Report

Oil spill identification

OSINET – Round Robin 2016

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![SINTEF]

Address:	# Report
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	# Oil spill identification
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ABSTRACT
The 11th Oil Spill Identification Round Robin test (RR2016) within the Bonn Agreement Oil Spill Identification Network of Experts (OSINET) has been organized by Rijkswaterstaat, Netherlands. This year's samples, one spill sample and three source samples, have been prepared by SINTEF.
The Spill sample was collected from a buoy in a drifting oil slick in the North sea close to the border between the Norwegian and British sector. There are several suspected sources, both from platforms and passing ships. Three of them are selected for comparison with the Spill sample.
Questions to be answered in the RR2016 case: which of the source samples is the source of the Spill sample? And what kind of weathering has taken place?

- The Source samples 1 and 2 are most likely refined products
- The Source sample 3 is a fresh light paraffinic crude oil
- The Spill sample is a paraffinic crude oil
- The Spill sample is heavily weathered with a high wax-content due to a mechanical wash out of the liquid components in the oil and the solid wax-components are remaining
- The Spill sample is non-match to Source 1 and Source 2.
- **The Spill sample is a positive match to Source 3**.

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1 Introduction

The 11th Oil Spill Identification Round Robin (RR2016) test within the Bonn Agreement Oil Spill Identification Network of Experts (OSINET) has been organized by Rijkswaterstaat, Netherlands. This year's samples, one spill sample and three source samples, have been prepared by SINTEF, Norway.

To secure that SINTEF received the same aliquot and concentration of samples as other laboratories within OSINET, SINTEF received the samples from Rijkswaterstaat, Netherlands on October 27th, 2016. SINTEF has followed the instructions given by the organizers for analysis and data treatment and compared the samples by means of the CEN (2012). The relevant compounds have been integrated and the results entered in the Excel spread sheet file produced by Paul Kienhuis, vs 62. In addition, all samples have been imported into the COSI database, and several of the chromatograms and figures given in this report are downloaded from the database.

2 Sample information

The scenario for the RR2016 describe that the Spill sample was collected from a buoy in a drifting oil slick in the North Sea close to the border between the Norwegian and British sector. There were several suspected sources, both from platforms and passing ships. Three of them seem to be more likely than others, and are selected for comparison with the Spill sample.

The samples received are described in Table 2-1 and Figure 2-1. Duplicate analyses were performed for all samples.

Table 2-1   Sample description and SINTEF ID.

SAMPLE ID	SINTEF ID	CosiWeb Id:	Sample description
Source 1	MC-2016-584	No-1-17.1 and 17.2	RR2016 Source 1
Source 2	MC-2016-585	No-1-17.3 and 17.4	RR2016 Source 2
Source 3	MC-2016-586	No-1-17.5 and 17.6	RR2016 Source 3
Spill	MC-2016-587	No-1-17.7 and 17.8	RR2016 Spill sample, collected from a drifting bouy

Figure 2-1   Samples received on October 27th, 2016.

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3 Materials and methods

3.1 Sample preparation and analysis

The participants were informed that the vials contained oil dissolved in dichloromethane (DCM): 5 mg/mL of the Spill and 18 mg/mL for the source samples. The Spill sample was analysed without dilution on the GC/FID and diluted 1:2 prior to GC/MS analysis. The source samples were diluted to give an approximate same concentration as the Spill sample. No clean-up was performed on the extracts.

Duplicate analyses were performed for all samples on the GC/FID and GC/MS. The GC/FID was equipped with a Zebron ZB-1 30m column 0.25mm ID and 0.25 μm film thickness using He as a carrier gas (2mL/min, constant flow), with an injection volume of 1 μL and the following temperature program: 40°C (1 min), 6°C/min up to 330°C (5 min). Instrument conditions given in CEN (2012) and in the instructions for COSI were used for the GC/MS. More specified MS conditions are given in the Excel-spreadsheet "SINTEF_NO Oilcomparison MS RR2016", including excluded masses.

4 GC/FID results

The GC chromatograms in *Figure 4-1* to *Figure 4-4* are normalized with the height of C25 and the overlays of the GC chromatograms are given in *Figure 4-5* to *Figure 4-7* (from COSI). Results from duplicate analyses were evaluated, but as the samples were very similar, the results are not shown.
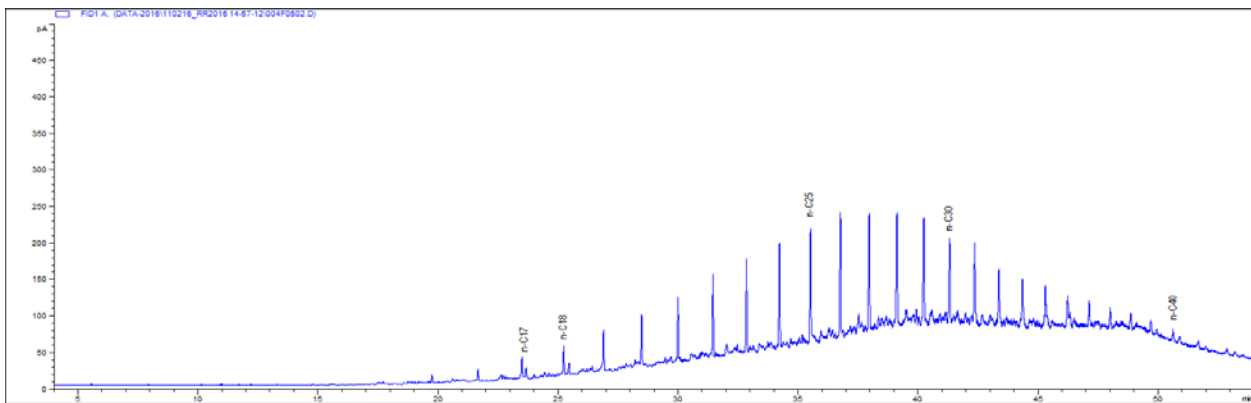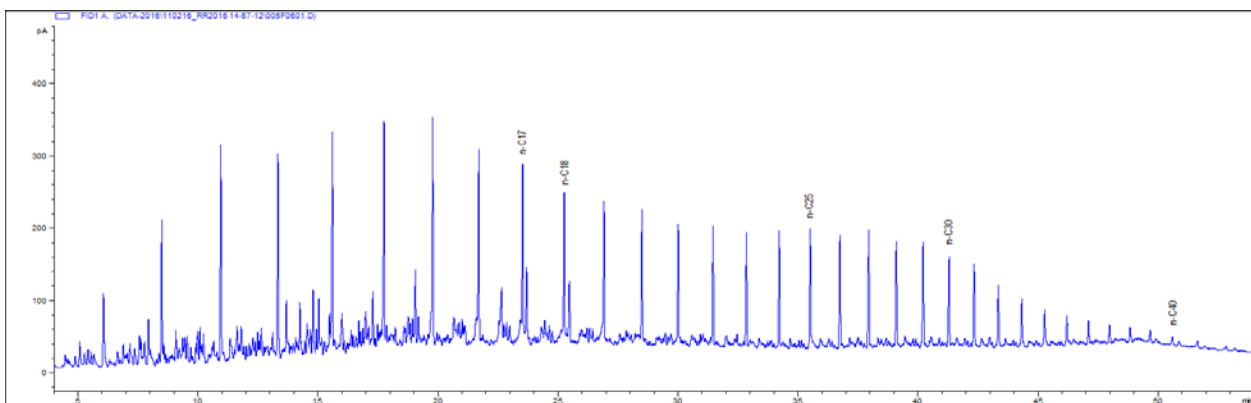

Figure 4-1   Source 1 (COSI Id.: No1-17.1).

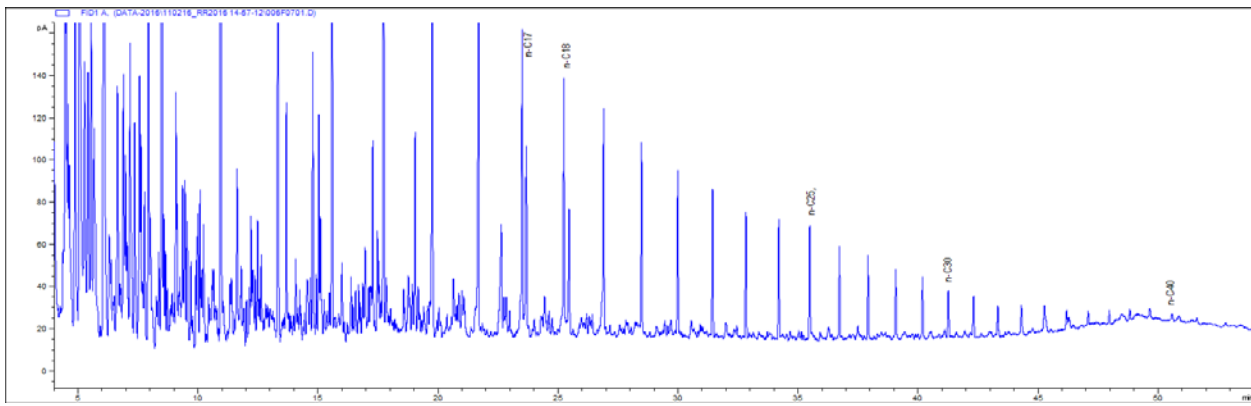*Figure 4-2   Source 2 (COSI Id.: No1-17.3)*

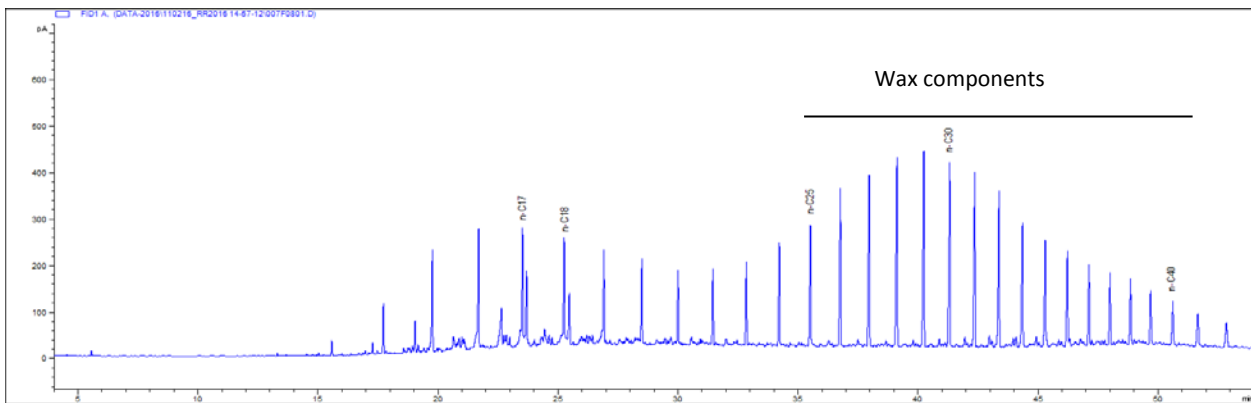*Figure 4-3　　　Source 3 (COSI Id.: No1-17.5)*

Figure 4-4　　　Spill (COSI Id.: No1-17.7)

4.1 Visual inspection, overlays

From the overlays, Source 1 has a UCM profile different from the Spill sample (*Figure 4-5*). Source 2 might be a mixture of a crude oil and a refined product and the baseline is equal compared to the spill (*Figure 4-6*). Source 2 cannot be ruled out as a possible source at this stage. The GC screening analysis indicates that the Source 3 and the Spill sample most likely are crude oils. The overlay of Source 3 and Spill (*Figure 4-7*) shows that Source 3 is a fresh paraffinic crude oil and the difference between the Spill and Source 3 could be due to the weathering.
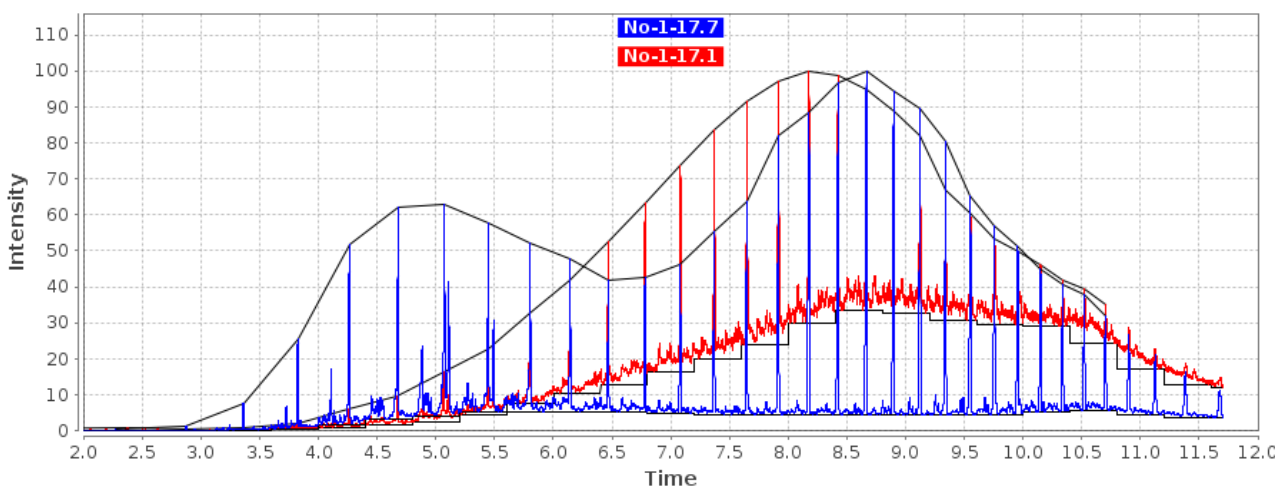

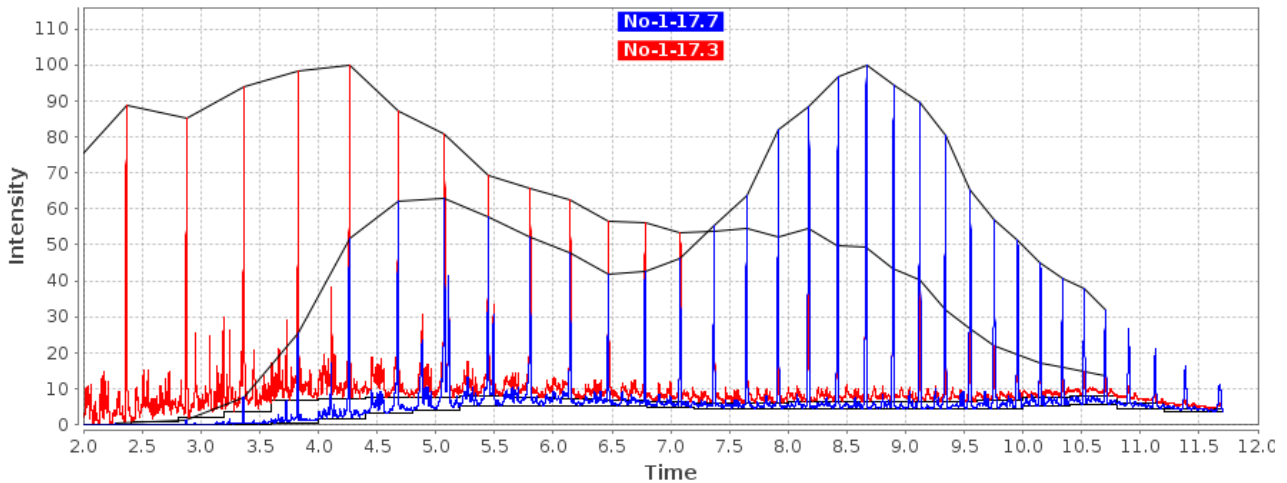*Figure 4-5　　　Overlay of GC chromatograms: Spill (blue) vs Source 1 (red)*

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Figure 4-6   Overlay of GC chromatograms: Spill (blue) vs Source 2 (red)
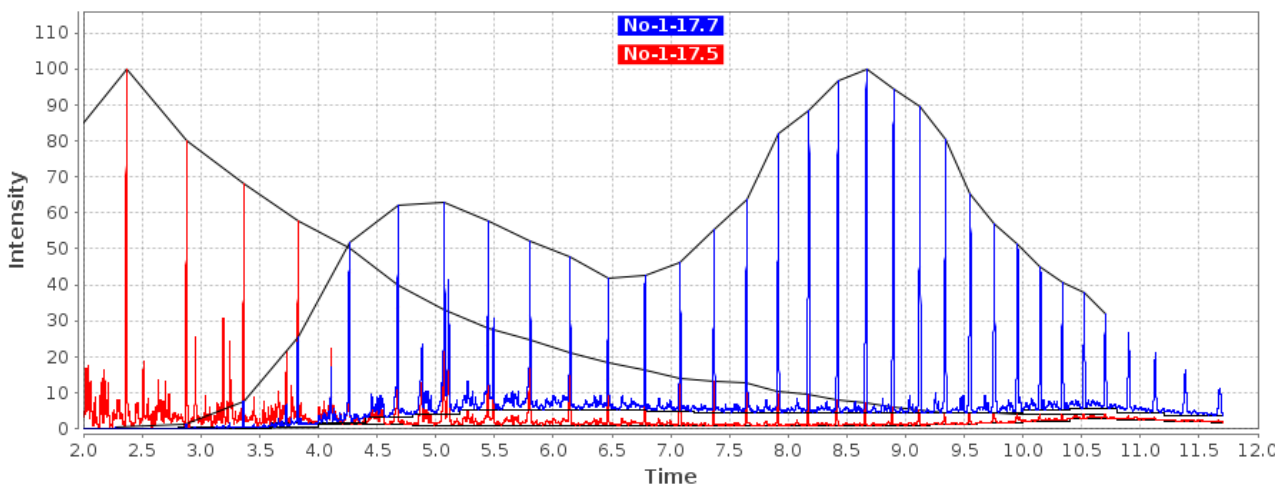

Figure 4-7   Overlay of GC chromatograms: Spill (blue) vs Source 3 (red).

4.1.1 Oil type, tentative

The n-alkanes are detected from C9 to C42 in the GC-method applied by SINTEF and the GC screening indicates that the samples most likely are crude oils. Source 1 is a heavily weathered oil with a UCM (unresolved complex materials), possibly a refined or a crude oil. Based on the GC/FID one cannot conclude whether Source 2 is a crude oil or a refined product. Source 2 can be a mixture of a crude oil and a refined product. Source 3 is more likely a fresh paraffinic crude oil and the Spill sample may be a heavily weathered paraffinic crude oil, with a high wax-content (n-alkanes from C25-C42).

4.1.2 Obvious differences

At this stage the obvious differences between the Spill sample and the tree sources is the high wax content (C25-C42) in the Spill (*Figure 4-1* to *Figure 4-4*). Source 1 has a high UCM compared to the Spill sample, as mentioned above and Source 2 might be a mixture of a crude oil and a refined product.

4.3 Isoprenoid ratios, GC-PW plots

The isoprenoid ratios are given in *Table 4-1* and are from COSI. GC-PW plots to compare evaporative loss between the Spill and sources are shown in *Figure 4-8* to *Figure 4-10* (from COSI). No conclusion can be made based on the GC-PW plots as this type of PW-plots do not seem to be suitable when the sources are compared to a spill sample elevated with wax.

The isoprenoid ratios are calculated from GCFID and are given in *Table 4-1*. Source 1 and Source 2 gave "Flag" when comparing the isoprenoid ratios with the Spill in COSI. Comparing Source 3 with the Spill gave <u>no</u> "Flag", that indicates that Source 3 can be a possible source to the spill.

Table 4-1   *The isoprenoid ratios between C17/pristane, C18/phytane, and pristane/phytane, based on peak heights (calculated from GC FID/COSI).*

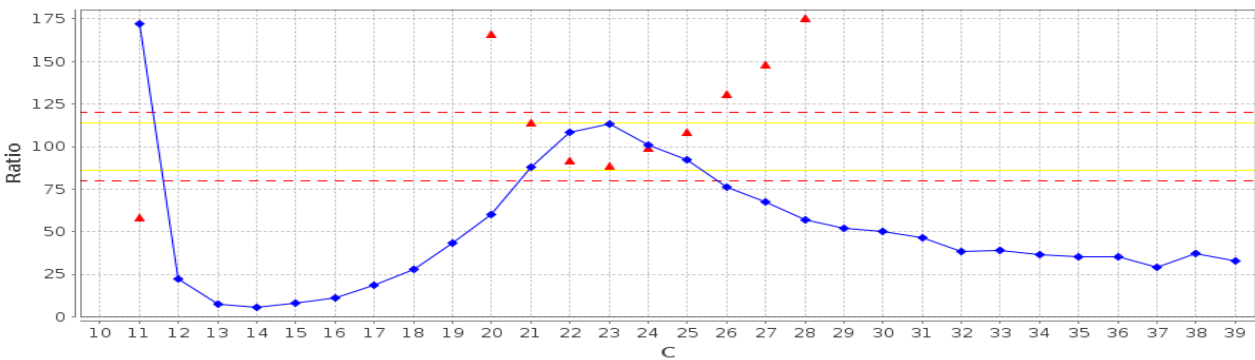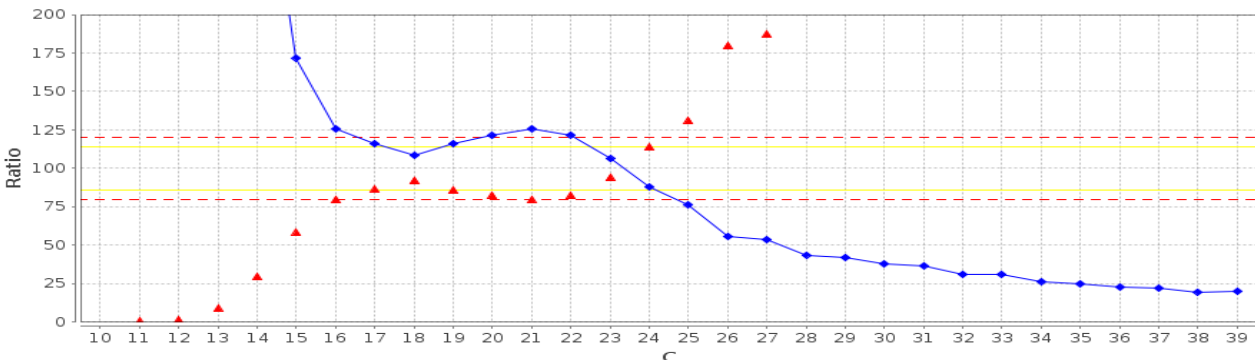| SINTEF ID	Sample ID	CosiWeb ID	C17/pristane	C18/phytane	Pristane/phytane
MC-2016-584	Source 1	No-1-17.1	1,82	2,11	0,86
MC-2016-585	Source 2	No-1-17.3	2,31	2,41	1,25
MC-2016-586	Source 3	No-1-17.5	1,61	2,02	1,49
MC-2016-587	Spill	No-1-17.7	1,57	2,06	1,46

Figure 4-8   *GC-PW plot: Spill (blue line) compared to Source 1.*

Figure 4-9   *GC-PW plot: Spill (blue line) compared to Source 2.*

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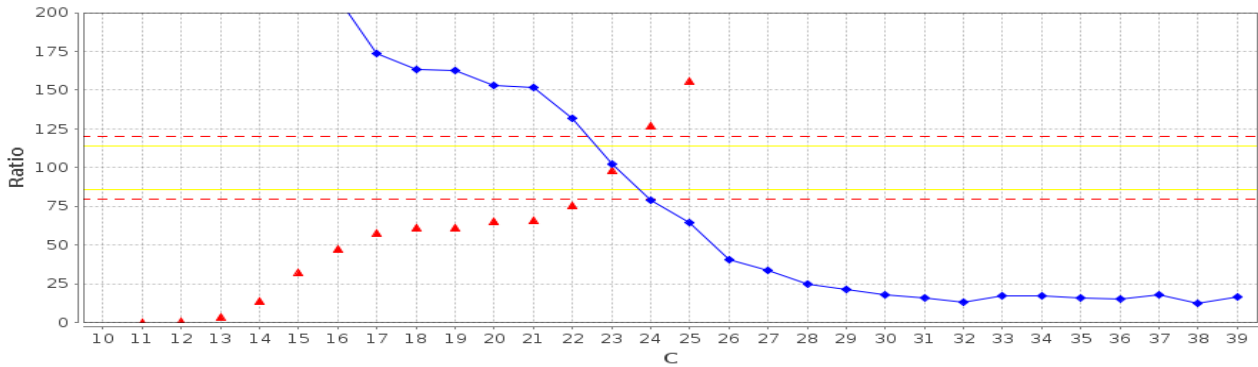OC2017 A-035

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Figure 4-10   GC-PW plot: Spill (blue line) compared to Source 3.

4.4 GC/FID conclusions

The n-alkanes are detected from C9 to C42 in the GC-method applied by SINTEF and the GC screening indicates that the samples most likely are crude oils. Source 1 is a heavily weathered oil with a UCM, but based on the GC/FID one cannot conclude whether Source 2 is a crude oil or a refined product. Source 2 can be a mixture of a crude oil and a refined product. Source 3 is more likely a fresh paraffinic crude oil and the Spill sample may be a heavily weathered paraffinic crude oil, with a high wax-content (n-alkanes from C25-C42).

Enrichment of wax in a paraffinic crude oil is a phenomenon that occurs during weathering. When an oil is in contact with a physical part, in this scenario a buoy, a mechanical wash out of the liquid components in the oil takes place and the solid wax-components are remaining as seen in the GC chromatogram of the spill sample. It has also been observed enrichment of wax in oil tare balls, which has been subjected to the same processes from the influence of waves. (CEN 2012, Appendix G and H).

Comparing the isoprenoid ratio for source 3 with the Spill gave <u>no</u> "Flag". It indicates that source 3 might be a possible source to the spill.

No source samples can be ruled out on this stage, and it is recommended to continue with GC/MS fingerprinting analysis of all samples.

5 GC/MS results

5.1 Visual inspection of the ion chromatograms

Ion chromatograms of m/z 191, 217, 218, 231, 234, 216, 192 and 198 are based on the reports downloaded from COSI and are given in Appendix A:

Error! Reference source not found.
Error! Reference source not found.*2*
Error! Reference source not found.*Comparison of Spill and Source 3*

5.1.1 Oil type

The C1-phenanthrenes/anthracenes (m/z 192) are often used to suggest the oil type: The indication of a refined product is a higher first duplet than the second duplet and a distinct 1-methyl anthracene peak (MA). In Source 1 the first duplet is higher than the second duplet, but there is no MA. In Source 2 the first duplet is higher than the second duplet with a distinct MA. This indicates that Source 2 is a refined product. In Source 3 and in the Spill sample the first duplets is lower than the second duplets and no presence of MA. This suggest that Source 3 and the Spill are paraffinic crude oils.

If retene (m/z 234) is present, it could be an indication of a crude oil and if absent it could be a refined product. The retene peak is very small and with low peak height, but present in both Spill and Source 3, it can hardly be detected in Source 1 and Source 2. BNT (m/z 234) is absent in Source 1 and Source 2, but a distinct high peak is present in Source 3 and in Spill. Retene could be destroyed in a cracking process, indicating a refined product as the oil type for source 1 and Source 2. See Figure A-1 to A-3.

5.1.2 Obvious differences

The differences are discussed based on visual inspection of selected ion chromatogram from COSI.

A specific feature in the hopanes m/z 191 is the presence of the peak 28ab in the spill. This may indicate that the spill is a crude oil from the North Sea (Wang et al. 2016).

Spill vs Source1

- When comparing biomarkers m/z 191 in the Spill with Source 1, the Oleanan (30 O) peak is present in the Source 1, but not present in the Spill sample. (*Figure 5-1*) The height of 29ab to hopane is higher in the Spill than in Source 1.
- It is obvious differences in the ion chromatograms for m/z 217 and 218 (*Figure A-1*)
- The ion pattern for m/z 231 (tri aromatic steranes) shows obvious differences for the Spill vs Source 1. In the early time window the peaks are like a "forest" compare to the spill. (Figure 5-2)
- For the m/z 216 the C1-fluoroanthenes/pyrenes ion chromatograms it is a visually difference in the peak heights (*Figure A-1*)
- Differences in the C1-dibenzothiphenes m/z 198 indicate that Source 1 is a refined product with a low sulphur content compare to the spill. (Figure 5-3).

These obvious differences in ion pattern and the differences in the GC/FID chromatograms, high UCM, compared to the Spill, ruled out Source 1 as a source to the spill.
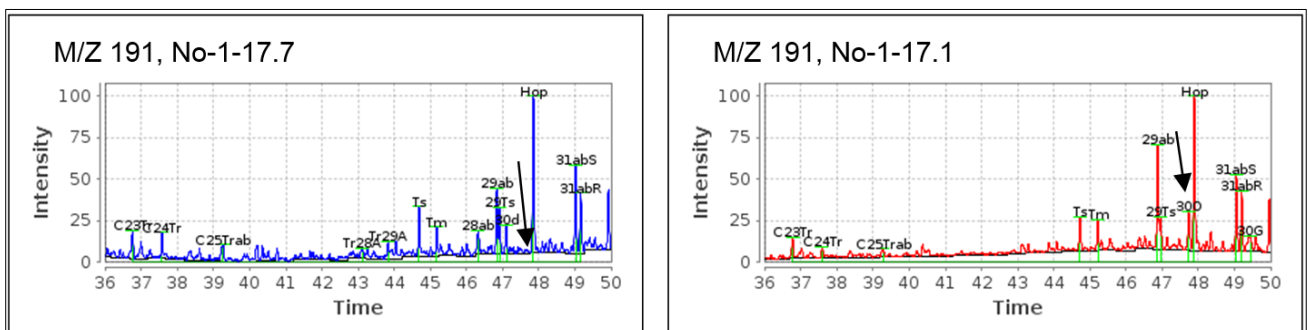

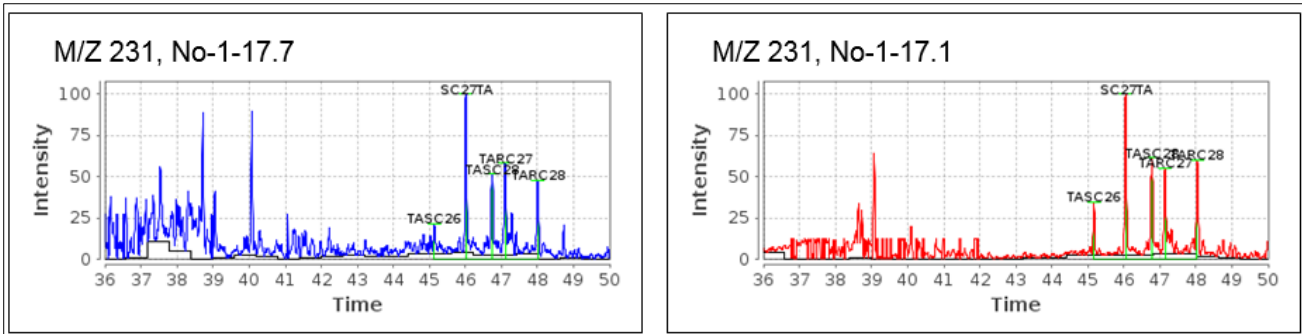*Figure 5-1   Comparison of m/z 191, Spill vs Source 1*

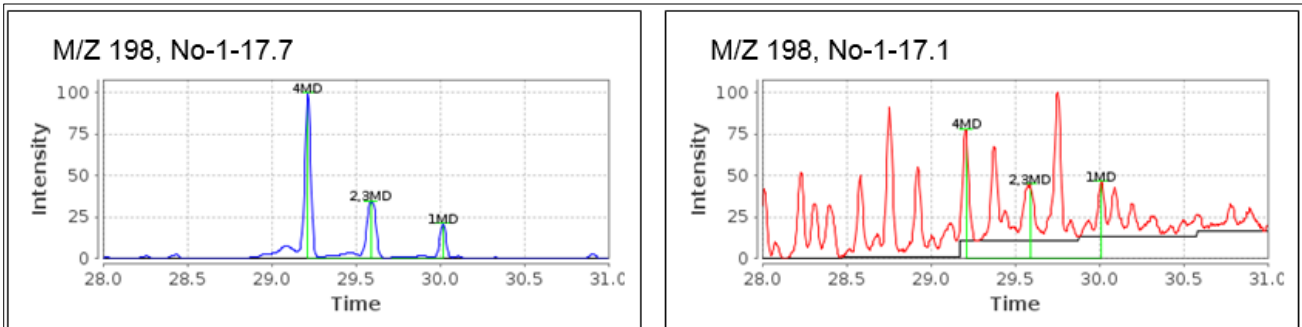Figure 5-2   *Comparison of m/z 231, Spill vs Source 1*

Figure 5-3   *Comparison of m/z 198, Spill with Source 1*

Spill vs Source2

- The height between the peak 30ab hopane and the 31 abs+r are different in the ion chromatogram for m/z191, (Figure 5-4).
- There is no Oleanan (30 O) peak present in the Source 2, (Figure 5-4).
- Both the 29ab and 28ab peak are higher in the Source 2 than in the Spill, (Figure 5-4).
- It is obvious differences in the ion chromatogram for m/z 217 and m/z 218, (Figure A-2).
- The ion pattern for m/z 231 (tri aromatic steranes) is different for the Spill vs Source 2 as for Source 1 as mention above, (Figure 5-5).
- The C1-phenanthrenes/anthracenes (m/z 192) are often used to suggest the oil type: The indication of a refined product is a higher first duplet than the second duplet and a distinct MA peak. These specific features for refined products is present in Source 2, but not in the Spill, (Figure 5-6).
- For the m/z 216 the C1-fluoroanthenes/pyrenes ion chromatogram it is a visually difference in the peak heights between the Spill vs Source 2 (*Figure A-2).*
- Differences in the concentration of C1-dibenzothiphenes m/z 198 indicate that Source 2 is a refined product with a low sulphur content compared to the Spill (Figure 5-7), possibly a bunker oil where most of the sulphur has been removed during the production.

These obvious differences ruled out Source 2 as a source to the spill.

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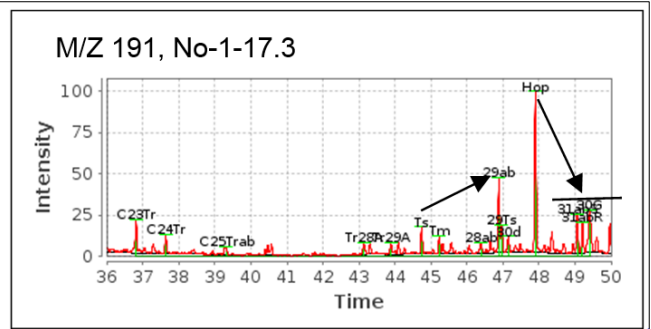**REPORT NO.**
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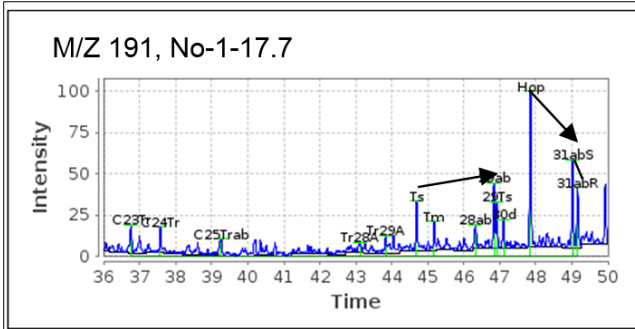Final

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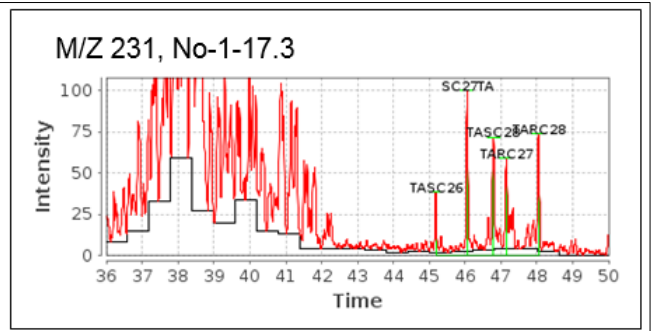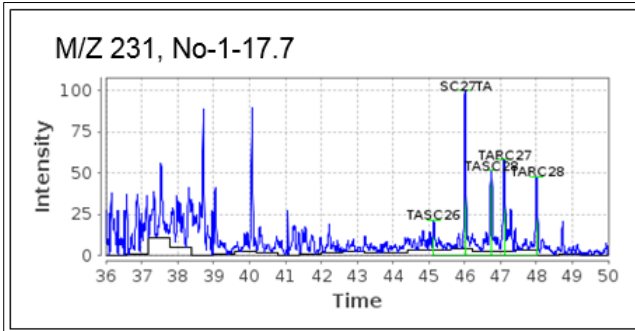Figure 5-4   Comparison of m/z 191, Spill vs Source 2

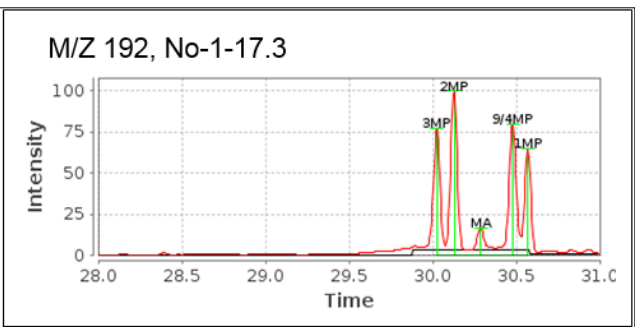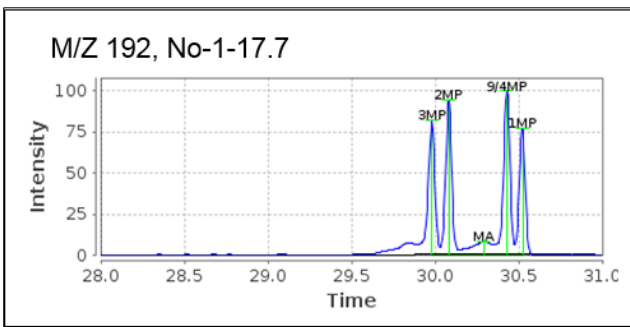Figure 5-5   Comparison of m/z 231, Spill vs Source 2

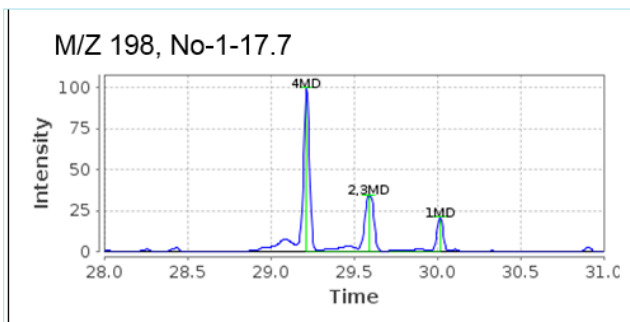Figure 5-6   Comparison of m/z 192, Spill vs Source 2
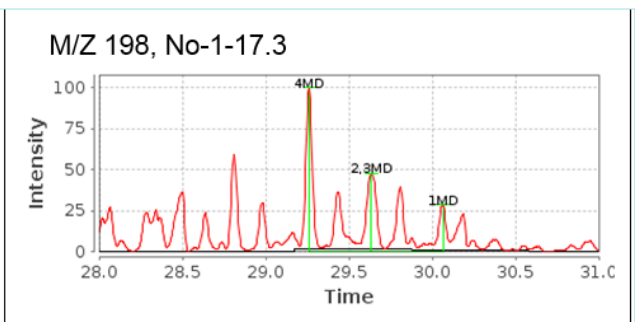
Figure 5-7   Comparison of m/z 198, Spill vs Source 2

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Spill vs Source3

- There are some visual difference in the ion chromatograms for the biomarkers m/z 191, (Figure 5-8) and m/z 231 (Figure 5-9) between the Spill and Source 3. It might be due to the differences in concentration of the samples. Source 3 is a fresh light paraffinic crude oil where a high content of lighter components are gone. This causes a big difference in the concentration of components with high boiling point, such as the biomarkers. It is visual in a higher base line for Source 3 for the biomarkers m/z 191 and 231. Both the spill and source 3 contain 28ab, which could indicate that the oils are crudes from the North Sea (Wang et al., 2016).
- It is no specific differences in the diasteranes m/z 217 and 218, (Figure A-3)
- There are no obvious visual differences in the ion chromatogram of the C1-phenanthrenes (m/z192) comparing the Spill with Source 3, (Figure 5-11).
- If retene (m/z 234) is present, it is an indication of a crude oil and if absent it could be a refined product. The retene peak is very small peak with low peak height, but present in both the Spill sample and Source 3, (Figure 5-10).
- Retene and BNT are present in the Spill sample and Source 3, and the ion chromatograms are very similar. This supports the conclusion that Source 3 and the Spill are crude oils.
- Visual differences in the m/z 216 ion chromatograms are observed in the Spill versus Source 3, (Figure 5-12) It has earlier been seen that these specific components are sensitive to sun light (photo oxidation) in reference to the excel spreadsheet provided by Paul Kienhuis. The scenario described that the Spill sample was collected from a buoy in a drifting oil slick and then it is very likely that the Spill sample has been photo oxidised while drifting on the sea surface. Photo oxidation can explain the high difference in the comparison of the normative ratios in relative difference in %, (Figure 5-14)
- The ion chromatogram of C1-dibenzothiophenes (m/z 198) in Source 3 and the Spill sample is mutually equal, (Figure 5-13)

Based on the visual comparison of the ion chromatograms between Source 3 and the Spill sample, Source 3 cannot be ruled out as the source to the spill. The differences observed are most likely caused by weathering.
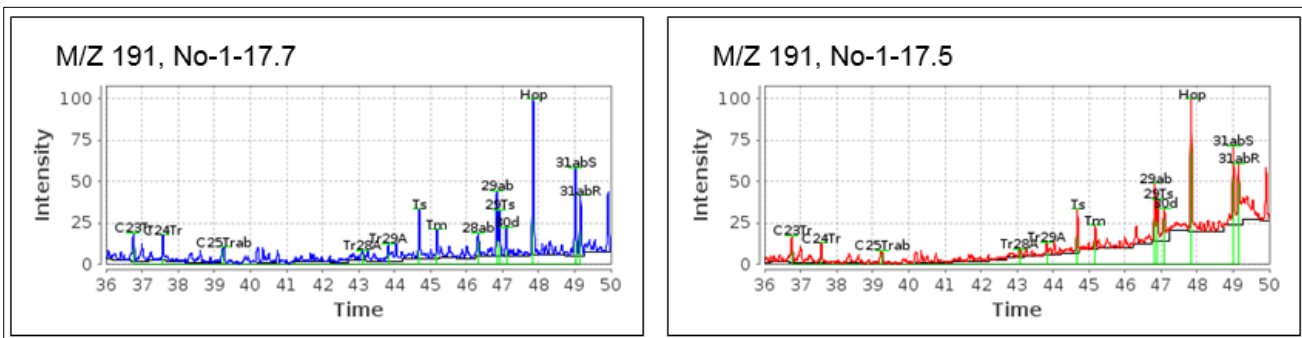

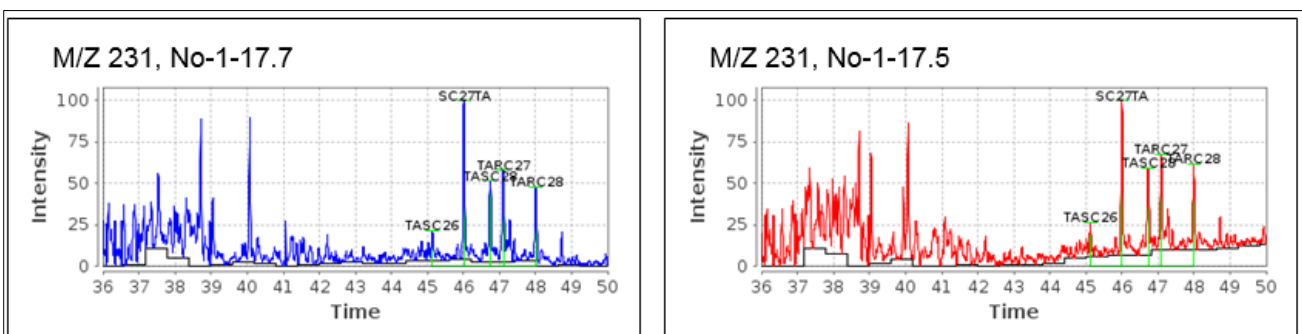Figure 5-8   Comparison of m/z 191, Spill vs Source 3

Figure 5-9   Comparison of m/z 231, Spill vs Source 3

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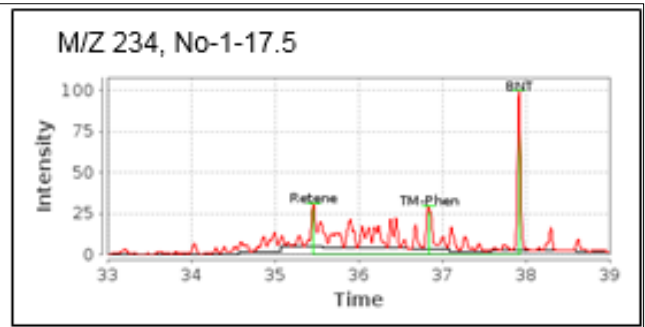
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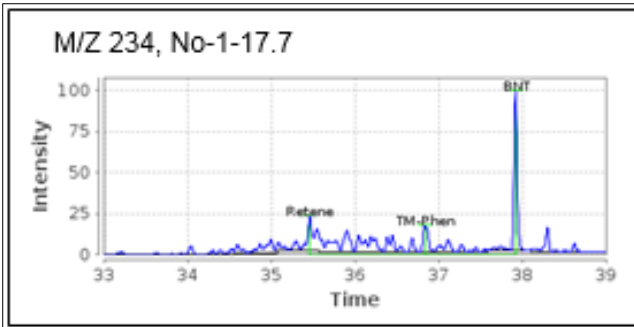VERSION
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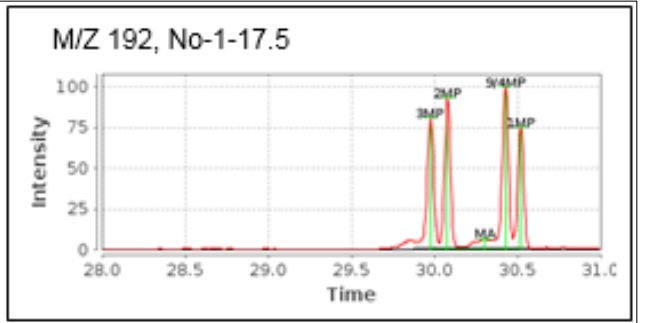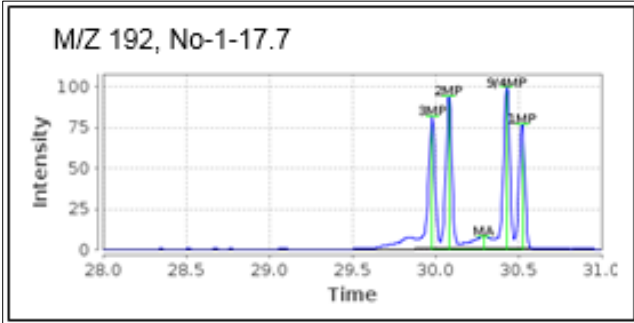Figure 5-10   Comparison of m/z 234, Spill vs Source 3

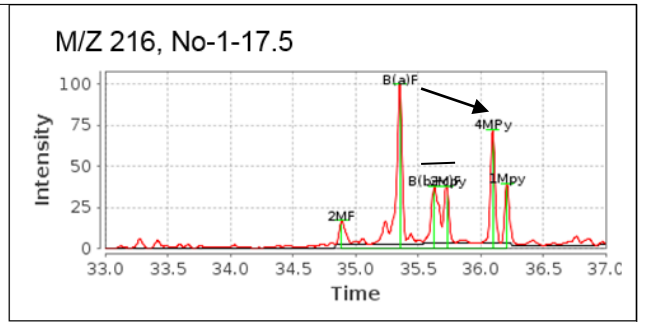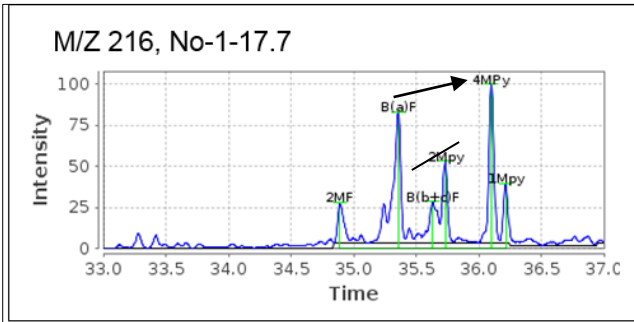Figure 5-11   Comparison m/z 192, Spill vs Source 3

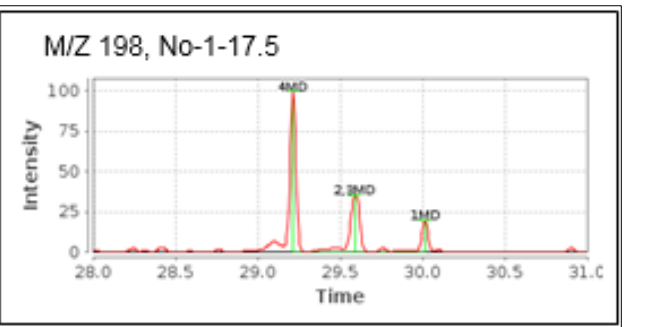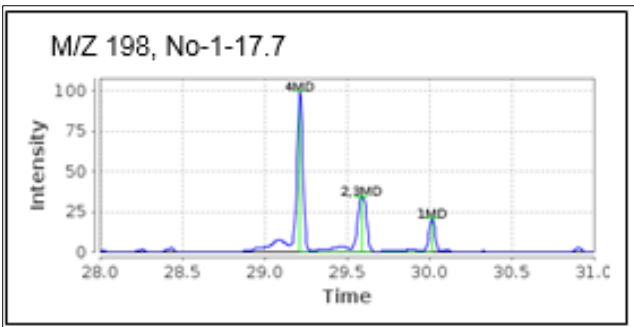Figure 5-12   Comparison of m/z 216, Spill vs Source 3

Figure 5-13   Comparison of m/z 198, Spill vs Source 3

5.2 Peak measurements GC/MS

The evaluation is based on the Excel spreadsheet provided by Paul Kienhuis (version 62).

5.2.1 Duplicate measurements

Results from duplicate measurement of Source 1, are shown and discussed in Appendix B.
The correlation between the duplicate samples is correlating very well, both the PW-plot and the ratio comparison.

5.2.2 MS-PW plots and diagnostic ratios - significant differences with the spill

The MS-PW plots and comparison of the normative diagnostic ratios are given in (**Error! Reference source not found.**).
These plots are based on the Excel spreadsheet provided by Paul Kienhuis and duplicate samples are compared.

The MS-PW plots and the calculated ratios when comparing the spill sample with Source 1 and Source 2, shows that nearly all normative ratios are above 14 % difference. These two source samples can be ruled out as source for the Spill sample, which also were concluded from the visual comparison.

The differences in the pristane/phytane ratio (Figure 5-14) is based on the MS-analysis. Results of duplicates has been used and it seems like it is a carry-over due to the high wax-content in the spill, because it is a higher response for phytane in duplicate b, (Excel spreadsheet). If the ratio is calculated from the GC/FID data (*Table 4-1*), the difference is small (1% according to COSI).

It is also observed a difference in the ratio of NR-BNT/T-M-Phen; but we do not know if it is caused by photo-oxidation or another weathering process. However, it is no reason to believe that this specific ratio will impact the conclusions.

The MS-PW plot and the calculated diagnostic ratios when comparing the Spill with Source 3 illustrate that the Spill is heavily influenced by weathering, and that the differences observed most likely can be caused by weathering (evaporative loss (pristane/phytane) and photo oxidization (m/ 216)). Source sample 3 is most likely the source of the spill.
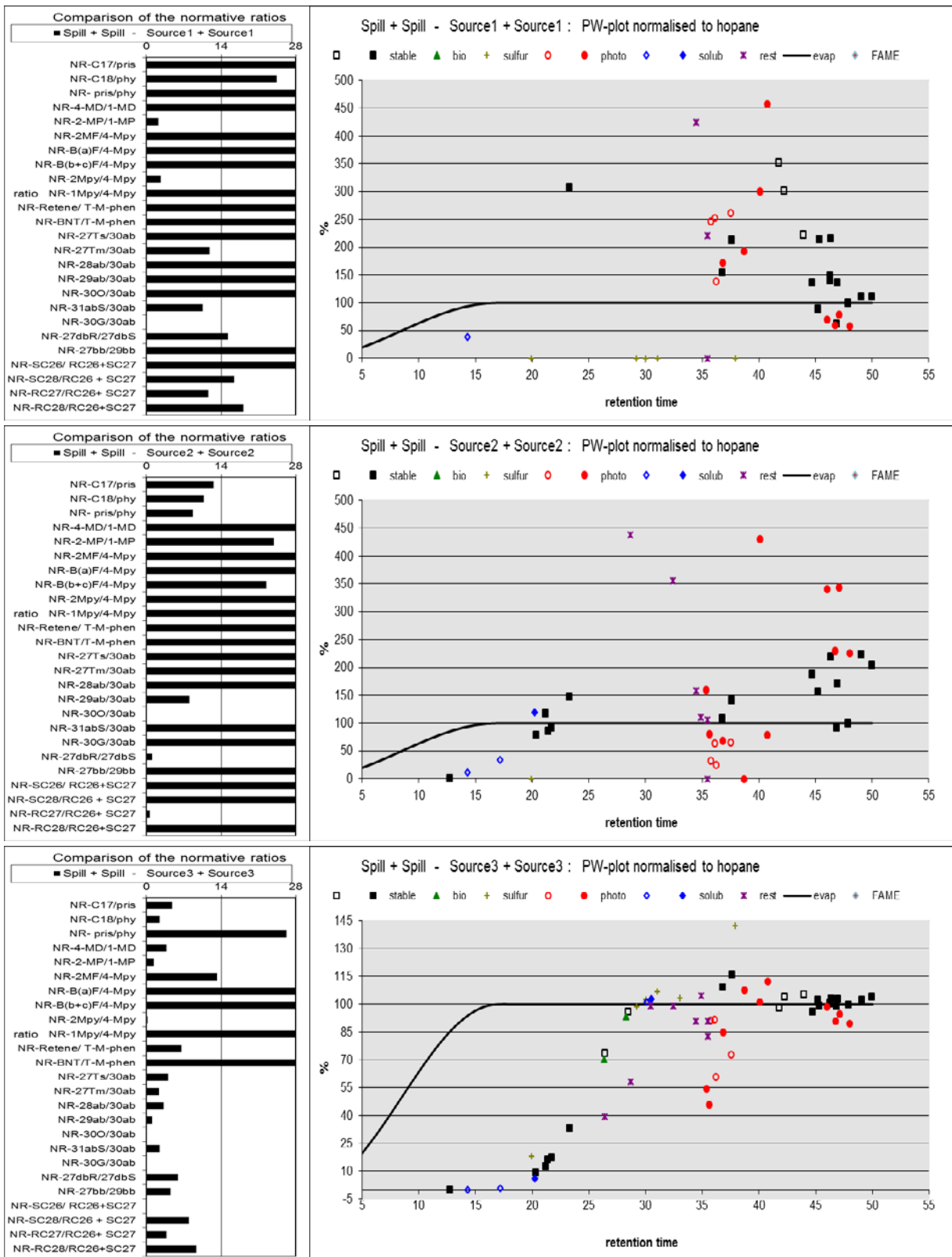
Figure 5-14   Comparison of Spill with source 1, 2, and 3: normative ratios

5.2.3 Reasons for selecting/deselecting DRs and data points in PW-plots

None of the normative ratios have been eliminated. For the informative ratios, the sesquiterpanes are influenced by weathering and there were no FAMEs present in any of the samples.

5.3 GC/MS conclusions

The diagnostic ratios are evaluated and it is assumed that the differences in m/z 216 are caused by photo oxidation and weathering processes as mention above in chapter 5.1.2 discussing the comparing of the Spill vs Source 3.

According to the PW-plot and the calculated diagnostic ratios, the following conclusions can be made based on the GC/MS results:

Source 1 and Source 2 are non-match to the spill.

Source 3 is a positive match to the spill.

6 Overall results

The scenario given for the Round Robin 2016 was as follows;
The Spill sample was collected from a buoy in a drifting oil slick in the North Sea close to the border between the Norwegian and British sector. There are several suspected sources, both from platforms and passing ships. Three of them are selected for comparison with the Spill sample.

Questions to be answered in the RR2016 case;
- Which of the source samples is the source of the spill sample?
- What kind of weathering has taken place?

Based on an evaluation of all samples, and taking into account that the Spill has been exposed to evaporative loss, sunlight, dissolution, and possibly biodegradation (depending on temperature), the following conclusion can be made:

- The Spill sample is non-match to Source 1 and Source 2.
- The Spill sample is positive match to Source 3.
- The weathering processes taking place is;
  - Enrichment of wax in a paraffinic crude oil is a phenomenon which occurs during weathering. When an oil is in contact with a physical part, in this scenario a buoy, a mechanical wash out of the liquid components in the oil and the solid wax-components are remaining.
  - Evaporative loss
  - Photo-oxidation due to exposure of sunlight, visual in m/z 216 (C1-fluoranthenes/pyrenes/benzofluorenes)

This scenario for Round Robin 2016 was a good and representative case for the use of the CEN (2012).

7 References

CEN (2012). 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. CEN/TR15522-2:2012).

OSINET (2016). Instructions for Oil Spill Identification Round Robin 2016 from Uta Kraus, Kees Kooistra and Paul Kienhuis of the 14th of October 2016.

Wang, Z., C. Yang, Z. Yang, C.E. Brown, B.P. Hollebone, and S. A. Stout (2016). Petroleum biomarker fingerprinting for oil spill characterization and source identification, in "Standard Handbook. Oil Spill Environmental Forensics. Fingerprinting and Source Identification. Second Edition". Stout, S.A., and Z. Wang (Eds), Elsevier. pp. 131-254, ISBN: 978-0-12-809659-8.
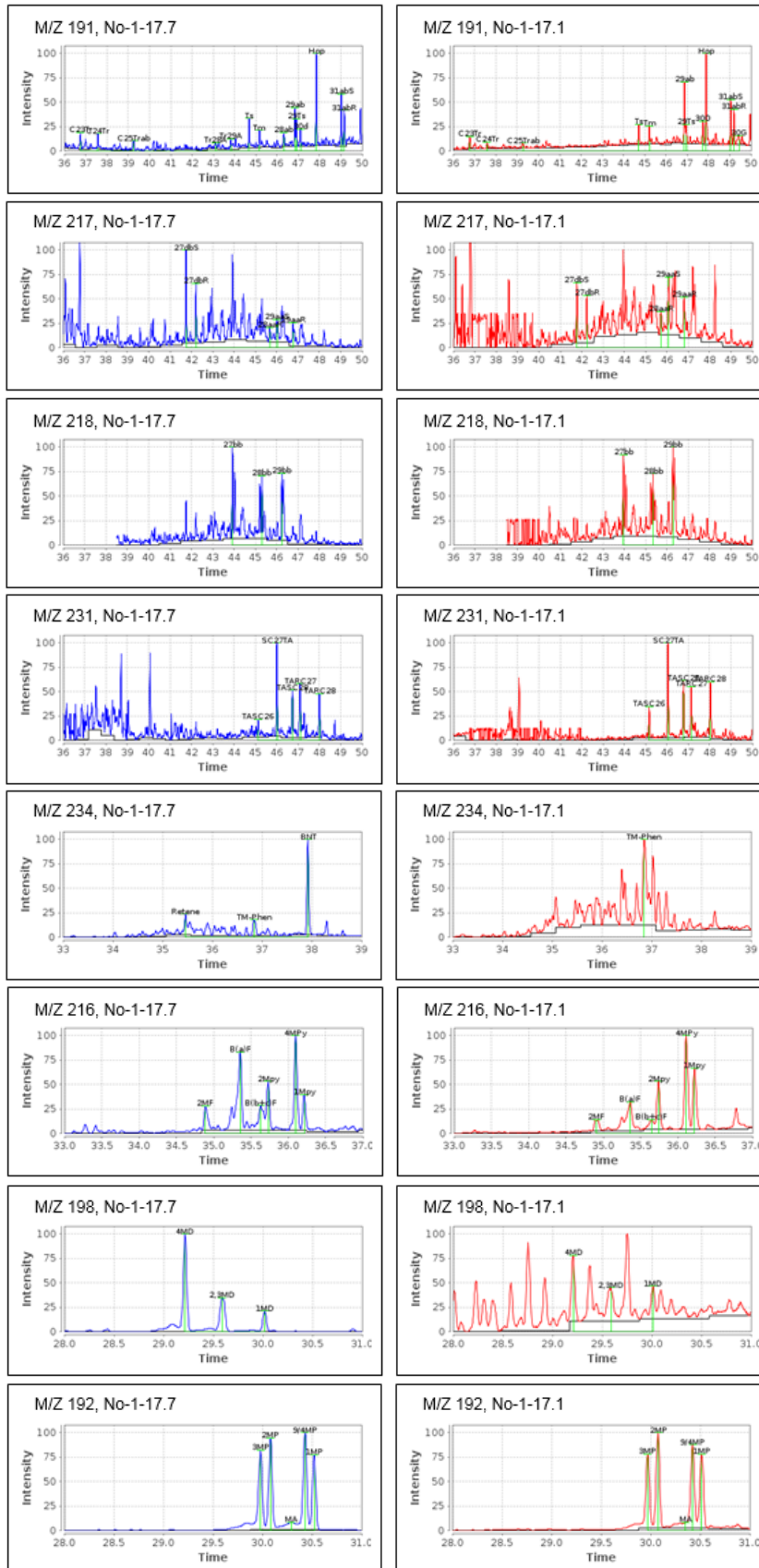
A Appendix Ion chromatograms

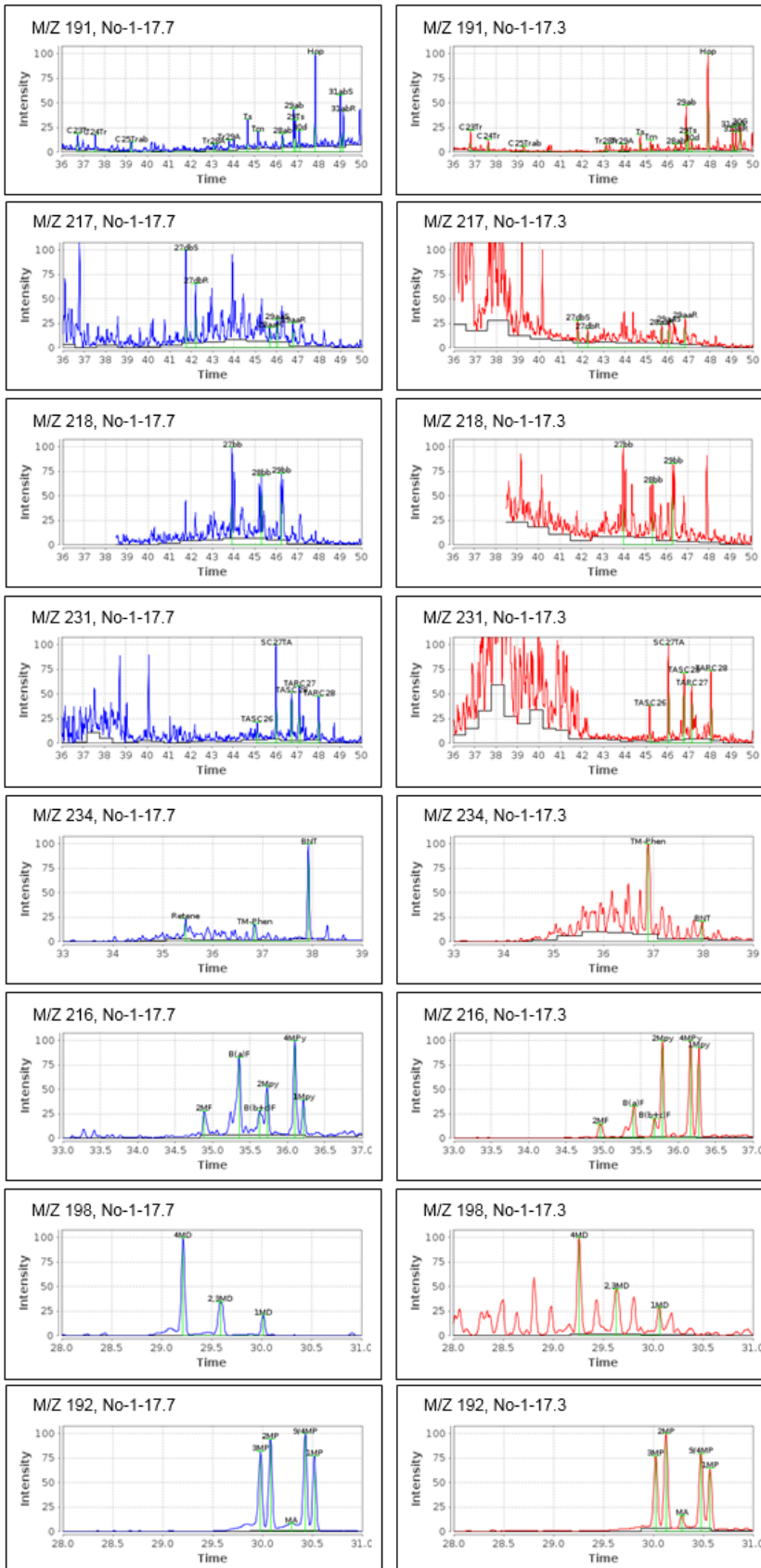*Figure A-1   Comparison of Spill vs Source 1*

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Figure A-2   Comparison of Spill vs Source 2

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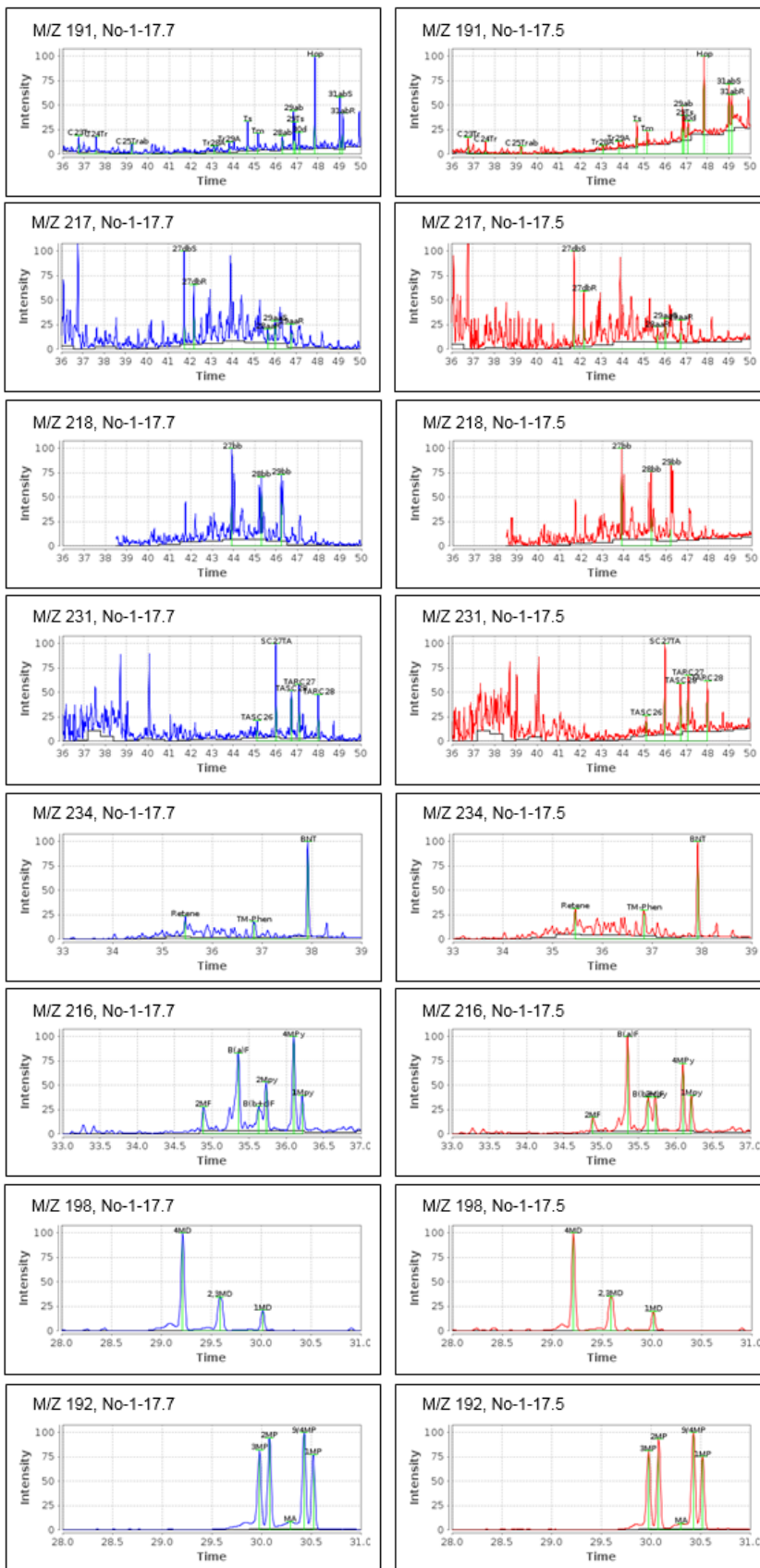REPORT NO.
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Figure A-3   Comparison of Spill vs Source 3

B Appendix Comparison of a duplicate injection of one of the samples

Duplicate injections were performed for all samples. MS-PW plots and calculated diagnostic ratios for Source 1 is shown in Figure B-1. The relative difference for all normative and informative ratios was below 14%.
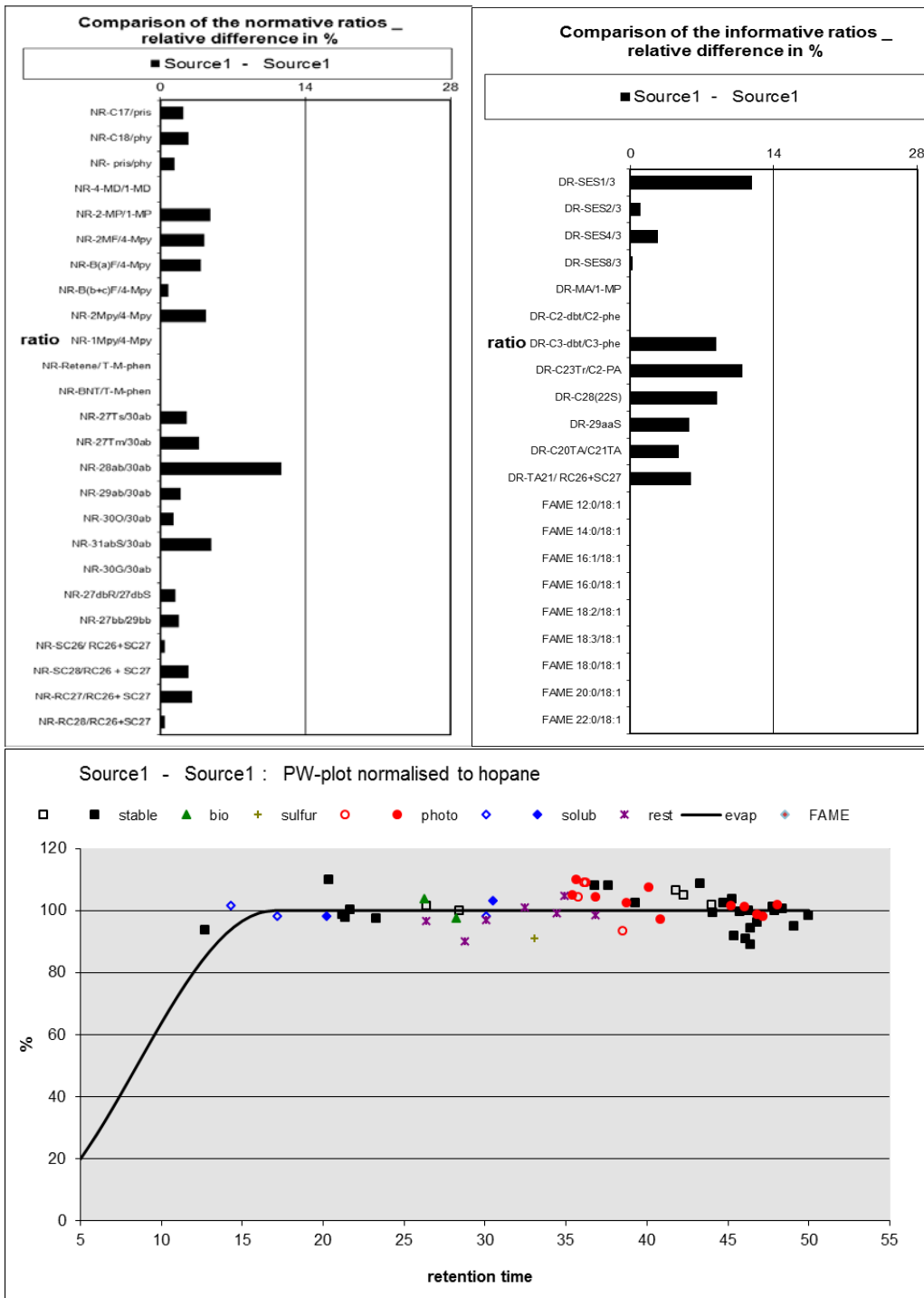

Figure B-1   Duplicate analysis of Source 1

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