



Round Robin 2008

Final Report



Introduction

At the last Bonn-OSINET meeting in Lelystad, NL, in May this year it was decided to:
„Organize a very straightforward ringtrial with a very simple evaluation of the results in order to stay in line with ISO 17025 accreditation and for some other reasons. The ringtrial will be organized by three people: Per Daling (samples), Paul Kienhuis (distribution), evaluation (Gerhard Dahlmann).“

Three samples were provided by Per, oil in DCM, from which subsamples were produced by Paul, which were sent to 24 laboratories end of August 2008. 23 result reports were received until end of November.

So, here is the summary of the results with just some remarks, which I found important.

The story

There was an "emergency" situation at a storage platform, that receives and stores crude oil from several production platforms, that resulted in an "controlled" release of crude oil stored in one of the platform legs. Much of the oil was recovered during a response operation close to the platform the same day within 2-5 hours (Day 1). A part of the slick was not recovered during the first day. During the night, the slick had drifted several miles, and into another oil field. When the recovery operation started the next day, two separate slicks were found here (slick A and slick B). The weather conditions during these days were: sea temp: 10 deg.C. wind:6-8 m/s

To be able to send all participants the same samples, the oil spill samples have been dissolved in DCM at a concentration of 10 mg/ml.

The samples are indicated as:

Source 1: (The oil from Day 1)
Spill 2: (The oil from slick A)
Spill 3: (The oil from slick B)

We like to ask you to analyse and compare the sample of Day 1 with the 2 slick samples and send in a report by email. The resulting report should not only consist of a simple yes or no, but also detailed reasons why a decision has been taken. The original reports will be combined in a final report, together with an evaluation of the overall results.

The truth

Spill 2 (slick A) originates from source 1 (discharged from let's say platform "A"). while spill 3 does not originate from source 1.

This case actually happened in the platform area of the northern North Sea. Many samples were taken from the spills during the combating operation and sent to SINTEF, No. Per Daling has chosen three „representative“ samples from source 1, spill 2, and spill3 for the purpose of this inter-calibration round.

Of course, the oil discharged from platform "A" was not left alone after the first day: according to trajectory modeling that took place during the night, slick A was approaching a neighbor platform (platform "B"). Slick A was also monitored / tracked by the response vessel, and samples from slick A were taken both before and after slick A had passed platform B during the combating operation next morning. At the time when the response operation took place fairly close to the platform "B", a significant amount of oil was released from platform "B". This release was documented by photos from the response vessel, and a MOB-boat from the response vessel went into slick B and secured samples of the slick for further documentation.

Strange things happen in oil production.

Results

Summary

		Source1/Spill2	Source1/Spill3
1	Petrobras, Br	M	NM
2	SKL, Se	M	NM
3	CSIC, Es	M	NM
4	NSW, Au	M	M
5	ESTC, Ca	M	(NM)
6	PESC, Ca	M	NM
7	ALET, Ca	M	NM
8	LVGMA, Lv	M	NM
9	NERI, Dk	M	NM
10	NCSEMC, Ch	M	NM
11	EERC, Ee	M	NM
12	ISPRA, It	M	NM
13	NBI, Fi	M	NM
14	NF, US	M	(M)
15	MUMM, Be	M	(NM)
16	NFI, NI	M	NM
17	EPA, Au	M	NM
18	RWS, NI	M	NM
19	Sintef, No	M	NM
20	CEDEX, Es	M	M
21	CEDRE, Fr	M	NM
22	ERT, Uk	M	M
23	BSH, De	M	NM

Table 1: Overall-results. M=match, NM= non-match, ()= not so sure, see text

All participants found a “match” between source 1 and spill 2.

The results of the comparison of source 1 with spill 3 cannot so easily be explained: 19 participants reported a “non-match” because significant differences were found. Further participants, although aware of those differences, came to the conclusions of “inconsistent” or “probable match”. This means that explanations were given here that there could be -or even there is probably- a connection between spill 3 and source 1 despite those differences. Others argued that those differences were small and could have been caused, for example, by the sampling technique.

Generally, the analyst was not provided with sufficient information and a sufficient number of samples in this case (as given above, a simplification had to be made for this RoundRobin-test).

If this would happen in an actual case, I would say: “non-match” with regard to the comparison of spill 3 with source 1 -and criticize the people on-scene for not having provided me with more samples from the spills and especially samples from the surrounding platforms. How should I know the “meaning” of smaller differences -or even whether there are any differences at all- in a very limited platform area.

Analyses

GC

Significant differences between source 1 and spill 3 could/should have been found already by the first “screening” of the samples -and nearly all participants found those differences here. It was reported that already the mere visual inspection of the chromatograms revealed that there was some “addition” in the diesel-range of spill 3 compared to source 1, including n-alkanes but also isoprenoids and even aromatics. Results presented in form of column-diagrams, PW-plots, and overlays of chromatograms showed that the relative concentrations of alkanes in the region C13 to C16 was about 25% higher in spill 3 than in source 1 (see below). This cannot be explained by weathering as spill 3 was at sea one day longer than source 1. It could of course be possible that source 1 may have been from a thin slick/sheen whereas spill 3 may have been a sample of a thick slick, where oil protected within an outer layer is more resistant to weathering (as also suggested). But if so, the fact that the concentration of C12, for example, was found to be identical in both samples, would then be a contradiction to this theory. Generally, differences of about 25% in some major components of the two oils would justify that the analysis of spill 3 is stopped here.

The comparison of source 1 with spill 2 reveals a possible match at this stage of analysis.

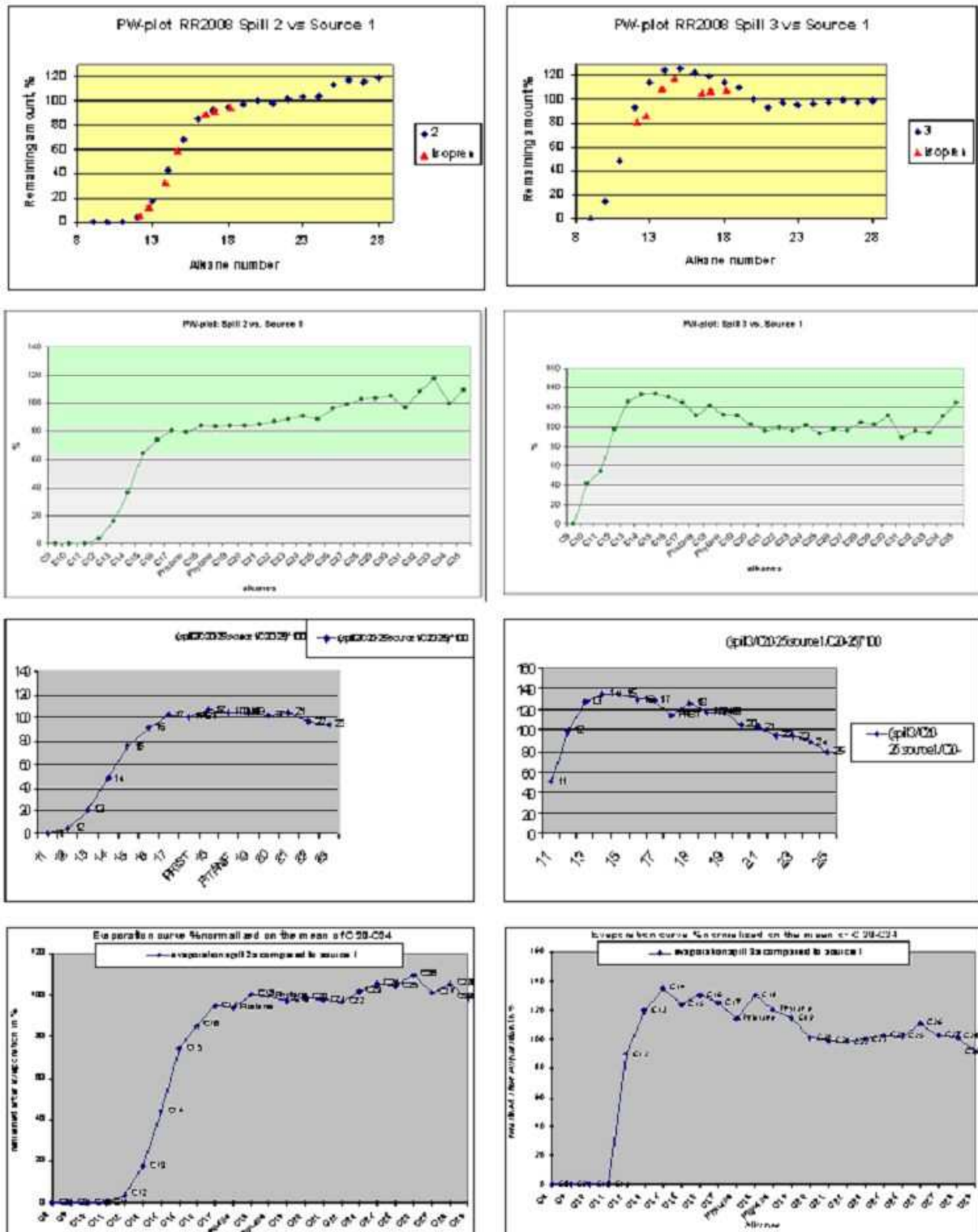


Fig. 1: PW-plots of source 1 and spill 2 (left), and source 1 and spill 3 (right). Look at 100% on the scales.

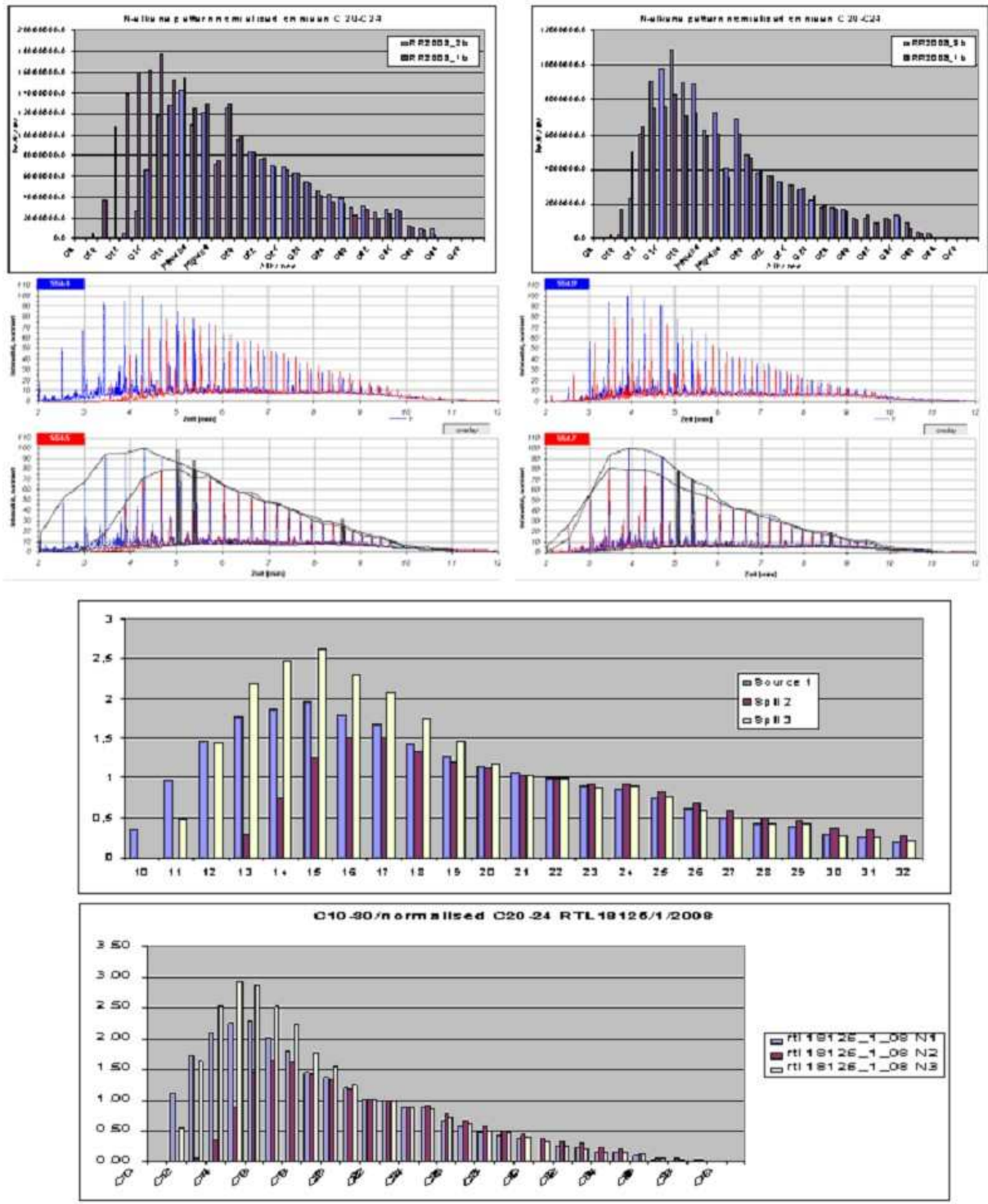


Fig. 2: Different visualizations of GC-screening results, demonstrating that the difference between source 1 and spill 2 may be caused by weathering. But when spill 3 is compared to source 1, “something seems to be added” in the region C13 to C 18.

GC/MS

The screening results could have been confirmed by GC/MS. Differences between source 1 and sample 3 were mainly present in the aromatics, whereas the biomarkers were very similar. When related to hopane, nearly all aromatics were higher in sample 3, which also here led to the impression that “something was added” in the diesel-range.

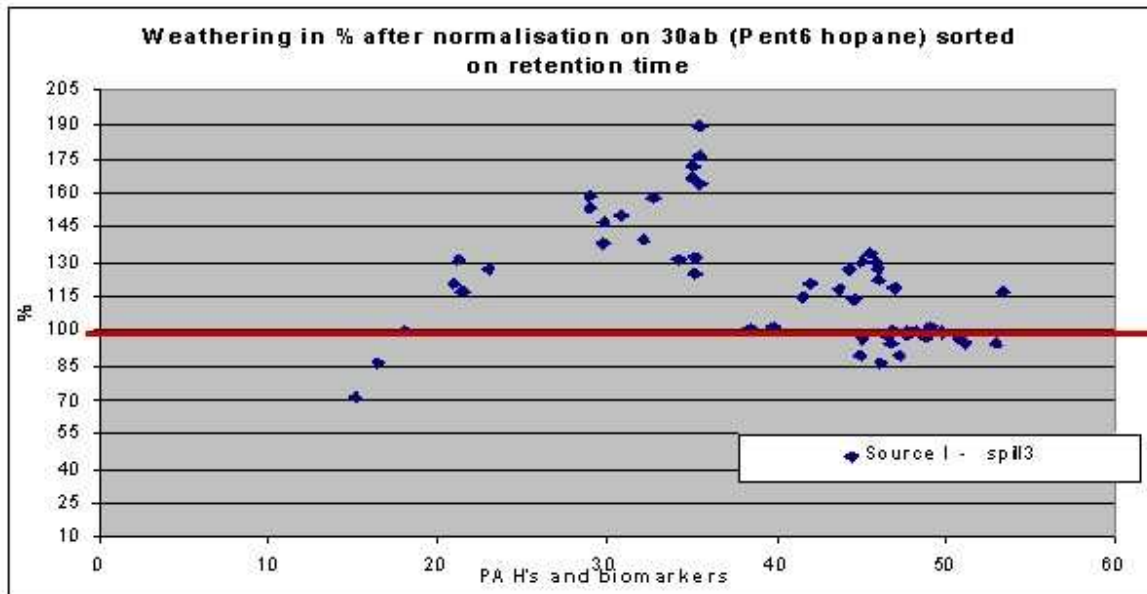


Fig. 3: GC/MS PW-plot (MUMM, Be)

Differences in the biomarker-ratios, if present at all, were caused by smaller peaks. A difference in the ratio 30d/hop, for example, was presented in different ways:

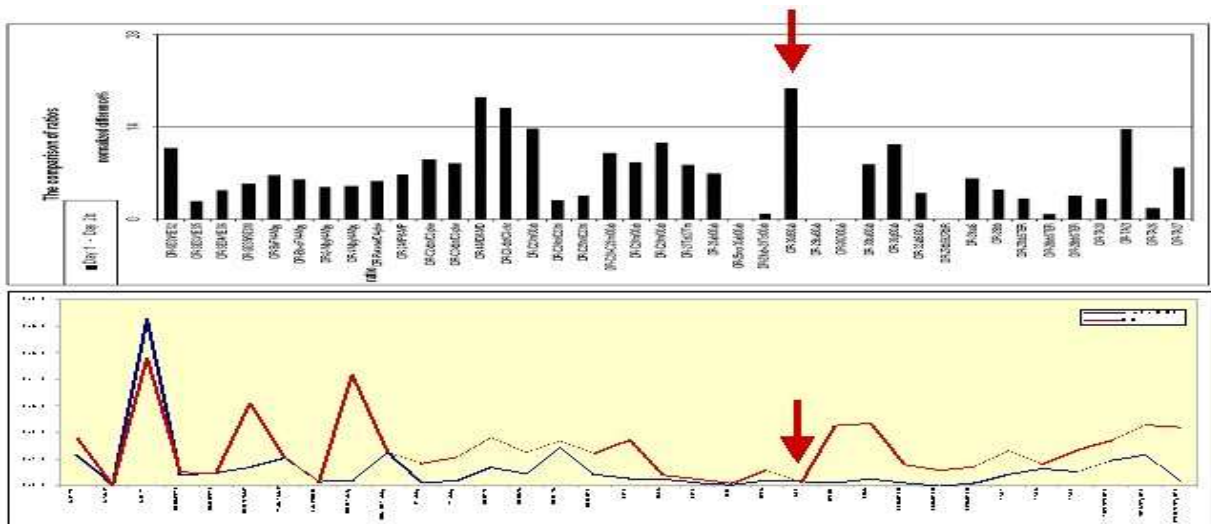


Fig. 4: Presentation of relative differences and the relative critical difference (RWS, NI, above), and absolute differences and absolute critical differences (ERT, Uk, below). Arrow: 30d/hop.

In the upper diagram in Figure 4, the difference in 30d is pronounced, whereas it can be seen in the lower diagram that this difference is small compared to the difference of other ratios (because 30d is a small peak).

When Source 1 was compared to Spill 2, differences were indeed smaller, and a “S”-shaped weathering curve could be found in the PW-plot:

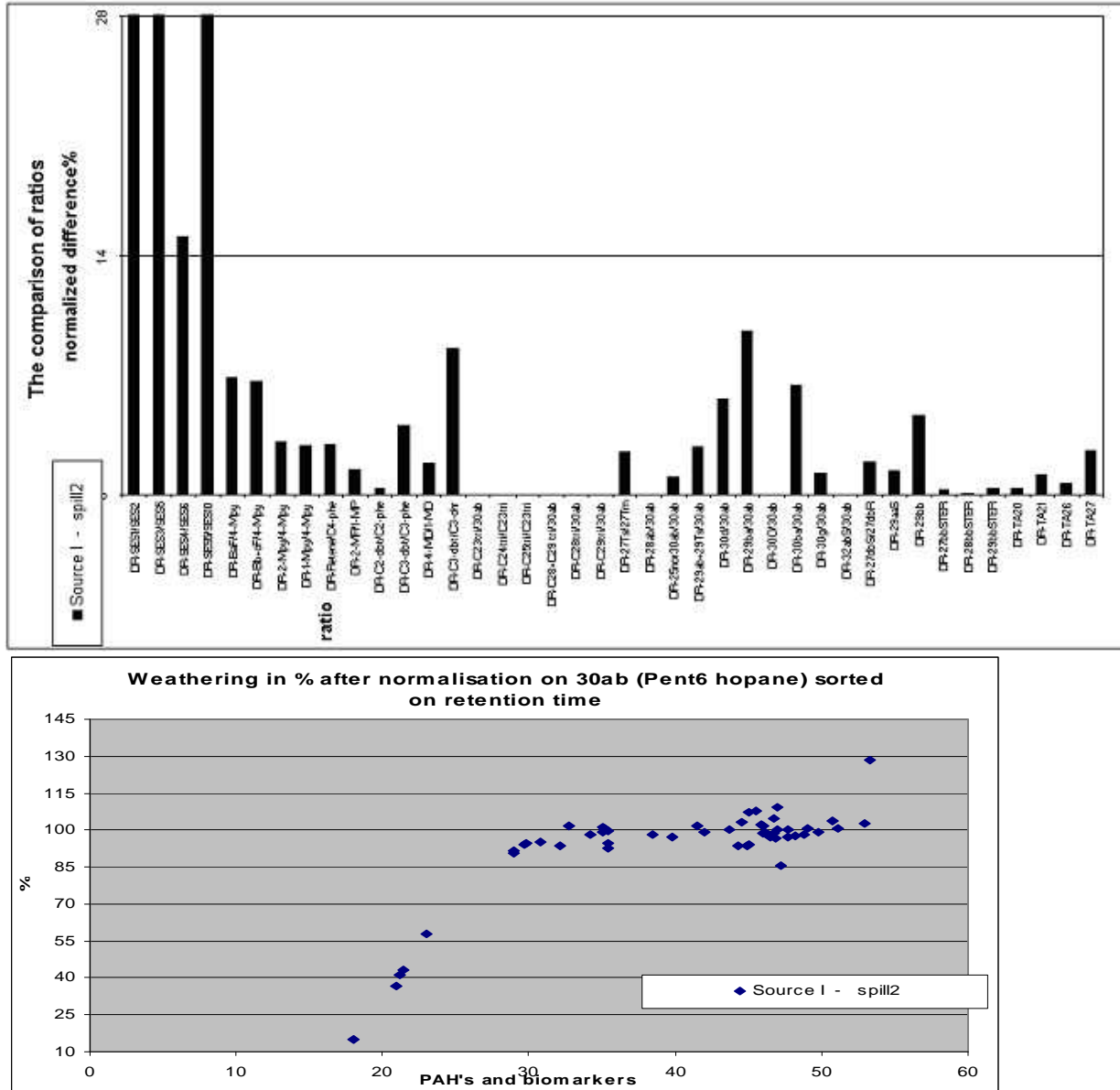


Fig. 5: Ratio-comparison above, MS-PW-plot below, Source 1/Spill 2 (MUMM, Be)

Just a short remark to the upper diagram in Figure 5: due to my experience in court trials, it might not be a good idea to present the high differences of the 4 sesquiterpenes here (just a tactical consideration and not a criticism). If it is absolutely sure from the beginning (screening results) that these compounds were highly effected by evaporation, there is no reason to measure, and especially to present them. Thus, “confusion” may be produced –and producing confusion is a common tactic of the defender.

Multivariate statistics

The “lack” of samples in this case and especially the “lack” of comparison samples from platforms of this area is especially striking, when multivariate techniques are used, and it is definitely not a failure of the PCA-technique, that the 3 samples are found to be very similar, when they are compared to any other oil samples:

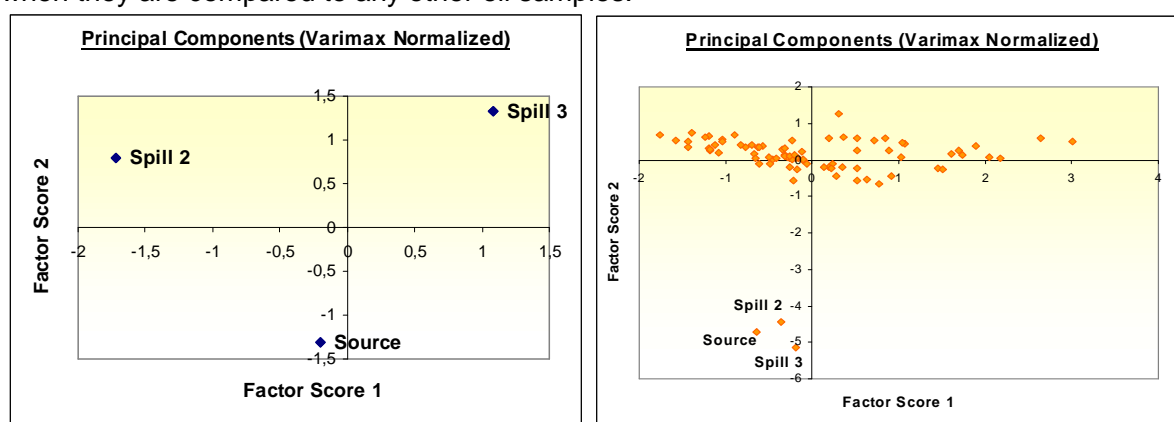


Fig. 6: PCA-score plots of the three samples alone (left), and compared to other samples (right), CEDEX, Es

As indicated in the CEDEX-report here, there is not sufficient information about the relative distance of the three samples (Figure 6 left). Compared to other arbitrarily chosen samples, the three samples are found to be very similar (two clusters, Fig. 6 right). Thus, both “shortcomings” of our RR-test mentioned above are correctly found out here. Turning this around, one can imagine that PCA would be a powerful tool here for coming to a conclusion and for demonstrating the findings, if many samples from the spills and many samples from the possible sources were available.

As also indicated here, the “similarity” of the three samples has to be verified by the single measurements. But that’s always needed, when PCA is used. The key-term here is “ground truth” any findings.

The COSI-system contains a huge database of oil samples including about 300 crude oils from all over the world. Beside by myself, this system is used so far by RWS, NI, and EERC, Ee. Of course, also here the “shortcomings” mentioned above are present, as the database cannot contain all crude oils from all wells of the world. It was also found out by EERC that the correlation coefficients between source 1/spill 2 and source 1/spill 3 were highly similar and there were only some smaller differences in the ratios between source 1 and spill 3 (nothing else than what is discussed in this report here so far).

But COSI immediately points to Norwegian Statfjord-crude oils as best matching oils over all other oil samples in the database:

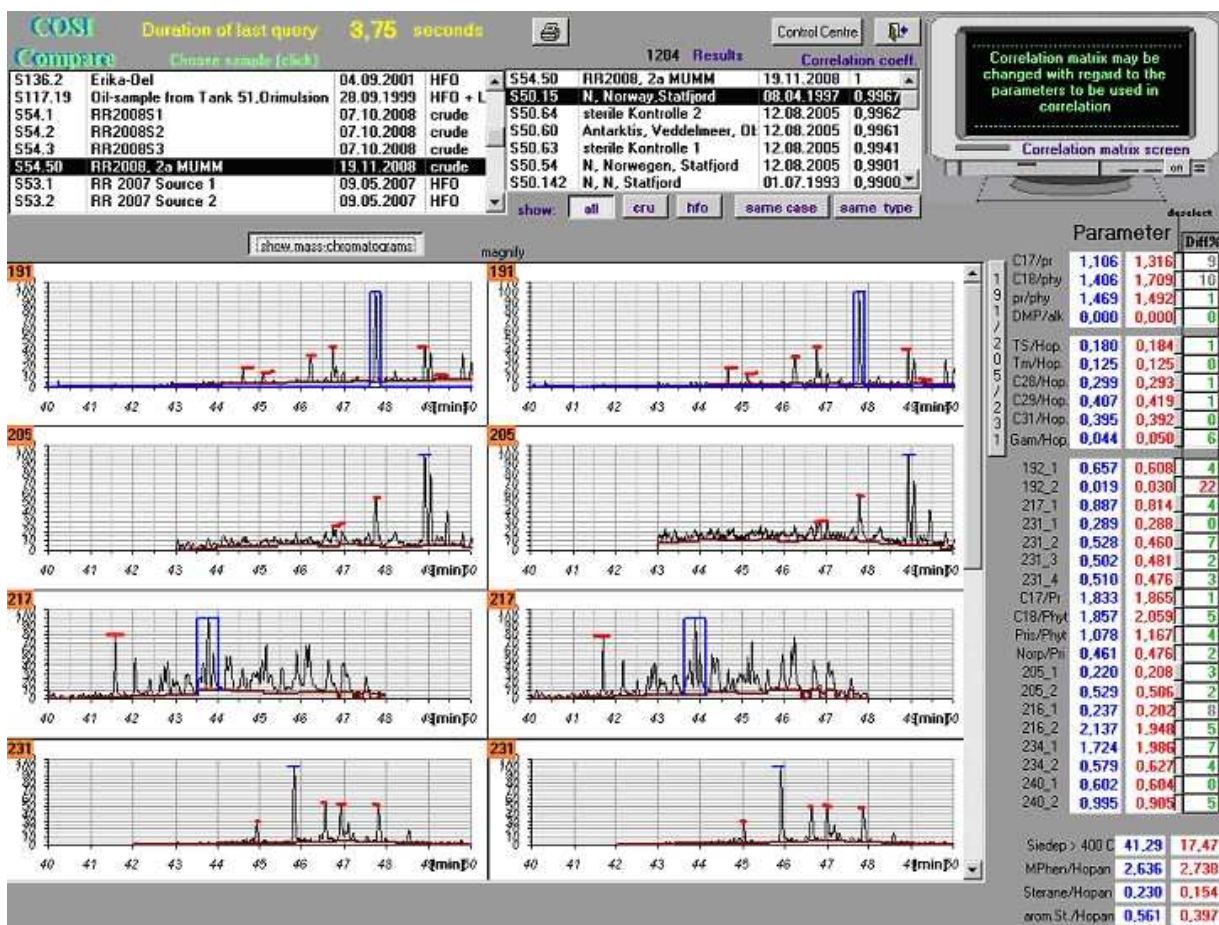


Fig. 7: COSI-results (left: spill 2, MUMM, Be)

In the example given above, spill 2 was analyzed by MUMM, and the raw data were sent to me for testing. When it is searched for this sample in the database, only Norwegian Statfjord oil samples appear as best matching oils (right table above in the figure. The samples S50.64, 60 and 63 originate from an experiment in the Antarctic, where Statfjord-crude was used –I should have given them a better description).

It is also interesting to note that all ratio differences (%Diff, right) are below our own analytical error (thus marked green), except 192_2 (M-antracene), which is a very small peak. But for the first time a different instrument (Varian Trace MS instead of HP/Agilent) and a different software (Excalibur instead of HP-Chemstation) was used here. Of course, the analytical parameters were adapted, as the automatic peak detection mechanism of COSI expects the compounds to be in distinct retention time intervals.

I do not know anything about the samples –except what is given in the Introduction above-, and I hope that I do not blame distinct oil producers by presenting a name of an oil field. I agree to Per, who indicated that “from a juridical point of view, it is not a good idea to mention the names of the platforms in the description of the case”, and I also agree that “there seems to be some “cowboy” like attitude offshore”. But Per has also made the proposal to use the samples as a test for COSI: can the origin be found out?. But this is done automatically as soon as a sample is added to the database, as every sample is compared to every other sample every time. If this is not wanted, one can use the switch “same case” (Figure 7, just below the right table, where the results are shown) and thus limit the comparison to samples from the same case.

Conclusion

As in former RoundRobins, simple “screening” of the samples revealed most important information. But experience and a sharp eye is needed, if the chromatograms are merely compared separately. The PW-plots, column diagrams, and overlays of the n-alkanes as given in Figures 1 and 2 are simple but effective tools for finding similarities and significant differences -but also for documentation. These were produced by the vast majority of the participants: when spill 3 was compared to source 1, something seemed to be added in the diesel-range, whereas the comparison of spill 2 with source 1 revealed a typical evaporation curve.

Differences in the compound ratios between source 1 and spill 3 were small and mainly present in the aromatics. Differences were pronounced, when the compounds were related to hopane (MS-PW-plots): nearly all compounds in the Diesel-range were higher in spill 3, which –together with the findings from GC-screening- could lead to the assumption that actually Diesel-oil was added.

I would liked to have the original samples from the platforms because I cannot believe that differences of this kind are present between crude oils of these nearby platforms. Diesel-oil is used on platforms for various purposes. It could thus be possible that a mixture of Diesel and crude oil was discharged by platform B.

All participants have verified the identity of spill 2 with source 1 by means of compound ratios, and all conclusions were given “with the highest certainty” here.

Such uniform results were not achieved in the former RoundRobins.

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