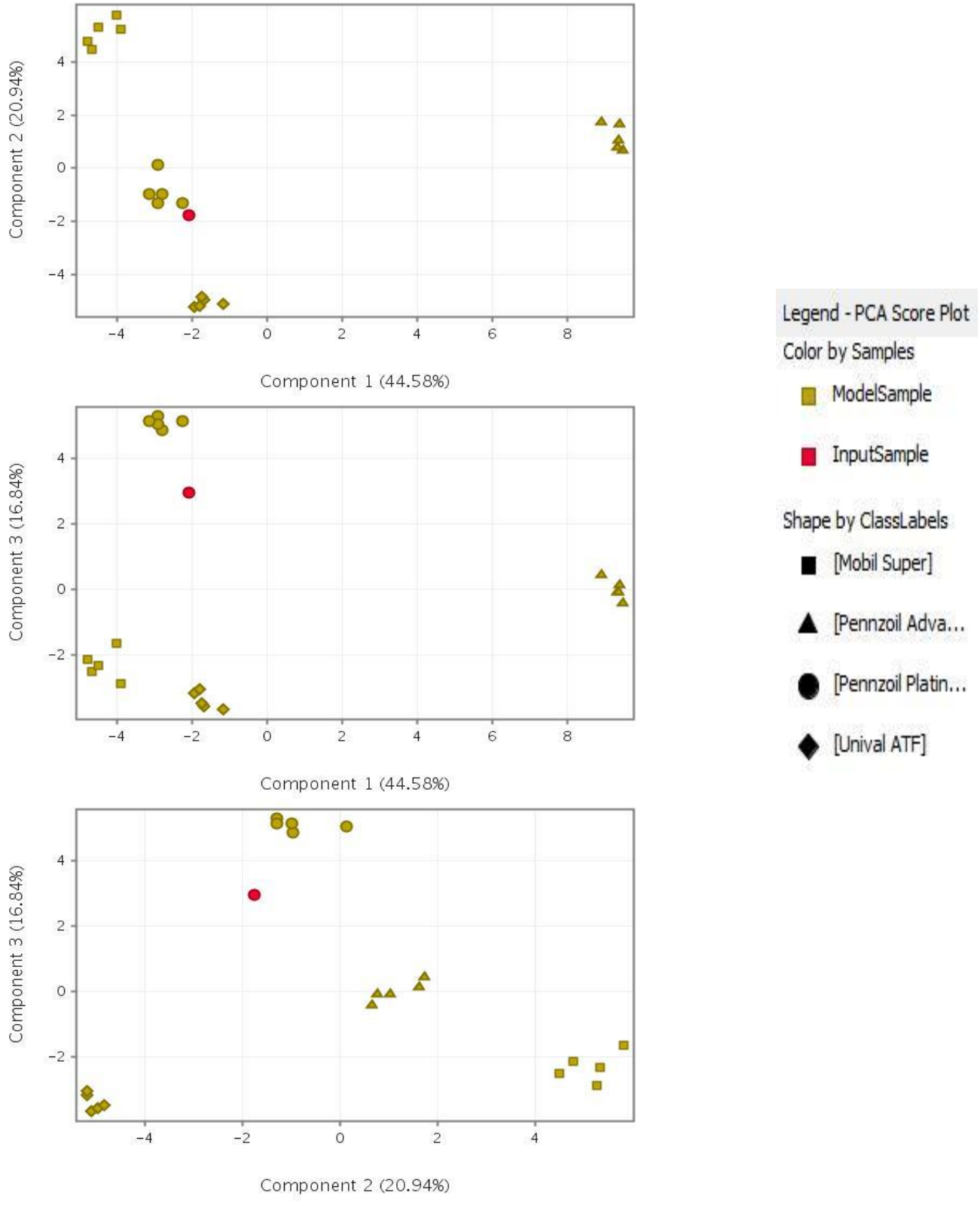
SI Figure 15 PCA score plots for model testing with last injection of an unweathered Mobil Super sample



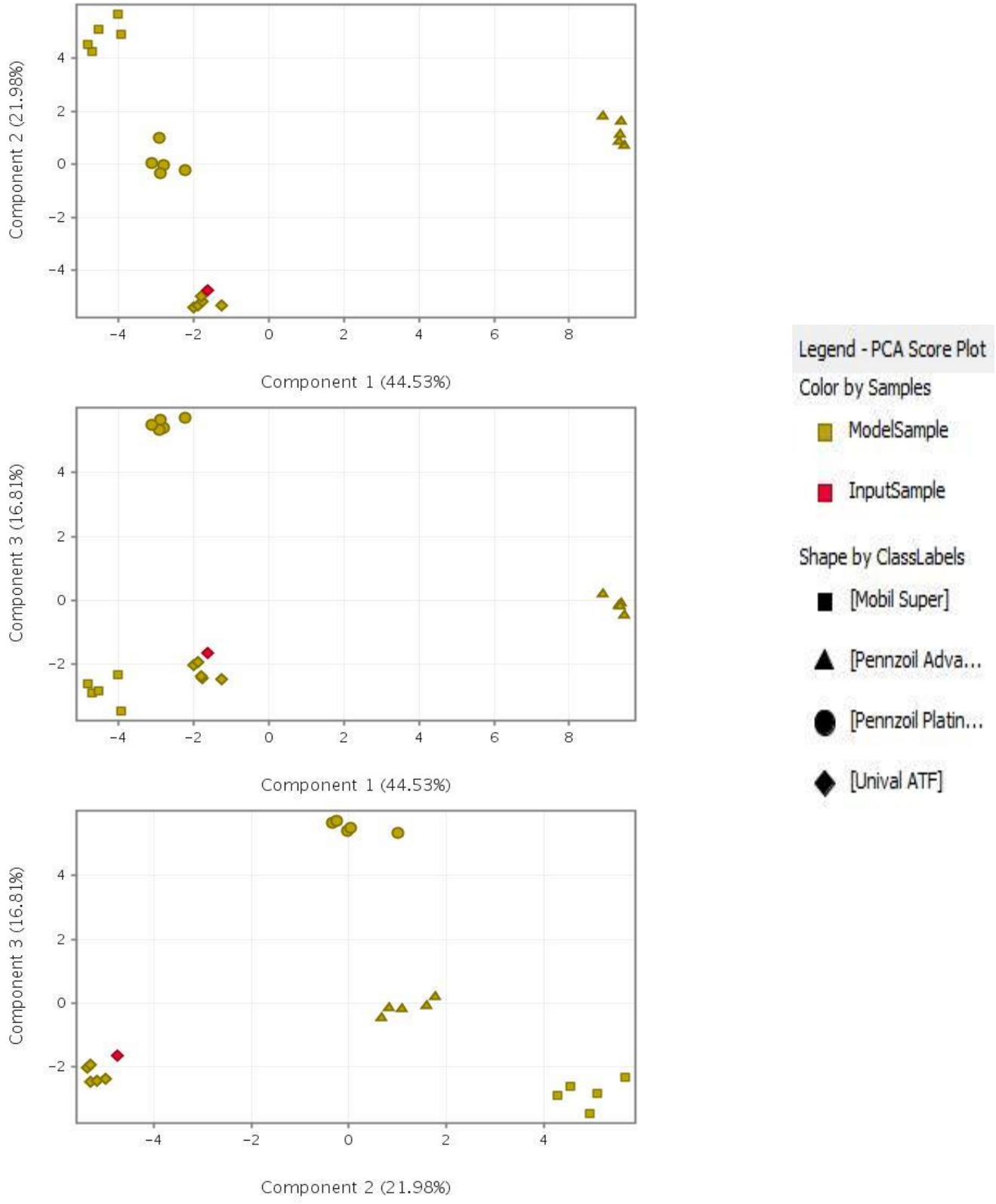
SI Figure 16 PCA score plots for model testing with last injection of an unweathered Pennzoil Advanced sample



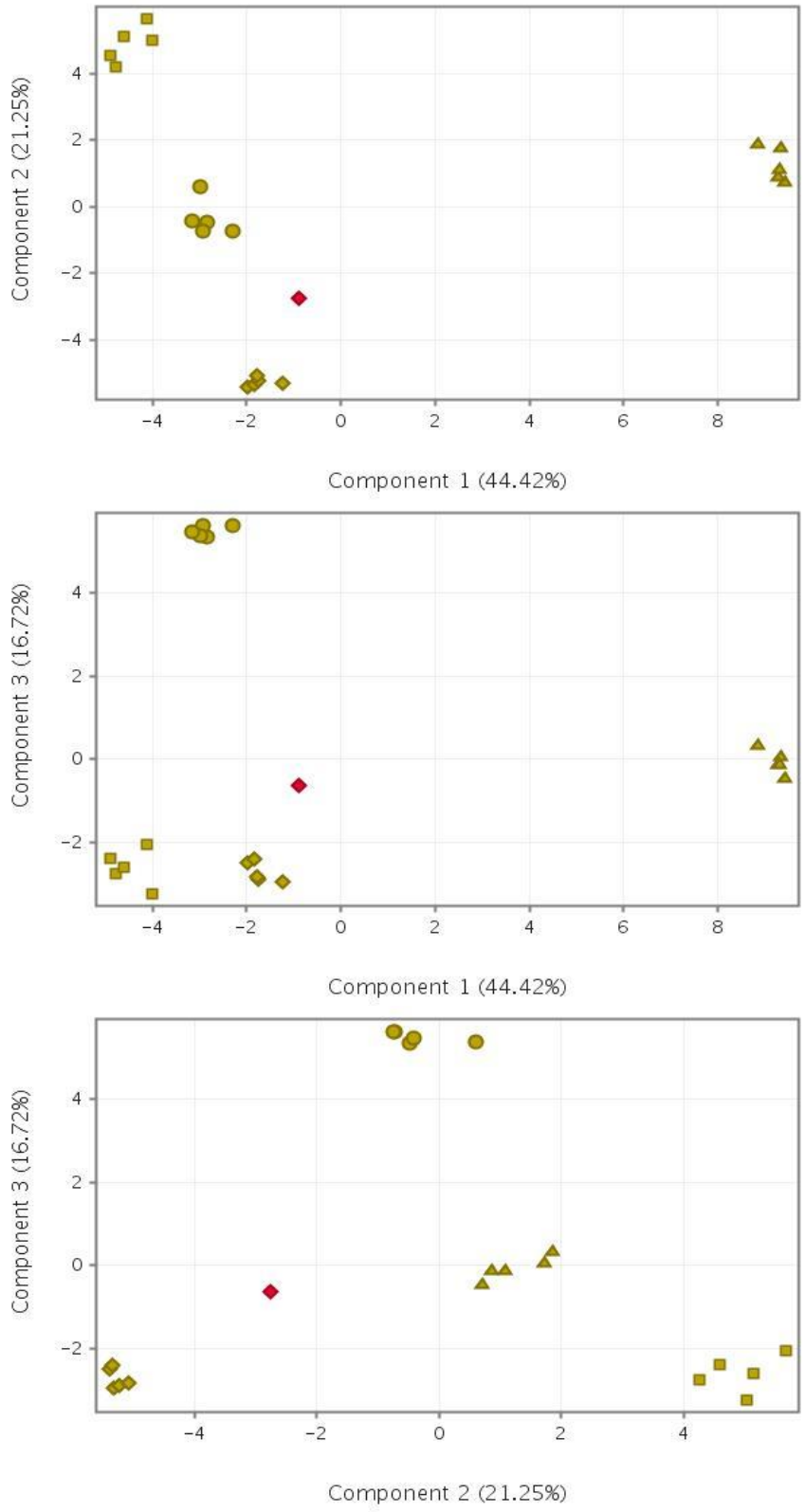
SI Figure 17 PCA score plots for model testing with last injection of an unweathered Pennzoil Platinum sample

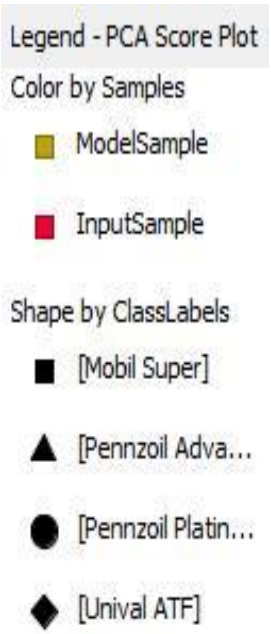


SI Figure 18 PCA score plots for model testing with last injection of an unweathered Unival ATF sample

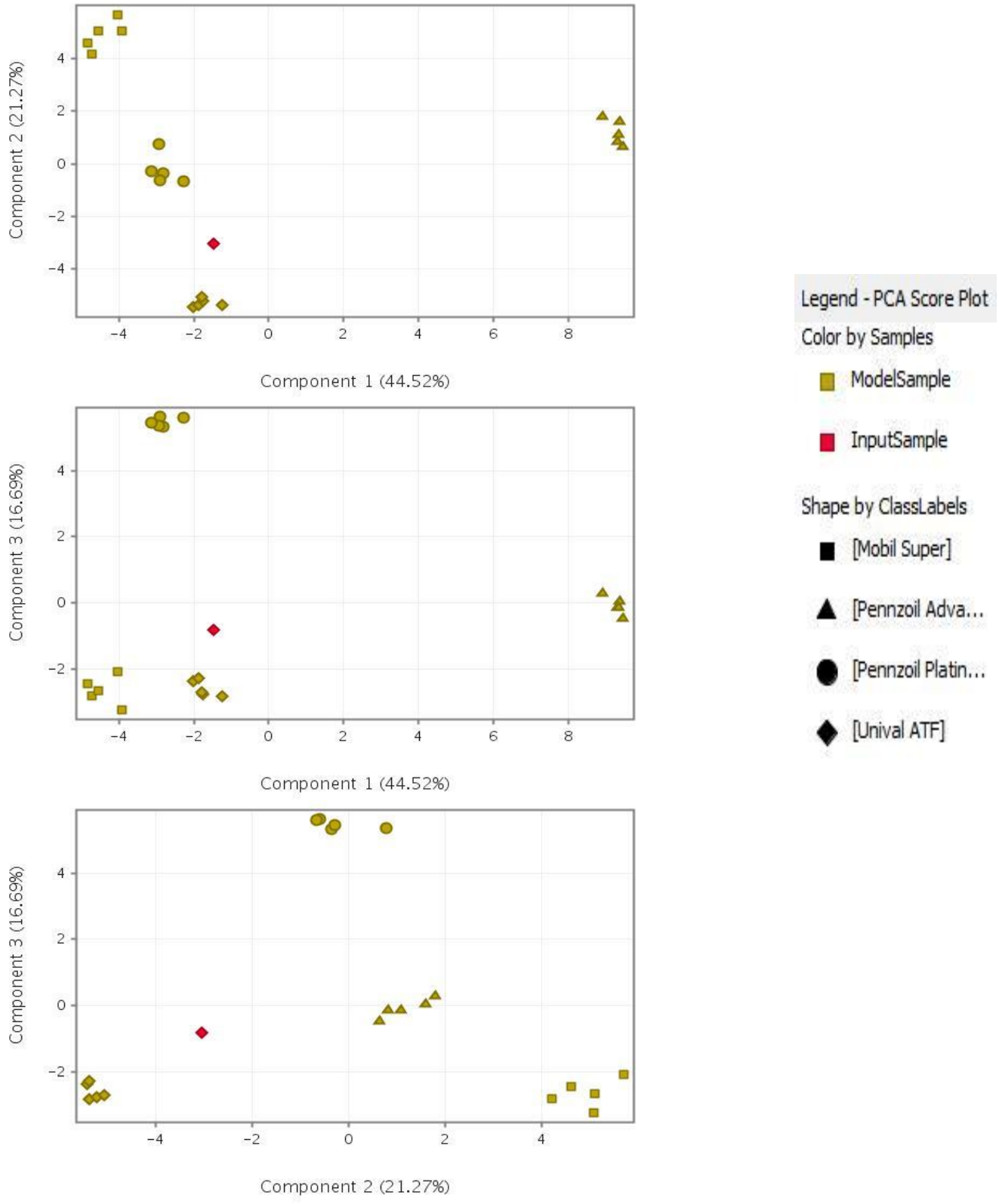


SI Figure 19 PCA score plots for first injection of QA1 prediction
*score plots for injection 2 to 6 are not included due to redundancy





SI Figure 20 PCA score plots for first injection of QA2 prediction
*score plots for injection 2 to 6 are not included due to redundancy



References

1. European Committee for Standardization (CEN)/TR 15522-2, *Oil Spill Identification – Waterborne Petroleum and Petroleum Products – Part 2 Analytical Methodology and Interpretation of Results Based on GC-FID and GC-MS Low Resolution Analyses*, 2012.