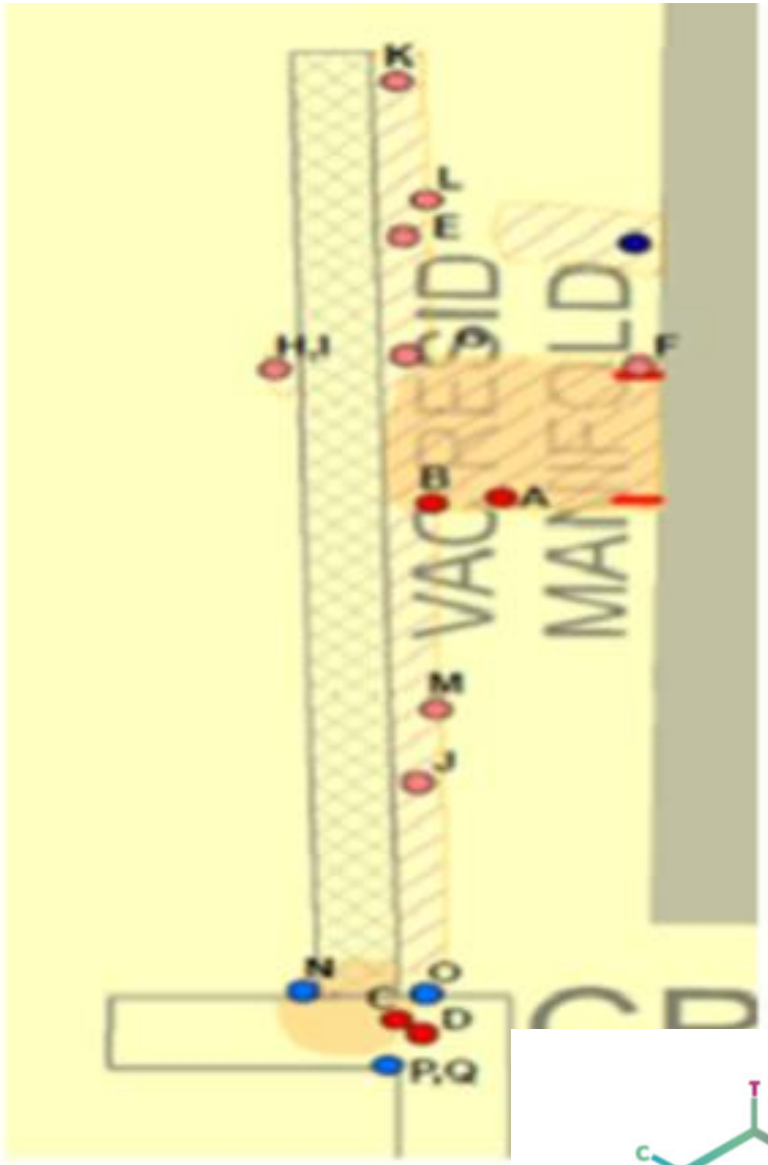

# GIBSON ENERGY

## Introduction to Deib and why as a company we use his services and OSINet Methods

October 2022

# Need For Forensic Fingerprinting – Proponents Angle

- Too often we have uncertainty over ownership and responsibility of liabilities for sites where multiple companies have historical facilities
- We need a defensible and accepted methodology differentiation / forensic fingerprinting to ascertain this ownership
- We use Deib consistently in circumstances like this due to his 40+ year expertise in analytical chemistry & forensics and because he is a leading proponent of the Oil Spill Identification Network of experts (OSINet) methods which were developed in the aftermath of the Tricolor spill in the English Channel in 2002 under the Bonn agreement have international recognized fingerprinting protocols
- We believe that this now recognized international methodology to differentiate sources will hold up in courts and eventually cascade from marine acceptance to land locked prairie regulatory acceptance
- **We thank Deib for his expertise and for spearheading these methods into the western Canadian oil patch**




# Discerning recent and historical spill material using European Standard EN 15522-2:2020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- ***1. D.A. Birkholz, Analytical Consultant, Inc.***
- ***2. Gibson Energy***
- ***3. WSP E & I Canada***


DEIB-CHEM FORENSICS

Forensic services in toxicology, chemistry biology sampling & statistics

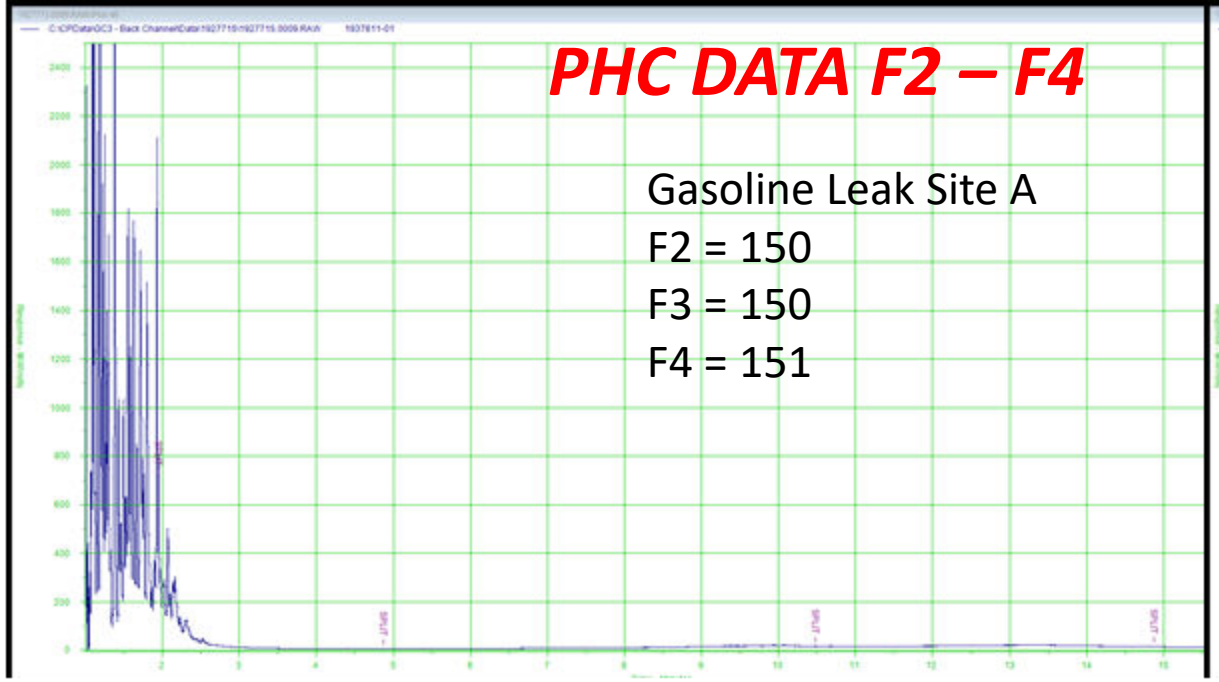
# Background

- Leak from branch of pipe connected to 3-Phase separator but no longer in use (not flowing)
- Investigation into extent of spill
- Sample taken from operational 3-Phase separator
- Spill material collected from one site following soil excavation (i.e. spill product and water mixture ‘Gasoline Leak Sample’)
- Soil samples collected from a number of sites where soil staining was observed
- All samples analyzed for petroleum hydrocarbons following CCME guidelines (i.e. BTEX AND PHC F1-F4 hydrocarbons)
- Review of PHC data resulted in the identification of sites of interest for further forensic testing using method EN 2020

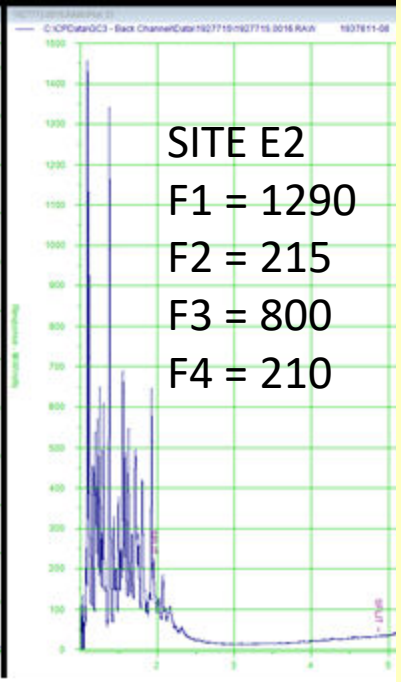
# Why Forensics

- Differentiation between historical releases and any current releases required.
- Eras of ownership can mean eras of differential liability.
- Forensics key for understanding of liability associated with areas of any future operational expansion
- EN2020 method ideally suited for this task.

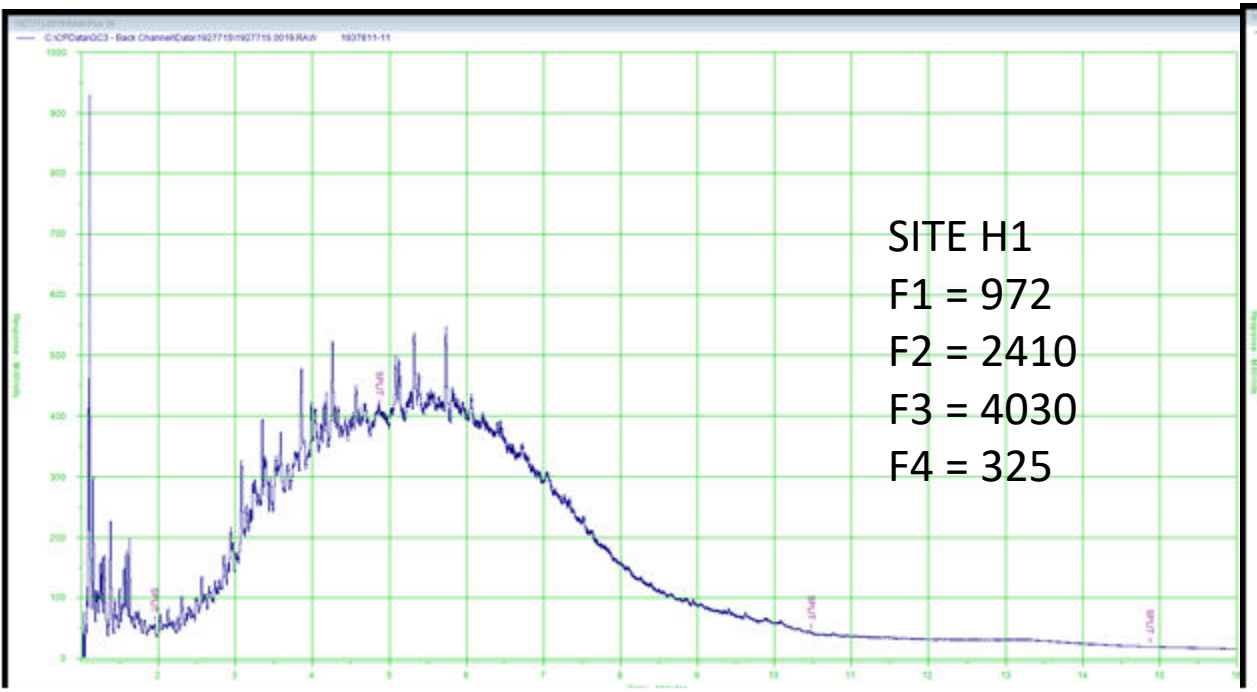
# PHC DATA F2 – F4



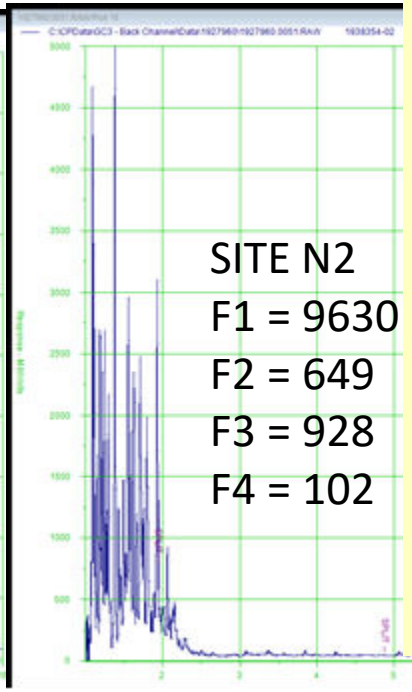
Gasoline Leak Site A
F2 = 150
F3 = 150
F4 = 151



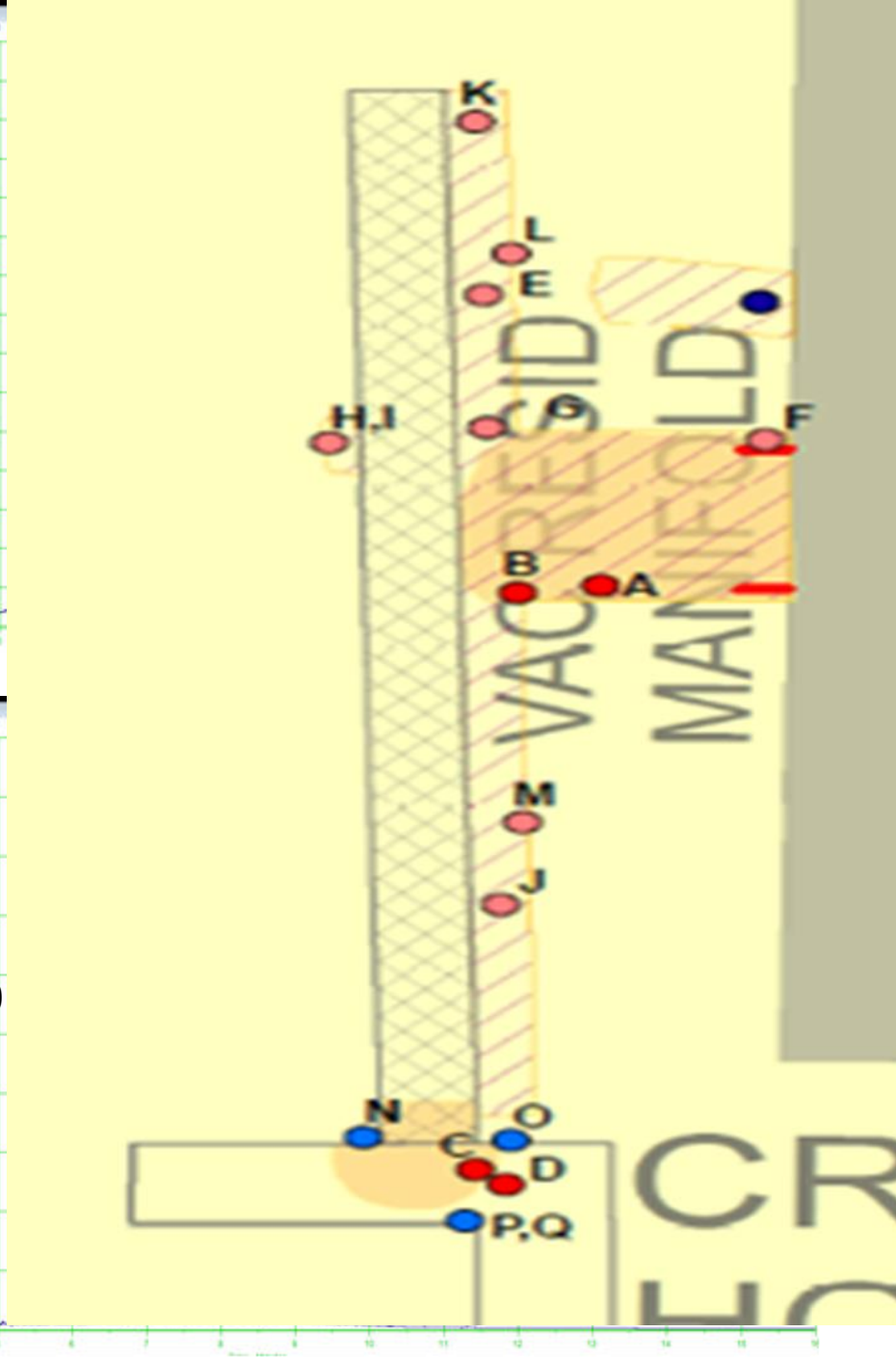
SITE E2
F1 = 1290
F2 = 215
F3 = 800
F4 = 210



SITE H1
F1 = 972
F2 = 2410
F3 = 4030
F4 = 325

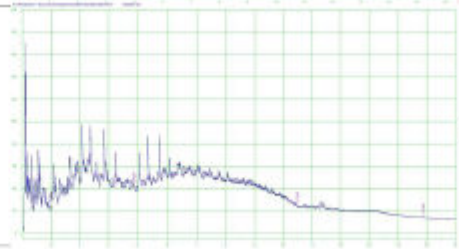


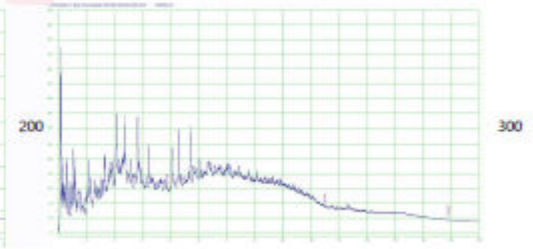
SITE N2
F1 = 9630
F2 = 649
F3 = 928
F4 = 102

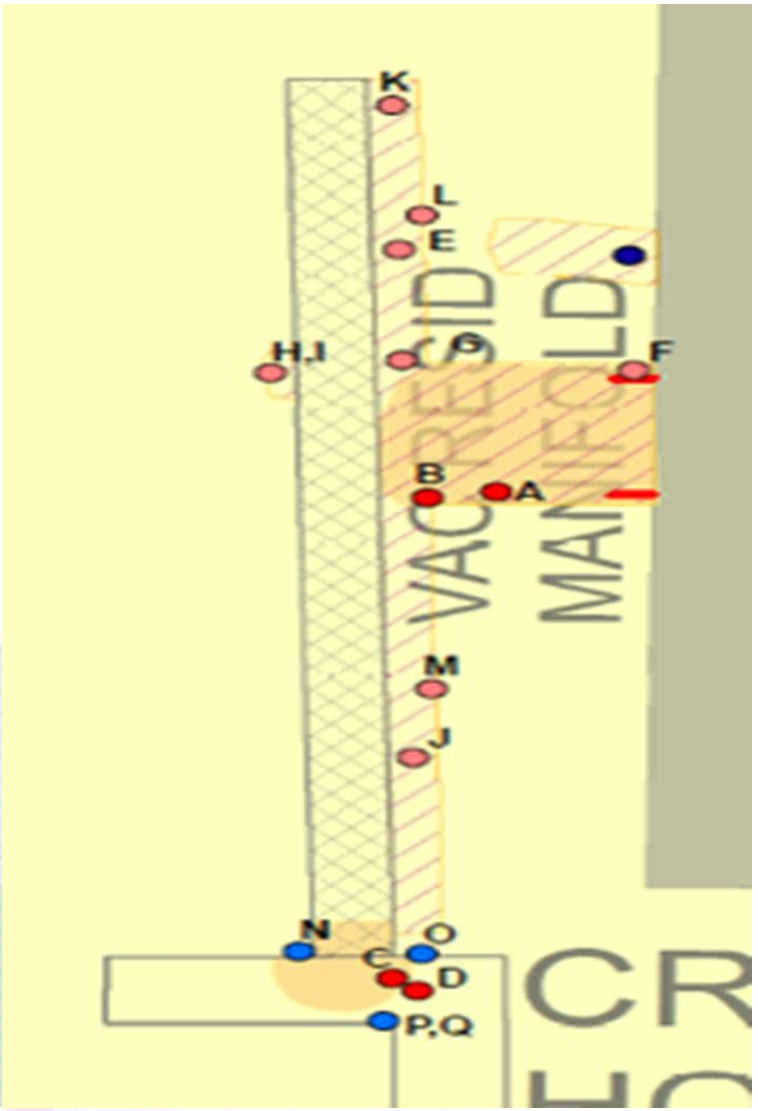


# PHC Data and Chromatograms for sites K, P and Q

| ID | Depth from soil surface (m) | Depth from top of sidewalk (m) | Colour | Benzene | Ethylbenzene | Toluene | Xylenes, total | F1 (C6-C10) | F2 (C10-C16) | F3 (C16-C34) | F4 (C34-C50) | Forensic candidate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K1 | 0.05 | 0.50 | brown | <0.02 | <0.05 | <0.05 | <0.05 | <7 | <4 | <8 | <6 | |
| K2 | 0.10 | 0.55 | slight st | <0.02 | <0.05 | <0.05 | <0.05 | 9 | 14 | 151 | <6 | |
| P1, Q1 duplicates | 0.10 | 0.71 | brown w | 1 | 7 | 0.44 | 3 | 456 | 628 | 1,160 | 299 | |





# OSINET Forensic Methods

- Bonn Agreement formulated in 2005 and network of expert chemists established specializing in oil spill identification techniques, now known as OSINET (oil spill identification, network).
- Bonn-OSINet was initiated with the objective to improve the quality of the laboratories and to stimulate cooperation and mutual assistance

***History of OSINET Analytical Methods:***

- Since 1991, the Nordtest method for oil spill identification (Nordtest, 1991) has formed an important forensic "platform" in relation to oil spill identification, not only in the Scandinavian countries, but also in other European countries following its recommendation in and adoption by the Bonn Agreement *Counter Pollution Manual.*

- CEN Technical Report, 2006
- CEN Technical Report, 15522-2, 2012
- EN 2020, Dec 2020.

# *Operating Principals of OSINET*

- Forensic research on the selection of appropriate chemicals and ratios to identify and measure in relation to spills of differing petroleum products. Dates back to 2002.
- Perform international round robin studies annually applying suggested measurements since 2002. Now every two years because there are many labs to evaluate - ***44 laboratories associated with 26 countries*** (2017 report).
- Perform statistical analyses and determine diagnostic power of chemical ratios.
- Those chemical ratios with high diagnostic power are deemed normative.
- Those with good, but lower diagnostic power, deemed informative.
- Continuing research and interlaboratory studies. Method EN2020 light petroleum products are being dealt with (e.g. condensates).
- Website dedicated to OSINET members sharing observations, publications, and findings.
- Forensic data is shared on a global basis using COSIWEB in order to identify spill material globally.
- Currently 6 Canadian Labs are OSINET members, 4 - Federal (Environment Canada) and 2 - private.
- Currently 3 US Labs are OSINET members, all private.

# Daubert Standard

- ***Daubert* standard** is a rule of evidence regarding the admissibility of expert witness testimony. Pursuant to Rule 104(a), in *Daubert* the U.S. Supreme Court suggested that the following factors be considered:[28]
  - Has the technique been tested in actual field conditions (and not just in a laboratory)?
  - Has the technique been subject to peer review and publication?
  - What is the known or potential rate of error?
  - Do standards exist for the control of the technique's operation?
  - Has the technique been generally accepted within the relevant scientific community?
  - Canadian Supreme Court "did list a number of factors that could be helpful in evaluating the soundness of novel science."
  - It is too early to say *Daubert*-like rules are likely to be applied in Canada in the near future. But Canadian class certification courts are starting to exercise an important evidentiary gatekeeping role (*Barry Glaspell (*bglaspell@blg.com*) is a senior class action counsel at Borden Ladner Gervais LLP, )*.

# ANALYTICAL METHODS – Petroleum Products

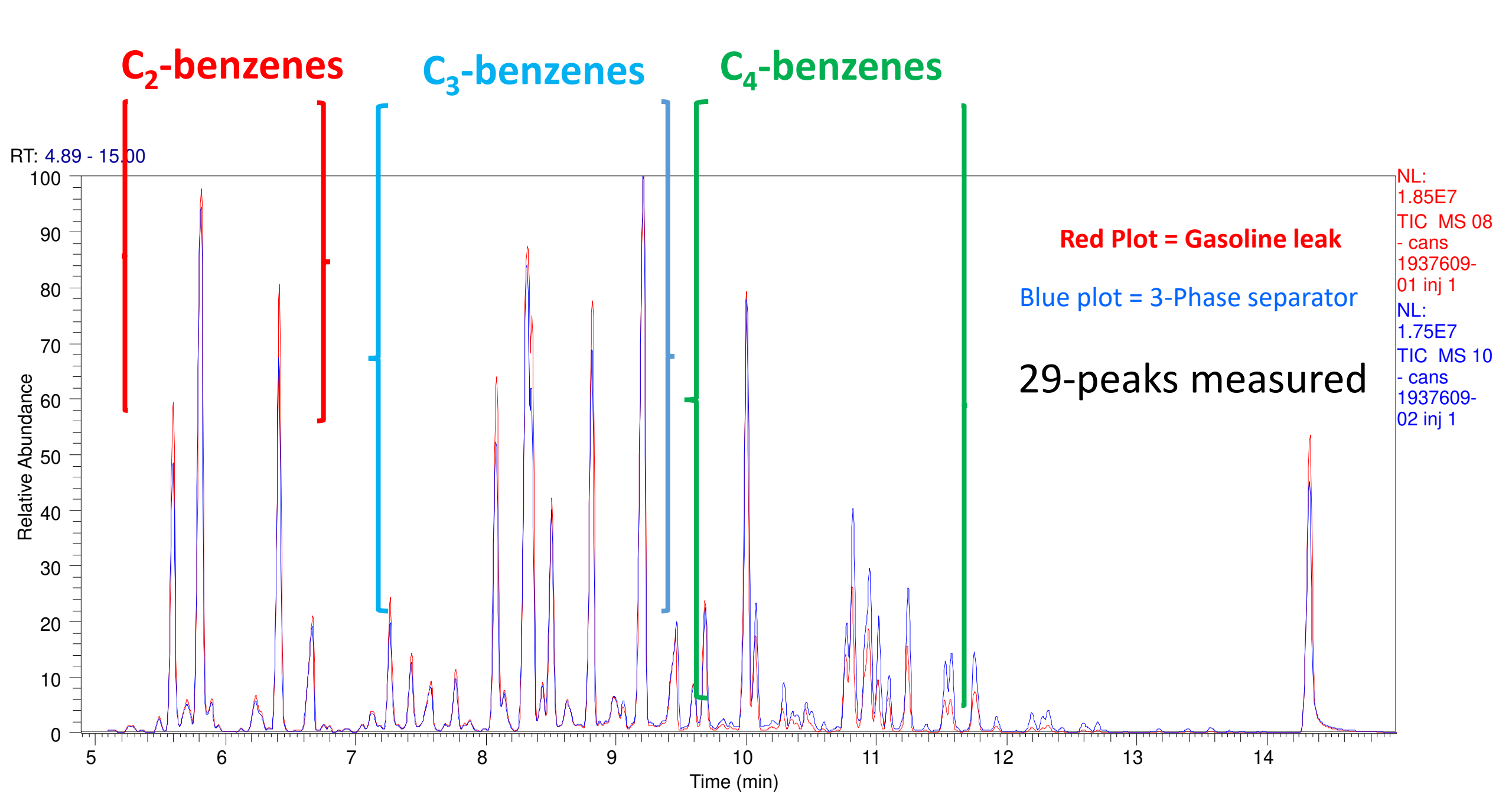
- An aliquot (500 ± 5 mg) of each product (Gasoline Leak and 3-Phase Separator gas) was weighed into a 12 mL vial and diluted to 5 mL with pentane. The mixture was placed in a freezer for 1 h to facilitate asphaltene precipitation. No precipitate was observed and therefore 200 µL of each pentane solution was diluted to 1 mL with dichloromethane solvent and analyzed.

# SOIL SAMPLES

- An aliquot (based upon soil PHC data) of soil was weighed into a new 1 quart new galvanized paint can as follows:
- (E2) – 44.5 g
- (H1) – 14.5 g
- (N2) – 12.1 g
- An aliquot of each liquid product (100 µL) was added to a Kimwipe and placed inside a new 1 quart galvanized paint can. Following the addition of 638 micrograms (µg) of surrogate (naphthalene-d8), along with a carbon strip (attached via a paper clip held to the lid of the paint can with a rare earth magnet) the cans were sealed and placed in an oven maintained at 70$^{o}$C for 24h.
- Following heat treatment, the cans were removed from the oven, allowed to equilibrate to room temperature and opened. The carbon strip was removed and placed into a 1 mL gas chromatographic vial. Carbon disulphide, 600 µL, was added to the vial containing the carbon strip. This solvent contained an internal standard, namely undecane-d24, at a concentration of 0.404 mg/mL.

# Chemical Analyses

- Chemical analyses were performed using gas chromatography/mass spectrometry (GC/MS) using EN2020. The main difference from the previous method CEN/TR 15522-2:2012, is that the method is extended to light diesel and condensate samples by including a range of low boiling compounds. Compounds measured = 144. Diagnostic ratios =  44-normative; 34 informative
- Analyses were performed in a single batch and contained 3 - 2016 composite LNAPL samples taken from another site as a reference oil. The 2016 LNAPL was used as a template to correctly identify petroleum biomarkers. All samples were analyzed in duplicate.
- All headspace samples were analyzed split 20:1. Liquid product samples were analyzed splitless.
- It is important to point out that oil samples can be stored indefinitely if stored at temperatures from above freezing to 30ºC (NOAA, 2011). Paracel Laboratories stored 2016 LNAPL as well as the samples listed in Table 1 in a refrigerator maintained at 5ºC.

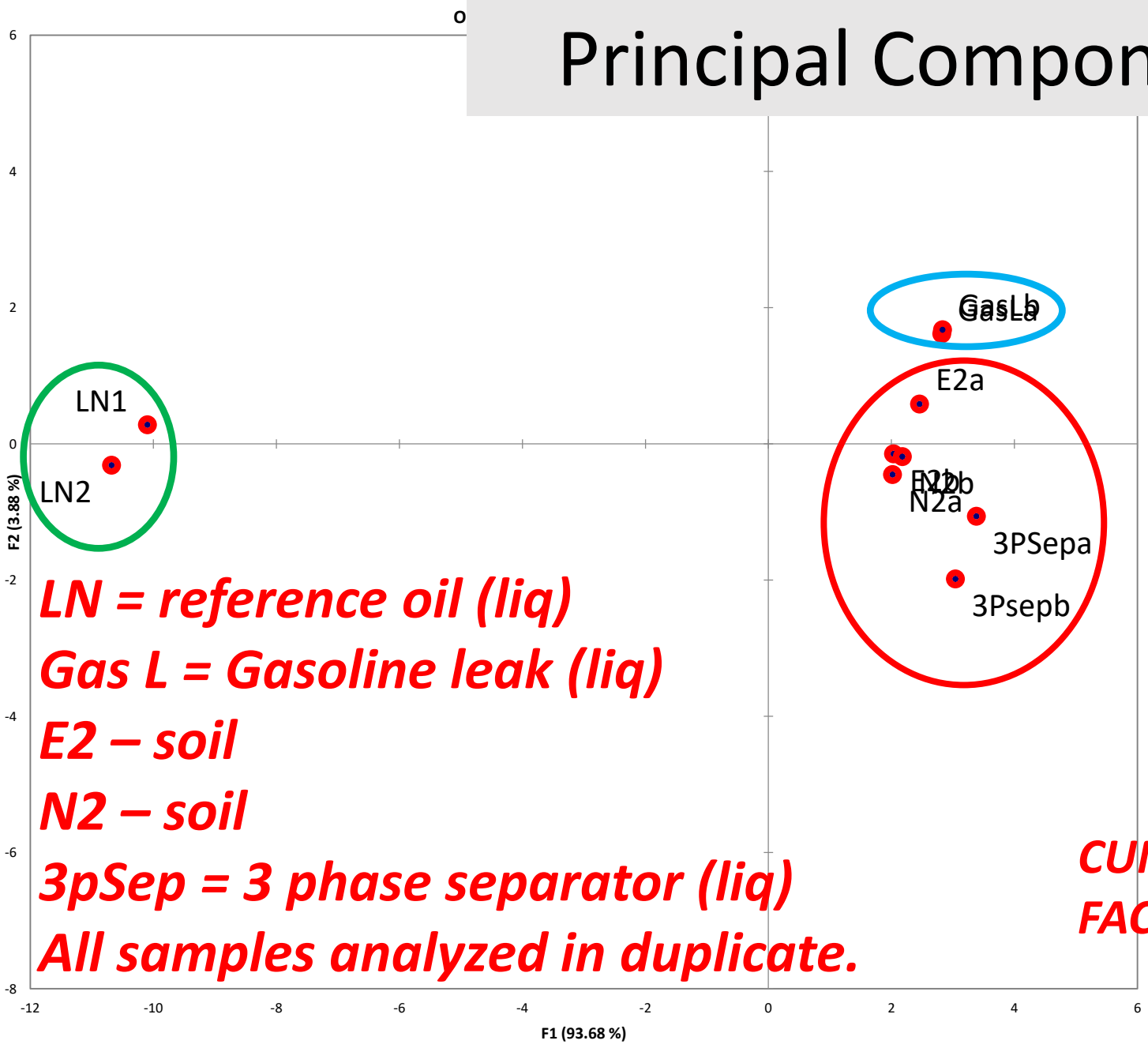



**GC/MS TOTAL ION CHROMATOGRAMS**

# Chemometrics

- GC/MS TIC data subjected to Atichison transformation
- Principal components analysis (PCA) using XLSTAT
- Score plots subjected to Agglomerative hierarchical clustering
- Dissimilarity: Euclidean distance (Ward’s method)
- Dissimilarity: Mahalanobis distance (unweighted pair group average)

# Principal Component Analysis




| Class | 1 | 2 | 3 |
|---|---|---|---|
| Objects | 2 | 6 | 2 |
| Sum of weights | 2 | 6 | 2 |
| Within-class variance | 0.002 | 1.106 | 0.349 |
| Minimum distance to centroid | 0.031 | 0.491 | 0.417 |
| Average distance to centroid | 0.031 | 0.883 | 0.417 |
| Maximum distance to centroid | 0.031 | 1.533 | 0.417 |
| | GasLa | 3PSepa | LN1 |
| | GasLb | 3Psepb | LN2 |
| | | E2a | |
| | | E2b | |
| | | N2a | |
| | | N2b | |

***LN = reference oil (liq)***

***Gas L = Gasoline leak (liq)***

***E2 – soil***

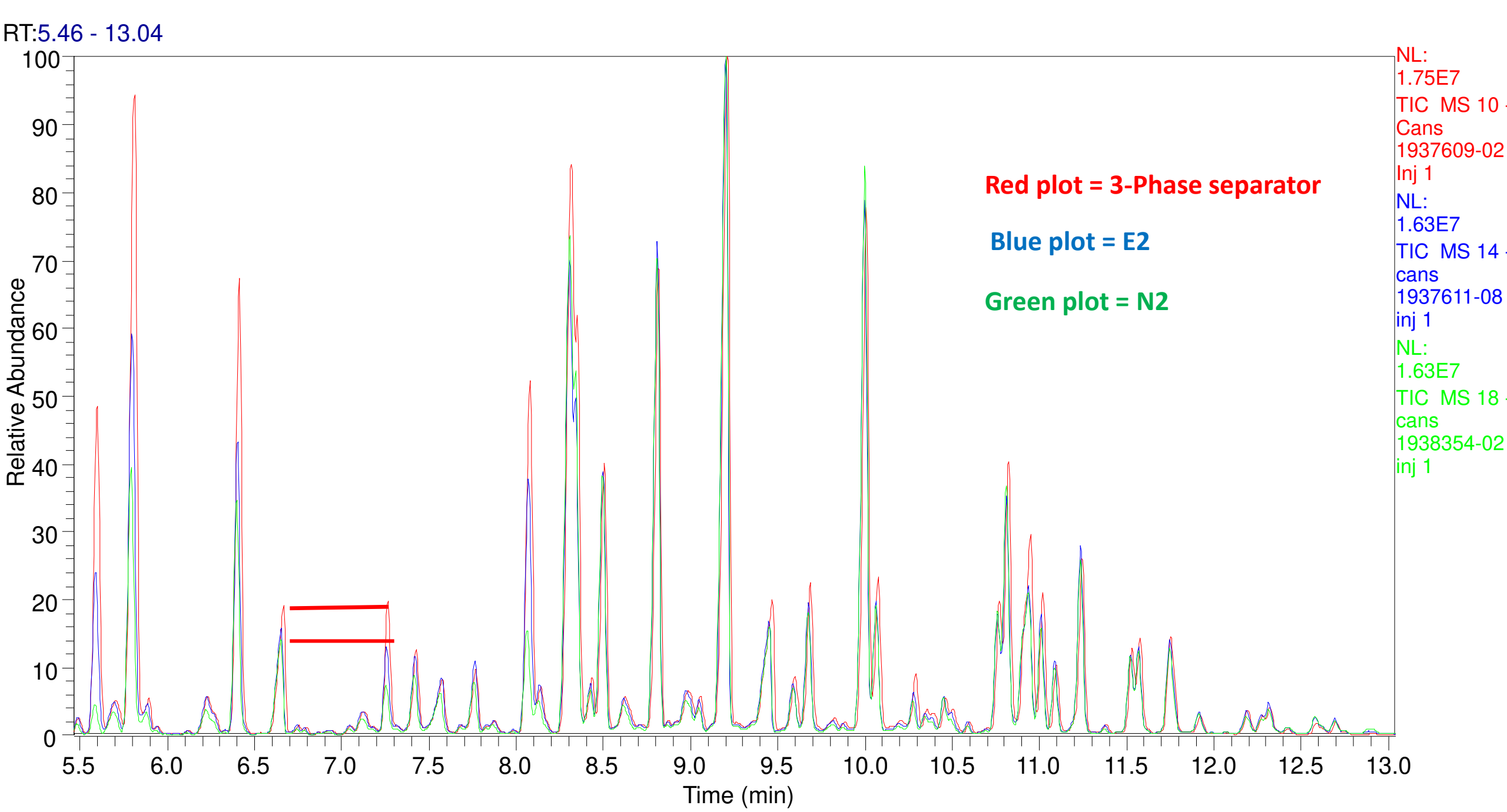
***N2 – soil***

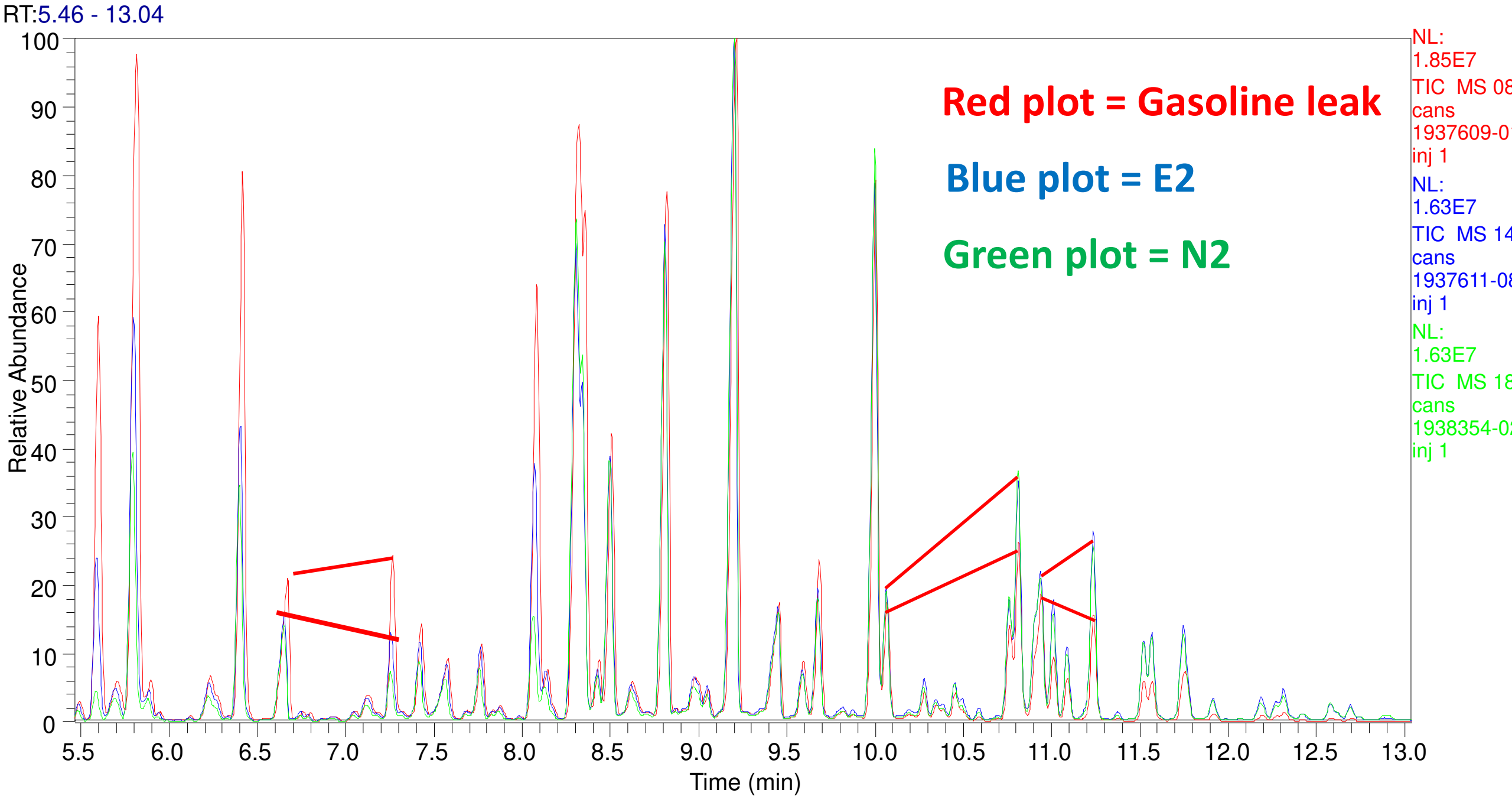
***3pSep = 3 phase separator (liq)***

***All samples analyzed in duplicate.***

***CUMULATIVE VARIABILITY % F1/F2 = 98%***

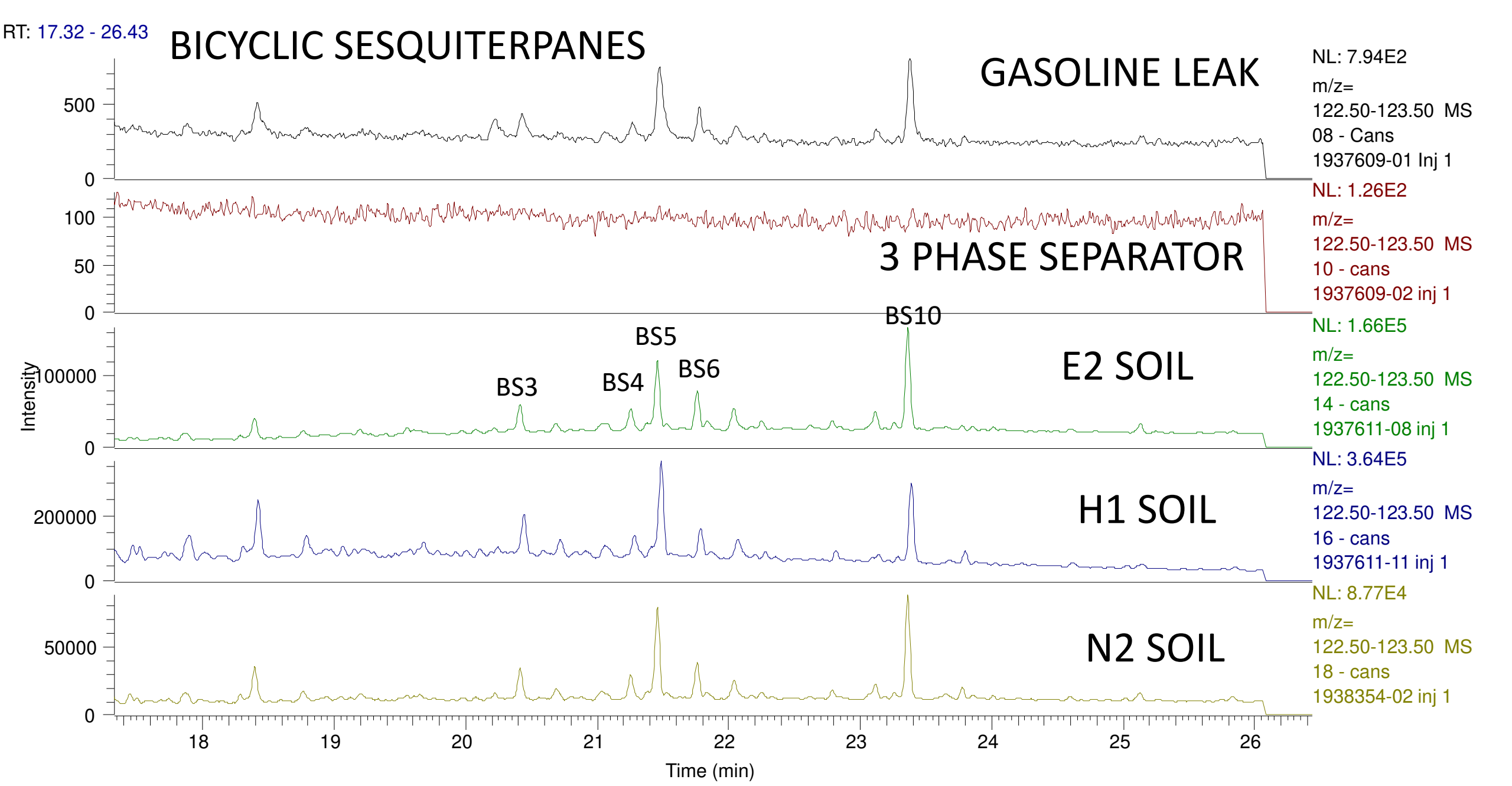
***FACTOR LOADINGS F1 = 0.85 – 1.0***


RT:5.46 - 13.04
Relative Abundance
Time (min)
Red plot = 3-Phase separator
Blue plot = E2
Green plot = N2
NL:
1.75E7
TIC MS 10 -
Cans
1937609-02
Inj 1
NL:
1.63E7
TIC MS 14 -
cans
1937611-08
inj 1
NL:
1.63E7
TIC MS 18 -
cans
1938354-02
inj 1


RT:5.46 - 13.04
Red plot = Gasoline leak
Blue plot = E2
Green plot = N2
Relative Abundance
Time (min)
NL:
1.85E7
TIC MS 08
cans
1937609-0
inj 1
NL:
1.63E7
TIC MS 14
cans
1937611-08
inj 1
NL:
1.63E7
TIC MS 18
cans
1938354-0
inj 1

# Preliminary Conclusions using Conventional Chemistry Alone

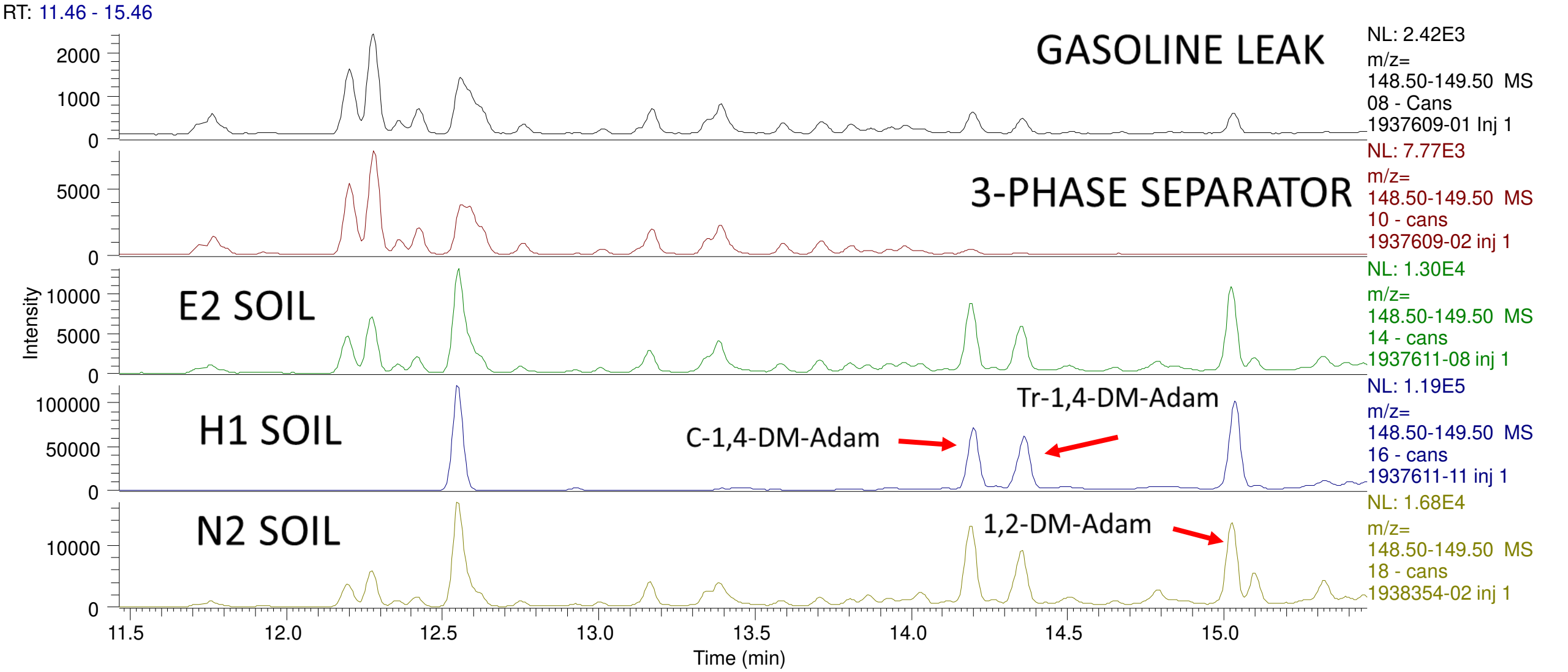
- Field observations, PHC data, chromatograms and chemometrics suggest that sites E2 and N2 are contaminated with material coming from a source similar to the 3-Phase Separator.
- In other words, current operations could be perceived as being responsible for the contamination observed.
- THIS SUGGESTS LIABILITY BUT IS THIS THE CORRECT CONCLUSION?


RT: 17.32 - 26.43
BICYCLIC SESQUITERPANES
GASOLINE LEAK
NL: 7.94E2
m/z=
122.50-123.50 MS
08 - Cans
1937609-01 Inj 1
3 PHASE SEPARATOR
NL: 1.26E2
m/z=
122.50-123.50 MS
10 - cans
1937609-02 inj 1
E2 SOIL
NL: 1.66E5
m/z=
122.50-123.50 MS
14 - cans
1937611-08 inj 1
BS3
BS4
BS5
BS6
BS10
H1 SOIL
NL: 3.64E5
m/z=
122.50-123.50 MS
16 - cans
1937611-11 inj 1
N2 SOIL
NL: 8.77E4
m/z=
122.50-123.50 MS
18 - cans
1938354-02 inj 1
Intensity
Time (min)

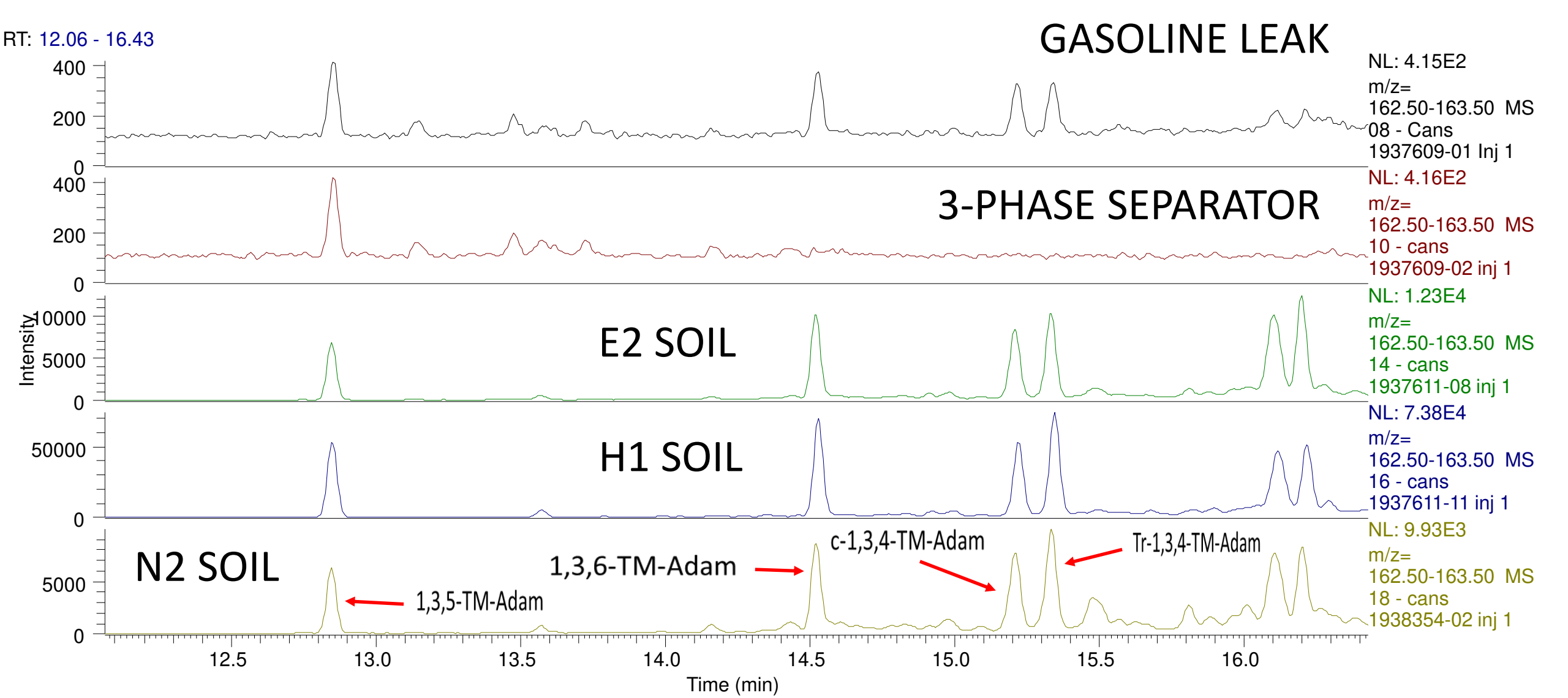
# *BICYCLIC SESQUITERPANE RATIOS*

| Ratio | Gasoline Leak | E2 SOIL | H1 SOIL | N2 Soil |
|---|---|---|---|---|
| BS4/BS5 | **0.32** | **0.32** | 0.22 | 0.26 |
| BS5/BS6 | **2.11** | 1.78 | 3.27 | 2.57 |
| BS3/BS10 | **0.33** | 0.27 | 0.50 | **0.30** |
| BS4/BS10 | **0.29** | 0.22 | **0.26** | 0.23 |
| BS5/BS10 | **0.90** | 0.68 | 1.20 | **0.88** |
| BS6/BS10 | **0.43** | **0.38** | 0.37 | 0.34 |

DATA IN GREEN A MATCH USING CRITICAL DIFFERENCE ANALYSIS




***DIMETHYL ADAMANTANES***

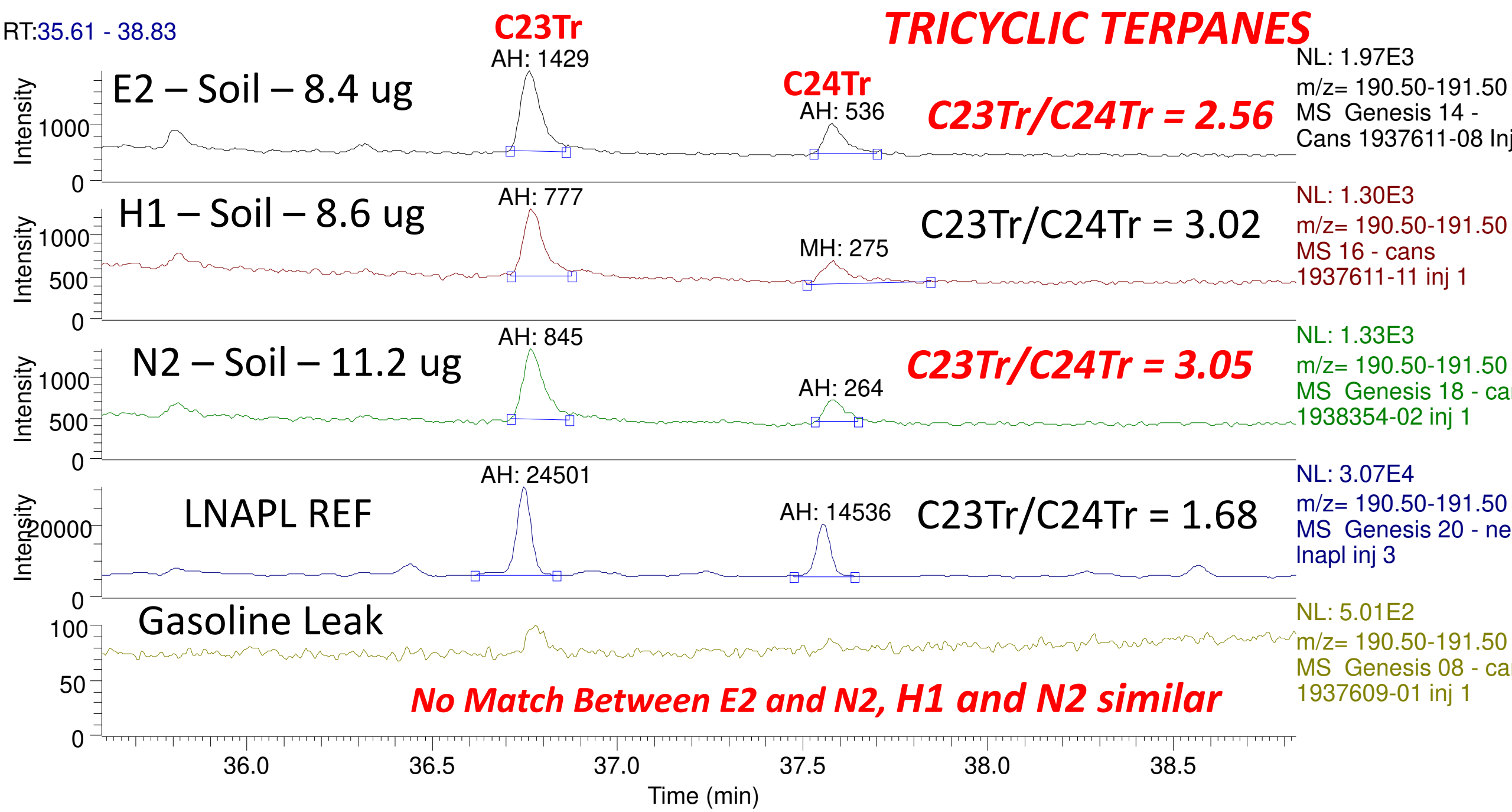



***TRIMETHYL ADAMANTANES***

# *DI- AND TRIMETHYL -ADAMANTANES*

| Ratio | Gasoline Leak | E2 SOIL | H1 SOIL | N2 SOIL |
|---|---|---|---|---|
| C-134-TM-ADAM/Tr-134-TM-ADAM | **0.95** | 0.82 | 0.72 | 0.78 |
| 135-TM-ADAM/134(C+TR)-TM-ADAM | **0.69** | 0.40 | 0.43 | 0.36 |
| 136-TM-ADAM/134(C+TR)-TM-ADAM | **0.61** | **0.55** | **0.55** | 0.50 |
| 135-TM-ADAM-136-TM-ADAM | **1.13** | 0.67 | 0.78 | 0.73 |
| C-14-DM-ADAM/TR-14-DM-ADAM | **1.44** | **1.48** | 1.17 | **1.50** |
| 14(TR+C)-DM-ADAM/12-DM-ADAM | **1.89** | 1.34 | 1.30 | 1.61 |

DATA IN GREEN A MATCH USING CRITICAL DIFFERENCE ANALYSIS


RT:35.61 - 38.83
TRICYCLIC TERPANES
C23Tr
AH: 1429
C24Tr
AH: 536
C23Tr/C24Tr = 2.56
E2 – Soil – 8.4 ug
NL: 1.97E3
m/z= 190.50-191.50
MS Genesis 14 -
Cans 1937611-08 Inj
AH: 777
MH: 275
H1 – Soil – 8.6 ug
C23Tr/C24Tr = 3.02
NL: 1.30E3
m/z= 190.50-191.50
MS 16 - cans
1937611-11 inj 1
AH: 845
AH: 264
N2 – Soil – 11.2 ug
C23Tr/C24Tr = 3.05
NL: 1.33E3
m/z= 190.50-191.50
MS Genesis 18 - ca
1938354-02 inj 1
AH: 24501
AH: 14536
LNAPL REF
C23Tr/C24Tr = 1.68
NL: 3.07E4
m/z= 190.50-191.50
MS Genesis 20 - ne
lnapl inj 3
Gasoline Leak
NL: 5.01E2
m/z= 190.50-191.50
MS Genesis 08 - ca
1937609-01 inj 1
No Match Between E2 and N2, H1 and N2 similar
Intensity
1000
0
500
20000
100
50
36.0
36.5
37.0
37.5
38.0
38.5
Time (min)

# Weathering Assessment: Evaporation

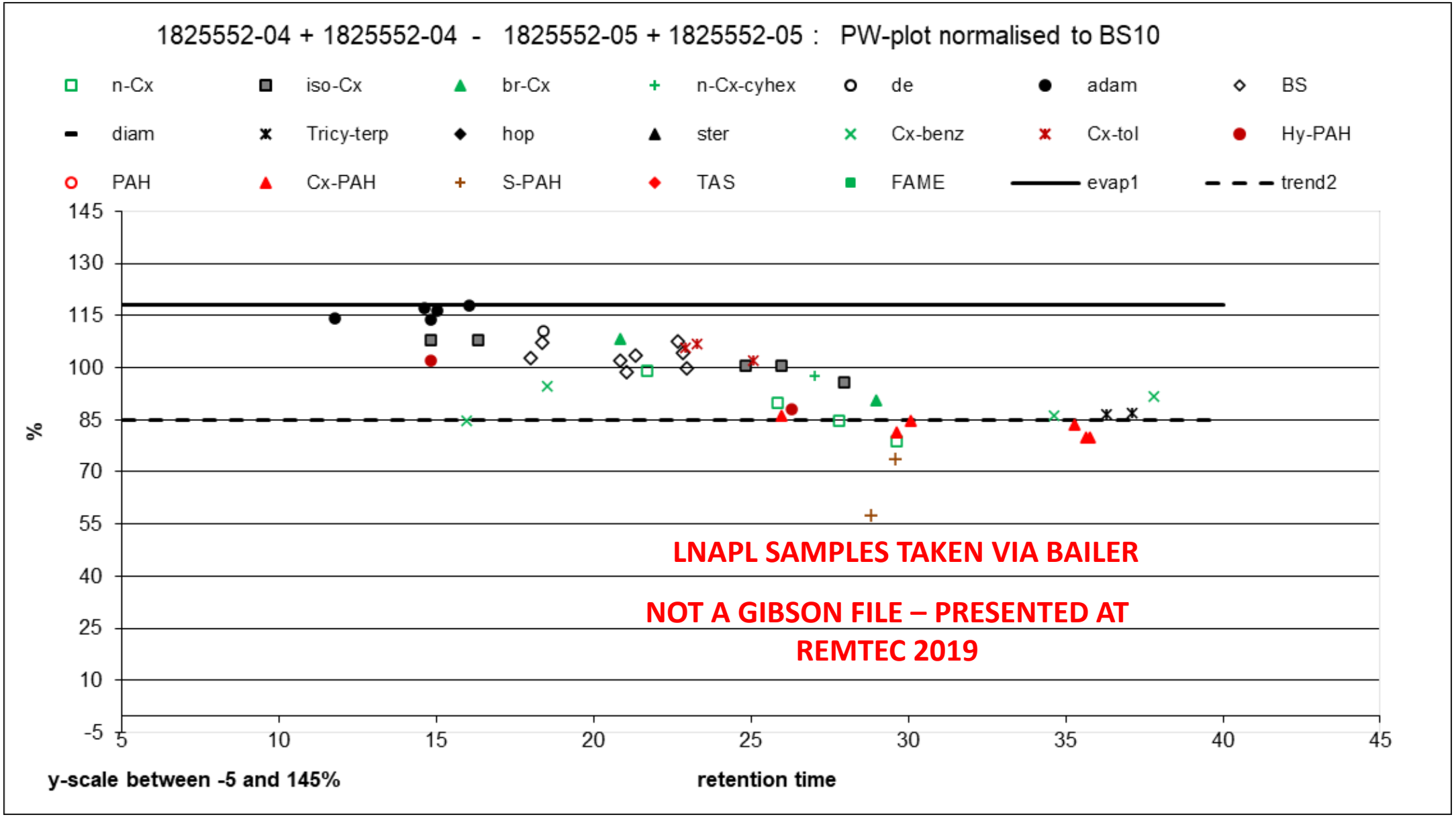
- Evaporation is the most significant weathering effect following release of light petroleum products such as gasoline and condensate
- Ratios assessing evaporation from gasoline include (Stout et al., 2006):
  - n-pentane/n-heptane (C5H12 / C7H16)
  - 2-methylpentane/2-methylheptane (C6H14/C8H18)
  - Isopentane/n-heptane (C5H12/C7H16)
  - n-heptane/n-decane (C5H12/C10H22)
- EN 2020 normalizes all biomarkers to bicyclic sesquiterpane 10 (BS 10), phytane or hopane – we used BS10
- In this study bicyclic sesquiterpanes (BS-1, -2, 3, -4, -5, -6, -8, -9, and 10) were detected ($C_{14}H_{26}$, $C_{15}H_{28}$, $C_{16}H_{30}$)
- Also detected were dimethyl- and trimethyl-adamantanes ($C_{12}H_{20}$ and $C_{13}H_{22}$)
- Bicyclic sesquiterpanes and adamantanes are stable to biodegradation but can be affected by evaporation. Using BS10 is a much better option for assessing evaporation of samples than those parameters identified in the literature.
- Also, the samples are more like condensate and middle distillates so use of gasoline weathering indices is inappropriate

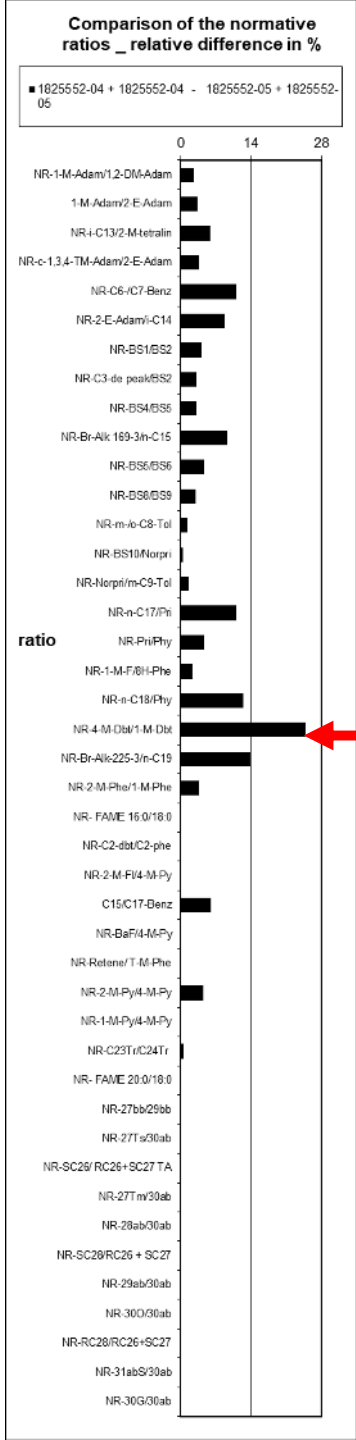
# Percent Weathering (PW) CALCULATIONS

$$\%C_{NSPILL} = C_{NSPILL}/C_{BS10SPILL} \,//\, C_{NSOURCE}/C_{BS10SOURCE}$$

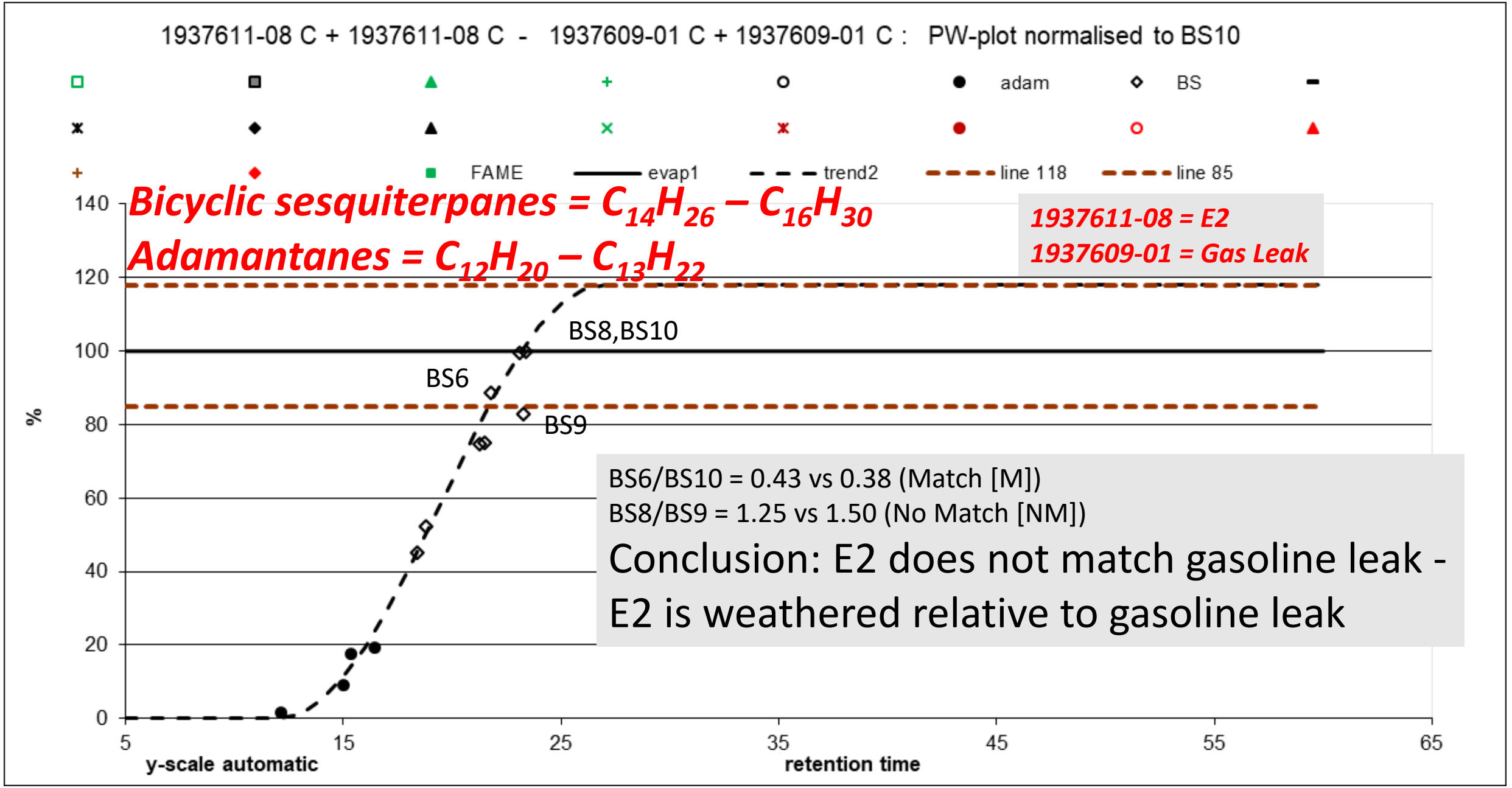
***EXAMPLE***

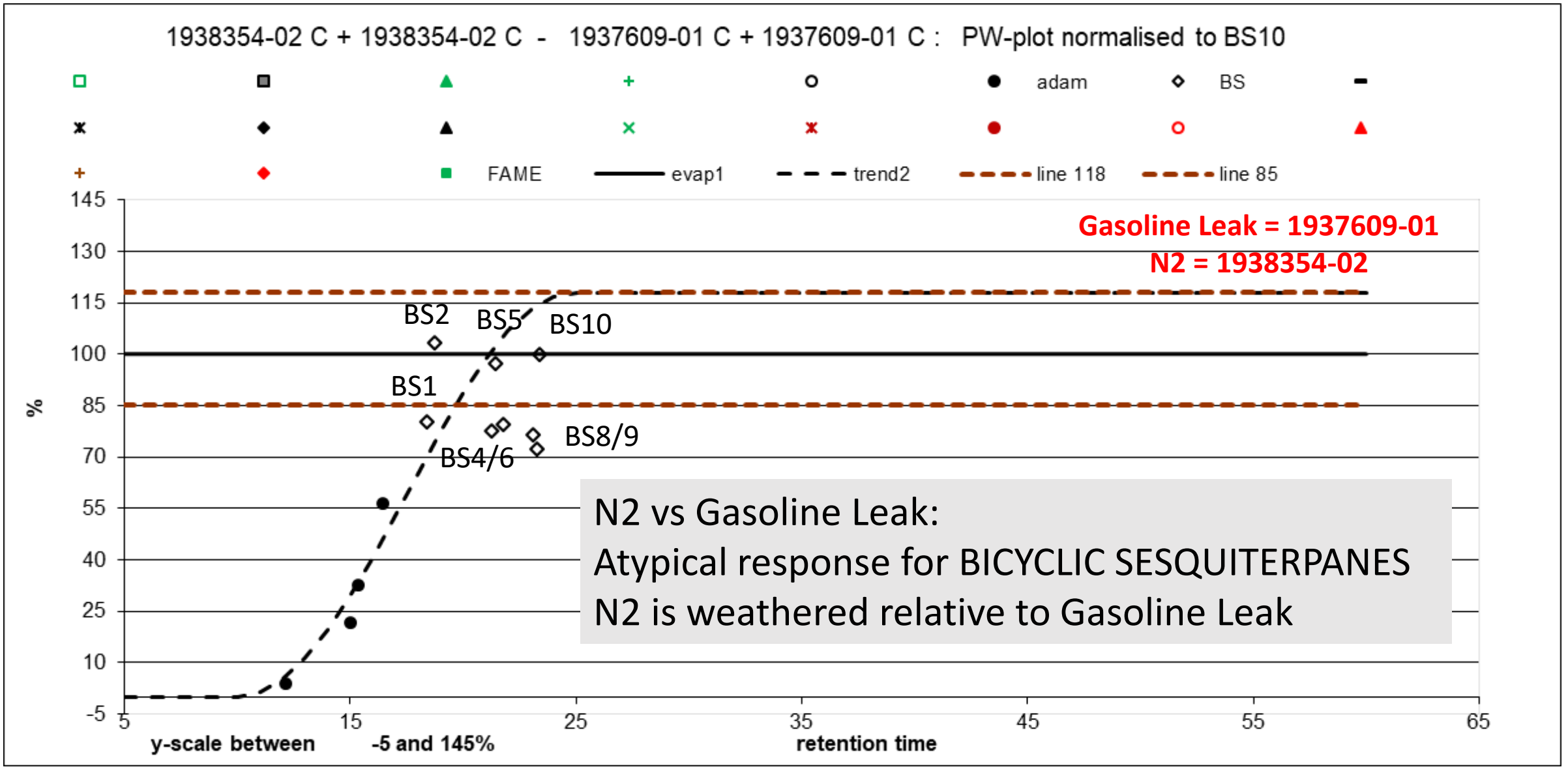
$$\%BS6_{SPILL} = C_{BS6SPILL}/C_{BS10SPILL}//C_{BS6SOURCE}/C_{BS10SOURCE}$$

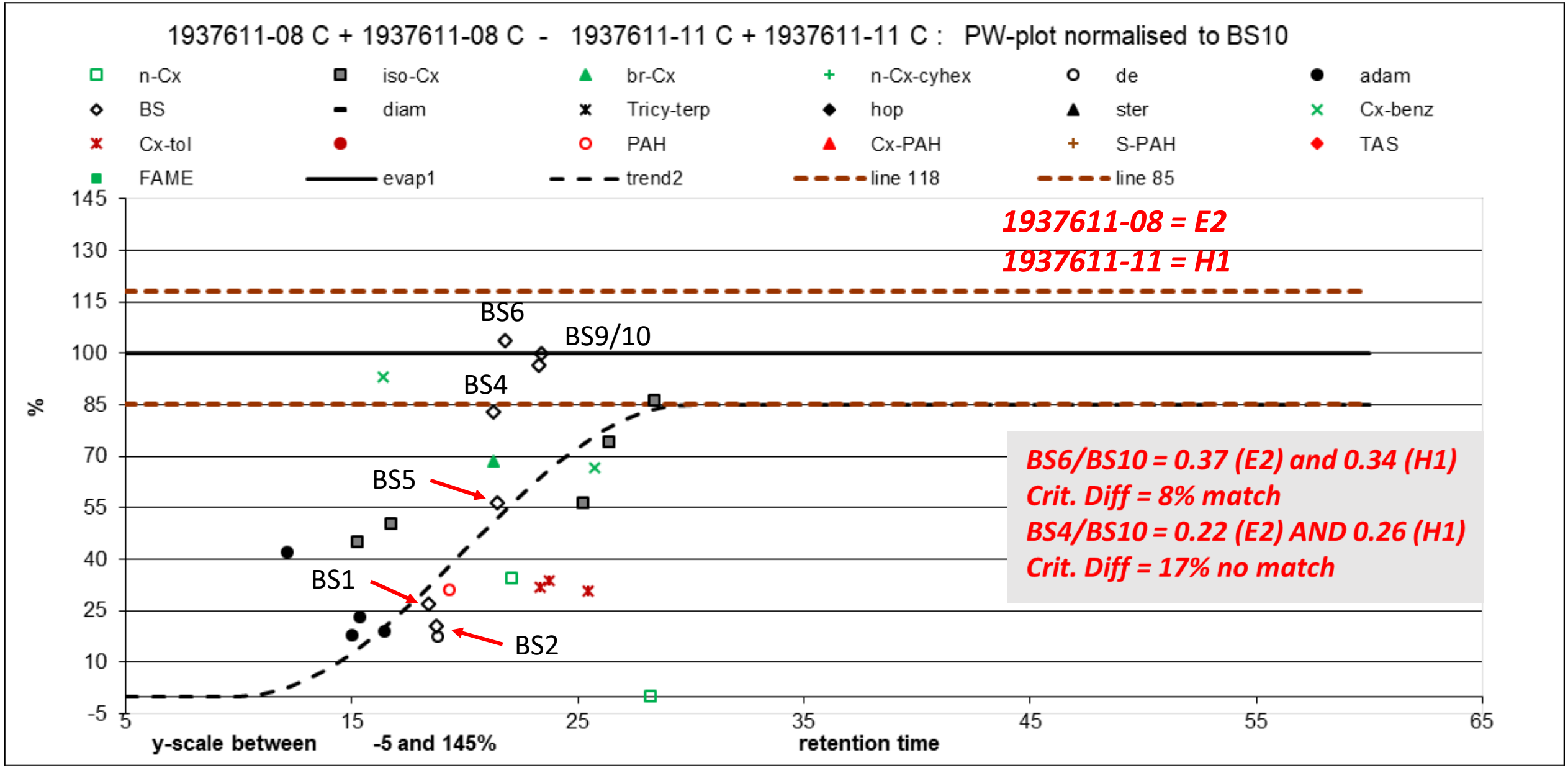


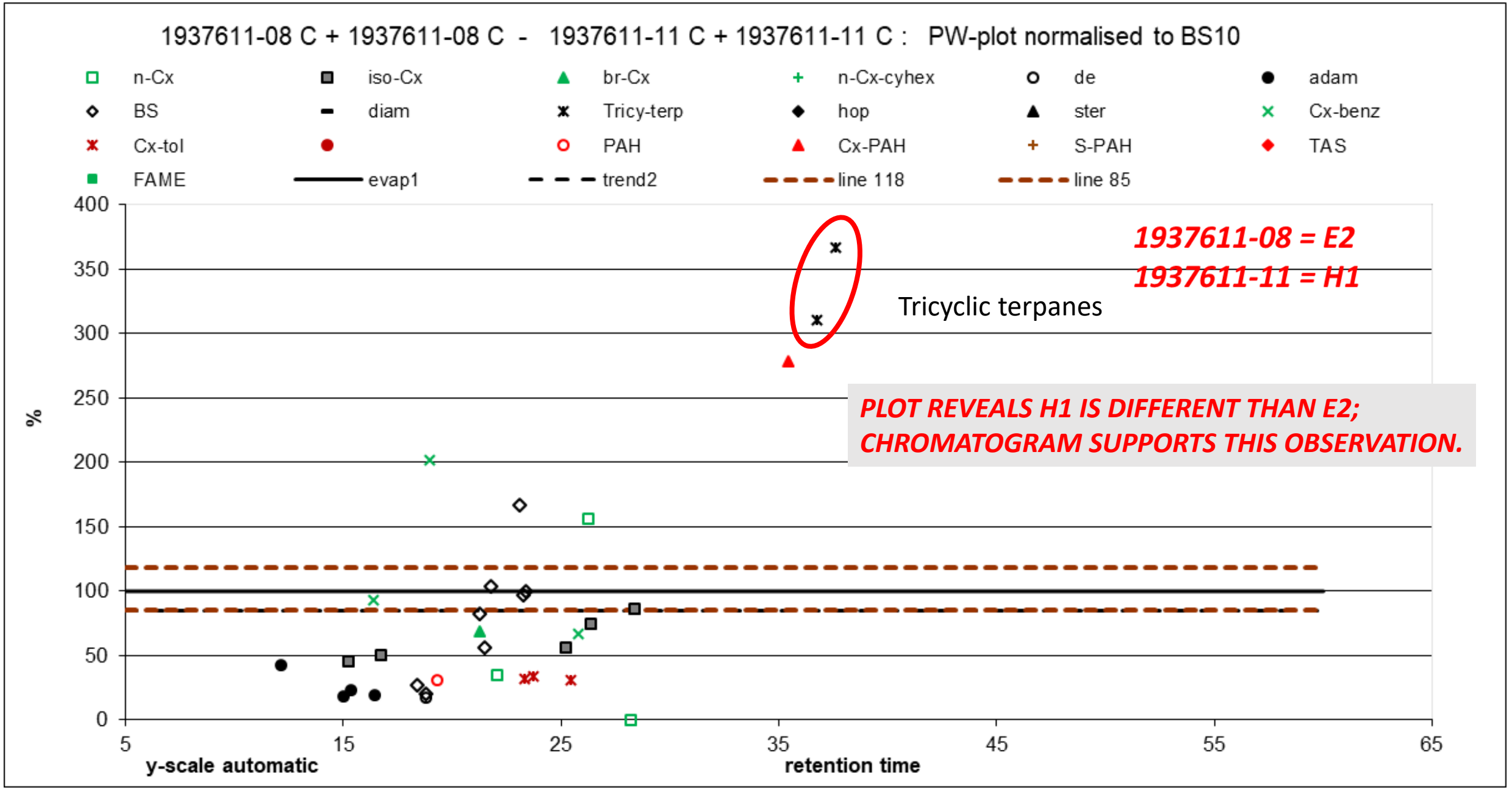



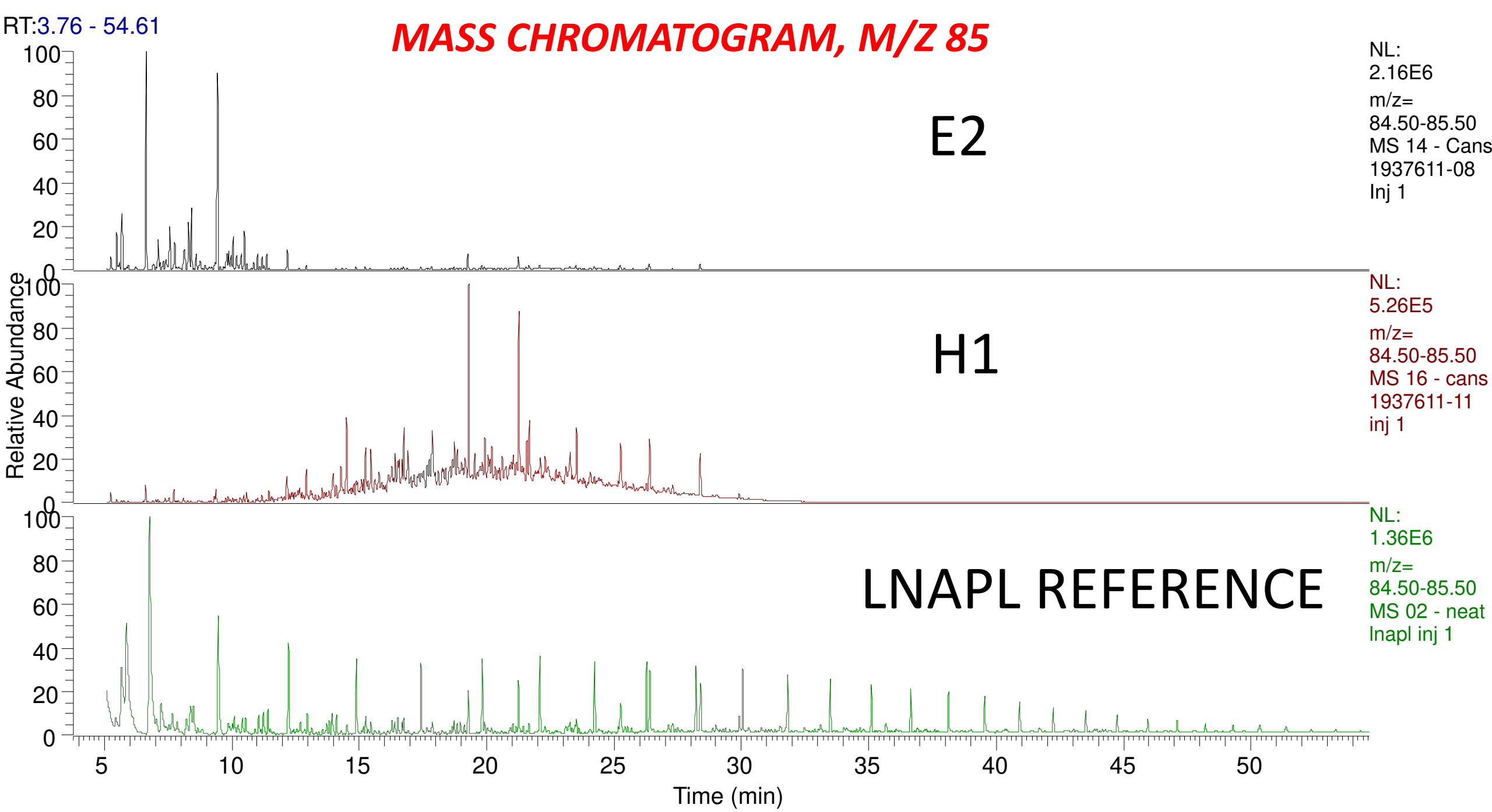

**TYPICAL WEATHERING PLOT COMPARISON** OF SOURCE (-05) WITH SAMPLE (-04). MIXTURE OF GASOLINE AND DIESEL FUEL. **ONE RATIO >14% RPD** BUT CAN BE EXPLAINED BY WEATHERING CONCLUSION BOTH ARE A POSITIVE MATCH

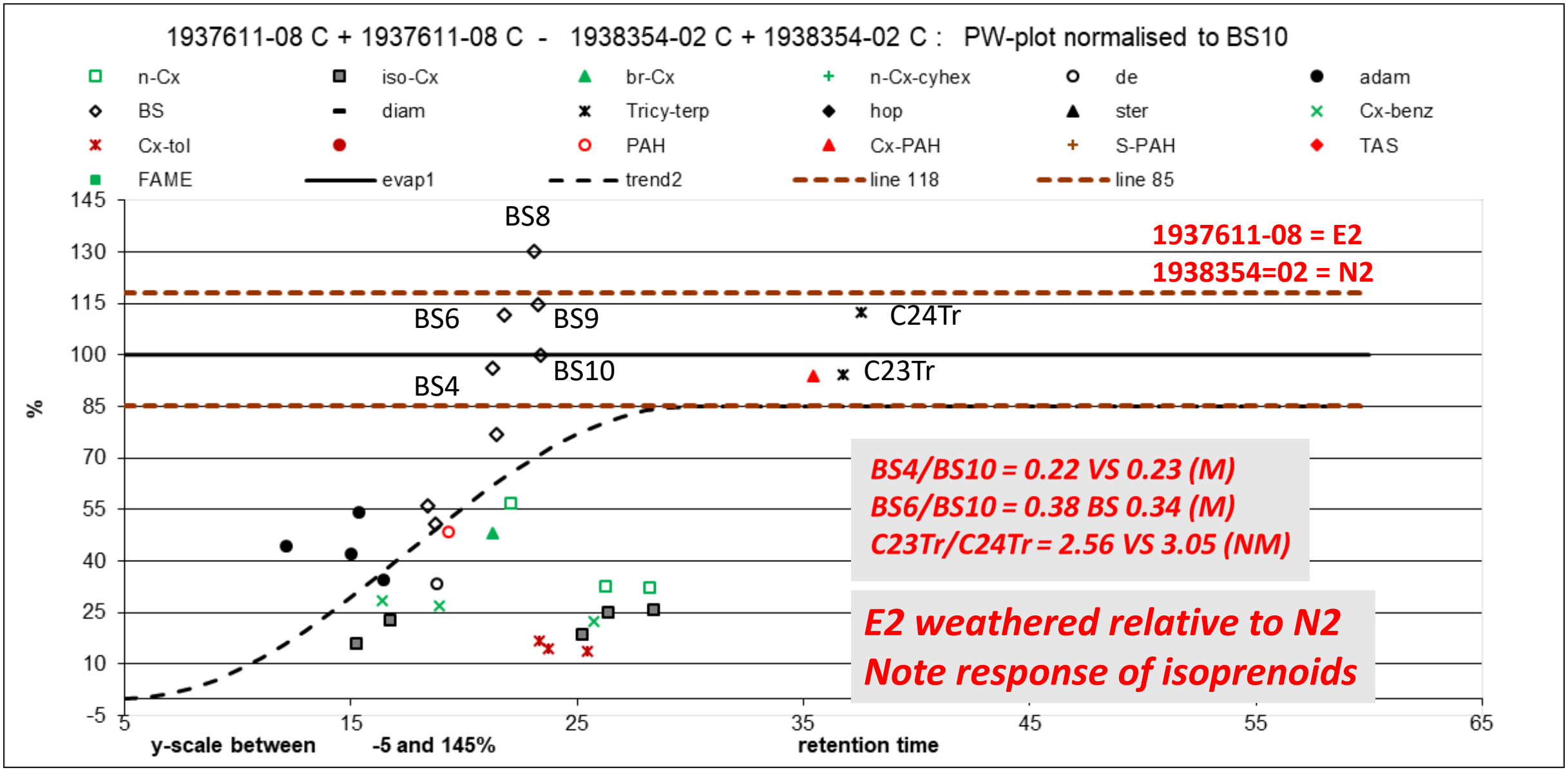

1937611-08 C + 1937611-08 C - 1937609-01 C + 1937609-01 C : PW-plot normalised to BS10
adam
BS
FAME
evap1
trend2
line 118
line 85
Bicyclic sesquiterpanes = C14H26 – C16H30
Adamantanes = C12H20 – C13H22
1937611-08 = E2
1937609-01 = Gas Leak
BS8,BS10
BS6
BS9
%
140
120
100
80
60
40
20
0
5
15
25
35
45
55
65
y-scale automatic
retention time
BS6/BS10 = 0.43 vs 0.38 (Match [M])
BS8/BS9 = 1.25 vs 1.50 (No Match [NM])
Conclusion: E2 does not match gasoline leak - E2 is weathered relative to gasoline leak

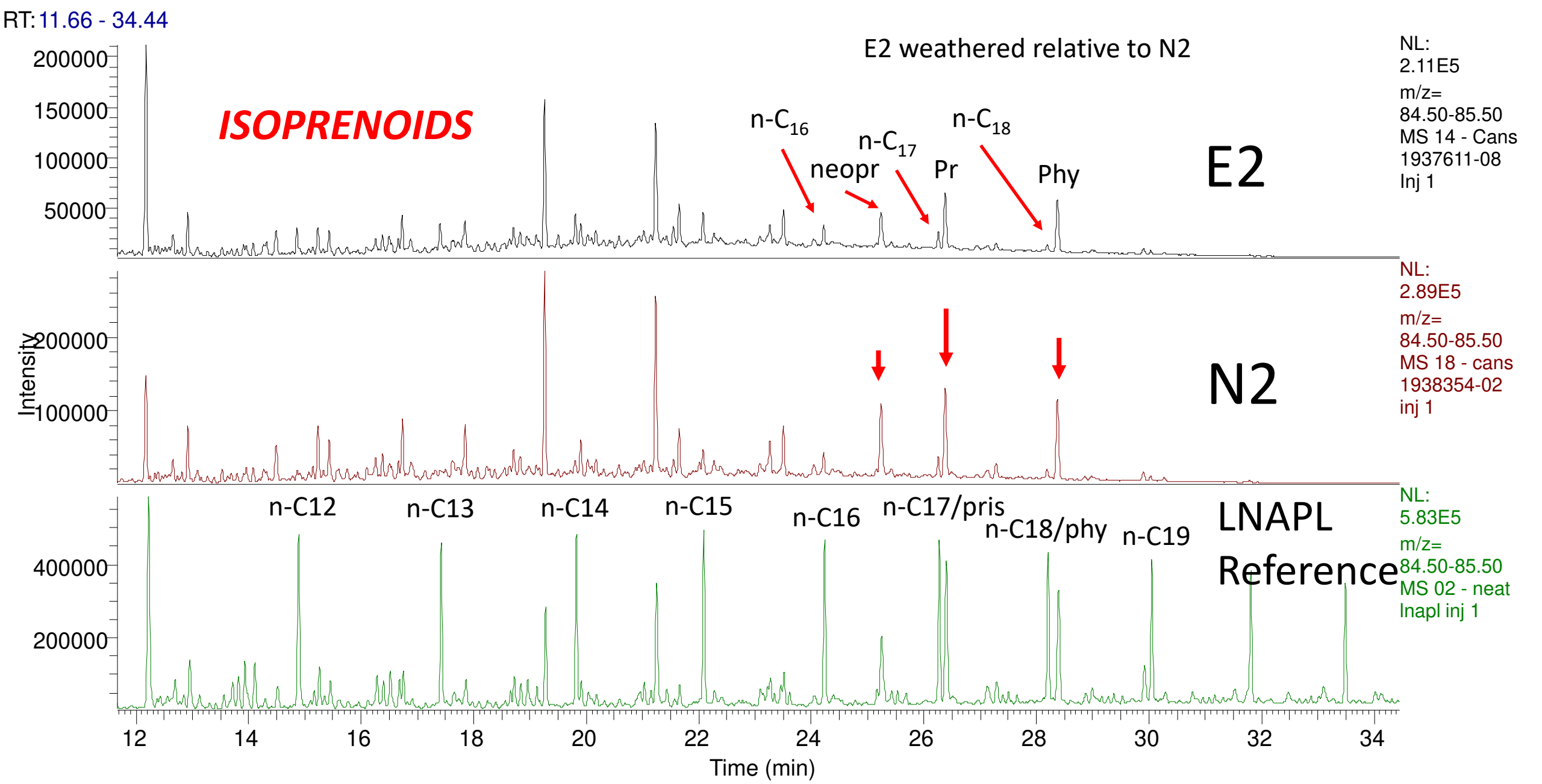

1938354-02 C + 1938354-02 C - 1937609-01 C + 1937609-01 C : PW-plot normalised to BS10
adam
BS
FAME
evap1
trend2
line 118
line 85
Gasoline Leak = 1937609-01
N2 = 1938354-02
BS2
BS5
BS10
BS1
BS8/9
BS4/6
N2 vs Gasoline Leak:
Atypical response for BICYCLIC SESQUITERPANES
N2 is weathered relative to Gasoline Leak
%
145
130
115
100
85
70
55
40
25
10
-5
5
15
25
35
45
55
65
y-scale between -5 and 145%
retention time

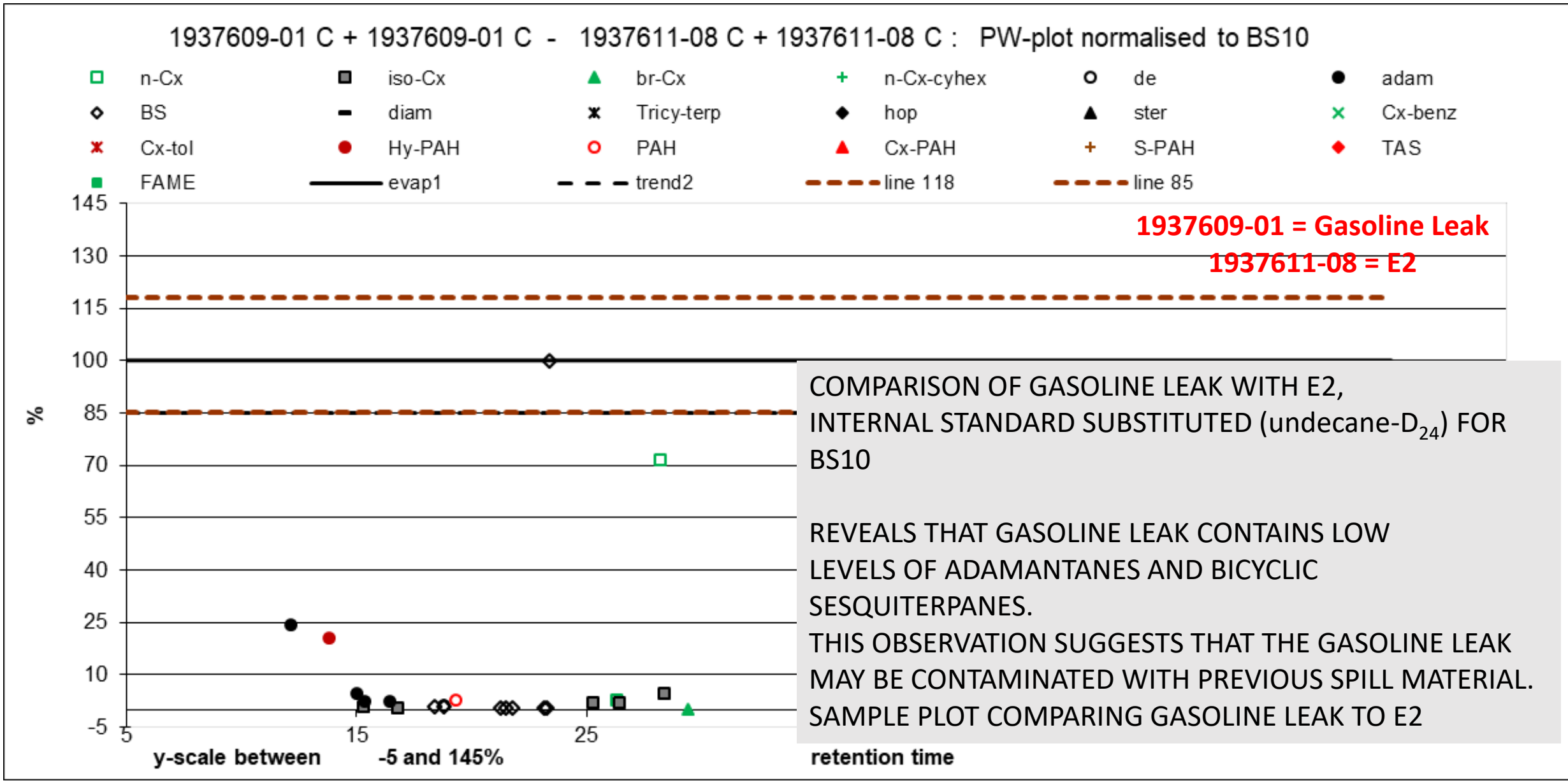

1937611-08 C + 1937611-08 C - 1937611-11 C + 1937611-11 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
1937611-08 = E2
1937611-11 = H1
BS6
BS9/10
BS4
BS5
BS1
BS2
BS6/BS10 = 0.37 (E2) and 0.34 (H1)
Crit. Diff = 8% match
BS4/BS10 = 0.22 (E2) AND 0.26 (H1)
Crit. Diff = 17% no match
%
145
130
115
100
85
70
55
40
25
10
-5
5
15
25
35
45
55
65
y-scale between -5 and 145%
retention time


1937611-08 C + 1937611-08 C - 1937611-11 C + 1937611-11 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
400
350
300
250
200
150
100
50
0
%
5
15
25
35
45
55
65
y-scale automatic
retention time
1937611-08 = E2
1937611-11 = H1
Tricyclic terpanes
PLOT REVEALS H1 IS DIFFERENT THAN E2;
CHROMATOGRAM SUPPORTS THIS OBSERVATION.


RT:3.76 - 54.61
MASS CHROMATOGRAM, M/Z 85
E2
NL:
2.16E6
m/z=
84.50-85.50
MS 14 - Cans
1937611-08
Inj 1
H1
NL:
5.26E5
m/z=
84.50-85.50
MS 16 - cans
1937611-11
inj 1
LNAPL REFERENCE
NL:
1.36E6
m/z=
84.50-85.50
MS 02 - neat
lnapl inj 1
Relative Abundance
Time (min)
0
20
40
60
80
100
5
10
15
20
25
30
35
40
45
50

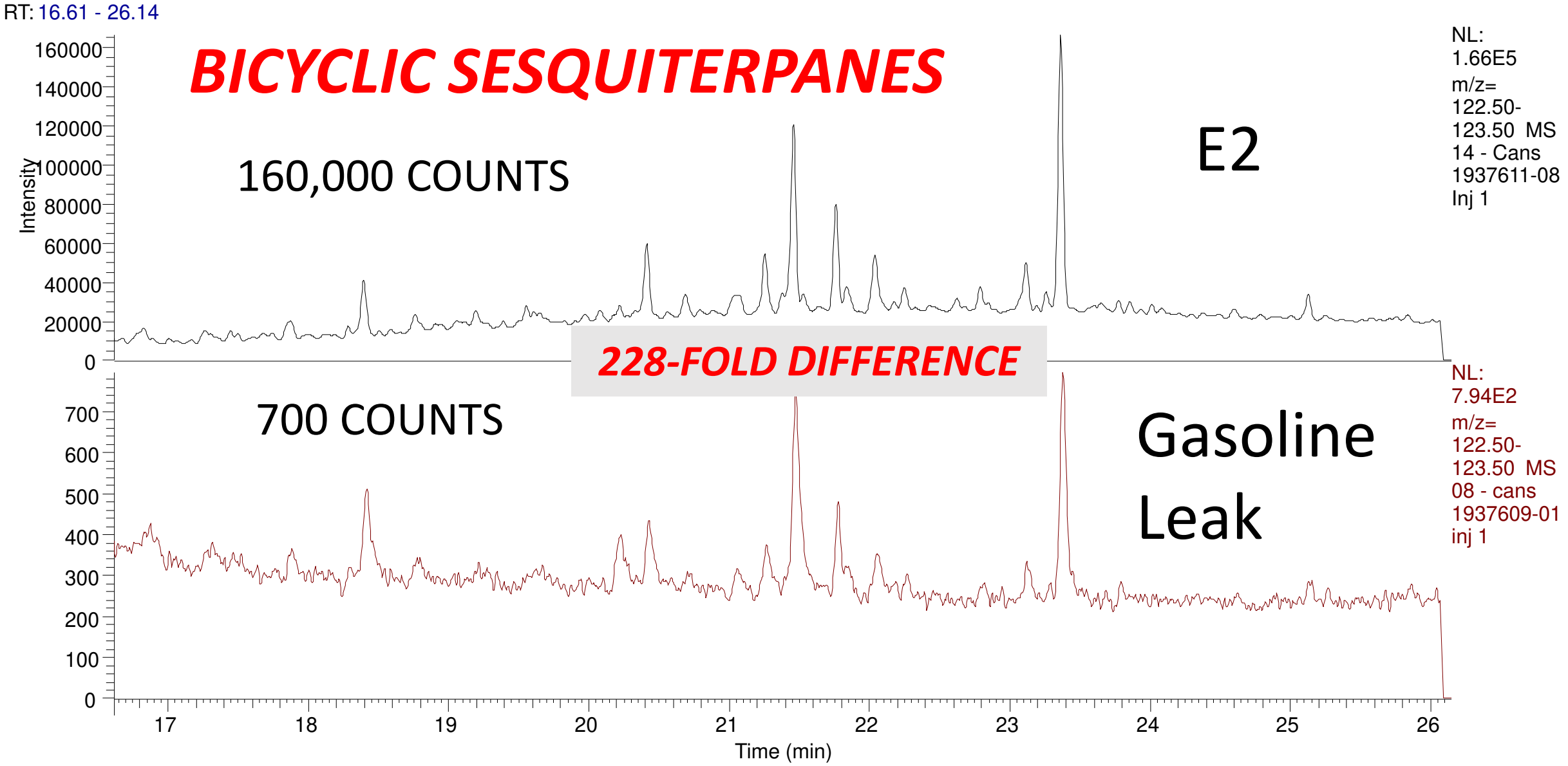

1937611-08 C + 1937611-08 C - 1938354-02 C + 1938354-02 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
%
145
130
115
100
85
70
55
40
25
10
-5
5
15
25
35
45
55
65
BS8
BS6
BS9
BS10
BS4
C24Tr
C23Tr
1937611-08 = E2
1938354=02 = N2
BS4/BS10 = 0.22 VS 0.23 (M)
BS6/BS10 = 0.38 BS 0.34 (M)
C23Tr/C24Tr = 2.56 VS 3.05 (NM)
E2 weathered relative to N2
Note response of isoprenoids
y-scale between -5 and 145%
retention time


RT: 11.66 - 34.44
E2 weathered relative to N2
ISOPRENOIDS
n-C16
neopr
n-C17
Pr
n-C18
Phy
E2
NL:
2.11E5
m/z=
84.50-85.50
MS 14 - Cans
1937611-08
Inj 1
N2
NL:
2.89E5
m/z=
84.50-85.50
MS 18 - cans
1938354-02
inj 1
n-C12
n-C13
n-C14
n-C15
n-C16
n-C17/pris
n-C18/phy
n-C19
LNAPL
Reference
NL:
5.83E5
m/z=
84.50-85.50
MS 02 - neat
lnapl inj 1
Intensity
200000
150000
100000
50000
400000
12
14
16
18
20
22
24
26
28
30
32
34
Time (min)

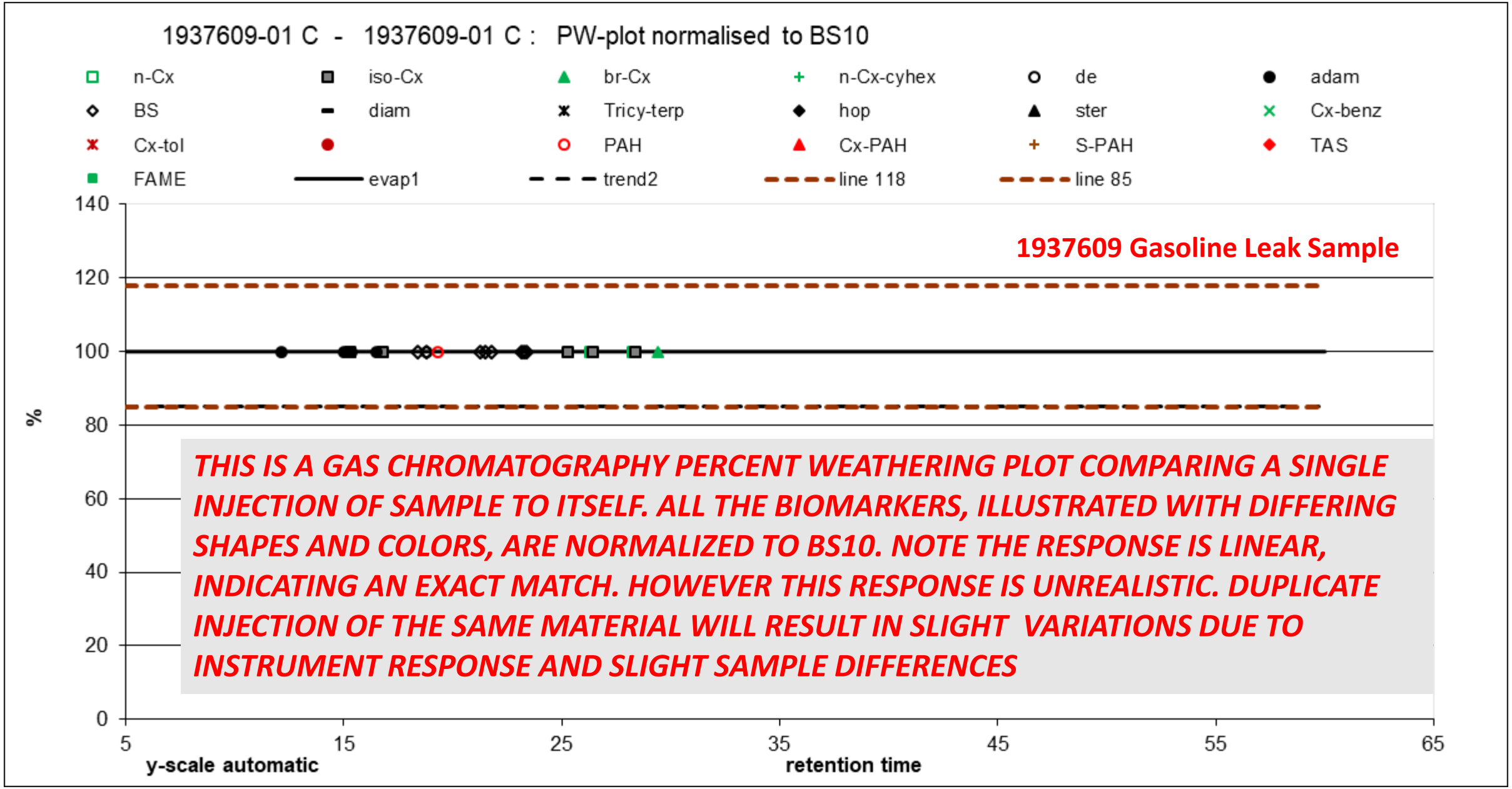


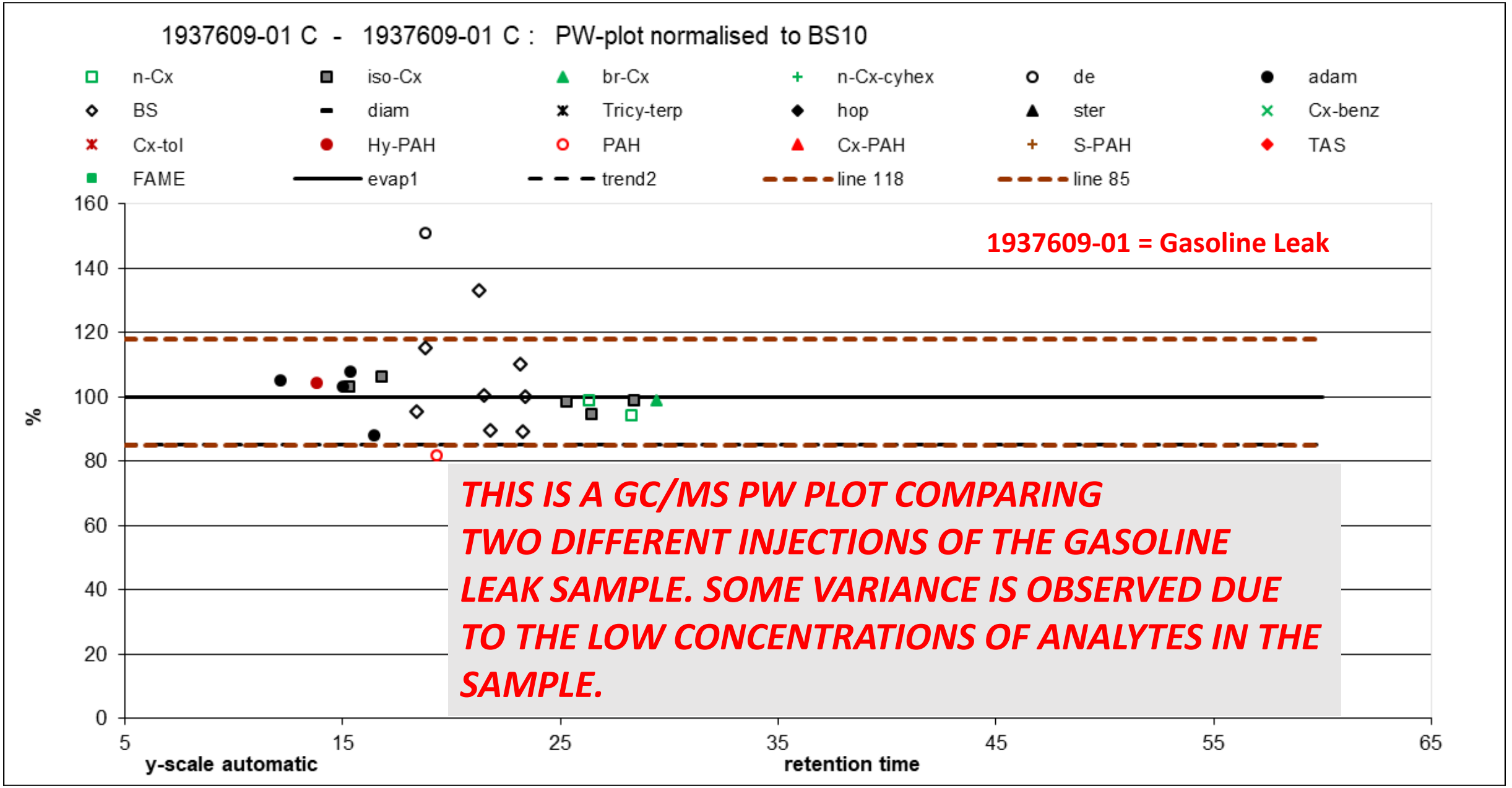

COMPARISON OF GASOLINE LEAK WITH E2, INTERNAL STANDARD SUBSTITUTED (undecane-$D_{24}$) FOR BS10

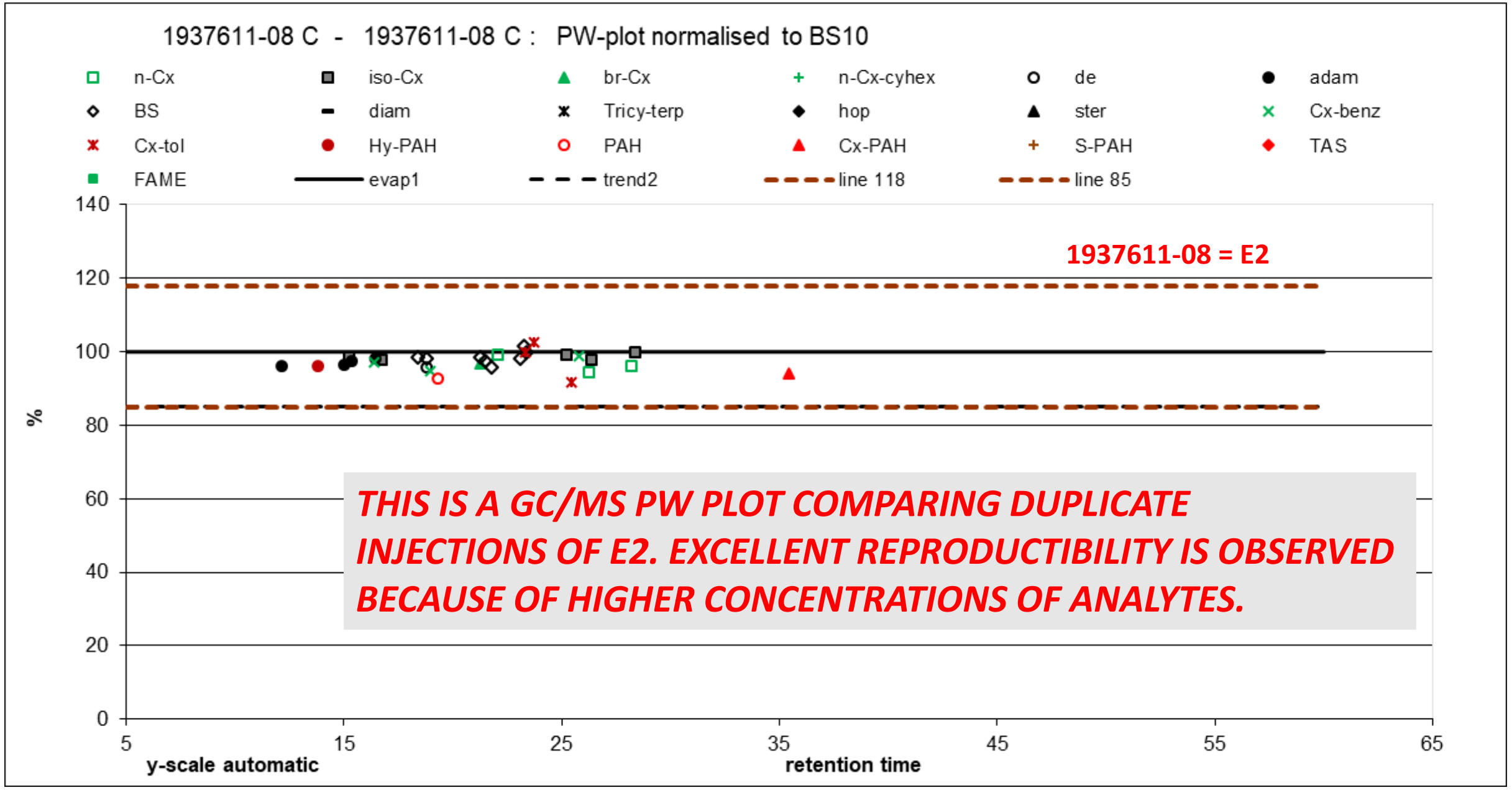
REVEALS THAT GASOLINE LEAK CONTAINS LOW LEVELS OF ADAMANTANES AND BICYCLIC SESQUITERPANES.
THIS OBSERVATION SUGGESTS THAT THE GASOLINE LEAK MAY BE CONTAMINATED WITH PREVIOUS SPILL MATERIAL.
SAMPLE PLOT COMPARING GASOLINE LEAK TO E2

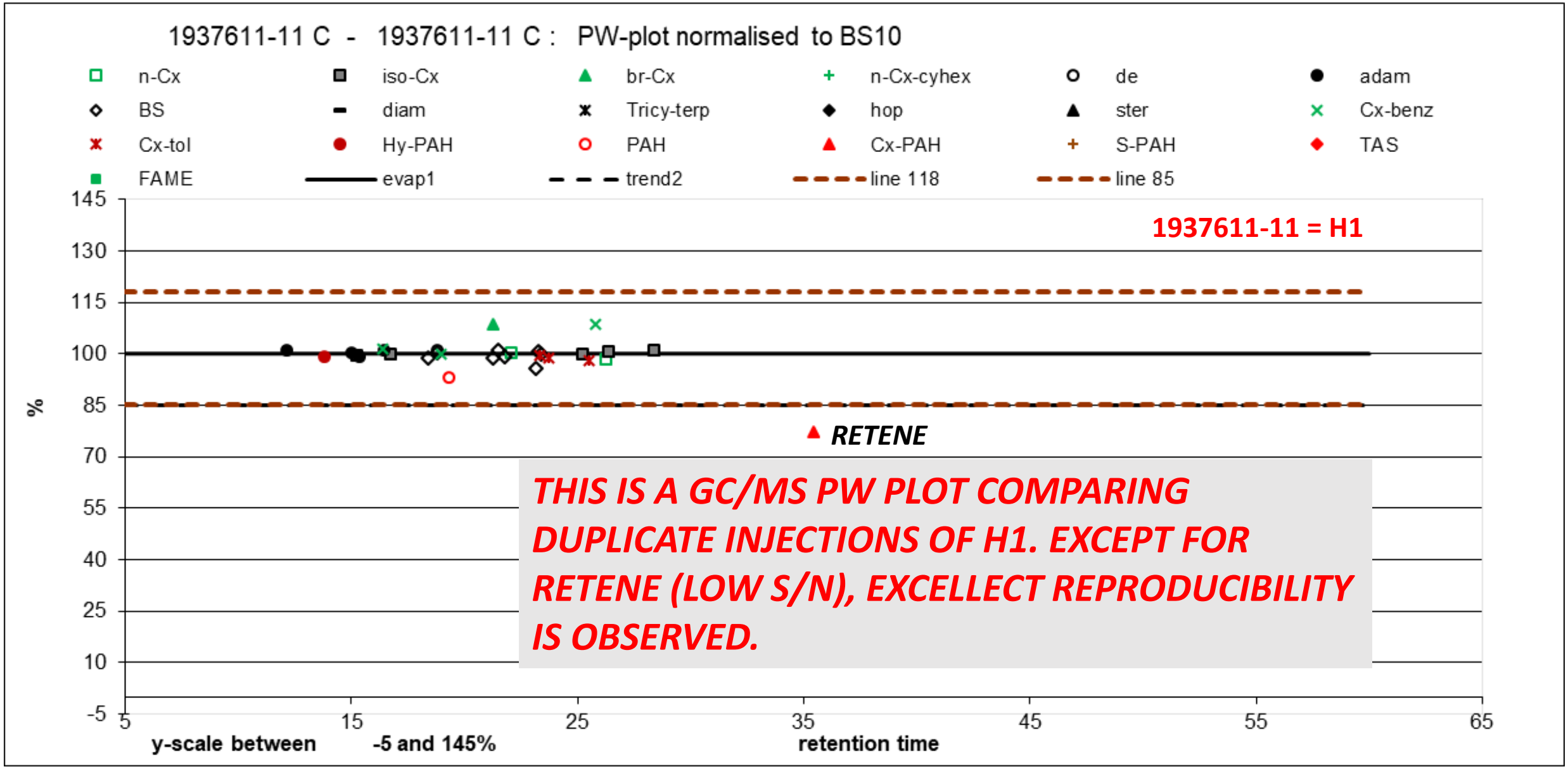

RT: 16.61 - 26.14
BICYCLIC SESQUITERPANES
160,000 COUNTS
E2
NL:
1.66E5
m/z=
122.50-
123.50 MS
14 - Cans
1937611-08
Inj 1
Intensity
160000
140000
120000
100000
80000
60000
40000
20000
0
228-FOLD DIFFERENCE
700 COUNTS
Gasoline
Leak
NL:
7.94E2
m/z=
122.50-
123.50 MS
08 - cans
1937609-01
inj 1
700
600
500
400
300
200
100
0
17
18
19
20
21
22
23
24
25
26
Time (min)

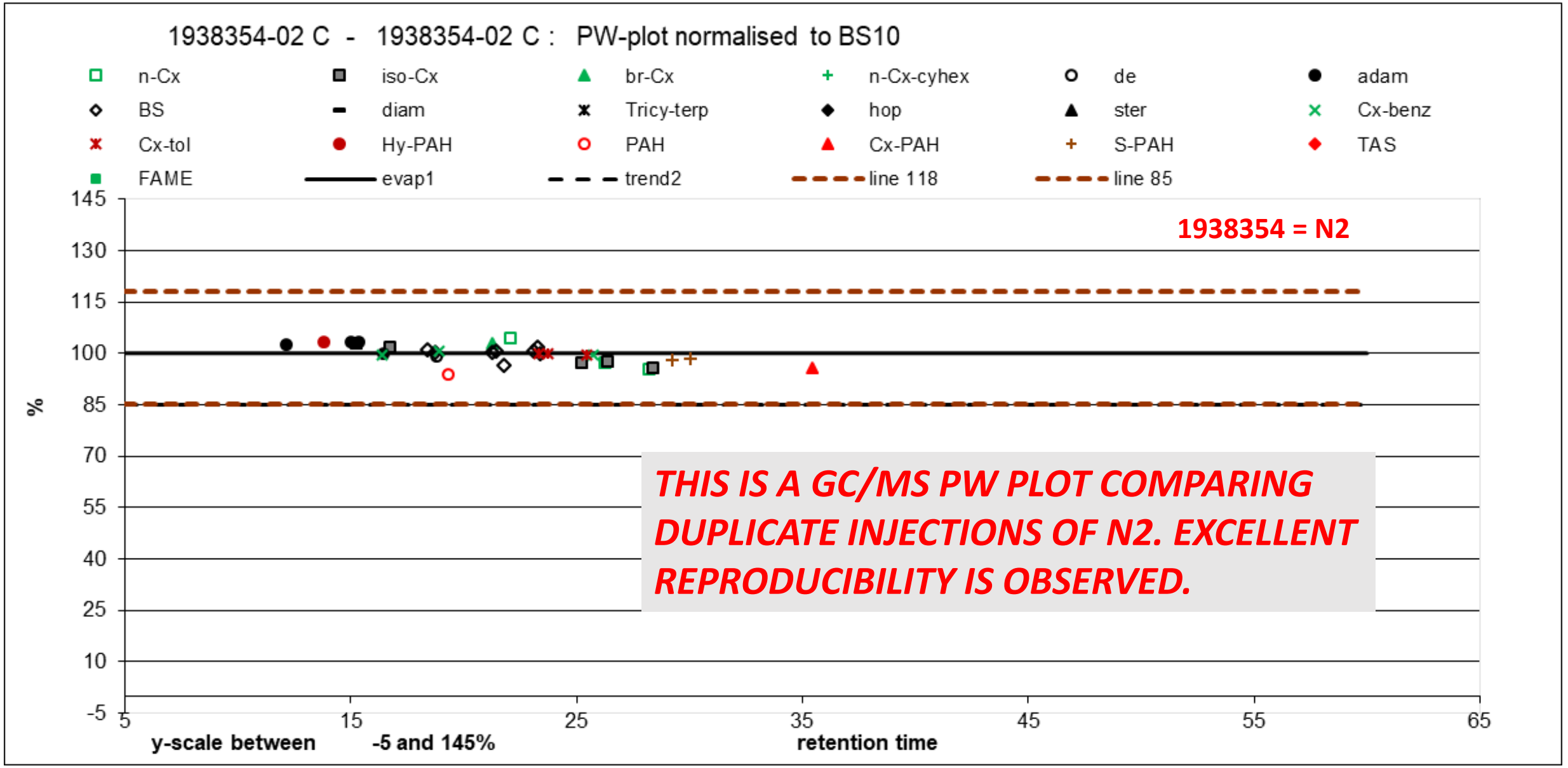
# QUALITY CONTROL


1937609-01 C - 1937609-01 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
1937609 Gasoline Leak Sample
THIS IS A GAS CHROMATOGRAPHY PERCENT WEATHERING PLOT COMPARING A SINGLE INJECTION OF SAMPLE TO ITSELF. ALL THE BIOMARKERS, ILLUSTRATED WITH DIFFERING SHAPES AND COLORS, ARE NORMALIZED TO BS10. NOTE THE RESPONSE IS LINEAR, INDICATING AN EXACT MATCH. HOWEVER THIS RESPONSE IS UNREALISTIC. DUPLICATE INJECTION OF THE SAME MATERIAL WILL RESULT IN SLIGHT VARIATIONS DUE TO INSTRUMENT RESPONSE AND SLIGHT SAMPLE DIFFERENCES
%
140
120
100
80
60
40
20
0
5
15
25
35
45
55
65
y-scale automatic
retention time


1937609-01 C - 1937609-01 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
Hy-PAH
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
160
140
120
100
80
60
40
20
0
%
1937609-01 = Gasoline Leak
THIS IS A GC/MS PW PLOT COMPARING TWO DIFFERENT INJECTIONS OF THE GASOLINE LEAK SAMPLE. SOME VARIANCE IS OBSERVED DUE TO THE LOW CONCENTRATIONS OF ANALYTES IN THE SAMPLE.
5
15
25
35
45
55
65
y-scale automatic
retention time

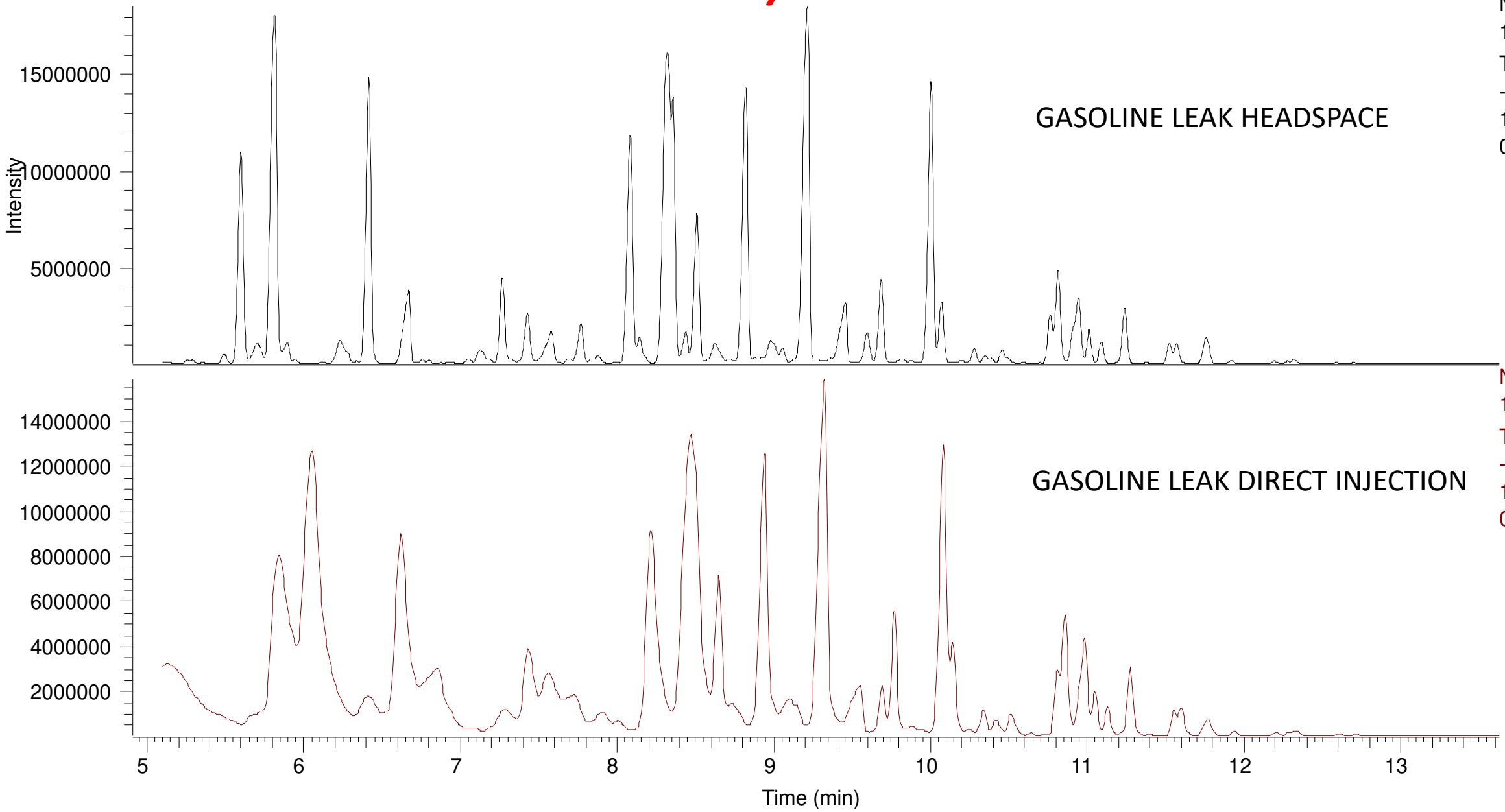

1937611-08 C - 1937611-08 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
Hy-PAH
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
1937611-08 = E2
THIS IS A GC/MS PW PLOT COMPARING DUPLICATE INJECTIONS OF E2. EXCELLENT REPRODUCTIBILITY IS OBSERVED BECAUSE OF HIGHER CONCENTRATIONS OF ANALYTES.
%
140
120
100
80
60
40
20
0
5
15
25
35
45
55
65
y-scale automatic
retention time


1937611-11 C - 1937611-11 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
Hy-PAH
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
1937611-11 = H1
RETENE
THIS IS A GC/MS PW PLOT COMPARING DUPLICATE INJECTIONS OF H1. EXCEPT FOR RETENE (LOW S/N), EXCELLECT REPRODUCIBILITY IS OBSERVED.
%
145
130
115
100
85
70
55
40
25
10
-5
5
15
25
35
45
55
65
y-scale between -5 and 145%
retention time


1938354-02 C - 1938354-02 C : PW-plot normalised to BS10
n-Cx
iso-Cx
br-Cx
n-Cx-cyhex
de
adam
BS
diam
Tricy-terp
hop
ster
Cx-benz
Cx-tol
Hy-PAH
PAH
Cx-PAH
S-PAH
TAS
FAME
evap1
trend2
line 118
line 85
1938354 = N2
THIS IS A GC/MS PW PLOT COMPARING DUPLICATE INJECTIONS OF N2. EXCELLENT REPRODUCIBILITY IS OBSERVED.
%
145
130
115
100
85
70
55
40
25
10
-5
5
15
25
35
45
55
65
y-scale between -5 and 145%
retention time

RT: 4.91 - 13.62

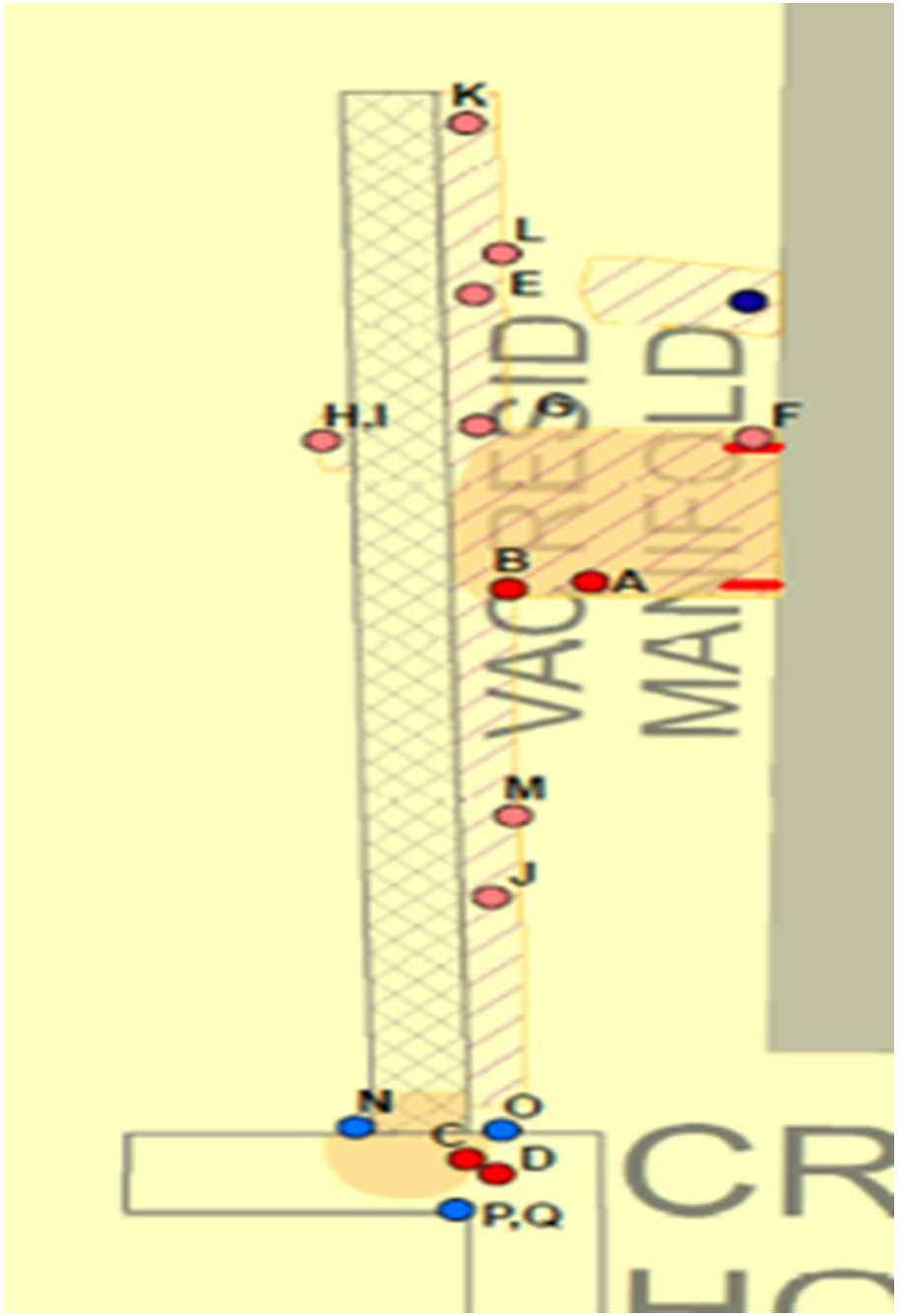
# GC/MS TOTAL ION CHROMATOGRAMS



| Sample Identification | Percent Naphthalene-D8 Recovery |
|---|---|
| | |
| injection 1 GAS LEAK | 51 |
| injection 2 GAS LEAK | 51 |
| injection 1 PHASE 3/SEP | 36 |
| injection 2 PHASE 3/SEP | 34 |
| injection 1 E2 | 49 |
| injection 2 E2 | 48 |
| injection 1 H1 | 58 |
| injection 2 H1 | 58 |
| injection 1 N2 | 50 |
| injection 2 N2 | 50 |

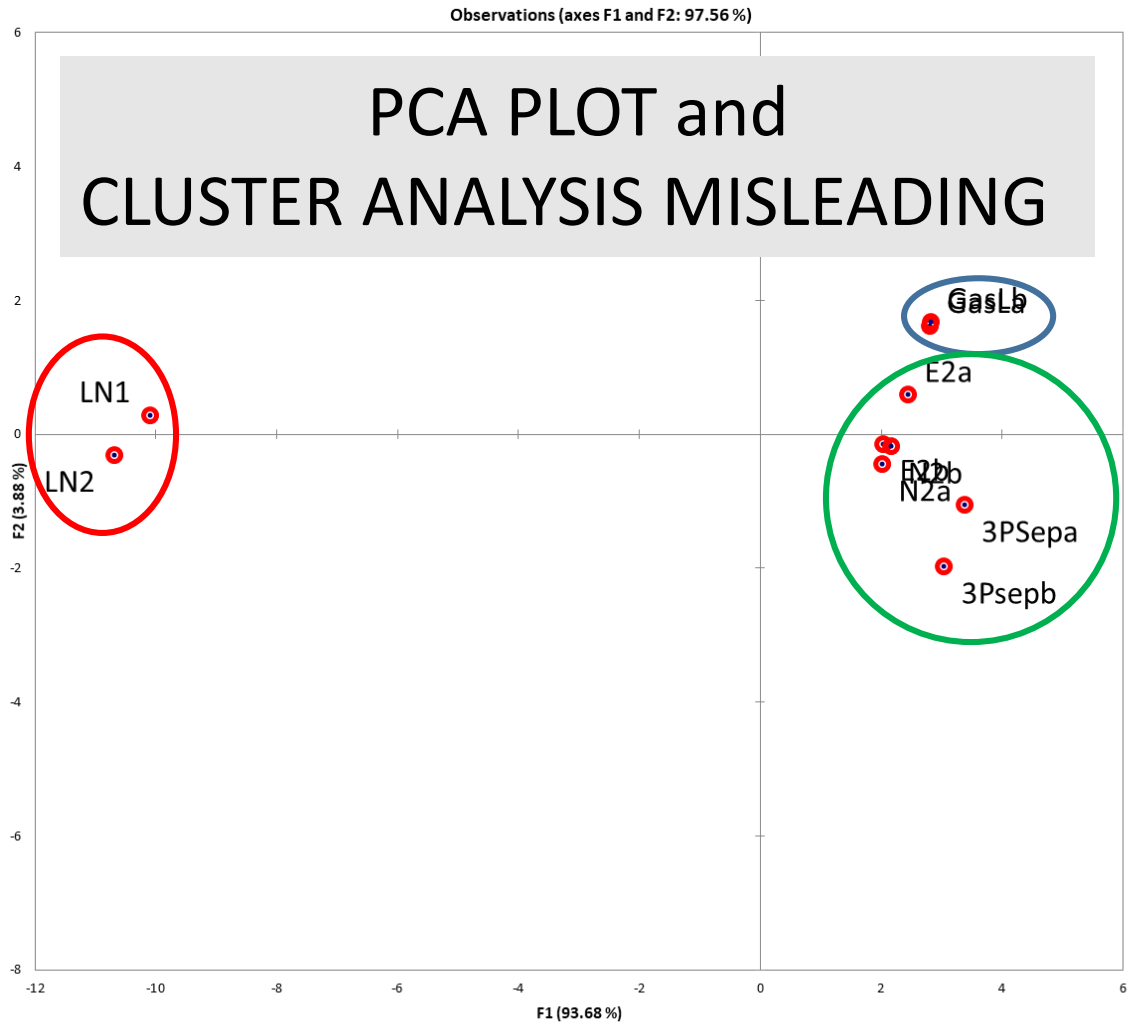
# CONCLUSIONS

- N2 AND E2 ARE NOT DERIVED FROM PHASE 3 SEPARATOR AS PREDICTED BY PRINCIPAL COMPONENTS ANALYSIS (PCA)
- N2 AND E2 ARE NOT DERIVED FROM A COMMON SOURCE. DIFFERING WEATHERING PROFILES INDICATE DIFFERING TIMES OF RELEASE AND RATIOS INDICATE DIFFERING SOURCES.
- THE GASOLINE LEAK MAY BE CONTAMINATED WITH HISTORIC SPILL MATERIAL (A). IT MAY BE A DIFFERENT CRUDE OIL STOCK AS WELL. HOWEVER, THE PCA AND CHROMATOGRAMS INDICATE A DIFFERENT SOURCE THAN THE PHASE 3 SEPARATOR GAS SAMPLE.



# CONCLUSIONS

- PRINCIPAL COMPONENTS ANALYSIS IS A USEFUL TOOL BUT NOT DEFINITIVE FOR DEFINING SPILL AND SOURCE RELATIONSHIPS, ESPECIALLY IF USED IN LITIGATION.
- DETERMINING HYDROCARBON RATIOS IS HIGHLY RECOMMENDED BUT WHICH ONES DO YOU CHOOSE ? THOSE DEFINED BY THE LITERATURE? THOSE DEFINED BY EN2020?
- ALSO, RATIOS CAN BE AFFECTED BY WEATHERING – HOW DO YOU DETERMINE THAT? THROUGH THE LITERATURE OR METHOD EN2020?
- IF INAPPROPRIATE RATIOS ARE EMPLOYED IN PCA THEN THE CONCLUSIONS MAY BE ERRONEOUS
- EN2020 PRESCRIBES CHEMICALS TO MEASURE AND RATIOS TO FOCUS ON, BASED UPON ***DIAGNOSTIC POWER***.
- EN2020 PRESCRIBES WEATHERING PROCEDURES BY NORMALIZING DATA TO BS10, PHYTANE AND/OR HOPANE.



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